Intramolecular Steric Factors in the Thermolysis of 4-Alkylidene-1-pyrazolines

Gerard N. LeFevre and Robert J. Crawford*

Contribution from the Department of Chemistry, The University of Alberta, Edmonton, Alberta, Canada T6G 2G2. *Received July 3, 1985*

Abstract: Secondary deuterium kinetic isotope effects and product proportions are measured for several methyl-substituted 4-methylene-1-pyrazolines and deuterated isotopomers. The kinetic data support a single-bond-cleavage mechanism, and the products indicate that three modes of ring closure are required. Evidence is presented for a series of monomethyl compounds to suggest that the mechanism is more complex than a two-step scheme would predict and that the interconversion of a series of intermediates **46** is required.

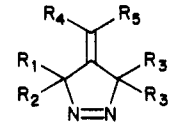
Linear azoalkanes (R—N=N—R) fit the general rule that tertiary carbon–nitrogen bonds undergo homolysis more rapidly than secondary which in turn react faster than primary.[1] Cyclic systems are not so well-behaved, and sometimes the replacement of a hydrogen by an alkyl group slows down the rate or has little or no effect.[2] In our studies of the thermolysis of 4-alkylidene-1-pyrazolines, we have observed some very unusual relative rates and enthalpy changes as we replaced hydrogens with methyls[3,4] (Table I). It is clear from examining the data that substituting hydrogen with a methyl leads to a significant decrease in the rate, e.g., compare **1**, **2**, and **4**. Substitution α to the nitrogen either has little effect or as in the case of **5** and **6** it significantly increases the activation energy.[5] We have studied the mechanism of thermolysis of **1** to alkylidenecyclopropanes in detail by examining the secondary deuterium isotope effects on both the rate and the product-determining steps.[3] The rate-determining step is consistent with the cleavage of one carbon–nitrogen bond to form an allylic diazenyl radical (Scheme I). The proportions of methylenecyclopropanes produced then depend upon an isotope effect for rotation of CH_2 in preference to CD_2 of the allylic system. While it is not clear that the nitrogen is involved in the product-determining step, it is necessary to have one of the α-methylenes stereochemically unique in order to accurately predict the product proportions.[3] The decrease in rate for **2** and **6** relative to **1** and **5** is due to steric crowding in the transition state caused by the decrease of the $C_3C_4C_6$ bond angle brought about by the homolysis of the C–N bond.[7] We have chosen to investigate in greater detail the thermolysis of 3-methyl-4-methylene-1-pyrazoline (**3**), 3,3-dimethyl-4-methylene-1-pyrazoline (**4**), and deuterium-labeled derivatives in an attempt to assess the extent that steric compression in the transition state may be responsible for some of the anomalous relative rates observed in Table I.

The bicyclic [2.2.1] analogues of the 4-alkylidene-1-pyrazolines have been carefully studied by Berson and his collaborators,[5] and they have presented compelling evidence for the singlet trimethylenemethane-like intermediate. By examining the monocyclic systems having distinguishing features at each of the carbons, we endeavoured to test for a nitrogen-free singlet intermediate in the less-constrained systems.

Results

The deuterated substrates, in Table II, were synthesized as outlined in Schemes II–V. Their isotopic purity was assessed by mass spectrometry and both proton and deuterium magnetic resonance spectroscopy. The Diels–Alder adduct **18** was prepared in 29% yield by heating methyl 3-methyl-2-butenoate and cyclopentadiene for 3 weeks at 140 °C in a sealed tube.[8] When lithium diisopropylamide and trioxane were used, the methyl ester **19** was prepared as a mixture of isomers. Lithium aluminum deuteride reduction followed by pyrolysis of **20** at 500 °C gave 2-isopropylidene-1,3-propanediol-*1,1-d*$_2$ in 87% yield. The dibromide **21** was prepared by Corey's procedure using dimethyl sulfide and *N*-bromosuccinimide.[9] Conversion of the dibromide to 4-isopropylidene-1-pyrazoline-*3,3-d*$_2$ (**15**) was achieved as described earlier.[10] Preparation of **16** was achieved as outlined

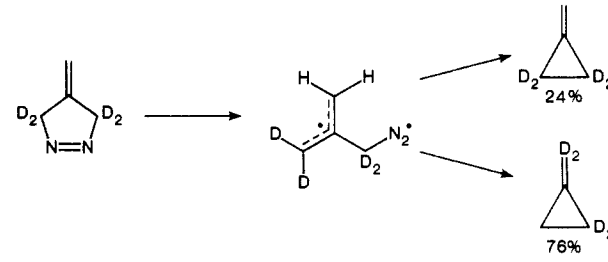
Table I. Activation Parameters and Relative Rates at 170 °C for Some 4-Alkylidene-1-pyrazolines



1

	compd	E_a, kcal mol^{-1}	log A	rel rate at 170 °C	ref
1a	R_1–R_4 = H	33.6 ± 0.7	13.75 ± 0.35	1.00	3
2	R_1–R_3 = H; R_4, R_5 = CH_3	35.9 ± 1.0	14.6 ± 0.9	0.55	2
3	R_1 = CH_3; R_2–R_5 = H	33.0 ± 1.0	13.4 ± 1.0	1.04	2
4	R_1, R_2 = CH_3; R_3, R_4, R_5 = H	35.3 ± 1.2	14.4 ± 0.6	0.70	2
5	R_1–R_3 = CH_3; R_4, R_5 = H	40.7 ± 0.4	15.5 ± 0.2	0.020	5
6	R_1–R_5 = CH_3	39.8 ± 0.4	13.6 ± 0.4	0.000 65	4

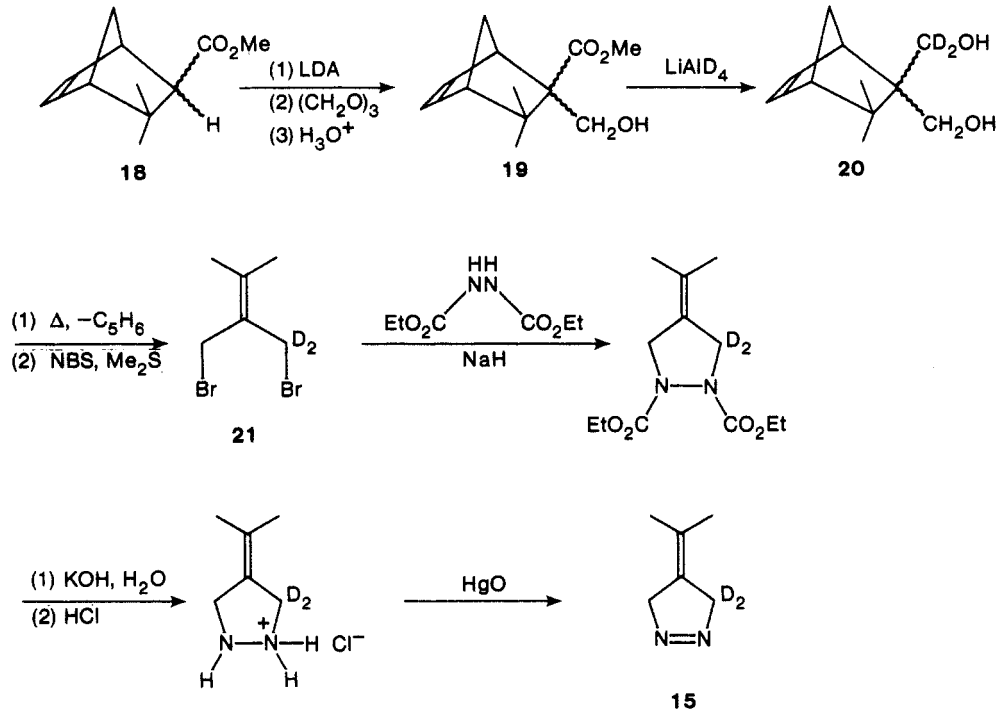
Scheme I



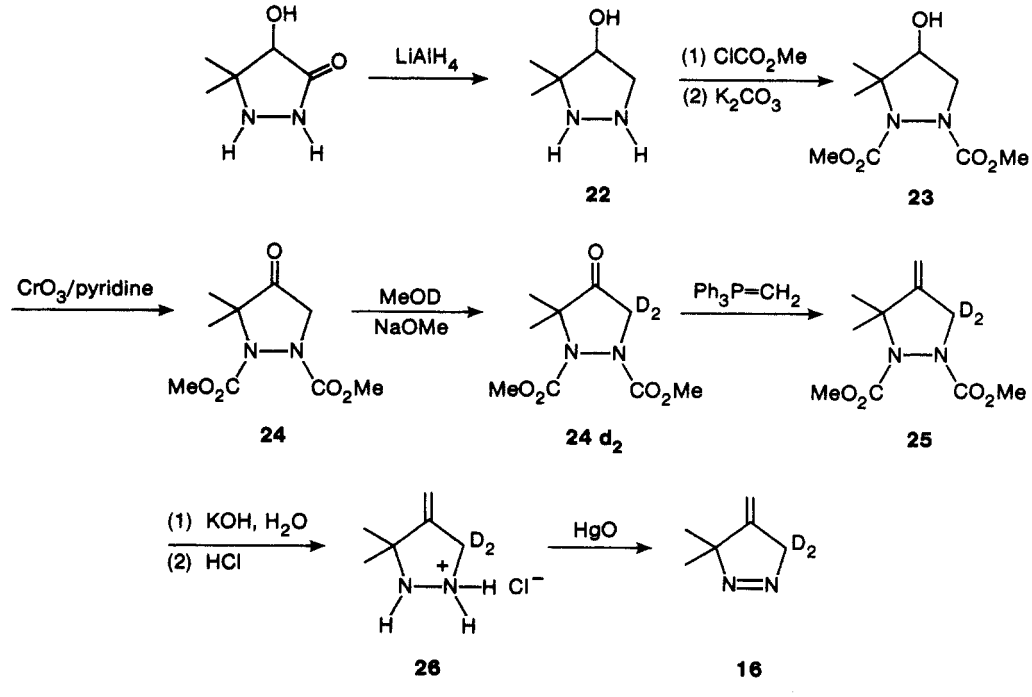
(1) Engel, P. E. *Chem. Rev.* **1980**, *57*, 99–150.
(2) Crawford, R. J.; Chang, M. H. *Tetrahedron* **1982**, *38*, 837–842.
(3) Chang, M. H.; Crawford, R. J. *Can. J. Chem.* **1981**, *59*, 2556–2567.
(4) Engel, P. S.; Shen, L. *Can. J. Chem.* **1974**, *52*, 4040–4044.
(5) (a) Berson, J. A. In "Diradicals"; Borden, W. T., Ed.; Wiley: New York, 1982. (b) Lazzara, H. G.; Harrison, J. I.; Rule, M.; Hilinski, E. F.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2233–2243. (c) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446–453.
(6) Crawford, R. J.; Tokunaga, H. *Can. J. Chem.* **1974**, *52*, 4033–4039.
(7) The X-ray structure of permethyl-4,4-bis-($\Delta^{1,2}$-pyrazolinylidene) has been determined by: Bushby, R. J.; Pollard, M. D. *Tetrahedron Lett.* **1978**, 3851–3854. And the $C_3C_4C_5$ bond angle is 103.8°. The $C_3C_4C_5$ bond angle of a 1-pyrazoline has also been determined as 99.1° (see: Rousseaux, M. P. *Acta Crystallogr.* **1978**, *288*, 720.
(8) Previous attempts resulted in a 5% yield, see: Alder, K.; Roth, W. *Chem. Ber.* **1957**, *90*, 1830–1837.
(9) Corey, E. J.; Kim, C. U.; Takeda, M. *Tetrahedron Lett.* **1972**, 4339–4342.
(10) Crawford, R. J.; Cameron, D. M.; Tokunaga, H. *Can. J. Chem.* **1974**, *52*, 4025–4032.

0002-7863/86/1508-1019$01.50/0

Scheme II



Scheme III



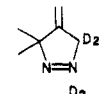
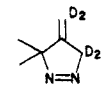
in Scheme III. Originally we had planned to synthesize 4-dideuteriomethylene-3,3-dimethyl-1-pyrazoline, using the ketone **24** with Wittig reactions, and other methyleneation methods;[11] these failed to give the desired products, either resulting in deuterium exchange or inappropriate materials. The deuterated 3-methyl-4-methylene-1-pyrazolines **11** and **12** were prepared as outlined in Schemes IV and V. Oxidative rearrangement of the allylic selenide **34** was particularly successful.[12] The 3-deuterio-3-methyl-4-methylene-1-pyrazoline (**14**) was prepared by the 1,3-dipolar addition of diazoethane-*1*-d_1 to allene.

Kinetic Measurements. The results of the gas-phase thermolysis of a series of 4-alkylidene-1-pyrazolines are reported in Table II. Each compound was transferred to a thermostated vessel maintained at a carefully regulated temperature. The initial pressure was generally 75–150 torr, well above the kinetic first-order fall-off range. Deuterated and nondeuterated compounds used for comparisons were run within a short period of one another, and the temperature was measured by using a multiple junction thermocouple placed in a well inside the 250-mL stainless steel reaction flask. The pressure was measured by using a transducer, and the data were digitized. The rates were calculated by using 16 or more points and had a correlation coefficient of 0.999 or better. The rates reported in Table II are the average of three or more runs, and the errors quoted are the 90% confidence limits. The secondary deuterium kinetic isotope effects (KIE) have all been corrected for incomplete deuteration by using analyses derived

(11) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613. Sowerby, R. L.; Coates, R. N. *J. Am. Chem. Soc.* **1972**, *94*, 4758–4759.

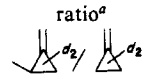
(12) Clive, D. L. J.; Chittattu, G.; Curtis, N. J.; Menchen, S. *J. Chem. Soc., Chem. Commun.* **1978**, 770–771.

Table II. Secondary Deuterium Kinetic Isotope Effects for Some 4-Methylene-1-pyrazoline Derivatives

compd	temp, °C	10^3k, s^{-1}	$(k_H/k_D)^{corr}$	$\delta\Delta G^{\ddagger}$, cal mol^{-1}	ref
10 	164.0 ± 0.1	1.94 ± 0.01			2
7 	164.0 ± 0.1	1.63 ± 0.02	1.19 ± 0.03[a]	157	2
8 	164.0 ± 0.1	1.82 ± 0.02	1.07 ± 0.02	59	2
9 	164.0 ± 0.1	1.51 ± 0.02	1.29 ± 0.03	221	2
3 	180.0 ± 0.1	3.01 ± 0.03			this work
11 	180.0 ± 0.1	2.55 ± 0.05	1.18 ± 0.03	149 ± 20	this work
12 	180.0 ± 0.1	2.86 ± 0.05	1.05 ± 0.02		this work
13 	180.0 ± 0.1	2.52 ± 0.02	1.19 ± 0.02	157 ± 20	this work
14 	180.0 ± 0.1	2.94 ± 0.02	1.02 ± 0.02	17 ± 17	this work
2 	180.0 ± 0.1	1.75 ± 0.02			this work
15 	180.0 ± 0.1	1.57 ± 0.01	1.12 ± 0.02	102 ± 16	this work
4 	180.0 ± 0.1	2.14 ± 0.01			this work
16 	180.0 ± 0.1	1.83 ± 0.02	1.18 ± 0.03	149 ± 20	this work
17 	180.0 ± 0.1	1.79 ± 0.05	1.20 ± 0.03	164 ± 20	this work

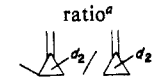
[a] Corrected for incomplete deuteration.

Table III. Product Proportions from the Thermolysis of 3-Methyl-4-methylene-1-Pyrazolines at 170 °C

reactant	ratio[a] 
3	3.95 ± 0.07[b]
11	4.08 ± 0.07
12	4.41 ± 0.09
13	4.56 ± 0.09
14	3.81 ± 0.07

[a] Equilibrium ratio at 170 °C is 0.743. [b] Determined by GC from three different samples each analyzed 3 times; the error indicated is the standard deviation of nine analyses.

Table IV. Product Proportions from the Thermolysis of Dimethyl-Substituted 4-Methylene-1-pyrazolines (170 °C)

reactant	ratio[a] 
2	1.54 ± 0.02
15	1.86 ± 0.08
4	4.43 ± 0.12
16	5.25 ± 0.33
17	5.25 ± 0.17

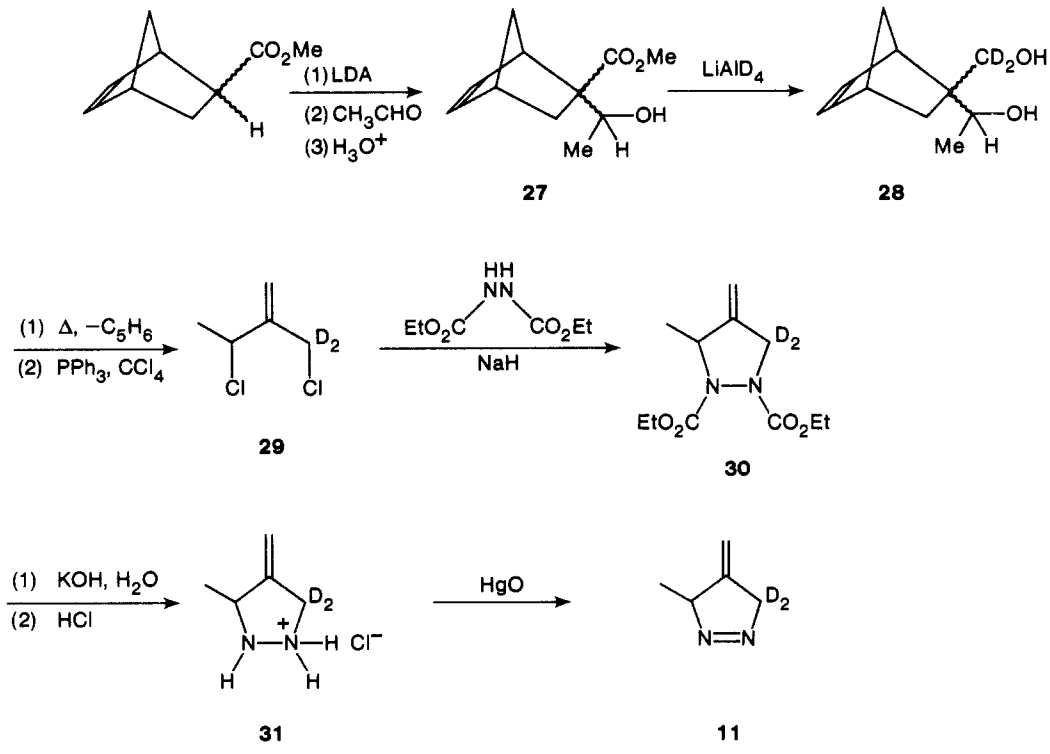
[a] The equilibrium ratio at 170 °C is 0.234.

from mass spectrometry. All samples were greater than 95% isotopically pure.

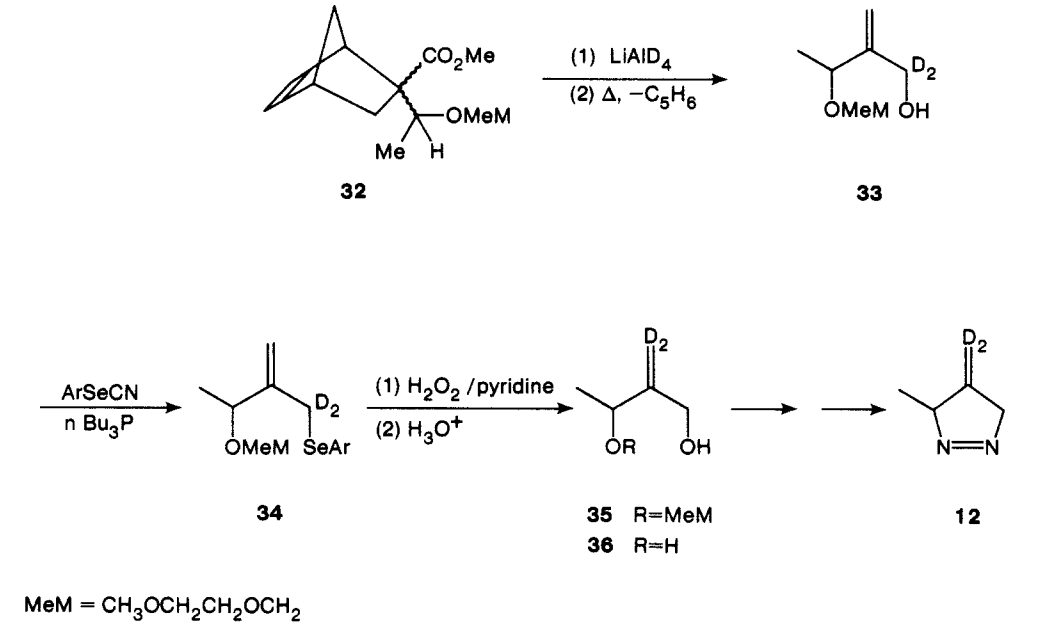
Product Studies. Only alkylidenecyclopropanes were produced upon the thermolysis of the pyrazolines studied. Tables III and IV give the gas chromatographic analyses of the structural isomers produced. These results were confirmed by both ^1H and ^2H NMR.[13] The products derived from the dimethyl compounds **15–16** were found to be slowly interconverting under the reaction conditions and the observed values have been corrected to zero time by standard kinetic procedures. It was also necessary to check for any degenerate rearrangement when dealing with the dideuterio

(13) There is no thermochemical preference by deuterium for the endo or exo position since a sample of tetradeuteriomethylenecyclopropane gives a 67:33 mixture at equilibrium.[9] Because of the long relaxation times associated with methylenecyclopropanes, we used CW methods where possible, or long delays between pulses for FT spectra.

Scheme IV

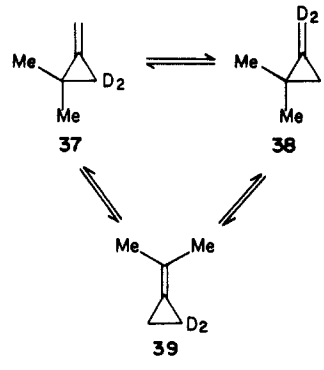


Scheme V



MeM = $CH_3OCH_2CH_2OCH_2$

compounds. The 2-methylmethylenecyclopropane-d_2 was found to be stable under the reaction conditions; however, the 2,2-dimethylmethylenecyclopropanes-d_2 (**37** and **38**) were intercon



verting slowly, and a correction was necessary for the degenerate rearrangement which is 21 times faster[14] than the isomerization to isopropylidenecyclopropane (**39**).

Discussion

The decrease in activation energy from 47.2[15] kcal mol^{-1} for azoethane to 42.8[16] for azo-2-methyl-2-propane is generally attributed to the stabilization of the incipient radical by the addition of methyl groups, and a decrease of 1–2 kcal mol^{-1} per methyl is common for homolytic cleavage reactions. The data in Table I demonstrated that analogous substitution at C-3 or C-5 generally increases the activation energy and decreases the rate. Using

(14) Le Fevre, G. N.; Crawford, R. J. *J. Org. Chem.* **1986**, *51*, in press.
(15) Sandhu, H. S. *J. Phys. Chem.* **1968**, *72*, 1857–1065.
(16) Levy, J. B.; Copeland, B. K. W. *J. Am. Chem. Soc.* **1960**, *82*, 5314–5318.

Table V. Percentage *exo*-Methylene-d_2 for the 2,2-Dimethylmethylenecyclopropane and 2-Methylmethylenecyclopropane Produced upon Thermolysis (170 °C)

reactant	% *exo*-d_2	reactant	% *exo*-d_2
15[a]	55 ± 1	**11**	64 ± 1
16[a]	52 ± 1	**12**	46 ± 1

[a] Corrected for the degenerate rearrangement of 2,2-dimethyl-3,3-dideuteriomethylenecyclopropane-d_2 to 2,2-dimethyldideuteriomethylenecyclopropane-d_2; see ref 13.

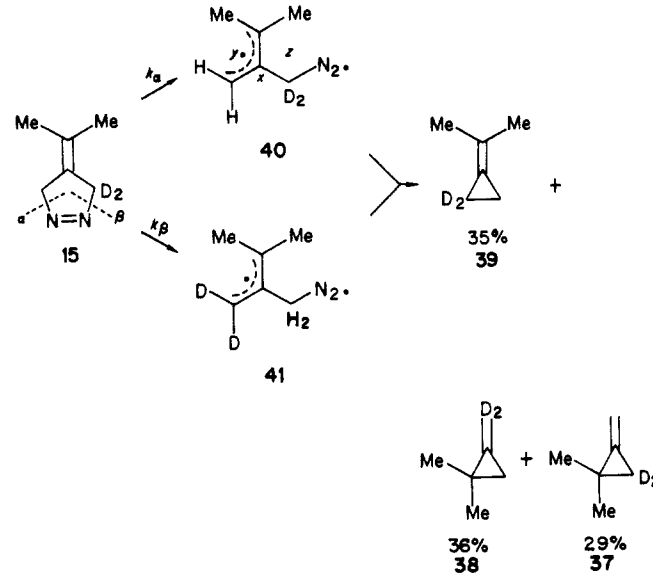
Table VI. Percentage Isomer Proportions of Methylenecyclopropanes Obtained by the Thermolysis (170 °C) of Deuterated Monomethyl-4-methylene-1-pyrazolines

	cyclopropanes			
	ethylidene-d_2		methylmethylene-d_2	
reactant	*E*	*Z*	endo	exo
11	13	7	51	29
12	8	11	37	44
7[a]	9	1	17	73
8[a]	1	9	80	10

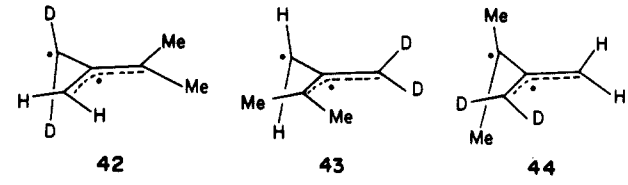
[a] See ref 3.

secondary deuterium isotope effects, we have observed rates consistent with a C–N bond-breaking process as the rate-determining step for the thermolysis of 4-methylene-1-pyrazolines.[3] Kinetically, we were not able to distinguish between a concerted breaking of two C–N bonds and a stepwise process. When the products were examined, we were able to fit all the deuterated methylenecyclopropanes to a scheme involving an allyldiazenyl intermediate, e.g., Scheme I. The data in Tables II–IV require that an intermediate be involved. Whereas the thermolysis rates follow the order **3** > **12** > **11**, the product ratios are **3** < **11** < **12**, the deuterium isotope effect being larger on the product-determining step when substitution is on the exocyclic methylene, and the KIE being larger when the deuterium substitution is on the endocyclic α-methylene.

Deuteration of the isopropylidene compound **2** to give **15** decreases the thermolysis rate 12%. This constitutes a free energy change of 51 ± 8 cal/mol per deuterium, considerably less than the generally accepted value of 80–120 cal mol^{-1} per deuterium.[17] If this is calculated as a single-bond-cleavage process and the thermolysis rate for **2** is $2k_\alpha$, then an intramolecular KIE (k_α/k_β) of 1.27 ± 0.04 is obtained and the value $\delta\Delta G^\ddagger$ per deuterium is 107 ± 14 cal mol^{-1}. Our previous mechanistic study required that the allyldiazenyl intermediates close by three modes *x*, *y*, and *z*.[18] If we assume, as was found earlier,[3] that the detuerated allylic methylene is slower to rotate into the cyclopropane conformation than is the CH_2 group[19] and use the value k_H/k_D = 1.40 obtained from the parent system, then the values of **x**/**y**/**z** of 0.38:0.25:0.37 are obtained. An attractive alternative is to consider the loss of nitrogen from the initially formed intermediates **40** and **41** to produce the corresponding Chesick diradicals **42** and **43**, respectively. Such diradicals would then be expected to close, using the least motion principle, to the corresponding methylenecyclopropanes. If we assume that the intermediates **42** and **43** are produced in the proportions 56:44 on the basis of the KIE and

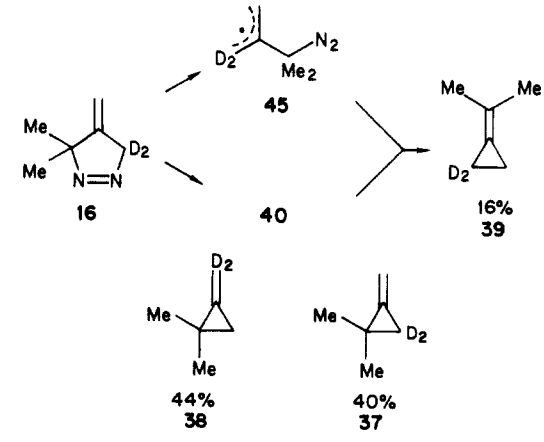


that **42** closes 62% of the time by rotation of the $(CH_3)_2C$ termini,



as is the case from the thermolysis of **2**, then the amount of **37** produced would be 35% and the yield of **39** via **42** would be 21%, leaving 14% to come via **43**, and thus predicting a yield of 28% for **38**, contrary to the experimental observations in Table V.

Replacing an α-hydrogen by methyl normally produces an acceleration of the thermolysis rate for azo compounds,[1] but such is not the case for the 4-methylene-1-pyrazoline system. Notably, the 3,3-dimethyl compound **4** undergoes thermolysis 30% slower than the parent **1**. Steric interactions can play a major role, if **4** is to attain a conformation such that the allylic resonance will accelerate the rate then the methyl groups can cause steric compression in the transition state; thus, the intermediate **45** for the thermolysis of **4** is expected to be a significant contributor. The secondary deuterium KIE for **16** is 75 ± 10 kcal mol^{-1} per deuterium, only slightly less than the 80–110 cal mol^{-1} values that characterize complete carbon–nitrogen bond rupture.[17] We thus



expect **16** to proceed principally through **45**. The 16% yield of isopropylidenecyclopropane would limit the participation via **40** to 45% of the reaction. The tertiary diazenyl radical **45** is expected to very rapidly loose nitrogen[21] and could be expected to form the

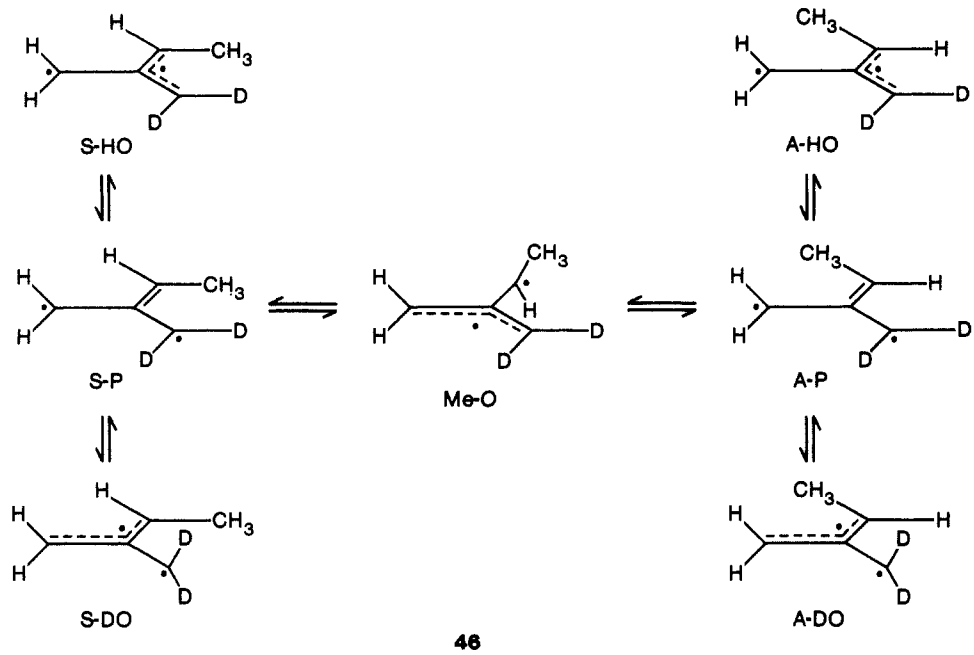
(17) Halevi, E. A. *Prog. Phys Org. Chem.* **1963**, *1*, 109–221. Zavitsas, A. A.; Seltzer, S. *J. Am. Chem. Soc.* **1964**, *86*, 1265–1267. Crawford, R. J.; Takagi, K. *J. Am. Chem. Soc.* **1972**, *94*, 7406–7416. Seltzer, S.; Dunne, F. T. *J. Am. Chem. Soc.* **1965**, *87*, 2628–2635. Seltzer, S.; Mylonakis, S. G. *J. Am. Chem. Soc.* **1907**, *89*, 6584–6589.

(18) The modes *x*, *y*, and *z* used here are equivalent to a partial rate ratio, i.e., $x = k_x/(k_x + k_y + k_z)$, $y = k_y/(k_x + k_y + k_z)$, etc., and require that the initial cleavage step is not reversible. None of our control experiments has demonstrated any detectable isomerization such as **2** ⇌ **4** or **11** ⇌ **12**.

(19) This type of isotope effect has been observed earlier in the isomerization of dimethylmethylenecyclopropane to ethylidenemethylcyclopropane, wherein k_H/k_D = 1.31 ± 0.04: Gajewski, J. J.; Chow, S. K. *J. Am. Chem. Soc.* **1977**, *99*, 5696–5707.

(20) Chesick, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 2720–2723.

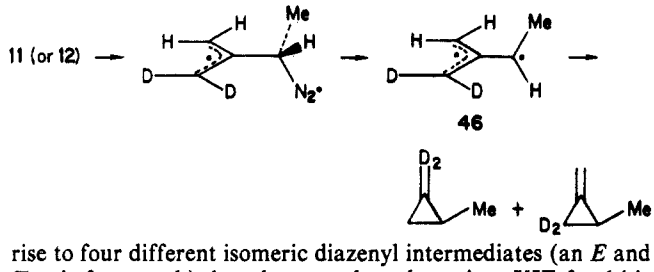
Scheme VI



46

Chesick intermediate **44**. If **44** is formed, then it would produce only the 2,2-dimethylmethylenecyclopropanes. This would account for the decrease yield of isopropylidenecyclopropane relative to that produced from **15**. If on the basis of the magnitude of the secondary deuterium KIE and the yield of isopropylidenecyclopropane we portion the thermolysis of **16** into a 60:40 ratio for the formation of **45** and **40**, and when the values of the x/y/z closure modes 0.38:0.25:0.37 obtained above for **40** are used, then the product ratio 16:44:40 observed for the isopropylidene-*exo*-d_2,*endo*-d_2 from **16** is predicted as 15:44:41, well within experimental error of the analytical procedures.[22]

Taken along with the kinetic data, the product distributions in Table VI place a number of constraints upon the mechanism of thermolysis of 3-methyl-4-methylene-1-pyrazoline (**3**). The secondary deuterium KIE for **11** (and **13**) imply that the C(5)–N bond is extensively broken in the rate-determining transition state. The rupture of the CH_2–N bond leads to a diazenyl radical that is expected to loose nitrogen rapidly[21] and to give rise to the Chesick intermediate **46**. Both **11** and **12** would give rise to **46**, and the product proportions from these compounds would be identical. Breaking the C(3)–N bond of **11** and **12** would give



rise to four different isomeric diazenyl intermediates (an *E* and *Z* pair from each), but the secondary deuterium KIE for **14** is small such as to imply that this process does not play a major role. Clearly, a more complex mechanism, or mixture of mechanisms, than has been suggested here is required to explain the monomethyl derivatives. Our observations lead us to conclude that the larger steric volume of methyl, relative to hydrogen, on the carbon attached to the nitrogen counteracts the inductive effect that normally gives rise to the order 3° > 2° > 1°, and thus the initial cleavage, as demonstrated by the secondary deuterium KIE, occurs at the methylene carbon–nitrogen bond (CH_2—N=). This cleavage results in a diazenyl radical[21] that rapidly loses nitrogen to produce a Chesick intermediate which closes in a conventional manner to form the methylenecyclopropanes. Such a mechanism is consistent with both the rates and products for all of the 4-methylene-1-pyrazolines. Anomalies arise in those cases wherein substituents are on the exo-cyclic methylene, and the products are more difficult to predict.

Table VII. Percentage Yield of Products Incorporating the Exocyclic Carbon of the Reactant into the Cyclopropane Ring of the Product (see Structure **1**, Table I)

compound		% cyclopropane C	ref
7		90%	2
1b	$R_1 = CD_3$; R_2–R_4 = H; $R_5 = CH_3$	>92%	*a*
1c	R_1, R_2, $R_5 = CH_3$; R_3, R_4 = H	>88%	
1d	R_1 = *t*-Bu; R_2–R_5 = H	96%	

[a] See: Crawford, R. J.; Tokunaga, H.; Schrijver, L. M. H. C.; Godard, J. Y. *Can. J. Chem.* **1978**, *56*, 998–1004.

To date, four different 4-alkylidene--pyrazoline derivatives having one alkyl substituent on the exocyclic methylene (i.e., RCH=) have been studied. In each case, the exocyclic carbon has a significantly greater tendency to become a cyclopropane carbon (see Table VII) than is the case for unsubstituted, or disubstituted (H_2C= or R_2C=), compounds. Quite remarkably, Dolbier and Burkholder[22] have observed a closely analogous situation for the 4-(fluoromethylene)- and 4-(difluoromethylene)-1-pyrazoline. They have suggested that a set of partially equilibrating trimethylenemethane species are produced, analogous to Scheme VI and that "subtle deviations from the symmetry of the parent (C_4H_6) TMM could give rise, either via E_a or $\Delta S^{\ddagger}$ differences, to the observed preferred cyclizations". Theoretical support for a variety of singlet TMM derivatives having a very low barrier to interconversion has been provided by Feller et al.[22] Which of the seven possible intermediates is first produced from the isomeric monomethyldideuterio substrates **7**, **8**, **11**, and **12** will no doubt depend upon the reaction dynamics of the leaving nitrogen and the ease of interconversion between the syn (5-HO, S-P, and S-DO) and anti series (A-HO, A-P, and A-DO). The substrates **7** and **8** generate initially intermediates in the **46**-A and **46**-S subset, whereas **10** and **11** may produce in both subsets depending upon the orientation of the methyl upon departure of the nitrogen.

(21) Engel, P. S.; Gerth, D. B. *J. Am. Chem. Soc.* **1983**, *105*, 6849–6851. Yamashita, K.; Kaminoyama, M.; Yamabe, T.; Fukui, K. *Chem. Phys. Lett.* **1981**, *83*, 78–82. Dannenburg, J. J.; Rocklin, D. *J. Org. Chem.* **1982**, *47*, 4529–4534. Klärner, F. G.; Volker, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 73–74.

(22) The values of k_H/k_D observed by Gajewski and Chow of 1.31 were used for ring closure of **44**. While the success of this type of calculation is supportive of the diazenylallyl intermediate **37**, there is a range of values that can predict these results and such examples do not constitute proof of the nitrogens involvement.

Conclusions

Evidence is presented to support the characterization of the rate-determining step of 4-methylene-1-pyrazoline thermolysis as being primarily affected by the cleavage of one carbon–nitrogen bond. An intermediate, or set of intermediates, is required to rationalize all the products. In the cases where methyl groups are placed α to the nitrogen, the reaction is slower and the normal kinetic order of 3° > 2° > 1° does not hold, but products are readily explained from a Chesick-type intermediate. Stereochemical tests will be required to detail the interconversion of possible TMM intermediates.

Experimental Section

The ^{1}H NMR spectra were obtained by using a Bruker WP-80 spectrometer, and a Bruker WH-400 high-field cryospectrometer. The ^{2}H NMR analyses were measured in the WH-400 using long delay times between pulses.

Exact masses were determined on an A.E.I. MS-50 mass spectrometer. Microanalyses were carried out by the Microanalytical Laboratory of the Department of Chemistry, University of Alberta.

The kinetic measurements were made by a procedure described previously.[3]

5-Carbomethoxy-6,6-dimethyl-2-norbornene (18). A mixture of freshly distilled cyclopentadiene (20 g, 0.303 mol and methyl 3-methyl-2-butenoate (87.5 g, 0.768 mol) was placed in four 90-mL Pyrex tubes, degassed, sealed, and heated to 140 °C for 3 weeks. When the tubes were opened, the contents were fractionally distilled to afford 16 g (29%) of **18**, bp 93–96 °C (20 torr), [lit. bp 68 °C (2.5 torr)].[8]

5-Carbomethoxy-6,6-dimethyl-5-(hydroxymethyl)-2-norbornene (19). A 2.3 M solution of *n*-butyllithium (37 mL, 85 mmol) was added at −78 °C to a solution of diisopropylamine (12.5 mL, 89 mmol) in THF (200 mL) under nitrogen atmosphere. After stirring for 1 h at −78 °C a solution of **18** (14.5 g, 81 mmol) in 50 mL of THF was added dropwise. After 3 h, a large excess of paraformaldehyde (28 g, 311 mmol) was added at once and again stirred at room temperature overnight. The product was purified by distillation, bp 89–95 °C (0.06 torr), to give 10 g (61% yield): ^{1}H NMR ($CDCl_3$) (2:1 mixture of isomers) (major isomer) δ 0.83 (s, 3 H), 1.12 (s, 3 H), 1.46 (m, 1 H), 1.72 (d, 1 H), 2.10 (s, 1 H, exch. with D_2O), 2.24 (s, 1 H), 3.08 (d, 1 H), 3.62 (s, 3 H), 3.64 (d, 1 H), 4.16 (d, 1 H), 6.08 (m, 1 H), 6.42 (m, 1 H), (minor isomer) δ 0.80 (s, 3 H), 1.08 (s, 3 H), 1.46 (m, 1 H), 1.52 (d, 1 H), 1.96 (d, 1 H), 2.32 (s, 2 H, 1 H exch. with D_2O), 3.24 (d, 1 H), 3.72 (s, 3 H), 3.88 (d, 1 H), 6.26 (m, 2 H); MS *m/e* (M^+) calcd 210.1251, obsd 210.1249.

6,6-Dimethyl-5-(hydroxymethyl)-5-(hydroxymethyl-d_2)-2-norbornene (20). Pulverized lithium aluminum deuteride (2.3 g, 55 mmol) in 100 mL of ether was stirred under nitrogen at the reflux for 2 h. A solution of **19** (9.5 g, 45 mmol) in 75 mL of ether was added at such a rate as to maintain a gentle reflux. The reaction mixture was refluxed overnight, and when it cooled, 2.3 mL of water, 2.3 mL of 15% sodium hydroxide, and 7 mL of water were added successively. Magnesium sulfate (10 g) was then added, and stirring was resumed for an additional hour. The organic solution was isolated by filtration, dried, and concentrated under reduced pressure. The product crystallized on standing to give 7.8 g (94% yield) recrystallized from ether/pentane: mp 215–217 °C.

For the nondeuterated material: Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.43; H, 9.82.

^{1}H NMR ($CDCl_3$) δ 0.83 (s, 3 H), 1.14 (s, 3 H), 1.36 (d, 1 H, J = 9.2 Hz) 1.76 (d, 1 H, J = 9.2 Hz), 2.28 (m, 1 H), 2.88 (m, 1 H) 3.52 (s, 2 H), 3.88 (m, 2 H), 6.20 (m, 2 H).

2-Isopropylidene-1,3-dibromopropane-1,1-d_2 (21). The nondeuterated material has been described previously.[2] Thermolysis of **20** (7.8 g, 42 mmol) produced 4.26 g (87% yield) of the diol which was purified by distillation, bp 84 °C (0.2 torr). The mass spectrum indicated 98.6 ± 0.1% d_2, based on the molecular ion peak. The dibromide, 2.23 g (59% yield), was obtained from the glycol by using the procedure of Corey et al.;[9] bp 50 °C (0.01 torr); ^{1}H NMR ($CDCl_3$) δ 1.82 (s, 6 H), 4.15 (s, 2 H), isotopic purity 99 ± 1%.

4-Isopropylidene-1-pyrazoline-5,5-d_2 (15). Transformations starting with **21** were carried out in a manner analogous to that for the nondeuterated material, i.e., first conversion of **21** to 1,2-dicarbethoxy-4-isopropylidenepyrazolidine-5,5-d_2 followed by hydrolysis to the hydrochloride salt and then oxidation. For the oxidation step, the hydrochloride salt (3.7 g, 25 mmol) was added in small portions over 3 h to a mechanically stirred slurry of red mercuric oxide (35 g) and anhydrous sodium sulfate (35 g) in 80 mL of absolute ether. The product was purified by distillation to give 2.1 g (77% yield): ^{1}H NMR (acetone-d_6) δ 1.64 (triplet, 6 H, J = 2 Hz), 4.86 (m, 2.18 H, J = 2 Hz), 91 ± 1% deuteration.

1,2-Dicarbomethoxy-3,3-dimethyl-4-hydroxypyrazolidine (23). A suspension of lithium aluminum hydride (50 g, 1.31 mol) in dry THF (800 mL) was added slowly to a well-stirred suspension of 5,5-dimethyl-4-hydroxy-3-pyrazolidone[25] (45 g, 346 mmol) in dry THF (800 mL) maintained under nitrogen at room temperature. After completion of the addition, the reaction mixture was heated slowly to ebullition. The mixture was then refluxed (2 h) and cooled and distilled water (50 mL), 15% sodium hydroxide (50 mL), and distilled water (150 mL) were added successively and the mixture stirred 1 h.

An aliquot of the solution was concentrated, dried, and recrystallized to give **22**: mp 85 °C; ^{1}H NMR (Me_2SO-d_6) δ 0.9 (s, 3 H), 1.0 (s, 3 H), 2.57 (dd, 1 H, J = 11, J = 3 Hz), 3.21 (dd, 1 H, J = 6, J = 11 Hz) 3.62 (br s, 3 H exch. with D_2O), 3.75 (dd, J = 6, J = 3 H); MS, *m/e* (M^+) calcd for $C_5H_{12}N_2O$ 116.0945, obsd 116.0950.

The remaining reaction mixture was cooled to −25 °C, and methyl chloroformate was added in large excess (100 mL). The mixture was stirred at room temperature for 2 days, the solids filtered and washed with ether, and the organic solution was concentrated to give a yellow oil. The major product (60%) was analyzed by GC–MS as the *O*-carbomethoxy derivative of **23**.

The crude oil was then dissolved in methanol (300 mL) and treated with potassium carbonate solution (112 g in 200 mL of water), stirred for 2 h, and then neutralized with acetic acid. The solution was then reduced to one-third of its volume by evaporation and extracted with ether by using a Soxhlet system for 2 days. The pure material was obtained by chromatography on a Kieselgel-60G column. Recrystallization from ether gave 40 g (50% yield): mp 76 °C; ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 3 H), 1.50 (s, 3 H), 3.75 (m, 6 H), 3.52 (m, 2 H), 4.06 (m, 2 H); MS, *m/e* (M^+) calcd 232.1055, obsd 232.1050.

Anal. Calcd for $C_9H_{16}N_2O_5$: C, 46.35; H, 6.94; N, 12.06. Found: C, 46.65; H, 7.06, N, 12.07.

1,2-Dicarbomethoxy-3,3-dimethylpyrazolidin-4-one (24). Chromium trioxide (25.8 g, 258 mmol) was added to a stirred solution of pyridine (41 g, 519 mmol) in 700 mL of methylene chloride. The burgundy solution was stirred at room temperature for 30 min, and then a solution of **23** (9.7 g, 42 mmol) in 20 mL of methylene chloride was added in one portion. After the solution was stirred an additional 2 h at room temperature, the solution was decanted from a tarry residue which was washed with 200 mL of ether. The combined organic fractions were filtered through a pad of Florosil and concentrated. Distillation gave 7.7 g (80% yield) of a colorless oil: bp 90 °C (0.1 torr): ^{1}H NMR ($CDCl_3$) 1.44 (s, 6 H), 3.70 (s, 3 H), 3.80 (s, 3 H), 4.0 (m, 2 H); IR 1776, 1715 cm^{-1} (C=O); MS, *m/e* (M^+) calcd 230.0898, obsd 230.0903.

24-d_2. A total of four exchanges were carried out on 9 g of **24** in methanol-*O*-*d* (8.1 g, 246 mmol) containing 0.03 g of sodium metal warmed to 45 °C. When the mixture was cooled and extracted into methylene chloride, the methylene signal at δ 4.0 was monitored. The final sample was of 95 ± 1% isotopic purity (54% recovery).

1,2-Dicarbomethoxy-3,3-dimethyl-4-methylenepyrazolidine-5,5-d_2 (25). Methyltriphenylphosphonium bromide (4.4 g, 12.3 mmol) and 40 mL of dry DME were added to a 200-mL three-necked flask fitted with a stirrer and dropping funnel and cooled to 0 °C under an atmosphere of nitrogen. A 1.57 M solution of *n*-butyllithium (7.15 mL) was added with vigorous stirring. The temperature was then increased to 65 °C and maintained for 3 h. When the solution was cooled to 0 °C, a solution of **24**-d_2 (2.3 g, 10 mmol) in 20 mL DME was added dropwise. The temperature was gradually increased to 50 °C, and stirring was maintained overnight. Acetone (1 mL) was added and the mixture stirred 30 min. After a conventional workup, the concentrated oil was eluted through a Kieselgel-60G column with ether/pentane (30/70). Distillation gave 1.06 g (46% yield), bp 80 °C (0.5 torr), of **25**: ^{1}H NMR (nondeuterated sample) ($CDCl_3$) 1.52 (s, 6 H), 3.72 (s, 3 H), 3.76 (s, 3 H), 4.96 (t, J = 2 Hz, 1 H), 5.02 (t, J = 2 Hz, 1 H), 4.26 (m, 2 H) (the deuterated sample lacked the signal at δ 4.26); MS, *m/e* (M^+) of nondeuterated material calcd 228.1106, obsd 228.1106. Mass spectrum indicated 96.0 ± 0.1% isotopic purity for **25**.

3,3-Dimethyl-4-methylenepyrazolidene-5,5-d_2 Hydrochloride (26). The procedure used was analogous to that of the nondeuterated material described earlier:[10] ^{1}H NMR (D_2O) δ 1.51 (s, 6 H), 4.12 (t, J = 2.2 Hz, 2 H), 5.26 (m, 2 H). For the nondeuterated material: Anal. Calcd for $C_6H_{13}N_2Cl$: C, 48.48; H, 8.82; N, 18.85. Found: C, 48.15; H, 8.80; N, 18.94.

3,3-Dimethyl-4-methylene-1-pyrazoline-5,5-d_2 (16). The hydrochloride **26** (0.9 g, 6.0 mmol) was added slowly to a stirred slurry of red

(23) Dolbier, W. R., Jr.; Burkholder, C. R. *J. Am. Chem. Soc.* **1984**, *106*, 2139–2142.

(24) Feller, D.; Tanaka, K.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1982**, *104*, 967–972 and references cited therein.

(25) Martynov, V. F.; Belov, I. B. *Zh. Obsch. Khim.* **1961**, *31*, 1509–1510.

mercuric oxide (9 g) and anhydrous sodium sulfate (9 g) in 25 mL of dry ether. The product was purified by distillation to give 0.357 g (54% yield) of **16**: bp 55 °C (27 torr); ^{1}H NMR ($CDCl_3$) δ 1.4 (s, 6 H), 5.0 (s, 1 H), 5.2 (s, 1 H); >95% isotopic purity.

3,3-Dimethyl-4-dideuteriomethylene-1-pyrazoline-*5,5*-d_2 (17). The procedure was analogous to that described previously[6] for the nondeuterated material except that 2-diazopropane was added to allene-d_4.[26] Mass spectrometry indicated 99 ± 1% isotopic purity. ^{1}H NMR consisted of a single peak at δ 1.4.

5-Carbomethoxy-5-(1-hydroxyethyl)-2-norbornene (27). *n*-Butyllithium (186 mL, 1.6 N) (298 mmol) was added, at −78 °C, under a nitrogen atmosphere, to a solution of diisopropylamine (30.3 g, 300 mmol) in 900 mL of dry THF. A solution of 5-carbomethoxy-2-norbornene (44 g, 290 mmol) in 120 mL of dry THF was added dropwise at −78 °C. After 1 h, a solution of freshly distilled acetaldehyde (20 g, 440 mmol) in 100 mL of THF wass added dropwise and the solution then allowed to warm to room temperature. A conventional workup gave 48 g (85% yield) of **27**, bp 80 °C (0.5 torr).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22; O, 24.46. Found: C, 67.27; H, 8.13; O, 24.51.

5-(1-Hydroxyethyl)-5-(hydroxymethyl-d_2)-2-norbornene (28). Pulverized lithium aluminum deuteride (5 g, 119 mmol) in 270 mL of dry ether was warmed for 3 h under a dry stream of nitrogen. When the solution cooled, a solution of **27** (31 g, 158 mmol) in 30 mL of dry ether was added. The mixture was refluxed overnight and when it cooled, 5 mL of water, 5 mL of 15% sodium hydroxide, and 15 mL of water were added successively. Ether extraction, drying, concentration, and distillation gave a product of 18.7 g of **28** (70% yield), bp 95–100 °C (0.2 torr). For the nondeuterated material: Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59; O, 19.02. Found: C, 71.38; H, 9.57; O, 19.17.

2-Methylene-1,3-Butanediol-*1,1*-d_2. A sample of **28** (18.7 g, 110 mmol) was thermolyzed by dropping onto a glass-bead column heated to 450 °C at 0.1 torr. The trapped product was purified by distillation to give 9 g (79% yield) of the desired diol: bp 112–113 (16 torr); ^{1}H NMR ($CDCl_3$) δ 1.31 (d, J = 6.5 Hz, 3 H), 3.98 (s, 2 H, exch. with D_2O), 4.40 (q, J = 6.5 Hz, 1 H); MS >99% isotopic purity. For the nondeuterated material: Anal. Calcd for $C_5H_{10}O_2$: C, 58.80; H, 9.87; O, 31.33. Found: C, 58.86; H, 9.80; O, 31.41.

3-Chloro-2-(chloromethyl-d_2)-*1*-butene (29). Dry triphenylphosphine (69 g, 263 mmol) was added to a stirred solution of 2-methylene-1,3-butanediol-*1,1*-d_2 (9 g, 87 mmol) in 90 mL of dry THF and 210 mL of carbon tetrachloride. When the solution was refluxed for 2 h under a stream of nitrogen, a large quantity of white solid was formed. When it cooled, 400 mL of pentane was added and the solids removed by filtration. Distillation gave 6.6 g of **24** (54% yield): bp 73 °C (57 torr); ^{1}H NMR δ 1.74 (d, 3 H) 4.76 (m, 1 H) 5.34 (d, 2 H). Mass spectral analysis indicated 99 ± 1% isotopic purity. The material was used without delay.

1,2-Dicarbethoxy-3-methyl-4-methylenepyrazolidine-*5,5*-d_2 (30). Sodium hydride (2.33 g, 69 mmol) was added to a solution of *sym*-dicarbethoxyhydrazine (12.1 g, 69 mmol) in 80 mL of HMPA maintained at 0 °C under a nitrogen atmosphere. After 6 h of stirring, **29** (9.3 g, 67 mmol) was added and the stirring continued an additional 72 h. A 0.65 M solution of sodium ethoxide in 107 mL of ethanol was added followed by sodium iodide (0.6 g), and stirring continued for 48 h at room temperature. Filtration, concentration, and ether extraction gave an organic layer which was dried over magnesium sulfate then concentrated and chromatographed on Kieselgel-60G. Distillation gave 5.6 g of **30** (35% yield): bp 68 °C (0.1 torr); ^{1}H NMR ($CDCl_3$), δ 1.30 (m, 9 H), 3.92 (d, J = 15 Hz, 0.04 H), 4.23 (m, 4 H) 4.60 (d, J = 15 Hz, 0.04 H) 4.71 (m, 1 H) 5.01 (d, 1 H) 5.07 (d, 1 H). The mass spectrum indicated 96.7 ± 0.1% dideuteration. MS, *m/e* (M^+) of the nondeuterated maerial calcd 242.1261, obsd 242.1260.

3-Methyl-4-methylenepyrazolidine-*5,5*-d_2 Hydrochloride (31). A solution of potassium hydroxide (1.5 g) in 15 mL of *n*-propanol, 1.5 mL of water, and **30** (0.9 g, 4 mmol) was maintained at 100 °C for 3 h under an inert atmosphere. The mixture was then distilled under vacuum (0.1 torr) and the distillate trapped at −80 °C. Acidification at 0 °C with excess concentrated hydrochloric acid gave 0.5 g (95% yield) of the hydrochloride **31**: ^{1}H NMR (D_2O) δ 1.41 (d, 3 H), 4.11 (m, 1 H), 5.23 (d, 1 H), 5.29 (d, 1 H), 4.0 (m, 0.05 H); exact mass calcd for nondeuterated material 99.0919, obsd 99.0874. Isotopic purity was 97 ± 1% by mass spectrometry.

3-Methyl-4-methylenepyrazoline-*5,5*-d_2 (11). The hydrochloride **31** (0.45 g, 3 mmol) dissolved in 2 mL of methanol was added slowly to a slurry of red mercuric oxide (3.4 g) and sodium sulfate 3.4 g) in 100 mL of ether. After 0.5 h of stirring, the solids were filtered off and washed with ether, and the organic layer was concentrated. The residue was purified by trap-to-trap distillation (0.16 g, 50% yield): ^{1}H NMR (C_6D_6) δ 1.19 (d, 3 H), 4.38 (m, 1 H), 4.59 (d, 1 H), 4.64 (d, 1 H), and trace signals at 4.57 and 4.38 indicating 97 ± 1% isotopic purity; ^{2}H NMR (C_6D_6) indicated >99.8% of total deuterium at the 5-position.

Preparation of Methoxyethoxymethyl Ether (32). The procedure of Corey[28] using chloromethyl 2-methoxyethyl ether (10.5 g, 8.4 mmol) of **27** (13 g, 66 mmol) in dry THF was used. The ether **32** was purified by distillation, bp 125–130 °C (0.5 torr), to give 14 g (74% yield); MS, *m/e* (M^+) calcd 284.1617, obsd 284.1621.

2-Methylene-*3*-*O*-[(2-methoxyethoxy)methyl]-1,3-butanediol-*1,1*-d_2 (33). Pulverized lithium aluminum deuteride (3 g, 75 mmol) in 100 mL of dry ether was used to reduce **32** (14 g, 49 mmol); after the solution refluxed overnight, the product was worked up in a manner analogous to **28**. Distillation gave 9.9 g (83% yield) of the norbornenyl β-hydroxymethoxyethoxymethyl ether, bp 120 °C (1 torr). For the nondeuterated material: Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44; O, 24.97. Found: C, 65.71; H, 9.50; O, 24.99.

Flash thermolysis was described above for **28** gave a 79% yield of **33**: bp 83 °C (0.2 torr): ^{1}H NMR ($CDCl_3$) δ 1.35 (d, 3 H), 2.42 (s, 1 H, exch. in D_2O), 4.40 (q, 1 H), 5.15 (s, 1 H), 5.20 (s, 1 H), 4.18 (d, 0.04 H), the MEM group signals were at δ 4.75 (s, 2 H), 3.70 (m, 4 H), 3.40 (s, 3 H). For the nondeuterated material: Anal. Calcd for $C_9H_{18}O_4$: C, 56.82; H, 9.54; O, 33.64. Found: C, 56.71; H, 9.51; O, 33.15.

Interconversion of 33 to 35. The alcohol **33** (1.9 g, 10 mmol) and 2-nitrophenylselenocyanate (2.72 g, 12 mmol) were dissolved in 30 mL of dry pyridine, and tri-*n*-butylphosphine (3 mL, 12 mmol) was added dropwise over 1 h according to the method of Clive.[12] Chromatographic workup on silica gel gave 2.76 g (73% yield) of a yellow oil; MS, *m/e* (M^+) for nondeuterated sample calcd 375.0579, obsd 375.0579.

Rearrangement of 34 to 35. The selenide **34** (6.16 g, 16 mmol) and 3 mL of pyridine were dissolved in 100 mL of methylene chloride, and an excess of 15% hydrogen peroxide (35 mL) was added. After an induction period, an exothermic reaction occurred with the formation of a large amount of precipitate and a change from yellow to orange. The solution was cooled, 50 mL of water was added, and the pH was lowered to 2 by using the hydrochloric acid. Filtration and ether extraction of the aqueous phase followed by drying and distillation gave 2.67 g of **35** (85% yield). ^{1}H NMR and ^{2}H NMR indicated 98 ± 2% deuterium exclusively in the vinylic position.

2-(Methylene-d_2)-1,3-butanediol (36). The ether **35** (3 g, 16 mmol) and 5.2 mL of 3 N hydrochloric acid in 25 mL of ethanol were heated for 1 h. Neutralization with sodium bicarbonate followed by filtration, concentration, and distillation gave 1.4 g (87% yield) of the diol **36**: bp 68 °C (0.1 torr); ^{1}H NMR ($CDCl_3$) δ 1.35 (d, 3 H) 2.87 (s, 2 H, exch. with D_2O), 4.22 (s, 2 H), 4.45 (q, 1 H). ^{2}H NMR indicated deuteration exclusively n the vinylic position.

Conversion of 36 to 12. The diol **36** was treated to the same sequence as **28** → **29** → **30** → **31** and upon oxidation gave **12**: ^{1}H NMR (C_6D_6) δ 1.18 (d, J = 7.5 Hz, 3 H), 4.38 (q, J = 7.5 Hz, 1 H), 4.40 (half of AB quartet, J = 21.7 Hz, 1 H), 4.59 (half of AB quartet, J = 21.7 Hz, 1 H), 4.57 (d, 0.039 H), 4.60 (d, J = 0.039 Hz), 96 ± 1% isotopic purity. ^{2}H NMR indicated >99% deuterium at the *exo*-methylene position.

Ethyl *N*-Ethyl-*1,1*-d_2-carbamate. Pulverized lithium aluminum deuteride (4.5 g, 120 mmol) in 100 mL of ether was refluxed for 1 h under nitrogen. When the solution was cooled, freshly distilled acetonitrile (4.6 g, 112 mmol) in 20 mL of ether was added dropwise followed by 1 h of reflux. When it was cooled to 0 °C, 4.5 mL of distilled water, 4.5 mL of 15% sodium hydroxide, and 12.5 mL of water were added successively. After it was cooled to −20 °C, ethyl chloroformate (50 g, 460 mmol) was added dropwise. The solids were removed by filtration, and after ether extraction, drying, and concentration, the carbamate, 7.6 g (57% yield), bp 78 °C (14 torr), was obtained: ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 3 H), 1.22 (t, 3 H), 4.12 (q, 2 H), 4.78 (s, 1 H, exch. with D_2O, 98 ± 2% isotopic purity.

Ethyl *N*-Nitroso-*N*-ethyl-*1,1*-d_2-carbamate. The procedure used was that described for the *N*-methyl derivative.[29] Starting from the carbamate (7.6 g, 64 mmol), a pink liquid, 6.8 g (72% yield), bp 70 °C (14 torr), was obtained: ^{1}H NMR ($CDCl_3$) δ 1.0 (s, 3 H), 1.46 (t, 3 H), 4.55 (q, 2 H) for the major isomer, and 1.12 (s, 7 H), 1.22 (t, 3 H), 4.10 (q, 2 H) for a minor isomer, 98 ± 2% isotopic purity.

3-Methyl-4-methylene-1-pyrazoline-*3*-d_1 (14). A solution of potassium hydroxide-*O*-*d* (2 g) and 15 mL of carbitol-*O*-*d* and 15 mL of ether was warmed to 50 °C in a 250-mL three-necked flask fitted with a stirrer, a dropping funnel, and a bent tube[30] leading to a condenser set for

(26) Morse, A. T.; Leitch, L. C. *J. Org. Chem.* **1958**, *23*, 990–993.

(27) Cope, A. C.; Ciganek, E.; LeBel, N. A. *J. Am. Chem. Soc.* **1959**, *81*, 2799–2804.

(28) Corey, E. J.; Gras, J. L.; Ulrich, P. *Tetrahedron Lett.* **1976**, 809–812.

(29) Hartman, W. N.; Phillips, R. "Organic Synthesis"; Wiley: New York, 1943; Collect. Vol. 2, pp 464–465.

downward distillation. A solution of ethyl *N*-nitroso-*N*-ethyl-*1,1-d*$_2$-carbamate (2 g, 13 mmol) in 20 mL of ether was added over 5 min. Fresh portions of ether were added until the distillate came over colorless. The orange solution of diazoethane-*1-d* in ether was cooled to −80 °C and transferred to a pressure bottle containing a large excess of allene (50 mL) at −80 °C. After a few hours at room temperature, the color disappeared and the reaction mixture was worked up as described previously;[31] 0.55 g (42% yield based on carbamate); ^{1}H NMR ($CDCl_3$) δ 1.49 (t, 3 H), 4.88 (half AB q, J = 21 Hz, 1 H), 5.04 (m, 1 H), 5.12 (m, 1 H), 5.02 (half AB q, J = 21 Hz, 1 H), 99% isotopic purity.

3-Methyl-4-methylene-*d*$_2$-1-pyrazoline-*5,5-d*$_2$ (13) was prepared as described previously[31] by the 1,3-dipolar addition of diazoethane[30] to allene-d_4:[26] ^{1}H NMR ($CDCl_3$) δ 1.51 (d, 3 H), 4.82 (q, 1 H), 99 ± 1% isotopic purity.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for support for this research. We thank the University of Alberta Mass Spectrometry Laboratory and the NMR Facility for the spectra they measured.

Registry No. 2, 55503-95-2; **3**, 67301-35-3; **4**, 55503-94-1; **11**, 99810-34-1; **12**, 99810-35-2; **13**, 99810-36-3; **14**, 99810-37-4; **15**, 99810-38-5; **16**, 99810-39-6; **17**, 99810-40-9; **18**, 83846-54-2; *exo*-**19**, 99810-41-0; *endo*-**19**, 99810-58-9; *exo*-**20**, 99810-42-1; *endo*-**20**, 99810-59-0; **20** (unlabeled derivative), 99810-60-3; **21**, 99810-43-2; **21** (1,3-diol), 99810-61-4; **22**, 99810-44-3; **22** (3-oxo derivative), 98069-71-7; **23**, 99810-45-4; **24**, 99810-46-5; **24**-d_2, 99810-64-7; **25**, 99810-47-6; **26**, 99810-48-7; **27**, 99810-49-8; **28**, 99810-50-1; **28** (unlabeled derivative), 62872-93-9; **29**, 99810-51-2; **30**, 99810-52-3; **31**, 99810-53-4; **32**, 99810-54-5; **33**, 99829-05-7; **33** (unlabeled derivative), 99810-69-2; **34**, 99810-55-6; **34** (unlabeled derivative), 99829-06-8; **35**, 99810-56-7; **36**, 99810-57-8; $Me_2C{=}CHCO_2Me$, 924-50-5; $ClCO_2Me$, 79-22-1; $Ph_3P{=}CH_2$, 3487-44-3; $MeC(=N_2)Me$, 2684-60-8; $D_2C{=}C{=}CD_2$, 1482-85-5; MeCHO, 75-07-0; $MeCH(OH)C(=CH_2)CD_2OH$, 99810-65-8; $MeCH(OH)C(=CH_2)CH_2OH$, 99810-66-9; $ClCH_2O(CH_2)_2OMe$, 3970-21-6; $2\text{-}O_2NC_6H_4SeCN$, 51694-22-5; $MeCD_2NHCO_2Et$, 99810-70-5; MeCN, 75-05-8; $ClCO_2Et$, 541-41-3; $EtO_2CN(CD_2Me)NO$, 99810-71-6; $H_2C{=}C{=}CH_2$, 463-49-0; $N_2{=}CH_2Me$, 1117-96-0; $EtO_2C(NH_2)_2CO_2Et$, 4114-28-7; cyclopentadiene, 542-92-7; 1,2-dicarbethoxy-4-isopropylidenepyrazolidine-*5,5-d*$_2$, 99810-62-5; 4-isopropylidenepyrazolidine-*5,5-d*$_2$ hydrochloride, 99810-63-6; 5-carbomethoxy-2-norbornene, 6203-08-3; norbornenyl β-hydroxymethoxyethoxymethyl ether-β,β-d_2, 99810-67-0; norbornenyl β-hydroxymethoxyethoxymethyl ether, 99810-68-1; 1-methyl-2-methylenecyclopropane-d_2, 99829-07-9; ethylenecyclopropane-d_2, 99829-08-0; 1,1-dimethyl-2-ethylidenecyclopropane-d_2, 99829-09-1; isopropylenecyclopropane-d_2, 99829-10-4; 1,1-dimethyl-2-(methylene-d_2)cyclopropane, 99810-72-7; 1-methyl-2-(methylene-d_2)cyclopropane, 67399-01-3.

(30) Wilds, A. L.; Meader, A. L. *J. Org. Chem.* **1948**, *13*, 763–765.
(31) Crawford, R. J.; Tokunaga, H.; Schrijver, L. H. M. C.; Godard, J. C. *Can. J. Chem.* **1978**, *56*, 998–1004.

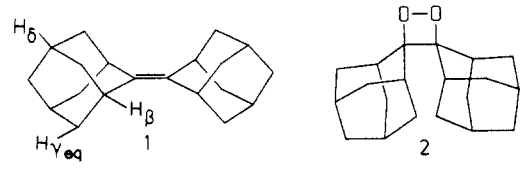
Dioxetane Radical Cations in Solution. An ESR and Cyclic Voltammetry Study

Stephen F. Nelsen,*† Daniel L. Kapp,† Fabian Gerson,‡ and Javier Lopez‡§

Contribution from S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, and Physikalisch-Chemisches Institut der Universität Basel, CH-4056 Basel, Switzerland. *Received April 26, 1985*

Abstract: The radical cation formed upon electrochemical oxidation either of adamantylideneadamantane **1** in an O_2-saturated solution or of the corresponding dioxetane **2** is shown by ESR spectroscopy to be **2**$^+$. This radical cation is relatively long-lived in CH_2Cl_2:CF_3CO_2H:$(CF_3CO)_2O$ solvent mixtures at low temperatures. The resolved hyperfine splittings are 0.325 mT (4 H) and 0.075 mT (6 H). Using deuterated derivatives, the larger splitting has been assigned to two pairs of γ_{eq}-protons and the smaller one to the two remaining pairs of γ_{eq}-protons and one pair of β-protons, with each β-proton situated in a different adamantylidene moiety of **2**$^+$ (the notation β and γ_{eq} refers to the structure of **1**). These data are consistent with a C_2 conformation of **2**$^+$ which is twisted at the dioxetane ring and does not enantiomerize on the hyperfine time scale at −110 °C. Dioxetane radical cations **11**$^+$ and **13**$^+$ generated from isopropylideneadamantane **10** and 3-pentylideneadamantane **12**, respectively, have also been studied under similar conditions by ESR spectroscopy. Their hyperfine data give no evidence of twisting at the dioxetane rings and provide a further example for the sensitivity of the long-range splittings to orientation of bonds relative to the spin-bearing orbital. Cyclic voltammograms indicate that the $E°'$ value for **2** is 0.66 V anodic of **1** at −78 °C, so that electron transfer from **1** to **2**$^+$ is exothermic by 15 kcal/mol.

In his review of the radical aspects of photooxygenation, Bartlett[1] reported an unpublished observation with M. J. Shapiro that $(p\text{-}BrC_6H_4)_3N^+$ converts adamantylideneadamantane **1** and $^3O_2$ to dioxetane **2**, pointing out the similarity of this reaction to the formation of endoperoxides from dienes, as described by Barton and co-workers.[2] He suggested[1] that both reactions proceed through the organic radical cation. In the same year, Haynes and co-workers,[3] as well as Tang and co-workers,[4] also argued for the intermediacy of diene radical cations in the conversion of dienes to endoperoxides. Later on, Nelsen and Akaba[5] reported the catalytic conversion of **1** to **2** by $(p\text{-}BrC_6H_4)_3N^+$, a reaction similar to those observed previously for the dienes.[2-4] Simultaneously, with Clennan and co-workers,[6] these authors[5] found that elec-



1

2

† S. M. McElvain Laboratories of Organic Chemistry.
‡ Physikalisch-Chemisches Institut der Universität Basel.
§ Present address: Ilford AG, CH-1701, Fribourg, Switzerland.

(1) Bartlett, P. D. "Organic Free Radicals"; Pryor, W. A., Ed.; American Chemical Society: Washington, DC, 1978; pp 26–28.
(2) Barton, D. H. R.; Haynes, R. K.; Leclerk, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2055.
(3) (a) Haynes, R. K. *Aust. J. Chem.* **1978**, *31*, 121, 131. (b) Haynes, R. K.; Probert, M. K.; Wilmont, I. D. *Ibid.* **1978**, *31*, 1737.
(4) Tang, R.; Yue, H. J.; Wolf, J. K.; Mares, F. *J. Am. Chem. Soc.* **1978**, *101*, 5248.
(5) Nelsen, S. F.; Akaba, R. *J. Am. Chem. Soc.* **1981**, *103*, 2096.
(6) Clennan, E. L.; Simmons, W.; Almgren, C. W. *J. Am. Chem. Soc.* **1981**, *103*, 2098.

0002-7863/86/1508-1027$01.50/0