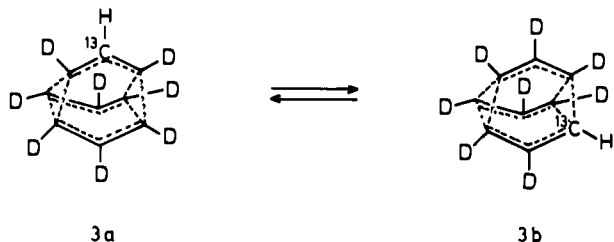
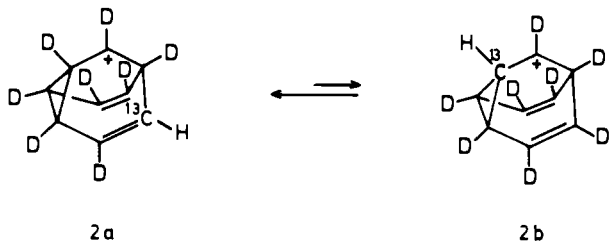


and 151 ppm, respectively (Figure 1d). The studies were started at ca. -151°C and the temperature then increased and later decreased. The sharp peaks due to **6** are thus missing from Figure 1d. Relative to the signals in Figure 1b, the upfield signal in Figure 1d is shifted downfield by 6 ppm and the downfield signal shifted upfield by about 1 ppm. This 6-ppm shift motivates our exclusion of ion **3** as the major ion responsible for the spectra. If ion **3** were the major ion showing the total degeneracy, we would expect the ^{13}C H group to show some preference for one of the two types of positions in this structure because of the difference in zero-point energy between the two types of CH bonds, i.e., the equilibrium constant for the equilibrium between **3a** and **3b** is different from 1. Such a preference would cause a chemical shift in the averaged



signal (Figure 1c), as was indeed observed (of 4.5 ppm). No shifts are expected, however, in the frozen-out signals (Figure 1d) relative to those of Figure 1b for ion **3**, since the deuteriums are predicted to show negligible influence on the chemical shifts of the ^{13}C nuclei in the ^{13}C H groups.⁷ However, the area ratio of the two signals might deviate from 6:3 due mainly to the difference in zero-point energy of the two types of ^{13}C H bonds.

If ion **2**, on the other hand, is the ion we observe, then shifts in the signals of Figure 1d relative to those of Figure 1b are expected, since each of the peaks originates from an averaging of magnetically nonequivalent carbon atoms in ^{13}C H groups, whose carbon-hydrogen bonds are likely to have different zero-point energies. The zero-point energy difference between CH bonds involving unsaturated carbons (including C_9) and saturated carbons favors in an equilibrium structure like **2a** (in which ^{13}C H is part of any of the double bonds or is a $^{13}\text{C}_9\text{H}$ group) over **2b** (or structures in which the ^{13}C H occupies any of the other saturated positions). The upfield signal comes from carbons



1,2,8,4-6, which exchange rapidly with one another. The downfield signal originates from the group of carbons 3,7, and 9. Since the CD groups probably prefer to occupy certain of the positions within each of the C groups, the ^{13}C H group is preferentially found at the remaining positions. Shifts will result in the frozen-out signals. The observed behavior of the ion is thus consistent with ion **2** and not **3**.

The average chemical shifts estimated for the barbaralyl cation using the 9-methyl-9-barbaralyl cation (**7**) and the shift differences of the carbon atoms in the 3-methyl-3-nortricyclyl and 3-nortricyclyl cations are 106 and 153 ppm, respectively.¹⁸ The close agreement between these values and those observed for the barbaralyl cation strongly suggest that this ion, like ion **7**, contains a cyclopropylcarbinyl cationic structural element (Scheme I).

A change from 6:3 to 5:3 is observed in the area ratio in Figure 1b upon substitution with the eight deuteriums (Figure 1d). The latter ratio was evaluated by using the chemical shift of the averaged signal in Figure 1c and those of Figure 1d. We therefore

(7) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1976; pp 107-110.

conclude that deuterium substitution increases the preference of the ^{13}C H group for the 3,7, and 9 positions at the expense of the remaining positions, i.e., the CD groups prefer to occupy non-olefinic positions. A similar behavior has previously been found with deuterium-labeled barbaralone.⁸ Furthermore, the small upfield shift (~ 1 ppm) indicates a slight preference of the ^{13}C H group for the olefinic positions (3 and 7) over the 9 position. Amongst the rapidly exchanging carbons 1,2,4-6, and 8 the ^{13}C H is also concluded to prefer an olefinic position over any of the other types of positions, since a 6-ppm downfield shift is obtained upon labeling with deuterium. The above conclusions are based on the chemical shifts for **2** estimated by using the shifts for the reference ion **7**. As expected, the deuterium isotope effects on the rearrangement rates are found to be small.

That the barbaralyl cation has 9-barbaralyl structure clarifies at least some aspects of the rearrangement mechanisms of **2**. Recent group-theoretical studies of ions **1**, **2**, and **3** and their rearrangements have shown that, if ion **2** is the most stable of these ions, **3** can be neither a transition state nor an intermediate in these rearrangements.¹⁶ Of the proposed mechanisms we are left with the series of divinylcyclopropylcarbinyldivinylcyclopropylcarbinyl cationic rearrangements shown in Scheme I. Ion **1** is likely to be a transition state or an intermediate in the totally degenerate rearrangement of **2**. The magnitude of the energy difference between ion **3** and ion **2** remains uncertain from the results obtained so far.

Acknowledgment. We thank the Swedish Natural Science Research Council for support.

(8) Barborak, J. C.; Sarangan, C.; Schleyer, P. von R. *J. Am. Chem. Soc.* 1971, 93, 5275-5277.

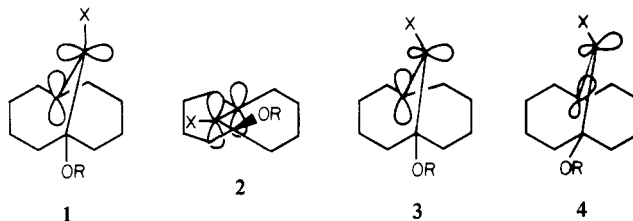
On the Question of Ground-State Perpendicular Olefins. Rehybridization of Twisted Olefins¹

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Received August 18, 1980

Investigations centered around the synthesis and reactions of bridgehead olefins² have inevitably generated interest in the structure of "anti-Bredt" double bonds. The structural options may be divided into three categories: (a) both trigonal carbons remain sp^2 hybridized without distortion of the σ framework, leaving each trigonal carbon and the three attached carbons in a plane and causing greatly diminished π overlap (none at all for **1**); (b) both trigonal carbons retain (partial or complete) ordinary



π overlap, necessitating distortion of the σ backbone (**2** shows extreme "bridge leaning" to give full π overlap); (c) the hybridization at the trigonal carbon(s) changes toward sp^3 with no (**3**, rehybridization at one carbon) or relatively little (**4**, rehybridization

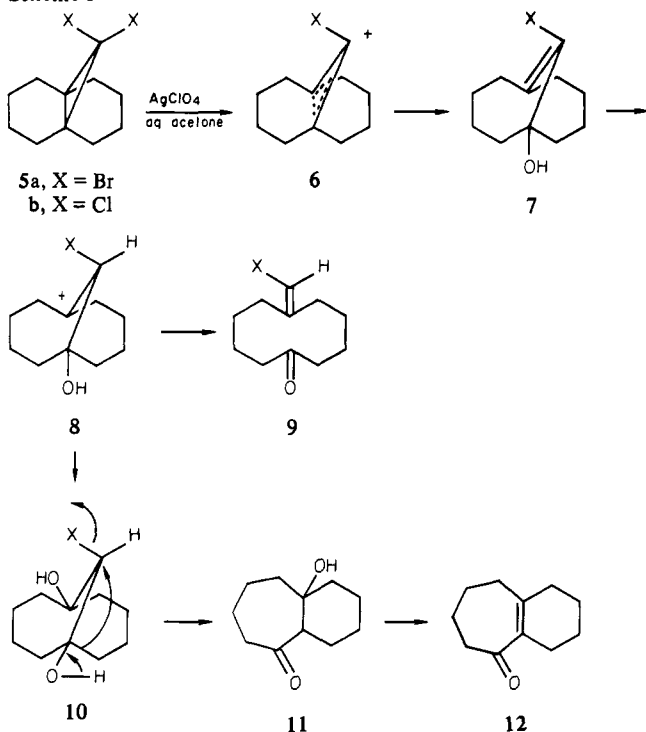
* Alfred P. Sloan Fellow, 1976-1980.

‡ NSF Trainee, 1974-77.

(1) This work was partially presented at the First International Symposium on Strained Ring Chemistry, Binghamton, NY, May 27, 1977.

(2) (a) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978. (b) Keese, R. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 528. (c) Buchanan, G. L. *Chem. Soc. Rev.* 1974, 3, 41. (d) Kobrigh, G. *Angew. Chem., Int. Ed. Engl.* 1973, 12, 464. (e) Shea, K. J. *Tetrahedron* 1980, 36, 1683.

Scheme I



at both carbons) distortion of the σ framework. Mock³ has proposed that twisted olefins pyramidalize (option c), while Keese^{2a} has stated that "a deformation of this kind (pyramidalization) must be a common feature of all strained bridgehead olefins". Keese listed three examples of rehybridized twisted bridgehead olefins, as determined by X-ray analysis. Other X-ray analytically confirmed examples of rehybridized twisted olefins include *trans*-2-cyclooctenyl 3,5-dinitrobenzoate,^{5a} 4,11-dioxatricyclo-[5.3.1.0^{3,5}]undeca-1,6-diene,^{5b} and tetradecahydro[2.2]paracyclophane.⁶ Nevertheless, the idea of a highly strained, perpendicular olefin (option a) persists.

In the absence of crystallographic data for unstable olefins, spectroscopic data might be used to sort out structural questions. Unfortunately, however, a photoelectron spectroscopic study was inconclusive, with respect to the rehybridization question, for bicyclo[4.2.1]non-1-ene.⁷ We wish to report a chemical approach to this problem for the olefin represented by 1-4(7).⁸

(3) (a) Mock, W. L. *Tetrahedron Lett.* **1972**, 475. (b) Radom, L.; Pople, J. A.; Mock, W. L. *Ibid.* **1972**, 479.

(4) Bridgehead olefins which are not twisted, but rather are very bent, also pyramidalize, as exemplified by 9,9',10,10'-tetra(dehydrobianthracene) [Viavattene, R. L.; Greene, F. D.; Cheung, L. D.; Majeste, R.; Trefonas, L. M. *J. Am. Chem. Soc.* **1974**, 96, 4342.

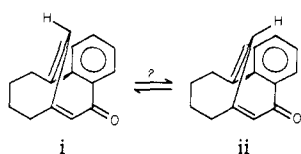
(5) (a) Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1974**, 13, 604. (b) Rastetter, W. H.; Richard, T. J.; Bordner, J.; Hennessee, G. L. *J. Org. Chem.* **1979**, 44, 999.

(6) (a) Coulter, C. L.; Trueblood, K. N. *Acta Crystallogr.* **1963**, 16, 667.

(b) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, 4, 204.

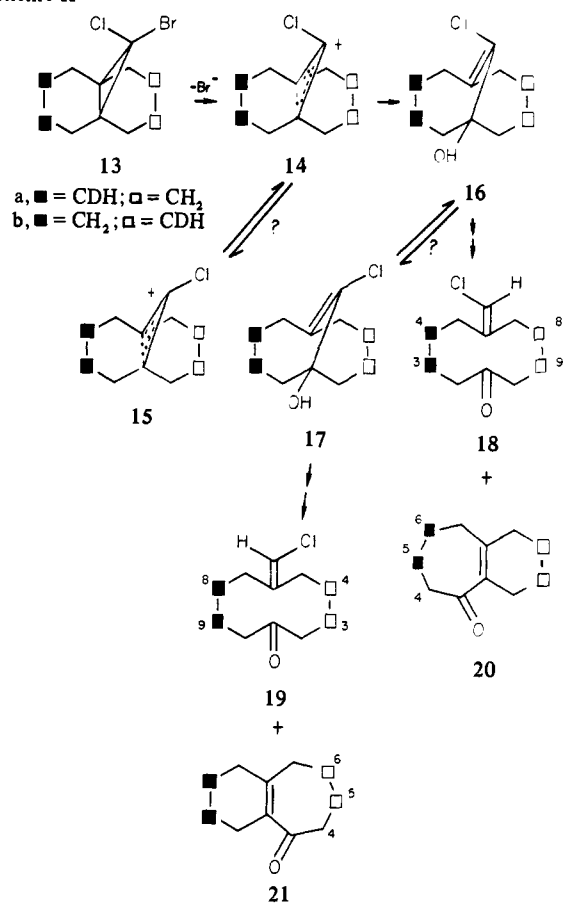
(7) Batich, C.; Ermer, O.; Heilbronner, E.; Wiseman, J. R. *Angew. Chem., Int. Ed. Engl.* **1973**, 12, 312.

(8) (a) During the course of this work, Lindner *et al.*^{8b} reported the stereoselective dimerization of (intermediate) bridgehead olefin i. However, this does not prove that i and ii do not interconvert, since ii did not yield a stereoselective product.^{8c}



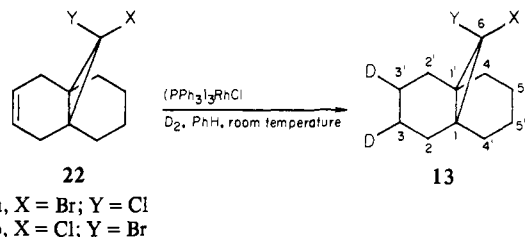
(b) Lidner, H. J.; Kitschke, B.; Liesner, M.; Seebach, D. *Helv. Chim. Acta* **1977**, 60, 1151. (c) After this paper was accepted, we learned from Professor Seebach that the stereoretentive reactions of both i and ii have been observed and are reported in the dissertation of Dr. K. M. Liesner (ETH, Zürich, 1980). We thank Professor Seebach for this information prior to publication.

Scheme II



We previously reported⁹ the mechanism for the solvolytic rearrangement of 5 (Scheme I).¹⁰ Intermediates 6 and 7 are both potentially symmetrical species, where the former could be a planar cyclopropyl cation¹¹ and the latter a perpendicular (90° twisted, 1) olefin. Solvolysis of a doubly labeled substrate, e.g., 13, would allow detection of symmetrical intermediates or transition states via a scrambling process (Scheme II) in which 14 and 15 and/or 16 and 17 interconvert to eventually afford mixtures of 18 and 19 and 20 and 21. Of course the observation of scrambling would not distinguish between the equilibration of intermediates shown in Scheme II and the presence of (more stable) symmetrical intermediates.

The synthesis of 13 involved CHBr₂Cl/KO-*t*-Bu addition to dihydrotetralin to afford a mixture of center (32%), end (10%), and bis (14%) adducts.¹² Separation of 22a (19%) and 22b (13%)



(9) (a) Warner, P.; Lu, S. *J. Am. Chem. Soc.* **1975**, 97, 2536. (b) Warner, P.; Palmer, R. F.; Lu, S. *Ibid.* **1977**, 99, 3773.

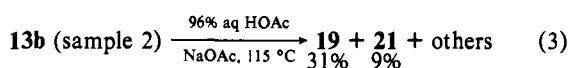
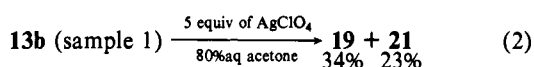
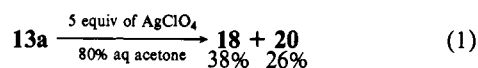
(10) (a) Ledlie, D. B. *J. Org. Chem.* **1972**, 37, 1439. (b) Reese, C. B.; Stebles, M. R. D. *Tetrahedron Lett.* **1972**, 4427. (c) Reese, C. B.; Risius, A. C. *Ibid.* **1976**, 4847.

(11) Several studies have indicated that planar cyclopropyl cations do not intervene in solution: (a) Warner, P.; Lu, S.-L.; Chang, S.-C. *Tetrahedron Lett.* **1978**, 1947. (b) Olah, G.; Liang, G.; Ledlie, D. B.; Costopoulos, M. *J. Am. Chem. Soc.* **1977**, 99, 4196. (c) Gray, R. W.; Chaples, C. B.; Vergnani, T.; Dreiding, A. S.; Liesner, M.; Seebach, D. *Helv. Chim. Acta* **1976**, 59, 1547.

(12) Previously, we^{9b} incorrectly reported these as a ca. 1:1 mixture of center and end adducts; at the time, the bis adducts were mistakenly grouped with the end adducts.

was achieved via a combination of repeated fractional crystallization (ca. 25 times from EtOH gave **22b**) and partial solvolysis (4-5 times in aqueous acetone gave **22a**); purity was readily monitored by ^{13}C NMR spectroscopy. The stereochemical assignments were made on the basis of the comparative line shapes of the ^1H NMR spectra of **22** and **5**.¹³ Deuteration of **22a** and **22b**, unsuccessful with diimide, was achieved by using Wilkinson's catalyst.¹⁴ From mass spectral studies, the deuterium incorporations¹⁵ were as follows. **13a** (containing 0-2% **13b**): 1.6% d_1 , 98.4% d_2 ; **13b** (sample 1, containing 4-6% **13a**): 2.5% d_1 , 95.7% d_2 , 1.9% d_3 ; **13b** (sample 2, containing 6.6% **13a**): 2.9% d_1 , 95.1% d_2 , 2.1% d_3 . From ^{13}C NMR spectra, it was obvious that essentially only one (different) type of carbon in each of **13a** and **13b** bore deuteriums; the location of the deuteriums is secure, as those carbons (3,5) resonate >8 ppm upfield from the others (1,2,4,6). However, it was not possible to determine much regarding minor amounts of scrambling, except that the **13b** samples contained 2-4% d_1 at C_2 .

Hydrolysis and acetolysis of **13-d**₀ have been described. In addition to the silver-assisted hydrolysis to **18-21**, we wanted to study the unassisted solvolysis. Conveniently, heating **13** in 96% aqueous HOAc (NaOAc buffer) at 115 °C afforded **18-21**. In the case of the deuterated samples, the following was found (yields are isolated):



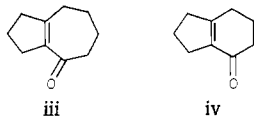
Monocyclic ketones **18** and **19** were analyzed by ^{13}C NMR spectroscopy: the undeuterated **9b** displayed the 11 expected peaks, whereas **18** and **19** each showed only 9 (the 2 carbons bearing deuterium appeared as small, nonintegrable triplets), where the 2 "missing" resonances in the spectrum of **18** were different from those in **19**. However, it was not possible to assign C_3 and C_4 vs. C_8 and C_9 , so the above result does not distinguish between gross retention (i.e., as written above) and gross inversion (i.e., **13a** \rightarrow **19**, etc.). On the other hand, the degree of stereospecificity could be calculated by comparison of the integrated areas of the ^{13}C NMR resonances in **9b**, **18**, and **19** (taking into account the small amounts of **13b** in **13a** and vice versa): (a) eq 1, 98 \pm 3.6% stereospecific (**18** should have contained 0-2% **19** and was calculated to contain 2.6 \pm 3.6% **19**), (b) eq 2, 100% stereospecific (**19** should have contained 4-6% **18** and was calculated to contain 4 \pm 1.7% **18**), (c) eq 3, 100% stereospecific (**19** should have contained 6.6% **18** and was calculated to contain 6.4 \pm 0.6% **18**).

The distinction between retention and inversion was made on the basis of mass spectral analyses of **20** and **21**. The key to the analysis is the loss of a C_3H_6 fragment to give the base peak; this loss is of C_4 , C_5 , C_6 .¹⁶ Thus the base peak ion for **20** (eq 1) was at m/e 122 (no deuteriums), while that for **21** (eq 2, 3) was at m/e 124. This information served to establish the stereoretentive nature of both the assisted and unassisted solvolyses. **In conclusion, neither 14 and 15 nor 16 and 17 interconvert, nor does a perpen-**

(13) The spectra, available on request, have been supplied to the referees.
(14) Jardine, F. H.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 1574.

(15) The "background" deuterium has been subtracted out; analysis was complicated because the parent ions were too weak, necessitating analysis of the P-Br ions.

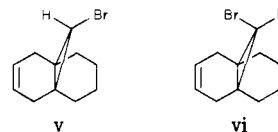
(16) This corresponds to a retro-Diels-Alder-type cleavage. The assignment is supported by observation of the same type loss to give the base peak for **iii** and a similar loss of C_2H_4 for **iv**.



dicular olefin (1) intervene in these reactions.¹⁷ While the precise structure of **16** (**17**) remains uncertain, a rehybridized structure appears to be the most reasonable alternative.¹⁸

Acknowledgment. This work was partially supported by the National Science Foundation, in the form of an energy traineeship to R.F.P.

(17) We have also found (M. Ah-King, unpublished results) that the bridgehead olefins derived from **v** and **vi** retain their configurations.



(18) On the basis of studies of bridgehead olefin formation from **22**, we can exclude the possibility that our results may be explained by conformational properties of the four-carbon bridges in **16(17)**; these will be detailed in our full paper.

On the Thermochemistry of α -Aminoalkyl Radicals¹

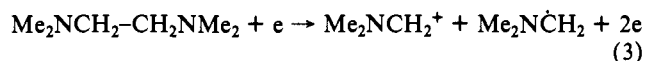
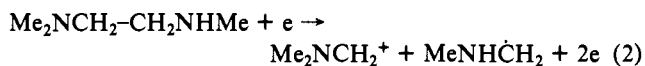
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Received October 30, 1980

Free radicals are stabilized by conjugative delocalization when the unpaired electron is adjacent to π bonds(s) or electron lone pair(s). Thus, the stabilization energies,² E_s , of allyl^{3,4} and benzyl⁴ radicals are 18 and 16 kcal mol⁻¹, respectively, while those for $\dot{\text{C}}\text{H}_2\text{OCH}_3$ ⁵ and $\dot{\text{C}}\text{H}_2\text{OH}$ ⁶ are 11 and 8 kcal mol⁻¹. However, the stabilizing effect due to a nitrogen lone pair has not been adequately quantified.

Colussi and Benson^{7,8} found $E_s(\dot{\text{C}}\text{H}_2\text{NH}_2) = 9$ kcal mol⁻¹ and consequently discounted earlier data^{8,9} which suggested that the stabilization energy afforded by an NMe_2 group was 19 kcal mol⁻¹, the premise being that E_s should not be significantly affected by N alkylation. To clarify this situation, we have measured the heats of formation and hence the stabilization energies for $\text{H}_2\text{N}\dot{\text{C}}\text{H}_2$, $\text{MeNH}\dot{\text{C}}\text{H}_2$, and $\text{Me}_2\text{N}\dot{\text{C}}\text{H}_2$.

The heats of formation of these α -aminoalkyl radicals were obtained from the appearance energies (AE) for the reactions $\text{H}_2\text{NCH}_2\text{-CH}_2\text{NH}_2 + e \rightarrow \text{H}_2\text{NCH}_2^+ + \text{H}_2\text{N}\dot{\text{C}}\text{H}_2 + 2e$ (1)



These appearance energies were measured by impact of an en-

*Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5.

(1) Issued as N.R.C.C. publication No. 19189.

(2) The stabilization energies are referred to $D(\text{CH}_3\text{-H})$ as the standard; see: Dewar, M. J. S.; Fox, M. A.; Nelson, D. J. *J. Organomet. Chem.* **1980**, *185*, 157-181. On this basis ethyl radical is stabilized by 6 kcal mol⁻¹.

(3) Rossi, M.; King, K. D.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1223-1230.

(4) Rossi, M.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1230-1235. See also: DeFrees, D. J.; McIver, Jr., R. T.; Hehre, W. J. *Ibid.* **1980**, *102*, 3334-3337 and references cited therein.

(5) Cruickshank, F. R.; Benson, S. W. *Int. J. Chem. Kinet.* **1969**, *1*, 381-390.

(6) Rossi, M.; Benson, S. W. *J. Phys. Chem.* **1969**, *73*, 733-737.

(7) Colussi, A. J.; Benson, S. W. *Int. J. Chem. Kinet.* **1977**, *9*, 307-316.

(8) See also: Parry, K. A. W.; Robinson, P. J. *Int. J. Chem. Kinet.* **1973**, *5*, 27-35. Collin, J. E.; Franksin, M. J.; Hyatt, D. *Bull. Soc. R. Sci. Liege* **1967**, *36*, 318-327. Shapiro, R. H.; Turk, J. *Org. Mass. Spectrom.* **1969**, *2*, 1067-1072. Sen Sharma, D. K.; Franklin, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 6562-6566.

(9) Richey, H. G., Jr.; Shull, D. W. *Tetrahedron Lett.* **1976**, 575-576.