The formation of only the *meta* isomer is diagnostic of reaction *via* a cationic species.[13,18,19] The potent reactivity of this species is illustrated by the high ratio of the *meta* isomer of **2**[20] as well as by the alkylation of nitrobenzene.[21]

The reactivity of **1**, **3**, and **4** in aromatic substitution is accommodated by the correlation of relatively low energies of activation with the loss of stable leaving groups.[3,14b,22] The present evidence that substitution at the bridgehead position of apocamphane derivatives occurs by a cationic process is consistent with previous suggestions in this[1,3] and related systems.[23,24] The common isomer ratio obtained in the different alkylations of chlorobenzene cannot be taken as favoring reaction *via* the 1-apocamphyl cation since reaction could occur through front-side displacement to π complexes,[25] equilibrating σ complexes, or other species such that product sensitivity to the nature of the leaving group would not be observed.

We wish to call attention to the fact that a family of reactions suitable for the formal production of highly reactive cations may be envisioned in which reaction is facilitated by the loss of a stable, nonnucleophilic leaving group.[4] Diazonium ions,[3] isocarboxonium ions,[26] and carboxylium ions[4] are members of this family, and other potential members can be imagined.[27] Regardless of whether or not such ions are truly reaction intermediates, the postulation of these species may prove useful in designing synthetic routes for substitution at positions of low incipient carbonium ion stability and for the generation of other highly reactive species.

Acknowledgment. We are grateful to the Public Health Service (GM-12595) and to the Alfred P. Sloan Foundation for support.

(18) (a) G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1964, pp 1362, 1467, 1548; (b) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Oxford, England, 1960, pp 77, 106.

(19) The formation of carbonium ions by the action of antimony pentafluoride on chloroformates and chlorosulfites has been reported by G. A. Olah, J. M. Bollinger, C. A. Cupas, N. Friedman, and J. Lukas, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract 56U.

(20) The previously reported alkylations of chlorobenzene[4a] showed only minor amounts of *meta* products.

(21) This appears to be the first cationic alkylation of nitrobenzene: G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1963, p 34.

(22) (a) A. Streitwieser, *J. Org. Chem.*, 22, 861 (1957); (b) G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

(23) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 5679 (1964).

(24) M. Wilhelm and D. Y. Curtin, *Helv. Chim. Acta*, **40**, 2129 (1957).

(25) (a) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **84**, 1688 (1962); (b) ref 21, pp 921–926.

(26) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959).

(27) For example, the reactions of sulfinylamines and isocyanates with nitrosonium salts reported by G. A. Olah, N. Friedman, J. M. Bolinger, and J. Lukas, *ibid.*, **88**, 5328 (1966).

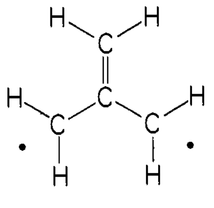
Peter Beak, Ronald J. Trancik
Department of Chemistry and Chemical Engineering
University of Illinois, Urbana, Illinois 61801

Received January 25, 1968

Trimethylenemethane, Proton Hyperfine Splitting

Sir:

Trimethylenemethane (I) has been postulated to be the central, stable intermediate in the low-temperature photochemical decomposition of 4-methylene-Δ^1-pyrazoline[1] and 3-methylenecyclobutanone.[2] The basis for this hypothesis lies in the detection of this ground-state triplet by electron spin resonance spectroscopy.[1,2] The observation that the same esr spectrum may be obtained from two independent precursors and the general agreement between the observed spectrum and that expected for such a symmetric diradical have been cited in support of the above hypothesis.[3]



I

The purpose of this communication is to present a striking new epr spectrum which not only establishes the skeletal structure of trimethylenemethane beyond question, but also affords a direct quantitative comparison with theoretical predictions of the ground electronic state of this molecule. This has been accomplished through the observation of the proton hyperfine splitting of trimethylenemethane in a single crystal. The new spectrum is essential to the structure proof in view of the special assumptions of bond length and spin density which were demanded in the comparison of the randomly oriented spectrum with theoretical expectation. In addition to being a stringent test of structure, the hyperfine splitting is of considerable theoretical interest as a direct measure of the electron spin density on the peripheral carbon atoms of the molecule.

The precursor to trimethylenemethane used in these experiments was 3-methylenecyclobutanone. A liquid at ambient temperatures, this material melts at −20°, Following a preliminary, but unsuccessful, search for a suitable crystalline host, it was decided to attempt to grow a single crystal of the pure starting ketone.[4–6] This attempt was successful. The crystal obtained was irradiated at −196° for 2 hr, giving rise in the esr to two major lines each of which was split into a number of hyperfine components. By suitable adjustment of the sample and rotation of the magnetic field, a maximum splitting of 525 G was reached.[7] This maximum corre-

(1) P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966).

(2) P. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967).

(3) Evidence for the thermal production of trimethylenemethane in the gas phase has been presented recently by R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966); R. G. Doerr and P. S. Skell, *ibid.*, **89**, 3062 (1967); P. S. Skell and R. G. Doerr, *ibid.*, **89**, 4688 (1967); and J.-P. Schirmann and F. Weiss, *Tetrahedron Letters*, 5163 (1967).

(4) We are very much indebted to Professor Melvyn R. Churchill and Dr. Peter Bird for their generous assistance in the early stages of crystal growing.

(5) Crystal growth was carried out in a sealed quartz capillary 1 mm in diameter which was scored 4 mm from the end. The use of a controlled stream of cold nitrogen ensured a slow rate of crystal growth. When crystal growth was complete, the capillary was immersed in liquid nitrogen and broken off at the scored point. It was then fastened horizontally to a ceramic rod. Adjustment of sample position and magnetic field then yielded reproducible spectra. The reproducibility depended critically on the appearance of the crystal during growth. Those crystals which grew as long thin rods running the length of the capillary were completely satisfactory. A second form which appeared as cubes during crystal growth could not be satisfactorily oriented in the magnetic field with the equipment at hand.

(6) C. A. Hutchison, Jr., and B. W. Mangum, *J. Chem. Phys.*, **29**, 952 (1958); **34**, 908 (1961); R. W. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchison, Jr., B. E. Kohler, and R. Silbey, *ibid.*, **43**, 2006 (1965); R. M. Moriarty, M. Rahman, and G. J. King, *J. Am. Chem. Soc.*, **88**, 842 (1966).

(7) The randomly oriented spectra previously obtained[1,2] were most

sponds to a parallel alignment between the magnetic field and the z axis of the molecule (defined as that Cartesian coordinate perpendicular to the plane of the molecule). In this orientation all the hydrogens are equivalent to *one* another with respect to the magnetic field, and each of the two major lines is split into seven, *and only seven*, hyperfine lines. One of the two identical septets is shown in Figure 1. The relative intensities of the peaks of the septets are expected to fall in the binomial ratio 1:6:15:20:15:6:1. The measured ratio of the spectrum shown in Figure 1 is 1.5:5.4:14.4:20:14.7:6:1.1. The splitting between the peaks is 8.9 G. This is the value predicted on the basis of valence-bond theory.[9] As a result of the neglect of negative spin density on the central carbon atom, Hückel molecular orbital theory predicts the lower value of 7.1 G.

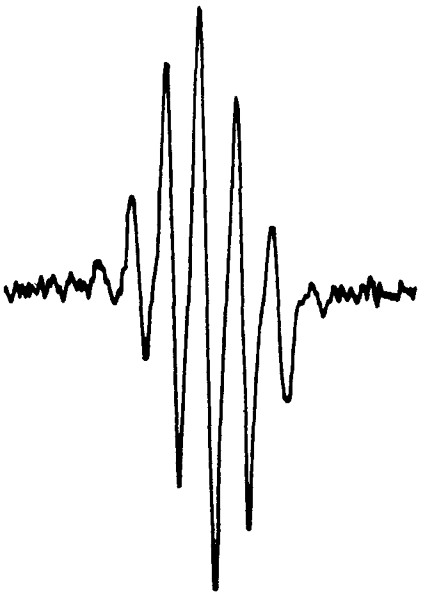


Figure 1. Single-crystal esr spectrum of trimethylenemethane (I). The septet shown, one of two, is the low-field peak. It is centered at 2940 G (klystron frequency 9150 Mc). Much more intense spectra show that *only* seven peaks are present. In the latter case, however, the use of higher power distorts the spectrum enough so that the expected binomial ratio of intensities is not reproduced as well as it is in the spectrum shown above.

The magnitude of the splitting between the two major lines shows the expected S-shaped angular dependence with respect to rotation of the magnetic field. At points below the maximum splitting the protons are no longer magnetically equivalent, and more complex unsymmetric splitting patterns are observed. The $\Delta m = 2$ transition[10] has also been observed in the present study. The latter transition shows rotationally dependent hyperfine structure, but this has not yet been studied in detail.

Acknowledgment. This work was generously supported by the National Science Foundation (Grant No. GP 6667) and The Research Corporation.

Paul Dowd, Avram Gold, Krishna Sachdev
Mallinckrodt Chemical Laboratory
Harvard University, Cambridge, Massachusetts
Received January 12, 1968

---

useful here in that one knew what maximum splitting to expect and that this splitting corresponded to the desired one in which the z axis of the molecule was parallel to the magnetic field.[8]

[8] E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

[9] H. M. McConnell, *ibid.*, **35**, 1520 (1961).

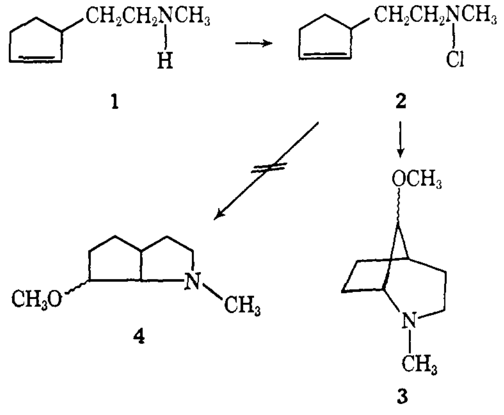
[10] J. H. van der Waals and M. S. deGroot, *Mol. Phys.*, **2**, 333 (1959); **3**, 190 (1960).

Solvolytic π Route to Azabicyclics

Sir:

Recent studies of alkyl migration to divalent, electron-deficient nitrogen[1] prompted us to explore the role of nitrenium ions in reactions analogous to other carbonium-ion-type processes. In view of the many well-established examples of the intramolecular addition of carbonium ions to double bonds,[2] we felt that the cyclization of nitrenium ions merited investigation,[3,4] especially in consideration of the biological importance of the azabicyclics. We now wish to report the conversion of a monocyclic olefinic N-chloramine into a bicyclic amino ether under solvolytic conditions.

When the amine **1** was treated with aqueous sodium hypochlorite, the N-chloramine **2** was obtained. Extraction of **2** with pentane followed by dilution of the pentane solution with methanol and evaporation of the pentane gave a methanolic solution of **2**. Refluxing this methanolic solution for 7 hr in the absence of silver ion or for 3 hr in the presence of silver nitrate (1.5 equiv) gave a single amino ether,[5] bp 92–94° (30 mm), in 55–65% yield. *Anal.* Calcd for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.54; H, 10.82; N, 9.09. In principle, cyclization could have occurred at either end of the double bond to yield either 8-methoxy-2-methyl-2-azabicyclo[3.2.1]octane (**3**) or 8-methoxy-2-methyl-2-azabicyclo[3.3.0]octane (**4**). Aside from es-



---

[1] P. G. Gassman and B. L. Fox, *J. Am. Chem. Soc.*, **89**, 338 (1967); P. G. Gassman and R. L. Cryberg, *ibid.*, **90**, 1355 (1968).

[2] P. D. Bartlett, S. Banks, R. J. Crawford, and G. H. Schmid, *ibid.*, 87, 1288 (1965), and references contained therein.

[3] The free-radical addition of nitrogen cation radicals and radicals to olefins has recently been reported: R. S. Neale, *ibid.*, 86, 5340 (1964); R. S. Neale and N. L. Marcus, *J. Org. Chem.*, 32, 3273 (1967); F. Minisoi, R. Galli, and M. Cecere, *Tetrahedron Letters*, 3163 (1966); K. Schrage, *ibid.*, 5795 (1966); and T. A. Foglia and D. Swern, *J. Org. Chem.*, **31**, 3625 (1966).

[4] Numerous examples of the addition of nitrenes to olefins have appeared. For leading references, see L. Horner and A. Christmann, *Angew. Chem.*, **75**, 707 (1963); R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964); J. S. McConaghy, Jr., and W. Lwowski, *J. Am. Chem. Soc.*, 89, 2357, 4450 (1967); see also W. Nagata, S. Hirai, Kawata, and T. Aoki, *ibid.*, **89**, 5045 (1967).

[5] In addition to the amino ether, small amounts of **1** were recovered.