Proton magnetic resonance techniques[7,8] are capable of measuring the rate of exchange directly but the resonance of the bound protons is resolved from that of the bulk protons only at temperatures below $-60°$. Rate data have been obtained only for mixed water-acetone solvents which give an extrapolated room temperature k of ca. $4-6 \times 10^6$ sec^{-1}.[7] Possible solvent effects and the large interval of extrapolation to room temperature make a direct comparison with the present results dubious.

The magnitude of the difference between the present result and the sound absorption and temperature jump data is not surprising. Differences of the same relative size have been noted previously for transition metal ions.[9] The rate constant for water exchange would be expected to be $^4/_3$ that of the rate constant for a ligand entering the first coordination sphere if it is assumed that only molecules on the faces of a first sphere octahedron of waters can enter a vacated site. The fact that the observed water rate is much greater than $^4/_3$ the ligand rate may be an indication of the extent to which water is electrostatically and/or sterically favored over the other ligands studied in competing for a vacated coordination site.

In principle one could determine from the intensity of the bound water signal the number of waters coordinated to magnesium ion in the first coordination sphere. No such attempt was made because of experimental errors, which were large enough to render meaningless any such results. Within experimental accuracy no chemical shift was observed between the first coordination sphere waters and pure water.

(7) R. G. Wawro and T. J. Swift, *J. Amer. Chem. Soc.*, 90, 2792 (1968).
(8) N. A. Matwiyoff and H. Taube, *ibid.*, 90, 2796 (1968).
(9) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37, 307 (1962).

James Neely, Robert Connick

Inorganic Materials Research Division of the Lawrence Radiation Laboratory and Department of Chemistry University of California, Berkeley, California 94720
Received December 31, 1969

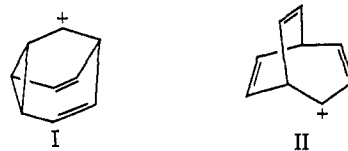## Direct Observation of the Degenerate 9-Methyl-9-barbaralyl Cation[1]

Sir:

The 9-barbaralyl cation (I) has previously been studied solvolytically,[2a–e] as well as under other conditions for short life,[2c,3a] usually in connection with attempts to investigate the bicyclo[3.2.2]nonatrienyl cation (II), a potentially "antibicycloaromatic" species.[3a,b] Earlier attempts to directly observe cations

(2) (a) J. C. Barborak, J. Daub, D. M. Follweiler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 91, 7760 (1969); (b) J. C. Barborak and P. v. R. Schleyer, *ibid.*, in press; (c) J. B. Grutzner and S. Winstein, to be published; (d) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, 23, 3943 (1967); (e) H. Westberg, Ph.D. Thesis, University of Washington, 1969.
(3) (a) M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, 89, 6356 (1967); (b) M. J. Goldstein, *ibid.*, 89, 6357 (1967).

I and II have been reported as unsuccessful.[2d,e] We now wish to report the successful generation and direct observation of the 9-methyl-9-barbaralyl cation (III), a partially degenerate derivative of I. Ion I has also been successfully generated in super acid media and its observation is reported in a following communication.[4]

Ion III was prepared by extraction of either 9-methyl-tricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-ol (IV)[5] or 2-methyl-bicyclo[3.2.2]nona-3,6,8-trien-2-ol (V)[6] from a CD_2Cl_2 solution into a mixture of FSO_3H-SO_2ClF (1:4 v/v) at ca. $-135°$ and was observed by nmr in the temperature range -135 to $-115°$. At $-116°$ ion III rearranged

$$k = 2.2 \times 10^{-3} \text{ sec}^{-1}$$
$$\Delta F^{\ddagger} = 11.0 \text{ kcal/mol}$$

(1)
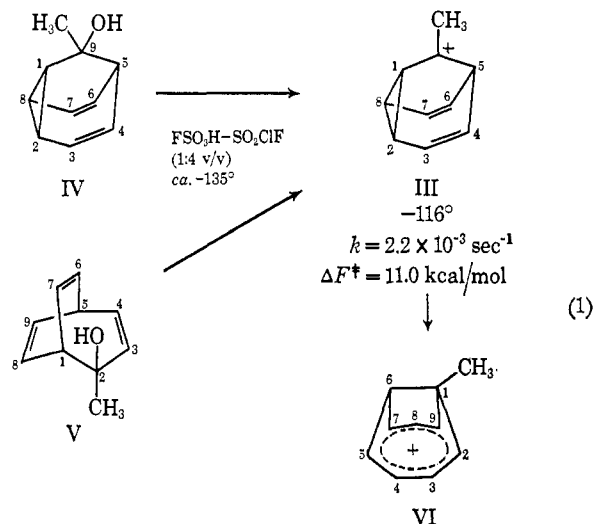
exclusively to the 1-methylbicyclo[4.3.0]nonatrienyl cation (VI), which was previously demonstrated to be a 1,4-bishomotropylium ion.[5] The structure 9-methyl-9-barbaralyl cation is assigned to ion III on the basis of its nmr data, compared to those of protonated barbaralone (VII),[7] protonated bicyclo[3.2.2]nona-3,6,8-trien-2-one (XII),[7] and dimethylcyclopropylcarbinyl cation (IX).[8] At $-135°$ the nmr of III (Figure 1a) shows six different groups of protons, in the approximate ratio $3:1:1:2:2:2$, with the chemical shifts τ 7.06, 5.23, 4.79, 4.20, 4.07, and 3.82, respectively. The $\Delta\tau_{X-IX}$ ($\tau_X - \tau_{IX}$) values observed for the bisected cation IX compared to dimethylcyclopropylcarbinol (X)[8] are ca. 2.9 for the α proton, ca. 3.5 for the β protons, and 1.46 for the *trans*-methyl group. These values, compared to the corresponding $\Delta\tau_{IV-III}$ values, indicate that III contains the structural element IX. As in protonated barbaralone (VII), the charge in III is not significantly delocalized onto the olefinic carbons
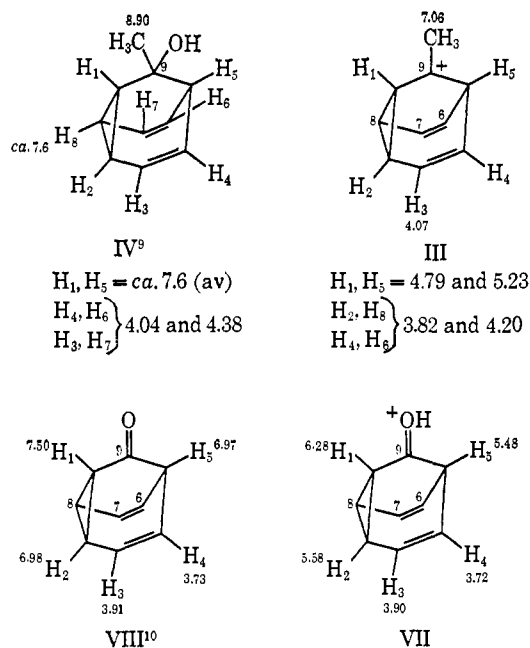
IV[9]

$H_1, H_5 = ca.\ 7.6$ (av)

$\left.\begin{array}{c} H_4, H_6 \\ H_3, H_7 \end{array}\right\}$ 4.04 and 4.38

III

$H_1, H_5 = 4.79$ and 5.23

$\left.\begin{array}{c} H_2, H_8 \\ H_4, H_6 \end{array}\right\}$ 3.82 and 4.20

VIII[10]

VII

(3, 4, 6, and 7). Structure XIII,[11] a potential representation for ion III, would be expected to have an average chemical shift[12] far downfield from that observed for XII (τ 3.27).[13] However, the average chemical shift actually observed for ion III (τ 4.28)[12] excludes XIII.

X

IX

XIII[11]
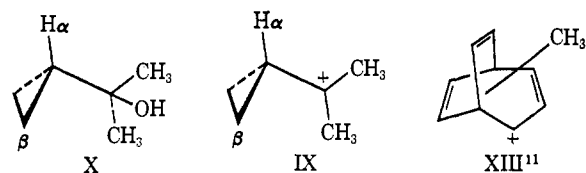
The nmr spectrum of III (Figure 1) shows reversible temperature dependence that indicates a degenerate rearrangement. The coalescence temperature for protons 1 and 5 (Figure 1b) is $-121°$. Figure 1b,c shows that protons 2 and 8 are averaging with protons 4 and 6. Furthermore, double-irradiation experiments[14] show that exchange of protons 1 and 5 with protons 2, 3, 4, 6, 7, and 8 is not rapid enough to be detected by transference of spin saturation. The unsymmetrical shape of the six-proton peak (2, 3, 4, 6, 7, and 8) suggests that protons 3 and 7 are not exchanging rapidly with protons 2, 8, 4, and 6. The degenerate rearrangement may proceed through more than one mechanism. One is the Cope[15] rearrangement (eq 2) observed in neutral molecules like 3,4-homotropilidene,[16a] 1,3,5,7-tetramethylbicyclo[5.1.0]octa-2,5-diene,[16b] and barbaralone.[17] Another reasonable mechanism is a concerted divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl rearrangement (eq 2).[2a–c,18] The barrier for

(9) CHFCl$_2$ solvent, TMS internal standard.

(10) Deuterioacetone solvent, TMS internal standard.

(11) The structure refers to the methyl group attached to any of the nine carbons in the ion.

(12) All protons except the methyl protons are averaged.

(13) M. Brookhart, Ph.D. Thesis, University of California, Los Angeles, 1968.

(14) R. A. Hoffman and S. Forsen, *Progr. Nuclear Magn. Resonance Spectry.*, 1, 173 (1966).

(15) H. Levy and A. C. Cope, *J. Amer. Chem. Soc.*, 66, 1684 (1944).

(16) (a) W. von E. Doering and W. R. Roth, *Tetrahedron*, 19, 715 (1963); (b) L. Birladeanu, unpublished results.

(17) J. B. Lambert, *Tetrahedron Lett.*, 27, 1901 (1963); experiments in these laboratories indicate that $\Delta S^{\ddagger}$ for the Cope in VIII is *ca.* 0 eu, and therefore $\Delta F^{\ddagger}$ is temperature independent.
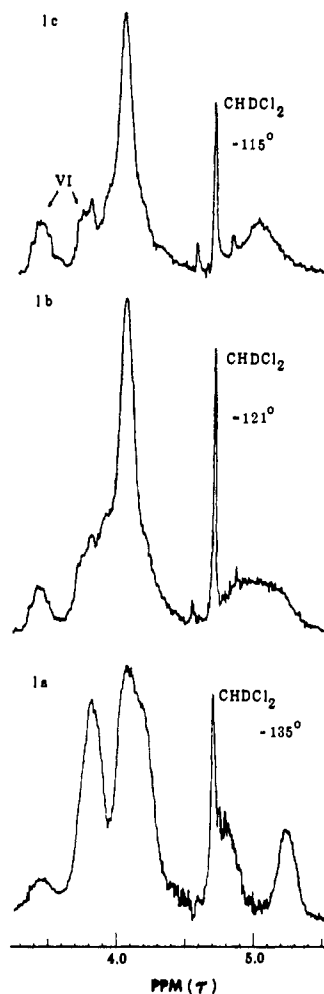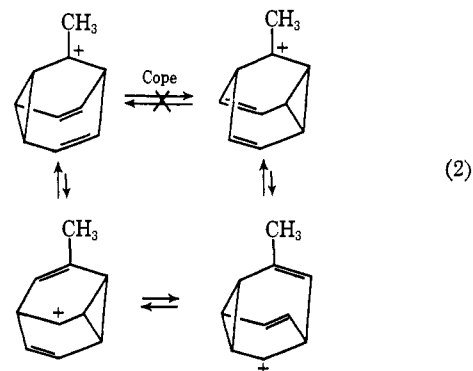

Figure 1. HA-100 nmr spectra of the 9-methyl-9-barbaralyl cation *vs.* temperature. Cation VI appears as an impurity. CHDCl$_2$ internal standard τ 4.70. The methyl absorption has been omitted.

the degenerate rearrangement of III is $\Delta F^{\ddagger} = 7.3$ kcal/mol ($k = 98$ sec^{-1} at $-121°$).[19] The Cope

(2)

rearrangement of barbaralone has a $\Delta F^{\ddagger} = 9.6$ kcal/mol[17] at $-48°$. The barrier is drastically changed on going to protonated barbaralone (VII). No averaging process is observed before decomposition; the estimated lower limit for the barrier is 13.8 kcal/mol at
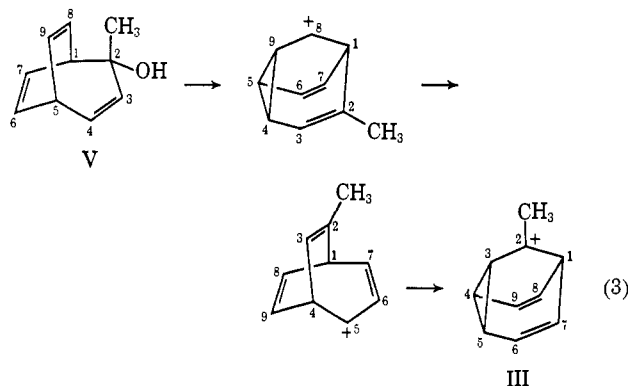
(18) This nomenclature was adopted in analogy to Doering's divinylcyclopropane rearrangement in homotropilidene.[2d]

(19) The rate constant is estimated from the formula $k = \pi/\sqrt{2} \cdot \delta\nu$,[20] which is valid at the coalescence temperature for an uncoupled two-spin system, but is approximately valid for this situation.

(20) J. J. W. Emsley, J. Feeney, and L. H. Sutcliff, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol, I, Pergamon Press, Oxford, 1965, p 481.

$-5°.$[23] This remarkable influence of the charge on the Cope rearrangement will probably be enhanced in III. This suggests an even higher barrier for a Cope averaging process for III than for VII. The barrier of 7.3 kcal/mol observed for III thus is suggested to be the barrier for the concerted divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl rearrangement (eq 2).[22]

Formation of III from V can be rationalized by invoking mechanisms (eq 3)[23] that involve the interconversion of barbaralyl and bicyclo[3.2.2]nonatrienyl cations. If bicyclo[3.2.2]nonatrienyl cations are inter-

mediates in the transformation of V to III, these by necessity have to be less stable than III. The exclusive rearrangement of III to VI shows that VI is the most stable of the species studied in this investigation, possibly because of its bishomoaromatic character.[5]

(21) $\Delta S^{\ddagger}$ is assumed to be ca. 0 eu.
(22) The concerted divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl rearrangement for VII is considered to be a high-energy process compared to the same process for III.
(23) Equation 3 is one of several possible mechanisms that contain the bicyclo[3.2.2]nonatrienyl cation.
(24) Fritz O. Fernstrom Fellow, 1969–1970.
(25) To whom inquiries should be addressed: Chemical Institute, Department of Organic Chemistry, Upsala University, Upsala, Sweden.
(26) Deceased Nov 23, 1969.

Per Ahlberg,[24,25] John B. Grutzner
David L. Harris, S. Winstein[26]
Contribution No. 2550, Department of Chemistry
University of California, Los Angeles, California 90024
Received February 19, 1970

The Gas to Condensed Phase Transition in Hot Atom Chemistry

Sir:

Interpretation of hot atom phenomena in gaseous media has become relatively straightforward.[1] In saturated systems primary products are formed by abstraction or displacement occurring by direct mechanisms (*i.e.*, single-step processes not involving persistent intermediates[1]). Secondary decomposition of such products may often occur but is usually identifiable. Condensed-phase hot atom phenomena are less well understood. While hot hydrogen reactions are

(1) R. Wolfgang, (a) *Progr. React. Kinet.*, 3, 99 (1965); (b) *Annu. Rev. Phys. Chem.*, 16, 15 (1965).

normally relatively phase independent,[2,3] yield spectra of hot halogen processes are often drastically different in gas and condensed media.[4] Despite much discussion of these differences their origin remains speculative.[4] This is largely because scavenger methods are unable to distinguish between direct hot reactions and thermal processes occurring in solvent cages.

We have approached this problem by taking a relatively well-understood low-pressure gas system and observing the effect of a continuous increase in density to that of a close-packed liquid or solid. A pioneering study of this type found an apparently linear rise in yields.[5] Interpretation of this, and related experiments on phase effects,[4] was hampered by lack of information regarding both primary processes (including possible reactions of the recoil species as ions) and the scavenging of thermalized entities.

Absolute yields of ^{18}F-labeled products from the reactions

$$^{18}F^* + CH_3F \longrightarrow CH_3{}^{18}F + F \text{ and } CH_2F{}^{18}F + H \quad (1)$$

were measured for densities from 0.0014 g cm^{-3} (gas at 1.1 atm) to 1.1 g cm^{-3}. This system was chosen because these and similar gas-phase reactions have now been studied quite extensively,[6–10] and because of the low critical temperature of CH_3F (44.9°).

Samples in sealed Pyrex ampoules at 55° were run up to twice the critical density. Beyond this it was necessary to lower the temperature to avoid excessive pressures.

Hot ^{18}F was produced by the ^{19}F(n,2n)^{18}F process, occurring within the ampoules. (The requisite fast neutrons resulted from 26-MeV protons causing p(d,n)2p reactions in heavy water.[11]) There was no apparent radiation damage; acetylene–benzene dosimeters indicated energy deposition $<10^{-2}$ eV/molecule.

Analysis was by radiogas chromatography.[7,12] CH_3-^{18}F, $CH_2F{}^{18}F$, and other low-boiling products were separated on a combined (3-m 40% hexamethylphosphoramide, 8-m 30% silicone oil (GE SF97) on chromosorb P) column at 25°. A thin-window flow-proportional counter[13] provided assays of ^{18}F-labeled products. Absolute yields are based on total available ^{18}F, as estimated using monitor samples irradiated simultaneously under the same or similar conditions.

In one series of runs, iodine at its saturation concentration and 6 mol % ethylene were both present as scavengers;[14] in another only iodine was used. Results

(2) M. Menzinger and R. Wolfgang, *J. Phys. Chem.*, 72, 1789 (1968).
(3) With relatively unstable molecules collisional stabilization causes major phase effects, *e.g.*, for CH_3NC, see C. T. Ting and F. S. Rowland, *ibid.*, 72, 763 (1968).
(4) J. E. Willard, *Annu. Rev. Phys. Chem.*, 6, 141 (1955).
(5) W. E. Rice and J. E. Willard, *J. Amer. Chem. Soc.*, 75, 6156 (1953).
(6) N. Colebourne and R. Wolfgang, *J. Chem. Phys.*, 38, 2782 (1963).
(7) N. Colebourne, J. F. J. Todd, and R. Wolfgang, (a) "Chemical Effects of Nuclear Transformations," Vol. 1, International Atomic Energy Agency, Vienna, 1965, p 149; (b) *J. Phys. Chem.*, 71, 2875 (1967).
(8) Y. N. Tang and F. S. Rowland, *ibid.*, 71, 4576 (1967).
(9) L. Spicer, J. F. J. Todd, and R. Wolfgang, *J. Amer. Chem. Soc.*, 90, 2425 (1968).
(10) Y. N. Tang, T. Smail, and F. S. Rowland, *ibid.*, 91, 2130 (1969).
(11) Technique developed by Dr. J. Hawke.
(12) R. Wolfgang and F. S. Rowland, *Anal. Chem.*, 30, 903 (1958).
(13) R. Wolfgang and C. MacKay, *Nucleonics*, 16, 69 (1958).
(14) We have no absolute assurance that in the dense samples the