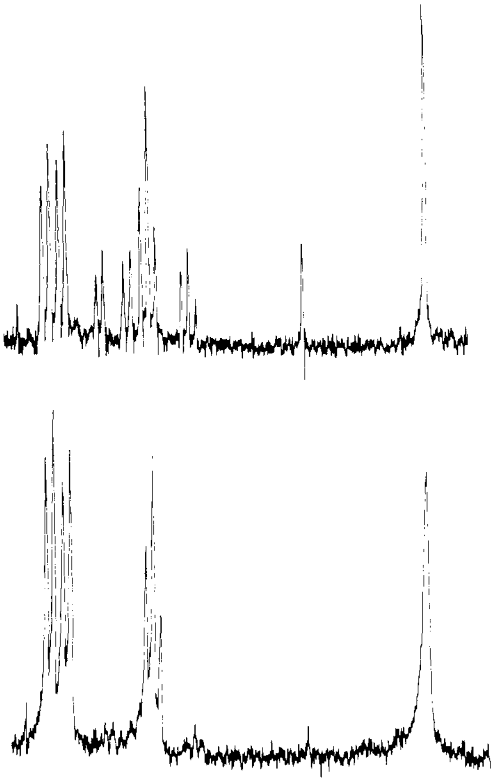


Figure 1. ^1H NMR spectrum of **1** in magic acid/SO_2: bottom spectrum at −60 °C; top spectrum at −20 °C.

and dication **3a** are clearly visible. Spectra taken at intermediate temperatures between −60 and −20 °C show intermediate amounts of **2a** and **3a.** Also, cooling the sample back to −60 °C regenerates the original spectrum. It is evident from the temperature-dependent spectra that the reversible protonation of **2a** is being observed under these conditions. Interestingly, when **1** is dissolved in the still stronger magic acid/SO_2ClF,[4] only the protonated carbocation **3a** can be detected at temperatures up to 0 °C.[5] It should be noted that these present results correlate very nicely with our earlier results in triflic acid.

Carbocation **2a** is not unique, for analogous results are obtained on **2c,** i.e., reversible protonation at C-2 in magic acid/SO_2 and irreversible protonation at C-2 in magic acid/SO_2ClF.[6] Surprisingly, perhaps, reversible protonation of **2b** at C-2 is observed both in magic acid/SO_2 and magic acid/SO_2ClF.[6,7] As might be expected from our original results, when there is only one electron-releasing substituent or none on the phenalenyl ring as on **2d** and **2e,** respectively, only **2d** and **2e** are observed in these highly acidic solvents.[6] Finally, the sesquixanthyl cation (**4**) is protonated irreversibly at the meta position in magic acid, both in SO_2 and SO_2ClF.[6,8]

In conclusion, it is clear that unequivocal evidence has been presented for the direct protonation of aromatic π carbocations. Furthermore, the present results in magic acid correlate very nicely (position of protonation on **2** and **4** and relative reactivity of **2a–d**) with our original results in triflic acid. Finally, it should be noted that these reversible reactions, properly calibrated, likely will represent a new method by which the acidity function (H_0) of these magic acid solvents can be measured. Studies in this area are continuing.

Acknowledgments. We thank the University of Tennessee for support and John Larsen for helpful comments.

References and Notes

(1) Richard M. Pagni and R. J. Smith, *J. Am. Chem. Soc.*, **101**, 506 (1979).

(2) Weiss et al. have observed a similar reaction. (a) R. Weiss and C. Priesner, *Angew. Chem., Int. Ed. Engl.*, 17, 445 (1978); (b) R. Weiss, C. Priesner, and H. Wolf, *ibid.*, **17**, 446 (1978).

(3) $(CH_3)_4N^+BF_4^-$ (δ 3.10) was used in all cases as internal standard: N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).

(4) This is based on the heats of ionization of alkyl halides in SbF_5/SO_2 and SbF_5/SO_2ClF: E. M. Arnett, C. Preto, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **101**, 522 (1979), and papers cited therein.

(5) The ^1H NMR of **1** dissolved in magic acid/SO_2ClF consists of δ 5.31 (br s, 2 H, H-2), 8.36 (t, J = 8 Hz, 2 H, H-5 and H-8), 9.26 (d, J = 8 Hz, 2 H, H-4 and H-9 or H-6 and H-7), and 9.47 (d, J = 8 Hz, 2 H, H-6 and H-7 or H-4 and H-9).

(6) NMR spectral data will be reported in our full paper.

(7) Based on substituent constants and field and resonance parameters one would expect the following order for stabilizing two positive changes: 2OH > 1OH plus $1OCH_2CH_3$ > $2OCH_2CH_3$. However, we have made no attempt to date in quantifying our data.

(8) The 2,2′,2″,6,6′,6″-hexamethoxytriphenylmethyl carbocation yields very complex temperature-dependent ^1H NMR spectra when dissolved in magic acid/SO_2.[6] Although the spectra have so far defied interpretation, it seems reasonable that protonation, possibly multiprotonation, of the carbocation has occurred here.

Robert J. Smith, Richard M. Pagni*
Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37916

Received April 2, 1979

High-Resolution ^{13}C NMR Spectra of Carbonium Ions in the Solid State

Sir:

It has recently been established[1-3] that well-resolved ^{13}C NMR spectra of solids can be obtained using a combination of pulsed NMR and "magic-angle" spinning techniques. Although initial studies have been carried out almost exclusively at ambient temperatures, full exploitation of this experiment requires variable-temperature capability.[4,5] The accessibility of low temperature, in particular, makes feasible the investigation by NMR of reactive intermediates in the solid state. Carbonium ions are classic examples of reactive intermediates and the NMR studies of Olah and co-workers[6] have led to detailed understanding of their structure in solution. Demonstration that high-resolution NMR spectra of carbonium ions can be obtained in the solid state, and particularly at low temperature, introduces the intriguing possibility of "freezing out" and observing structures which are involved in low-energy exchange processes. In this communication, we report the first high-resolution ^{13}C NMR spectra of carbonium ion salts in the solid state.

Diethoxycarbonium hexachloroantimonate (I) was chosen as representative of those carbonium ion structures in which the charge is effectively localized on a single carbon center.[7] The solid-state ^{13}C NMR spectra of this species at low (−105 °C) and ambient (27 °C) temperatures are shown in Figure 1.

At both temperatures, the resolution is sufficient to clearly identify the different carbon atoms in the system. Of particular interest is that the methylene carbons appear as two separate signals. This result is in accord with the solution proton spectrum[8] at −30 °C, which shows two methylene-proton resonances. The inequivalence is thought to arise from restricted rotation about the C–O bonds in the preferred (Figure 1) cis,trans isomer. To compare the carbon shifts with solution values, we determined the ^{13}C spectrum of I at −45 °C in ($CDCl_3$-CD_3NO_2). The chemical-shift values (parts per million from Me_4Si) in the solid (solution) follow: C-1, 176.7 (177.1); C-2,2′, 82.6, 76.8 (81.8, 75.8); C-3,3′, 13.2 (13.9, 12.6).[9] The close agreement in chemical-shift data indicates that the preferred conformation that exists in the crystal lattice is the same as the stable conformer in solution at low temperature. In solution, the spectrum is a function of temperature with averaging of the shift inequivalence occurring at 30 °C;

0002-7863/79/1501-4770$01.00/0

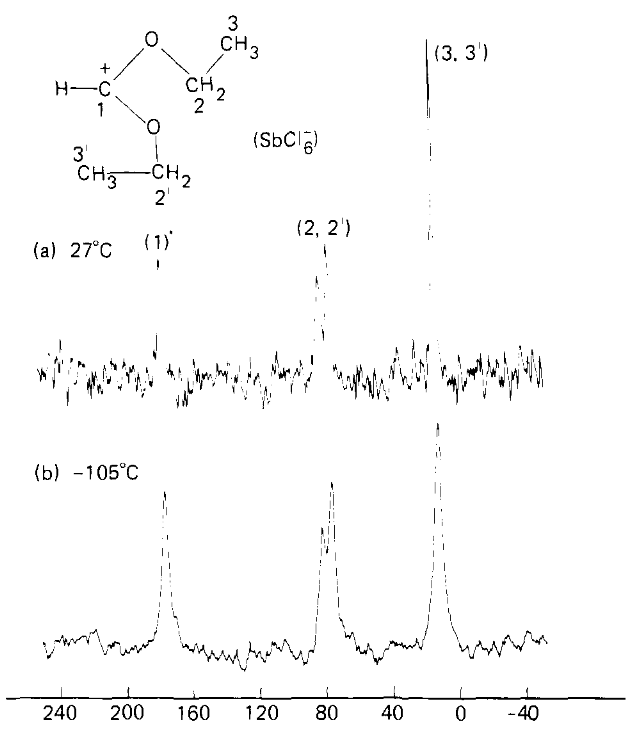


Figure 1. ^{13}C NMR spectra (15.08 MHz) of diethoxycarbonium hexachloroantimonate (I) at −105 (bottom) and 27 °C (top). Spectra were obtained using single 5-ms cross-polarization contacts with a 44-kHz proton-carbon matching condition;[1] 3880 scans with a 3-s delay and 29 000 scans with a 1-s delay were used at 27 and −105 °C, respectively. Spinning rates were ~3 kHz.[4,5]

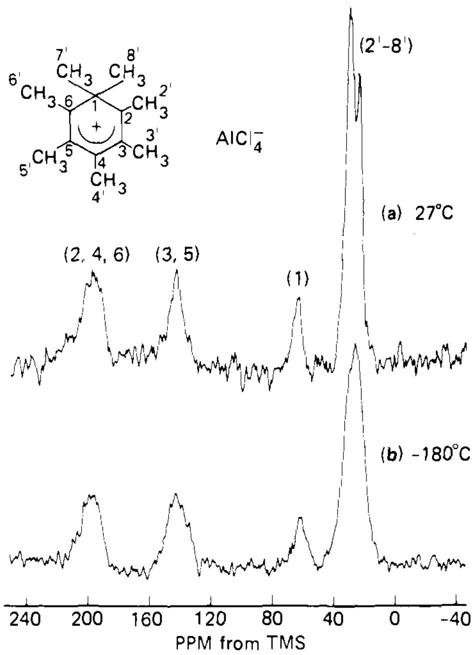


Figure 2. ^{13}C NMR spectra (15.08 MHz) of heptamethylbenzenonium tetrachloroaluminate (II) at −180 (bottom) and 27 °C (top). Conditions were the same as used to obtain the spectra of I, except that 7800 scans with a 10-s delay and 3100 scans with a 2-s delay were used at 27 and −180 °C, respectively.

in the solid, the spectrum remains unchanged from −180 to 27 °C.

Figure 2 shows the ^{13}C NMR spectrum of heptamethylbenzenonium tetrachloroaluminate (II) at low (−180 °C) and ambient (27 °C) temperatures. This species was chosen as representative of a large class of carbonium ions where the positive charge is distributed over a number of carbon centers in a π-bonding network.[7] Although the line widths at 27 °C are two to three times those of the diethoxycarbonium ion,[10] the spectra are still sufficiently well resolved to assign most of the carbon resonances. The chemical shifts measured for the solid-state spectra are within 1-4 ppm of those reported from high-resolution NMR studies in solution.[11] The lack of any substantial shift differences between the spectra in the two phases indicates that there has been little perturbation in the charge distribution in the solid.

An interesting feature of the two carbonium ion spectra is the line width which, for both compounds, is large compared with that obtained[3,4] from polycrystalline hydrocarbons (~10-20 Hz). Since these salts are crystalline materials,[7] it is unlikely that the line widths are due to a distribution of isotropic chemical shifts. Such distributions have been observed for amorphous polymers[1] but not for crystalline regions of semicrystalline polymers.[12,13] Therefore, this broadening is attributed to dipolar interaction of the carbons with the quadrupolar chlorine nuclei in the counterions. At the 1.4T field strength of the spectrometer, dipolar coupling of carbons with the chlorine nuclei (which experience a strong electrostatic quadrupole interaction[14]) should not be removed by magic-angle spinning.[15] The enhancement in resolution at ambient temperature for both I and II may be due to reduction of C-Cl coupling by molecular motion in the solid. Although the C-Cl dipolar interaction limits the resolution, the distance dependence of this coupling, $(R_{\text{C-Cl}})^{-3}$, represents a potential source of information on the geometry of the ion pair. For compound II, the width of the resonance of the C-3,5 ring carbons is ~1.5 (27 °C) to 2 (−180 °C) times[10] that of the C-1 ring carbon. This result suggests closer proximity of the AlCl$_4^-$ counterion to the portion of the ring in which the positive charge is expected to be localized. Indeed, the X-ray structure[16] of II shows much shorter C-Cl distances for C-3,5 compared with C-1. The differential in line widths between I and II may be due to more facile rotation of the SbCl$_6^-$ moiety in the solid, leading to a reduced C-Cl coupling either by motional narrowing or enhanced spin-lattice relaxation of the chlorine nuclei, with concomitant self-decoupling from the carbons.[17]

Similar results to those presented above have been obtained for other carbonium ion species.[18] Collectively, they demonstrate the feasibility of using "magic-angle" spinning NMR spectroscopy to characterize carbonium ions in the solid state at low temperatures. The resolution of the experiments is adequate for structural assignments, and more importantly, it appears that there are no large chemical-shift changes induced by "solid-state" effects. The latter finding may not always obtain and will have to be verified for each different *type* of reactive intermediate under study before attempting to extend correlations established in solution to the solid state.

These results illustrate the potential of this technique as a new avenue for the study of reactive intermediates. We are currently extending this type of spectroscopy to other, less well characterized, carbonium ions.

Acknowledgments. The inventive technical assistance of R. D. Kendrick is acknowledged and the authors thank J. J. Mayerle for help in calculating the correct C-Cl distances in II.

References and Notes

(1) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384–405, and references therein.
(2) Garroway, A. N.; Moniz, W. B.; Resing, H. A., *ACS Prepr. Div. Org. Coatings Plastic Chem.* **1976**, *36*, 133–138.
(3) Lippmaa, E. T.; Alla, M. A.; Tuherm, T. In "Magnetic Resonance and Related Phenomena", *Proc. Congr. AMPERE, 19th, 1976* **1976**.
(4) Fyfe, C. A.; Lyerla, J. R.; Yannoni, C. S. *J. Am. Chem. Soc.* **1978**, *100*, 5635–5636.
(5) Fyfe, C. A.; Mossbrugger, H.; Yannoni, C. S. *J. Magn. Reson.*, in press.
(6) Stothers, J. B. "Carbon-13 NMR spectroscopy"; Academic Press: New York, 1972; pp 217–238.

(7) Materials were synthesized using the following literature preparations. I: Meerwein, v. H.; Bodenbenner, K.; Barner, P.; Kunert, F.; Wunderlich, K. *Justus Liebigs Ann. Chem.* **1960**, *632*, 38–55. II: von E. Doering, W.; Saunders, M.; Boyton, H. G.; Earhart, W. H.; Wadley, E. F.; Edwards, W. R.; Laber, G. *Tetrahedron* **1958**, *4*, 178–185.

(8) Borch, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5303–5305.

(9) Determined on a Varian CFT-20 spectrometer operating at 20 MHz for ^{13}C NMR.

(10) The line widths of I are ~35 Hz at 27 °C (except for the methyl resonance which is 16 Hz) and 65 Hz at −180 °C. The line widths of resonances from the C-1 and C-3,5 carbons of II are 80 and 130 Hz, respectively, at 27 °C and 120 and 250 Hz, respectively, at −180 °C. Ring carbons 2 and 6 are not resolved from the resonance due to C-4; thus single-carbon line-width data is not available for these carbons.

(11) Rezvukhin, A. I.; Mamatyuk, V. I.; Koptyug, V. A. *Z. Org. Khim.* **1972**, *8*, 2443.

(12) Fyfe, C. A.; Lyerla, J. R.; Volksen, W.; Yannoni, C. S. *Macromolecules*, in press.

(13) Earl, W; VanderHart, D. L. *Macromolecules*, in press.

(14) Cotton, F. A.; Harris, C. B. *Proc. Natl. Acad. Sci. U.S.A.* **1966**, *65*, 12–15.

(15) Lippmaa, E. T.; Alla, M. A.; Pehk, T. J.; Engelhardt, G. *J. Am. Chem. Soc.* **1978**, *100*, 1929–1931.

(16) Baenziger, N. C.; Nelson, A. D. *J. Am. Chem. Soc.* **1968**, *90*, 6602–6607. The labeling of atoms is incorrect in Table V. The correct labeling shows that the shortest C–Cl distances (ångstroms) are the following: C-1, 4.37; C-2, 3.90; C-3, 3.46; C-4, 3.37; C-5, 3.80; C-6, 3.99.

(17) Spiess, H. W.; Haeberlen, U.; Zimmerman, H. *J. Magn. Reson.* **1977**, *25*, 55–66.

(18) A preliminary account of this work was presented at the 20th Experimental NMR Conference, Asilomar, Calif., Feb. 20, 1979.

J. R. Lyerla, C. S. Yannoni*
IBM Research Laboratory, San Jose, California 95193

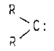
D. Bruck, C. A. Fyfe*
Guelph-Waterloo Centre for Graduate Work in Chemistry
Guelph Campus, Department of Chemistry
University of Guelph, Guelph, Ontario, Canada

Received March 21, 1979

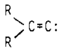
Extended Unsaturated Carbenes.[1]
Generation and Reaction of Allenylidene Carbenes, $(R)_2C{=}C{=}C{=}C:$, with Olefins

Sir:

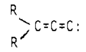
Carbenes **1** are well established and highly useful members of the family of reactive intermediates.[2] More recently unsaturated carbenes, consisting of alkylidene **2** and alkenylidene **3** carbenes, have been generated and shown to possess novel properties and chemistry.[3] However, to date no extended unsaturated carbenes beyond **3** have been reported. Such extended unsaturated carbenes would be of interest in their own right in addition to serving as a means of simple entry into cumulene chemistry. In this communication we report the generation and interaction of the next homologous unsaturated carbenes, specifically allenylidene carbenes **4**, with some olefins.


$R_2C:$

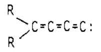
1


$R_2C{=}C:$

2

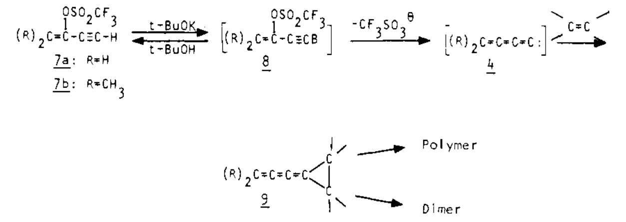

$R_2C{=}C{=}C:$

3

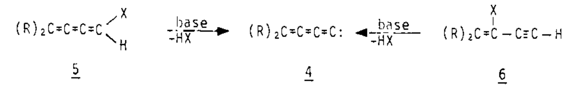

$R_2C{=}C{=}C{=}C:$

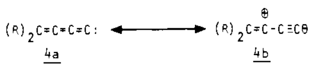
4

Scheme I

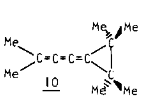


A priori, allenylidene carbenes **4** may be generated using base via α-elimination from an appropriately functionalized cumulene **5** or by γ-elimination from a properly functionalized enyne **6**. These two modes of allenylidene carbene generation are analogous to the generation[3] of alkenylidene carbenes **3** from allenyl and propargyl halides. Since to our knowledge cumulenyl halides **5** are unknown[4] and not readily accessible, we chose triflate functionalized enynes[5] **6** as progenitors of carbene **4**. Reaction of 5.0 mmol of alkynylvinyl triflates[5] **7a** and **7b** with a mixture of excess olefin in 1,2-dimethoxyethane at 0 °C maintained over an argon atmosphere and containing 5.5 mmol of potassium *tert*-butoxide proceeded as shown in Scheme I. Rapid loss of a proton and formation of anion **8** was indicated by reisolation of deuterium incorporated triflate **7b** in deuterated media.[6] Subsequent loss of the triflate ion results in carbene **4** which is a resonance hybrid of the neutral carbene **4a** and the dipolar form **4b**. The contribution of the dipolar form **4b** is presumably minimized by both the relatively high energy of a vinyl cation[7] in comparison with normal carbenium ions and the nonpolar nature of the reaction medium. Carbene **4** is readily trapped by olefins resulting in adduct **9**, whose subsequent fate is strongly dependent upon substituents in both the carbene and the olefin.

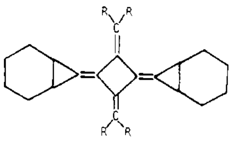




Addition of the parent triflate **7a** to tetramethylethylene (TME) results in a polymer most likely via oxygen initiated free radical polymerization of adduct **9**.[8] Using triflate **7b** and TME, the monoadduct **10** is isolated as transparent plates. In



10



11a: R=H
11b: R=CH3

Table I. Spectral Data for Products **10**, **11a**, and **11b**

compd	mp, °C	mass spectra *m/e* (rel int)	UV[a], λ_{max}, nm (ϵ)	IR,[b] cm^{-1} (int)	^1H NMR,[c] δ ppm (no., mult)	^{13}C NMR,[d] δ (ppm)
10	58–60	162 (100), M^+	306 sh, (150) 264 (10800) 236 sh, (3900)	2065 (m)	1.17 (12 H, s) 1.80 (6 H, s)	163.5, 121.1, 116.2, 111.7, 30.2 (e), 28.3, 24.6, 21.1
11a	102–104 dec	264 (94), M^+ 165 (100)	256 (1750) 202 (11450)	1900 (m) 1710 (w) 860 (s)	0.63 (2 H, m) 1.19 (8 H, br m) 1.70 (6 H, s)	151.6, 129.7, 118.2, 97.6, 22.8, 21.3, 21.2
11b	114–116 dec	320 (100), M^+	264 (4000) 245 (4000) 207 (19200)	1955 (m) 1710 (w)	0.60 (2 H, m) 1.13 (8 H, br m) 1.70 (6 H, s)	195.3, 103.6, 100.2, 40.1, 21.7, 21.4, 19.4, 16.0

[a] Heptane. [b] 10% CCl_4. [c] CCl_4, internal standard Me_4Si. [d] $CDCl_3$, internal standard Me_4Si, proton decoupled. [e] Impurity.

0002-7863/79/1501-4772$01.00/0