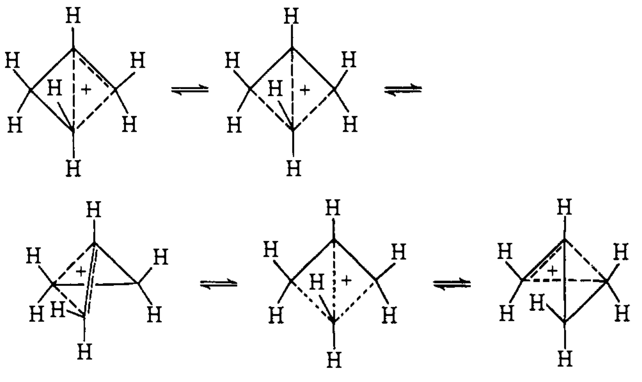
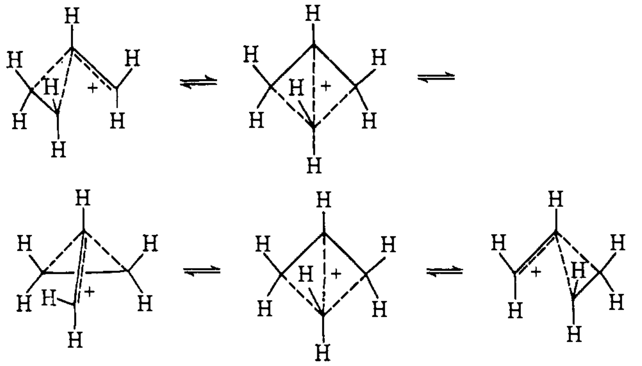


equilibrating bicyclobutonium ions



equilibrating "bisected" cyclopropylcarbinyl cations

methylcyclopropylcarbinyl (**7**) < cyclopropylcarbinyl (**6**). All of the cyclopropylcarbinyl cations show delocalization of charge by the cyclopropyl ring, but only with the primary system do we observe the truly unique behavior which indicates the limiting nonclassical nature of the ion. Present work reinforces our contention that the ^{13}C chemical shifts are an excellent, direct experimental way of determining the "nonclassical" character of carbonium ions.

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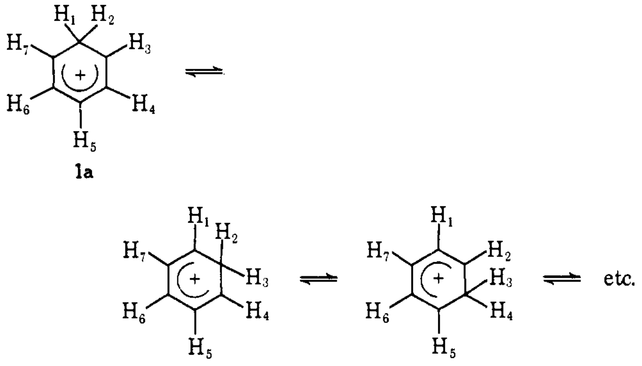
Stable Carbonium Ions. IC. The Benzenonium Ion ($C_6H_7^+$) and Its Degenerate Rearrangement[1]

Sir:

Mass spectroscopic studies[2] have shown the formation of $C_6H_7^+$ as a fragmentation ion produced upon electronic bombardment of benzyl alcohol. Substantial research has been reported on proton-addition complexes of aromatic hydrocarbons.[3-12] Olah and Kuhn[6,9] achieved the synthesis and isolation of stable alkylbenzenonium fluoroborate and fluoroantimonate salts. Although Perkampus and Baumgarten[13] reported solid-state infrared and ultraviolet spectra for the ternary system benzene–HCl–GaCl$_3$, a well-characterized description of $C_6H_7^+$ in solution has not been presented until now.[14]

We wish to report the observation of the simple benzenonium ion ($C_6H_7^+$) as a stable long-lived species. When a saturated solution of benzene in sulfuryl chloride fluoride at −50° is added dropwise with vigorous stirring to a 1:2 (v/v) solution of 1:1 (mol/mol) hydrogen fluoride–antimony pentafluoride in SO$_2$ClF at −78°, a suspension is formed. The clear supernatant solution has a pmr spectrum (Figure 1) consisting of a single sharp peak at δ 8.09 (apart from the acid and the H_3O^+ peaks), which we assign to the degenerate $C_6H_7^+$ ion **1a–c**, undergoing rapid hydrogen migration.



1a

1b

1c

When the mixed solvent system SO$_2$ClF–SO$_2$F$_2$ was employed,[15] the pmr spectrum could be observed at as low a temperature as −134°. At this temperature the separate absorptions for the four different types of protons of the "frozen-out" benzenonium ion are apparent (*cf.* **1a**): the methylene protons (H_1, H_2) giving a broad signal at δ 5.84, H_4 and H_6 at 8.40, H_5 at 9.20, and H_3 and H_7 at 9.42 ppm (Figure 2). Warming the solution to −70° regenerates the singlet absorption at δ 8.09 ppm.

The temperature dependence of the spectrum was used to calculate the rate constants and activation parameters of the hydrogen migration. The line shapes for various rate constants were calculated and recorded by means of a multiple-site exchange program.[16] The axial (C_{2v}) symmetry of the ion allowed us to treat this case as a four-site problem. Fitting the data to the Arrhenius equation gave an activation

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[14] The species thought to be $C_6H_7^+$ in SO$_2$ solution of benzene–HF–SbF$_5$[9] was obviously the sulfinated product (*vide infra*).

[15] The solution (0.5 ml) is added to SO$_2$F$_2$ (*ca.* 0.2 ml) in an nmr tube at −78°.

[16] The Fortran IV program was written by C. S. Johnson, Jr., *Advan. Magnetic Resonance*, **1**, 33 (1965), and adapted for use on a Univac 1108 computer by Mr. W. Heyd of this department.

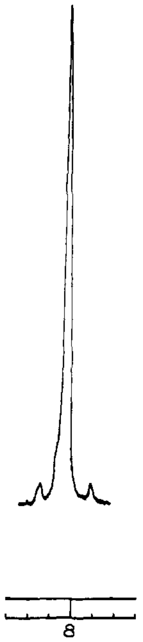
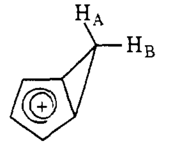


Figure 1. Spectrum (60 MHz) of $C_6H_7^+$ in $HF-SbF_5-SO_2ClF$ at −80°.

energy, E_a, of 10± kcal mol^{-1} and a preexponential factor, A, of $10^{15.9 \pm 1.6}$.

The broadness of the methylene absorption at δ 5.84 ppm can be explained by proton exchange with the acid solvent system, which is not completely stopped at the low temperature attained. The deuterated analog of ion **1** formed from benzene-d_6 in $HF-SbF_5-SO_2ClF$ indeed undergoes slow deuterium–hydrogen exchange at −134° which is much accelerated at higher temperatures. Broadening due to the nonequivalence of the aliphatic methylene protons in a 4-π-electron Möbius-type[17] analog (**2**) of the homotropylium cation (a homo-Möbius cyclopentadienyl cation) seems unlikely due to steric prohibition of a Möbius strip closure in a five-membered ring system.[18]



2

The singlet peak at δ 8.09 ppm is flanked by large ^{13}C satellites (Figure 1), as would be expected for the degenerate ion (theoretically, each 3.3% of the ^{12}C peak), giving a value of $J(^{13}C\text{–}H)_{av}$ = 26 Hz. This average value of a C–H coupling constant is a result of a rapid exchange involving all seven protons and six carbon atoms, similarly as observed by us in the case of the cyclopentyl cation.[19] Using the indor technique previously described[19] (monitoring the downfield ^{13}CH satellite or the main ^{12}CH peak) the ^{13}C chemical shift of **1** at −78° was found to be $\delta(^{13}C)$ +48 ppm (from CS_2). Both the average coupling constant and chemical shift values are in good agreement with those calculated for the rapidly equilibrating set of benzenonium ions (σ complexes) **1a–c** using either a static model, **3a–c**, or reported ^{13}C data from the mesitylium ion (2,4,6-trimethylbenzenonium ion).[20]

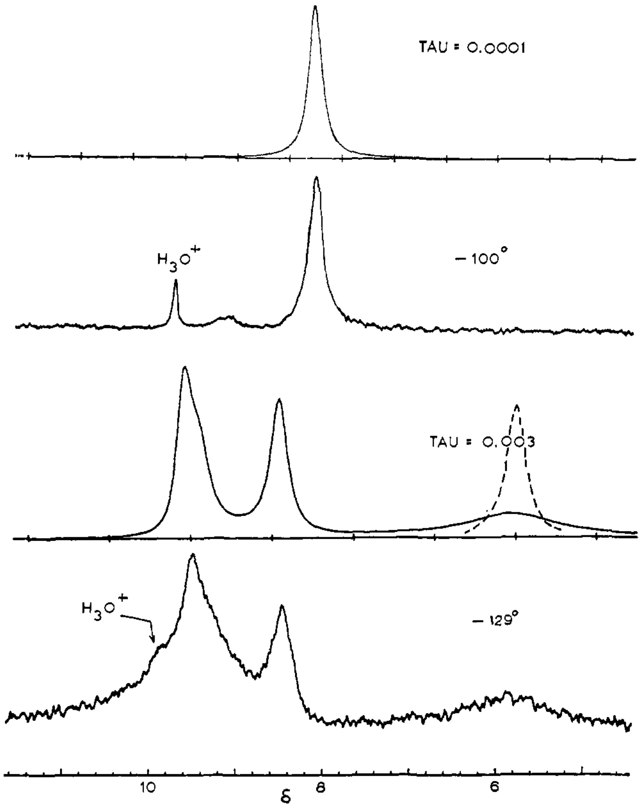
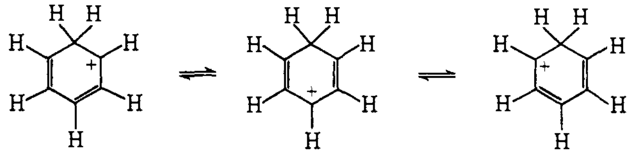


Figure 2. Computed and observed spectra of degenerate (top) and "frozen-out" (bottom) benzenonium ion. Dashed line indicates computed methylene proton absorption in the absence of exchange with acid (see text).



3a **3b** **3c**

From the static model, $J(^{13}C\text{–}H)_{av}$ is calculated from four cyclohexadiene-type olefinic (167 Hz), two sp^3-type cyclohexane methylene (125 Hz), and one isopropyl cation-type (169 Hz)[21] couplings, equilibrated over six carbons as: $J(^{13}C\text{–}H)_{av} = [(4 \times 167) + (2 \times 125) + (1 \times 169)]/(6 \times 7) = 26$ Hz.

Similarly the ^{13}C chemical shift can be calculated from the values for olefinic carbons in cyclohexadiene, the methylene carbon in the 2,4,6-trimethylbenzenonium ion,[20] and the isopropyl cation carbon:[19] $\delta(^{13}C)_{av} = [(4 \times 66) + (1 \times 139) + (1 \times -125)]/6 = +46$ ppm (CS_2). The ^{13}C chemical shifts for the 2,4,6-trimethylbenzenonium ion (**4**) have been reported by Koptyug[20] and serve as an excellent model for **1**. Since the sub-

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[17] (a) E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964); (b) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966).

[18] Larger cyclic 4*n* π-electron cations like the cyclononatetraenyl cation could be stabilized by a Möbius-type interaction; our studies in this regard will be reported.

[19] A. M. White and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2943 (1969).

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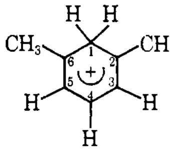
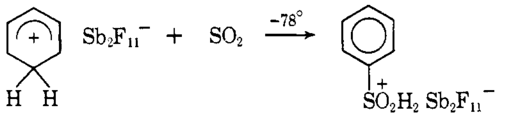


$\delta(C_1)$ +139 ppm
$\delta(C_{2,4,6})$ −0.5 ppm
$\delta(C_{3,5})$ +58 ppm

4

stitution of a hydrogen atom for a methyl group in carbonium ions generally causes only a slight change (shielding of about 10 ppm) in the ^{13}C shift,[22] the data from the 2,4,6-trimethylbenzenonium ion can be used directly to calculate the average ^{13}C shift in **1**: $\delta(^{13}C)_{av} = [139 + (3 \times -9.5) + (2 \times 58)]/6 = 47$ ppm (CS_2).

When sulfur dioxide is added to the HF–SbF_5–SO_2ClF solution of **1** at −78°, an immediate reaction occurs to form protonated benzenesulfinic acid, $C_6H_5S(OH_2)^+$, as evidenced by a two-proton pmr singlet at δ 9.54 ppm (S–OH) and the five-proton aromatic absorption at 7.96 ppm.



Winstein's group[23] has reported that monoalkylbenzenes in FSO_3H–SbF_5–SO_2 solution form sulfinated alkylbenzenes and suggested that the SO_2–SbF_5 complex is responsible for the electrophilic sulfinations. This suggestion could explain the results of previous investigations of monoalkylbenzenonium ions in sulfur dioxide solutions,[9] *i.e.*, formation of sulfinated products. Similar observations were made concerning ions produced from monoalkyl- and halobenzenes, which were obtained and studied in detail in super acid systems free of SO_2 and diluted where necessary with SO_2ClF.[24] While the SO_2–SbF_5 complex is an effective electrophilic sulfinating agent, we felt that in super acid media the reaction of the benzenonium ions themselves with SO_2 can also be responsible for the observed sulfinations. In our previous studies the reaction of benzenonium ions as isolated salts with nucleophiles was studied. Ion **1** is not sufficiently stable for isolation, but its solution behavior supports its reactivity with SO_2. Alternatively there could be an equilibrium, even at −78°, of **1** and benzene, with added SO_2 promoting deprotonation. Benzene then could undergo sulfination by SO_2–SbF_5 or SO_2H^+. At this low temperature sulfination would be expected to be slow and would hardly account for the experimental observation of fast quantitative conversion of **1** into benzenesulfinic acid. It should be mentioned that dialkylbenzenes and higher polyalkylbenzenes are sufficiently basic to form alkylbenzenonium ions which, at low temperatures, generally do not react with SO_2. Observation of these ions in SO_2 solution was therefore not affected by the solvent.

Our studies indicate that we have observed the heretofore elusive benzenonium ion (**1**) in solution as an equilibrating set of degenerate ions which can be frozen out at −134° to the static benzenonium ion. Our investigations relating to the benzenonium ion and monoalkylbenzenonium ions are published in full in a forthcoming paper.

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Structure of the Methylcyclobutyl Cation

Sir:

Methylcyclopentyl cation was recently reported to undergo ready interchange of the α and β ring protons and to exchange ring and methyl protons and carbons less readily.[1] The rates were similar to those found for analogous processes in the classical *t*-amyl cation.[1,2]

With the hope of studying similar processes in methylcyclobutyl cation, we treated the corresponding tertiary chloride **I** (prepared from methylenecyclobutane and HCl gas at 0°[3]) with SbF_5 and SO_2ClF in the usual manner at low temperature. A solution giving an nmr (−80°) spectrum which consisted of two singlets at τ 6.11 and 7.13 (measured from external $(CH_3)_4Si$) with an area ratio of 2:1 was obtained. Cooling a sample prepared with a SO_2ClF–SO_2F_2–SbF_5 solvent system[4] to −125° produced only broadening of both peaks, probably due to increased viscosity. Splitting was observed (−25°) appropriate for coupling between groups of three and six equivalent protons (Figure 1).

1-Chlorotrideuteriomethylcyclobutane (II) was prepared from trideuteriomethyl iodide (approximately 90% deuterium) *via* a Grignard reaction on cyclobutanone and subsequent treatment of the alcohol formed with concentrated HCl and pentane at room temperature. The ion from II was prepared and its nmr spectrum at −60° was only a singlet (half-height width 1.7 Hz) at τ 6.07 and a small peak at 7.1 due to residual hydrogen from the methyl group of the chloride. Apparently the ring hydrogens are identical and 1 ppm downfield from the methyl position. The coupling constant (0.9 Hz) is unusually low compared to that for the coupling of methyl and α hydrogens of the methylcyclopentyl cation (4.0 Hz).[5]

Several possible explanations might fit these results: (1) a series of rapid hydride and possibly methide shifts could exchange ring hydrogens; (2) the ion could have a static highly symmetrical structure with six equivalent methylene protons; (3) it could be a rapidly equilibrat-

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[3] H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952); we are grateful to Gary Taylor for supplying the methylenecyclobutane.

[4] G. A. Olah and A. M. White, *ibid.*, **91**, 3956 (1969).

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