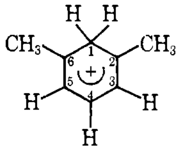
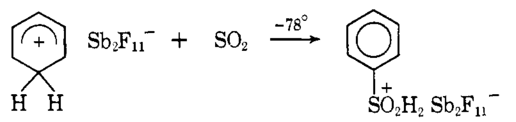


$\delta(C_1)$ +139 ppm
$\delta(C_{2,4,6})$ −0.5 ppm
$\delta(C_{3,5})$ +58 ppm

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.

Acknowledgment. Support of this work by the National Science Foundation and the C. F. Mabery Fund of Case Western Reserve University is gratefully acknowledged.

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[22] Substitution of a methyl by a hydrogen brings about a shielding of 3–10 ppm: (a) B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 5319 (1967); (b) D. M. Grant and E. G. Paul, *ibid.*, **86**, 2984 (1964); (c) L. M. Jackman and D. P. Kelly, *J. Chem. Soc., B*, in press.

[23] M. Brookhart, F. A. L. Anet, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 5657 (1966); M. Brookhart, Ph.D. Thesis, University of California, Los Angeles, Calif., 1968.

[24] G. A. Olah, C. U. Pittman, Jr., E. Namanworth, and M. B. Comisarow, *J. Amer. Chem. Soc.*, **88**, 5571 (1966); G. A. Olah and T. E. Kiovsky, *ibid.*, **89**, 5692 (1967); **90**, 2583 (1968).

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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[1] M. Saunders and J. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 7756 (1969).

[2] M. Saunders and E. L. Hagen, *ibid.*, **90**, 2436 (1968).

[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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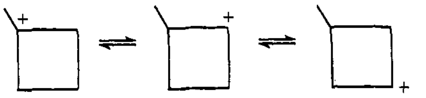
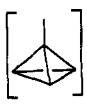
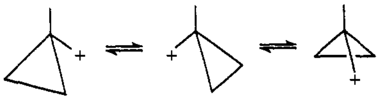


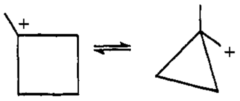
(1)



(2)



(3)



(4)

ing cyclopropylcarbinyl cation; (4) the cyclobutyl cation could be in rapid equilibrium with the corresponding cyclopropylcarbinyl cation.

Mechanisms 2, 3, and 4 would produce ^{13}C satellites at positions appropriate for the various coupling constants.[6,7] Mechanism 1, however, would require ^{13}C satellites of triple the normal intensity at spacings corresponding to one-third the normal splittings due to averaging of direct and indirect coupling constants.

The calculated theoretical shift for the ring hydrogen peak for explanations 2 or 3 (this value is based on shifts from ion III (see below); it is the weighted average of τ 5.6 for the four cyclopropyl hydrogens and 0.5 for the two carbinyl protons) is τ 3.9. This is far below the observed value. A similarly calculated shift (this value is the weighted average of τ 5.8 for the four α-methylene hydrogens and 7.5 for the two β-methylene hydrogens which are derived from data on the methylcyclopentyl cation[5]) for a methylcyclobutyl ion whose α and β hydrogens are all averaged by rapid interchange is τ 6.4, approximately the experimental value. Mechanism 4, with the equilibrium favoring the cyclobutyl cation, fits the data best.

Our observation that similar treatment of 1-chloromethyl-1-methylcyclopropane[8] gives a cation with an nmr spectrum identical with that of the ion from I is also consistent with possibility 4.

At −25°, the ion from I isomerized slowly (assuming a normal log A, we obtained an E_a of about 20 kcal/mol) to III whose spectrum consisted of a multiplet at τ 0.49 (1 H), a multiplet centered at 5.6 (5 H), and a doublet at 6.63 (3 H), $J = 6.3$ Hz (coupling constant measured on both 100- and 60-MHz instruments). Comparison with cyclopropylcarbinyl-type cations[9] leads to the assignment of (methyl)cyclopropylcarbonium ion (III) as its structure. To check the assignment, 1-chloroethylcyclopropane was prepared.[10] The ion from this chloride was found to be identical with III. This mixture of ions was allowed to reach equilibrium at room temperature (several minutes). A final low-temperature spectrum indicated that about 2% of the cyclobutyl ion remained. This corresponds to a K_{equil} of 50 and a ΔF of approximately 2 kcal/mol.

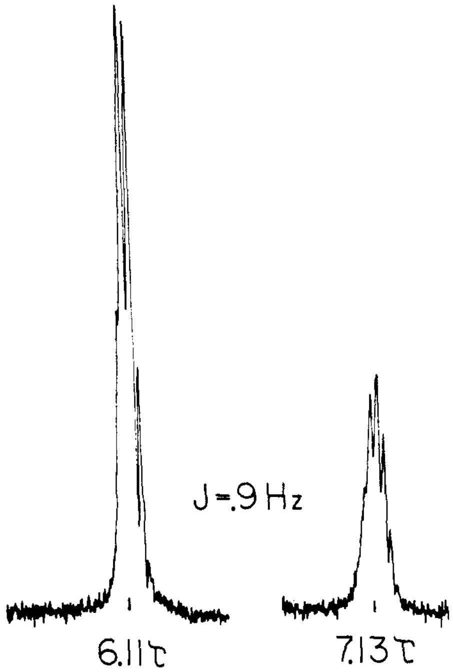


Figure 1.

Isomerization of the trideuteriomethylcyclobutyl cation was also carried out. The ratio of the ring hydrogen to methyl hydrogen peaks in the *unrearranged* material remained unchanged during the reaction, *i.e.*, there was no significant amount of mixing of ring and methyl hydrogen.

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(6) G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **88**, 1818 (1966).

(7) G. A. Olah and A. M. White, *ibid.*, **91**, 3954 (1969).

(8) W. Kirmse, M. Kapps, and R. B. Hager, *Chem. Ber.*, **99**, 2855 (1966).

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(11) Fellow of the Alfred P. Sloan Foundation.

(12) National Institutes of Health Predoctoral Fellow.

Characteristics of the Abrupt Change from the Participation to the Nonparticipation of a Neighboring Group

Sir:

Most changes in molecular structure which result in a change in neighboring group participation also involve a change in the steric environment of the centers being studied. At this time we wish to report our results on a series of molecules of essentially identical steric environment in the vicinity of the reactive sites. In this series we observe an abrupt cessation of neighboring group participation with a resultant dramatic change in the characteristics of the reaction being studied.

In a previous report[1] we presented data on the solvolysis of the systems represented by **1** and **2** where X was p-methoxy, hydrogen, and p-trifluoromethyl. These compounds solvolyzed over a rate range of 10^7 and provided definitive evidence that in certain cases neighboring group participation is a linear function of

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(1) P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **91**, 1545 (1969).