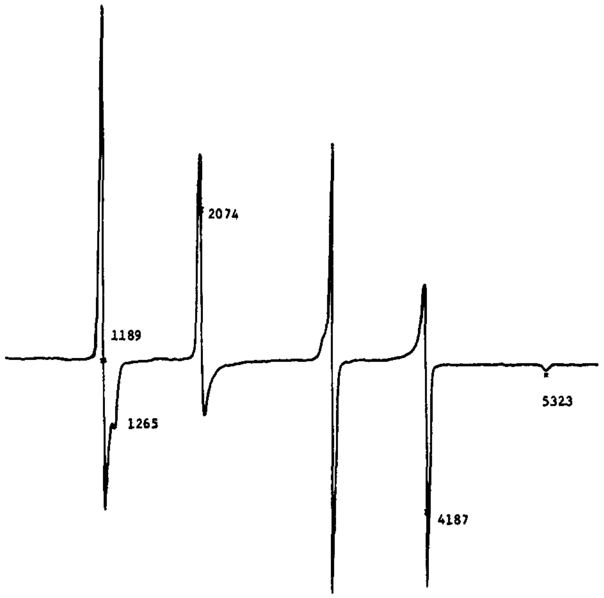
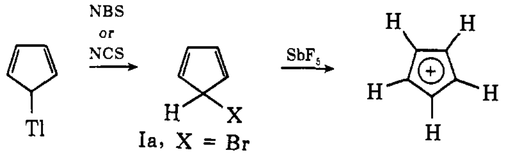


Figure 1. The epr spectrum of $C_5H_5^+$ at 78°K in a matrix of SbF_5.

studied,[5-7] in all of which the ground state is a singlet. However, when hexachlorocyclopentadiene is treated with SbF_5 it is converted to pentachlorocyclopentadienyl cation, which is in fact a ground-state triplet.[5,8] From this it was reasonable to expect that the unsubstituted cyclopentadienyl cation, if it could be prepared, would also be a ground-state triplet species.

Methods have recently become available for preparing 5-iodocyclopentadiene,[9] 5-bromocyclopentadiene,[10] and 5-chlorocyclopentadiene.[10] These are attractive precursors of unsubstituted cyclopentadienyl cation, although they do not afford this cation under mild solvolytic conditions.[9] We now wish to report that 5-bromocyclopentadiene (Ia) can be converted to the unsubstituted cyclopentadienyl cation II on treatment with SbF_5, and that this cation is indeed a triplet.



Ia, X = Br
b, X = Cl

II

Solutions of the 5-bromo- or 5-chlorocyclopentadienes (I) are prepared by treatment of thallium cyclopentadienide with the *N*-halosuccinimide in various solvents. The products (I) are identified both from the Diels–Alder dimers they form on warming the solutions and from their adducts with *N*-phenyltriazolinedione. To prepare the cation II, Ia (*ca.* 1 mmol) was prepared in di-*n*-butyl phthalate and vacuum transferred into one side of a molecular beam reaction apparatus.[11] Concurrently, 2 g (9 mmol) of SbF_5 was transferred from a bulb on the other side of this apparatus into the reaction chamber held at 78°K. When the transfer was complete a magnetic stirring bar was used to powder the product and it was transferred as a solid at 78°K into an epr tube.

The epr spectrum (Figure 1) of the product at 78°K showed triplet signals at 1189 ± 5, 1265, 2074 ± 2, 4187 ± 2, and 5323 ± 2 G. (A line at 3283 G (g = 2.010) is assigned to monoradical impurities.) The g_{xy} value is 2.0023 ± 0.0011 and the D value is calculated[12] to be 0.1868 ± 0.0005 cm^{-1}. The same (but weaker) spectrum was obtained from 5-chlorocyclopentadiene (Ib). In addition, the triplet spectrum[5,8] of $C_5Cl_5^+$ was observed in this latter case, apparently from contamination of Ib with hexachlorocyclopentadiene.

Figure 1 is certainly the epr spectrum of the triplet state of II. The coincidence of the x and y lines (E < 0.001, indicating plane regular polygonal symmetry) and the weakness of the z line are expected for II and are consistent with results[5,8] for the $C_5Cl_5^+$ triplet. The value of D for II is somewhat larger than the 0.1495-cm^{-1} value for $C_5Cl_5^+$, as expected since II is less delocalized. Curie law studies indicate that II, like $C_5Cl_5^+$, is in fact a ground-state triplet.[13] Thus, one of the most significant predictions of molecular quantum mechanics for $C_5H_5^+$, the cyclopentadienyl cation, has been confirmed.

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(13) Good Curie law behavior was observed for most samples down to liquid helium temperature. Although some showed deviations near 10°K, this was related to the prior history of the sample.

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A Molecular Beam Method for Preparing Carbonium Ion Solutions

Sir:

Through addition of solutions of alkyl halides to solutions of SbF_5 at low temperature, it has been possible to prepare stable solutions of many simple organic cations.[1,2] We have encountered two circumstances where this procedure is limited. Ions which can readily rearrange to isomers are difficult to obtain pure. The reaction of halides with SbF_5 is strongly exothermic; hence the heat released on the addition of each drop of reactant raises the temperature locally. Thus, *sec*-butyl cation which rearranges rapidly to *tert*-butyl cation only at −30° was always obtained rearranged to the extent of at least 25% even when the preparation was performed slowly using a dilute solution of the halide at a *bath temperature* of −120°.

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Unsaturated halides, even those leading to the highly stable allyl cations, are also difficult precursors. Here, even if some ion were formed from the initial quantity of halide, further amounts would invariably lead to polymerization since addition of cation to the double bond is usually faster than ionization. Such ions have, until now, been prepared in other ways.[3,4]

We report here a new method which permits the preparation of pure samples of easily rearranged carbonium ions and which also allows the use of unsaturated halides as precursors of allyl cations. The key idea is the formation of molecular beams of the reactants through introduction *via* nozzles into a highly evacuated chamber. These beams impinge on a surface cooled with liquid nitrogen to form an intimate solid mixture of the reagents. Only a faint haze of material is deposited on the sides of the chamber. This shows that the pressure is low enough to avoid collisions in the gas phase.

The apparatus used in this technique is shown in Figure 1. Flasks of SbF_5 and the appropriate organic chloride precursor (attached through a short length of capillary tubing if the chloride is very volatile) are attached to the side arms of the apparatus and degassed thoroughly. The chamber is cooled and evacuated and the transfer is begun. The rate of introduction of the two reagents is controlled through the temperatures of the flasks containing the reagents. Where the volatility of the halide requires it, a capillary can be interposed between the halide flask and the rest of the apparatus. The reactants meet only on the bottom of the central chamber. The reaction may occur then or on later warming to −120°. SO_2ClF or another solvent may be distilled in from the vacuum line to decrease the viscosity of the ion sample. Mixing can be facilitated by sealing a glass-covered magnetic stirring bar in the central chamber. The solution is decanted while at −100° or lower to nmr tubes which are attached to the side of the chamber.

sec-Butyl cation was prepared using this method by the simultaneous distillation over 30 min of 2.5 g of SbF_5 at 3° and 0.1 ml of *sec*-butyl chloride at −28° through a 40 × 0.5 mm capillary tube. Following preparation of the ion 1.5 ml of SO_2ClF was added by distillation and the solution was warmed to −100° and then transferred to the nmr tubes which were sealed off and removed. Integration of the 100-MHz nmr spectrum showed 95% unrearranged *sec*-butyl cation and 5% rearranged ion as the *tert*-butyl cation to be compared with the 75% *sec*-butyl cation and 25% *tert*-butyl cation resulting from the best previous preparation.

When 100 mg of 3-chloro-3-methylbut-1-ene and 8 g of SbF_5 were introduced into the apparatus, a solution was obtained with a spectrum which we assigned to 1,1-dimethylallyl cation. A complex group of peaks was observed between τ 1.5 and 2.1 assigned to the allyl protons and a singlet of twice the area at τ 6.4 ascribed to the methyls. The presence of such a small chemical shift between the inside and outside allylic protons is not unexpected, since most of the charge must be on the tertiary center rather than the primary carbon. The observation of a single peak for the two methyl groups can mean either that the chemical shift difference happens to be zero or that there is a low barrier for rotation around the bond to the vinyl group. This would again be not unexpected if the charge were localized on the tertiary carbon. No change in the spectrum was observed from −90 to +80°. We could not ascertain from the observed spectrum whether the vinyl protons form an ABC multiplet or an A_2B multiplet.

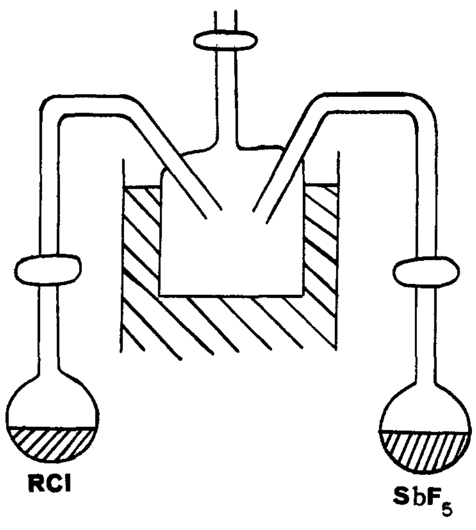

Figure 1.

When 1-chloro-3-methylbut-2-ene was used as a precursor, the same peaks were present but in addition a set of extraneous peaks could be observed. We believe that these are due to a dimer formed by attack of a molecule of cation on a neighboring molecule of the precursor before it has a chance to ionize. This hypothesis was supported by observing that using a very high ratio of SbF_5 to chloride led to lower quantities of extraneous peaks. This isomer would be expected to be more susceptible to attack by another cation, since it has a secondary–tertiary double bond in contrast to the primary–secondary double bond of the tertiary chloride.

Thus far, cyclopentenyl,[5] cyclopentadienyl,[6] and dimethylisobutyl[7] carbonium ions have been prepared by this method for the first time. It is likely that many additional interesting cations which have not previously been available could be prepared in this way.

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Enzymatic Preparation of an Optically Active Phosphotriester, Asymmetric Only at Phosphorus

Sir:

In this communication we describe the first preparation of an optically active triester of phosphoric acid,