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Molecular Beam Method for Preparing Stable Solutions of Carbonium Ions

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Abstract: A method is described for carrying out the reaction of SbF$_5$ and alkyl halides by using deposition of molecular beams of the reagents on a surface cooled to liquid nitrogen temperature to produce stable solutions of carbocations. This procedure is advantageous for preparing ions from unsaturated precursors or when the ions formed can easily isomerize.

Introduction

In 1964, Olah and co-workers[1] described a reaction between SbF$_5$ and alkyl halides, carried out by mixing solutions of these reagents, which yields carbonium ions (carbocations) as stable solutions where these ions can be examined by using NMR spectroscopy.[2] Since then, numerous publications have appeared concerning structural features,[3] rearrangement rates,[4] and thermodynamic parameters[5,6] in these stable carbocations. The purpose of this paper is to provide a detailed description of an improved technique[7] for carrying out this reaction for preparing stable solutions of carbocations, which we have found to be advantageous over the previously described experimental methods and which we have called the molecular beam method.

Difficulties of Previous Methods. The earlier methods reported work effectively for preparing many carbocations but two serious kinds of difficulty can arise in certain cases. The most common problem results from attempts to ionize unsaturated precursors. Quite often, after the first small amount of ion has been formed from the initial drop of precursor, further addition leads *only* to polymerization, because the addition of carbonium ions to double bonds or other unsaturated groups is an extremely facile reaction step[8] and usually occurs much more rapidly than formation of the desired unsaturated ion. Neither very slow addition nor efficient stirring makes any difference in these cases.

If the ion to be prepared can readily rearrange to a more stable cation, one often finds that an appreciable amount of the rearrangement product has been formed even though the reaction has been run using solutions cooled to a temperature where the desired ion would be stable. We feel that the reason for this is that the ionization reaction is so exothermic that, as each drop of the halide solution is added, local heating occurs which can cause isomerization before the heat is dissipated through stirring.

Very slow addition of a dilute solution with good stirring *can* alleviate this difficulty, but then a dilute solution of the ion is obtained which may not be strong enough to yield a good NMR spectrum. A case where this difficulty arises is the preparation of *sec*-butyl cation from *sec*-butyl chloride where even the use of a dilute solution still resulted in the formation of an appreciable amount of *tert*-butyl cation.[9]

The Molecular Beam Method. Briefly, the present procedure involves transfer of alkyl halides and antimony pentafluoride through separate nozzles into an evacuated chamber where they condense on a liquid-nitrogen-cooled glass surface. SO$_2$ClF, another solvent, or a substance intended to react with the initially formed cation may be added through a third nozzle in the apparatus if this is desired. The resulting intimate, solid mixture is then dissolved in SO$_2$ClF at low temperature and transferred to an NMR tube for study.

Scope. The principal advantage of this technique is that the

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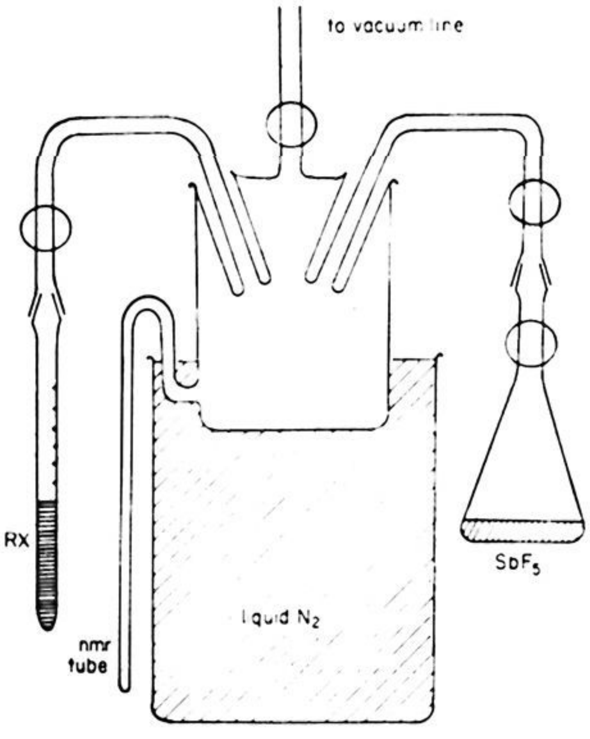

Figure 1.

precursor is matrix-isolated in excess SbF_5 at temperatures close to −196 °C during the vacuum deposition and polymerization is thereby strongly inhibited. After introduction of the solvent, the solution can readily be kept below −120 °C during the transfer and NMR observation to allow observation of relatively unstable carbocations. The relative concentrations of RX, SbF_5, and SO_2ClF are easily controlled over a wide range and are uniform in the deposited solid during the preparation.

The molecular beam method is, of course, not applicable to cases where the precursor is nonvolatile. However, even *slightly* volatile substances can be used if even a few milligrams of material can be transferred with the aid of high vacuum in a reasonable time.

This basic technique has been used routinely at Yale for the last 7 years in the preparation of cation solutions and has been found to be more convenient than the previously used procedure which involved slow addition of solutions of the reagents on the vacuum line.

We found that clean solutions of cyclopentenyl[10] and cyclohexenyl[11] cations can be easily made from the allyl halides using the molecular beam method. This technique was also used in the first preparation of the cyclopentadienyl cation.[12] In this case, the highly unstable cyclopentadienyl halide precursers could not be handled normally because of rapid polymerization; therefore they were produced in a generating flask directly attached to the molecular beam apparatus and transferred into it as they were formed and volatilized.

A modified version of this procedure has been employed by using an apparatus with *three* addition nozzles instead of two for the purpose of adding carbonium ions to olefins in a single preparative step.[8] We are sure that reactions of carbocations with other reagents could also be investigated in the same way.

We have also used our procedure to prepare many other cations which have been previously made using other methods, since we have found that we can readily obtain solutions which yield quite clean NMR spectra.[13-15] It seems clear to us that, at this point, the molecular beam procedure should be the method of choice for preparing carbocations and should be seriously considered for any reaction where highly reactive, volatile reactants are involved.

Experimental Section

Before the apparatus (Figures 1 and 2) is attached to the vacuum line, a 5-mm NMR tube for proton spectroscopy or a 10-mm tube for carbon spectroscopy or both, each tube containing external standards of 5% Me_4Si in CD_3COCl (used for the spectrometer lock) is sealed on. The glass capillary which contains the external standard is prepared on the vacuum line by distilling CD_3COCl and a small amount of Me_4Si into the tube. For a 5-mm NMR tube, a 2-mm capillary is used; for a 10-mm tube, a 4-mm o.d. glass tube is used. The CD_3COCl/Me_4Si solution is sealed in the appropriate tube under vacuum and a solid glass rod of approximately the same diameter is fused to the top of the glass tube in order to prevent the capillary from floating in the dense reaction solution.

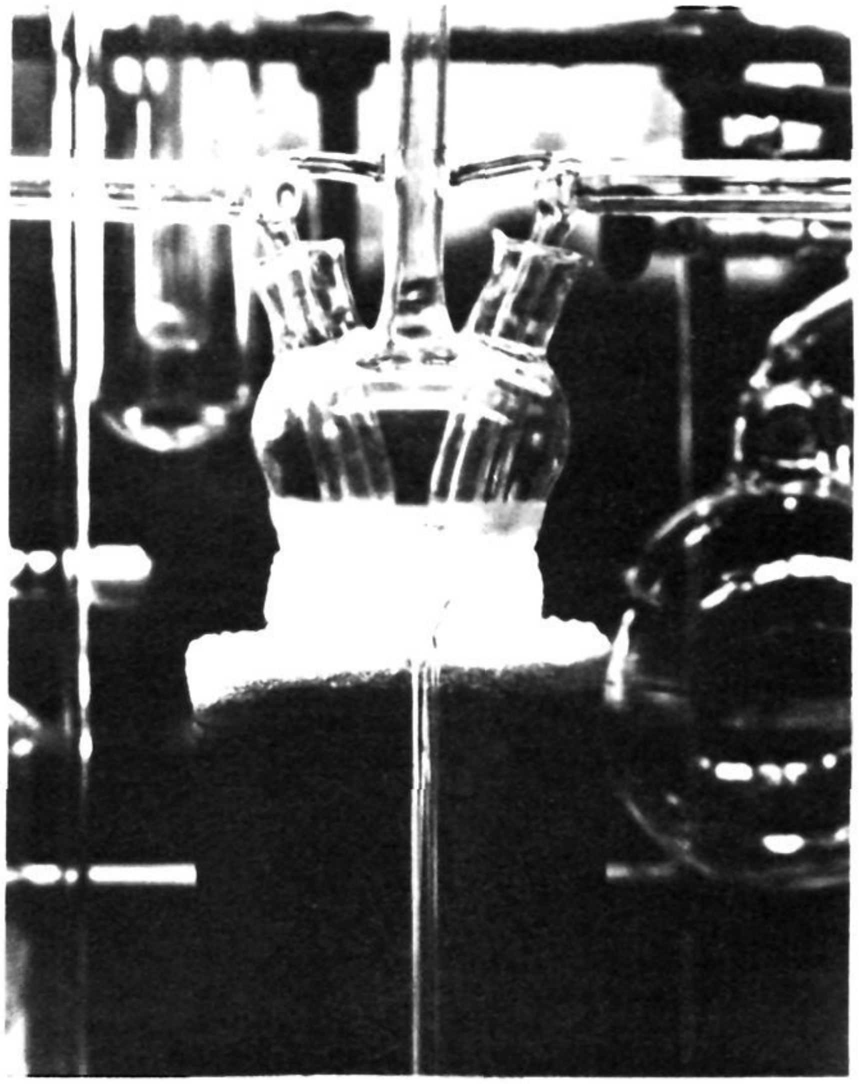

Figure 2.

In order to align the external lock tube with the glass rod, a die is used which holds them in line while they are fused together. The head of the rod is flattened so that it just fits inside the appropriate NMR tube. This tends to keep the external standard and lock tube centered.

A tared, evacuated flask containing SbF_5 is attached to one arm of the apparatus. A Teflon stopcock is used on this flask since SbF_5 reacts with stopcock grease. At 0 °C the SbF_5 distills at about 1 g/15 min. This rate is suitable for most preparations. Typically about 2 g of SbF_5 is transferred.

Another evacuated sample holder containing RX, usually a 1-mL pipet with calibrated markings that has been sealed at the delivery end and has a Teflon needle valve at the other, is attached to the second arm. For compounds with boiling points of less than 100 °C, a narrow diameter pipet is convenient to avoid too rapid transfer. The rate of addition is controlled as well with the Teflon needle valve and through the temperature of a bath surrounding the holder. Usually about 0.15 mL is distilled in about 20 min, but we have used much less material in order to prepare solutions of ions from unsaturated precursors as dilute as 0.01 M.

All materials must be thorougly degassed by using freeze-thaw cycles before beginning the transfer. Before the codistillation is begun, warm solvent is placed in the nozzle jackets to make sure that SbF_5 does not condense in the nozzle. In some cases when the transfer of a very small amount of a halide is desired, we have made a dilute solution of it in SO_2ClF. The RX and SO_2ClF are codistilled from a narrow tube to prevent fractionation since most of the halides used are considerably less volatile than SO_2ClF.

The apparatus shown in Figures 1 and 2 is attached to the vacuum line and a pressure not in excess of 1×10^{-5} Torr is obtained in the system, and then the chamber is immersed in liquid nitrogen. Next, the solvent SO_2ClF is distilled into the chamber from a reservoir on the vacuum line at a rapid rate. The solvent is distilled first, since the heat generated by heats of condensation and fusion may cause unwanted rearrangements or reactions of the stable carbocations if they are sensitive to heat and if the solvent were distilled in last. Usually about 2.0–2.5 mL of solvent is added. This quantity will result in a final concentration of the solution of less than about 0.75 M. This is the maximum concentration we have been able to prepare with this technique. If it is desired that the concentration be higher, it is possible to remove some of the solvent and/or SbF_5 by distillation.

The usual practice is next to distill in some SbF_5 and then to open the needle valve so that RX distills at a slow, even rate of about 0.005 mL per min. The two reactants condense on the surface cooled by liquid nitrogen. Maintaining low pressure during the preparation is important in order that all the SbF_5 deposits as desired on the cold surface. If the pressure is too high, SbF_5 is dispersed by collisions in the gas phase into the RX nozzle. Then some of the RX reacts with this deposit and forms a layer of reactive cations and polymer in the RX nozzle where a small amount collects. This diminished the amount of RX which reaches the chamber. Polymeric material from the nozzle can also drip into the chamber upon warming and contaminate the sample.

Once the desired amounts of RX and SbF_5 are deposited, the stopcock is closed and the apparatus is removed from the vacuum manifold. The chamber is then placed in a thick slurry of 1:1 ethanol: methanol and liquid nitrogen at −125 °C and the NMR tubes are simultaneously placed in a Dewar containing an identical slurry.

The tubing which connects the NMR tubes to the chamber is wrapped in glass wool and periodically soaked with the −125 °C slurry. The slurry is slowly allowed to warm to about −120 °C at which time the SO_2ClF melts and begins to dissolve the intimate mixture of RX and SbF_5. This process can be hastened by removing the chamber from the Dewar for short periods of time and swirling the solution.

Once all of the solid has dissolved, the apparatus is tipped so that the desired amount of material pours into each NMR tube. The depth of the solution in the NMR tubes is important because the cooling system of most spectrometers only cools a limited length of the tube. Any material above this level might be subjected to higher than desired temperatures. With the desired amount of solution in each tube, the apparatus is returned to the vacuum line, where the chamber and tubes were placed in Dewars filled with liquid nitrogen. After the solution freezes, the entire apparatus is again evacuated to remove any gas which might be present. The NMR tubes are sealed off and stored at liquid nitrogen temperature.

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1,4,5,8-Tetramethylnaphthalene Dication and Related Radical Cations

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Abstract: The oxidation of 1,4,5,8-tetramethylnaphthalene in SbF_5/SO_2ClF solution at −80 °C yields the 1,4,5,8-tetramethylnaphthalene dication. Hexahydropyrene and 1,2,3,4,-tetramethylnaphthalene, under similar conditions, give an equilibrium of the corresponding dication and radical cation, $Ar^{2+} \rightleftharpoons Ar^{+\cdot}$, whereas oxidation of dibenzopyracyclene gives only the radical cation. Study of the cations was carried out by ^{13}C NMR spectroscopy. The reasons, particularly peri-strain of the contrasting oxidation tendencies of the studied, 1,4,5,8-substituted naphthalenes, are discussed.

Introduction

The ease of oxidation of polycyclic aromatic hydrocarbons is well recognized.[3-10] In our previous work,[11] we reported the two-electron oxidation of an extensive series of arenes by SbF_5/SO_2ClF solution to dipositive ions and their study by ^{13}C NMR spectroscopy. In continuation of our work on dications, we wish to report the oxidations of 1,4,5,8-tetramethylnaphthalene (**1**), hexahydropyrene (**2**), dibenzopyracyclene (**3**), and 1,2,3,4-tetramethylnaphthalene (**4**) under similar conditions and their carbon-13 NMR spectroscopic study.

Results and Discussion

A series of 1,4,5,8-tetra-substituted naphthalenes was examined for the formation of stable dications in SbF_5/SO_2ClF solution. The dications and/or their exchanging systems with the corresponding radical cations were observed by ^{13}C NMR spectroscopy. Results are summarized in Table I. The tetra-α-substituted naphthalenes represent borderline cases for the formation of dications by oxidation with SbF_2 in SO_2ClF. The dication of octamethylnaphthalene has been reported in preceding work,[11] but neither naphthalene itself nor any of the

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