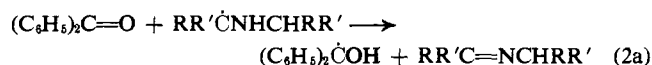
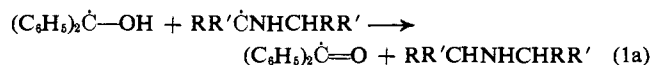


steric factors diminish the rate of the second step (eq. 2a).



The reverse of reaction of type 1, thermodynamically favorable but frequently not observed for kinetic reasons,⁹ may then intervene and reduce the observed rate of photoreduction (eq. 1a). Evidence for such reversibility has been seen in photoreduction of benzophenone in optically active methyl 2-octyl ether.⁷



The tertiary amine reacts quite slowly, comparable to the hydrocarbons; half of the rate, as compared with *n*-butylamine or with the secondary amine, may be lost because of absence of the reaction related to eq. 2, and the remainder again possibly because of reversibility.⁷ The low reactivity of *t*-butylamine may indicate that α -C-H is necessary for high reactivity, while the low reactivity of the tertiary amine indicates that presence of α -C-H is clearly not sufficient. The 5:1 relative reactivity of 2-propanol and cyclohexane in our work is similar to that observed in competitive experiments.¹⁰

It remains possible that the abstractions of hydrogen occur in the reverse order, triplet ketone abstracting hydrogen from nitrogen and the radical transferring α -H from carbon to ground-state ketone. Experiments with suitably deuterated amines and with optically active amines will give information about this and about the reversibility. Experiments with suitable diamines may lead readily to heterocyclic compounds.

(9) S. G. Cohen, D. A. Laufer, and W. V. Sherman, *J. Am. Chem. Soc.*, **86**, 3060 (1964).

(10) C. Walling and M. J. Gibian, *ibid.*, **86**, 3902 (1964).

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Received May 3, 1965

Stable Carbonium Ions. XIII.¹

Generation of Stable Alkyl, Alkylaryl, and Cycloalkyl Carbonium Ions from Alcohols in Fluorosulfonic Acid and Antimony Pentafluoride

Sir:

Attempts to generate simple alkyl, arylalkyl, and cycloalkyl carbonium ions in sulfuric acid or oleum solution generally result in the formation of complex mixtures in which the stable carbonium ions present are of the methylated cyclopentenyl cation type (stabilized allylic cations²).

Sulfuric acid and oleum as solvents have the serious disadvantage that they are quite viscous and possess relatively high freezing points. This generally results in the need to carry out the investigations at or above +10°. At these temperatures the rate of secondary reactions leading to the cyclized allylic type ions is so high that no simple alkyl (cycloalkyl) carbonium ions

(1) Part XII: G. A. Olah and M. B. Comisarow, *J. Am. Chem. Soc.*, **86**, 5682 (1964).

(2) For a summary, see N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, (1964).

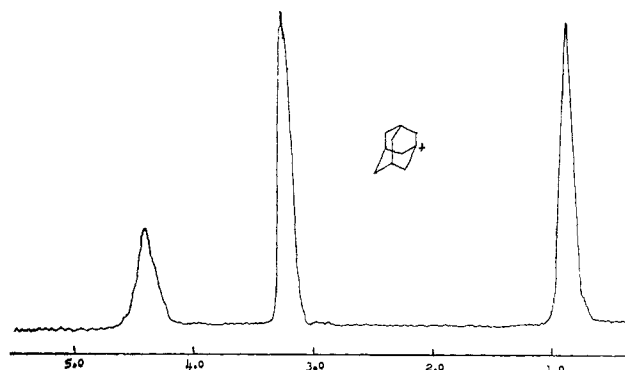


Figure 1.

corresponding to the alcoholic precursors are observable.

One of us was previously able to report that stable alkyl (cycloalkyl) carbonium ions are formed from halide (fluoride, chloride) precursors in neat antimony pentafluoride or mixed SbF_5-SO_2 , SO_2F_2 , SOF_2 , or SO_2ClF solvent systems.³

It was of substantial interest to try to extend the scope of forming stable carbonium ions by using alcohols as precursors. In many instances the alcohols as precursors are much more readily available, and their conversion to the corresponding halides without isomerization can represent serious problems.

We would like now to report our observations concerning the generation of stable carbonium ions from alcohols under conditions where no rearrangements (a characteristic of sulfuric acid and oleum systems) take place.

Fluorosulfonic acid is one of the strongest pure acids that has yet been studied.⁴ H_0 for the neat acid is about -12.6 (compared with -11 for 100% sulfuric acid and -10 for anhydrous hydrogen fluoride). At the same time fluorosulfonic acid has a low freezing point (-87.3°) and can be readily purified. As to be expected very few coacids are capable of enhancing the acidity of fluorosulfonic acid. Gillespie and his co-workers, however, observed that antimony pentafluoride acts as acid in fluorosulfonic acid solution by enhancing ionization according to $SbF_5 + 2FSO_3H = H_2SO_3F^+ + SbF_5(SO_3F)^-$. Solutions of SbF_5 in fluorosulfonic acid are considered the most acidic media that have yet been studied.

When alcohols like *t*-butyl alcohol, *t*-amyl alcohol, methylethylphenylcarbinol, diphenylethylcarbinol, 2-*exo*-norborneol, and 1-adamantanol were dissolved in fluorosulfonic acid-antimony pentafluoride solutions diluted with sulfur dioxide (in order to achieve better mixing of the less viscous solutions and to avoid the possibility of local overheating) at temperatures ranging around -60°, stable, slightly colored solutions are formed. The p.m.r. spectra of these solutions (Figures 1-5) show the corresponding carbonium ions with generally good resolution.

We have also found that solutions of the alcohols in SbF_5-SO_2 show formation of the corresponding carbonium ions, indicating ionization in the strong Lewis

(3) G. A. Olah, *et al.*, *J. Am. Chem. Soc.*, **86**, 1360, 5680 (1964).

(4) R. J. Gillespie in "Friedel-Crafts and Related Reactions," Vol. 1, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

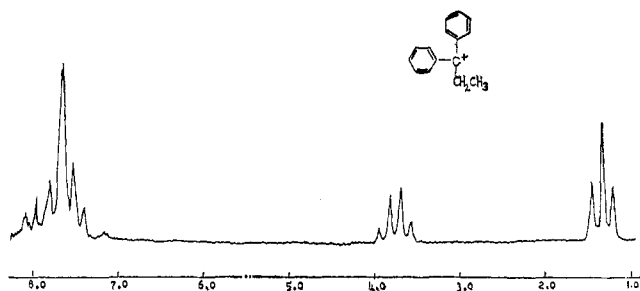


Figure 2.

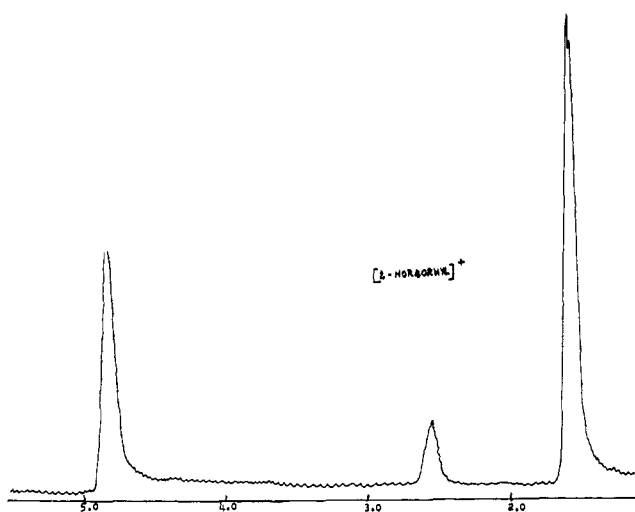


Figure 3.

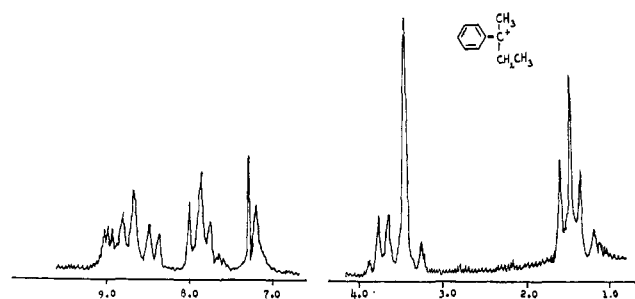


Figure 4.

acid itself



The resolution of the spectra; however, is generally poorer, and frequently substantial peak broadenings occur.

When solutions of alcohols in fluorosulfonic acid or fluorosulfonic acid-sulfur dioxide were prepared, tertiary carbonium ions could be generally observed, but peak broadenings (due to exchange) and side products are observed. Secondary and primary alcohols form generally only the monosulfates. It is, however, noteworthy that benzhydryl alcohol, 1-adamantanol, and 2-*exo*-norborneol at -60° in neat fluorosulfonic

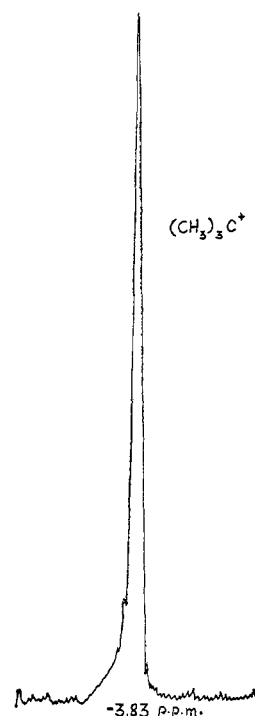


Figure 5.

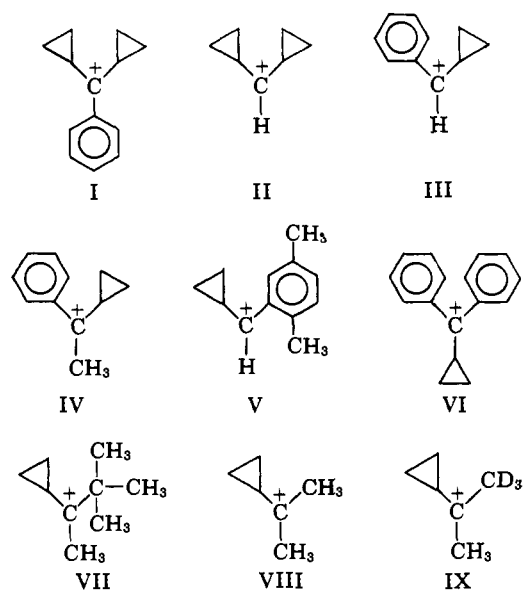
acid gave very well-resolved spectra of the corresponding carbonium ions.

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Stable Carbonium Ions. XIV.¹ Cyclopropylcarbonium Ions

Sir:

We wish to report the direct observation of a series of cyclopropylcarbonium ions (I-IX), including the first



(1) Part XIII: G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **87**, 2997 (1965).