other glycols were reagent grade commercial materials used without further purification.

Nmr Spectra, Preparation of Diprotonated Glycols, and Study of Their Cleavage. A Varian Associates Model A-56-60A spectrometer with variable-temperature probe was used for all spectra. The preparation of the samples and the procedure for the kinetic study were described in an earlier paper for alcohols.[2]

Acknowledgment. Support of this work by grants of the National Science Foundation and the National Institutes of Health is gratefully acknowledged. The award of a postdoctoral fellowship by the North Atlantic Treaty Organization is also acknowledged (J. S.).

Stable Carbonium Ions. LIV.[1] Protonation of and Hydride Ion Abstraction from Cycloalkanes and Polycycloalkanes in Fluorosulfonic Acid–Antimony Pentafluoride

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received June 12, 1967*

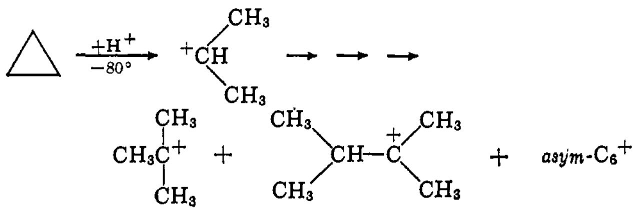
Abstract: The behavior of cycloalkanes and polycycloalkanes in the strong acids FSO_3H-SbF_5 and $HF-SbF_5$ with and without SO_2ClF as diluent was investigated. At temperatures above 0° ring cleavage occurs to give acyclic alkylcarbonium ions. At lower temperatures hydride ion is abstracted and cycloalkyl cations are formed.

In previous work,[3,4] we have investigated the formation of carbonium ions from alkanes in the strong acids FSO_3H-SbF_5 and $HF-SbF_5$. Hydride ion is abstracted in the decreasing order of reactivity from the tertiary, secondary, and primary positions. Secondary and primary carbonium ions formed under these acidic conditions are stabilized by immediate rearrangement (frequently with fragmentation or dimerization) to tertiary carbonium ions. The methylcyclopentyl cation[5] is the only cycloalkyl cation which has been investigated previously. It was therefore of interest to extend our investigations to the study of the formation of carbonium ions from cycloalkanes and polycycloalkanes in strong acids.

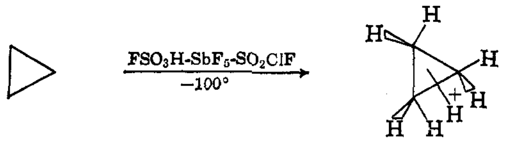
Results and Discussion

Cycloalkanes are protonated in FSO_3H-SbF_5 or $HF-SbF_5$ solution with subsequent hydrogen abstraction or cleavage, depending on reaction conditions. Which reaction path is taken depends on (a) the reaction temperature, (b) the acid strength, and (c) the ring size. At low temperatures (generally −60 to −100°) hydride abstraction is favored; at higher temperatures cleavage occurs. Decreasing acid strength tends to favor cleavage.

Cyclopropane is protonated and cleaved in $FSO_3H-SbF_5-SO_2ClF$ or $HF-SbF_5-SO_2ClF$ solution above −80° to give acyclic products. Through various di- and trimerization processes and fragmentations, the products are, in varying amounts, the *t*-butyl and *t*-hexyl cations (the pmr spectra of which are well known from our previous work).[2,3,6] The cyclopropyl cation itself is not stable in these systems, as shown previously.[4]



At −100° cyclopropane behaves differently. In $FSO_3H-SbF_5-SO_2ClF$ solution it forms a species the pmr spectrum of which shows four lines, probably two doublets at −2.30 and −2.10 ppm (J_{H-H} = 6 Hz) and a septuplet at −6.40 ppm (J = 6 Hz) (Figure 1), besides some ring-opened ions. On warming to −80°, the pair of doublets collapses to a single doublet (Figure 2). This transformation is reversible. The pmr spectral observation could indicate that protonated cyclopropane (I) is formed: the single proton (on the face of the cyclopropane ring or in an "edge"-protonated but equilibrating system) gives rise to the septuplet at δ −6.40 coupled to six methylene hydrogens, which in turn appear as a doublet. On comparison of the chemical shifts with those of comparable open-chain ions, such as isopropyl cation,[6] the allyl cation,[7] and cyclopropyl cations,[8] one finds the nmr absorption of the assumed protonated cyclopropane shifted upfield. A large anisotropy effect must be thus responsible for this effect.



I ?

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[1] Part LIII: G. A. Olah and J. Sommer, *J. Amer. Chem. Soc.*, **90**, 927 (1968).

[2] National Institutes of Health Postdoctoral Research Investigator, 1965–1967.

[3] G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2227 (1967).

[4] G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967).

[5] G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *ibid.*, **89**, 2692 (1967).

[6] G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, **86**, 1360 (1964).

[7] G. A. Olah, and M. B. Comisarow, *ibid.*, **86**, 5682 (1964).

[8] R. Breslow, H. Hover, and H. W. Chang, *ibid.*, **84**, 3168 (1962).

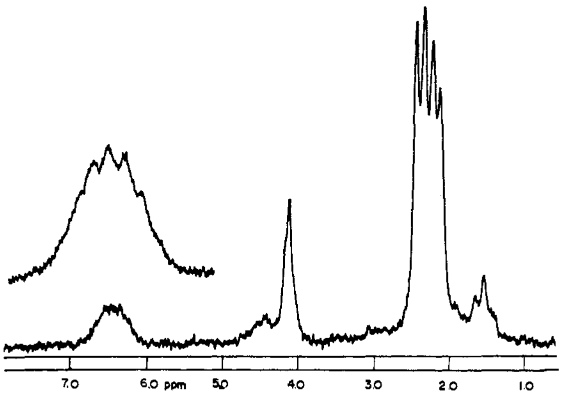
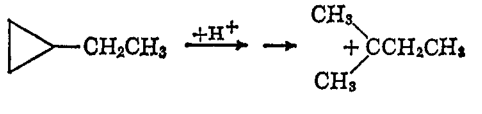


Figure 1. Nmr spectrum of cyclopropane in FSO_3H-SbF_5-SO_2ClF at −100°.

The fact that the methylene groups give rise to a pair of doublets at −100° suggests that the hydrogens above and below the plane of the ring have different magnetic environments and they are both coupled to a single hydrogen, the geminal coupling being too small to be observed.

Much must be done, however, including decoupling experiments (made difficult due to the thermal instability), study of deuterated derivatives, and a thorough quantitative study of quenching products (again very difficult in this system) and investigation of related substituted cyclopropanes before species I can be definitely identified. Our efforts in this direction are continuing. At the present time data are insufficient to claim that the nmr spectra observed are those of a monomeric cyclopropane derivative and not of a secondary ring-opened product or whether we indeed observed the elusive protonated cyclopropane. It also must be noted that, due to the extreme sensitivity of the system, to obtain resolved spectra as that shown in Figure 1 is difficult and necessitates extreme care.

Ethylcyclopropane undergoes protolytic ring opening and rearrangement to the *t*-amyl cation under all conditions studied.



Isopropylcyclopropane loses the methine hydrogen of the isopropyl group when treated with FSO_3H-SbF_5 in SO_2ClF at −100°. The dimethylcyclopropylcarbonium ion (II)[9] is noteworthy, since the two methyl groups are magnetically nonequivalent. The steric configuration of the ion is such that one methyl group lies in the face of the cyclopropyl ring and thus will experience its diamagnetic anisotropy. The methyl groups therefore appear as two singlets separated by 0.54 ppm (bisected form).

Concurrently with hydride abstraction, protonation occurs which leads through ring opening to tertiary hexyl cations.

We were able to observe the dimethylcyclopropylcarbonium ion up to a temperature of 0° (previously it was observed only below −35° when generated from the alcohol. The difference in stabilities is presumably due to differences in the medium used for generating the ions). Two of the *t*-hexyl ions, methyldiethylcarbonium ion and dimethylpropylcarbonium ion, rearranged at this temperature to the dimethylisopropylcarbonium ion. The doublet due to this ion was superimposed on the upfield singlet of one of the methyl groups of ion II.

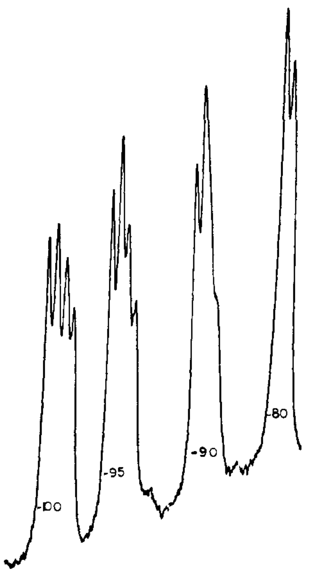
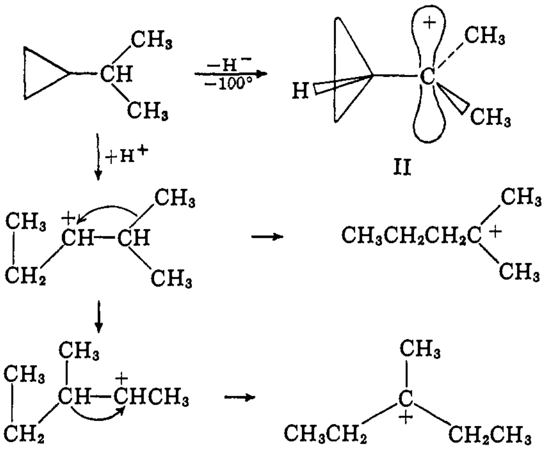


Figure 2. Nmr spectra of the methylene groups of species I between −80 and −100°.



II

Cyclobutane in the highly acidic solvent media gives at −100° a pmr spectrum which consists of a multiplet at −6.50 ppm, a broadened peak at −5.63 ppm, and doublets at −4.50 (J = 9 Hz) and −4.05 ppm (J = 7 Hz) (Figure 3). If protonation of cyclobutane had occurred, subsequent cleavage and rearrangement would be expected to give the *t*-butyl cation which, however, was not observed. Hydride abstraction is therefore likely. We tentatively interpret the spectrum shown in Figure 3 as either that of the cyclobutyl cation (III) or that of the mixture of the cyclobutyl cation (III) and the cyclopropylcarbinyl cation (IV). If the spectrum is that of only ion III it must exist in a configuration in which the three methylene groups are arranged in such a manner that they form two magnetically equivalent groups of hydrogen atoms, which would be all coupled to the methine hydrogen (vicinal and geminal coupling could be expected to be insignificant). The only suitable configuration to satisfy this requirement would be a tri-

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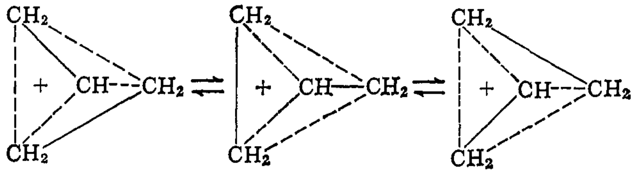
[9] C. U. Pittman and G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 2998 (1965).

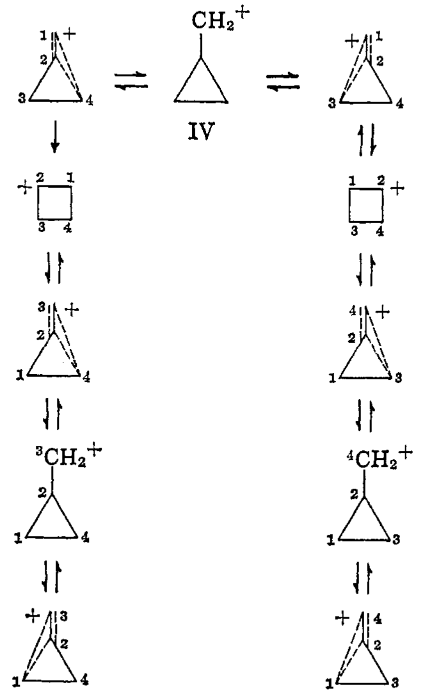
cyclobutonium ion. In it the CH+ would be located above a cyclopropane ring (consisting of three methylene groups bonded with one full and two half-bonds), alternately bonded with one full and two half-bonds to the ring carbon atoms.[10]



(III)

The nmr observation, however, also could be accounted for by a mixture of ions III and IV or by a rapidly equilibrating system. At the present time we have no definite evidence to exclude the possibility that the spectrum shown in Figure 3 is that of a single species (ion III) or a mixture of ions III and IV. Rapid equilibration could also take place according to the following scheme. Interconversion through the six possible bicyclobutonium ions would let the cyclobutyl cation (III) appear in the pmr spectrum just like the tricyclobutonium ion. This by no means would be taken, however, as to indicate experimental evidence for existence of a nonclassical structure. The relatively slow nmr method will only see the mean average of all existing conformations, each one of which can be perfectly "classical" as are the three cyclopropylcarbinyl and two cyclobutyl cations, which are intraconverted in the equilibration process.[11]

Quenching the solution of cyclobutane in SO_2ClF–FSO_3H–SbF_5 with methanol gave an 80% yield consisting of 90% methyl cyclopropylcarbinyl ether and 10% methyl cyclobutyl ether, but no methyl allylcarbinyl ether.



A detailed investigation of the cyclobutyl–cyclopropylcarbinyl–allylcarbinyl cation system is in progress in our laboratories and will be reported in detail in a later publication. Above −100° cyclobutane is protonated and immediately cleaved and rearranges to the *t*-butyl cation.

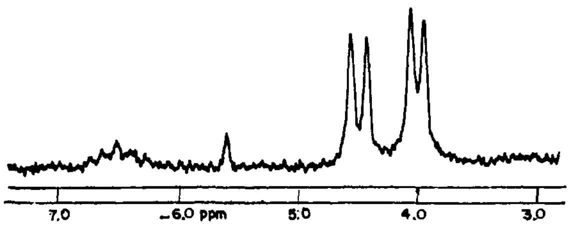
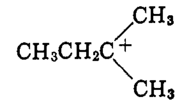
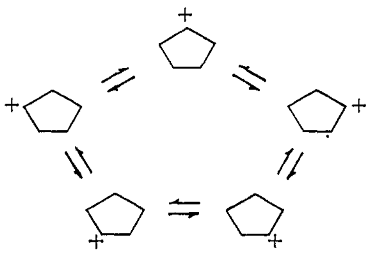


Figure 3. Nmr spectrum of cyclobutane in FSO_3H–SbF_5–SO_2ClF at −100°.

Bicyclo[1.1.0]butane polymerizes in FSO_3H–SOF_5–SO_2ClF solution even at −125°, and no conditions were found to be able to observe any well-identified products.

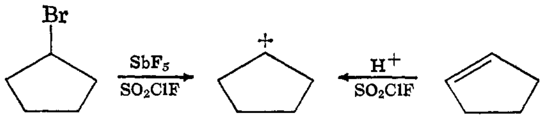
Cyclopentane is protonated in FSO_3H–SbF_5 or HF–SbF_5 solution above −10° and yields *via* cleavage and rearrangement the *t*-amyl cation. Below −10° in solution diluted with SO_2ClF the pmr spectrum exhibits only one singlet (at −4.75 ppm). The spectrum is unchanged even at such low temperatures as −130°. Only through rapid 1,2-hydride shifts around the ring can all hydrogen atoms become magnetically equivalent.





V

The cyclopentyl ion (V) can also be generated from cyclopentyl bromide and cyclopentene. Quenching its solution in SO_2ClF–FSO_3H–SbF_5 with methanol yields, in high yield, cyclopentyl methyl ether.



V

Cyclohexane in FSO_3H–SbF_5 loses, at room temperature, a hydride ion in 90% of the reaction and gives the methylcyclopentyl cation (VI), which is formed through rearrangement of the incipient cyclohexyl ion.[5] The cyclohexane (10%) goes to the dimethylisopropylcarbonium ion,[3,4] which indicates protonation followed by immediate ring opening and rearrangement to the stable dimethylisopropylcarbonium ion.

With increasing temperature the ratio of hydride abstraction *vs.* cleavage is decreasing so that at 60° only ring opening occurs.

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(10) J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, 73, 3542 (1951).

(11) R. Breslow, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, 262.

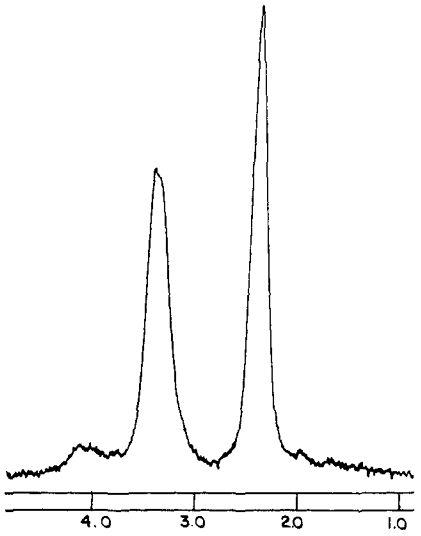
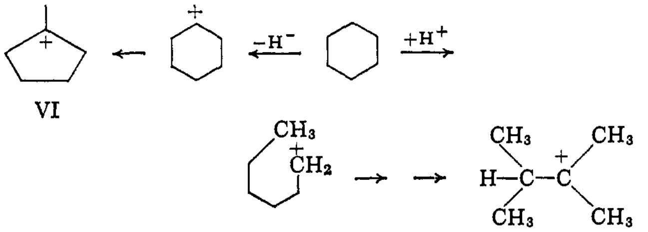
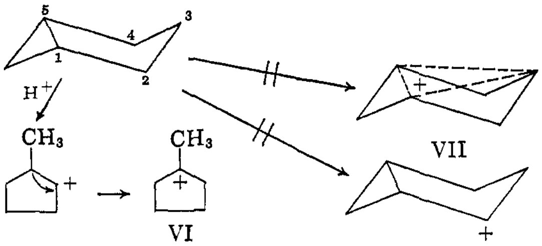


Figure 4. Nmr spectrum of decalyl cation (VIII) at −80°.

Methylcyclopentane follows the same reaction pattern as cyclohexane. Since, however, a tertiary hydrogen atom is ionized easier than a secondary, hydride abstraction is more favored (giving ion VI) over cleavage than in cyclohexane and therefore the latter occurs only at temperatures above 25°. We reported the 1-methylcyclopentyl cation previously.[5]

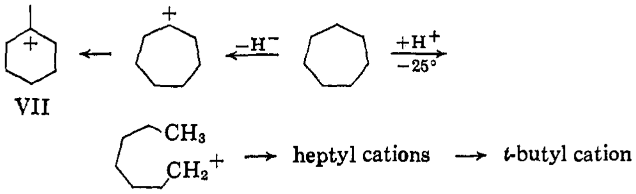


Bicyclo[3.1.0]hexane could be[9] expected to ionize *via* hydride ion abstraction either in the 3 position with simultaneous 1–5 carbon–carbon σ bond delocalization to give the nonclassical trishomocyclopropenyl cation (VII)[12] or in the 2 or 4 position to give a cyclopropylcarbinyl cation. Hydride abstraction could not, however, be detected. Instead, protonation of the cyclopropyl ring occurs with breakage of the 1,6 bond. The incipient secondary 2-methylcyclopentyl ion rearranges immediately to the 1-methylcyclopentyl cation (VI).

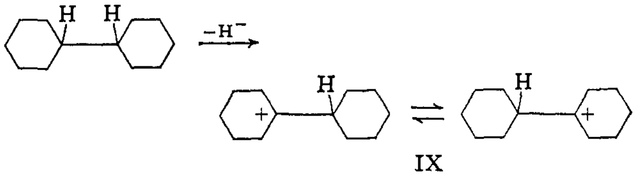


Cycloheptane is protonated in FSO_3H-SbF_5 at room temperature, followed by ring opening, rearrangement, and fragmentation. The heptyl cations are not stable[3,4] under these conditions, and the *t*-butyl cation is the only detectable product.

At −60°, through hydride abstraction the cycloheptyl cation is formed and rearranges immediately to the 1-methylcyclohexyl cation (VIII).

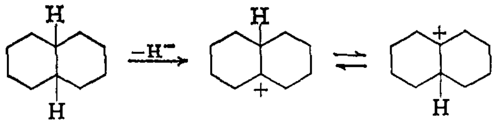


The bicyclic hydrocarbon bicyclohexane in FSO_3H-SbF_5 solution loses one or two tertiary hydrogen atoms. Analogous to the isopropyldimethylcarbonium ion[3,4] the tertiary hydrogen then undergoes a rapid 1,2-hydride shift. The pmr spectrum consists of multiplets at −4.10, −3.10, and −2.10 ppm for the α, β, and γ–δ hydrogens in the equilibrating ion IX.



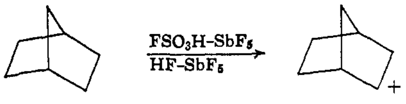
IX

Decalin behaves similarly to bicyclohexane. A rapid, reversible hydride shift between carbon atoms 9 and 10 in the spectrum of the decalyl cation L (X) appears as three multiplets (−4.08, −3.38, and −2.39 ppm) for the equilibrating 9,10-hydrogen atom and for the α- and β-methylene groups (Figure 4).



X

Norbornane in FSO_3H-SbF_5 and HF-SbF_5 gives the 2-norbornyl cation (XI)[13,14] at all temperatures. Above 0°, however, increasing amounts of fragmentation products are formed, primarily the *t*-butyl cation.



XI

The temperature dependence of the spectrum of the 2-norbornyl cation as observed previously can be seen in either neat acid solution or in a solution of SO_2ClF. However, in the former case the temperature of complete equilibration (where the three peaks of the spectrum will collapse to one broad peak due to the increasing rate of the 2,3-hydride shift) is 100° higher than if the solution is diluted with SO_2ClF. We would like to suggest the same explanation for this observation as previously given in the case of the *t*-amyl cation.[3,4]

Adamantane ionizes *via* hydride ion abstraction to the 1-adamantyl cation,[15] known from our previous work. *endo*-**Trimethylenenorbornane** (tricyclo-

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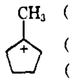
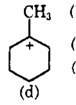
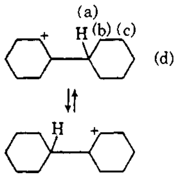
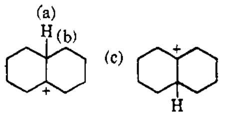
[12] S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron Suppl.*, 8, 621 (1966).

[13] P. von R. Schleyer, W. E. Watts, R. C. Fort, M. B. Comisarow, and G. A. Olah, *J. Amer. Chem. Soc.*, 86, 5679 (1964).

[14] M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, 86, 5680 (1964).

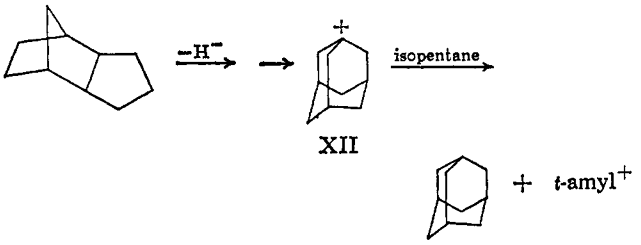
[15] P. von R. Schleyer, R. C. Fort, W. E. Watts, M. B. Comisarow, and G. A. Olah, *ibid.*, 86, 4195 (1964).

Table I. Nmr Shifts (in ppm) and Coupling Constants (in Hz) of Cycloalkyl Cations

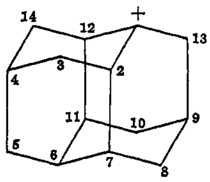
Cation	Structure	δ values,[a] ppm				Temp, °C
		(a)	(b)	(c)	(d)	
V, Cyclopentyl			−4.75 (s)			−10 to −100
VI, Methylcyclopentyl		−4.20 (q) 4.0	−3.98 (p) 4.0	−2.45 (m)		25 to −60
VIII, Methylcyclohexyl		−4.33 (m)	−3.97 (p) 3.5	−2.61 (m)	−2.29 (m)	−60
IX, Bicyclohexyl		−4.10	−3.10	−2.10		−60
X, Decalyl		−4.08	−3.38	−2.39		−80
XI, Norbornyl		−5.35	−3.15	−2.20		−30
			−3.3			90
XII, Adamantyl		−5.12	−4.10	−2.37		25
XIII, Congressyl (diamantyl)	Positions	7, 11 −4.67 9 −4.40 (m)	2, 12 −4.10 (m)	13 −3.50 (d, 4.5)	3,4,5,6, 8,10,14 −2.03 (m)	−30

[a] δ values in SO_2ClF, (multiplicity) J values (H–H) in hertz. Chemical shifts are solvent dependent. In neat FSO_3H–SbF_5 they are ~0.3 ppm downfield from those in SO_2–FSO_3H–SbF_5, or SO_2ClF–FSO_3H–SbF_5. Downfield from capillary TMS. Abbreviations used: p, pentuplet; d, doublet; q, quintet; m, multiplet.

$[5.2.1.0^{2,6}]$decane) ionizes and rearranges in FSO_3H–SbF_5 solution to give the 1-adamantyl cation (XII) with the *t*-butyl cation and other unknown fragmentation products formed in side reactions. The 1-adamantyl cation is formed in 35% yield of the total of products. Upon addition of pentane to the acid solutions, adamantane can be isolated. Pentane acts as a source of hydride ion converting the adamantyl cation to the hydrocarbon, forming simultaneously the *t*-amyl cation. When an excess (200%) of tricyclodecane is used, adamantane could be isolated in 50% yield based on reacted tricyclodecane (*endo*-trimethylenenorbornane). Quenching the solution of the adamantyl cation with water or methanol gives a nearly quantitative yield of 1-adamantanol and methyl 1-adamantyl ether. The method, therefore, seems to have preparative importance to prepare 1-adamantyl derivatives in a one-step method with good yields from the easily available tricyclodecane.



Diamantane (pentacyclo$[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]$tetradecane, congressane) contains two different types of tertiary hydrogen atoms (two apical hydrogen atoms in the 4 and 9 positions and six belt hydrogen atoms in the 1, 2, 6, 7, 11, and 12 positions). Either one can be expected to be ionized as a hydride ion in FSO_3H–SbF_5 solution. Ionization of one of the apical hydrogen atoms would result in a highly symmetrical carbonium ion with a relatively simple nmr spectrum. The spectrum observed in the solution of diamantane in FSO_3H–SbF_5 solution is indicative of ionization of one of the belt hydrogen atoms (XIII)[16] (Figure 5).



XIII

Analogous to the adamantyl ion, the tertiary H_7 and H_{11} atoms would be assigned to the band at lowest field (−4.67 ppm), the secondary H_9 atom at −4.40 ppm. Of the α-hydrogen atoms, the tertiary H_2 and H_{12} appear at −4.10 ppm, whereas the secondary H_{13} appears as a doublet (−3.50 ppm), coupled to H_9. All other hydrogen atoms (3, 4, 5, 6, 8, 10, and 14) appear as a multiplet centered at −2.03 ppm.

Experimental Section

Cycloalkanes used were commercial chemicals of highest available purity. Further purification, if needed, was carried out by stan-

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(16) R. C. Fort and P. von R. Schleyer, *Advan. Alicylic Chem.*, **1**, 283 (1966), also found that the bromination of diamantane (a carbonium ion reaction) takes place preferentially in the "belt" position.

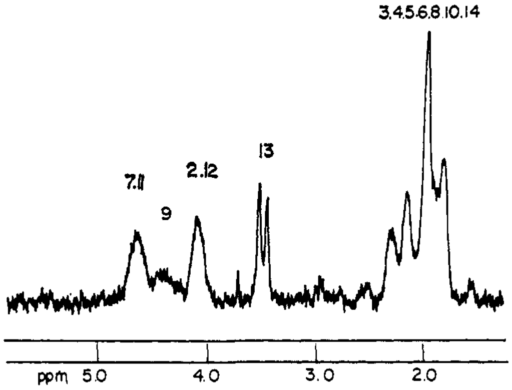

Figure 5. Nmr spectrum of the diamantyl (congressyl) cation (XIII) in neat FSO_3H-SbF_5 solution at −30°.

dard methods. Bicyclo[3.1.0]hexane was prepared according to Simmons and Smith.[17]

Nmr spectra were obtained on a Varian Associates Model A-56-60A nmr spectrometer equipped with a variable-temperature probe. Spin-spin decoupling experiments were done on Varian Associates Model HA-60IL and A-60A spectrometers. Very low temperature work (−120°) was carried out on the HA-60IL instrument using a special low-temperature probe. Table I summarizes the nmr shifts and coupling constants of cycloalkyl cations.

Generation of Cycloalkyl Cations in Neat FSO_3H-SbF_5. In a typical experiment, the cycloalkane and a tenfold (weight) excess of the acid (1:1 mixtures of FSO_3H and SbF_5) were vigorously stirred at room temperature, until they formed a homogeneous colorless mixture. The reaction is carried out under exclusion of moisture and is generally completed in 10 to 30 min.

Generation of Cycloalkyl Cations in $FSO_3H-SbF_5-SOCl_2F$. To a mixture (1:1) of SO_2ClF and FSO_3H-SbF_5 the alkane is added, diluted with SO_2ClF when necessary. On mixing, reaction willoccur at all temperatures above −120°. Un-ionized material will be supervalent. If the acid concentration is decreased, un-ionized alkane will be present in solution together with the carbonium ion.

Quenching of Cycloalkyl Cations. A. With Methanol. The acid solution of the carbonium ion diluted with SO_2ClF or SO_2 is added dropwise to a vigorously stirred slurry of Na_2CO_3 in methanol which is cooled by a Dry Ice-acetone bath. After warming the solution to room temperature, the formed ether is extracted with pentane and isolated after evaporation of the solvent. Methanolysis of all reported ions was carried out and gave generally 70–80% or higher yields of the expected methyl ether.

B. With Water. The solution of the carbonium ion in FSO_3H-SbF_5 or $HF-SbF_5$ is diluted with SO_2ClF or SO_2 and added dropwise to a slurry of ice and sodium carbonate in SO_2 at −78°. After the solution has been warmed up to room temperature the formed alcohol is extracted with ethyl ether and isolated by evaporation of the solvent.

Preparation of Adamantane and Its Derivatives. To 10 g of FSO_3H-SbF_5 (0.032 mol) is added in small amounts 8.6 g (0.064 mol) of tricyclo[5.2.1.$0^{2,6}$]decane over a period of 1 hr. After the addition of 10% of the organic precursor, the adamantyl ion will start to precipitate. Either vigorous stirring or shaking is necessary. After the addition (30 min) has been completed, the slurry is extracted with *n*-pentane. After washing the pentane solution with a solution of sodium carbonate in water, the solvent is evaporated and 4.3 g (0.016 *M*) of adamantane is isolated. Recrystallization is in most cases unnecessary.

1-Adamantanol and methyl 1-adamantyl ether are prepared in the fashion described above for quenching of carbonium ions with methyl alcohol.

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Stable Carbonium Ions. LV.[1] Protonated Alicyclic Ketones

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Abstract: The pmr parameters of O-protonated alicyclic ketones in $SbF_5-FSO_3H-SO_2$ and FSO_3H-SO_2 solutions at −60° have been determined. Analysis of the pmr data leads to the conclusion that the structure of protonated ketones is best represented by the oxonium ion resonance form, with little contribution from the hydroxycarbonium ion form.

Evidence has been presented recently[3] that protonation of aliphatic ketones leads to an equilibrium mixture of stereoisomers observable by pmr spectroscopy. It was considered that the cause of stereoisomerism is the double-bond character of the protonated carbonyl group. There is evidence from the pmr study that the hydroxycarbonium ion as a resonance form contributes only in a minor way to the structure of the protonated species, the main resonance form being the oxonium ion. In other words, the nature of this carbon–oxygen bond is only slightly modified by protonation and the positive charge is located mainly on the oxygen atom. The present pmr study was undertaken to provide additional experimental support for this suggestion. Pmr studies of protonated alicyclic ketones have not been reported in the literature.[4]

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[4] After our work was completed, in a communication M. Brookhart, G. C. Levy, and S. Winstein, *ibid.*, **89**, 1735 (1967), reported the observation of the $C{=}OH^+$ absorption in some protonated alicyclic ketones as deshielded singlets.