

Figure 2.

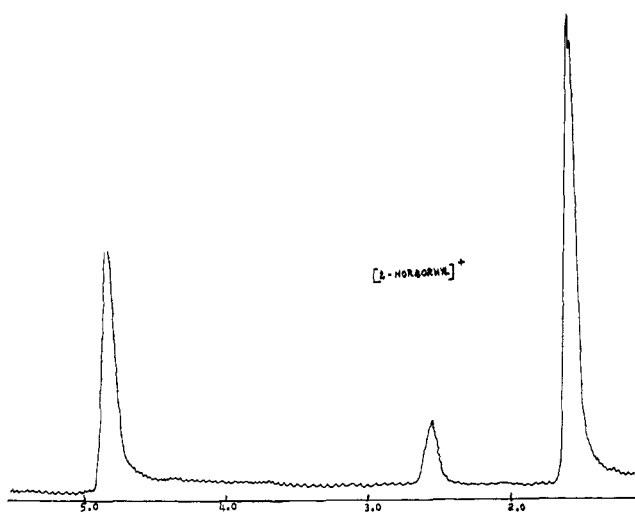


Figure 3.

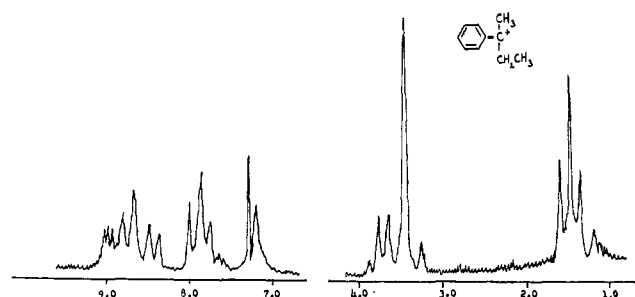


Figure 4.

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

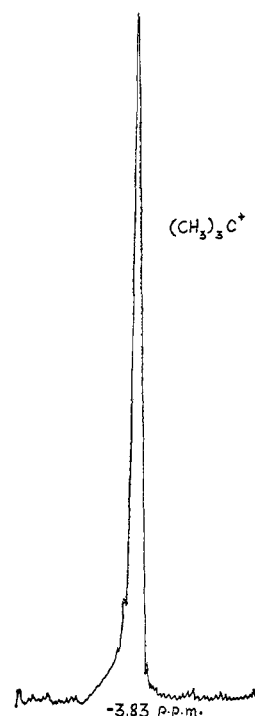


Figure 5.

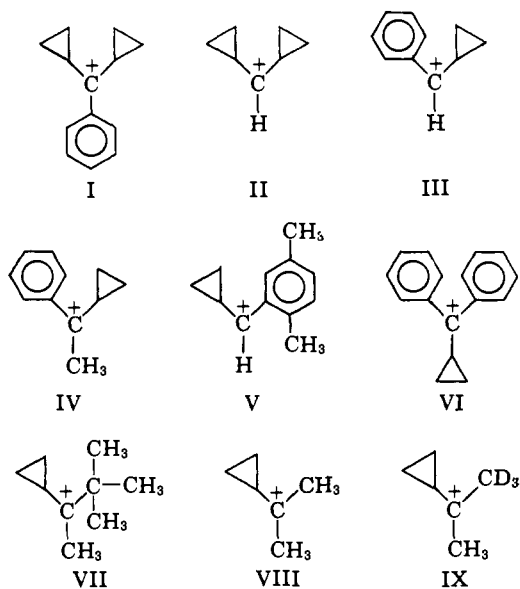
acid gave very well-resolved spectra of the corresponding carbonium ions.

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Stable Carbonium Ions. XIV.¹ Cyclopropylcarbonium Ions



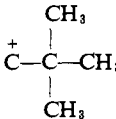
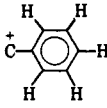
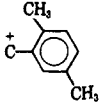
Sir:

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).

Table I. P.m.r. Shifts of Cyclopropylcarbonium Ions^a

Carbonium ion			C ⁺ H					
	α	β						
Dicyclopropylphenyl	-3.00 to -3.30	-2.85 to -2.45					-7.55 to -8.10	
Dicyclopropyl	-2.92 to -3.45	-2.35 to -2.74	-8.14					
Cyclopropylphenyl	-2.86 to -3.28	-2.33 to -2.62	<i>b</i>				-7.15 to -8.42	
Cyclopropylphenylmethyl	-3.56 to -3.90	-2.82 to -2.98		-2.52			-7.34 to -8.27	
Cyclopropyl-2,5-dimethylphenyl	-2.96 to -3.32	-2.40 to -2.86	<i>b</i>				-7.3 to -8.20	-2.04 and -2.33
Cyclopropyldiphenyl	-3.40 to -3.95	-2.35 to -2.74					-7.30 to -7.85	
Cyclopropylmethyl- <i>t</i> -butyl	-3.17 to -3.56	-2.30 to -2.90		-2.40	-1.10			
Cyclopropyldimethyl	-3.44 to -3.95			-3.14 <i>cis</i> -2.60 <i>trans</i>				

^a At -60° , in $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$ solution from external TMS. ^b Under phenyl hydrogen peaks.

known mono- and dicyclopropyl ions. The only previously known cyclopropylcarbonium ions, like the tricyclopropylcarbonium ion, were reported by Deno, *et al.*² We also would like to report the first observations on the orientation of a cyclopropyl ring next to positive carbon.

The cyclopropylcarbonium ions were generated by adding the corresponding alcohols to $\text{FSO}_3\text{H}-\text{SO}_2-\text{SbF}_5$ solutions at -78° with vigorous stirring, as described in the preceding communication.¹ The n.m.r. spectra were then taken at low temperatures (generally at -60 to -65°). In all cases the α - and β -hydrogens on the cyclopropyl rings were resolved. The integrated areas were in accord with the structure in every case. Ions I-IX were all stable at -65° with the exception of VII, which slowly decayed over a 30-min. period. All observed ions were destroyed on raising the temperature to -25° . The products from warming VII to room temperature were a mixture of cyclopentenyl cations.³ Figure 1 exemplifies the resolution of the spectra obtained. Table I contains the n.m.r. band positions and assignments of ions I-IX.

The n.m.r. spectrum of the dimethylcyclopropylcarbonium ion (VIII, Figure 1) is especially noteworthy. The methyl groups are not equivalent, but separated by 0.54 p.p.m. We believe this demonstrates

the cyclopropyl ring lies in a plane which is perpendicular to the plane of the $\text{C}^+<\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$ system (Chart I). Thus the plane of the cyclopropyl ring is parallel to the axis of the vacant p-orbital. In this orientation

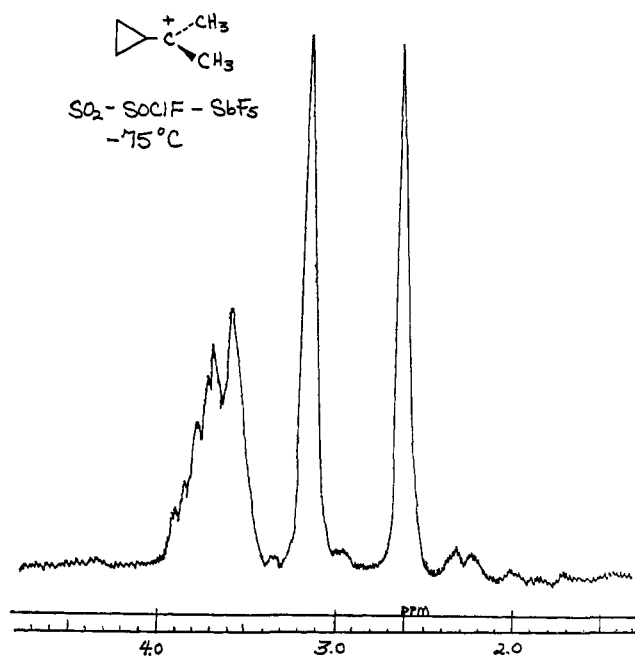


Figure 1.

(2) N. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *J. Am. Chem. Soc.*, **84**, 2016 (1962).

(3) N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *ibid.*, **85**, 2991 (1963).

Chart I. Steric Configuration of the Dimethylcyclopropylcarbonium Ion

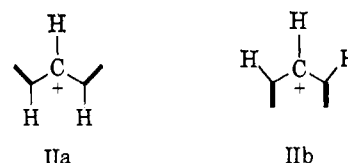


the cyclopropyl ring now lies *cis* to one methyl group and *trans* to the other. Models show clearly that the *cis*-methyl now lies in the face of the cyclopropyl ring where the *cis*-methyl group will experience the diamagnetic anisotropy of the cyclopropyl ring and thus will be found at higher field than the *trans*-dimethyl group. It is known in several cases that diamagnetic anisotropy causes such geometrically positioned hydrogens to be shifted upfield from 0.3 to 0.5 p.p.m. in uncharged systems.^{4,5} This is in agreement with the 0.54 p.p.m. difference we observed. 1,1,1-Trideuterio-2-cyclopropyl-2-propanol was prepared, and the n.m.r. spectrum of the corresponding carbonium ion (IX) was found to be identical with that of ion VIII except the two methyl peaks at -3.14 and -2.60 p.p.m. were only one-half as intense as in VIII.

Evidence for delocalized orbitals in the cyclopropyl ring has been reported from ultraviolet,^{6,7} infrared,⁸ n.m.r.^{2,3} and theoretical^{9,10} studies. The cyclopropyl ring's "banana bonding"⁷ contrasts sharply with the π -orbitals of benzene which lie above and below the plane of the benzene ring. Thus the cyclopropyl ring might be expected to lie perpendicular to the plane of the $C^+ < \begin{matrix} CH_3 \\ CH_3 \end{matrix}$ in order to give maximum orbital overlap with the vacant p-orbital instead of being coplanar as with the benzene ring. No rotation of the cyclopropyl ring was observed in n.m.r. studies on warming up to -35° . Here the ion was rapidly destroyed, with no coalescence of the methyl bands observed.

The large downfield shifts of the α - and β -hydrogens demonstrate a large amount of charge delocalization into the β -positions of the cyclopropyl ring. This is in agreement with the references for delocalized orbitals cited.⁶⁻¹⁰ Generally both α - and β -hydrogens are shifted about 3 p.p.m. downfield from their positions in the precursor alcohols.

In ion II the hydrogen on the central, charged carbon atom appears as a sharp triplet at -8.14 p.p.m. with $J = 13$ c.p.s. This symmetrical triplet shows that both α -hydrogens in II are equivalent and that no coupling to the β -hydrogens is found. We favor the orientation IIa over IIb. It is interesting to compare the position of the hydrogen at the central carbon with the corresponding hydrogens in the isopropyl cation¹¹ (in neat SbF_5 , -13.5 p.p.m.) and the benzhydryl



cation¹² (in SO_2-SbF_5 , -9.8 p.p.m.). The value of -8.14 p.p.m. for $+C-H$ in ion II indicates that the cyclopropyl rings probably delocalize more charge than the phenyl rings in the benzhydryl cation. However; since the diamagnetic anisotropy effects cannot be clearly separated from the electron withdrawal effects, only a qualitative observation can be made.

(12) G. A. Olah, *ibid.*, **86**, 932 (1964).

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The Direct Observation of Dicyclopropylcarbonium Ions

Sir:

Since the first report on the physical properties of the tricyclopropylmethyl cation¹ several cations of the cyclopropylalkenyl type have been observed and briefly reported.^{2,3} In the accompanying communication by Pittman and Olah it has been found that a wide variety of mono- and dicyclopropylcarbonium ions can now be directly observed in $FSO_3H-SbF_5-SO_2$ at -60° . Our own group has had success with similar experiments in FSO_3H at -50° , and these are added to Pittman and Olah's report.

Figure 1 is the n.m.r. spectrum of the 1,1-dicyclopropylethyl cation (I). The relative areas of the bands of the α -H, β -H, and CH_3 are 2.2:8.0:3, in agreement with 2:8:3. Support for the identification of this ion was obtained by preparing the analog of I in which both α -hydrogens of the cyclopropane rings were replaced by deuterium. The spectrum of the di-deuterated form of I at -50° showed (1) the complete disappearance of the α -H bands, (2) the α - CH_3 again at -2.28 p.p.m., and (3) the collapse of the β -hydrogen bands to a broad singlet at -2.56 p.p.m. At -30° the singlet is resolved into bands at -2.54 and -2.58 , which are identically shaped. It would seem that the coupling constants between β -hydrogens must be small.

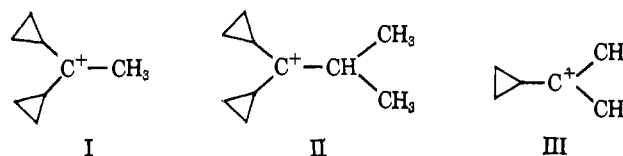


Figure 2 is the n.m.r. spectrum of the 1,1-dicyclopropyl-2-methylpropyl cation (II). The relative areas of the two band systems are 10.9:6, in accord with the 11:6 ratio of methine (CH) plus cyclopropyl hydrogens to methyl hydrogens.

- (1) N. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *J. Am. Chem. Soc.*, **84**, 2016 (1962).
(2) N. Deno, *Progr. Phys. Org. Chem.*, **2**, 148 (1964).
(3) N. Deno, *Chem. Eng. News*, **42**, 88 (1964).

(4) S. Forsen and T. Norin, *Tetrahedron Letters*, No. 39, 2845 (1964).

(5) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).

(6) R. H. Eastman, *ibid.*, **76**, 4115, 4118 (1954); **77**, 6643 (1955).

(7) E. M. Kosower and M. Ito, *Proc. Chem. Soc.*, 25 (1962).

(8) A. P. Cross, *J. Am. Chem. Soc.*, **84**, 3206 (1962); D. H. Williams and N. S. Bhacca, *ibid.*, **85**, 2861 (1963); K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).

(9) A. S. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(10) C. A. Coulson and W. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

(11) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastion, *J. Am. Chem. Soc.*, **86**, 1360 (1964).