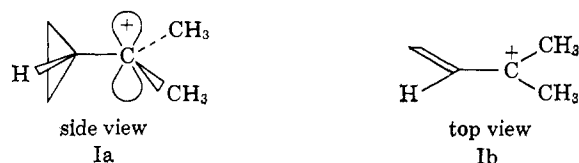


Chart I. Steric Configuration of the Dimethylcyclopropylcarbonium Ion

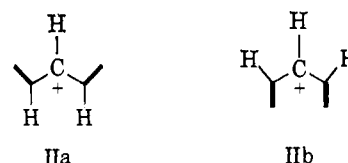


the cyclopropyl ring now lies *cis* to one methyl group and *trans* to the other. Models show clearly that the *cis*-methyl now lies in the face of the cyclopropyl ring where the *cis*-methyl group will experience the diamagnetic anisotropy of the cyclopropyl ring and thus will be found at higher field 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.<sup>4,5</sup> 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,<sup>6,7</sup> infrared,<sup>8</sup> n.m.r.<sup>2,3</sup> and theoretical<sup>9,10</sup> studies. The cyclopropyl ring's "banana bonding"<sup>7</sup> contrasts sharply with the  $\pi$ -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  $-35^\circ$ . Here the ion was rapidly destroyed, with no coalescence of the methyl bands observed.

The large downfield shifts of the  $\alpha$ - and  $\beta$ -hydrogens demonstrate a large amount of charge delocalization into the  $\beta$ -positions of the cyclopropyl ring. This is in agreement with the references for delocalized orbitals cited.<sup>6-10</sup> Generally both  $\alpha$ - and  $\beta$ -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  $\alpha$ -hydrogens in II are equivalent and that no coupling to the  $\beta$ -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 cation<sup>11</sup> (in neat  $SbF_5$ ,  $-13.5$  p.p.m.) and the benzhydryl



cation<sup>12</sup> (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.

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### The Direct Observation of Dicyclopropylcarbonium Ions

Sir:

Since the first report on the physical properties of the tricyclopropylmethyl cation<sup>1</sup> several cations of the cyclopropylalkenyl type have been observed and briefly reported.<sup>2,3</sup> 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  $-60^\circ$ . Our own group has had success with similar experiments in  $FSO_3H$  at  $-50^\circ$ , 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  $\alpha$ -H,  $\beta$ -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  $\alpha$ -hydrogens of the cyclopropane rings were replaced by deuterium. The spectrum of the di-deuterated form of I at  $-50^\circ$  showed (1) the complete disappearance of the  $\alpha$ -H bands, (2) the  $\alpha$ - $CH_3$  again at  $-2.28$  p.p.m., and (3) the collapse of the  $\beta$ -hydrogen bands to a broad singlet at  $-2.56$  p.p.m. At  $-30^\circ$  the singlet is resolved into bands at  $-2.54$  and  $-2.58$ , which are identically shaped. It would seem that the coupling constants between  $\beta$ -hydrogens must be small.

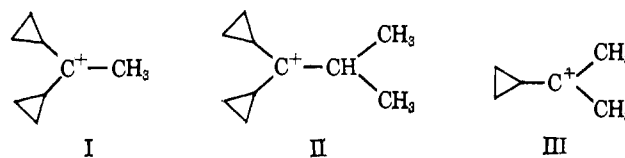


Figure 2 is the n.m.r. spectrum of the 1,1-dicyclopropyl-2-methylpropyl cation (II). The relative areas of the two band systems are 10.9:6, in accord with the 11:6 ratio of methine (CH) plus cyclopropyl hydrogens to methyl hydrogens.

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(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).

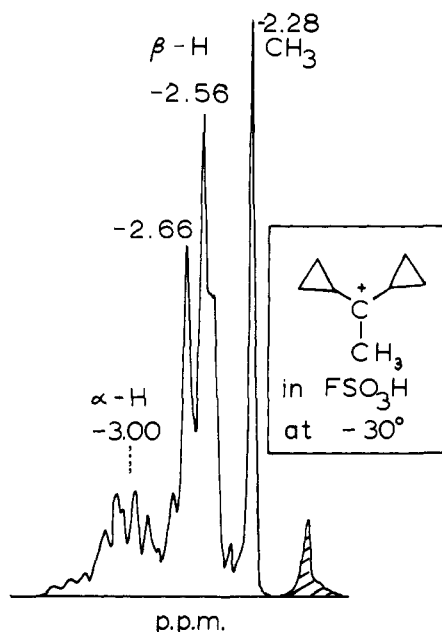


Figure 1.

Satisfactory n.m.r. spectra were obtained for analogs of I in which the methyl group was replaced by the cyclohexyl and apocamphyl groups. However, when the methyl group was replaced by *t*-butyl, the ion was much less stable and no satisfactory n.m.r. spectrum was obtained.

Pittman and Olah report the n.m.r. spectrum of the dicyclopopylmethyl cation. The spectrum of this ion can also be observed in  $\text{FSO}_3\text{H}$  at  $-50^\circ$ , and the resolution is nearly as good. Using an internal tetramethylammonium ion standard (taken to be at  $-3.10$  p.p.m. relative to tetramethylsilane, TMS), the center of the triplet was at  $-8.24$ . Pittman and Olah report  $-8.14$ , using an external TMS standard.

The carbonium ions were produced by dissolving the corresponding alcohol in  $\text{CHCl}_3\text{-CCl}_4$  and extracting the solution with  $\text{FSO}_3\text{H}$  at  $-70^\circ$ . This introduced a trace of  $\text{CHCl}_3$ , and this can be used as an internal standard and taken to be at  $-7.27$  p.p.m. The alcohols were produced by the appropriate combination of  $\text{RMgBr}$  or  $\text{RLi}$  with a ketone or acid chloride. Some of the alcohols have been reported.<sup>4,5</sup> The identity of the new compounds was verified by both n.m.r. spectra and carbon and hydrogen analyses.

Pittman and Olah report the direct observation of III and, coupled with their data on the trideuterated derivative, the identification seems unequivocal. They recognize that the nonidentical methyl groups are strong evidence for the bisected structure<sup>2</sup> for cyclopropyl-carbonium ions. Further support for the bisected structure comes from the demonstration by Bartell and co-workers<sup>6</sup> that cyclopropanecarboxaldehyde exists in about equal amounts of *cis* and *trans* isomers, and both forms have the cyclopropyl ring bisected by the plane of the trigonal carbon.

2-Cyclopropyl-2-propanol was dissolved in  $\text{FSO}_3\text{H}$

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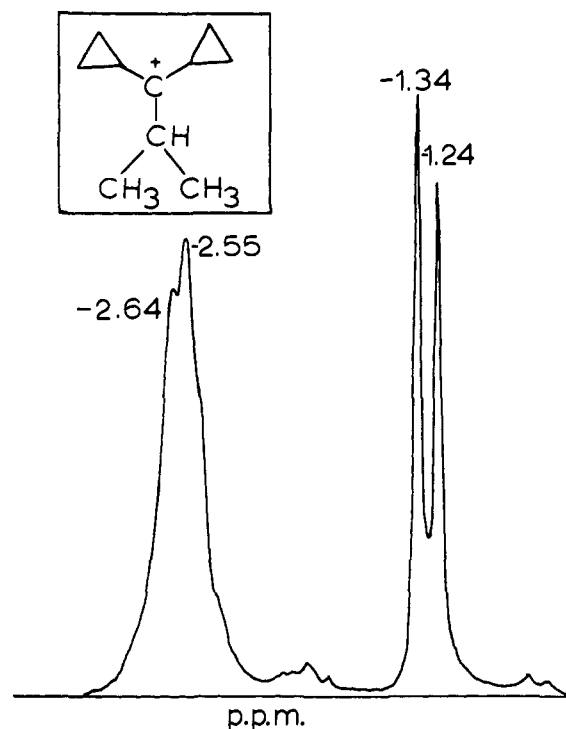


Figure 2.

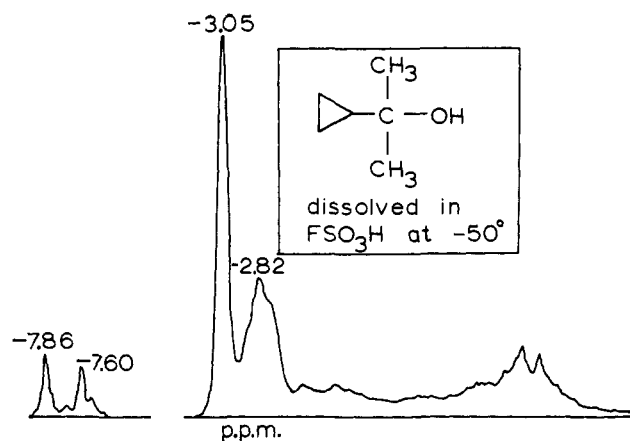


Figure 3.

at  $-50^\circ$ , and the spectrum shown in Figure 3 was observed. This spectrum is not that of III despite the fact that the conditions were close to those of Pittman and Olah. It is tentatively identified as that of the trimethylallyl (2-methylpentenyl) cation. This could form by dehydration of the alcohol, opening of the cyclopropyl ring by protonation, and appropriate  $\text{CH}_3$  and H shifts.

Homologs of III containing one or two isopropyl groups in place of the methyl groups form cyclopentenyl cations immediately at  $-50^\circ$ , presumably by migration of the carbonium site and internal alkylation of the cyclopropane ring to form a 5-membered ring. Specifically, 2-cyclopropyl-3,5-dimethyl-3-pentanol forms the 1-isopropyl-2,3-dimethylcyclopentenyl cation in  $\sim 50\%$  yield in  $\text{FSO}_3\text{H}$  at either  $-50^\circ$  or  $+25^\circ$ .

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### Transient Intermediates in Inner-Sphere Electron-Transfer Reactions Involving Polyatomic Bridging Ligands

Sir:

One of the important questions which arises in connection with the mechanisms of inner-sphere electron-transfer reactions involving polyatomic bridging ligands, e.g., in the reductions of  $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$  (where  $\text{X} = \text{CN}, \text{NO}_2, \text{NCS}$ , etc.) by reductants such as  $\text{Cr}^{2+}(\text{aq})^1$  or  $\text{Co}(\text{CN})_5^{3-}$  to give  $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{2+}$

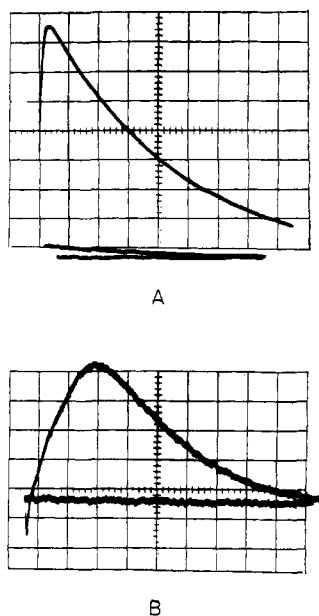


Figure 1. Stopped-flow oscillograms showing transient intermediates in the oxidation of  $\text{Co}(\text{CN})_5^{3-}$  by pentaamminecobalt(III) complexes at 25°. (A) oxidant,  $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$  ( $1.0 \times 10^{-3} M$ );  $2.0 \times 10^{-4} M \text{Co}(\text{CN})_5^{3-}$ ;  $0.0125 M \text{CN}^-$ ; wave length, 380  $\mu\text{m}$ ; time scale, 2 sec./major division. (B) Oxidant  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  ( $2.0 \times 10^{-3} M$ );  $2.0 \times 10^{-3} M \text{Co}(\text{CN})_5^{3-}$ ;  $3.0 \times 10^{-2} M \text{CN}^-$ ; wave length, 320  $\mu\text{m}$ ; time scale, 1 sec./major division.

and  $\text{Co}(\text{CN})_5\text{X}^{3-}$ , respectively, relates to the position of attack of the reductant on the bridging ligand, and to the configuration of the initial oxidation product which in some cases is thought to differ from the final product. It has been suggested,<sup>4</sup> for example, that the reduction

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of  $(\text{NH}_3)_5\text{CoNCS}^{2+}$  by  $\text{Cr}^{2+}(\text{aq})$  involves attack at the S atom, followed by electron transfer via the intermediate  $[(\text{NH}_3)_5\text{Co}-\text{NCS}-\text{Cr}(\text{H}_2\text{O})_5]^{4+}$ , to yield the S-bonded complex  $(\text{H}_2\text{O})_5\text{Cr}-\text{SCN}^{2+}$  as the initial oxidation product; but the latter, if formed, apparently rearranges to the stable N-bonded isothiocyanato product  $(\text{H}_2\text{O})_5\text{Cr}-\text{NCS}^{2+}$  too rapidly to be detected.

The studies reported here are pertinent to this theme and appear to be the first examples in which direct evidence for the position of attack in such reactions has been obtained through the detection of the transient initial oxidation products.

The studies in question relate to the oxidation of  $\text{Co}(\text{CN})_5^{3-}$  by several pentaamminecobalt(III) complexes,  $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$ . As previously shown,<sup>2,3</sup> the general rate law for these reactions has the form  $-d[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}]/dt = k_i[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}][\text{Co}(\text{CN})_5^{3-}] + k_o'[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}][\text{Co}(\text{CN})_5^{3-}][\text{CN}^-]$ , the first term corresponding to the inner-sphere oxidation of  $\text{Co}(\text{CN})_5^{3-}$  through the bridged intermediate  $[(\text{NH}_3)_5\text{Co}-\text{X}-\text{Co}(\text{CN})_5]$ , to  $\text{Co}^{\text{III}}(\text{CN})_5\text{X}$ , and the second term to the outer-sphere oxidation of  $\text{Co}(\text{CN})_5^{3-}$  to  $\text{Co}(\text{CN})_6^{3-}$ .

For  $(\text{NH}_3)_5\text{Co}-\text{NO}_2^{2+}$  (containing an N-bonded nitro ligand)<sup>5</sup> as oxidant, the values of  $k_i$  and  $k_o'$ , at 25° and  $\mu = 0.2$ , were found to be  $3.4 \times 10^4 M^{-1} \text{sec}^{-1}$  and  $3 \times 10^4 M^{-2} \text{sec}^{-1}$ , respectively. At 0.0125  $M \text{CN}^-$  about 99% of the oxidation of  $\text{Co}(\text{CN})_5^{3-}$  proceeds by the inner-sphere ( $k_i$ ) path to yield  $\text{Co}(\text{CN})_5\text{NO}_2^{3-}$  ( $\text{NO}_2$  also N-bonded to Co) as the final product. Stopped flow measurements<sup>2</sup> (Figure 1A) clearly reveal that under these conditions the disappearance of  $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$  ( $t_{1/2} = 0.1 \text{ sec.}$ ) does not coincide with the formation of the final product but rather of a transient intermediate which decays much more slowly ( $t_{1/2} = 7 \text{ sec.}$ ) to  $\text{Co}(\text{CN})_5\text{NO}_2^{3-}$ . The transient exhibits strong absorption in the wave length region ( $\sim 380 \mu\text{m}$ , Figure 1A) where both  $\text{Co}(\text{NH}_3)_5\text{NO}_2^{3+}$  and  $\text{Co}(\text{CN})_5\text{NO}_2^{3-}$  are nearly transparent, but which is characteristic of pentacyanocobaltate(III) complexes containing O-bonded ligands (e.g.,  $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$   $\lambda_{\text{max}} 380 \mu\text{m}$ ,  $\epsilon_{\text{max}} 240$ ). These observations are consistent with attack of  $\text{Co}(\text{CN})_5^{3-}$  on an oxygen atom of the bridging  $\text{NO}_2$  ligand, resulting in electron transfer through the intermediate  $[(\text{NH}_3)_5\text{Co}-\text{NO}_2-\text{Co}(\text{CN})_5]$  to produce O-bonded  $\text{Co}(\text{CN})_5\text{ONO}^{3-}$  initially, and subsequent isomerization of the latter to  $\text{Co}(\text{CN})_5\text{NO}_2^{3-}$ . The first-order rate of isomerization was unaffected by increasing the  $\text{Co}(\text{CN})_5^{3-}$  concentration from  $1 \times 10^{-5}$  to  $2 \times 10^{-4} M$ , suggesting that the isomerization under these conditions occurs intramolecularly rather than via ligand transfer between  $\text{Co}(\text{CN})_5\text{ONO}^{3-}$  and  $\text{Co}(\text{CN})_5^{3-}$ .

Similar evidence for a transient intermediate was obtained with  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  (C-bonded)<sup>6</sup> as oxidant. The values of  $k_i$  and  $k_o'$  for this oxidant at 25° and  $\mu = 0.2$  were found to be  $2.9 \times 10^2 M^{-1} \text{sec}^{-1}$  and  $4.5 \times 10^3 M^{-2} \text{sec}^{-1}$ , respectively, both paths in this case giving rise to  $\text{Co}(\text{CN})_6^{3-}$  as the final product. At 0.03  $M \text{CN}^-$ , with the inner-sphere path accounting for some 70% of the reaction, the disappearance of  $\text{Co}(\text{NH}_3)_5\text{CN}^{2+}$  ( $t_{1/2} = 0.8 \text{ sec.}$ ) coincided with the

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