

**Figure 1.** L Band ESR spectra of **1**: (a) experimental in a solid solution of polystyrene-2% divinylbenzene copolymer beads at 298°K; (b) computed for an ensemble of randomly oriented radicals on the basis of a second-order perturbation treatment,  $D = 82$  G.

$\Delta m = 3$  refers to the transition between the levels identified by the approximate quantum numbers  $m = -3/2$  and  $m = +3/2$ . The transition is observed because the magnetic dipolar interaction admixes, at most orientations of the molecule relative to the external field, components with  $m = \pm 1/2$  into each of the levels  $m = -3/2$  and  $m = 3/2$ . The amplitudes of the admixtures are of order  $D/H$ ,  $D$  being the dipole-dipole coupling parameter and  $H$  the external field. Owing to the shifts in energy produced by the dipolar interaction and to the aforementioned admixtures, the spectrum at each orientation of the quartet molecule consists of three lines near  $H = \omega/\gamma$  ( $\Delta m = 1$ ), a pair of lines near  $H = \omega/2\gamma$  ( $\Delta m = 2$ ), and a single line at  $H = \omega/3\gamma$  ( $\Delta m = 3$ ).  $\omega$  is the angular frequency of the radiation,  $H$  the field, and  $\gamma$  the magnetogyric ratio of the electron. Nonrotating randomly oriented molecules yield spectra with characteristic shapes in each of the three regions,<sup>6</sup> the  $\Delta m = 3$  transition being a single fairly sharp line, just as is the  $\Delta m = 2$  transition in a triplet molecule. Appearance of the sharp  $\Delta m = 3$  transition requires that three electron spins be coupled to each other.

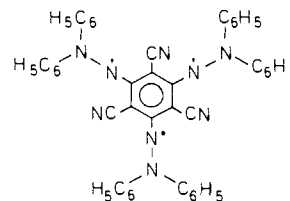
The intensities of the three transitions  $\Delta m = 1, 2,$  and  $3$  are in the approximate ratio  $1:(D/H)^2:(D/H)^4$ .<sup>7</sup>

The **1**,<sup>8</sup> whose spectrum we report here, has  $D \sim 80$  G. At the commonly used X band frequency the intensity of the  $\Delta m = 3$  transition would be only  $3 \times 10^{-5}$  relative to  $\Delta m = 1$ . It has, obviously, not been observed at X band despite careful search for it. We, therefore, turned to lower frequency, L band, with frequency  $1 \times 10^9$  Hz. The L band spectrometer is less sensitive by a factor of about 100 in the minimum number of spins which it is capable of detecting than the X band one, but owing to the large volume of material which it accommodates, its concentration sensitivity appears to be superior.

The **1**, synthesized at the University of Freiburg,<sup>5</sup> was dissolved in a toluene solution of polystyrene-2% divinylbenzene copolymer beads. A uniformly colored solid remained after evaporation of the toluene. Its spectrum is characteristic of a randomly oriented solid solution. No

signs of the spectrum of microcrystals of the radical are observed.

The L band spectrum at room temperature is shown in Figure 1a. A computed spectrum is shown in Figure 1b. The agreement is good except for the positions marked by asterisks. The extra feature at the latter positions arise from a contamination of bishydrazyl. The  $\Delta m = 3$  resonance, which can arise only from molecules with three spins, stands out clearly.



**Acknowledgments.** The spectrometer has evolved over many years. It was perfected under a grant from the Hartford Foundation to Professor Barry Commoner. We are grateful to Professor Commoner for his generous permission to use the instrument. Its development was carried out by J. Townsend, S. Fuller, A. Lindauer, and R. Brennan. The compound was prepared by Dr. F. Rieser. Dr. E. Ohmes assisted in computation of the spectrum.

The work has been supported by the National Science Foundation, Deutsche Forschungsgemeinschaft, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

## References and Notes

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- (7) One of us, S.I.W., was seduced into the present experiment by the erroneous belief that  $\Delta m = 3$  would have intensity  $(D/H)^2$  relative to  $\Delta m = 1$ . The phases of the admixture are such that cancellation of the components of order  $D/H$  in the transition moment occurs, leaving only a moment of order  $(D/H)^2$  and intensity  $(D/H)^4$ . The transition is excited by the component of oscillating field rotating in the opposite sense to the normal one.
- (8) 1,3,5-(2,4,6-Tricyanobenzene)tris( $N,N'$ -diphenylhydrazyl), 1

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Received February 5, 1975

## Generation, Nuclear Magnetic Resonance Spectra, and Structure of 9-Pentacyclo[4.3.0.0<sup>2,4</sup>.0<sup>3,8</sup>.0<sup>5,7</sup>]nonyl Cations

Sir:

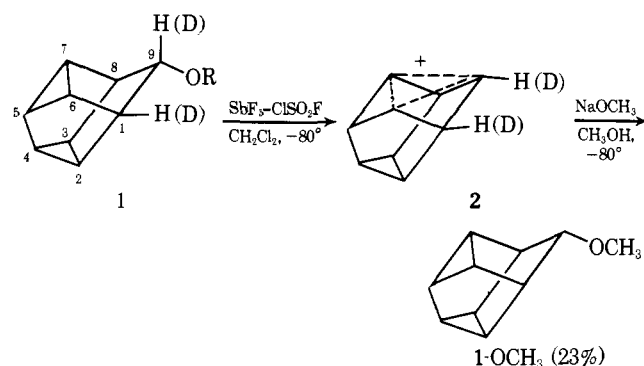
The hydrolysis of 9-pentacyclo[4.3.0<sup>2,4</sup>.0<sup>3,8</sup>.0<sup>5,7</sup>]nonyl *p*-nitrobenzoate (**1-OPNB**) proceeds with a very large rate enhancement ( $10^{10}$ - $10^{12}$ ) and leads to a statistical, but stereospecific, rearrangement which regenerates the parent pentacyclic alcohol (**1-OH**) with positions 6, 7, and 9 and positions 1, 5, and 8 each having been completely exchanged.<sup>1</sup> These observations were explained by ionization

Table I. Proton and Carbon-13 NMR Data<sup>a</sup> for 9-Pentacyclo[4.3.0.0<sup>2,4</sup>.0<sup>3,6</sup>.0<sup>5,7</sup>] nonyl Cations

	Charged sites		Bridgehead sites			Cyclopropane sites			Other sites			
	Position(s)	$\delta_H$	$\delta_C$	Position(s)	$\delta_H$	$\delta_C$	Position(s)	$\delta_H$	$\delta_C$	Substituent	$\delta_H$	$\delta_C$
	6,7,9	2.25	29.53 <sup>b</sup>	1,5,8	3.97	31.43 <sup>c</sup>	2,3,4	2.38	41.28 <sup>d</sup>			
	6,7 9	2.00	29.89 69.12	1,8 5	3.82 4.07	37.40 34.95	2,3 4	2.38 2.38	40.66 39.63	CH <sub>3</sub>	1.90	16.11
	6,7 $\rightleftharpoons$ 2,3 9	2.25	37.32 87.62	1,8 5 $\rightleftharpoons$ 4	4.60 3.43	37.03 40.14				C <sub>6</sub> H <sub>5</sub>	7.63	$\left\{ \begin{array}{l} 135.48 \\ 132.52 \\ 131.12 \\ 124.59 \end{array} \right\}$ (o,m) (p)

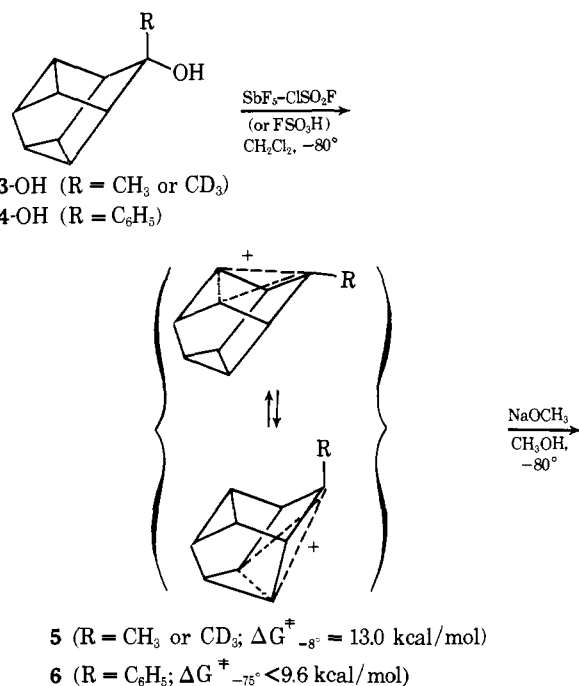
<sup>a</sup> <sup>1</sup>H NMR and <sup>13</sup>C NMR chemical shifts are reported relative to tetramethylsilane but were measured relative to internal CH<sub>2</sub>Cl<sub>2</sub> assuming the chemical shifts of CH<sub>2</sub>Cl<sub>2</sub> are  $\delta_H$  5.28 and  $\delta_C$  54.50. <sup>b</sup>  $J^{13}CH = 204$  Hz. <sup>c</sup>  $J^{13}CH = 179$  Hz. <sup>d</sup>  $J^{13}CH = 185$  Hz.

of 1-OPNB with exclusive participation of the anti cyclopropane ring giving rise to the threefold symmetric trishomocyclopropenium ion **2**.<sup>2</sup> We now wish to report the direct observation this [CH]<sub>9</sub><sup>+</sup> cation, as well as its 9-methyl (**5**) and 9-phenyl (**6**) derivatives.



The parent pentacyclic alcohol (**1-OH**) was prepared by lithium aluminum hydride reduction of the corresponding ketone, now more readily available from the ethylene ketal of the 1-bromo ketone through reduction with lithium-*tert*-butyl alcohol and ketal hydrolysis.<sup>3,4</sup> This approach also provided access to the 1-deuterio (reduction with *tert*-butyl alcohol-*O-d*) and 9-deuterio (reduction of ketone with LiAlD<sub>4</sub>) labeled alcohols. The reaction of the ketone (or its 1-deuterio derivative) with methyl lithium (or CD<sub>3</sub>MgI) and phenylmagnesium bromide gave the 9-methyl (**3-OH**) and 9-phenyl (**4-OH**) pentacyclic alcohols, respectively.

Rapid mixing of a solution of **1-OH** (~0.6 mmol) in methylene chloride (0.2 ml) with a solution of antimony pentafluoride (0.9–1.2 mmol) in sulfuryl chlorofluoride (~0.3 ml) at –80° gave rise to a long-lived ion which upon quenching with sodium methoxide in methanol at –80° produced **1-OCH<sub>3</sub>** (23%). The proton NMR spectrum of the ion exhibited three somewhat broad ( $W_{1/2}$  10–15 Hz) singlets ( $\delta$  2.25, 2.38, 3.97) of equal intensity and was un-



changed until the onset of decomposition at ca. +10°. The appearance of this spectrum is as expected for the threefold symmetric nonclassical ion **2** and rigorously excludes a classical carbonium ion. The three signals may be assigned to the charged sites (H<sub>6,7,9</sub>), cyclopropane ring sites (H<sub>2,3,4</sub>),

and bridgehead sites ( $H_{1,5,8}$ ), respectively, upon inspection of the spectra obtained from the 1-deuterio and 9-deuterio derivatives of **1-OH**. The carbon-13 NMR spectrum of **2** similarly displays three absorptions of approximately equal intensity which are assigned as indicated in Table I according to the effects of deuterium substitution.<sup>5</sup>

The methyl substituted ion **5** was similarly generated by reaction of **3-OH** with antimony pentafluoride in sulfuric chlorofluoride at  $-80^\circ$ . The proton NMR spectrum of **5** ( $R = CD_3$ ) exhibits four absorptions ( $\delta_H$  2.00, 2.38, 3.82, and 4.07) in the ratio 2:3:2:1. The signal at  $\delta$  3.82 may be assigned to the equivalent bridgehead sites ( $H_{1,8}$ ) since its intensity is reduced to one proton in the deuterated ion. The three-proton peak at  $\delta$  2.38 is attributed to the superposition of the two types of cyclopropane sites ( $H_{2,3}$  and  $H_4$ ) rather than the charged sites since the chemical shift is identical with that of the corresponding cyclopropane ring protons in the parent ion. This spectrum shows a reversible temperature dependence upon warming. At ca.  $0-5^\circ$  the bands at  $\delta$  2.00 and 2.38 merge into a single peak at  $\delta$  2.19 ( $\sim 4$  H), the band at  $\delta$  4.07 disappears, and that band at  $\delta$  3.82 remains unchanged. This behavior is consistent with a degenerate bridge-flip rearrangement which exchanges  $H_{2,3}$  with  $H_{6,7}$  and  $H_4$  with  $H_5$ . Owing to decomposition, it was not possible to achieve sufficiently rapid exchange of  $H_4$  and  $H_5$  to observe the peak expected at the average position. The free energy of activation at coalescence ( $\Delta G^\ddagger_{-80} = 13.0$  kcal/mol) is remarkably close to that found for the analogous bridge-flip rearrangement of the 7-methylnorbornadienyl ion ( $\Delta G^\ddagger_{-140} = 12.4$  kcal/mol).<sup>7</sup> The carbon-13 NMR spectrum of **5** ( $R = CH_3$ ) at  $-80^\circ$  shows seven peaks which may be assigned as indicated in Table I on the basis of off-resonance decoupling, relative intensities of signals for carbons bearing one proton, the effect of deuterium substitution at C-1, and comparison with chemical shifts of the corresponding carbons in **2**.

The long-lived ion from the 9-phenyl precursor (**4-OH**) was best generated with fluorosulfonic acid. Since the proton NMR spectrum shows only three signals ( $\delta$  2.25, 3.40, and 4.60) in the ratio 4:2:2, in addition to the aromatic ring protons, and is unaffected by temperature changes in the range  $-75$  to  $-25^\circ$ ,<sup>8</sup> the phenyl substituted ion evidently is undergoing a rapid bridge-flip rearrangement on the NMR time scale. This conclusion is supported by the observation of four signals (other than those for the aromatic ring carbons) in the carbon-13 NMR spectrum. Thus, the NMR chemical shifts reported in Table I for positions 2,3,6,7 and 4,5 are time-averaged values.

The relatively high field position of the charged carbons bearing the substituent in the carbon-13 NMR spectra of **5** ( $\delta_{C_9} + 69.12$ ) and **6** ( $\delta_{C_9} + 87.62$ ) as compared to the charged carbons in the 1-methylcyclopentyl ( $\delta_{C_1} + 337$ ) and 1-phenylcyclopentyl ( $\delta_{C_1} + \sim 265$ ) carbonium ions<sup>9</sup> is convincing evidence for the delocalized trishomocyclopropenium structures for both substituted ions. This conclusion is in line with the inability of a *p*-anisyl substituent to "level" homocyclopropylcarbinyl participation (and by inference either a methyl or phenyl substituent since their leveling capabilities are much less than that of the *p*-anisyl group) in the solvolysis of 8-*p*-anisyl-endo,anti-tricyclo[3.2.1.0<sup>2,4</sup>]oct-8-yl *p*-nitrobenzoate.<sup>10</sup> The high field position of the NMR signals for both the protons and carbons at the charged sites in **2** is consonant with data recently reported by Masamune and coworkers for the parent trishomocyclopropenium ion ( $\delta_{H_1}$  1.15;  $\delta_{C_1} + 4.7$ ) and its ethano-bridged analog ( $\delta_{H_{2,4}}$  2.10,  $\delta_{H_3}$  1.44;  $\delta_{C_{2,4}} + 19.58$ ,  $\delta_{C_3} + 0.0$ ).<sup>11</sup> The high <sup>13</sup>C-H coupling constant at the charged sites ( $J_{13C_1-H} = 204$  Hz) is indicative of a high s-character for these C-H bonds and typical of nonclassical ions.<sup>9</sup>

**Acknowledgment.** We wish to thank the A. P. Sloan Foundation and the National Institutes of Health for partial support of this research.

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Received December 23, 1974

## Mechanism of Electrophilic Cleavage of Iron-Carbon $\sigma$ Bonds by Mercury(II) Chloride

Sir:

The electrophilic cleavage of transition metal-carbon  $\sigma$  bonds by mercury(II) salts is a reaction of considerable importance<sup>1-3</sup> and current mechanistic interest.<sup>4-18</sup> When the cleaving reagent is  $HgX_2$  ( $X = Cl, Br, \text{ or } I$ ), this reaction has been reported<sup>11-16</sup> to follow eq 1.



Our interest in the mechanism of insertion and eliminative cleavage<sup>19</sup> reactions at iron-carbon  $\sigma$  bonds<sup>14,20,21</sup> prompted a study of the electrophilic scission of  $\eta^5-C_5H_5Fe(CO)_2R$  by  $HgCl_2$ . Here we report a novel finding that this cleavage does not always proceed according to eq 1 but rather affords products which are dependent on the nature of the alkyl fragment R. We also present a mechanism that differs considerably from those proposed previously for mercury(II) cleavage reactions of other complexes.

Reactions of  $\eta^5-C_5H_5Fe(CO)_2R$  (generally  $5 \times 10^{-3}$  to  $5 \times 10^{-2} M$ ) with ca. tenfold excess of  $HgCl_2$  in THF at  $25^\circ$  proceed via three distinct pathways, as shown in eq 2-4.

