

- (13) The temperature dependences of the  $^{13}\text{C}$  NMR shifts attributable to an equilibrium process suggest the possibility of concomitant temperature dependences for the  $^1J_{^{13}\text{C}\text{H}}$  couplings. The  $^1J_{^{13}\text{C}\text{H}}$  values of the methine and methylene resonances in this system were measured at intervals from  $-76$  to  $-132$   $^\circ\text{C}$  but no systematic temperature dependences were observed. The broadness of the resonances lines ( $\nu_{1/2} \sim 12$  Hz, probably because of long-range carbon-proton couplings) precluded detection of small changes in these couplings. Nonetheless, the low- and high-field methylene proton resonances<sup>3d</sup> of  $\text{C}_4\text{H}_7^+$  at 60 MHz shifted upfield by 0.06 and 0.12 ppm, respectively (relative to external  $\text{CF}_2\text{ClH}/(\text{CH}_3)_4\text{Si}$ ), between about  $-85$  to  $-115$   $^\circ\text{C}$ . The  $^1\text{H}$  NMR resonance of the methine proton of  $\text{C}_4\text{H}_7^+$  was too broad to permit accurate measurement of its temperature dependence. The methylene proton shifts of the O-protonated cyclobutanol present in these solutions (see ref 8) remained essentially constant over this temperature range.
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### Observation by Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Hydride Shifts in $\text{C}_4\text{H}_7^+$ Derived from Cyclopropylcarbinol- $l$ - $^{13}\text{C}$ in $\text{SbF}_5\text{-SO}_2\text{ClF-SO}_2\text{F}_2$ Solution<sup>1</sup>

Sir:

The interconversion in carbocationic reactions of cyclobutyl, cyclopropylcarbinyl, and allylcarbinyl derivatives has been the subject of many investigations since its discovery in 1950.<sup>2,3</sup> Although controversy continues to surround the precise nature

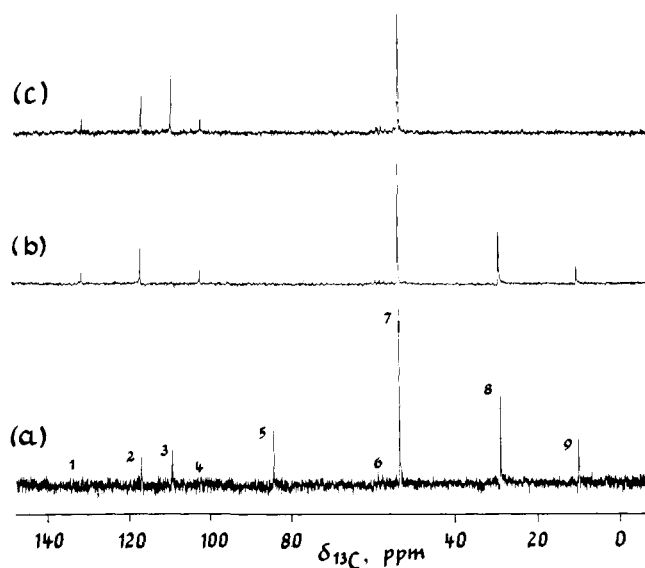
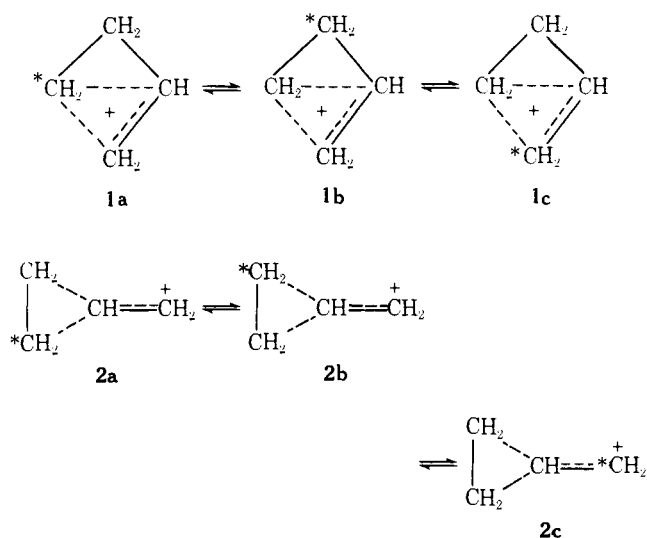
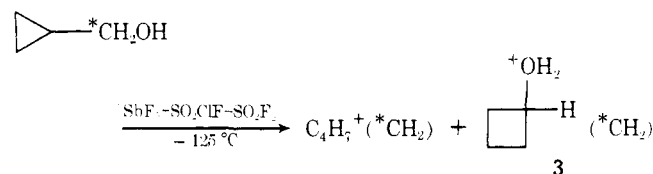


Figure 1. Fourier transform, 20-MHz  $^{13}\text{C}$  NMR spectra (at  $-100$   $^\circ\text{C}$  of  $\text{SbF}_5\text{-SO}_2\text{ClF-SO}_2\text{F}_2$  solutions): (a)  $\text{C}_4\text{H}_7^+$  and O-protonated cyclobutanol **3** from cyclopropylcarbinol; (b)  $\text{C}_4\text{H}_7^+$  and O-protonated cyclobutanol **3** from cyclopropylcarbinol- $l$ - $^{13}\text{C}$  (43% enrichment); (c)  $\text{C}_4\text{H}_7^+$  after warming the solution described in (b) to  $-70$   $^\circ\text{C}$  for 20 min and cooling to  $-100$   $^\circ\text{C}$ . The resonance lines are assigned as follows: 1, 2, 4 =  $\text{CF}_2\text{ClH}$  of external  $\text{CF}_2\text{ClH}/(\text{CD}_3)_2\text{O}$  used as reference and field-frequency lock signal; 3, 7 = CH and average  $\text{CH}_2$ , respectively, of  $\text{C}_4\text{H}_7^+$ ; 5, 8, 9 = C-1, C-2 + C-4, and C-3, respectively, of **3**; 6 =  $(\text{CD}_3)_2\text{O}$  of external reference.

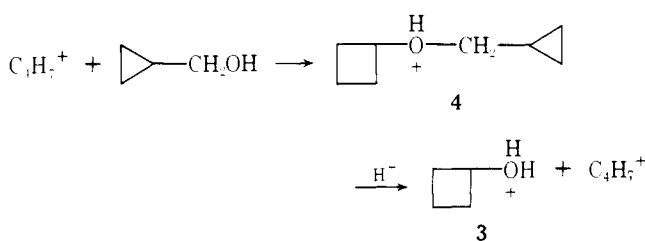
of the "nonclassical"  $\text{C}_4\text{H}_7^+$  cationic intermediate(s) involved in these transformations, the very rapid equilibration of the methylene carbons is well established. At present, opinion is divided as to whether the equilibration process involves rapidly interconverting bicyclobutonium ions (**1a-c**) or "bisected" cyclopropylcarbinyl cations (**2a-c**).<sup>2,3</sup> In contrast, no evidence has been reported to indicate that hydride migrations occur in these intermediates.<sup>2-6</sup> We now report that the  $^{13}\text{C}$  NMR spectrum of an isotopically labeled  $\text{C}_4\text{H}_7^+$  under stable-ion conditions provides unequivocal evidence for slow occurrence of such hydride shifts.

An  $\text{SbF}_5\text{-SO}_2\text{ClF-SO}_2\text{F}_2$  solution of  $\text{C}_4\text{H}_7^+$  was prepared according to previously described techniques at about  $-125$   $^\circ\text{C}$ , employing cyclopropylcarbinol- $l$ - $^{13}\text{C}$  (43%  $^{13}\text{C}$ ).<sup>4h,7-9</sup> A second  $\text{SbF}_5\text{-SO}_2\text{ClF-SO}_2\text{F}_2$  solution of  $\text{C}_4\text{H}_7^+$  was prepared



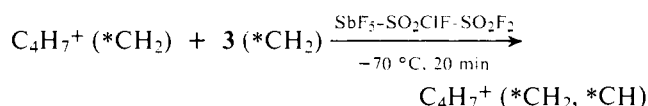
for comparison purposes from nonisotopically enriched cyclopropylcarbinol under the same conditions.<sup>10</sup> The FT 20-MHz  $^{13}\text{C}$  NMR spectra of these solutions at  $-100$   $^\circ\text{C}$  are shown in Figure 1.<sup>11</sup> These  $^{13}\text{C}$  NMR spectra display resonances of an additional, previously unreported,<sup>2,3,4h</sup> species with  $\delta_{^{13}\text{C}}$  84.2 (d, 167), 29.2 (t, 143), and 10.1 (t, 149) as well as the resonances of the methine and averaged methylene carbons of the  $\text{C}_4\text{H}_7^+$  cation at  $\delta_{^{13}\text{C}}$  109.1 (d, 182) and 53.6 (t, 179), respectively.<sup>2,3,4h,11</sup> The 60-MHz  $^1\text{H}$  NMR spectrum of this new species in  $\text{SbF}_5\text{-SO}_2\text{ClF-SO}_2\text{F}_2$  at  $-100$   $^\circ\text{C}$  consists of a doublet ( $J = 3$  Hz, 2 H) at  $\delta$  8.78, a broad multiplet centered at 5.6 (1 H), and two broad, partially coincidental multiplets centered at 2.8 (4 H) and 2.1 (2 H). Comparison of these  $^1\text{H}$  and  $^{13}\text{C}$  NMR parameters with those reported for cyclobutanol<sup>12</sup> and O-protonated alcohols<sup>13</sup> shows that this substance is O-protonated cyclobutanol (**3**), a wholly (\*-)

able product in view of the reported<sup>4b</sup> facile conversion of cyclopropylcarbinol to cyclobutanol under acidic conditions. The relative resonance intensities observed for C-1, C-2,4 and C-3 in the <sup>13</sup>C NMR spectra of **3**, prepared from cyclopropylcarbinol and cyclopropylcarbinol-*l*-<sup>13</sup>C, shows that its carbon-13 label has become essentially randomly distributed between the two nonequivalent sets of methylene sites but has not involved the methine carbon. Because, above -70 °C, **3** is irreversibly converted in SbF<sub>5</sub>-SO<sub>2</sub>ClF-SO<sub>2</sub>F<sub>2</sub> solution to C<sub>4</sub>H<sub>7</sub><sup>+</sup>, the observed scrambling of the label in the transformation of cyclopropylcarbinol to **3** suggests either a transalkylation mechanism by way of the conjugate acid of cyclobutyl cyclopropylcarbinyl ether (**4**) (which would have scrambled



methylene in the cyclobutyl group) or "internal-return isomerization".<sup>2,4b,15</sup> Although solvolysis studies have firmly established that cyclopropylcarbinol-cyclobutyl-allylcarbinyl interconversions are often accompanied by internal return involving C<sub>4</sub>H<sub>7</sub><sup>+</sup> X<sup>-</sup> ion pairs, it is not certain that analogous behavior could occur in the highly ionizing, superacidic media. We can only speculate as to the nature of X<sup>-</sup> if such an ion pair were formed, but SbF<sub>5</sub>OH<sup>-</sup> and Sb<sub>2</sub>F<sub>10</sub>OH<sup>-</sup> are reasonable possibilities.

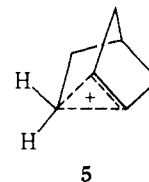
The solution of C<sub>4</sub>H<sub>7</sub><sup>+</sup> and **3** prepared from cyclopropylcarbinol-*l*-<sup>13</sup>C (43% <sup>13</sup>C) was warmed to -70 °C for 20 min and subsequently recooled to -100 °C and its <sup>13</sup>C NMR spectrum was again recorded (Figure 1c).<sup>11</sup> This spectrum has C<sub>4</sub>H<sub>7</sub><sup>+</sup> as the single detectable species, and comparison of the relative intensities of the methine and average methylene resonances (Figure 1c) with those for the original solution (Figure 1b) demonstrates that the carbon-13 label is now randomly distributed in both the methylene and the methine positions.



This result demonstrates that hydride migrations from methylene to methine carbons of C<sub>4</sub>H<sub>7</sub><sup>+</sup> occur under these superacidic conditions at -70 °C. The rate of this process remains slow on the 60-MHz <sup>1</sup>H and 20-MHz <sup>13</sup>C NMR time scales at -61 °C. Because, below -60 °C, this rearrangement does not result in significant broadening of either the <sup>1</sup>H or <sup>13</sup>C NMR resonances, and, above -60 °C, C<sub>4</sub>H<sub>7</sub><sup>+</sup> rapidly decomposes in SbF<sub>5</sub>-SO<sub>2</sub>ClF-SO<sub>2</sub>F<sub>2</sub> solution to unidentified products, it was only possible to determine a limiting value of the rate. The line width (ν<sub>1/2</sub> < 10 Hz) of the methylene carbon resonance at -61 °C shows that *k* < 65 s<sup>-1</sup>, and, thus, Δ*G*<sup>‡</sup> is greater than 10 kcal/mol.<sup>16,17</sup>

We have reported<sup>18</sup> that the <sup>13</sup>C shifts of C<sub>4</sub>H<sub>7</sub><sup>+</sup> under stable-ion conditions change with temperature in a way which indicates that more than one isomeric cation is present. Analysis of the temperature dependences of these shifts indicate that the bicyclobutonium ion **1** is the most stable of the rapidly equilibrating species present. The nature of the higher energy isomer(s) participating in this equilibrium is less certain, but a strong possibility is the bisected cyclopropylcarbinyl cation (**2**). However, this cation is not well constituted for hydride migrations of the type observed. It appears more

reasonable to draw on the close structural similarity of **1** to the nonclassical 2-norbornyl cation (**5**)<sup>19</sup> and to suggest that the hydride shifts correspond to either the 3,2- or the 6,2,1-hydride shifts which are well known to occur in **5** under both kinetic and stable-ion conditions.<sup>19</sup> Because the hydride-shift transition



state lies at least 10 kcal above the normal state(s) of C<sub>4</sub>H<sub>7</sub><sup>+</sup>, it is also possible that the classical cyclobutyl ion is the intermediate and undergoes the 1,2-hydride shifts of the kind which are very fast for the cyclopentyl cation.<sup>19a,c</sup> Notwithstanding the ambiguity of the identity of the C<sub>4</sub>H<sub>7</sub><sup>+</sup> species which is undergoing hydride shifts, our results demonstrate that the Δ*G*<sup>‡</sup> for a hydride shift from a methylene to a methine position for **1** must be greater than 10 kcal/mol. This Δ*G*<sup>‡</sup> is at least 5 kcal/mol higher than that for degenerate 1,2-hydride shifts in secondary carbocations such as the cyclopentyl cation.<sup>19c</sup> A similar high Δ*G*<sup>‡</sup> has been reported for the 3,2-hydride shifts in **5**.<sup>19</sup> Further work will be required to determine whether the Δ*G*<sup>‡</sup>s for hydride shifts in these nonclassical ions are the result of common electronic<sup>19a,c</sup> or common geometric<sup>19c</sup> features.

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- (9) This solution was made up from 0.067 g of cyclopropylcarbinol-*l*-<sup>13</sup>C (43% <sup>13</sup>C), 1.0 g of SbF<sub>5</sub>, 1 mL of SO<sub>2</sub>ClF, and 1 mL of SO<sub>2</sub>F<sub>2</sub>.
- (10) This solution was made up from 0.072 g of cyclopropylcarbinol, 1.0 g of SbF<sub>5</sub>, 1 mL of SO<sub>2</sub>ClF, and 1 mL of SO<sub>2</sub>F<sub>2</sub>.
- (11) The FT 20-MHz <sup>13</sup>C NMR spectra shown in Figure 1 were obtained with a Varian Associates, Model FT-80, NMR spectrometer equipped with a deuterium field-frequency lock system, a broadband <sup>1</sup>H decoupler and a variable-temperature accessory. All spectra were obtained with the same spectral parameters. The chemical shifts were measured from the CF<sub>2</sub>ClH resonance of an external (capillary) CF<sub>2</sub>ClH/(CD<sub>3</sub>)<sub>2</sub>O reference lock and converted to parts per million relative to external (CH<sub>3</sub>)<sub>4</sub>Si utilizing δ<sub>13C</sub> (external (CH<sub>3</sub>)<sub>4</sub>Si) = δ<sub>13C</sub> (CF<sub>2</sub>ClH) + 116.60. Values in parentheses are the proton-coupled multiplicities and <sup>1</sup>J<sub>CH</sub> values (in hertz), respectively.
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## Homolytic Substitution at Saturated Carbon: Mass Spectrometry and Free-Radical Chemistry

Sir:

Homolytic substitution at saturated carbon is a much sought after process in free-radical chemistry.<sup>1,2</sup> We wish to point out the following: (1) a long observed and well-investigated fragmentation of simple aliphatic halides in mass spectrometers is an unrecognized<sup>3,4</sup> example of this sought free-radical reaction; (2) stereochemical evidence for this fragmentation, reported here, is consistent with favored inversion of configuration at the homolytic substitution site; (3) a thermochemical explanation, in line with Ingold and Roberts' ideas,<sup>3</sup> can account for the observation of this reaction in mass spectrometers.

(1) In 1962 McLafferty hypothesized that hydrocarbon loss in the mass spectra of certain long-chain aliphatic halides takes place as pictured in Figure 1 for *n*-hexyl chloride.<sup>5</sup> Deuterium labeling of the  $\alpha$  and  $\delta$  positions demonstrates that these methylene groupings are both retained and as well occupy equivalent positions in the product  $m/e$  91 ion.<sup>6,7</sup> The variation of relative intensity of the  $m/e$  91 ion with electron beam energy<sup>8</sup> and the observation of a strong metastable peak for the formation of this ion<sup>9</sup> are consistent with a low energy of activation rearrangement mechanism.<sup>10</sup> Photoelectron spectroscopy of aliphatic halides shows the lowest energy ionization to involve promotion of a nonbonding electron from halogen.<sup>11,12</sup> This evidence identifies the reaction in Figure 1 as homolytic intramolecular displacement ( $\text{S}_{\text{H}}1$ )<sup>3</sup> of ethyl radical from the  $\delta$  carbon by chlorine radical cation.

(2) Because the stereochemistry of a homolytic displacement step is of great interest<sup>3,4</sup> we have prepared<sup>13</sup> the cis and trans isomers of 4-*tert*-butylcyclohexyl bromide (**1**) and 4-*tert*-butylcyclohexyl chloride (**2**). These materials, with a desirable fixed steric relationship between the  $\delta$ -alkyl grouping and the potentially displacing halogen radical cation, show, as seen in Table I, enhanced loss of the pendant *tert*-butyl group in the trans over the cis isomers. This stereoselectivity which expresses itself in both the percent of total ionization for loss of *tert*-butyl radical,  $\% \Sigma_{50}(\text{M} - \text{C}_4\text{H}_9)^+$ , and as increased competitiveness with rearrangement loss of isobutane,<sup>14</sup>  $(\text{M} - \text{C}_4\text{H}_9^+/\text{M} - \text{C}_4\text{H}_{10}^+)$  (Table I), is consistent with assisted

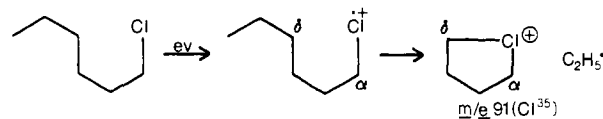


Figure 1.

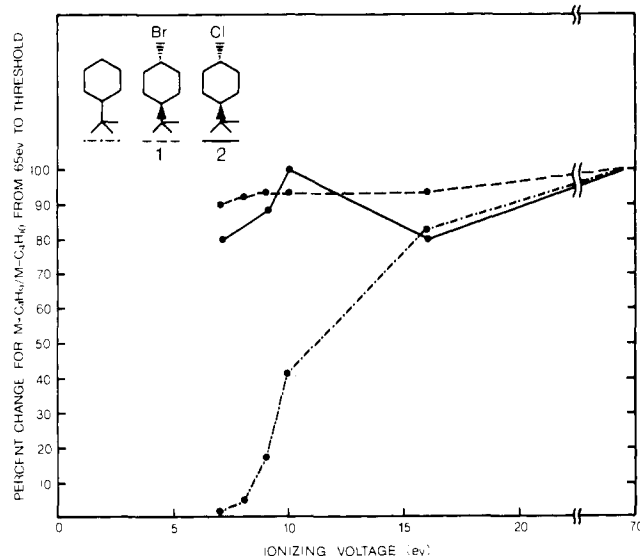


Figure 2. The lines represent the designated molecules as shown and were calculated by setting the  $\text{M} - \text{C}_4\text{H}_9/\text{M} - \text{C}_4\text{H}_{10}$  ratio at 70 eV (Table I) (the electron voltages were measured directly from the ion source terminals and are uncalibrated) equal to 100% and comparing the lower electronvolt values with it. The numbers are the averages of many independent determinations with average deviation of about  $\pm 10\%$  (absolute) for **1** and **2** at the lowest electronvolt values and  $\pm 30\%$  (absolute) for *tert*-butylcyclohexane. The precision increased at higher electron voltages. Measurements were made on a Du Pont 21-490 mass spectrometer at a source temperature of  $130^\circ\text{C}$ .

Table I.<sup>a,b</sup> Stereoselectivity (Trans/Cis) for Loss of the 4-*tert*-Butyl Group

	Br	Cl
	trans/cis	trans/cis
$\% \Sigma_{50}(\text{M} - \text{C}_4\text{H}_9)^+$	79/21	73/27
$(\text{M} - \text{C}_4\text{H}_9^+)/(\text{M} - \text{C}_4\text{H}_{10}^+)$	90/10	84/16

<sup>a</sup> Data were taken on a Hitachi RMU-6 mass spectrometer at 70 eV and  $\sim 130^\circ\text{C}$  source temperature. Independent experiments were carried out on a Du Pont-21-490 mass spectrometer and gave results within experimental error of these above. <sup>b</sup> See text. Numbers are expressed as ratio of trans to cis for percent total ionization above  $m/e$  50 ( $\% \Sigma_{50}$ ) with average deviation of  $\pm 5\%$  and ratio of loss of *tert*-butyl to isobutane  $((\text{M} - \text{C}_4\text{H}_9)^+ / (\text{M} - \text{C}_4\text{H}_{10})^+)$  with average deviation of  $\pm 10\%$ .

back-side displacement of alkyl radical by the halogen cation radical through the boat conformation of the intact molecular ions of *trans*-**1** and **-2**.<sup>15</sup>

Such a process of assisted displacement should show the characteristics of a rearrangement reaction and would be accessible to the lowest energy molecular ions in contrast to simple cleavage loss of the *tert*-butyl group. The experimental data in Figure 2 provide a test of this notion by presenting a comparison of the  $(\text{M} - \text{C}_4\text{H}_9)^+ / (\text{M} - \text{C}_4\text{H}_{10})^+$  ratio for