

about 2500.  $m/z$  (relative intensity) 1971 ( $M + Na$ )<sup>+</sup> (2), 1949 ( $M + H$ )<sup>+</sup> (7), 1108 (17), 1023 (1), 910 (4), 841 (22), 823 (11), 738 (11), 653 (16), 651 (3), 568 (3), 523 (4), 454 (12), 440 (39), 429 (23), 410 (5), 395 (6), 355 (46), 307 (39), 282 (28), 270 (44), 232 (43), 215 (60), 202 (55), 199 (70), 197 (44), 128 (55), 93 (100). When NaCl is added to the matrix, the ( $M + Na$ )<sup>+</sup> peak becomes much more prominent than ( $M + H$ )<sup>+</sup>.

**NMR Spectroscopy.** The 1D <sup>1</sup>H NMR spectra and the 2D experiments were performed on a WM 500 spectrometer (Bruker) equipped with an Aspect 2000 computer using DIS NMR P 830601 software. Internal Me<sub>4</sub>Si was used as standard. Concentration for all the spectra was 0.02 M.

Solvent titration experiments were carried out by adding a peptide solution in Me<sub>2</sub>SO-*d*<sub>6</sub> in aliquots to a CD<sub>3</sub>OH solution, thus maintaining a fixed concentration of 0.02 M.

The applied pulse sequence allowing the <sup>1</sup>H-<sup>1</sup>H relayed COSY ex-

periment was (90°-*t*-90°-*τ*-180°-*τ*-90°-acquisition) (11-*μ*s 90° pulse, 1.5-s relaxation delay, *τ* = 28 ms). The matrix was symmetrized. The spectral width in  $F_1$  and  $F_2$  was 5000 Hz, the number of data points in  $F_2$  was 2048, and 512 increments of 32 scans were recorded. Before Fourier transformation the data were multiplied with an unshifted sine bell. Zero filling was applied only in  $F_1$ .

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## Deuterium Isotope Effects on the <sup>13</sup>C NMR Spectra of 1-Methylcyclobutyl and Trishomocyclopropenyl Cations<sup>1</sup>

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**Abstract:** Saunderson's deuterium isotopic perturbation technique using <sup>13</sup>C NMR spectroscopy has been applied to the 1-methylcyclobutyl and trishomocyclopropenyl cations **1** and **9**. The <sup>13</sup>C NMR chemical shift of the nondeuterated methylenes of  $\alpha,\alpha$ -dideuterio-1-methylcyclobutyl cation is shielded by 1.27 ppm at -50 °C to 1.41 ppm at -90 °C, implying an equilibrium isotope effect. The observed isotope effect between -50 and -90 °C is interpreted with the involvement of  $\sigma$ -delocalized cyclopropylcarbinyl cations **2**, which rapidly exchange methylene carbons in accordance with the previous <sup>13</sup>C NMR spectroscopic studies. However, at lower temperature (-154 °C), the observed spectrum shows no equilibrium isotope effect and closely resembles the spectrum obtained for the all-protio ion (except for a small intrinsic deuterium isotope effect), consistent with a symmetrical  $\sigma$ -bridged structure **6** and not a set of rapidly equilibrating bicyclobutonium ions **4**. Study of Winstein's trishomocyclopropenyl cation **9** upon deuterium substitution at the 3-position shows negligible isotope effect on methine signals ( $\leq 0.2$  ppm), indicative of the static  $\sigma$ -bridged structure.

The isotopic perturbation method developed by Saunders and co-workers<sup>2</sup> to distinguish rapidly equilibrating systems with low energy barriers (double minima) from symmetric systems (single minimum) has become a versatile tool to study degenerate carbocation rearrangements. By asymmetric deuterium substitution, using <sup>13</sup>C NMR spectroscopy, the  $\sigma$ -bridged nature of several carbocations such as 2-norbornyl,<sup>3</sup> 2-bicyclo[2.1.1]hexyl,<sup>4</sup> cyclopropylcarbinyl,<sup>5</sup> and Coates's 9-pentacyclo[4.3.0.0<sup>2,4</sup>.0<sup>3,8</sup>.0<sup>5,7</sup>]nonyl cations<sup>3</sup> has been demonstrated. Other rapidly equilibrating carbocationic systems such as tetramethylethyl,<sup>6</sup> pentamethylethyl,<sup>6</sup> and dimethylcyclopropenyl<sup>7</sup> cations, which are degenerate in solution even at -140 °C, were shown to be regular trivalent carbenium ions by this method. In fact, a recent solid-state cross-polarization magic-angle spinning <sup>13</sup>C NMR study<sup>8</sup> on the latter cations also

indicates their regular trivalent carbenium nature. We now report preparation of deuterium-substituted 1-methylcyclobutyl and trishomocyclopropenyl cations **1** and **9** and their <sup>13</sup>C NMR spectroscopic study at low temperatures, which show no equilibrium isotope effect excluding equilibrating ions. Independent evidence for the  $\sigma$ -bridged nature of both cations **1** and **9** was obtained from <sup>13</sup>C NMR spectroscopic data.<sup>9,10</sup>

### Results and Discussion

**1-Methylcyclobutyl Cation.** The structure of 1-methylcyclobutyl cation **1** under stable ion conditions has been investigated.<sup>9,11-14</sup> In the <sup>13</sup>C NMR spectrum at -80 °C, the ion **1** in SbF<sub>5</sub>/SO<sub>2</sub>ClF solution exhibits three absorptions;  $\delta$ (<sup>13</sup>C) 163.1 (s), 48.7 (t) and 25.4 (q). The observation of a single average absorption for the methylenes indicates a fast threefold degenerate rearrangement on the NMR time scale. The mechanism for such a process was rationalized<sup>12,13</sup> by the involvement of rapidly equilibrating bisected  $\sigma$ -delocalized 1-methylcyclopropylcarbinyl cations **2** exchanging

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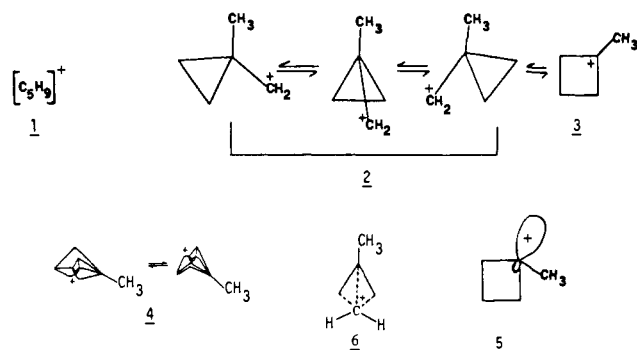
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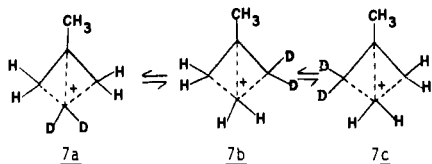
through classical 1-methylcyclobutyl cation **3**. The possibility of equilibrating  $\sigma$ -delocalized bicyclobutonium ions **4** was also considered.<sup>12</sup>



Cooling the solution of ion **1** to  $-156\text{ }^\circ\text{C}$  resulted in the broadening and splitting of the methylene peaks into two separate absorptions at  $\delta(^{13}\text{C})$  72.72 and  $-2.83$  in the ratio 2:1. The quaternary carbon at  $\approx \delta(^{13}\text{C})$  163.1 and the methyl group at 25.4 remained relatively unchanged. Such behavior was rationalized by Sorensen and Kirchen<sup>14</sup> to be due to freezing out of an  $\text{sp}^3$ -hybridized 1-methylcyclobutyl cation structure **5**. Our subsequent studies have shown, however,<sup>9</sup> that the structure of **1** can best be represented as a set of rapidly equilibrating degenerate nonplanar bicyclobutonium ions **4** interconverting through a symmetrical  $\sigma$ -delocalized species **6** that render the  $\beta$ -methylene carbon pentacoordinated or the symmetrical ion **6** itself. The primary evidence for the  $\sigma$ -bridged structure comes from the observation of highly shielded methylene carbon  $\delta(^{13}\text{C})$   $-2.83$  in the  $^{13}\text{C}$  NMR spectrum at  $-156\text{ }^\circ\text{C}$ .

$\text{LiAlD}_4$  reduction of 1-methylcyclopropane carboxylic acid in diethyl ether gave the corresponding  $\alpha,\alpha$ -dideuterio-1-methylcyclopropylcarbinol, which was ionized to the cation at  $-78\text{ }^\circ\text{C}$  in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution. In the  $^{13}\text{C}$  NMR spectrum of the deuterated ion, the peak for nondeuterated methylene was found shielded by between 1.27 ( $-50\text{ }^\circ\text{C}$ ) and 1.41 ppm ( $-90\text{ }^\circ\text{C}$ ) compared to the unlabeled ion, indicating a definite equilibrium isotope effect. The carbon bearing the deuterium (quintet,  $J_{\text{C-D}} = 27.4\text{ Hz}$ ) was found deshielded from the undeuterated methylenes by 2.91 ppm at  $-50\text{ }^\circ\text{C}$ . The small change in the equilibrium isotope effect with temperature from  $-50$  to  $-90\text{ }^\circ\text{C}$  on the undeuterated methylenes ( $\approx 0.14\text{ ppm}$ ) is interpreted with the involvement of  $\sigma$ -delocalized cyclopropylcarbinyl cations **2**, which exchange the methylene carbons.

Cooling the solution of the deuterated ion to  $-154\text{ }^\circ\text{C}$  splits the undeuterated methylenes into two peaks at  $\delta(^{13}\text{C})$  71.30 and  $-2.14$ , respectively. The quaternary carbon and the methyl group are observed at  $\delta(^{13}\text{C})$  161.72 and 25.06. These chemical shifts compare closely with those observed<sup>9,14</sup> for the all-proton ion except for small intrinsic deuterium isotope induced shifts, indicating the ion at  $-154\text{ }^\circ\text{C}$  to be indeed the bridged ion such as **6** and not a set of equilibrating bicyclobutonium ions such as **4**. The ion **6** can also be represented as a resonance hybrid of bicyclobutonium structures **4**. Also the observation of the deuterated methylenes deshielded from the undeuterated methylenes at  $-50\text{ }^\circ\text{C}$  seems to indicate that in the equilibrium which averages methylenes, structure **7a** (wherein the carbon bearing deuterium is pentacoordinate) is less preferred over structures **7b** and **7c**. Such



deshielding isotope effect has been earlier observed in the case of the  $\alpha$ -monodeuterated parent cyclopropylcarbinyl cation  $[\text{C}_4\text{H}_6\text{D}^+]$  by Saunders and Siehl<sup>5a</sup> and more recently by Roberts and co-workers.<sup>5d</sup> Since the methylene hydrogens are non-equivalent in the parent cyclopropylcarbinyl cation both positive

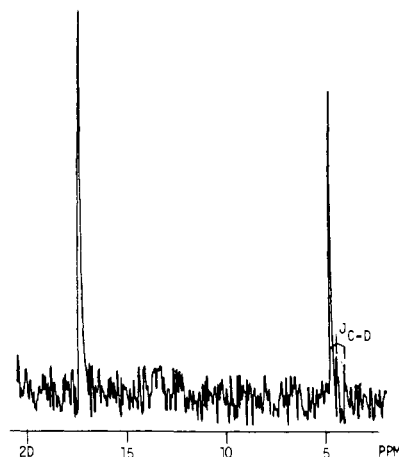
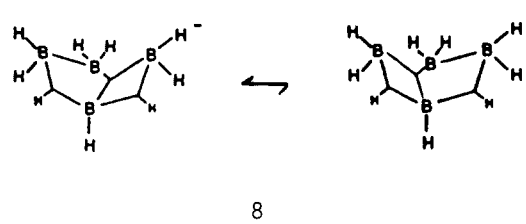


Figure 1. Proton-decoupled 50-MHz  $^{13}\text{C}$  NMR spectrum of 3-deuteriobicyclo[3.1.0]hexyl cation in  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution at  $-80\text{ }^\circ\text{C}$ .

(shielded) and negative (deshielded) isotope effects were observed, indicating that pentacoordinated carbon in  $[\text{C}_4\text{H}_6\text{D}^+]$  shows an unusual preference for deuterium depending whether it is exo or endo. No such complications exist in the case of **1** since the exo and endo protons show same chemical shift.<sup>11</sup> Support for the symmetrical structure **6** also comes from consideration of the carbocation polyborane analogy developed by Williams and Field.<sup>15</sup> The *arachno*-tetraborane anion  $\text{B}_4\text{H}_9^-$  **8** has a similar structure to **6**. Hehre and co-workers<sup>16</sup> have calculated relative energies



of different  $[\text{C}_3\text{H}_9]^+$  isomer using ab initio molecular orbital theory at 4-31G split-valence basis set level. They concluded that a geometry with bisected 1-methylcyclopropyl carbinyl cation structure (such as **2**) was the most stable one followed by bicyclobutonium type structure **4**. However, the present deuterium isotope studies does indicate that the frozen-out structure for **1** is indeed **6**, which is midway between the equilibrating bicyclobutonium ion structures **4** (a resonance hybrid).

**Trishomocyclopropenyl Cation.** Winstein's trishomocyclopropenyl cation **9** under stable ion conditions was first prepared by Masamune and co-workers<sup>10</sup> by the ionization of *cis*-bicyclo[3.1.0]hexyl chloride. Subsequently it has also been prepared<sup>17</sup> by the ionization of *cis*-bicyclo[3.1.0]hexan-3-ol in protic acid free  $\text{SbF}_5/\text{SO}_2\text{ClF}$ . The evidence for the bridged nature of **9** comes



mainly from  $^{13}\text{C}$  NMR spectroscopic data wherein highly shielded bridged methines and methylenes are observed at  $\delta(^{13}\text{C})$  4.90 and 17.60, respectively. Now we would like to provide additional evidence for the bridged nature of **9** by deuterium substitution at the 3-position.

Ionization of *cis*-3-deuteriobicyclo[3.1.0]hexan-3-ol in highly purified protic acid free  $\text{SbF}_5/\text{SO}_2\text{ClF}$  solution provided 3-deuteriotrishomocyclopropenyl cation **10**, whose  $^{13}\text{C}$  NMR

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spectrum at  $-80\text{ }^\circ\text{C}$  for the undeuterated methine and methylene at  $\delta(^{13}\text{C})$  4.93 and 17.60 (Figure 1) is almost identical with those of the symmetrical all-proton ion **9** ( $\delta(^{13}\text{C})$  4.90 and 17.60).<sup>13</sup> The deuterated methine triplet ( $J_{\text{C-D}} = 24.9\text{ Hz}$ ) was found less than 0.2 ppm shielded from the undeuterated methine peak, indicating only an isotopic perturbation of resonance. These observations fully support the symmetrical nonclassical structure of **9**. Similar results have been obtained by Saunders and co-workers<sup>3</sup> previously on the related Coates's cation<sup>18</sup> (i.e., the trishomocyclopropenyl-9-pentacyclo[4.3.0.0<sup>2,4</sup>.0<sup>3,8</sup>.0<sup>5,7</sup>]nonyl cation) by deuterium substitution at the C<sub>9</sub> position.

### Conclusion

The application of Saunderson's isotopic perturbation method of equilibria to 1-methylcyclobutyl cation **1** and trishomocyclo-

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propenyl cation **9** supports their  $\sigma$ -bridged nonclassical structures.

### Experimental Section

The  $\alpha,\alpha$ -dideuterio-1-methylcyclopropylcarbinol and *cis*-3-deuterio-bicyclo[3.1.0]hexan-3-ol were prepared by LiAlD<sub>4</sub> reduction of 1-methylcyclopropanecarboxylic acid (purchased from Aldrich) and bicyclo[3.1.0]hexan-3-one<sup>19</sup> in diethyl ether.

**Preparation of Ions.** Freshly double-distilled SbF<sub>5</sub> was used. To SbF<sub>5</sub> dissolved in about fourfold excess of SO<sub>2</sub>ClF at dry ice/acetone temperature ( $-78\text{ }^\circ\text{C}$ ) was added with vigorous stirring a cooled slurry or solution of the appropriate precursor in SO<sub>2</sub>ClF so as to obtain approximately 10-15% solution of the ion.

<sup>13</sup>C NMR spectra were obtained with Varian Model XL-200 NMR spectrometer equipped with a low-temperature broad-band probe. Chemical shifts are referenced from capillary tetramethylsilane.

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## Enthalpies of Hydration of Alkenes. 3. Cycloalkenes

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**Abstract:** The enthalpies of reaction of cyclopentene, cyclohexene, 1-methylcyclopentene, methylenecyclopentane, 1-methylcyclohexene, methylenecyclohexane, bicyclo[2.2.1]hept-2-ene, and bicyclo[2.1.1]hex-2-ene with trifluoroacetic acid were measured. This gives the difference in energy between exo- and endocyclic double bonds with very good precision and gives differences in driving force for addition reactions in the bicyclic systems. In the series cyclopentene, bicycloheptene, and bicyclohexene, the enthalpies of reaction with trifluoroacetic acid are 9, 15, and 23 kcal/mol, respectively. The enthalpies of conversion of the corresponding alcohols to the trifluoroacetates also were measured, allowing the enthalpies of formation of the alcohols to be determined. It is found that the enthalpy change for replacing a hydroxy group by methyl is essentially constant for a given type of alcohol (i.e., primary, secondary, or tertiary), but it varies considerably between groups.

We have developed a procedure whereby the enthalpies of hydration of alkenes may be measured experimentally.<sup>1</sup> It involves the reactions of the alkene and of the product alcohol with trifluoroacetic acid containing trifluoroacetic anhydride, leading in both cases to the same trifluoroacetate products. The difference in enthalpies of reaction along with the enthalpy of reaction of water allows the calculation of the enthalpy of hydration.

The data may be used to determine the relative energies of related alkenes, as well as the enthalpies of formation of the product alcohols. The procedure possesses the generality associated with enthalpies of hydrogenation of alkenes<sup>2</sup> but provides data of higher precision and leads to an alcohol as the product rather than the nonfunctionalized alkane. When the enthalpies of formation of the alkenes are known, the method allows the enthalpies of formation of the alcohols to be determined. This is of particular value since there is a relative lack of such information for alcohols.

We have applied the procedure to the study of the series of C<sub>5</sub>, C<sub>6</sub>, and C<sub>7</sub> *n*-alkenes.<sup>1,3</sup> It was possible to show that some of the earlier combustion data for the hexenes were significantly in error and to revise the  $\Delta H_f$ . Enthalpies of formation of the 2-, 3-, and 4-heptanols and 3-hexanol were obtained.

We now report the continuation of this study using a series of cyclic alkenes which are of greater chemical interest than the *n*-alkenes. The compounds include cyclopentene (**1**), cyclohexene

**Table I.** Enthalpies of Trifluoroacetylation of Alkenes

compound	state	<i>n</i> <sup>a</sup>	$\Delta H_r$ , <sup>b</sup> cal/mol
cyclopentene ( <b>1</b> )	<i>l</i>	3	$-9167 \pm 44$
cyclohexene ( <b>2</b> )	<i>l</i>	4	$-10355 \pm 25$
<i>cis</i> -3-hexene	<i>l</i>		$-10514 \pm 29^c$
1-methylcyclopentene ( <b>3</b> )	<i>l</i>	3	$-7250 \pm 3$
methylenecyclopentene ( <b>4</b> )	<i>l</i>	3	$-10900 \pm 21$
1-methylcyclohexene ( <b>5</b> )	<i>l</i>	4	$-8739 \pm 21$
methylenecyclohexane ( <b>6</b> )	<i>l</i>	4	$-10710 \pm 24$
bicyclo[2.2.1]hept-2-ene ( <b>7</b> )	<i>c</i>	10	$-14575 \pm 54$
	<i>l</i>		$-15333 \pm 55$
bicyclo[2.1.1]hex-2-ene ( <b>8</b> )	<i>l</i>	3	$-23757 \pm 117$

<sup>a</sup>Number of runs. <sup>b</sup>Uncertainties are twice the standard deviation of the mean (2 $\sigma$ ). <sup>c</sup>Reference 1. The value corresponds to the formation of the 3-trifluoroacetate as the product.

**Table II.** Enthalpies of Fusion

compound	<i>n</i> <sup>a</sup>	$\Delta H$ (cal/mol)
1-methylcyclopentanol	3	$2011 \pm 4$
1-methylcyclohexanol	3	$2599 \pm 7$
<i>exo</i> -bicyclo[2.2.1]heptan-2-ol	3	$621 \pm 11$
bicyclo[2.1.1]hexan-2-ol	3	$545 \pm 6$
bicyclo[2.2.1]hept-2-ene	3	$758 \pm 8$

<sup>a</sup>Number of runs.

(**2**), 1-methylcyclopentene (**3**), methylenecyclopentane (**4**), 1-methylcyclohexene (**5**), methylenecyclohexane (**6**), bicyclo[2.2.1]hept-2-ene (norbornene, **7**), and bicyclo[2.1.1]hex-2-ene (**8**). The reactions of **1** and **2** with trifluoroacetic acid proceeded

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