

### <sup>13</sup>C N.M.R. Spectroscopic Measurement of the Rotational Barrier in the 1-Cyclopropyl-3-methylbuta-1,2-dienyl Cation. Preference for the Bisected Conformation of an $\alpha$ -Cyclopropyl-vinyl Cation

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The cyclopropyl rotational barrier in the 1-cyclopropyl-3-methylbuta-1,2-dienyl cation has been measured using 100 MHz <sup>13</sup>C n.m.r. spectroscopy.

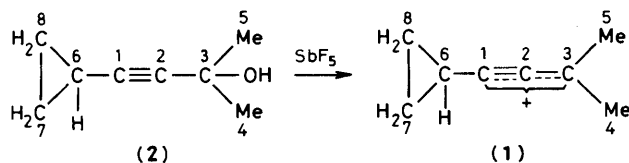
It is well known that electron-donating substituents at the  $\alpha$ - or  $\beta$ -position in vinyl cations stabilize these reactive intermediates.<sup>1</sup> Recently we have generated  $\alpha$ -vinyl-substituted vinyl cations as stable species in solution.<sup>2</sup> Subsequently we have shown by <sup>13</sup>C n.m.r. spectroscopy that combined  $\alpha$ -vinyl and  $\beta$ -cyclopropyl substitution leads to effective delocalization of positive charge in this type of vinyl cation.<sup>3</sup>

Stable alkyl- and aryl-substituted,  $\beta$ -vinyl-stabilized, vinyl cations, *i.e.* allenyl cations, have been prepared,<sup>4</sup> whereas  $\alpha$ -cyclopropyl stabilization, although well established in solvolytic studies,<sup>1</sup> has not been demonstrated for stable vinyl cations in solution. Combined  $\alpha$ -cyclopropyl,  $\beta$ -vinyl stabilization of a vinyl cation is demonstrated here for the first time by the n.m.r. spectroscopic observation of the 1-cyclopropyl-3-methylbuta-1,2-dienyl cation (**1**). We also report the first

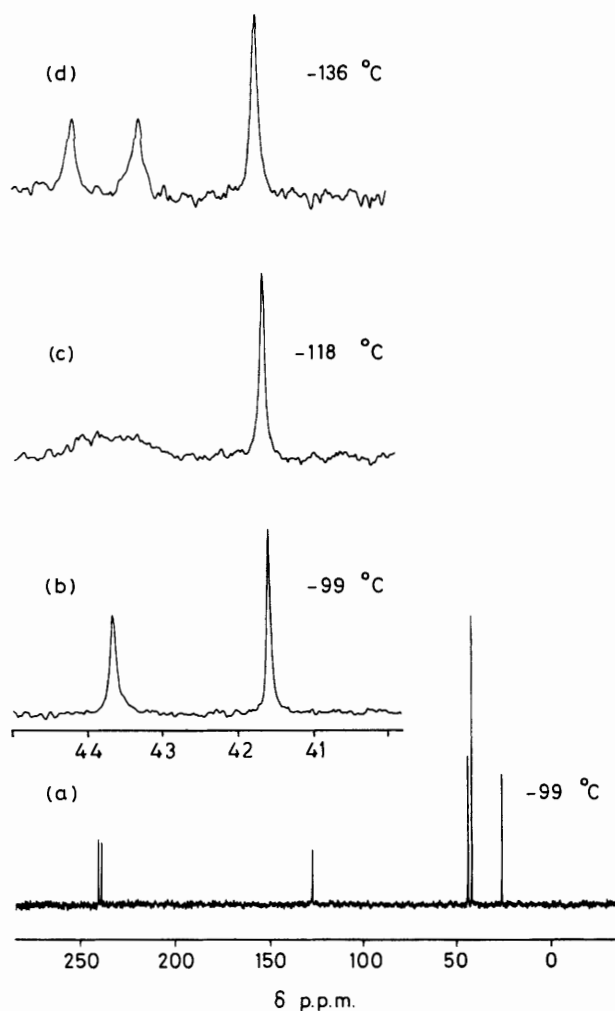
measurement of the rotational barrier in this  $\alpha$ -cyclopropyl allenyl cation.

Generation of stable vinyl cations *via*  $sp^2$ -C-X bond heterolysis has not been achieved to date.<sup>5</sup> Cation (**1**) was therefore generated not from a vinylic precursor but *via*  $sp^3$ -C-X bond cleavage from alcohol (**2**)<sup>†</sup> by reaction with SbF<sub>5</sub>. Yellow solutions of (**1**) in SO<sub>2</sub>ClF-SO<sub>2</sub>F<sub>2</sub> were obtained using advanced techniques already described.<sup>6</sup> The <sup>13</sup>C n.m.r. spectrum of (**1**) at -99 °C (Figure 1a) shows six peaks ( $\delta$  240.45, C-3; 238.89, C-1; 127.31, C-2; 43.69, C-4 and C-5 41.64, C-7 and C-8; 25.74 p.p.m., C-6). Assignments were made on the basis of proton-coupled spectra and specific proton decoupling. The C-3 signal shows long-range coupling to six methyl protons and could thus be distinguished from C-1.

The downfield shifts of C-1 and C-3 indicate extensive charge delocalization between these two positions. Charge delocalization into the cyclopropyl ring is indicated by the 33 p.p.m. downfield shift of C-7 and C-8 and the 26 p.p.m. downfield shift of C-6 in the cation (**1**) compared to the



<sup>†</sup> <sup>13</sup>C N.m.r. of (**2**) in CDCl<sub>3</sub>;  $\delta$  80.29, C-1; 85.24, C-2; 64.93, C-3; 31.53, C-4 and C-5; -0.87, C-6; 7.92 p.p.m., C-7 and C-8.

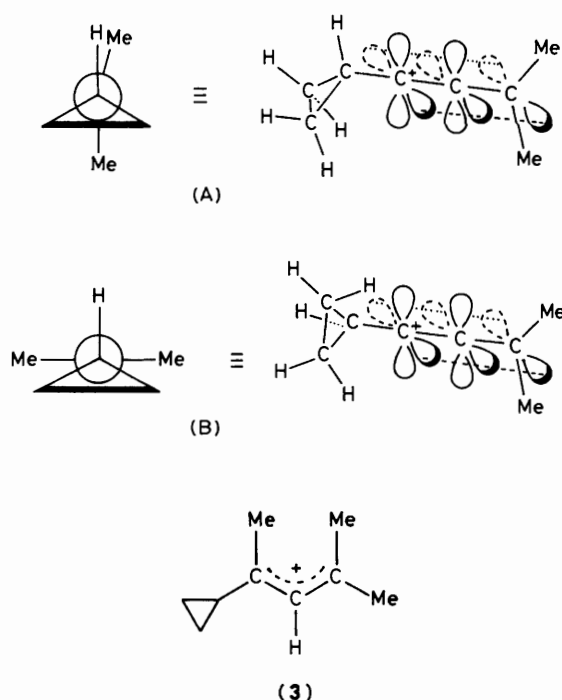


**Figure 1.** (a) 100.62 MHz  $^{13}\text{C}$  N.m.r. spectrum of cation (1) in  $\text{SO}_2\text{ClF}-\text{SO}_2\text{F}_2$  (2:1) at  $-99^\circ\text{C}$ . (b)–(d) Expansions showing the temperature dependence of the methyl group signals at selected temperatures.

precursor (2). The averaged methyl signal (C-4 and C-5) at 43.69 p.p.m. shows kinetic line broadening at  $-99^\circ\text{C}$  and coalescence at  $-120^\circ\text{C}$  (Figure 1). Two peaks are observed below  $-123^\circ\text{C}$ . At  $-141^\circ\text{C}$  the peaks are 0.88 p.p.m. apart and the line width equals the line width of non-exchanging carbon signals. From line shape analysis rate constants were obtained which gave the Arrhenius parameters  $E_A = 7.2 \pm 0.2$  kcal/mol $\ddagger$  and  $\log A = 12.7 \pm 0.3$ .

Theoretical evidence predicts that  $\alpha$ -cyclopropyl-substituted vinyl cations, like trigonal cations, prefer to adopt the bisected geometry.<sup>7</sup> A basic feature of this conformation is the lack of a symmetry plane through the C-1-cyclopropane bond. Whereas two alike substituents orthogonal to this plane are magnetically nonequivalent in trigonal cations, this cannot be realized in the parent  $\alpha$ -cyclopropyl-vinyl cation or its  $\beta$ -disubstituted homologues. In contrast allenyl cations like (1) have two orthogonal double bonds leaving  $\gamma$ -substituents orthogonal to the delocalized C-1-p-orbital.

There are two limiting conformations for cation (1), the bisected conformation (A) and the perpendicular conformation (B). Only in conformation (A) are the two methyl groups



non-equivalent. The low temperature spectrum of (1) (Figure 1d) thus proves directly the preference for the bisected conformation (A). It also shows that vinyl cations, like trigonal cations,<sup>8</sup> adopt the conformation involving the most extended conjugation.

If one assumes that cyclopropyl stabilization of the cation is eliminated in the perpendicular rotated transition state (B), the barrier  $E_A$  is a direct measure of cyclopropyl stabilization in cation (1). The barrier in (1) is significantly lower than in the dimethyl-cyclopropylmethyl cation ( $E_A = 13.7 \pm 0.4$  kcal/mol $\ddagger$ ),<sup>9</sup> because cation (1) is stabilized in addition by  $\beta$ - $\pi$ -allyl-type resonance. The 2-cyclopropyl-4-methylpent-3-enyl cation (3) which might serve as a close trigonal analogue to (1) has a very similar rotational barrier ( $\Delta G^\ddagger = 7.9$  kcal/mol $\ddagger$  at  $-85^\circ\text{C}$ ).<sup>8</sup> This indicates a similar requirement for  $\alpha$ -cyclopropyl stabilization in tertiary allyl and allenyl cations.

This work was supported by the Deutsche Forschungsgemeinschaft.

Received, 26th January 1984; Com. 116

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$\ddagger$  1 kcal = 4.184 kJ.