Energy Separation between Secondary and Tertiary Bicyclo[2.1.1]hexyl Cations. Partial Bridging in Carbocation Structures

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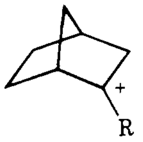
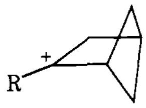
Abstract: The 2-bicyclo[2.1.1]hexyl cations show thermodynamic and spectroscopic properties which are intermediate between those found in 2-norbornyl cations on the one hand and cyclopentyl or aliphatic cations on the other. The free-energy difference between isomeric secondary and tertiary carbocations was found to be 7.0–9.8 kcal/mol compared to 5.5 and ≤11.4 kcal/mol for the analogous norbornyl and cyclopentyl member. Applying Saunders' equilibrium isotope effect (CD_3 vs. CH_3) to the bicyclo[2.1.1]hexyl case gives an enthalpy difference of 150 cal/mol, compared to the previously determined values of 60 and 180 cal/mol for the norbornyl and cyclopentyl cations, respectively. This thermodynamic data correlates well with known ^{13}C chemical shift NMR spectroscopic data, suggesting a common origin for these effects. A C2–C6 partial bond description, with charge delocalization to C1, rationalizes all these observations. It is important to recognize that the bonding in some carbocations precludes a ready classification into "classical" or "nonclassical" categories and one should rather think in terms of a whole range of intermediate bonding situations.

A determination of the energy separation between secondary and tertiary (CH_3) 2-norbornyl cations **1**, in solution, employing several unrelated experimental procedures, has consistently yielded a figure of about 5.5–7.5 kcal/mol.[1] This can be compared to that found for simple aliphatic cations, the figure of 10–15 kcal/mol being generally accepted.[1d,2] This paper reports a determination of the free-energy[3] difference ΔG between secondary and tertiary 2-bicyclo[2.1.1]hexyl cations **2**. It is significant that one finds a value *intermediate* between those reported above.



1a, R = H
b, R = CH_3



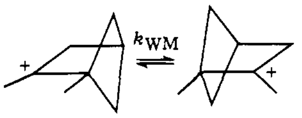
2a, R = H
b, R = CH_3

Results

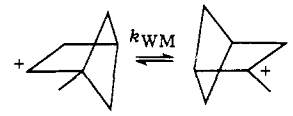
The procedure by which one uses activation free energy data to calculate ground-state properties of cations will necessarily vary depending on the particular rearrangement rate processes being studied. For 2-bicyclo[2.1.1]hexyl cations **2**, the procedure differs from that used in the norbornyl cation case[4] and is shown in Figures 1 and 2. The high-energy secondary cation **2c** is of course not directly observable. One can, however, determine the forward rate constant k_f because the group equivalences in **2c** differ from those in **2b** and the overall result is an exchange of the equivalent carbons 5 and 6 with carbon 3 or of the complete equivalence of the proton sets a, b, and c in Figure 1. The exchange matrix for the latter is also shown in Figure 1. The only significant factor which might complicate this analysis would be an unsymmetrical geometry for **2c**. The straightforward sequence depicted in Figure 1 and this second latter case are shown in Figure 2. In both cases, the exchange matrix is the same. The rearrangement depicted in the middle barrier in the lower energy profile of Figure 2 corresponds to a symmetrization process which is inherent in a symmetric **2c** intermediate. Only if this barrier were higher than the $\Delta G^{\ddagger}_{\text{reverse}}$ barrier would any complication arise.[5]

The ^1H and ^{13}C NMR spectra of the 2-methyl-2-bicyclo[2.1.1]hexyl cation **2b** have been reported[6] and shown qualitatively to undergo the exchange process depicted in Figure 1. Since we wished to determine accurate activation parameters, we have repeated the preparation of **2b** and have determined the ^1H NMR line shapes at a number of accurately determined temperatures. These spectra are shown in Figure 3, starting with a "frozen-out" spectrum at −99.5 °C and continuing up to −51 °C, where decomposition becomes rapid. The three sets of protons, a, b, and c, involved in the exchange are marked in the −99.5 °C spectrum.[7] To simulate the observed spectrum as accurately as possible, and hence obtain the most accurate rate constants, all of the protons (exchanging and nonexchanging) have been included. The matching agreement is generally excellent and this is further verified by the good Eyring plot obtained from this data. The activation parameters thus obtained are $\Delta H^{\ddagger} = 10.3 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger} = 2.9 \pm 2.1$ eu, and $\Delta G^{\ddagger} = 9.8$ kcal/mol. This $\Delta G^{\ddagger}$ value has been included in Figure 2 and one now needs to determine $\Delta G^{\ddagger}_{\text{reverse}}$ in order to complete the calculation.

A conventional rate determination of $\Delta G^{\ddagger}_{\text{reverse}}$, starting from **2c**, is manifestly impossible because of the very small barrier involved. However, one can look at this type of Wagner–Meerwein (WM) rearrangement using the 1,2-dimethyl-2-bicyclo[2.1.1]hexyl cation **3**, where the rearrangement is degenerate (and hence potentially accessible using NMR line-broadening techniques). Since the **2c** → **2b** process involves a secondary → tertiary cation conversion, one can very confidently predict that this rate would be even faster ($\Delta G^{\ddagger}$ smaller) than that involved in the **3** ⇄ **3′** process, which itself turns out to be extremely fast.

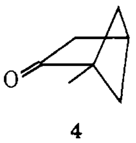


3 **3′**



2c **2b**

Cation **3** has not been previously reported. It was prepared starting from the known 1-methyl ketone **4**,[8] by methyllithium treatment to give the tertiary alcohol **5** and conversion of this to the chloride **6** with concentrated hydrochloric acid. The ^{13}C NMR spectrum of this ion shows only four peaks, δ 199.2 (C1 and 2), 60.6 (C3, 5, and 6), 34.6 (C4), and 22.7 (1- and 2-



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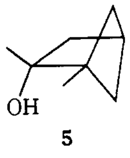

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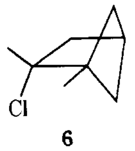

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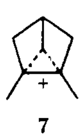

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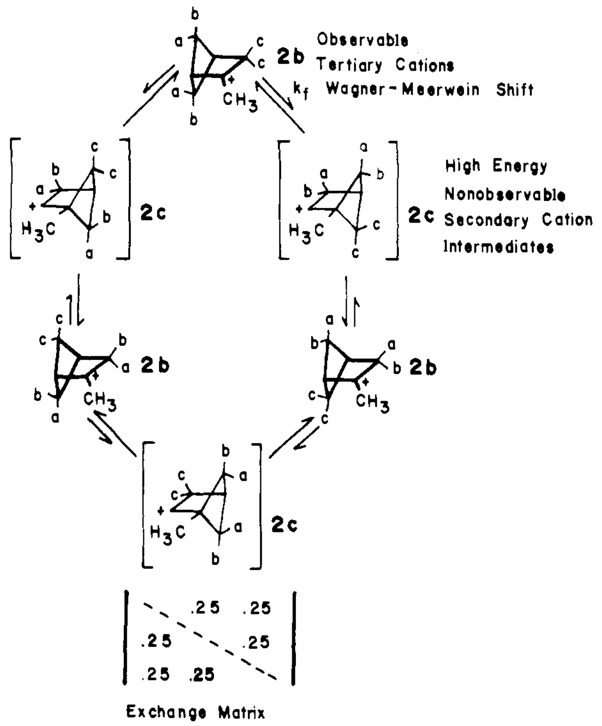


Figure 1. Exchange process and matrix for the three chemically nonequivalent sets of protons. Two of the tertiary ions shown are enantiomers by virtue of the magnetic labeling, as are two of the secondary ions.

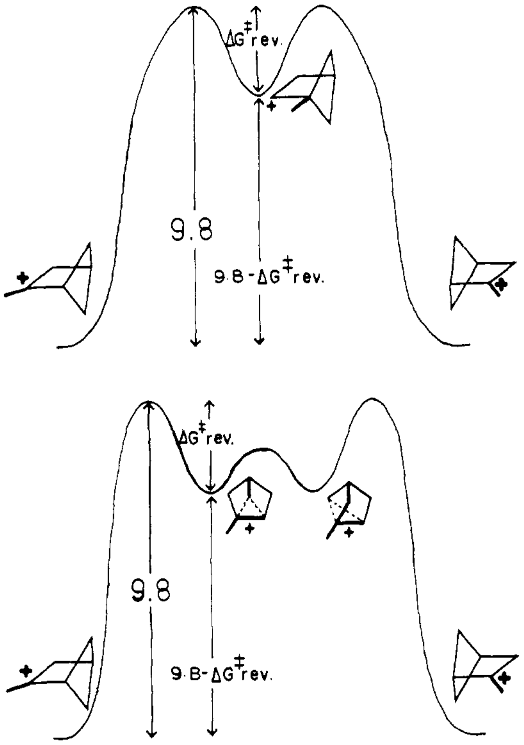


Figure 2. "Reaction coordinate" diagram of the overall rearrangement. The top curve assumes a planar secondary ion intermediate, whereas the bottom curve considers the possibility that extensive C2-C6 bonding will render the secondary ion intermediate nonplanar. Included in the diagram is our experimentally determined value for the barrier (kcal/mol).

CH_3), thus indicating a very rapid WM shift (see later evidence excluding a symmetrical structure **7**). With care in the cation preparation, one can cool this solution to −156 °C and even at this extreme temperature there is only slight (viscosity?) broadening of the averaged C1-C2 carbon peak (it is in fact this averaged peak which would have broadened first, assuming that one had succeeded in bringing the rate within

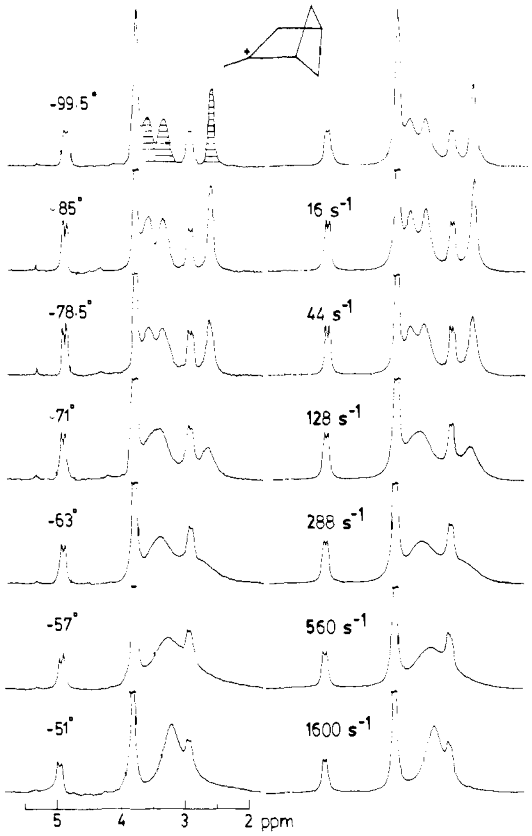


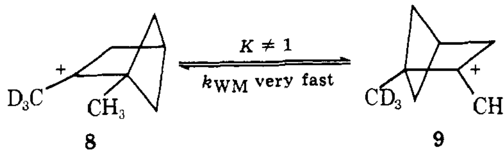
Figure 3. Left: experimental line shapes at different temperatures for the ^1H NMR spectrum of the 2-methyl-2-bicyclo[2.1.1]hexyl cation (**2b**). The peaks involved in the exchange have been shaded in the −99.5 °C spectrum. Right: simulated spectra, with rate constants, based on the exchange process shown in Figures 1 and 2.

the NMR detection range, because the intrinsic separation of these carbons is expected to be very large, about 225 ppm or 5085 Hz).[9] Simulation of the actual C1-C2 line shape for a two-carbon exchange process shows that the WM rate constant for **3** ⇄ **3′** must be equal to or greater than 5×10^7 s^{-1} at −142.5 °C, $\Delta G^{\ddagger} \leq 2.8$ kcal/mol. From Figure 2, one can now determine the ΔG tertiary-secondary difference as 7.0-9.8 kcal/mol.

An attempt was also made in this study to freeze out a possible WM shift in the parent 2-bicyclo[2.1.1]hexyl cation **2a**, since previous workers[6,10] had not determined the ^{13}C NMR spectrum at these extremely low temperatures. Not unexpectedly, this also fails. From this evidence, the cation is either symmetrical or has a WM shift barrier of ≤3.5 kcal/mol.[11]

Proof of the Equilibrating Nature of 3. As discussed previously, the NMR spectrum of **3** is consistent with either a symmetrical structure **7** or one involving a very rapid WM shift **3** ⇄ **3′**. That the latter is the case can be shown easily.

The degeneracy of the WM shift in **3** could be broken in several structural ways[12] but the most direct is to substitute CD_3 for one of the CH_3 groups (structures **8** and **9**). Saunders[13] has previously used this procedure on the 1,2-dimethyl-2-norbornyl cations and others. The ^{13}C NMR spectrum of the **8** ⇄ **9** mixture shows a separation of the averaged C1 and C2 carbons of 46.48 ppm at −128 °C. This chemical shift separation is temperature dependent, as expected for an equilibrium process, and the data are given in Figure 4. A ln



8 **9**

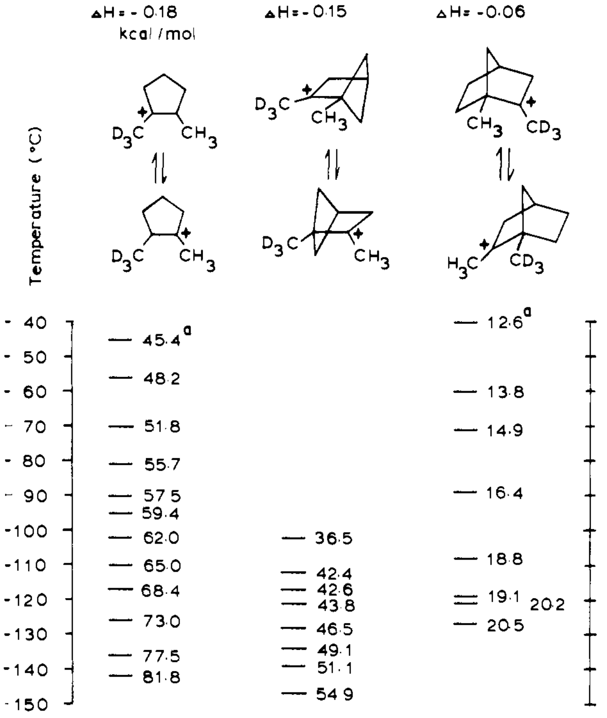


Figure 4. Chemical-shift separation (δ) as a function of temperature between the averaged C1 and C2 carbons (ppm). In each case C1 and C2 average to a single line when these positions are substituted with two methyl groups rather than a methyl and a trideuteriomethyl group. (a) Data of ref 13a.

K^{14} vs. $1/T$ plot is shown in Figure 5 and this gives $\Delta H = -0.15 \pm 0.01$ kcal/mol, $\Delta S = -0.22 \pm 0.05$ eu. That **9** is more stable than **8** is expected but this can also be experimentally determined from the relative intensities of the two ^{13}C peaks involved here (less NOE enhancement and T_1 relaxation in the CD_3 case).

Discussion

We have previously accepted that the 2-norbornyl cation structure involves extensive C2-C6 bonding[1c] with concomitant charge delocalization from C2 to C1. It could be a fully symmetrical structure *or* an equilibrating pair. We would attribute the modestly smaller secondary-tertiary cation energy difference to this delocalization.

One of the advantages of a partial bonding picture[1c] is that it can accommodate a whole range of C2-C6 bond strengths depending on the actual cation involved. This is where the 2-bicyclo[2.1.1]hexyl cations come into the picture. When one compares this system to the 2-norbornyl cations on the one hand and "normal" aliphatic species on the other, the properties being compared fall in an *intermediate* range. Thus, the 2-bicyclo[2.1.1]hexyl cations seem clearly not as well disposed geometrically for C2-C6 bonding and charge delocalization.

The comparisons one can make are the following: (1) the intermediate value for the secondary-tertiary cation energy difference (Table I); (2) the intermediate value for the CD_3 equilibrium isotope effect in equilibria involving the 1,2-dimethyl-2-norbornyl cation, the 1,2-dimethylbicyclo[2.1.1]-hexyl cation **3**, and the 1,2-dimethylcyclopentyl cation. These data are shown in Figure 4. The small separation in the norbornyl case argues for some delocalization,[16] making the C1 position more resemble C2 and thus lowering the known hyperconjugative preference for CH_3 vs. CD_3 on a C^+ carbon.[13] One could argue that there is also a *small* delocalization effect operating in **3** since the separation is smaller than in the cyclopentyl case and ΔH is smaller; (3) the ^{13}C chemical shift for the C^+ carbon (assuming that charge-density correlations hold) in the 2-methylnorbornyl cation **1b** is 270.2 ppm,[17] in 2-methyl-2-bicyclo[2.1.1]hexyl (**2b**), 322.0 ppm,[6] and in methylcyclopentyl, 336.7 ppm.[18] The averaged C1-C2 chemical shift in the 2-norbornyl cation is 125.0 ppm,[19] in the 2-bicyclo[2.1.1]hexyl cation 157 ppm,[10] and in the secondary butyl cation 171.6 ppm.[20] In addition, one could have brought in comparisons of C1 chemical shifts and of H-1 and H-6exo proton positions. Farnum and Wolf[21] have used such chemical-shift comparisons in the aryl-substituted 2-norbornyl cation series.

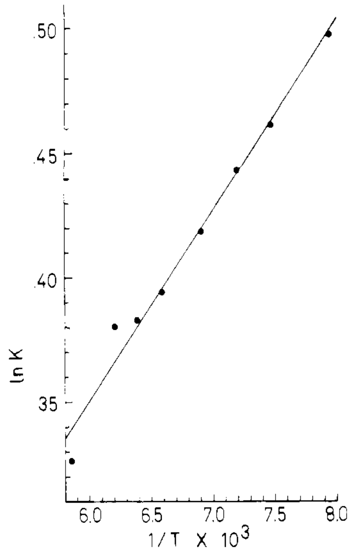
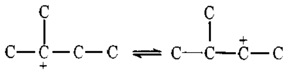
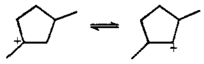
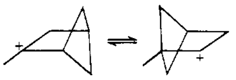
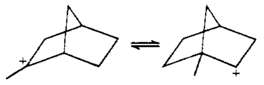
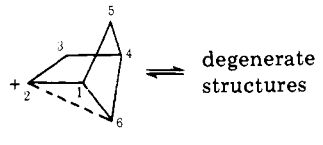


Figure 5. Plot of ln K vs. $1/T$ for the equilibrium constant between cations **8** and **9**.

Table I. Free-Energy Differences of Secondary and Tertiary Carbocations in Superacid Solvent Determined by a Similar Procedure

reaction	ΔG, kcal/mol	ref
 $C-\overset{C}{\underset{+}{C}}-C-C \rightleftharpoons C-\overset{C}{C}-\overset{+}{C}-C$	10-13	2a,b
	≤12.5, ≤11.4	2e,15
	7.0-9.8	this work
	5.5	1b,c

Solvolysis results with the 2-bicyclo[2.1.1]hexyl system have been interpreted in favor of bridged structures by some authors[22] and in terms of "classical" ions by others.[23] In the MINDO/3 theoretical results of Dewar,[24] the bicyclo[2.1.1]-hexyl cation was found to be a better candidate for symmetrical bridging than 2-norbornyl, but more recent results by Lenoir[25] show the reverse. In the original paper on the observable bicyclo[2.1.1]hexyl cation, Saunders, Wiberg, et al.,[10] argued for a bridged structure, whereas Olah et al. later opted for a "carbenium" or "classical" formulation for the ground state.[6] The most recent paper by Saunders et al.[26] simply describes this cation as "highly σ-delocalized" and in our opinion this is the best description, i.e., the ion is unsymmetrically bridged (C1-C6 > C2-C6) (structure **10**). To accommodate the symmetrical NMR spectrum, this ion must undergo a very rapid C2-C6 → C2-C5 bridging switch and also the degenerate Wagner-Meerwein shift whereby the C1-C6 and C2-C6 bonds interchange. Partial bonding descriptions are a universal



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phenomenon in organic chemistry and are well supported in carbocations by molecular orbital calculations.[27] Such descriptions lack precision, but in many cases this is exactly what one wants under the circumstances.

Experimental Section

Preparations of Ions. A solution of the appropriate chloride in $CFCl_3$ was added, with vigorous stirring, to a cooled (ca. −130 °C) 1:4 SbF_5/SO_2ClF or 1:3:3 $SbF_5/SO_2ClF/SO_2F_2$ solution contained in an NMR tube. The former mixture was used for **2b**, the latter for all the others. Approximately 100 mg of precursor was used for the ^{13}C spectra. In the ^1H spectra, between 15 and 35 mg of precursor was used.

NMR Spectroscopy. Both the ^1H (90.0 MHz) and ^{13}C (22.63 MHz) spectra were recorded on a Bruker WH-90 spectrometer operating in the FT mode. The ^{19}F signal of SO_2ClF was used as a lock. The ^1H spectra of ions were referenced to external Me_4Si and ^{13}C spectra to internal $CFCl_3$, taking the center of the $CFCl_3$ doublet as 117.9 ppm. Temperatures were measured by inserting a tube containing silicone oil and a thermocouple into the probe. The reported temperatures are averages of readings taken before and after the actual measurement.

Line-Broadening Calculations. The simulated spectra were all calculated, by digital computation of the exchange modified Bloch equation, using the experimentally observed line widths (T_2). The H1 and H4 protons of the 2-methyl-2-bicyclo[2.1.1]hexyl cation (**2b**) were entered as doublets but the couplings in the remaining protons were not resolved and showed up experimentally (and simulated) as a broadened line. The rate constants were assigned in two steps, a rough range obtained initially and then a more accurate comparison to simulated spectra calculated with only small jumps in the rate constants. The ^{13}C line-broadening results were obtained in a similar way. Experimental C1–C2 peaks were matched with calculated curves on the assumption that the observed line broadening is due to a slowing down of the WM shift. This assumption is almost certainly wrong but this procedure does give an absolute minimum rate constant (or maximum $\Delta G^{\ddagger}$) for the process. In some cases, one gets the smallest maximum $\Delta G^{\ddagger}$ by not evaluating the most extreme temperature spectra since these are considerably broader than those at perhaps 10 °C higher temperature.

2-Bicyclo[2.1.1]hexanone was prepared from 1,5-hexadien-3-ol by the method of Bond.[28]

1-Methyl-2-bicyclo[2.1.1]hexanone (**4**) was prepared from 2-methyl-1,5-hexadien-3-ol (prepared via a Grignard reaction using the method of Dreyfuss[29]) by a procedure analogous to that given above:[8] IR 1759 cm^{-1}; ^1H NMR ($CDCl_3$) 2.66 (1 H, m), 2.14 (2 H, m), 2.00 (2 H, m), 1.59 (2 H, dd), and 1.15 (3 H, s) ppm.

2-Methyl-2-bicyclo[2.1.1]hexanol[6] **and 1,2-dimethyl-2-bicyclo[2.1.1]hexanol** (**5**) were obtained by adding methyllithium to the corresponding ketones. Compound **5** had ^{13}C NMR ($CFCl_3$) 77.5, 55.9, 46.5, 44.3, 42.7, 33.9, 23.7, and 13.9 ppm, and was not purified further.

2-Methyl-2-chlorobicyclo[2.1.1]hexane and 1,2-dimethyl-2-chlorobicyclo[2.1.1]hexane (**6**) were prepared by stirring a $CFCl_3$ solution of the alcohol with concentrated HCl for 2.5 h at 0 °C. The layers were separated and the $CFCl_3$ layer was dried over anhydrous K_2CO_3. Evaporation of the $CFCl_3$ solutions yielded the essentially pure chlorides. 2-Methyl-2-chlorobicyclo[2.1.1]hexane had ^{13}C NMR ($CDCl_3$) 75.2, 54.3, 45.7, 40.7, 39.3, 38.8, and 30.2 ppm. Compound **6** had ^{13}C NMR ($CFCl_3$) 76.8, 58.3, 48.5, 44.8, 42.2., 34.9, 27.5, and 14.4 ppm.

1-Methyl-2-trideuteriomethyl-2-bicyclo[2.1.1]hexanol was obtained by adding CD_3MgI to ketone **4.** The resulting alcohol was converted to the chloride, as above. As expected, a mixture of 1-trideuteriomethyl and 2-trideuteriomethyl chlorides was obtained.

2-Bicyclo[2.1.1]hexanol was prepared as previously described.[30]

2-Chlorobicyclo[2.1.1]hexane was obtained by stirring a $CFCl_3$ solution of the corresponding alcohol with PCl_5 (excess) for 2.5 h at 0 °C. The resulting mixture was washed with cold water and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the chloride: ^{13}C NMR ($CFCl_3$) 59.1, 48.4, 39.8 (2 C), 39.6, and 36.8 ppm.

Acknowledgment. We thank the National Research Council of Canada for generous financial support.

References and Notes

(1) (a) H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **89**, 74 (1970); (b) E. Huang, K. Ranganayakulu, and T. S. Sorensen, *J. Am. Chem. Soc.*, **94**, 1780 (1972); (c) R. Haseltine, N. Wong, T. S. Sorensen, and A. J. Jones, *Can. J. Chem.*, **53**, 1891 (1975); (d) E. M. Arnett and C. Petro, *J. Am. Chem. Soc.*, **100**, 2563 (1978); (e) H. C. Brown and Min-Hon Rei, *ibid.*, **86**, 5008 (1964); (f) K. L. Servis, S. Borčić, and D. E. Sunko, *Tetrahedron*, **24**, 1247 (1968).

(2) (a) M. Saunders and E. L. Hagen, *J. Am. Chem. Soc.*, **90**, 2436 (1968); (b) M. Saunders, P. Vogel, E. L. Hagen, and J. Rosenfeld, *Acc. Chem. Res.*, **6**, 53 (1973); (c) J. L. Fry, J. M. Harris, R. C. Bingham, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2540 (1970); (d) L. Radom, J. A. Pople, and P. von R. Schleyer, *ibid.*, **94**, 5935 (1972); (e) D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, **9**, 204–205 (1972); (f) E. W. Bittner, E. M. Arnett, and M. Saunders, *J. Am. Chem. Soc.*, **98**, 3734 (1976).

(3) Entropy effects appear to be small so that ΔH and ΔG can be used interchangeably.

(4) R. Haseltine, E. Huang, K. Ranganayakulu, T. S. Sorensen, and N. Wong, *Can. J. Chem.*, **53**, 1876 (1975).

(5) Even if this were the highest barrier our figures would not be much changed; see footnote 11.

(6) G. A. Olah, G. Liang, and S. P. Jindal, *J. Am. Chem. Soc.*, **98**, 2508 (1976).

(7) Olah et al.[6] give two different assignment versions in structure **2** and Table I of their paper. The high-field peak is certainly H5[6] endo but a definite assignment of the other two is not possible. This uncertainty has no bearing on the analysis.

(8) T. W. Gibson and W. F. Erman, *J. Org. Chem.*, **37**, 1148 (1972).

(9) C1 in cation **2b** appears at 81.6 ppm. Addition of a methyl group should deshield this carbon by ca. 5 ppm, giving us an estimate of 86.6 ppm for C1. From the position of the averaged peak, this places C2 at 311.8 ppm, a very reasonable figure.

(10) G. Seybold, P. Vogel, M. Saunders, and K. B. Wiberg, *J. Am. Chem. Soc.*, **95**, 2045 (1973).

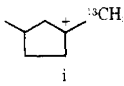
(11) A symmetrical formulation for **2a** does not make C3, 5, and 6 all equivalent. This requires a step identical with that depicted in Figure 2, lower profile, middle barrier. Since these carbons are experimentally equivalent, this barrier must be small.

(12) T. S. Sorensen and K. Ranganayakulu, *Tetrahedron Lett.*, 2447 (1972).

(13) (a) M. Saunders, L. Telkowski, and M. R. Kates, *J. Am. Chem. Soc.*, **99**, 8070 (1977); (b) M. Saunders and M. R. Kates, *ibid.*, **99**, 8071 (1977).

(14) The intrinsic ^{13}C chemical shift separation of C1 and C2 (Δ) was taken as 225 ppm; see footnote 9.

(15) This result was obtained from unpublished data of the authors. Observation of the time-dependent ^{13}C NMR spectrum of



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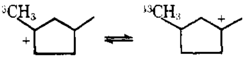
at a temperature of −115 °C allowed us to follow the rearrangement



ii iii

by conventional kinetics.

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