

2,3-Dimethyl-2-norbornyl Cations. Rearrangements and Equilibria

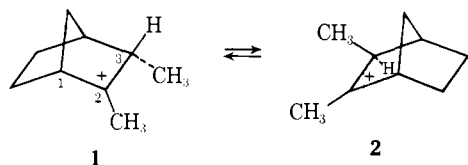
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Abstract: Both the 2,3-*endo*-dimethyl-2-norbornyl (**1**) and very probably the 2,3-*exo*-dimethyl-2-norbornyl (**2**) cation have been directly observed. Contrary to the recent conclusions of Olah and Liang, it is suggested that the more stable isomer is **1**. Using both ¹H and ¹³C nmr line broadening, it has been possible to accurately determine the rate of the *exo*-3,2-hydride shift in **1** and to determine the rate and equilibrium constant for the interconversion of **1** and **2**. The rate of the *endo*-3,2-hydride shift in **2** is found experimentally to be slower than the rate of interconversion of **1** and **2** and to have a free energy of activation of at least 5.5 kcal/mol greater than that for the *exo*-3,2-hydride shift.

By directly observing many of the well-known carbocation rearrangements of substituted norbornyl cations, in particular, the absolute rate at which these occur and the thermodynamic stability of the carbocations themselves, one is able to better rationalize how the (often) myriad products typically produced by acid catalysis or solvolysis (and involving these ions as *intermediates*) will depend upon the particular reaction conditions (acid strength, reaction time, temperature, the nucleophile in solvolysis, whether conditions allow a reversibility of the reaction, etc.). This is illustrated by a comparison of the way in which the observable α -fenchyl cation (2,7,7-trimethyl-2-norbornyl) rearranges^{2a} and the way α -fenchene rearranges under acid-catalysis conditions.^{2b}

Resulting from such studies is the not surprising finding that classes of ion to ion rearrangements appear to occur at a very similar rate in a variety of these methyl-substituted norbornyl cations. It is our hope that it will be possible to observe *directly* all the important examples and to assign a unique activation energy for each. As a result, in considering an unknown system in which several competing rearrangement processes might be possible, one would be in an advantageous position to make a rational assessment of the probable product(s). Carbocations capable of just such competing rearrangement possibilities are the 2,3-*endo*-dimethyl-**1**- and 2,3-*exo*-dimethyl-2-norbornyl-**2** cations. We consider in this study three rearrangement possibilities: (1) an *exo*-3,2-hydride shift in **1**; (2) a rearrangement which interconverts **1** and **2**; and (3) an *endo*-3,2-hydride



shift in **2**. These are shown in this paper by a variety of techniques to have the following relative rate:

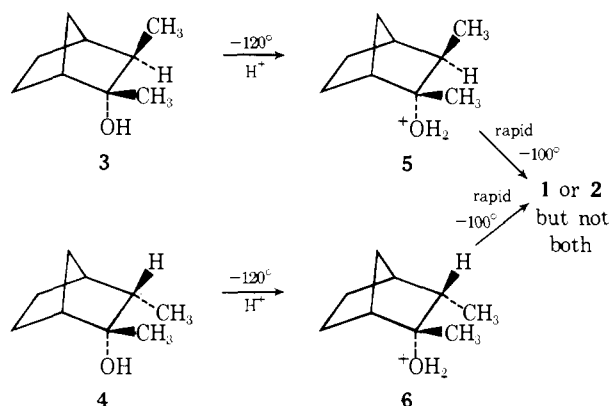
$$k_{\text{exo-3,2-hydride}} \gg k_1 \approx k_2 > k_{\text{endo-3,2-hydride}}$$

Furthermore, interesting and unexpected thermodynamic differences exist between **1** and **2**,³ and it has been possible to directly measure the energy difference between **1** and **2** and to state which isomer is in fact the more stable.⁴

Results and Discussion

Stereochemical Assignment of the C3 Methyl Group in **1 and **2**.** In our initial work on this system, only one of the ions (**1** or **2** but which?) could be obtained. Thus, both the alcohols **3** and **4**, previously known⁵ and of unambiguous stereochemistry, on addition to 3:1 SO₂ClF-FSO₃H at

-80°, yield the same nmr spectrum (Figure 1). This spectrum can be satisfactorily analyzed as coming from a single cation species which at this temperature (-80°) is undergoing a very rapid 3,2-hydride shift (averaging among others the C2-C3 methyl groups). When the alcohols **3** and **4** are added to the acid at -120°, the nmr spectra obtained are characteristic of a protonated alcohol, presumably **5** and **6**, respectively. On warming each to *ca.* -100°, the peaks due



to the protonated alcohol disappear and are replaced by the peaks of the same single ion shown in Figure 1. Since both alcohols yield a single ion, it is apparent that the rate of interconversion of **1** and **2** is fast on a conventional kinetic time scale at -100°, and that one of the carbocation isomers is very much more stable than the other. The former result actually came as no surprise to us since the same result had been obtained previously in related work with α - and β -fenchene.^{2a} Addition of either of these to FSO₃H-SO₂ClF at -120° results in the same carbocation nmr spectrum. The rearrangement process (see later) which interconverts the α - and β -fenchyl cations (2,7,7- and 2,5,5-trimethyl-2-norbornyl, respectively) is the same mechanism which would be expected to interconvert **1** and **2**.

Since the known geometry of the alcohol precursors **3** and **4** provides no evidence for the structure of the single cation observed, one has to rely on indirect evidence. The assignment of the 3-*endo*-methyl structure **1** to the spectrum shown in Figure 1 is based on the following reasoning and experimental evidence.

(1) Related work with a 1,2,3-trimethyl-2-norbornyl system^{2a} shows the 3-*endo*-methyl structure in these cases to be the more stable. The assignment of the stereochemistry in these cations was originally made on the assumption that protonation of the corresponding 2-norbornene precursor occurred from the *exo* side and also on certain nmr chemical shift observations, but the assignments have since been

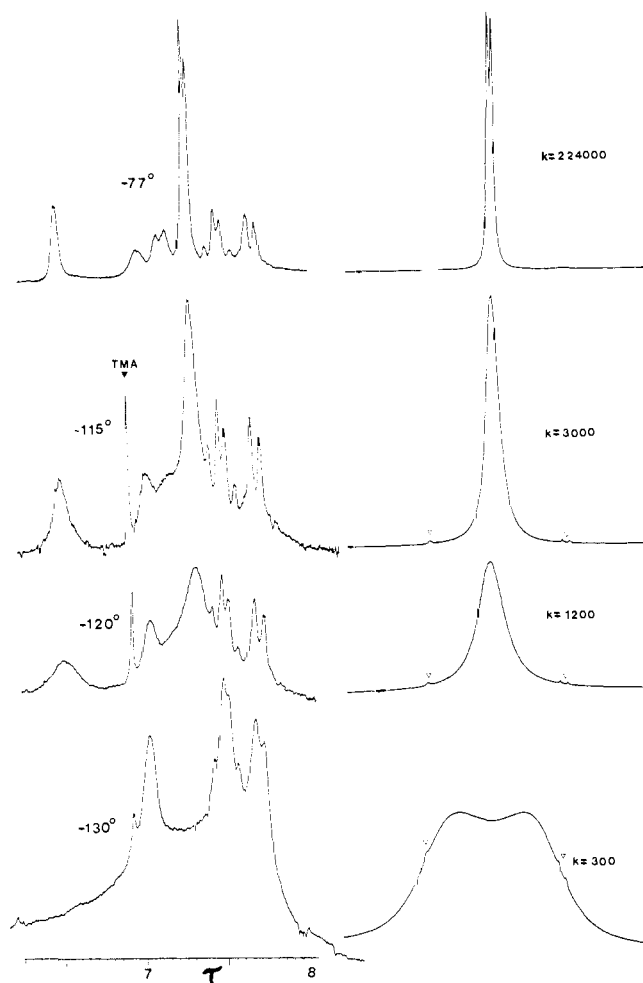


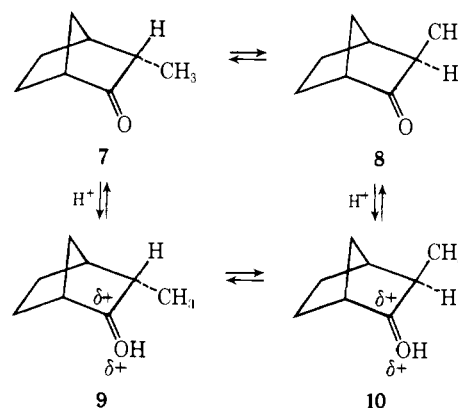
Figure 1. Left: Selected experimental ^1H spectra of **1**, TMA is tetramethylammonium cation, the internal reference. Right: Computed spectra of the methyl groups in **1**, assuming a 3,2-hydride shift. The very small peaks are the computed peaks of **2**.

confirmed by unambiguous syntheses.⁶

(2) A kinetic study of the 1,2,3,4-tetramethyl-2-norbornyl system⁷ shows that the rate of an exo-3,2-hydride shift in the 3-*endo*-methyl isomer is faster than that of an endo-3,2-hydride shift in the 3-*exo*-methyl isomer by a factor of at least 10^5 . Furthermore, the actual absolute rate of the 3,2-hydride shift in **2** (see Results section) is very similar to that measured for the exo-3,2-hydride shift in the tetramethyl case. If our stereochemical assignment of **1** and **2** were reversed, the results would require the endo hydride shift to be very much faster than the exo hydride shift, a result completely contrary to much previous solvolysis evidence.⁸ In order to obtain still further evidence, we have studied equilibria involving the related ketones **7** and **8**, both as neutral species and as protonated (hydroxy carbocation) species **9** and **10**. It had been reported previously¹⁰ that the two ketones form a nearly 1:1 mixture on base equilibration; however, it is not clear in these examples that complete equilibration had been reached since the equilibrium was approached from one direction only. In this work, starting separately from both pure ketones, the equilibrium percentages of the two are $40 \pm 2\%$ **8** and $60 \pm 2\%$ **7** in methanol solution at 65° . In 80 and 90% H_2SO_4 , where the ketones are expected to be nearly completely protonated,¹¹ the corresponding percentages are: in 80% H_2SO_4 , $32 \pm 2\%$ **10** and $68 \pm 2\%$ **9**; in 90% H_2SO_4 , $27 \pm 3\%$ **10** and $73 \pm 3\%$ **9**, both at 95° . The 3-*endo*-methyl ketone **7** is only marginally more stable than **8**. In the hydroxy carbocations **9** and

Table I. Rates for Exo-3,2-Hydride Shift in **1** at Various Temperatures

$T, ^\circ\text{C}$	Rate constant, sec^{-1}
-91.8	$\sim 1 \times 10^5$
-96.4	$\sim 5 \times 10^4$
-100.4	1.8×10^4
-105.8	1×10^3
-112.1	5×10^2
-117.1	2×10^2
-120.3	1.2×10^2
-127.4	5×10^1
-130.5	3×10^1
-137.1	1.25×10^1



10, some additional factor results in the 3-*endo*-methyl structure **9** becoming yet slightly more stable. It seems reasonable to regard the geometry and electron delocalization of the hydroxy carbocations **9** and **10** as somewhat intermediate between that in the ketones and the carbocations **1** and **2**. Thus, the factor which is responsible for making **1** more stable than **2** is showing up partially in its effect on the equilibrium ratio of **9** and **10**.

The above three arguments convince us that the major (Figure 1) isomer has the 3-*endo*-methyl structure **1**. We next turn our attention to the three-rearrangement reactions outlined in the introductory section.

The Degenerate Exo-3,2-Hydride Shift in 1. The absolute rate of the 3,2-hydride shift in **1** has been obtained in several solvent systems from both ^1H and ^{13}C nmr line-broadening studies. In Figure 1 are shown four representative ^1H spectra of the ion at different temperatures together with the corresponding calculated line shapes considering in this particular case only the two methyl groups. Comparisons of calculated and observed spectra were based mainly on the peak shape (not shown) of the averaged H_1 - H_4 protons and beyond coalescence, the H_1 proton. The methyl peak shapes were also used, although these are not easily compared in the slow exchange region because of other overlapping peaks sitting over them. In Table I are listed the calculated rates as a function of temperature, and this gives $\Delta H^* = 6 \pm 1$ kcal/mol, $\Delta G^* = 6.6$ kcal/mol at -117° , $\Delta S^* = -4 \pm 7$ eu. The coalescence point for the methyl protons occurs at *ca.* -130° . In Table II are listed the chemical shifts of the carbocation **1**.

In order to further check the derived rate constants, we have also obtained the ^{13}C nmr spectrum as a function of temperature. This offers the advantage of simplifying the calculations (errors which may be inherent in the proton-spectra calculations due to the neglect of second-order coupling effects are eliminated) and allowing a matching over a much wider temperature range. The experimental and calculated line shapes are shown in Figure 2, the test rate constants being those derived at each temperature from the

Table II. Magnetic Resonance Parameters for **1**

H ₁	H ₃	H ₄	H ₅	H ₆	H ₇	CH ₃ -2	CH ₃ -3	
~5.1 ^{a,b}	7.10 ^c	~7.1 ^d	7.35 (d), <i>J</i> = 11 ^e	8.46 (d), <i>J</i> = 11 ^e	7.99 C7 anti 8.13 C7 syn AB quartet <i>J</i> = 11	~7.0 ^f	~8.5 ^g	
C1	C2	C3	C4	C5	C6	C7	CH ₃ -2	CH ₃ -3
78.6 ^{a,h}	274.7	62.6 ⁱ	48.2	27.5 ^j		38.9	26.0	11.4

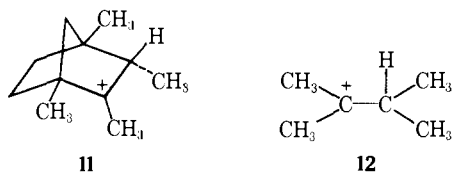
^a In τ parts per million relative to internal tetramethylammonium cation at 6.90. ^b At -141° , the peak is not completely sharpened up from the 3,2-hydride shift, and the expected doublet is not observed, only a broad peak. ^c Very broad. ^d Interpolated from the averaged H₁-H₄ position at 6.09 and the H₁ position. ^e Below the coalescence temperature these peaks are obscured by the broad C3 and C2 methyl groups. The values reported are for the averaged H5 endo-H6 endo (8.46) and H5 exo-H6 exo (7.37). The coupling is the averaged geminal-vicinal coupling. The averaged H5 exo-H6 exo peaks are further broadened from unresolved coupling with H₁. These peaks and H7 protons are misassigned in ref 4. ^f These peaks are still somewhat broad at -141° , so that the exact positions are difficult to obtain. At higher temperatures, the averaged peak occurs at 7.70 (d), *J* = 4.5 (the averaged coupling with H₃). ^g In parts per million from external TMS, all values except those for the methyl groups and C7 are regarded as provisional. ^h This position interpolated from the measured average of C1-C4 and the "frozen-out" position of C4. ⁱ Obtained by interpolation from the known C2-C3 position and the "frozen-out" position of C2. ^j The "frozen-out" peaks could not be located. However, from the observed broadening of the averaged peak, one can estimate that the inherent positions of the C5 and C6 carbons are *ca.* 200-300 Hz separated.

proton spectra analysis (Table I). The agreement is good enough so that no additional adjustments to the calculations were needed. In the ¹³C nmr matching, individual rates are much less accurate than ¹H, but the much extended temperature range of the former may mean that ΔH^* values are as accurate or more so compared with the proton case. At -150° , it was just possible to observe several of the peaks of the partially "frozen-out" spectrum, and this has enabled a tentative assignment of all the carbons except C5 and C6. These are listed in Table II and were used in the calculations, an estimated separation of *ca.* 250 Hz being used to position the C5 and C6 carbons so as to give the observed degree of broadening for the particular rate constant used.¹²

It is instructive to compare the ¹H and ¹³C nmr spectra to show the wide temperature range over which broadening occurs in the latter. The C2-C3 coalesced carbons show obvious broadening at -50° ,¹³ the C1-C4 coalesced carbons begin broadening noticeably at -100° , while the others begin about -110° . In the proton spectra, the broadening is not very obvious until the temperature reaches -100 or -110° .

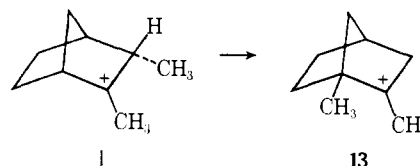
Carbon-13 nmr spectra over the complete temperature range were obtained using the solvent systems FSO₃H-SO₂ClF-SO₂F₂, FSO₃H-SO₂ClF, and SbF₅-SO₂ClF-SO₂F₂. No really measurable rate differences were found for the exo-3,2-hydride shift in any of these systems (or in any of the systems used for the proton nmr studies).

The actual rate of the exo-3,2-hydride shift in **1** is quite similar to that previously measured⁷ for the tetramethyl ion **11** ($\Delta G^* = ca.$ 7.1 kcal/mol at -115°) so that this rate now appears to be a unique value associated with a tertiary-tertiary exo-3,2-hydride shift in the norbornyl cation system.¹⁴ In relation to other 1,2-hydride shifts, it is faster than the 3,2 shift in the parent norbornyl cation¹⁵ but much slower than the tertiary-tertiary hydride shift in the acyclic ion **12**.¹⁶



The Interconversion Rate and Equilibrium Constant between the 3-exo-Methyl- (2) and 3-endo-Methyl-2-norbornyl (1) Cations and the Indirect Detection of the Former. On warming a solution of **1** above -70° , a very subtle event

takes place in the measured nmr spectrum. This is shown in Figure 3 for the averaged methyl peaks only (somewhat comparable changes also occur in the averaged H₁-H₄ signal and to some extent in the H₅ endo-H₆ endo peak). The averaged methyl peaks in **1** begin to broaden ever so slightly, reach a maximum broadness about -45° , and then sharpen up again at still higher temperatures. The change might normally be passed off as magnet inhomogeneity were it not for the complete reproducibility of the spectra (four complete series were done). The experiment shown in Figure 3 is slightly hampered by the fact that at the highest temperatures, -20° , the cation **1** is rearranging irreversibly at a rapid rate into the 1,2-dimethyl-2-norbornyl cation (**13**), a



reaction previously noted in our original communication.³ Nevertheless, a spectrum of **1** again showing the sharp methyl doublet on the high-temperature side of the broadening could be obtained by working rapidly.

An event of the type shown in Figure 3 is indicative of a rapid (nmr time scale) exchange between two species of very unequal population. The major ion is, of course, **1**, and, in the case in hand, there are two reasons for believing that the minor component is the elusive 3-exo-methyl isomer **2**. (1) In the closely related 1,2,3-trimethyl-2-norbornyl cations (see previous discussion regarding the stereochemistry of **1**), the corresponding 3-exo-methyl isomer is present (along with the major 3-endo-methyl ion) in small amounts but in this case directly observable. This indicates to us that the equilibrium constant for **1** \rightleftharpoons **2** will probably not be excessively small. (2) The mechanism interconverting the two geometric isomers, **1** and **2**, is expected to involve a Wagner-Meerwein rearrangement followed by a 6,2-hydride shift and then the reverse Wagner-Meerwein process (abbreviated WM-6,2-WM rearrangement) and is shown in eq 1. The rate of this overall process in four other norbornyl cations has been carefully measured (1,3), and this rate is virtually identical with that derived in this study on the assumption of a 3-exo-methyl cation minor partner, **2**, causing the broadening shown in Figure 3.

In attempting to match the experimental line broadening shown in Figure 3, it might appear at first sight that the problems were insurmountable since one does not know the

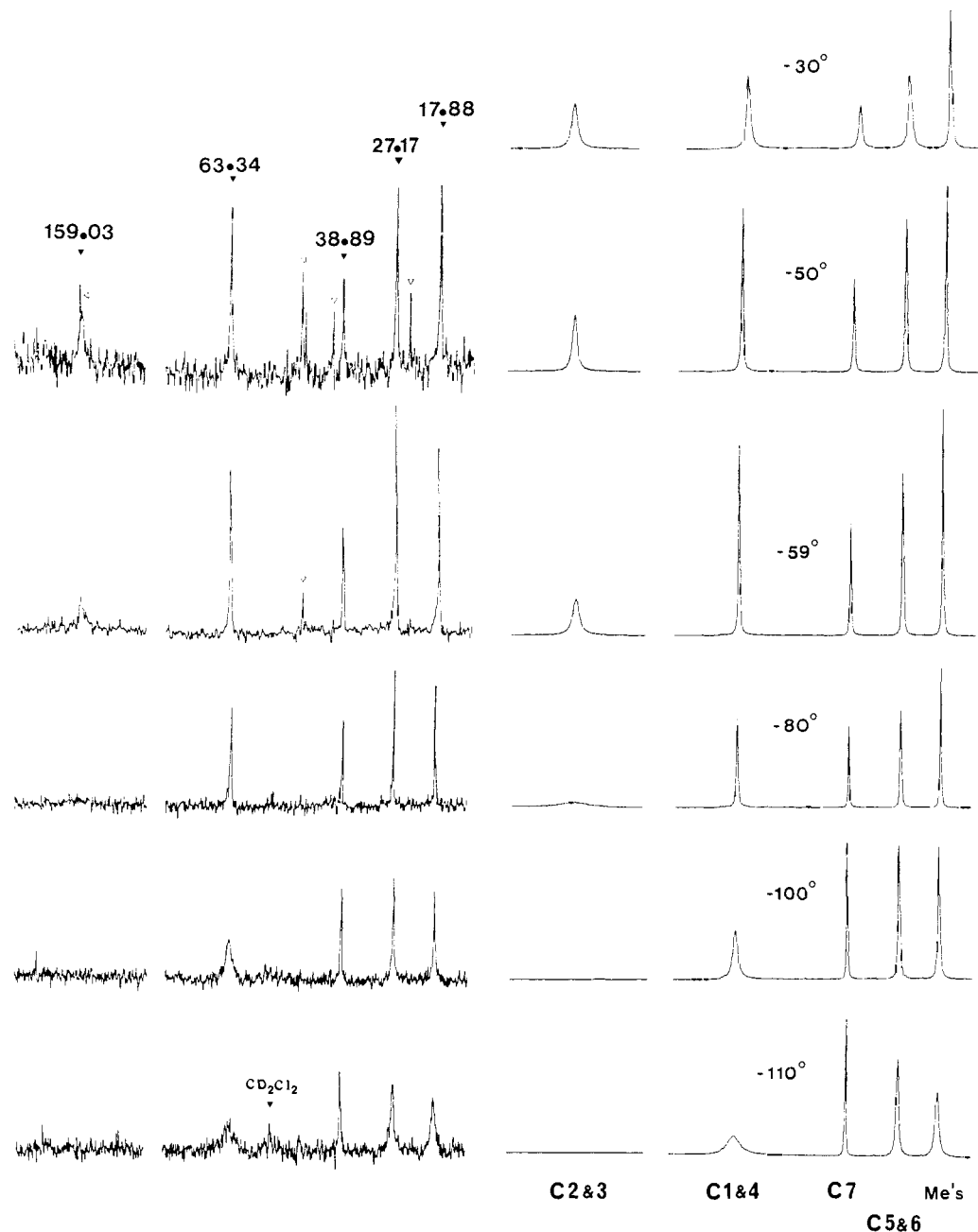
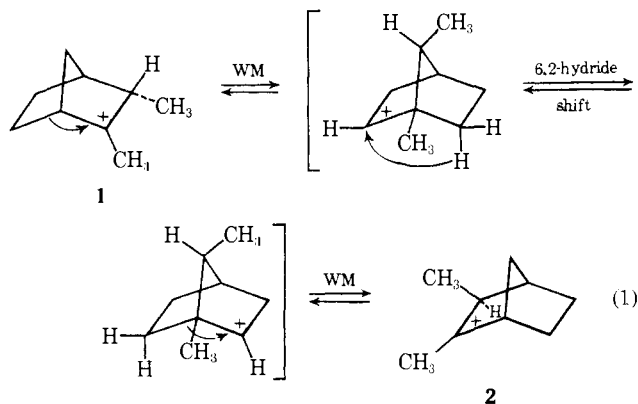


Figure 2. Left: Selected experimental ^{13}C spectra of **1**. Positions are in parts per million from external TMS. In the top two spectra, the extra peaks (∇) are due to the 1,2-dimethyl-2-norbornyl cation (**1** is rearranging to this). Right: Computed spectra using the rate constants for the 3,2-hydride shift in Table I and for the WM-6,2-WM process in Table III and using $K = 2.75\%$ (-44°).



chemical shifts of **2**, the relative populations of **1** and **2**, or the rate constants for the interconversion of **1** and **2**. In

practice, the chemical shifts expected for the methyl groups in **2** can be well approximated from a wealth of chemical shift data on similarly positioned methyls in other polymethyl-2-norbornyl cations. In any case, the line-broadening calculated results are virtually unaffected by small changes in the assumed chemical shifts in **2**. To determine the best equilibrium constant K and rate constant k , one can allow both to vary independently, and this has been done. From this time-consuming analysis, it seems certain that the minor isomer **2** percentage at -44° (the temperature of maximum broadness of the peaks shown in Figure 3) must be bracketed between 1.5 and 4.0%, with a middle figure of 2.5–3.0% agreeing best. The corresponding best value rate constant at -44° is 17 sec^{-1} for k_{forward} in the process $\mathbf{1} \rightleftharpoons \mathbf{2}$ (eq 1). For higher and lower temperatures, K was allowed to vary according to the equation, $\Delta H - T\Delta S = -RT \ln K$. The statistical entropy difference between **1** and

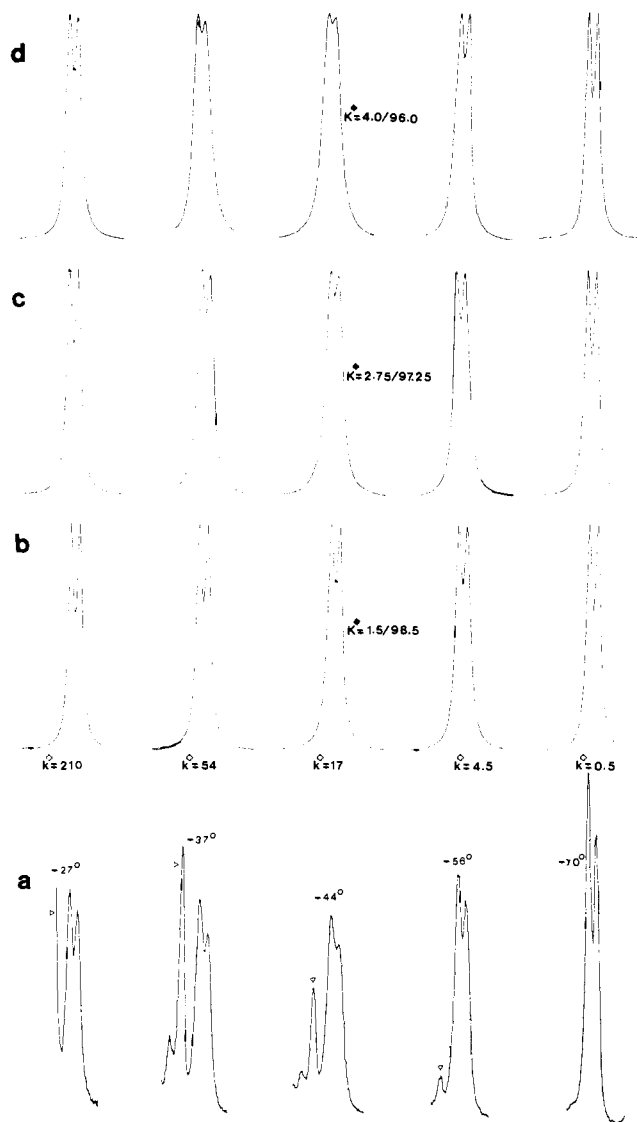


Figure 3. (a) Experimental ^1H spectra of only the methyl doublet in **1** showing the behavior of this peak with changes in temperature. The "growing" peak to the left is due to the 1,2-dimethyl-2-norbornyl cation (**1** is rearranging to this). (c) Calculated spectra assuming $K = 2/1 = 2.75\%$ at -44° , varying the rate constant and K for the process $\mathbf{1} \rightleftharpoons \mathbf{2}$, the rate of the 3,2-hydride shift in **1** being very fast. (b,d) Calculated spectra, as above, assuming $K = 1.5$ and 4% , respectively, at -44° . This shows that the broadening in the experimental spectra is bracketed by these values.

2 was taken as $R \ln 2$ because of the twofold degeneracy in **1** caused by the rapid exo-3,2-hydride shift and assuming that other bond entropy-type contributions in **1** and **2** will cancel. The best fitting (now varying only the rate constant) calculated line shapes for $K = 2.75\%$ (-44°) of **2** are compared in Figure 3 with the experimental curves. In order to show the sensitivity of the procedure to variations in the assumed K , we have also included, for comparison, calculations using the same rate constants for exchange but using $K = 1.5\%$ (-44°) and $K = 4.0\%$ (-44°) of **2**. The rate constants calculated for the (best) $K = 2.75\%$ (-44°) series are recorded in Table III. A least-squares plot of $\log k$ vs. $1/T$ results in $\Delta H^* = 13.2$ kcal/mol. This compares reasonably well with values of $\Delta H^* = 11$ kcal/mol for this same WM-6,2-WM process in other systems where the measurements are much more exact. Actual individual rate constants compare even better, e.g., $\Delta G^* = 11.9$ kcal/mol for $\mathbf{1} \rightarrow \mathbf{2}$ compared with 11.3 for the 2-methyl-2-norbornyl cation, both

Table III. Rates for the Forward Reaction $\mathbf{1} \rightleftharpoons \mathbf{2}$ at Various Temperatures

$T, ^\circ\text{C}$	Rate constant, sec^{-1}	$T, ^\circ\text{C}$	Rate constant, sec^{-1}
-61.4	1.9	-40.5	36
-55.9	4.5	-36.5	54
-49.9	9	-31.9	79
-44.6	17	-27.6	210

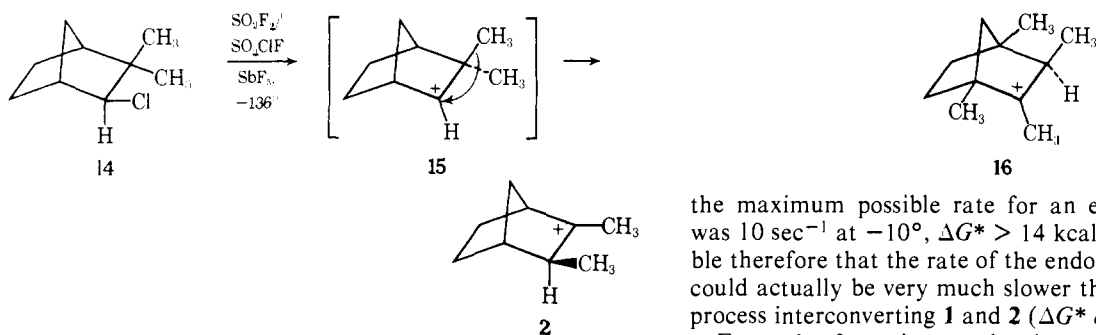
at -44° .

Once again, one sees a constancy in absolute rates for the same rearrangement; in this case, the WM-6,2-WM (eq 1) process and a value of $\Delta H^* = 11$ kcal/mol appear typical. The most valuable part of the foregoing analysis is the determination of K for $\mathbf{1} \rightleftharpoons \mathbf{2}$ since the WM-6,2-WM parameters are much better determined in other systems.

Effect of the WM-6,2-WM Process on the ^{13}C Spectra. In the calculated line broadening for the ^{13}C spectra, an 18×18 kinetic matrix using three separate rate constants (for the exo-3,2-hydride shift and the forward and reverse WM-6,2-WM rearrangement)¹⁷ was employed. The WM-6,2-WM process turns out however to have no effect on the calculated line shapes until the temperature reaches about -40° , too high to obtain experimental ^{13}C spectra. As it is, the -50° spectrum shown in Figure 2 contains peaks due to the rearrangement ion, the 1,2-dimethyl-2-norbornyl cation (**13**). We show in Figure 2, however, a theoretical spectrum for -30° showing a further predicted broadening of the ^{13}C lines. We predict in fact that the ^{13}C peak(s) for the C2-C3 carbons in **1** remain(s) broadened over the entire range 25 to -150° , a hypothetical value at the high-temperature end.

Correlation of the Calculated K for $\mathbf{1} \rightleftharpoons \mathbf{2}$ with Direct Experimental Data. A 2.75% concentration of the minor isomer **2** (see preceding discussion) would have been detectable under the experimental conditions in this work, but this value refers to -44° , and these ^1H nmr peaks are calculated to be broadened beyond recognition at this temperature. At higher temperatures (past coalescence), they will have "fused" with the much larger methyl peaks of **1**. At lower temperatures, one calculates that the minor isomer **2** peaks should become sharp at about -90° ; however, the calculated K has diminished to 1% of **2** at this temperature (see Figure 1). Using a concentrated solution of carbocation, a search was made at -90° for the C2 methyl peak of **2**, expected (see next section) at τ 6.91, a reasonably clear region of the spectrum of **1** at this temperature. A very small peak with a concentration of no more than 1.5% (assuming three H area) is present in this region, however the safest statement to make is that at -90° , K for the minor isomer **2** could not be more than 1.5%. One thus can verify directly that the upper limit suggested in the earlier calculations for the K of **2** is correct, using a completely independent type of measurement (or nonmeasurement).

The Probable Direct Observation of the Elusive 3-exo-Methyl Cation **2.** Armed with a rate constant k for the rearrangement $\mathbf{1} \rightarrow \mathbf{2}$ and K , one can, of course, calculate a rate for $\mathbf{2} \rightarrow \mathbf{1}$. If one is to be successful in preparing and observing **2**, the rate constant for this process should be less than $1 \times 10^{-3} \text{ sec}^{-1}$ ($t_{1/2} \sim 10$ min). Extrapolation of the $k_{1 \rightarrow 2}$ rate and K data using the value of 11.5 kcal/mol for E_a ¹⁸ one calculates that the $\mathbf{2} \rightarrow \mathbf{1}$ rate will equal $1 \times 10^{-3} \text{ sec}^{-1}$ at -132° . As an ion precursor, the tertiary alcohol **3** has already been ruled out since this simply forms the protonated alcohol **5** at this temperature (see previous section). One also wishes to avoid ion formation reactions which are likely to be exothermic during the mixing stage. For these reasons, 3,3-dimethyl-2-exo-chloronorbornane (**14**)¹⁹ was cho-



sen as the precursor. On ionization in $\text{SbF}_5\text{-SO}_2\text{ClF-SO}_2\text{F}_2$ solution, one would expect to obtain initially the 3,3-dimethyl-2-norbornyl cation (**15**), and this would be expected to undergo a rapid, stereospecific, *exo*-3,2-methyl shift²⁰ to give **2**. The fact that a rearrangement is necessary to produce **2** may also be helpful in removing excess energy produced during the ionization process.

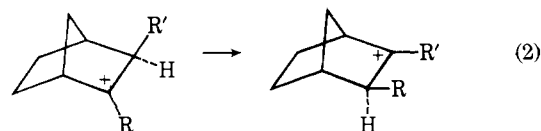
Addition of a very cold solution of $\text{SbF}_5\text{-SO}_2\text{ClF}$ to a solution of the chloride **14** in $\text{SO}_2\text{ClF-SO}_2\text{F}_2$ contained in an nmr tube cooled at allyl chloride slush bath temperature (-136.4°), results in a clear, light yellow, carbocation solution which was rapidly transferred to the nmr probe, pre-cooled to -140° . The temperature was then raised 5° , and spectra were recorded. At this temperature, -135° , the 3-*endo*-methyl ion **1** is by coincidence at the coalescence point for the *exo*-3,2-hydride shift. This makes for broad peaks of low amplitude and is ideal for trying to observe **2**. In the observed spectrum, characteristic peaks were found at τ 5.0 (*ca.* 1 H), 6.3 (*ca.* 1 H), 6.91 (*ca.* 3 H), and 7.33 (*ca.* 1 H). The high-field region contains broad overlapping peaks and was not useful. The peak at τ 5.0 is particularly characteristic of a Cl proton, and its shape (an apparently unresolved doublet in the slightly viscous solution) is as expected. The other peaks are consistent with the ion being **2**, *viz.*: 6.3 (H-6 *exo*), 6.91 (the methyl at C2), and 7.33 (the C4 proton). Even more significant, these peaks disappear (together) rapidly at -130° , *k*, *ca.* $1.4 \times 10^{-3} \text{ sec}^{-1}$, and the resulting solution now consists only of the cation **1** peaks. The circumstantial evidence all points to the elusive 3-*exo*-methyl cation **2** as the species responsible for the nmr peaks. It is difficult to judge the initial purity of **2**, but it appears to be better than 50%.²¹

Rate of a Possible Endo-3,2-Hydride Shift in 2. We consider finally the last of the three rearrangement processes discussed in the introductory section. It is apparent that all along we have been assuming that the *endo*-3,2-hydride shift in **2** is slow; *e.g.*, this reaction was not considered (in contrast to the *exo* shift in **1**) in the previous section dealing with the nmr spectrum of **2**. There was a good reason for this since the observed line broadening shown in Figure 3 (*i.e.*, -44° region) can only be caused if the methyl peaks for the minor isomer **2** are located at their "frozen-out" positions. If they had been averaged by a rapid *endo*-3,2-hydride shift, the averaged methyls would have been virtually coincident in chemical shift with those of the averaged methyls in **1**. Interconversion between **1** and **2** would *not* in this case have caused any line broadening of the methyl peaks in **1** and would most likely have gone undetected. Putting an upper limit on a possible *endo*-3,2-hydride-shift rate is very difficult, but it seems unlikely that this rate could exceed the interconversion rate of **1** and **2** so that we suggest a minimum ΔG^* of 12 kcal/mol for this process. The *minimum* free-energy difference between the *exo*- and *endo*-3,2-hydride-shift processes is therefore of the order of 5.5 kcal/mol.

In the 1,2,3,4-tetramethyl-2-norbornyl cation (**16**),

the maximum possible rate for an *endo*-3,2-hydride shift was 10 sec^{-1} at -10° , $\Delta G^* > 14 \text{ kcal/mol}$.⁷ It seems possible therefore that the rate of the *endo*-3,2-hydride shift in **2** could actually be very much slower than the WM-6,2-WM process interconverting **1** and **2** ($\Delta G^* \text{ ca. } 11 \text{ kcal/mol}$).

From the foregoing results, it seems probable that the lowest energy route for the hypothetical process shown below (eq 2) does not involve the single-step *endo*-hydride



shift but would instead involve the seven-step sequence, WM, 6,2-hydride shift, WM, *exo*-3,2-hydride shift, WM, 6,2-hydride shift, WM.²²

Why Is the 3-*endo*-Methyl Cation More Stable? It appears unlikely that nonbonded steric interactions are involved since in the related ketones, the energies of the respective isomers are nearly equal. If anything, one might suppose that there would be *more* steric interactions in the 3-*endo*-methyl cation isomer since it is possible to imagine a twisting motion in **1** which brings the 2-position p orbital of the cation center colinear with the 3-position *exo* proton and thus forces the C2 methyl group into a more eclipsing relationship with the C-3 *endo*-methyl group.

A hyperconjugation argument seems more reasonable, *i.e.*, that the empty p orbital of the ion overlaps preferentially with the *exo* substituent, and that a proton is favored over a methyl group. In addition, there is a statistical entropy effect which favors **1**, but this is of only moderate importance in energy terms.

Experimental Section

3-*exo*-Methylnorbornan-2-one (8) was prepared by the procedure of Corey.^{10b} The crude material contains a small amount of the starting norbornan-2-one and also 3-*endo*-methylnorbornan-2-one (**7**). Base equilibration (refluxing methoxide-methanol) afforded an equilibrium mixture of **8** and **7**. Preparative glc (Carbowax 20M) gave pure **7** and a mixture of **8** and norbornan-2-one. Reinjection of this mixture onto an SE-30 column afforded pure **8**.

2-*exo*-3-*exo*-Dimethylnorbornan-2-ol (3) and **2-*exo*-3-*endo*-dimethylnorbornan-2-ol (4)** were prepared from the crude ketone mixture and methyllithium. The solid di-*exo*-methyl alcohol **3** (the higher retention) could be easily separated by preparative glc on Carbowax 20M. The first glc fraction was reinjected on SE-30 to separate **4** from 2-norbornanol. The nmr spectrum of **3**, CCl_4 solution, shows a clean doublet at 9.15, $J = 7 \text{ Hz}$, and a sharp singlet at 8.89, representing the two methyl groups. The nmr spectrum of **4** shows a doublet at 9.31, $J = 7 \text{ Hz}$, and a singlet at 8.94. However, there is a much smaller doublet and singlet combination at 9.26 and 8.92 which probably represents one of the 2-*endo*-methyl alcohols. This is, however, a minor impurity in **4**. Both **3** and **4** have been previously reported.⁵

2-*exo*-Chloro-3,3-dimethylnorbornane (14) was prepared from camphenilol using the procedure of Brown.¹⁹ The actual product of this reaction is a mixture of **14** and 2-*exo*-chloro-7,7-dimethylnorbornane.

Ketone Equilibration Studies. For the base equilibration, pure ketones **7** and **8** were refluxed for 8 days in individual methanol-methoxide (dilute) solutions. The relative peak areas (hydrogen flame ionization) were equated with concentrations of the two ketones. For the acid equilibration, the ketones were dissolved in both 80 and 90% sulfuric acid and kept under N_2 at 95° for 70-90 hr.

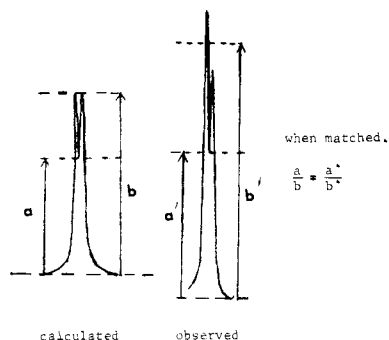


Figure 4.

Care was taken to analyze only the material remaining in the sulfuric acid solution since a film of material (presumably the ketones and water) collects on the condenser.

Preparation and Nmr Spectra of the Ions. The ion preparations were done using previously described procedures.²³ ¹H nmr spectra were recorded on a Varian Associates HA-100. Temperatures were monitored using a thermocouple directly inserted into the nmr tube. ¹³C nmr spectra were recorded on a Bruker HFX-90 Fourier transform spectrometer. Between 1 and 2K scans were collected for each temperature. Temperatures for the ¹³C spectra are based on a direct reading thermocouple, previously standardized. The heteronuclear fluorine lock material, trifluoromethyltrichloroethene, was contained with TMS in a 5-mm capillary. The chemical-shift data for **1** are reported in Table I. The protonated alcohols **5** and **6** were characterized by very broad peaks at *ca.* τ -1.3 ($-\text{O}^+\text{H}_2$) and at 8.81 in **6** and 8.75 in **5** (methyl protons). All these peaks are absent in the carbocation **1**, which tends to be present to some extent as well in the solutions. These peaks decrease simultaneously at around -90 to -100° to give only the carbocation **1** peaks.

Line-Broadening Calculations. ¹³C spectra (one mutual exchange and the interconversion of **1** and **2**) were calculated using multisite exchange (Lorentzian line shapes were used) programmed for a CDC 6400 and Calcomp plotter. For the ¹H spectra involving the exo-3,2-hydride shift, both the mutual exchanges of the H1 and H4 protons and of the C2 methyl and C3 methyl groups were used. In the former case, there is no problem since a first-order coupling treatment suffices, the C1 proton expected to be a 6.5-Hz AX doublet (this feature was not observed at -140° because of the viscous nature of the solution at this temperature; however, this doublet appears in numerous other norbornyl cations of this type, and the observed -140° peak was broad enough to contain this feature) and C4 a slightly broadened singlet. In the case of the methyl protons, the "frozen-out" positions are well represented by a singlet (CH₃-C2) and an AX₃ doublet (CH₃-C3). However, the coalesced peak (see Figure 1) shows partial second-order coupling, *i.e.*, AB₆, the H3 proton A being 60 Hz to the low-field side of the averaged methyl peak (which shows the averaged coupling of *ca.* 4.5 Hz), giving $J/\delta = 7.5$. However, a computer program involving the exchange of a minimum seven-spin system AB₃C₃ \rightleftharpoons AC₃B₃ would be extremely expensive, particularly since a large number of computed spectra are required. For most matching purposes, the H1-H4 protons were used, matching the half-width at half-height with experimental spectra. The exchange involved in the WM-6,2-WM process need not be taken into account in this calculation since it is very slow, $K < 0.1 \text{ sec}^{-1}$, at the temperatures concerned.

For the WM-6,2-WM process calculations, a multisite exchange involving only the methyl groups in **1** and **2** was used. Once again, a second-order coupling should in theory be used, *i.e.*, minimumly AB₃C₃DE₃F₃ \rightleftharpoons DE₃F₃AB₃C₃, in addition to the mutual exchange involving AB₃C₃, but in this case is completely impractical considering that several hundred calculations were needed to "zero in" on the proper values of K and the rate constant. In the kinetic matrix, values of $k_{\text{exo-3,2-hydride shift}}$ were extrapolated to the temperature of interest using the Arrhenius relationship. The forward rate constant for **1** \rightarrow **2** was varied, and the rate constant for **2** \rightarrow **1** was expressed as $k_{1 \rightarrow 2}/K$. The equilibrium constant was independently varied. Matching with the experimental curves (Figure 3) was accomplished by noting the ratio of the total height of the peak relative to the total height of the valley. In the experimental

spectra where both halves of the doublet are of unequal height, an averaged value was used. This is shown schematically in Figure 4. In all calculations, the experimental peak widths obtained for nonexchanging (or completely exchanged) conditions were used and were kept constant.²³

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References and Notes

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- (2) (a) E. Huang, K. Ranganayakulu, and T. S. Sorensen, *J. Amer. Chem. Soc.*, **94**, 1779 (1972); (b) reviewed in "Rodd's Chemistry of Carbon Compounds," 2nd ed, Part II, S. Coffey, Ed., Elsevier, Amsterdam, 1969, pp 243-249.
- (3) Part of this work has been very briefly communicated previously; E. Huang, K. Ranganayakulu, and T. S. Sorensen, *J. Amer. Chem. Soc.*, **94**, 1780 (1972).
- (4) G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, in press, have also published their findings concerning this system. However, these authors did not directly observe either of the rearrangements discussed in this work and have made, in our opinion, an assignment of the wrong stereochemistry to the observed (major) ion. We thank these authors for a preprint of their paper.
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- (11) E. M. Arnett, R. P. Quirk, and J. W. Larsen, *J. Amer. Chem. Soc.*, **92**, 3977 (1970), report a pK_a value of -6.2 for norbornanone.
- (12) The actual values "guessed" for C5 and C6 respectively were 22.8 and 33.2 ppm. These actually correspond very well to the corresponding carbons in the 2-methyl-2-norbornyl and 2,3,3-trimethyl-2-norbornyl cations: T. S. Sorensen and A. J. Jones, unpublished results.
- (13) In a published ¹³C spectrum of **1**,⁴ Olah and Liang show the C2-C3 coalesced carbon peak as a sharp singlet at a stated temperature of -90° . In the proton coupled spectrum, this peak (a doublet) is somewhat broadened but readily discernible. In our results, both experimental and calculated, this peak was broadened beyond recognition at this temperature. Since the exo-3,2-hydride shift rate does not appear to be solvent dependent, we have no explanation for the obvious discrepancy in results.
- (14) We have found a similar rate even when a C7 syn methyl group is present, indicating that such a group causes no particular steric problems. It has also been possible to directly observe the deuterium isotope effect for this shift, $k_H/k_D \sim 8$ at -120° .
- (15) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **92**, 4627 (1970).
- (16) At -140° , there is no indication of broadening in the coalesced C⁺-CH carbons (¹³C spectrum) which indicates that either the ion is bridged as the ground state, or that the rate constant for the 1,2-hydride shift is greater than 10^7 sec^{-1} ($\Delta G^\ddagger < 4 \text{ kcal/mol}$). The great difference in the rate of the hydride shift in the ions **1** and **12** is illustrated very well if one notes that in **1**, the C⁺-CH carbons were beginning to broaden at -50° . This also serves to show the incredibly fast rate (from calculations) needed to give a sharp coalesced ¹³C line when the averaging carbons are separated by 5000 Hz, or more (hence the 10^7-sec^{-1} minimum figure quoted above).
- (17) The ¹³C chemical shift positions had to be assumed, of course, for cation **2**. These were taken as having the same values as the corresponding carbons in cation **1**. In any case, the ¹³C chemical shift separations are so large that the small shift errors likely involved in this procedure have no practical effect on the actual extent of the calculated broadening in the cation **1** peaks.
- (18) For reasons which are apparent (see discussion on this in the text), the derived value of ΔH^\ddagger for the **1** \rightleftharpoons **2** reaction is subject to considerable error, and we prefer to use an activation energy obtained in more accurate studies, in this case, the E_a is that derived from the 2-methyl-2-norbornyl cation.
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- (20) In the camphene hydro cation and in two other related structures, this shift has been found to be extremely stereospecific. In addition, the absolute rate for the process is such that even at -135° , the reaction should be rapid.
- (21) Initially at -135° , several other, but small and broad, low-field peaks were observed at τ 3.79, 4.50, and 5.66. These decrease considerably even before there is much rearrangement of the initially observed **2**.
- (22) The principle of least motion takes a battering in this instance.
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