Predicting the Most Favored Path and the Overall Rate of Multistep 2-Norbornyl Cation Rearrangements. The Assignment of a Trial Activation Energy for Each Unique Step

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Received October 31, 1974

R. HASELTINE, E. HUANG, K. RANGANAYAKULU, T. S. SORENSEN, and N. WONG. Can. J. Chem. **53**, 1876 (1975).

Observable 2-norbornyl cations undergo at least five different rearrangement reactions, all of which are known from previous work on this system. In this paper, these rearrangement categories have been subdivided to reflect secondary–tertiary energy and rate differences and a trial set of activation free energies $\Delta G^{\neq}$ is derived for each subdivided step. The most important of these parameters is the energy difference between secondary and tertiary (methyl) systems which was estimated as 5.5 kcal/mol. These parameters allow one, for the first time, to make a rational assessment of the overall reaction course of multistep rearrangement reactions in this system, for example, those observed in a number of bicyclo[2.2.1]heptyl(norbornyl) terpene systems.

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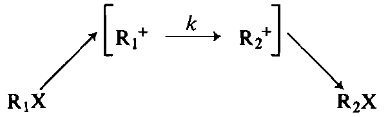
Les cations norbornyl-2 que l'on peut observer subissent au moins cinq réactions de réarrangement différentes et elles étaient toutes connues à partir de travaux antérieurs sur ce système. Dans ce travail, on a subdivisé ces catégories de réarrangement afin de mettre en relief les différences d'énergie et de vitesse des cations secondaires *vs.* tertiaires et on a établi des valeurs préliminaires pour les énergies libres d'activation $\Delta G^{\neq}$ de chaque étape des subdivisions. Le paramètre le plus important est la différence d'énergie entre les systèmes secondaires et tertiaires (du méthyle) qui serait de 5.5 kcal/mol. En utilisant ces paramètres, on peut pour la première fois faire une attribution raisonable pour l'évolution globale des réactions de réarrangement de ce système impliquant plusieurs étapes; à titre d'exemple on peut faire des attributions pour les réactions observées dans un certain nombre de systèmes terpéniques du bicyclo[2.2.1]heptyle(norbornyle). [Traduit par le journal]

Introduction

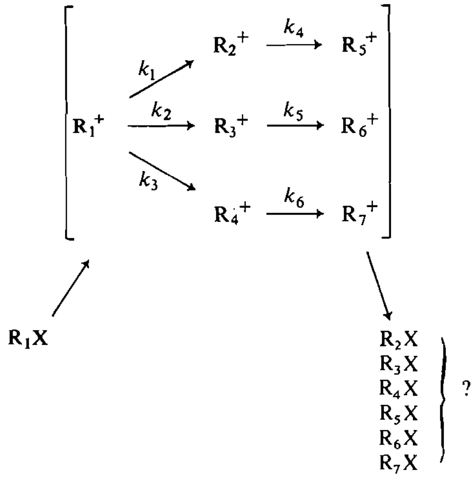
Organic molecular rearrangements occur by a variety of mechanisms but for hydrocarbons the most important class involves the intermediacy of carbocations, the actual molecular rearrangement taking place in the carbocation intermediate (eq. 1).

[1]



Working in very stong acids, it is now possible to prepare many of these carbocation "intermediates" and to directly measure the rate of the critical cation$_1$ → cation$_2$ step. For simple reactions of the eq. 1 type, this measurement is mainly of interest to the physical organic chemist since, regardless of the absolute rate of the cation step, the product remains the same. Let us consider, however, a more realistic case, given in eq. 2.

[2]

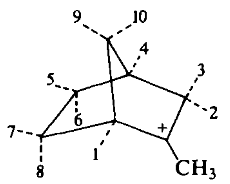


In this case, the product formed is critically dependent on what R_1^+ does and may also be dependent on the behavior of the primary rearrangement ions. If one knew the relative rates (or activation barriers $\Delta G^{\ddagger}$) of the k_1–k_6 processes, one would be in a position to rationally assess what the probable product might be.

Previously, it has been verified that the products formed from the acid-catalyzed treatment of α-fenchol (which differ greatly in composition depending on the severity of the reaction) correlate with the measured rates of the various rearrangements involving the corresponding observable α-fenchyl cation (1). Since these cation → cation absolute rates were not previously known, one could not of course have predicted the actual products formed in the α-fenchol acid-catalysis reactions. However, in this paper it is suggested that one can build up from a number of these "base" measurements, a reasonably consistent set of activation energy parameters (constants), each constant being characteristic of a particular single-step rearrangement process of the kind given in eq. 2.

The choice of the 2-norbornyl cation system as an illustrative example of eq. 2 is dictated by two factors: (*i*) a given norbornyl cation has at least five different structural "chess moves", *i.e.* given by k_1, k_2, k_3, etc. in eq. 2, which it can undergo at any one stage and (*ii*) there has been an enormous amount of solvolysis and acid-catalysis work (which can be used for comparison purposes) carried out on methyl-substituted 2-norbornyl systems, including all of the monomethyl analogs (2) and a great many di- (3) and trimethyl (4) systems. Many of the di- and trimethyl systems studied (like α-fenchol) are terpenes or rearrangement products derived from these.

Although the division is somewhat artificial (see further), we will use as "base" systems, the activation energy parameters derived from the observed rearrangements of the parent 2-norbornyl cation, the 2-methyl cation, and a number of trimethyl and higher methylated norbornyl cations. One can then test the validity (predictive power) of these parameters on the rearrangement reactions involving the complete set of 10 tertiary dimethyl-2-norbornyl cations **1** (accompanying paper) (5). Six of these ions, and hence their rearrangement reactions, were completely unknown until after the formulation of the trial activation energy parameters and hence offered a genuine test of the validity of these. The other four ions and their rearrangement reactions were known and hence the treatment involving these is somewhat artificial.



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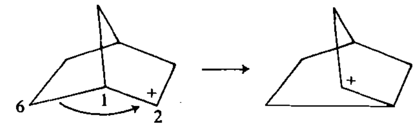
Results and Discussion

Rearrangement Processes Considered

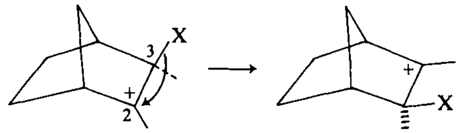
In organizing this paper, it seems best to outline the various rearrangements which the 2-norbornyl system can undergo and then to consider whatever specific subdivision of these main categories which may be necessary. Following this, we will discuss the particular rearrangement (or rearrangements) which allows one to assign an activation energy value to that particular step. Some previously communicated work and procedures (1, 6) will be described in full in this paper but the focus of the presentation differs somewhat (*e.g.* one communication (1) covered a number of sequential rearrangements involving initially the α-fenchyl cation system).

The rearrangement processes considered (the first three are well known) for the 2-norbornyl cation system were the following.

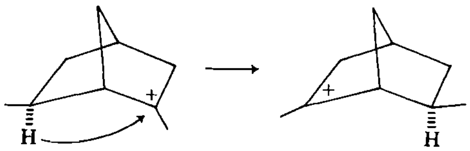
(*1*) A Wagner–Meerwein shift of the C6—C1 bond to C6—C2:



(*2*) An *exo*-3,2-substituent shift:

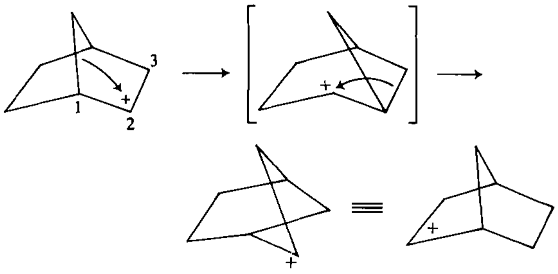


(*3*) An *endo*-6,2-hydride shift:

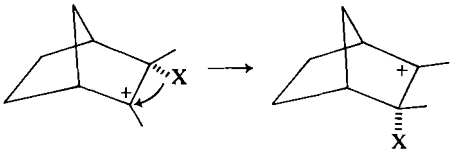


(*4*) An overall two-step process involving the shift of the C1—C7 bond to C2 to give a high energy, unobservable, 2-bicyclo[3.1.1]heptyl cation intermediate and then the shift of the original C2—C3 bond to C1. This overall sequence has been termed a double Wagner–Meerwein

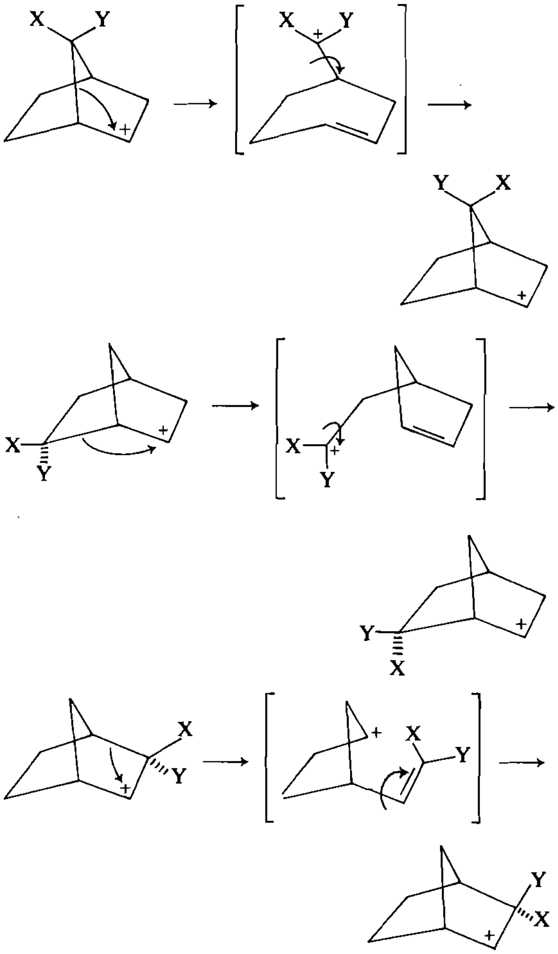
(DWM) rearrangement (7):



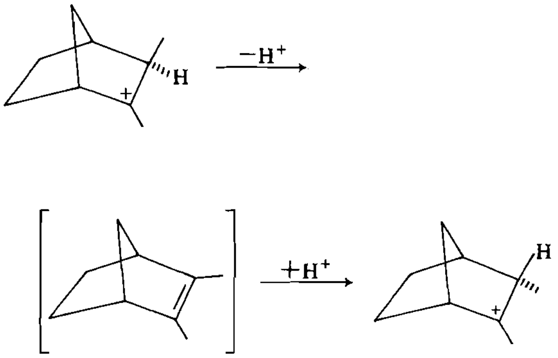
(*5*) An *endo*-3,2-substituent shift:



(*6*) Ring opening – bond rotation – ring closure processes:



(*7*) In addition to the above, a process involving deprotonation–reprotonation might occur.



This last process is expected to differ from all of the others in that the rate of the reaction should be markedly sensitive to the strength of the strong acid solvent (8). Based on present knowledge (9), the rearrangement rates of processes *1*–*6* will not be appreciably affected by changes in the strong acid solvent system used.

Subdivision of the Major Categories

One could not possibly expect the rearrangement rates of the processes *1*–*6* to be insensitive to a variety of substituents on the basic 2-norbornyl ring system. Fortunately, much of the solvolysis and acid-catalysis work in the chemical literature involves only methyl or hydrogen as substituents (*e.g.* terpenes) and in this work, the same restriction is applied. It would also be expected that steric effects would be an important factor, particularly if one had very many methyl substituents. In setting up the "base" activation energy parameters, we have tried to avoid model systems where rearrangement rates might be seriously changed by some steric factor. Nevertheless this must remain a nagging problem.

One factor demonstrably affecting the rates and the thermodynamic stability of the ions which cannot be ignored concerns the substitution at C2, *i.e.* either an H (secondary 2-norbornyl) or CH_3 (tertiary 2-norbornyl). The other factor concerns the *exo*- and *endo*-3,2-substituent shift, *i.e.* the rate is demonstrably different for a methyl *vs.* a proton shift. These considerations lead to the following further subdivision of the major categories (Scheme 1).

Major process	*Subdivisions considered*							
1	1TT	1TS	1ST	1SS				
2	2HTT	2HTS	2HST	2HSS	2MTT	2MTS	2MST	2MSS
3	3TT	3TS	3ST	3SS				
4	4TT	4TS	4ST	4SS				
5	5HTT	5HTS	5HST	5HSS	5MTT	5MTS	5MST	5MSS

SCHEME 1. Abbreviations: T = tertiary, S = secondary, the first letter refers to the reactant ion and the second to product, H = hydrogen, M = methyl, the major rearrangement processes take the same number as was used to list them.

The ring opening – rotation – ring closure processes, *6a–c*, have been left out of Scheme 1. Although all three rearrangements, *6a* (10, 11), *6b* (12), *6c* (11), have been proposed in part for stable 2-norbornyl cations, it appears that not only is the activation energy quite high but that also, in some cases, a ring opening would lead irreversibly to cycloallyl cations (11). The deprotonation–reprotonation sequence *7* has also been left out since experimentally this process does not appear to play a significant role in the mono- , di- , or trimethyl-2-norbornyl cation rearrangements. In any case, if one uses the strongest acid systems available, *e.g.* $R^+ \ SbF_6(SbF_5)_n^-$ salts, the activation energy for this process could be made very high and the process effectively shunted aside. Other marginally possible processes, *e.g. endo*-5,2-hydride shifts, have not been observed and likely have a high activation energy barrier associated with them.

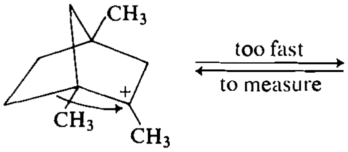
Obtaining the $\Delta G^{\neq}$ Parameters for Each Subdivided Rearrangement Process

The experimental evidence available for assigning $\Delta G^{\neq}$ parameters comes, as will be seen, in varying degrees of reliability. Some observable 2-norbornyl cation rearrangement processes involve a single specific step and this is then easily assigned a $\Delta G^{\neq}$ value. Other rearrangements involve two or more steps but the sequence can be uniquely assigned. However, in other multistep rearrangements it is not possible to assign an unique sequence or to even ascertain the particular rearrangement steps. A good discussion of this situation is given in two recent papers by Collins and co-workers (7). They show that one can bring about any overall 2-norbornyl cation transformation by using only combinations of the first three rearrangement processes given in Scheme 1, albeit the number of steps may be very large. In practice, one is forced to assign a specific mechanism sequence from among many theoretical possibilities. We will use the computerized treatment of Collins and co-workers (7), where appropriate, together with our further subdivision of each major step and then give our reasons for the choice of a specific sequence[1] in discussing an overall multistep rearrangement.

In most cases, only a $\Delta G^{\neq}$ activation energy value was experimentally obtained. However, in those rearrangements where both $\Delta G^{\neq}$ and $\Delta H^{\neq}$ were measured, they have turned out to be very similar, *i.e.* $\Delta S^{\neq} \sim 0$ and $\Delta G^{\neq} \sim$ constant. Also, since one is dealing with rate *comparisons*, the term $T\Delta S^{\neq}$ would become significant only if the temperature of the "base" measurement rearrangement and the observed rearrangement differed considerably.

Rearrangement 1TT

Only a lower limit $\Delta G^{\neq}$ value can be obtained for this shift since it cannot be "frozen out" in the n.m.r. spectrum of the 1,2,4-trimethyl-2-norbornyl cation **2** (1) or in higher methylated analogs (12). Cation **2** can be obtained as the "ultimate rearrangement" product of the tertiary α-fenchenehydro cation (1) and the structure was proven from quenching experiments wherein the



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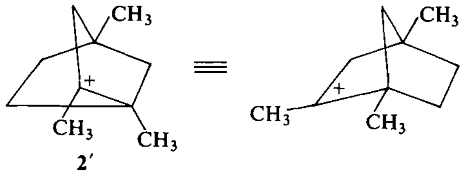

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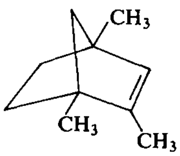
[1] From basic thermodynamic principles, all sequences are probably being followed and the occasional explorer molecule may indeed complete even the most unfavorable path. In the discussion, therefore, one is concerned about the route followed by > 99% of the reactant carbocations.

two new "fenchenes" **3** and **4** were obtained and characterized (see Experimental). In addition, a small amount of what is likely the alkene **5** was obtained. The carbon-13 n.m.r. spectrum of **2** is particularly useful for obtaining an upper limit estimate for the 1TT activation energy barrier since the process is degenerate in this ion and the C1—C2 n.m.r. peak is a composite of peaks which are expected to be separated widely in the "frozen out" structure. The rate constant for an n.m.r. averaging process needed to give a sharp coalesced peak is dependent on the intrinsic separation of the individual peaks, and if one makes a reasonable choice of a 4000 Hz separation for C1 and C2 in **2** (based on values for C1 and C2 obtained for the 2-methyl-2-norbornyl cation (ref. 13 and footnote 2)), one can show by standard n.m.r. theory that a rate constant of $>10^6$ s^{-1} (see accompanying paper (17)) is needed to produce the relatively sharp peak observed (14) for **2** at −140 °C. This leads to a maximum possible $\Delta G^{\neq}$ value of 4 kcal/mol. Since this barrier is so small, one may wonder whether the ion might not have a symmetrical structure and hence there would be no 1TT process involved at all. Previous work with unsymmetrical cations of this type has shown, however, that the averaged chemical shifts are temperature dependent in exactly the manner expected for an equilibrating pair of ions, where the more stable isomer becomes more dominant at low temperatures (the van't Hoff relationship) (14). Other evidence also indicates equilibrating structures (15, 16).



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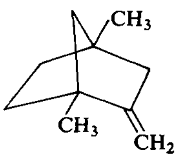

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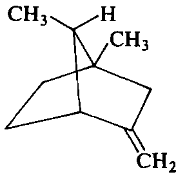

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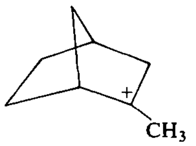
Rearrangement 1SS

For consistency in the computerized treatment, a secondary 2-norbornyl cation will be treated as an equilibrating structure, *i.e.* as having a 1SS process. (A discussion of the structure problem is given in an accompanying paper (17).) Olah *et al.* have recently published (18) a ^{13}C n.m.r. spectrum of the 2-norbornyl cation which shows a sharp coalesced C1—C2 peak at −150 °C. Using identical calculations to those used for the 1TT case, one calculates a maximum activation energy barrier of 4 kcal/mol.

Rearrangements 1TS and 1ST

Assuming a simple transition state model, these two processes involve the same potential energy surface. If one knew the energy difference between a secondary and a tertiary(methyl) 2-norbornyl cation and only one of the two activation energies, one could always obtain the other. This applies not only for the WM process but for all five major divisions in Scheme 1. Thus, the value assigned to this secondary–tertiary energy difference is quite critical. Fortunately, a method exists for estimating such a value. In the first (fastest rate) degenerate rearrangement of the 2-methyl-2-norbornyl cation **6** (prepared from 2-methylnorbornanol or the corresponding chloride), in a second (slower rate) degenerate rearrangement in the camphenehydro cation (6, 19) and in the overall process interconverting the tertiary α- and β-fenchenehydro cations (1), one has a process which can be unequivocally assigned to the three-step sequence 1TS, 3SS, 1ST. A careful matching of the observed n.m.r. line broadening in **6** with computed spectra has been carried out and from this analysis one obtains, in the usual way, $\Delta G^{\neq} = 11.3$ kcal/mol at −49 °C, $\Delta H^{\neq} = 11.0 \pm 1$ kcal/mol. Some of the experimental and calculated spectra for the line broadening in **6** are shown in Fig. 2. The activation energy for the 3SS step in the 2-norbornyl cation has been reported by Olah *et al.* (20) $\Delta G^{\neq} = 5.8$ kcal/mol at −141 °C, $\Delta H^{\neq} = 5.3$ kcal/mol. If this same value is applicable to the 3SS step in a 1-methyl secondary cation, then one can construct the transition state diagram shown in Fig. 1, leading to an estimate of 5.5 kcal/mol for the secondary–tertiary energy difference. Concerning the 1TS and 1ST processes, one would expect the activation energy for the 1ST process to be, at worst, the same as the 1SS process, *i.e.* <4 kcal/mol. This leads to a value of <9.5 kcal/mol for 1TS and, although the argument is



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[2] A. J. Jones and T. S. Sorensen, unpublished results.

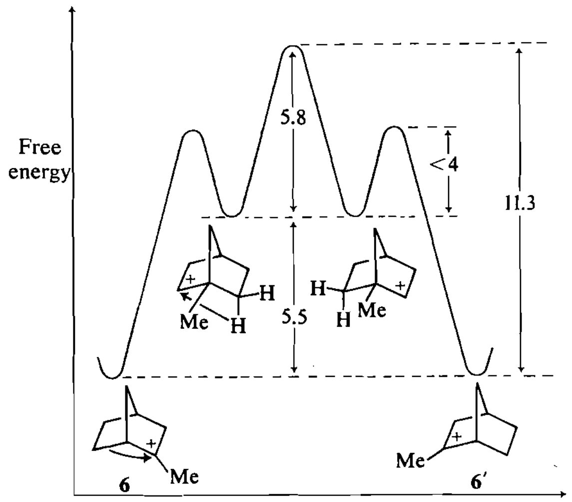


FIG. 1. "Reaction coordinate" diagram showing the derivation of the energy difference between a 1-methyl secondary norbornyl cation and a 2-methyl tertiary norbornyl cation.

circular, this confirms the assumed equilibrium kinetic treatment made in Fig. 1, *i.e.*

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C,$$

where

$$k_{-1} > k_2$$

and B is a steady state-intermediate.

Rearrangement 2HTT

This process can be directly measured (n.m.r. line broadening) as a single degenerate step in the 1,2-*endo*-3,4-tetramethyl-2-norbornyl cation (11), $\Delta G^{\ddagger} = 7.1$ kcal/mol, and also in even higher methylated analogs, 7.4 kcal/mol (12).

Rearrangement 2HSS

This process occurs as a degenerate rearrangement in the 2-norbornyl cation and has been analyzed by Olah *et al.* (20) $\Delta G^{\ddagger} = 11.4$ kcal/mol at −29 °C, $\Delta H^{\ddagger} = 10.2 \pm 0.6$ kcal/mol. In the analysis of the observed line broadening, one cannot distinguish between an *exo*-3,2-hydride shift and an *endo* equivalent or a mixture of both but, in the corresponding TT process, the *exo* shift is favored over the corresponding *endo* shift by at least 6.9 kcal/mol (see below). There is also much solvolysis evidence showing that *exo* shifts are highly preferred (21) in the secondary system.

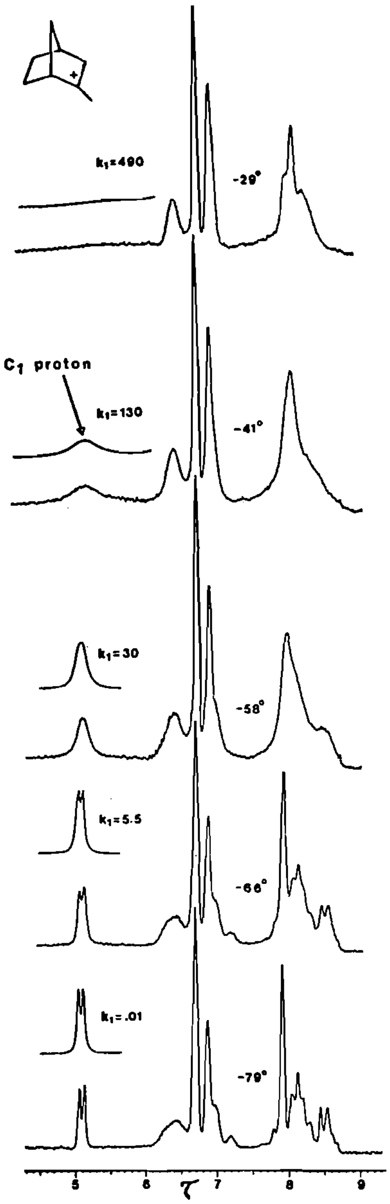


FIG. 2. ^{1}H n.m.r. spectrum of the 2-methyl-2-norbornyl cation showing the experimental line broadening due to the most rapid of two degenerate rearrangements occurring in this ion. The H1 proton at *ca.* τ 5.1 was used for the rate analysis with the calculated spectrum shown above each experimental peak. At temperatures above −40 °C, the amplitude of the H1 signal in the experimental spectra was increased considerably over that shown in this diagram.

Rearrangements 2HTS and 2HST

As explained previously, only one of these needs to be measured. This can be done from an

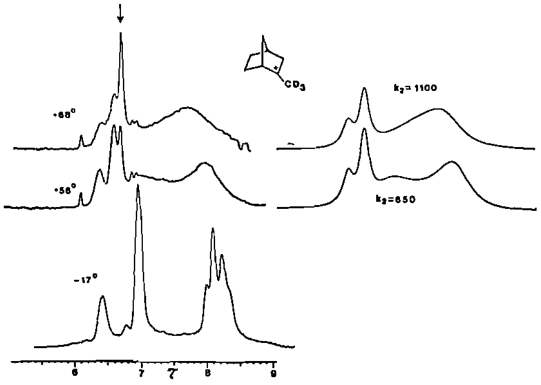
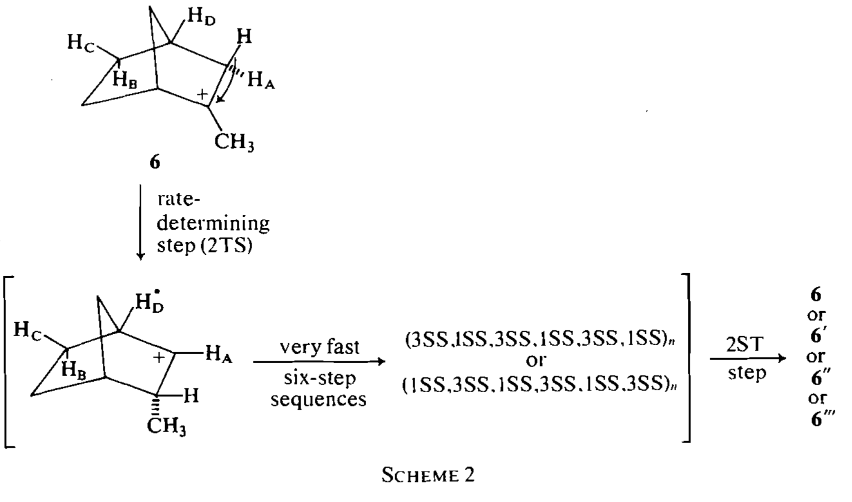


FIG. 3. ^{1}H n.m.r. spectrum of the 2-deuteriomethyl-2-norbornyl cation showing the experimental line broadening (left) due to the slower of two degenerate rearrangements occurring in this ion. At the right are two calculated spectra for this exchange, k_1 being set from the data obtained in Fig. 2. The peak designated by ↓ is the C2 deuteriomethyl group which is being exchanged with H at the higher temperatures.

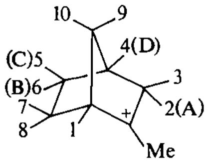
analysis of the second (slower) degenerate rearrangement observed for the 2-methyl-2-norbornyl cation **6**. Examples of the actual line broadening experimentally observed at 0 °C and above for **6** are illustrated in Fig. 3. The rearrangement sequence responsible for this broadening is not immediately obvious because there appear at first sight to be several degenerate sequences which might cause the observed broadening. However, the fact that the *exo*-6 proton peak (H7 in Fig. 4) does not broaden (at least initially) allows one to assign the process as follows (Scheme 2).

The overall topology of the process is to rotate the protons A, B, C, and D one turn for each six-step sequence. The overall proton equivalences are shown in Fig. 4, together with the kinetic exchange matrix used. This matrix embodies the assumption that one will statistically partition the protons A, B, C, and D equally among the four positions available to these before returning to the tertiary ion via a 2ST step. This requires the rate of the 2ST step to be much slower than the 1SS and 3SS processes, a requirement that may not be strictly true. The calculated $\Delta G^{\ddagger}$ values are <4 and 5.8 kcal/mol for the 1SS and 3SS processes *vs.* a calculated 9.7 kcal/mol for the 2ST process. Even if there is some bias towards returning to the original configuration, as compared to the other three, the effect on the calculated $\Delta G^{\ddagger}$ value will probably not be large (the calculated value will always be on the high side). The specific proton exchanges listed in Fig. 4 were also confirmed using the D1SST technique of Forsén and Hoffmann (22). Thus, irradiation of the averaged C5—C7 protons (Fig. 3) at +15 °C, causes the overlapping C3—C4 signal to nearly disappear and *vise versa*. The *exo*-H6 proton is not appreciably affected.

Using the equivalences shown in Fig. 4, the calculated and experimental line shapes are compared in Fig. 3 for various rate constants. The approximations used in the calculations are detailed in the Experimental. Only the calculated spectra in the intermediate exchange region can validly be used for comparison to experimental spectra. From this, one obtains $\Delta G^{\ddagger}$ = 15.2



SCHEME 2



First exchange (k_1)	Second exchange (k_2)	Overall exchange
$H_1 = H_8$	$H_2 = H_4 = H_5 = H_6$	$H_1 = H_8$
$H_2 = H_3$	H_9	$H_2 = H_3 = H_4 = H_5 =$ $= H_6 = H_9 = H_{10}$
$H_5 = H_{10}$	H_{10}	
$H_6 = H_9$	H_7	
H_7	H_8	H_7
H_4	H_3	
	H_1	

k_1							$-k_1$		
	$k_1+\frac{3k_2}{4}$	$-k_1$	$\frac{-k_2}{4}$	$\frac{-k_2}{4}$	$\frac{-k_2}{4}$				
	$-k_1$	k_1							
	$\frac{-k_2}{4}$		$\frac{3k_2}{4}$	$\frac{-k_2}{4}$	$\frac{-k_2}{4}$				
	$\frac{-k_2}{4}$		$\frac{-k_2}{4}$	$k_1+\frac{3k_2}{4}$	$\frac{-k_2}{4}$			$-k_1$	
	$\frac{-k_2}{4}$		$\frac{-k_2}{4}$	$\frac{-k_2}{4}$	$k_1+\frac{3k_2}{4}$				$-k_1$
$-k_1$							k_1		
				$-k_1$				k_1	
					$-k_1$				k_1

FIG. 4. Overall exchanges occurring in the 2-methyl-2-norbornyl cation and the kinetic matrix used in the exchange.

kcal/mol, using a matching just before coalescence, *i.e.* the +56 °C spectrum in Fig. 3. Subtracting 5.5 results in the $\Delta G^{\ddagger}$ value of 9.7 kcal/mol for the 2HST process.

At higher temperatures (>65 °C), there is evidence that still another degenerate process in cation **6** is beginning to show up since the *exo*-H6 proton starts to broaden. This is very likely due to the sequence 1TS,2HSS,3SS,2HSS,1ST.

Rearrangement 2MTT

This single-step process has been directly measured as a degenerate process in the camphenehydro cation (6, 19), $\Delta G^{\ddagger}$ = 8.3 kcal/mol at −104 °C, $\Delta H^{\ddagger}$ = 8.2 ± 1 kcal/mol, and in two higher methylated analogs (12), $\Delta G^{\ddagger}$ = 9.4 kcal/mol.

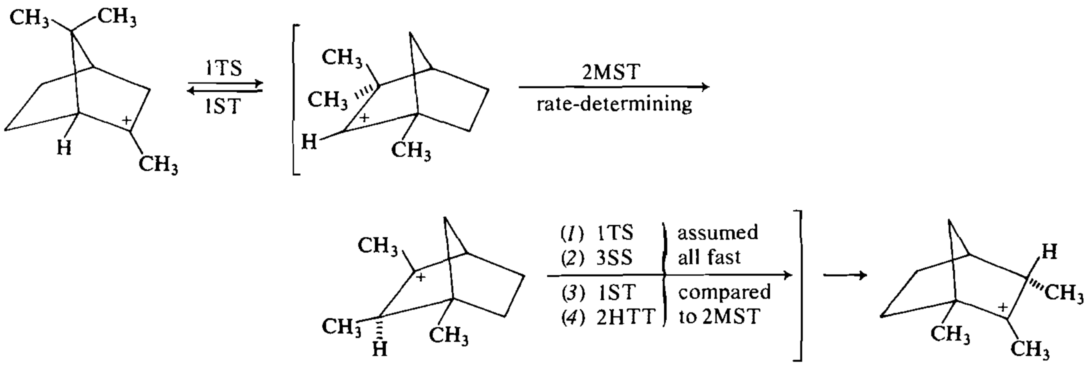
Rearrangement 2MSS

No satisfactory value could be arrived at for this process. However, we believe that the $\Delta G^{\ddagger}$ value should be as high or higher than the process 2MST (which can be determined). Tentatively, therefore, 2MSS is assigned a lower limit value, $\Delta G^{\ddagger} \gtrsim$ 7.6 kcal/mol. However in some cases, methyl shifts are slower than the corresponding proton shifts. Since the 2HSS value is 11.4 kcal/mol, it would not be unreasonable to expect a 2MSS value even higher than this.

Rearrangements 2MTS and 2MST

The best estimate for the 2MST rearrangement comes from the observed rearrangement of the tertiary α-fenchenehydro cation **7** to the 1,2-*endo*-3-trimethyl-2-norbornyl cation **8**, for which the mechanism in eq. 3 appears the most reasonable (from graph theory there are many other longer sequences possible). The overall activation energy is 13.1 kcal/mol ≡ 2MST. The reverse 2MTS step is assigned a value 13.1 − 5.5 = 7.6 kcal/mol.

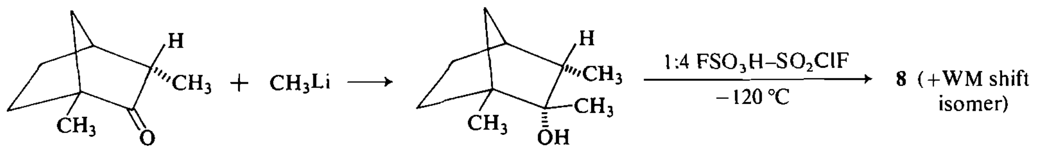
[3]



8 (+WM shift isomer)

The structure of cation **8** was confirmed by an unequivocal synthesis starting from the known ketone **9** (eq. 4).

[4]



9 **10**

Rearrangement 3TT

No direct measurement of this parameter is available from any of the mono- or trimethyl-2-norbornyl cation rearrangements studied in this work. However a maximum $\Delta G^{\ddagger}$ value of 11.3 kcal/mol is estimated (below) for the 3TS process and the same value is tentatively used for 3TT.

Rearrangement 3SS

This degenerate process has been observed in the 2-norbornyl cation, $\Delta G^{\ddagger} = 5.8$ kcal/mol at -141 °C, $\Delta H^{\ddagger} = 5.3$ kcal/mol (20).

Rearrangements 3TS and 3ST

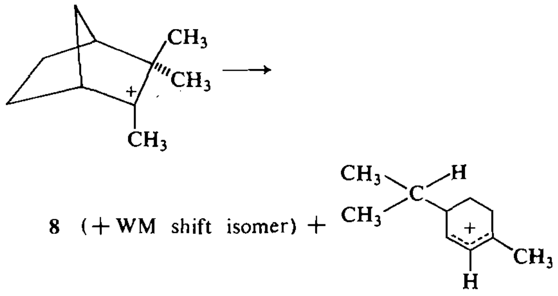
It seems reasonable to assume that the process 3ST will have a $\Delta G^{\ddagger}$ value of no more than the 3SS value, *i.e.* $\Delta G^{\ddagger} = 5.8$ kcal/mol is assigned. This results in a maximum value of 11.3 kcal/mol for 3TS.

Although the $\Delta G^{\ddagger}$ values assigned to the *endo*-6,2-hydride shifts (process *3*) appear rather uncertain, they are all small enough so that this step will rarely be rate determining in an overall multistep rearrangement.

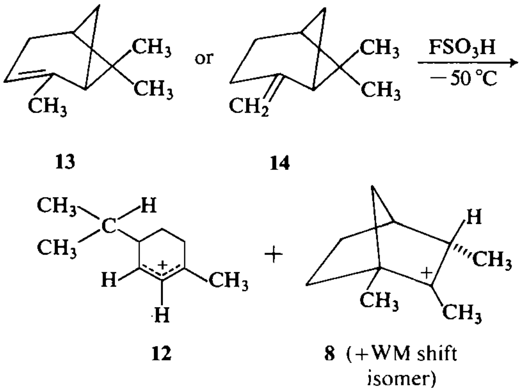
Rearrangement 4

Assigning a $\Delta G^{\ddagger}$ value for this two-step process has proven difficult since, as previously mentioned, one can always find a theoretical sequence of steps for any 2-norbornyl cation rearrangement not *requiring* this process. This point is discussed in detail by Johnson and co-workers (7). There are, however, two kinds of experimental results which offer reasonably good evidence for process *4*.

(*a*) The camphenehydro cation **11** rearrangement to give **8** also yields as a side reaction the cyclohexenyl cation **12** (the ratio of **8** (+WM shift isomer) to **12** is about 62:38) (6, 19). That the simultaneous formation of both these ions may be indicative of the intermediacy of the 2-bicyclo[3.1.1]heptyl cation formed in process *4* is shown by protonation reactions carried out in this study on α- and β-pinene **13** and **14**. Addition of these to FSO_3H at -50 °C or 1:4

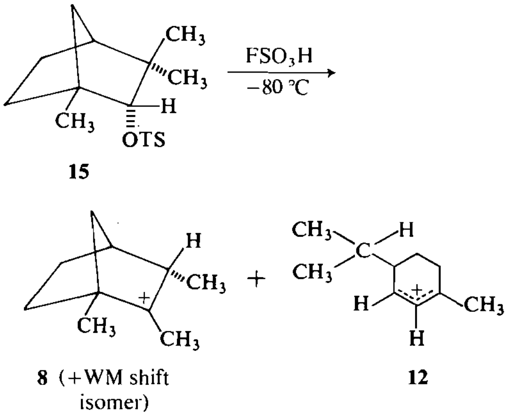


$FSO_3H–SO_2ClF$ at −120 °C and then warming to −50 °C yields the same two cations **8** and **12**, although the ratio favors the cycloallyl cation **12** (eq. 5).

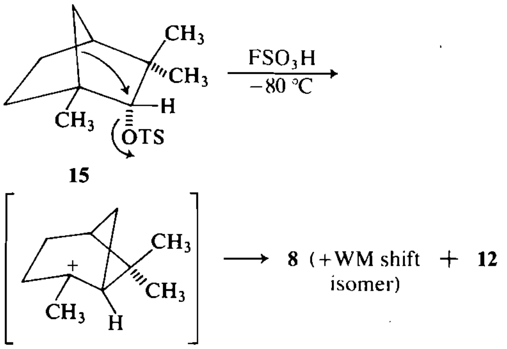
[5]


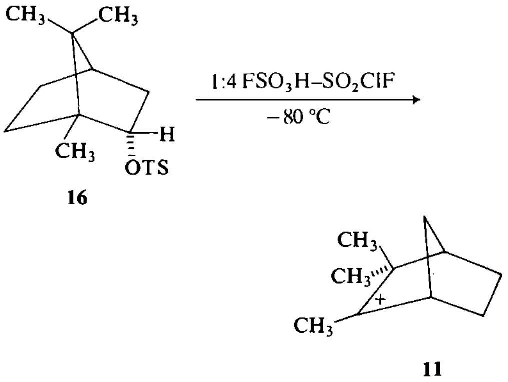
The actual ratio is somewhat difficult to determine since there is considerable polymer formation but it is about 3:1 favoring **12**. There is often some difference in the partitioning behavior of a steady-state intermediate and the partition which occurs when one attempts to directly prepare the intermediate (see refs. 8 and 23 for some previously discussed examples of this).

(*b*) The addition of α-fenchyl tosylate **15** (*endo* leaving group) to fluorosulfonic acid at −80 °C yields the same two cations **8** and **12** (eq. 6), in about the same proportions as are produced from the camphenehydro cation rearrangement.

[6]


What makes this result odd is that **12** is not a normal product of the tertiary α-fenchenehydro cation **7** rearrangement sequence (which one might have expected from **15** via a WM shift) and mechanistically its formation is difficult to rationalize *unless* there is bond migration (eq. 7) in the solvolysis, to yield the 2-bicyclo[3.1.1.]-heptyl cation intermediate, which then partitions as previously noted. This same problem arises in rationalizing the approximately 50% of ring-opened products produced in the deamination of α-fenchylamine (24). However this interpretation of the solvolysis of **15** is negated somewhat by the observation that borneol tosylate **16** in $FSO_3H–SO_2ClF$ at −80 °C does not yield detectable amounts (<10%) of **8** or **12**, which would be expected if a similar 7,1–7,2 bond migration had occurred. The sole product is the WM shift species, the camphenehydro cation **11** (eq. 8).

[7]


[8]


The deamination of bornylamine does yield ring-opened products (24); however, the percentage of these is somewhat less than in the fenchyl case, just the opposite of what might have been expected, so it may still mean that the fenchyl system for some reason is directly yielding the 2-bicyclo[3.1.1]heptyl cation system, while the bornyl is not.

On balance, we feel that there is some evidence that the 2-bicyclo[3.1.1]heptyl system is an intermediate in some observable 2-norbornyl cation rearrangements.

Considering the rearrangement *4* subcategories (Scheme 1), one finds that if C1 and C2 are substituted by identical groups, *i.e.* H or CH_3, then a rearrangement *1* process accomplishes the same permutation as a rearrangement *4* process, except that the former interchanges the C1 and C2 carbons and attached substituent while the latter does not. Since none of our labelling can distinguish such differences we can forget about these categories, the $\Delta G^{\ddagger}$ value for process *1* being much lower than that expected for process *4*.

Rearrangements 4TT and 4SS

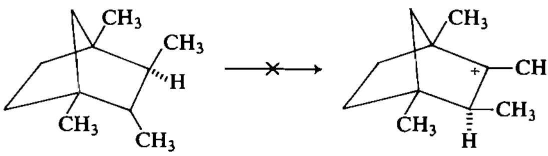
The sequences 4TT and 1TS,4SS,1ST accomplish the same permutations (7) and cannot be distinguished. The experimental barrier for the camphenehydro cation **11** giving **8** and the ring-opened cyclohexenyl cation **12** is 17.5 kcal/mol. As explained previously, one can rationalize the formation of both products on the assumption of common bicyclo[3.1.1]heptyl cation intermediate but the evidence certainly does not require this mechanism. Tentatively, we assign a barrier $\gtrsim$ 18 kcal/mol for either 4TT or 1TS, 4SS,1ST, whichever is less. In other words, if the actual barrier is 4TT, then the 18 kcal/mol is directly appropriate. If the 1TS,4SS,1ST sequence is lower, then the 4SS barrier would be assigned as $\gtrsim 18 - 5.5 = \gtrsim 12.5$ kcal/mol.

Rearrangement 5HSS

Several results (11, 21) suggest that an *exo*-3,2-hydride shift will be much faster than the *endo* shift. The process 5HSS accomplishes the same overall permutations (unless the C2 and C3 protons are labelled) as the apparently much easier 2HSS process and the former need not be considered further (*i.e.* it would represent a very minor pathway).

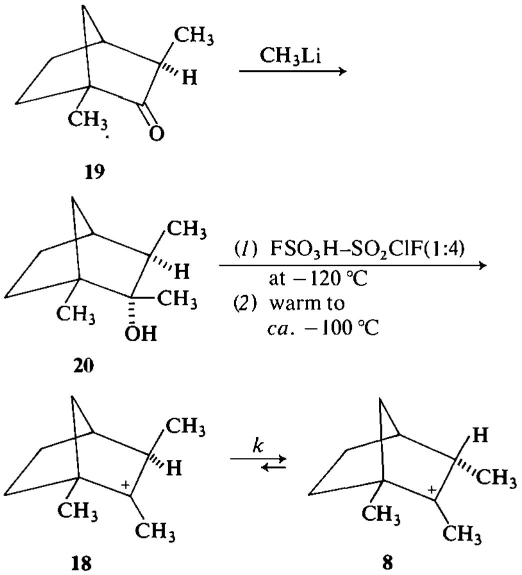
Rearrangement 5HTT

There is no observable n.m.r. line broadening in the 1,2-*exo*-3,4-tetramethyl-2-norbornyl cation (**17**) up to at least −10 °C, such as might have occurred from an *endo*-3,2-hydride shift (11) and we can assign a minimum $\Delta G^{\ddagger}$ value of *ca.* 14.2 kcal/mol. The interconversion of the 1,2-*exo*-3-trimethyl-2-norbornyl cation (**18**) prepared by an unambiguous route starting from the known ketone **19** and the alcohol **20** and the 1,2-*endo*-3-trimethyl-2-norbornyl cation (**8**) (eq. 9), for which $k = 3.0 \pm 0.5 \times 10^{-4}\ s^{-1}$ at −90 °C, $\Delta G^{\ddagger} = 13.6$ kcal/mol, can be most expeditiously explained using an *endo*-3,2-hydride shift, a five-step sequence involving 5HTT,1TS,3SS,1ST, 2HTT. However, there are other ways that this transformation could have occurred, for example, using only the first three processes; this requires a minimum of eight steps for the lowest calculated 15.2 kcal/mol (2HST) barrier, perilously close to the observed 13.6 kcal/mol barrier. Tentatively, a $\Delta G^{\ddagger}$ value of $\gtrsim$ 14.0 kcal/mol is assigned for 5HTT.



17 **17′**

[9]



18 (+WM shift isomer) **8** (+WM shift isomer)

Rearrangements 5HTS and 5HST

Starting from a tertiary cation energy base, the 2HTS(2HST) process requires 15.2 kcal/mol. If one looks at the minimum $\Delta\Delta G^{\ddagger}$ difference between 2HTT and 5HTT, *i.e. ca.* 7 kcal/mol, and applies this difference to the 5HTS and 5HST processes, one obtains barriers in excess of 20 kcal/mol. Since these processes are never *required* in any of the overall transformations, the molecules ($\gg$99%) will always find easier routes.

Rearrangement 5MTT

The rearrangement has been observed in a hexamethyl-2-norbornyl cation system (12), $\Delta G^{\ddagger} = 19.5$ kcal/mol. Since a 2MTT process, $\Delta G^{\ddagger} = 8.9$ kcal/mol, accomplishes the same permutation of groups, unless the methyls at C2 and C3 are labelled, one need not consider 5MTT any further.

Rearrangements 5MSS, 5MST, and 5MTS

If one adds the same $\Delta\Delta G^{\ddagger}$ difference observed between 2MTT and 5MTT to the 2MSS, 2MST, and 2MTS values derived previously, one arrives at $\Delta G^{\ddagger} > 20$ kcal/mol (from a tertiary cation energy base) for the title processes. Since these processes are not *required* for any of the overall transformations they could only represent very minor pathways.

Of all the *endo*-3,2-substituent shift processes, only 5HTT appears to have a reasonable chance of being important.

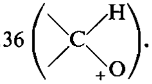
Concluding Discussion

The $\Delta G^{\ddagger}$ values obtained for each of the rearrangements *1–5* represent the "best" values which can be derived from the limited number of "base" measurements investigated to date. The most unsatisfactory situation concerns the 2MSS step. The problems created by this uncertainty are readily apparent when we come to test the predictive power of the parameters (following paper). The uncertainty with process *4* is not as serious since we have some confidence that the barrier for this is quite high and sequences not requiring process *4* can usually be found.

Experimental

Carbocations and protonated alcohol solutions were prepared and referenced using previously described procedures (11, 25). Nuclear magnetic resonance spectra were obtained on a Varian Associates HA-100 equipped with a variable temperature probe. Probe temperatures were monitored by placing a thermocouple directly into the spinning n.m.r. tube. Preparative g.l.c. separations were performed using either (*A*) a 12 ft. × 3/8 in. column of 30% Carbowax 20M on Chromosorb 60–80 or (*B*) a 10 ft. × 3/8 in. column of 20% SE-30 on Chromosorb 60–80.

1,2,4-Trimethyl-2-norbornyl Cation 2

The ^{1}H n.m.r. chemical shifts for this cation have been reported in a communication (1). The cation was obtained by protonating α-fenchene, prepared from α-fenchyl tosylate and g.l.c. separation (column *A*, 90 °C) from small amounts of ζ-fenchene and cyclofenchene (26); from β-fenchene, prepared by g.l.c. separation (column *A*) of the complex mixture obtained by dehydrating α-fenchol with solid potassium bisulfate (27) (α- and β-fenchene are the highest retention products and are only poorly resolved but by cutting the front part of this combined "peak" pure β-fenchene can be obtained); from cyclofenchene or from α-fenchol itself, obtained by lithium aluminum hydride reduction of fenchone (28). In the α- and β-, and cyclofenchene cases, one initially obtains at −120 °C a mixture of the tertiary α- and β-fenchenehydro cations, the chemical shifts of these have been reported in the communication (1). On warming the solutions one obtains first a 1,2,3-trimethyl-2-norbornyl cation system and finally at around −15 °C, cation **2**. In the case of α-fenchol, one initially obtains in FSO_3H the protonated alcohol, characterized by ^{1}H n.m.r. peaks at τ 8.67, 8.78, and 8.87 (3H each, the methyl groups) and 5.36 . At −18 °C, this solvolyzes within 0.5 h to yield a mixture of the 1,2,3-trimethyl species and **2**. After 0.5 h at 0 °C, only **2** is left.

On cooling a solution of **2** in 4:1 SO_2ClF–FSO_3H down to −120 °C, there is no evidence that the degenerate WM shift is being slowed down enough to see ^{1}H n.m.r. line broadening.

Structure Proof of 2. Isolation of Two New Fenchenes

The structure of cation **2** is reasonably assigned from the n.m.r. spectrum but is confirmed from quenching experiments. Solutions of **2** were prepared at −80 °C using 10% w/v of α-fenchol in FSO_3H and letting the solution stand 0.5 h at 0 °C. This acid solution was then added dropwise to an ice-cold, well stirred, aqueous sodium hydroxide solution containing a small upper ether layer. The aqueous solution was extracted twice with ether and the ether dried over anhydrous potassium carbonate. The organic residue showed two "peaks" on g.l.c. analysis (column *B*): a large shorter retention peak and a more diffuse higher retention one, about 3:1 area ratio. Both were collected in quantity. Rechromatography on column *A* of the first fraction yielded three well-separated peaks. The lowest retention product was very small and not further investigated. The highest retention product was a liquid with *m*/*e* 136. The n.m.r. spectrum (CCl_4) showed peaks at τ 8.82 and 8.85 (3H each, methyl groups at C1 and C4), 7.94 (broad, 2H, C3 protons), 5.42 and 5.54 (1H each, t, $J = 2$, the C2 *exo*-methylene protons). This allows one to assign the structure as 1,4-dimethyl-2-methylenebicyclo[2.2.1]heptane **4**, which can also be labelled η-fenchene. The structure is further confirmed by ozonolysis of **4**, whereby the pure ketone, 1,4-dimethylbicyclo[2.2.1]heptan-2-one, was obtained by preparative g.l.c. separation (column *B*); i.r. 1750 cm^{-1}, C=O; n.m.r. (CCl_4), τ 8.74 and 8.90 (3H each, the C1 and C4 methyl groups), 8.10 (broad, 2H, the C3 protons); 2,4-DNPH derivative, m.p. 128–130 °C (lit. (29) m.p. 129–129.5 °C). Readdition of **4** to FSO_3H at −80 °C yields the cation **2**. The middle retention product was also a liquid, *m*/*e* 136; n.m.r. (CCl_4), τ 8.76 and 8.79 (3H each, C1 and C4 methyl groups), 8.41 (d, $J = 1.5$, 3H, C2 methyl group), 4.71 (broad, 1H, the alkene proton at C3). The m.s. fragmentation shows a large even ion at *m*/*e* 108 (−28 for the reverse Diels–Alder product ethylene). These data allow one to assign the structure as 1,2,4-trimethylbicyclo-[2.2.1]hept-2-ene (**3**) which can also be labelled θ-fenchene. Readdition of **3** to FSO_3H at −80 °C gives **2**. The ratio of **4**/**3** is about 4:1. In theory, there should be no more alkenes produced from **2** but rechromatography of the second column *B* peak on column *A* yields a complex series of peaks. The largest is the highest retention peak which was collected, a liquid, *m*/*e* 136. From the n.m.r. spectrum (CCl_4), the compound is not pure but has major peaks at τ 9.17 (d, J = 6.75), 8.91 and 8.96, 5.34 and 5.57. Readdition of this alkene to 4:1 SO_2ClF–FSO_3H at *ca.* −120 °C yields **2** and in part a cation assigned as 2,4-*anti*-7-trimethyl-2-norbornyl cation; n.m.r. τ 5.37 (d, J = 5.5, C1 proton), 6.78 (C2 methyl), 8.59 (C4 methyl), and 8.86 (possibly an unresolved doublet, *anti*-C7 methyl). This rearranges to **2** at very low temperatures and was not further investigated. The alkene can be assigned as 4-*anti*-7-dimethyl-2-methylenebicyclo[2.2.1]heptane (**5**).

2-Methyl-2-norbornyl Cation 6. Degenerate Rearrangements

Cation **6** was prepared in a number of solvent systems, FSO_3H, FSO_3H–SO_2ClF (1:4), SbF_5–SO_2, FSO_3H–SbF_5 and the rearrangement rates do not vary to any measurable extent. The cation was prepared in *ca.* 5% w/v concentration either from the tertiary alcohol, *exo*-2-methylnorbornan-2-ol or the tertiary chloride, *endo*-2-methyl-2-chloronorbornane. The 2-CD_3 alcohol was used in some cases and was prepared from norbornanone and CD_3MgI. The chemical shifts of **6** have been reported by Olah *et al.* (20) but their assignment should be corrected. Our results show that the C6-*endo* and a C5 proton assignment should be interchanged. Cation **6** undergoes two degenerate rearrangements. The rate of the faster process was obtained by matching computed spectra of the H1 proton doublet (AX) with calculated spectra assuming various exchange rates with the H6-*endo* proton (simulated as a broad singlet of half-width 24 Hz). The experimental coalesced H1–H6-*endo* proton peak appears very close to the C2 methyl peak but could be observed using the 2-CD_3 cation. No peak matchings were attempted at or beyond coalescence because the H6-*exo* and H3 protons interfere to some extent and also the very approximate line shape assigned to H6-*endo* will be a factor in the coalesced peak line shapes (but will not affect the more exact matchings done only on the C1 proton doublet prior to coalescence). The second degenerate rearrangement occurs at temperatures above 0 °C (in FSO_3H–SbF_5 (1:2)) and can be assigned to the process given in Scheme 2. The kinetic matrix used is shown in Fig. 4. Monstrous problems arise in treating this line broadening since all 10 protons are coupled in an interwoven manner, some involving second-order effects. Programs to handle such large exchanges are impossibly expensive even if one could determine all of the unknown coupling constants. The approximations used in the calculations consist in treating all protons (except C2) as uncoupled singlets, using various line widths to mimic coupling to some extent. The values used were as follows: H1, doublet, J = 7, line-width 5 Hz; *exo*-H3, 12; *endo*-H3, 12; H4, 7.5; *exo*-H5, 15; *endo*-H5, 10; *exo*-H6, 19; *endo*-H6, 24; *anti*-H7, 7; *syn*-H7, 7. In spite of these severe approximations, we expect that spectra in the intermediate exchange region should be relatively good since the exchanging protons are separated by large chemical shifts and consequently the peaks are very broad (see Fig. 3) in this region (and relatively unaffected by the exact line shape of the "frozen out" peaks.

Interconversion of the α- and β-Fenchenehydro Cations

On adding α-, β-, or cyclofenchene to FSO_3H–SO_2ClF (1:4) at *ca.* −120 °C, one obtains only the equilibrium mixture of the α- and β-cations, *K* being near unity. On warming very rapidly (there is also an irreversible transformation occurring rapidly as one warms the solution, next sextion) to −78 °C, the interconversion becomes rapid enough so that the DISST technique of Forsén and Hoffman (22) can be used to estimate the interconversion rate. Irradiation of the combined *endo*-H6 region (*ca.* τ 8.6) results in a 50% decrease in the combined H1 proton region. Assuming T_1 = 2 s (30), this gives an order of magnitude rate constant, $k = 1\ s^{-1}$, $\Delta G^{\neq}$ = *ca.* 11.2 kcal/mol. For confirmation, this technique was also applied to the degenerate rearrangements observed for cation **6**, where both line broadening and the DISST technique can be used. For the faster of the two degenerate rearrangements in **6**, the DISST technique gives $k = 1\ s^{-1}$ at −87.0 °C, compared to the extrapolated estimate of $0.85\ s^{-1}$ from the log *k vs.* $1/T$ plot using line-broadening data. The DISST technique was also used to confirm qualitatively the exchanges suggested for the slower degenerate rearrangement in **6**.

α- and β-Fenchenehydro Cations → 1,2-endo-3-Trimethyl-2-norbornyl Cation 8 (+ WM Shift Isomer)

This rate was followed by determining the height of the growing C1 and C2 methyl peaks of **8** (+ WM shift isomer) as a function of time using a standard first-order plot. At −92 °C, $k = 5.1 \pm 0.2 \times 10^{-4}\ s^{-1}$, $\Delta G^{\neq}$ = 13.1 kcal/mol (average of two runs).

Structure Proof of Cation 8 (+ WM Shift Isomer)

The ketone 1-*endo*-3-dimethylbicyclo[2.2.1]heptan-2-one (**9**), was prepared by first alkylating 1-methylbicyclo-[2.2.1]heptan-2-one using trityl sodium and methyl iodide (31). The product is mainly the *exo*-3-methyl compound **19** (g.l.c.) with traces of **9** and some starting material. Equilibration in refluxing $NaOCH_3$–CH_3OH gives an equilibrium mixture now slightly richer in **9** (*ca.* 55%) and this was isolated by preparative g.l.c. (column *A*, 155 °C). The ketone has been reported (31). Treating 0.210 g (1.52 mmol) of **9** in ether with excess methyl lithium in ether at 0 °C yields, after work-up, an oil, 0.236 g, which solidifies in the freezer; i.r., no C=O, 3420 cm^{-1} (b), OH; n.m.r. (CCl_4), τ 8.97, 9.03, 9.20 (d, J = 7 Hz, all 3H, the three methyl groups of **10**). Judging from the lack of doubling of n.m.r. peaks, the product is likely to be mainly the *exo*-2-methyl isomer. Addition of the alcohol **10** to FSO_3H–SO_2ClF (1:4) at −120 °C and warming to −100 °C gives **8** (+ WM shift isomer). The chemical shifts for **8** (+ WM isomer) have been reported previously (1). Some of these are temperature dependent, as expected (14). Solutions of **8** can be quenched (−20 °C), as for **2**, and pure 1,2,3-trimethylbicyclo[2.2.1]hept-2-ene (ε-fenchene) can be isolated by preparative g.l.c. (column *A*). There are also produced in this quenching a number of other alkenes with an exocyclic methylene group, probably corresponding in part to elimination at the C2 methyl in **8** and also from the C2 methyl of the WM shift isomer. However, there are more products than this will account for. Cation **8** (+ WM shift isomer) is produced on adding ε-fenchene to $FSO_3H–SO_2ClF$ (1:4) at *ca.* −120 °C.

1,2-endo-3-Trimethyl-2-norbornyl Cation 8 → 1,2,4-Trimethyl-2-norbornyl Cation 2

The rate of this reaction was measured by following the increase in the C4 methyl peak height of **2** as a function of time. The reaction was run at −15.0 °C in a cryostat and samples were periodically quenched at −78 °C and the n.m.r. spectrum determined at −50 °C. Nitromethane was used to obtain a constant reference peak height, $k = 1.1 \pm 0.2 \times 10^{-4}\ s^{-1}$, $\Delta G^{\neq} = 18.5$ kcal/mol (average of two determinations).

Protonation of α- and β-Pinene

α-Pinene or β-pinene was dissolved in an equal volume of $CDCl_3$ and added slowly to either pure FSO_3H with stirring at −50 °C in a 5 ml round-bottom flask or directly to an n.m.r. tube containing a 1:4 mixture of $FSO_3H–SO_2ClF$ at *ca.* −120 °C. The spectra were reasonably clean and could be analyzed at low temperatures but on warming, broad featureless n.m.r. peaks characteristic of polymers appeared. Both products **8** and **12** are stable at these temperatures so the reason for the polymerization is not known.

α-Fenchyl Tosylate and Borneol Tosylate

These compounds were prepared by standard procedures and are both known (32).

1,2-exo-3-Trimethyl-2-norbornyl Cation 18 → 1,2-endo-3-Trimethyl-2-norbornyl Cation 8

Cation **18** (+ WM shift isomer) was prepared from the corresponding tertiary alcohol **20**. The preparation of **20** follows that of **10**, except that the 1-*exo*-3-dimethyl ketone **19**, needed in this case, had to be isolated by a double preparative g.l.c. collection of the initial alkylation mixture referred to in the preparation of **10**. On column *A*, the ketone **19** and the starting material can be separated as a single peak from the 1-*endo*-3-dimethyl ketone **9**. Reinjection on column *B* separates the starting ketone and **19**. Methylation (0.209 g, 1.51 mmol) with excess methyl lithium, as previously, yields an oily tertiary alcohol (0.226 g); i.r., no C=O, 3430 cm^{-1}, OH. The n.m.r. spectrum (CCl_4) indicates a mixture of the *exo*-2 and *endo*-2 methyl alcohols, peaks at τ 8.94, 9.00, 9.06, and 9.14 (d, J = 7 Hz). The 8.94 and 9.06 peaks add up to approximately 3H and presumably are the *exo*-2 and *endo*-2 methyl groups, the C1 and C3 methyls overlapping in both isomers. Both isomers yield the same cation so the stereochemistry at C2 is unimportant for our purposes. Addition of **20** to $FSO_3H–SO_2ClF$ (1:4) at *ca.* −120 °C and then warming to −100 °C yields **18** (+ WM shift isomer). The chemical shifts for this rapidly equilibrating pair have been reported (1) and as expected (14), the C1 and C2 methyl shifts are temperature dependent. The interconversion rate was followed by determining the increase of the standardized C1 and C2 methyl peak heights of **8** (+ WM shift isomer) as a function of time. Reversible first-order kinetics were used since a small amount of **18** (+ WM shift isomer) exists at equilibrium, **8**/**18** = 6.3 ± 0.3, $k_{18 \rightarrow 8} = 3.0 \pm 0.5 \times 10^{-4}\ s^{-1}$ at −90 °C, $\Delta G^{\neq} = 13.6$ kcal/mol (average of three runs).

The authors wish to thank the National Research Council of Canada for generous financial support.

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