Solution carbocation stabilities measured by internal competition for a hydride ion

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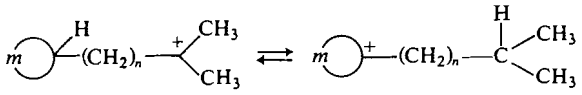
Although many techniques are known which allow one to compare the stabilities of solution carbocations, that involving the intermolecular competition for a hydride ion is conceptually (but not experimentally) the simplest procedure. This paper describes a variant of this which is experimentally more reliable and which uses intramolecular equilibria where the two competing systems are held together by a $-(CH_2)_n-$ chain, e.g.



By systematically varying "n" in this example (n = 0, 1, 2, or 3), it has been found that a methylene chain of two or more carbons is necessary in order to minimize steric interactions between the end "systems". It has also been found that all cycloalkyl rings studied (except cyclohexyl) stabilize a cation centre much better than an aliphatic equivalent, i.e. $-\overset{+}{C}(CH_3)_2$, in agreement with solvolysis rate studies. The same situation was found when comparing this aliphatic "system" against the 2-norbornyl cation (bicyclic) or against the tricyclic 2-adamantyl cation. In fact, in these cases the equilibria are too lop-sided to obtain numerical values for the equilibrium constants concerned. Finally, three carbocations were looked at where the 2-norbornyl cation structure was pitted against the structurally very related cyclopentyl, bicyclo[2.1.1]hexyl, and bicyclo[3.2.1]octyl cations. In all cases, the 2-norbornyl cation is the more stable. ^{13}C nmr spectroscopy was used as the analytical tool to measure (or attempt to measure) the equilibrium constants. Depending on the *rate* of the equilibration process, three different techniques are involved and the relative merits of these are discussed in the latter part of the paper.

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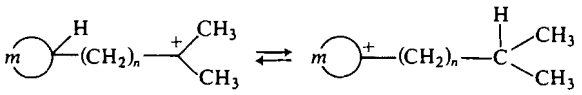
Parmi toutes les techniques connues qui permettent de comparer les stabilités des carbocations en solution, celle qui implique la compétition intramoléculaire de l'ion hydrure est conceptuellement (mais non expérimentalement) la plus simple. Ce travail décrit une variante de cette technique qui est plus fiable expérimentalement et qui utilise les équilibres intramoléculaires lorsque les deux systèmes en compétition sont maintenus ensembles par une chaîne de $-(CH_2)_n-$, comme dans



En faisant varier "n" d'une façon systématique dans cet exemple (n = 0, 1, 2 ou 3) on a trouvé qu'une chaîne contenant au moins deux unités méthylènes est nécessaire afin de minimiser les interactions stériques entre les systèmes terminaux. On a également trouvé que tous les cycloalkyles étudiés (à l'exception du cyclohexyle) stabilisent mieux le centre cationique que les équivalents aliphatiques c'est-à-dire $-\overset{+}{C}(CH_3)_2$; ceci est en accord avec les études de vitesse de solvolyse. On a trouvé la même situation en comparant ce "système" aliphatique avec le cation norbornyle-2 (bicyclique) ou avec le cation tricyclique adamantyle-2. En fait, dans ces cas les équilibres sont trop dissymétriques pour obtenir les valeurs numériques des constantes d'équilibres concernées. Finalement, on a étudié trois carbocations où la structure du cation norbornyle-2 est opposée aux cations cyclopentyle, bicyclo[2.1.1]hexyle et bicyclo[3.2.1]octyle qui sont structurellement très reliés. Dans tous les cas, le cation norbornyle-2 est le plus stable. On a utilisé la spectroscopie de rmn du ^{13}C pour mesurer (ou pour essayer de mesurer) les constantes d'équilibre. Dépendant de la vitesse du processus d'équilibration, on utilise trois techniques différentes et on discute de leurs mérites relatifs dans la dernière partie de cette publication.

[Traduit par le journal]

Introduction

The comparative base strengths of anions in general, and carbanions in particular, can be measured by setting up solution equilibria in which two anions compete for a proton, e.g.

[1] $R_1-H + R_2^- \overset{K}{\rightleftharpoons} R_1^- + R_2H$

This classic procedure (1) has an opposite charge analogy, in which solution cations formally compete for a hydride ion, e.g.

[2] $R_1-H + R_2^+ \overset{K}{\rightleftharpoons} R_1^+ + R_2H$

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Where R^+ is a carbocation, one can in principle use this procedure to study the relative stabilities of carbocations. However, it should be noted that while the proton transfer process (reaction [1]) can be defined in terms of pK_a's, this is not true of reaction [2]. Furthermore, much information relating to relative carbocation stabilities is available from a host of other techniques, such as solvolysis rate comparisons, calorimetry of ionization processes (2), mass spectrometry and ion cyclotron resonance (3) (reaction [2]-type *gas-phase* equilibria are now accurately known for a large number of systems), pK_a-type equilibria (4), kinetics of various acid-catalyzed reactions, ionization equilibria (5), etc. Nevertheless, reaction [2] solution equilibria, if the measurements could be made general for a wide variety of cation structures, would be unsurpassed as a "true" measure of solution cation stability since the hydrogen being competed for is the smallest transfer "group" possible, minimizing as much as one can steric contributions. This can be contrasted, for example, with the simplest traditional pK_a equilibrium (reaction [3])

[3] $\text{>C=C<} + (H^+) \rightleftarrows \text{>C(H)—C}^+\text{<}$

Not only are these equilibria very hard to measure (6) (because of polymerization) but we believe that one must take account of more steric factors in this case.

Although many studies involving [2]-type reactions have appeared in the past, they have focussed primarily on kinetics (7) or synthetic applications, the numerical equilibrium constant being of secondary concern. However, Kramer and co-workers have reported some studies devoted entirely to measuring [2]-type equilibria (8).

A serious drawback to intermolecular equilibria involves experimental difficulties associated with an oxidation of the hydrocarbon component (9) of these equilibria by the excess strong acid solvent system used in generating the cation component, leading to "messy" nmr spectra. Furthermore, in choosing solvent systems where both cation and hydrocarbon are soluble, one is reduced to solvents such as dichloromethane, where extensive ion-pairing may result, coincidentally, also a problem with some carbanion equilibria. For example, in the study by Kramer *et al.* (8), the results quoted are markedly influenced by the choice of both the solvent and the Lewis acid.

Our approach to the above problems is to link the R_1 and R_2 fragments, modifying reaction [2] as follows:

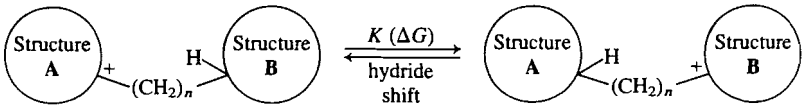
[4] $R_1\text{—H} + R_2^+ \overset{K}{\rightleftharpoons} R_1^+ + R_2H$

Each species is now a cation so that solubility problems no longer exist and oxidation is certainly a less serious problem.

Other studies have in the past used the position of a suitable *intramolecularly-generated* carbocation equilibrium in order to probe various phenomena related to carbocation stabilities, e.g. the hyperconjugative order (10). However, the recent availability of routine ^{13}C nmr spectroscopy now makes it potentially possible to study a wider variety of such equilibria.

We were therefore interested in looking at intramolecular equilibria related to the above intermolecular processes and as a consequence of this in: (*a*) the design of suitable carbocation systems for such equilibrium measurements and (*b*) an examination of the relative practical merits of various ^{13}C nmr techniques needed to obtain the equilibrium constant numerical data.

The design of the desired organic systems can be schematically represented as follows:



I II

The major uncertainty initially was in knowing how large to make "*n*" so that structures **A** and **B** would not directly interfere with each other, the aim being of course to mimic intermolecular equilibria as closely as possible. We therefore prepared a number of systems in which only "*n*" was allowed to vary.

A consequence of changing "*n*" is that the *rate* for the equilibration will also change (based on the known behavior of simple model systems) (11, 12).

Depending on how fast this equilibration rate is, there are three separate ^{13}C nmr techniques which could be used to measure the equilibrium constant K: (A) for very fast rates, only averaged nmr peaks will be observed and K can be calculated if reasonable estimates can be made for the chemical shifts of the individual components. Also, these averaged peaks will be measureably temperature-dependent if K is not too large or too small. (B) for intermediate exchange rates, an nmr line-broadening technique could be used, in particular the application of techniques designed to detect potentially very lop-sided equilibria (13), and (C) for moderately slow rates, one could expect to quantitatively detect peaks characteristic of both ions **I** and **II**.

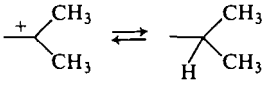
In evaluating these three techniques, we will be concerned with two factors: (*a*) the potential ability of the technique to detect very large and very small K values and (*b*) a confidence factor which ultimately comes into play when pushing these techniques to their practical limits.

Results

All of the carbocations were prepared *in situ* from the corresponding alcohol using previously described techniques (14). The alcohols were prepared by standard Grignard or alkyl lithium reactions. Nuclear magnetic resonance procedures for determining K's will be discussed later. Each specific cation is given an arabic number, but when we wish to discuss the series in a general way we use the Roman numerals **I** ⇄ **II**.

*Effect of varying "*n*" in* ***I*** ⇄ ***II***

A series of cations were prepared in which one end was simply



and this "structure" we equate as being equivalent to a normal acyclic tertiary carbocation, e.g. *t*-butyl. In this study, the other "structure" was a cycloalkyl group (ring size = 4–8) (monocyclic), or 2-norbornyl (bicyclic) or 2-adamantyl (tricyclic). For the purposes of investigating the effect of n, only the cyclohexyl system **1** ⇄ **2** (structures in Table 1) was suitable, all other systems involving at least some equilibria which were too lop-sided to quantitatively measure. The data are summarized in Table 1.

There is an increase in K as n is increased, but the change from $n = 2$ to $n = 3$ is minimal and we conclude that direct proximity effects between the two "structures" have become insignificant for $n = 2$ and 3.

Effect of ring size

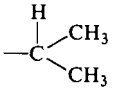
A series of cations were prepared, where $n = 0$, 1, and 2 and the ring size $m + 1 = 5$, 7, and 8 (general structures **3** and **4**, see Table 2). The alcohols for the $m + 1 = 4$ series were also prepared but the corresponding cations could not be prepared, a ring expansion to a cyclopentyl or a cyclohexyl ring occurring too fast. The data are summarized in Table 2.

For the $n = 0$ series, equilibrium constants could be measured for $m + 1 = 5$ and 7, but not 8. However, for $n = 1$ or 2, only minimum estimates were obtained. This situation is not unexpected if one looks at the Table 1 data.

The 2-norbornyl comparisons (cations **5** and **6** in Table 3) were also made for the $n = 0$, 1, and 2 series and are summarized in Table 3. These equilibria are even more lop-sided than those in Table 2 and even the $n = 0$ equilibrium constant cannot be obtained.

Finally the tricyclic 2-adamantyl comparisons (cations **7** and **8** in Table 4) were made. In this case only the $n = 1$ equilibrium constant could be measured.

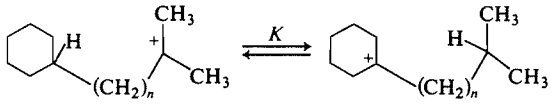
As it turns out, most of the presently chosen equilibria are too lop-sided to obtain numerical K values, i.e. the combination of the sp^2 C^+ centre in the cyclic, bicyclic, or tricyclic ring and the CH sp^3 centre in



is much better than the alternative. In principle, it would probably be possible to devise a series of overlapping equilibria which would permit one to evaluate all of the K's looked at here, but this would require more study. However, since the tertiary 2-norbornyl cation "structure" has been the subject of numerous studies, it seemed worthwhile to look at cation equilibria in which the 2-norbornyl cation was pitted against the structurally-related cyclopentyl cation, and also against related tertiary bicyclic frameworks, in the hope that this closer similarity of the two "structures" would yield measurable K's. The comparisons are shown below with dark lines emphasizing the similarities in the two "structures". An $n = 2$ connection was used to minimize direct interactions.

For **9** ⇄ **10**, the equilibrium constant was 15 at −90°C, while for **11** ⇄ **12**, only ion **12** was observed at equilibrium, $K \geq 30$ at −90°C. Similarly, it can be

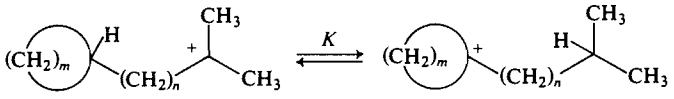
TABLE 1. Effect of varying "n" on the **1** ⇄ **2** equilibrium



1 **2**

Ion	n	K	$-G$ (kcal)	Temperature (°C)	Nmr method used
1*a*–**2***a*	0	0.045	−1.0	−105	A
1*b*–**2***b*	1	0.33	−0.35	−113	C
1*c*–**2***c*	2	1	0.00	−106	C
1*d*–**2***d*	3	1.2	0.09	−74	A

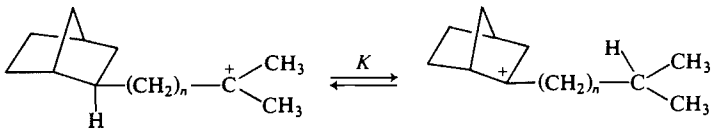
TABLE 2. Equilibrium constants (or minimum estimates) for the equilibria **3** ⇄ **4**, where $m + 1 = 5$, 7, and 8 and $n = 0$, 1, or 2



3 **4**

Ion	m	n	K	$-\Delta G$ (kcal)	Temperature (°C)	Nmr method used
3*a*–**4***a*	4	0	25	1.1	−105	A
3*b*–**4***b*	4	1	≥1000	≥2.6	−85	B
3*c*–**4***c*	4	2	≥35	≥1.2	−116	C
3*d*–**4***d*	6	0	50–100	1.2–1.4	−123	A
3*e*–**4***e*	6	1	≥20	≥1.0	−110.5	C
3*f*–**4***f*	6	2	≥35	≥1.2	−102	C
3*g*–**4***g*	7	0	≥200	≥1.8	−128 to −102	A
3*h*–**4***h*	7	1	≥1000	≥2.6	−81	B ($K \geq 20$, method C)
3*i*–**4***i*	7	2	≥35	≥1.2	−105	C

TABLE 3. Minimum equilibrium constant estimates for the equilibria **5** ⇄ **6**



5 **6**

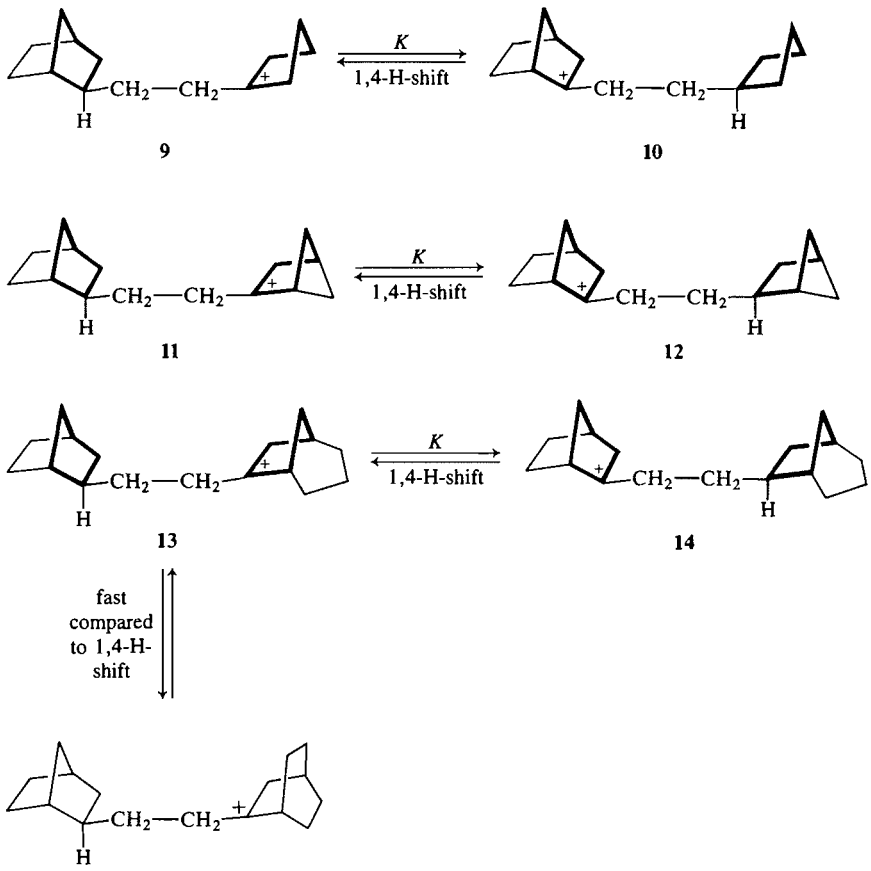
Ion	n	K	$-\Delta G$ (kcal)	Temperature (°C)	Nmr method used
5*a*–**6***a*	0	≥200	≥2.2	−119 to −63	A
5*b*–**6***b*	1	≥1000	≥2.6	−118 to −61	B
5*c*–**6***c*	2	≥50	≥1.8	−117 to −40	C

deduced that the **13** ⇄ **14** equilibrium lies completely on the side of **14**, $K \geq 400$ at −90°C. This case is somewhat complicated by another equilibrium involving cation **15** and this is discussed later.

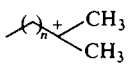
Discussion

As with carbanion equilibria, the equilibrium constant for **I** ⇄ **II** is *not* necessarily a direct measure of the stability of the two cation "structures" in **I** and **II**. One must also consider the two sp^3 CH centres and their relative stabilities, although these will not normally be expected to be the dominant factors involved.

The situation in kinetic solvolysis work is also related, although this involves a variety of larger leaving groups and transition-state developed "cations". Nevertheless, the rather incomplete equilibrium constant data (or limits) for the cycloalkyl vs. acyclic carbocation "structures" is completely in accord with previous solvolysis rate comparisons. These are shown in Table 5.



The equating of the *t*-Bu solvolysis data in Table 5 with our



"structure" can be justified by noting the similarity of the solvolysis data for *t*-BuCl, 2-methyl-2-chlorobutane, and 2-methyl-2-chloropentane (less than a factor of two difference among these) (15).

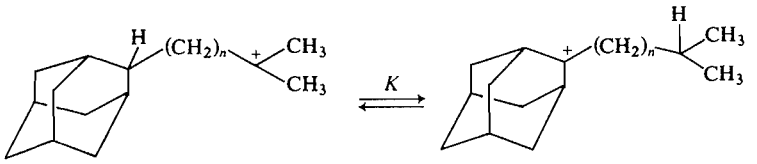
The K equilibrium constant data for $n = 2$ in Table 5 employs the nmr method C and, as will be discussed subsequently, this is not very sensitive. It is entirely possible, based on the more sensitive (nmr method B) $n = 1$ data, that these K values are indeed much larger than the lower limits quoted in Table 5. It is entirely reasonable, of course, that the present K equilibrium constant data would be larger than $k_{cyclic}/k_{t\text{-}Bu}$ because the temperature of the K measurements is quite low (favoring larger K's) and in addition, fully developed cations are involved. The "I-strain" concept (16) generally accounts for both the internal solvolysis comparisons and the equilibrium constant data; however, other factors like C—H hyperconjugation are probably involved as well.

The 2-norbornyl results in ions **5** ⇄ **6**, **9** ⇄ **10**, **11** ⇄ **12**, and **13** ⇄ **14** are also interesting in the context of comparisons to solvolysis data. Both *exo*- and *endo*-2-methyl-2-norbornyl esters or halides lead, of course, to the same carbocation intermediate. They typically differ greatly in solvolysis rate, however, and it is not immediately obvious which comparisons, if any, one should make. The data in Table 6 are illustrative.

The first column shows that tertiary cyclopentyl solvolysis rates typically fall between tertiary *exo*- and *endo*-2-norbornyl. Column two shows that the k_{exo}/k_{endo} difference also applies to a chloride-leaving group and column three shows the solvolysis comparison of acyclic, monocyclic, and *exo*-bicyclic chlorides.

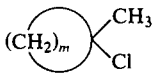
In view of the 1:355 solvolysis ratio, the complete dominance of ion **6** in the **5** ⇄ **6** equilibrium is to be expected. Ion **5**, although not present in detectable amounts, would be expected

TABLE 4. Equilibrium constants (or minimum estimates) for the equilibria **7** ⇄ **8**



7 **8**

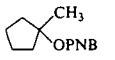
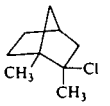
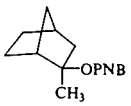
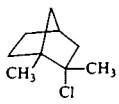
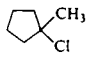
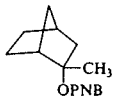
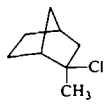
Ion	n	K	$-\Delta G$ (kcal)	Temperature (°C)	Nmr method used
7*a*–**8***a*	0	≥200	≥2.2	−120 to −68	A
7*b*–**8***b*	1	330	2.2	−79	B
7*c*–**8***c*	2	≥50	≥1.4	−88	C

TABLE 5. Solvolysis data for  vs. K data from this work

Ring size (m + 1)	k (cyclic)[a] / k (acyclic) (tBu)	K (n = 1 data) nmr method B	K (n = 2 data) nmr method C
5	43.7	≥1000	≥35
6	0.35	0.33	1.0
7	38.0	[b]	≥35
8	100.0	≥1000	≥35

[a]Data from ref. 42.
[b]Ion too unstable to use method B.

TABLE 6. Solvolysis data for various tertiary 2-norbornyl compounds

Compound	Relative k[a]	Compound	Relative k[b]	Compound	Relative k[c]
	1		178	*t*-BuCl	1
	4.75		1		66
	0.00536				355

[a]In 80% acetone, data of ref. 43.
[b]In ethanol, data of ref. 18.
[c]In ethanol, data of ref. 44.

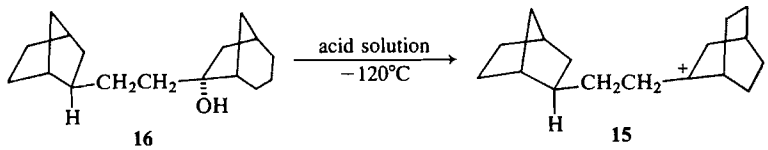
to have the *exo* stereochemistry on steric grounds and this can actually be verified for the **9** ⇄ **10** equilibrium.

The comparisons in **9** ⇄ **10**, **11** ⇄ **12**, and **13** ⇄ **14** are more relevant since one is comparing rather similar structures. The stability of **10** over **9** seems to clearly involve an "extra" stability associated with the tertiary 2-norbornyl cation. For example, having the sp^3 centre (as in **10**) should preferentially disfavor the simple cyclopentyl ring (more eclipsing interactions), but this is obviously more than made up for by some favorable effect, presumably associated with the 2-norbornyl cation "structure".

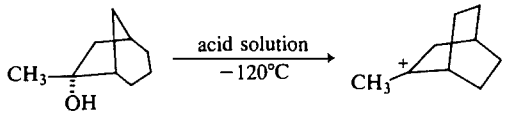
An even closer comparison comes from the rather exotic **11** ⇄ **12** equilibrium and this serves to

show that ring strain *per se* is not involved in stabilizing the 2-norbornyl cation, the 2-bicyclo-[2.1.1]hexyl "structure" being much more strained and also clearly disfavored as a cation site in the **11** ⇄ **12** comparison.

A three-carbon "backside" bridge is also much less favorable than the two-carbon one in 2-norbornyl, as shown by the **13** ⇄ **14** equilibrium. This equilibrium is somewhat more complicated than the others since we do not actually see cation **13**. Even carrying out the addition of the alcohol **16** to the acid solution at −120°C, the initially expected **13** has rearranged to **15** ($K \geq 20$). Model system experiments starting with alcohol **17** confirm this observation, i.e. ionization of **17** at −120°C gives "immediately" >90% of the known (14) 2-methylbicyclo[2.2.2]octyl cation **18**.



16 **15**

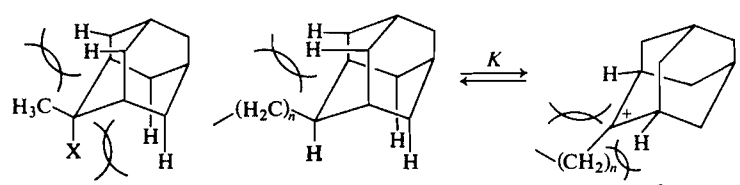


17 **18**

At about −90 to −100°C, cation **15** rearranges to **14** (via **13** and a 1,4-H-shift) since a *neutral* bicyclo[3.2.1]octane skeleton is more stable than the [2.2.2] skeleton (17). The **15** ⇄ **14** equilibrium lies completely to the right ($K \geq 20$), but since one already knows that **13** is less stable than **15**, one has a combined result giving a minimum K of 400 for the **13** ⇄ **14** equilibrium.

Overall, the K's for the 2-norbornyl "structures" correlate much better with *exo*-leaving-group solvolyses, the implication being that these are "normal" and that factors *other* than the intrinsic cation stability are involved in the transition-state for *endo*-solvolyses. This has been a point of contention for a number of years and our results are consistent with the arguments of Brown (18). These "interpretation problems" also point out the advantages of using equilibria as a measure of cation stability.

The 2-adamantyl equilibria also correlate with solvolysis data, i.e. *t*-BuBr/2-methyl-2-adamantyl bromide rates are about 1:10 (19). These enhanced rates are usually attributed to the removal of 1,3-diaxial interactions in going to the sp^2 carbocation intermediate and are also found in dehydration studies (20). However, in the ion equilibria where the 2-position of adamantane is sp^3-hybridized, i.e. ion **7**, only one 1,3-diaxial interaction is important (hydrogen occupying the other position) and this is balanced in the sp^2-hybridized case, structure **8**, by eclipsing interactions of the 2-alkyl group with hydrogens on the 1- and 3-carbons of the adamantyl ring, as shown below:



solvolysis starting material **7** **8**

However, interactions in **7** may be the dominant factor and it is significant in this regard that in the one case where a K could be measured (Table 4, $n = 1$, the isobutyl group), molecular mechanics calculations (20) suggest the least steric gain in going from the sp^3-hybridized adamantane to the corresponding sp^2-hybridized cation. The calculated relief in the isopropyl case ($n = 0$) is

considerably larger and would account for the fact that K is larger here than in the $n = 1$ case.

It is somewhat surprising that one sees no 1-adamantyl cations in the equilibria. Although a 1,2-hydride shift in **8** is probably proscribed (21), there is ample opportunity to form a 1-adamantyl cation by a 1,3-hydride shift from **7***a*, a 1,4-shift from **7***b*, or a 1,5-shift from **7***c*.

Overall conclusions on the equilibrium results

Solvolysis rate comparisons, when used to probe cation stabilities, are obviously capable of a much greater range than the equilibria looked at in this study. However, as previously noted, solvolysis data are more complex and, besides cation stability and steric effects associated with $sp^3 \rightarrow sp^2$ hybridization changes, are also concerned with internal return (ion-pairing), stereoelectronic participation, solvent effects, leaving group effects, etc., as witnessed by comparing *exo*- and *endo*-2-norbornyl solvolysis rates (which lead to the same cation). The equilibrium method described in this work is restricted at present to subtle comparisons such as cyclopentyl vs. 2-norbornyl in cations **9** $\rightleftarrows$ **10**. Eventually, of course, one could probably devise overlapping equilibria which would allow one to compare quantitatively all of the "systems" looked at in this study, as well as a host of others.

An even better approach is suggested by the elegant work of Arnett and co-workers (2), who have developed calorimetric techniques to measure cation stabilities, including methods for measuring the heat of isomerization of cations, e.g. 4-methyl-2-norbornyl → 2-methyl-2-norbornyl (22). The cations described in this work which are related by 1,4-H shifts rearrange slowly enough to be potential candidates for such calorimetry. Direct K (ΔG) measurements and $\Delta H_{\text{isom.}}$ measurements tend to be complementary techniques, since the latter are best applied where energy differences are relatively large, the former where they are small.

With regard to comparisons to gas-phase ion work, we do not feel that we have enough data yet to make very many meaningful comparisons, i.e. the effect of solvation on cation stabilities.

Discussion of the nmr methods used to determine K

As mentioned in the Introduction, three ^{13}C nmr methods were used in determining K (methods A, B, and C).

Method A

For the 1,2-hydride shift equilibria ($n = 0$ case), the associated rate constant is very fast over the temperature range of our measurements. One sees only averaged spectra for ions **I** and **II**. In those cases where there is no temperature dependence of the chemical shift and where the spectrum "fits" a single isomer, we obviously cannot measure any K value and only a lower limit has been estimated. It does not matter which alcohol one starts with to prepare the cation (both were used for **1***a* $\rightleftarrows$ **2***a* and for **3***a* $\rightleftarrows$ **4***a*) and one has to determine the presence of **I** or **II** from the detailed analysis of the actual ^{13}C shifts (easily done by looking at the methyl signals in ions **1–8**).

A detectable equilibrium for the $n = 0$ case is signalled by noting a temperature dependence for the "averaged" C^+—CH and CH—C^+ carbon peaks in **I–II**, the higher field combination moving downfield on increasing the temperature and the other moving upfield. Other peaks will possibly shift as well but to a much smaller extent. There are four unknowns here: (*1*) the chemical shift separation Δ_1 for the C^+ carbon in **I** and the CH carbon in **II**; (*2*) Δ_2 for the C^+ of **II** and the CH of **I**; (*3*) ΔH (assumed independent of temperature); and (*4*) ΔS. Normally, one assumes that $\Delta_1 = \Delta_2 = \Delta$, and then adjusts Δ to give a good ln K vs. $1/T$ van't Hoff plot, $K = \Delta - \delta/\Delta + \delta$, where δ = the observed separation of the C^+—CH and CH—C^+ peaks at a given temperature.

In the cyclohexyl vs. dimethyl case, ions **1***a* $\rightleftarrows$ **2***a*, there is no question but that an observable equilibrium exists. The data for these ions are shown in Table 7.

The best fit van't Hoff plot gives $K = 0.045$ at $-105°C$, $\Delta H = 1.2$ kcal/mol, and $\Delta = 254$ ppm (Fig. 1). Since the peaks being averaged in Table 7 are ca. 5700 Hz apart, the temperature dependence is large. For the remaining peaks in **1***a*–**2***a*, only small changes are observed (nevertheless providing enough information to assign **1***a* as the major species).

The data for the cyclopentyl vs. dimethyl case, ions **3***a* $\rightleftarrows$ **4***a*, are shown in Table 8. A van't Hoff plot gives $\Delta = 285$ ppm, $K = 25$ at $-105°C$, and $\Delta H = -1.9$ kcal/mol. One has uncertainties in K because this number is very dependent on the Δ value used.

As expected, there are situations, for example **3***d* $\rightleftarrows$ **4***d*, where one sees even smaller changes and in the right directions. One knows that K cannot be smaller than a certain value but one cannot be very certain that the actual value calculated is correct. In general, one should be able to detect K's between 200 and 0.005 by this procedure but the confidence factor will be lower as one approaches these extremes.

TABLE 7. Chemical shift values for the averaged C^+—CH and CH—C^+ peaks in $1a \rightleftarrows 2a$[a]

	^{13}C shift (ppm)		
Temperature (°C)	C^+ (1*a*)—CH (2*a*)	C^+ (2*a*)—CH (1*a*)	δ separation (ppm)
−133	320.9	77.3	243.6
−126	319.5	78.2	241.3
−116	317.7	80.0	237.7
−105	314.9	82.8	232.1
−96	313.3	84.7	228.6
−84	310.2	87.5	222.7

[a]Saunders and Lloyd have also looked at this equilibrium and the one shown in Table 8; their results are similar to ours (ref. 45, ref. 46, footnote 31).

TABLE 8. Chemical shift values for the averaged C^+—CH and CH—C^+ peaks in $3a \rightleftarrows 4a$

	^{13}C shift (ppm)		
Temperature (°C)	C^+ (4*a*)—CH (3*a*)	C^+ (3*a*)—CH (4*a*)	δ separation (ppm)
−128	336.2	60.5	275.7
−116	333.1	63.5	269.6
−105	329.1	66.8	262.3

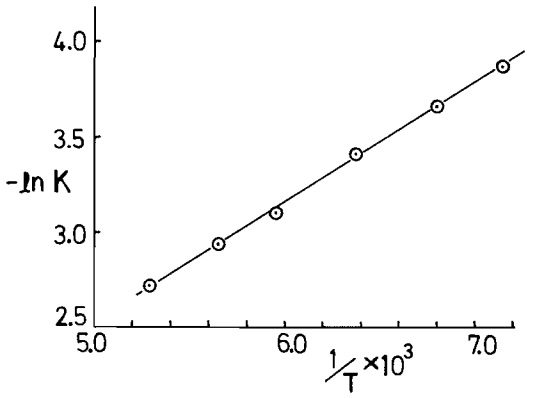


FIG. 1. Van't Hoff plot for the equilibrium $1a$–$2a$, using the data in Table 7.

For the single $n = 3$ case studied, ions $1d \rightleftarrows 2d$, a 1,5-hydride shift is involved. Over a large temperature range from about −80 to −120°C, intermediate exchange kinetics made the averaged C^+—CH and CH—C^+ signals too broad to detect. Eventually, at about −70°C, they sharpen sufficiently to detect and using nmr method A, an equilibrium constant was calculated.

Standard deviation type errors for method A are very small.

Method B

Equilibrium in the $n = 1$ cases involves a 1,3-hydride shift. From previous work by Brouwer and Saunders (11, 12), it was expected that these shifts would be moderately fast on the nmr time scale (very fast on a conventional kinetic time scale). Consequently, either of the alcohols related, for example, to cations **1***b* and **2***b* can be used to prepare the equilibrium mixture. To determine the equilibrium constant, one could in principle use methods A, B, or C (see subsequent discussion). However, the temperature where averaged spectra would be obtained (method A) is too high for the survival of any of the cations studied in this work. Method C will apply at low temperatures under "frozen-out" exchange conditions. This procedure is the method of choice where both isomers can in fact be detected, but only in the cyclohexyl vs. dimethyl case (**1***b*–**2***b*) was this situation found. In all other cases, we have applied (or tried) method B.

Method B involves cases where one sees only one isomer at low temperatures (frozen-out conditions). As one warms the solution, one looks for line-broadening due to exchange with the "hidden" equilibrium partner. This method has been discussed in detail elsewhere (13). Cations **I** ⇄ **II** are particularly suitable for such a treatment if one focuses on the C^+ and CH carbons of the major isomer. The corresponding minor exchange partners (CH and C^+ respectively) are separated by about 6000 Hz in each case (there is very little uncertainty involved in estimating this separation using model systems). Since the potential line-broadening is a linear function of this separation, one should see *selective* broadening of these two peaks and much smaller changes, if any, in the others. In addition, these peaks should resharpen at still higher temperatures. This method is capable

of detecting much larger or smaller K's than either A or C, and this is nicely shown in the 2-adamantyl vs. dimethyl case, ions **7***b* ⇄ **8***b*. In this system, the peaks for the C^+ and CH (in isobutyl) carbons each reach a maximum broadness, in excess of the natural line-width, of ca. 20 Hz at −79°C, corresponding to a K of ca. 330. The rate constant for **8***b* → **7***b* is ca. 120 s^{-1}, $\Delta G^{\ddagger} = 9.3$ kcal/mol at −79°C. No other peaks are significantly broadened and a subsequent resharpening of the C^+ and CH carbon peaks was also observed. Selected spectra are shown in Fig. 2.

This method is quite capable of detecting K's between 1000 and 0.001 using a 22.63 MHz instrument (and even wider ranges with higher fields). In those cases where we still have detected no line-broadening, e.g. 2-norbornyl vs. dimethyl, **5***b* ⇄ **6***b*, one can place a lower limit on K *providing one is willing to accept that we have passed through a temperature where the equilibrium rate would have maximized the line-broadening if it had been detectable*. In the two cases where detectable changes were observed, $\Delta G^{\ddagger}$ for the 1,3-hydride shift was 8.9 and 9.3 kcal/mol (cf. 8.5 for the 2,4-dimethylpentyl cation) (11). It therefore appears reasonable to expect a similar $\Delta G^{\ddagger}$ (and temperature of maximum broadness) for all of these ions, particularly since the 1,3-hydride shift is not constrained by unfavorable geometries.

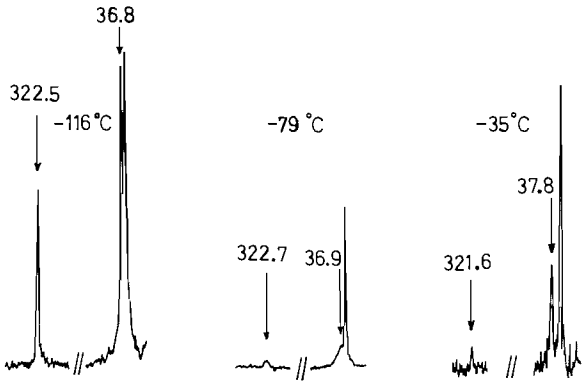


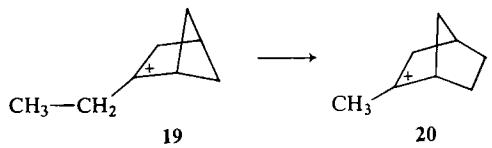
FIG. 2. Three (partial) ^{13}C nmr spectra of cation **8***b* taken at three temperatures (others are not shown). The spectrum at the left is the "frozen out" spectrum of **8***b* showing the C^+ and isobutyl CH peaks. The spectrum at −79°C (maximum broadness) shows the *specific* line-broadening caused by the dynamic exchange with cation **7***b* (which is "hidden" in the spectrum at −116°C because its concentration is very small). The peak to the right of the one at 36.9 (C_6) is included in the diagram to illustrate that the other peaks in **8***b* are *not* broadened. At −35°C, the peaks are "resharpened" and are from the averaged **7***b*–**8***b* situation. However, they have remained at almost the same chemical shift because of the very small concentration of **7***b* involved here.

In the case of the cycloheptyl vs. dimethyl cation, we were unable to reach −80°C (ring-contraction), so this can place a restriction on the use of method B.

Method B requires some faith that one understands the rearrangement under consideration since, as mentioned, one often does not directly "see" the minor equilibrium partner. However, the selectivity involved in the line-broadening would be very difficult to interpret in any alternative way and we believe that this method has a good confidence factor over the K range that we quote. The error limits are probably within ±20% of the quoted K values.

Method C

Equilibrium via a 1,4-hydride shift (either direct or a combination of 1,2-shifts) was already known from model systems to be a slow process on an nmr time scale (11). Therefore, this nmr method is simply involved in trying to "see" peaks from both isomers. Ultimately for large or small K's the limitation is determined by signal/noise considerations. In order to verify that a 1,4-shift is reasonably fast on a conventional kinetic time scale, we prepared both alcohols related to cations **1***c* and **2***c* and to **3***c* and **4***c* and found the same ^{13}C nmr spectrum for the ions at −100°C, i.e. equilibration has occurred. The equilibration reaction was directly observed in the case of **9** ⇄ **10** and **11** ⇄ **12**, where the less stable cations **9** and **11** were first prepared at −120°C and the isomerization to **10** and **12**, respectively, could be followed at ca. −90 to −100°C. That **10** and **12** are the species formed is clear from a detailed analysis of the ^{13}C peak positions and comparisons to the ^{13}C shifts and reactivity of model systems, for example, the ring expansion of **11** was shown to be slow by preparing the 2-ethyl-2-bicyclo[2.1.1]hexyl cation **19** and noting that the quantitative expansion to the 2-methyl-2-norbornyl cation **20** occurred only at much higher temperatures than that involved in a 1,4-hydride shift.



19 **20**

In the case of cations **3***f*–**4***f*, **3***i*–**4***i*, **5***c*–**6***c*, and **7***c*–**8***c*, only one species was observed, but one can confidently presume equilibration conditions were present based on the near constancy of the 1,4-hydride shift rate in the four cases where this was checked.

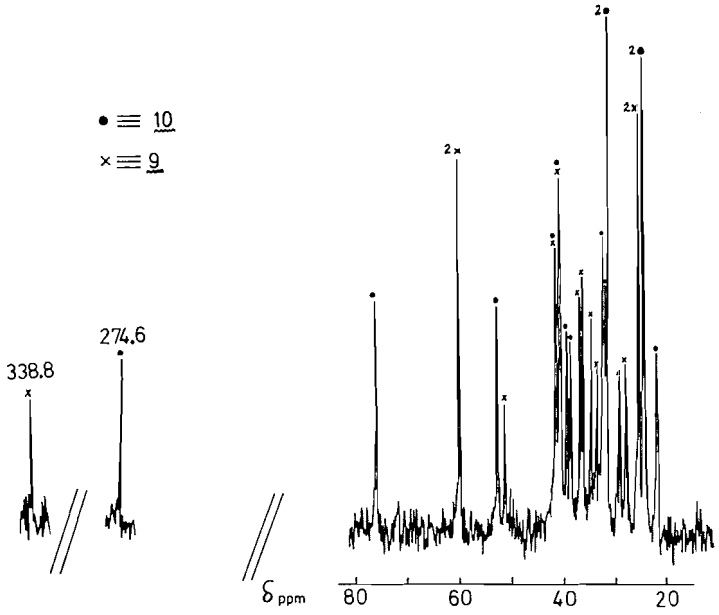
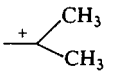


FIG. 3. Illustration of the "Method C" procedure for determining K values. This spectrum (1000 scans at −90°C) was recorded at an intermediate point in the rearrangement of **9** to **10** to show the "fingerprinting" capabilities of the ^{13}C nmr spectra (only two lines are overlapped in the two ions). With longer times, the **9** ⇄ **10** equilibrium is reached.

The S/N limits for the *absence* of detectable amounts of the minor partners in the above cases employed a search for the characteristic methyl signals from



which occur (or would occur) at about 45 ppm, a region fairly free of other ^{13}C peaks. In most cases, spectra were obtained after about 4000 accumulations, which has sufficient S/N to place an upper limit of about 3% on the maximum possible minor isomer. Thus, this method is not as sensitive as A or B, depending of course on how many accumulations one is able or willing to obtain.

Where equilibrium constants can be measured, one has a high confidence rating. For example, in ions **9** and **10**, there are fourteen peaks possible for each ion and in mixtures, twenty-two of these are completely resolved, i.e. "fingerprinting" comparisons have numerous peaks to use. This is shown in Fig. 3. The error limits are probably within ±10% of the reported K values.

Carbocation structures

All of the ions prepared in this work are new, but in all cases, the corresponding methyl-substituted species has been reported. In the ions prepared in this work, only in the case of cation **4***g* are any anomalies noted in the expected (based on the methyl-substituted species) ^{13}C peak positions and this case has been discussed elsewhere (23). The ^{13}C shifts which are relevant to determining K's or for structure assignment are given in Table 9.

Like the methyl analog, the cyclohexyl cations show evidence of a chair – twist boat conformational equilibrium and the cyclooctyl cations show a conformational line-broadening for some of the ^{13}C peaks.

Carbocation rearrangements

All of the cations eventually irreversibly rearrange. In the monocyclic cations, ring expansions or contractions readily occur, leading to cyclohexyl cations. Thus, none of the cyclobutyl ions could even be prepared, the cyclopentyl cations ring expand at ca. −80°C, a rate rather similar to the simple 1-ethyl analog (24), the cycloheptyl cations readily contract at about −90°C to −100°C, again similar to the 1-methyl analog (24), and the cyclooctyl cations also ring contract. In most cases, the products of these reactions were the same 1-isoalkylcyclohexyl cations which had already been characterized.

The 2-norbornyl cations are stable to about −30°C and the initial ring-expanded product is likely a 2-bicyclo[2.2.2.]octyl cation system. The 2-adamantyl cations are also stable to about −30°C. In the one case where rearrangement peaks were recorded, peaks characteristic of 1-adamantyl

TABLE 9. Diagnostic ^{13}C chemical shifts in the carbocations which were used to identify or calculate equilibrium constants

Cation	^{13}C chemical shifts and assignments	T (°C)[m]	Comments
1*a*–**2***a*	See Table 7		
1*b*	331.3 (C^+), 46.1 (CH_3's), 42.9 (CH)	−113	*a*
2*b*	328.4 (C^+), 22.9 (CH_3's), 31.4 (CH)	−113	*a*
1*c*	332.9 (C^+), 38.2 (CH), 45.2 (CH_3's)	−119	*b*
2*c*	328.6 (C^+), 29.3 (CH), 22.2 (CH_3's)	−119	*b*
1*d*–**2***d*	~204 (broad), ~160 (broad), 32.0 (CH_3's)	−74	*c*
3*a*–**4***a*	See Table 8		
4*b*	337.1 (C^+), 30.8 (CH), 22.5 (CH_3's)	−112	*d*
4*c*	338.1 (C^+), 28.2 (CH), 21.7 (CH_3's)	−116	
3*d*–**4***d*	331.1 (C^+—CH), 58.4 (CH—C^+), 21.7 (CH_3's)	−123	*e*
4*e*	327.3 (C^+), 32.0 (CH), 23.0 (CH_3's)	−124	*f*
4*f*	332.8 (C^+), 28.7 (CH), 21.9 (CH_3's)	−117	
4*g*	313.7 (C^+), 53.7 (CH), 25.3 (CH_3's)	−93	*g*, *h*
4*h*	333.5 (C^+), 23.1 (CH_3's)	−89	*h*
4*i*	331.8 (C^+), 30.6 (CH), 21.8 (CH_3's)	−81	*h*
6*a*	269.0 (C^+), 76.6 (C-1), 41.7 (CH of *i*Pr), 20.7 (CH_3's)	−80	*i*
6*b*	278.2 (C^+), 77.1 (C-1), 29.4 (CH of *i*Bu), 22.4, 22.6 (CH_3's)	−95	*i*
6*c*	275.0 (C^+), 76.4 (C-1), 28.4 (CH of *i*Pent), 21.9 (CH_3's)	−87	*i*
8*a*	319.2 (C^+), 54.3 (CH of *i*Pr), 19.0 (CH_3's)	−109	
8*b*	322.7 (C^+), 36.9 (CH of *i*Bu), 24.1 (CH_3's)	−79	*j*
8*c*	320.5 (C^+), 30.3 (CH of *i*Pent), 22.0 (CH_3's)	−105	
9	338.8 (C^+), 60.9 and 26.4 (both 2C), α and β-C of C-5 ring	−80	
10	274.6 (C^+), 76.7 (C-1 of 2-norbornyl), 25.4 and 32.5 (both 2C), α and β-C of neutral C-5 ring	−80	
11	326.4 (C^+), 79.4 (C-1 of bicyclo[2.1.1.]hexyl)	−100	*k*
12	275.1 (C^+), 76.7 (C-1 of 2-norbornyl)	−90	*k*
14	276.6 (C^+), 76.4 (C-1 of 2-norbornyl), 20.1 (C-6 of a neutral bicyclo[3.2.1]octyl system)	−90	*l*
15	333.8 (C^+), 61.9 (C-1 of 2-bicyclo[2.2.2]octyl), 29.5 and 23.7 (both 2C), the C-6, C-7 and C-5, C-8, carbons of the 2-bicyclo[2.2.2] system	−108	
19	329.1 (C^+), 78.8 (C-1), 57.1 (C-5, C-6), 55.7 (CH_2 of Et), 48.3 (C-3), 36.2 (C-4), 9.1 (CH_3 of Et)	−90	

[a]Dynamic line-broadening occurs at higher temperatures due to the **1***b* ⇄ **2***b* rate process becoming fast on the nmr time-scale.
[b]At other temperatures one sees changes in the ratio of **1***c* and **2***c*.
[c]The methyl carbons move to lower field at lower temperatures, indicating that while enthalpy favors **1***d*, entropy favors **2***d*.
[d]The C^+ and CH peaks did not broaden up to −85°C.
[e]Total chemical shift vs. temperature changes were only about 2 ppm over a 25°C span.
[f]Rearranges before the temperature needed for the 1,3-H-shift to show dynamic nmr line-broadening.
[g]See ref. 23 for a full description of this system.
[h]A dynamic chair–twist boat ⇄ twist boat–chair conformational interchange broadens some of the peaks. See ref. 14 for an analysis of the 1-methyl analog.
[i]Line-broadening, due to the well-known (25) 6,2-H-WM-6,2-H rearrangement, begins to show up at the higher temperatures.
[j]See Fig. 2, showing the line-broadening due to the exchange with the "hidden" **7***b*.
[k]See Fig. 3, showing an intermediate spectrum in the rearrangement of **11** to **12**.
[l]The peak at δ 20.1 is not compatible with a bicyclo[2.2.2]octane ring (26).
[m]In all cases, the spectra were also run at a number of other temperatures.

cations were observed, although the rearrangement appears to be "deep-seated".

Experimental

General procedures

Mass spectra were obtained on a Varian CH-5 mass spectrometer. ^1H nmr spectra of neutral precursors were obtained on a Varian HA-100, Varian A-60, or Hitachi Perkin-Elmer R24B spectrometer. ^{13}C nmr spectra were obtained using a Bruker WH-90 or Varian XL-200 spectrometer, in $CDCl_3$ unless otherwise stated. Boiling points and melting points are uncorrected.

Preparation of alcohol precursors

Alkyl lithium reagents were prepared by standard procedures. The appropriate ketone, dissolved in ether, was added dropwise under argon at 0°C and then the mixture was refluxed for several hours. After work-up, the alcohols were isolated by fractional distillation. Yields using isopropyl lithium were generally poor (enolization) but purity of product was the main concern. ^{13}C and/or ^1H nmr spectroscopy and mass spectrometry were used to characterize the liquid products and to check the alcohol purity.

1-(1-Methylethyl)-1-cyclobutanol, bp 51°C/12 mm, *m/e* = 114.

1-(1-Methylethyl)-1-cyclopentanol, bp 63–66°C/11 mm, lit. (27), 53°C/6 mm, ^{13}C nmr ($CFCl_3$): δ 84.9, 38.8, 37.8, 24.4, and 18.0.

1-(1-Methylethyl)-1-cyclohexanol, bp 70–77°C/11 mm, lit. (27), 77°C/13 mm, ^{13}C nmr ($CFCl_3$): δ 72.8, 38.3, 34.7, 26.5, 22.3, and 17.0.

1-(1-Methylethyl)-1-cycloheptanol, bp 42°C/0.09 mm, lit. (28), 96°C/12 mm, ^{13}C nmr ($CFCl_3$): δ 76.9, 39.7, 38.8, 30.2, 23.3, and 17.7.

1-(1-Methylethyl)-1-cyclooctanol, bp 133–135°C/26 mm, reported in patent literature (29), ^{13}C nmr ($CFCl_3$): δ 75.5, 36.2, 34.7, 28.5, 25.5, 22.5, and 17.0.

2-(1-Methylethyl)-2-bicyclo[2.2.1]heptanol, bp 85–89°C/13 mm, *m/e* = 154, reported with no details (30), ^{13}C nmr ($CFCl_3$): δ 81.3, 45.8, 44.9, 39.0, 38.0, 36.7, 28.6, 23.3, 17.7, and 16.3.

2-(1-Methylethyl)-2-tricyclo[3.3.0.0^{3,7}]decanol, mp 59°C, lit. (31), 72.8–73.8°C, ^{13}C nmr ($CFCl_3$): δ 75.4, 39.0, 35.2, 34.4, 33.8, 30.0, 27.8, and 15.5.

Isobutyl lithium reactions also gave generally poor yields

because of the facile reduction of ketones by this particular reagent.

1-(2-Methylpropyl)-1-cyclobutanol, bp 58°C/10 mm, *m/e* = 128.

1-(2-Methylpropyl)-1-cyclopentanol, bp 69–71°C/10 mm, lit. (32), 120°C/22 mm, ^{13}C nmr ($CFCl_3$): δ 82.6, 50.9, 40.8, 25.3, 24.8, and 23.9.

1-(2-Methylpropyl)-1-cyclohexanol, bp 80–83°C/10 mm, lit. (32), 95°C/15 mm, ^{13}C nmr ($CFCl_3$): δ 71.7, 52.3, 38.5, 26.3, 25.1, 23.8, and 22.6.

1-(2-Methylpropyl)-1-cycloheptanol, bp 98–102°C/10.5 mm, lit. (32), 120°C/16 mm.

1-(2-Methylpropyl)-1-cyclooctanol, bp 116–118°C/9 mm, *m/e* = 184.

2-(2-Methylpropyl)-2-bicyclo[2.2.1]heptanol, bp 91–93°C/10 mm, *m/e* = 168.

2-(2-Methylpropyl)-2-tricyclo[3.3.0.0^{3,7}]decanol, mp 51°C, lit. (33), 57°C.

Isopentyl alcohols were prepared using the Grignard reagent or where noted, the lithium reagent, and yields were good in most cases.

1-(3-Methylbutyl)-1-cyclobutanol, isolated on a small scale by molecular distillation, bath temperature 50–75°C at 10 mm, *m/e* = 142, ^{13}C nmr: δ 75.8, 37.5, 36.0, 32.5, 28.5, 22.7, and 12.3.

1-(3-Methylbutyl)-1-cyclopentanol, bp 88–89°C/11 mm, *m/e* = 156, ^{13}C nmr: δ 82.5, 39.7, 39.3, 33.8, 28.6, 23.9, and 22.7.

1-(3-Methylbutyl)-1-cyclohexanol, bp 60–62°C/0.025 mm, reported in patent literature (34), ^{13}C nmr: δ 71.4, 40.2, 37.5, 32.0, 28.6, 26.0, 22.7, and 22.4.

1-(3-Methylbutyl)-1-cycloheptanol, using Li reagent, bp 115–121°C/10 mm, reported in patent literature (29).

1-(3-Methylbutyl)-1-cyclooctanol, using Li reagent, bp 86–92°C/0.25 mm, *m/e* = 198.

2-(3-Methylbutyl)-2-bicyclo[2.2.1]heptanol, bp 58–60°C/0.05 mm, *m/e* = 182, ^{13}C nmr: δ 79.5, 46.8, 45.8, 40.2, 38.7, 37.2, 32.3, 28.6, 22.7, and 22.2.

2-(3-Methylbutyl)-2-tricyclo[3.3.0.0^{3,7}]decanol, using Li reagent, mp 65°C, *m/e* = 204 (M − 18).

Cation solutions **1***a*–**2***a*, **1***c*–**2***c*, **3***a*–**4***a*, and **3***c*–**4***c* were also prepared from the corresponding sidechain alcohols.

2-Cyclohexyl-2-propanol, bp 76–78°C/9 mm, lit. (27), 85°C/15 mm, ^{13}C nmr ($CFCl_3$): δ 72.5, 50.0, 28.1, 27.3, and 27.2.

4-Cyclohexyl-2-methyl-2-butanol was prepared from 3-cyclohexylpropanoic acid by reaction of the acid chloride with 2 mol of methyl lithium, bp 108–110°C/11 mm, lit. (35), 96–97°C/7 mm.

2-Cyclopentyl-2-propanol, bp 35–36°C/0.35 mm, lit. (27), 50°C/3 mm, ^{13}C nmr ($CFCl_3$): δ 71.9, 51.8, 28.4, 27.7, and 26.6.

4-Cyclopentyl-2-methyl-2-butanol, prepared like the cyclohexyl analog, bp 90–93°C/11 mm, *m/e* = 138 (M − 18).

Cation **1***d*–**2***d* solutions were prepared from *5-Cyclohexyl-2-methyl-2-pentanol*, bp 70–76°C/0.09 mm, ^{13}C nmr ($CFCl_3$): δ 70.5, 44.7, 38.5, 38.1, 33.9, 29.4, 27.0, 26.8, and 22.0. This alcohol was prepared from the known (36) 3-cyclohexyl-1-bromopropane and acetone via the lithium reagent of the former.

Cations **9** and **10** both originated from the alcohol related to **9**.

*1-[2-(*exo*-2-bicyclo[2.2.1]heptyl)ethyl]-1-cyclopentanol*, bp 125–130°C/0.5 mm, solidifying at 25°C. *Anal.* calcd. for $C_{14}H_{24}O$: C 80.7, H 11.6; found: C 80.9, H 12.0. This alcohol was prepared by adding cyclopentanone at 0°C to the Grignard reagent from 1-bromo-2-(*exo*-2-bicyclo[2.2.1]heptyl)ethane and was formed in near quantitative yield.

*1-Bromo-2-(*exo*-2-bicyclo[2.2.1]heptyl)ethane*, bp 45–46°C/0.6 mm, was prepared from the known (37) alcohol (Br_2, triphenylphosphine, in acetonitrile) (38). In our case, the alcohol was prepared by esterification and $LiAlH_4$ reduction of the commercially-available carboxylic acid. The bromide had ^{13}C nmr: δ 62.4 (CH_2—Br), 40.8 (CH), 40.0 (CH_2), 37.6 (CH_2), 36.5 (CH), 35.5 (CH), 32.0 (CH_2), 30.0 (CH_2), and 28.7 (CH_2).

*2-[2-(*exo*-2-Bicyclo[2.2.1]heptyl)ethyl]-2-bicyclo[2.1.1]hexanol* was prepared like the cyclopentyl analog and was used to prepare both cations **11** and **12**, bp 103–106°C/0.3 mm, solidifies to a slightly oily solid at 25°C. *Anal.* calcd. for $C_{15}H_{24}O$: C 81.8, H 11.0; found: C 82.0, H 11.6. The alcohol is expected to be a mixture of two diastereomers and the ^{13}C nmr spectrum indicates this. The 2-bicyclo[2.1.1]hexanone was prepared by the method of Bond (39).

*6-[2-(*exo*-2-Bicyclo[2.2.1]heptyl)ethyl]-6-bicyclo[3.2.1]octanol* was prepared like the cyclopentyl analog using 6-bicyclo-[3.2.1]octanone (40) as the ketone, bp 128–140°C/0.6 mm, solidifies at room temperature. *Anal.* calcd. for $C_{17}H_{28}O$: C 82.2, H 11.5; found: C 82.0, H 11.7. This alcohol is likewise a mixture of diastereomers, but is expected to have the *endo*-alcohol configuration at C-6 (40).

Preparation of the cations

All of the cations were prepared by adding the weighed alcohol (80–200 mg dissolved in 200–500 μL of $CFCl_3$) to 2 mL of a 1:4 mixture of Magic acid (1:1 SbF_5–FSO_3H) and SO_2ClF. The acid solution was cooled to ca. −130°C in a liquid N_2 slush bath prior to the alcohol addition. In all cases, except the cyclobutanols, carbocations were obtained with unrearranged alcohol carbon skeleton (although H-shifts often occurred). 1-(1-Methylethyl)-1-cyclobutanol gave the 1,2-dimethylcyclopentyl cation (41), 1-(2-methylpropyl)-1-cyclobutanol gave mainly the cations **3***a*–**4***a*, and 1-(3-methylbutyl)-1-cyclobutanol gave **1***a*–**2***a* cleanly.

Nuclear magnetic resonance spectra of the cations

All ^1H and ^{13}C nmr spectra were obtained on a Bruker WH-90 FT-NMR spectrometer and previously described procedures were used for temperature calibration, lock, etc. (14). ^1H nmr spectra were obtained in a few cases but are not very useful for determining *K* values and are not further reported. ^{13}C nmr spectra were obtained at approximately 10–15°C intervals and generally involved about 4000 accumulations. Complete ^{13}C assignments were made for each cation, except for **11**, **12**, **14**, and **15** which are very complex, from off-resonance spectra and comparisons to the known 1-methyl analogs. Table 9 records the peaks of importance to the actual or attempted *K* determinations. Complete ^{13}C nmr assignments are available on request or are in the thesis of N.E.O. Any special observations on the ^{13}C spectra, such as dynamic line-broadening, are given in Table 9. Nuclear magnetic resonance procedures used to determine the *K*'s have already been discussed.

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