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A Study of Multiple Ring Expansion and Ring Contraction Rearrangements in Observable Cycloalkyl Cations

Roger P. Kirchen, Ted S. Sorensen,* and Kim E. Wagstaff

Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4. Received December 30, 1977

Abstract: Tertiary cycloalkyl cations involving ring sizes $n = 4$ (small ring), $n = 5$–7 (common ring), $n = 8$–11 (medium ring), and $n = 12$–20 (macroring) have been prepared. These cations have been found to undergo a very general ring expansion or contraction reaction, often in a multiple or repetitive sense. These rearrangements are facile at temperatures varying between -70 and $-100\ °C$ and have activation barriers from 12 to 15.5 kcal/mol. Two regions of thermodynamic stability were found, the cyclohexyl ring and macrorings where $n > 14$ carbons. The cyclodecyl ring system sits on the energy watershed with some molecules contracting (40%) and others expanding (60%). The cyclododecyl ring system was found to be an excellent starting point for expansions to very large ring cations, involving the incorporation of up to eight carbon atoms, and some potential exists for the use of this procedure in the synthesis of large rings.

Carbocyclic ring expansion or contraction processes are a common feature of organic chemistry.[1] Many of these rearrangements occur by way of carbocation intermediates and are therefore of interest in "observable carbocation studies" where the kinetics and thermodynamics of the actual expansion or contraction step can be directly probed.

There have been a number of observable ion studies involving ring interconversions among alkyl-substituted cycloallyl cations $(C_nH_{2n-3}{}^+)$[2] but surprisingly few investigations involving the corresponding cycloalkyl cations $(C_nH_{2n-1}{}^+)$.[3]

Particularly attractive targets for further study are the 1-*n*-alkylcycloalkyl cations **2**, since a plausible mechanism for interconverting these rings has been known for a number of years. In 1968, two groups[4] reported that the *tert*-amyl cation **1** undergoes a three-step degenerate rearrangement (eq 1): (1)

1,2-hydride shift to give a secondary ion, (2) 1,2-alkyl shift within the secondary ion manifold, and (3) 1,2-hydride shift to give back the tertiary ion (overall $\Delta G^{\ddagger} = 14.8$ kcal/mol).

If one now applies this sequence to tertiary cycloalkyl cations **2** (eq 1), one expects to find a *general* ring contraction-ring expansion process, where step 2 involves the actual expansion or contraction. However, even more significant, the mechanism can in principle be repeated and the ring might therefore continue stepwise to either contract or expand until a thermodynamically stable ring size is attained.

A good way of mentally visualizing such multiple rearrangements would be to think of the cycloalkyl ring as a molecular CH_2-chain lasso, with the C^+ center, together with the three-step eq 1 mechanism, functioning as a sort of "slip-knot" (see Figure 1). The incorporation of the end methyl group of the side chain into an expanding ring would be unlikely for both
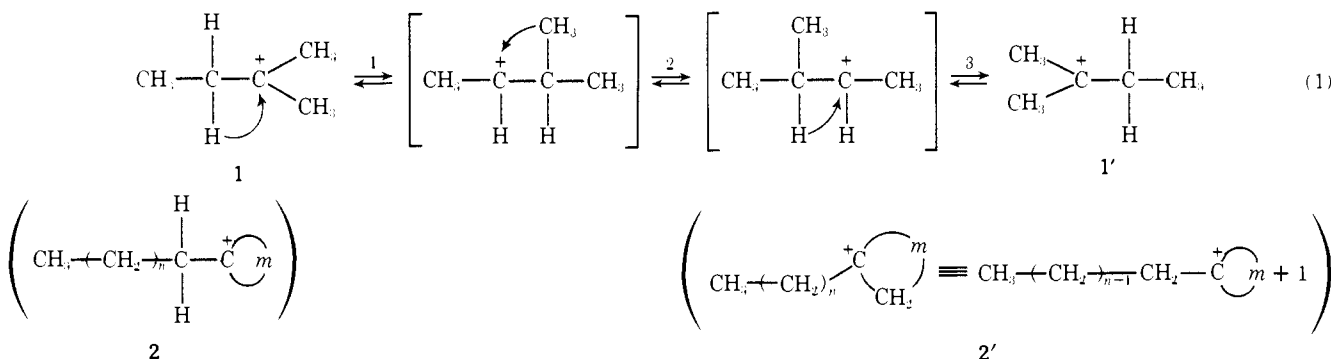
Table I. ^{13}C NMR Chemical Shift Positions in the Cations[a]

cation	temp, °C	C+	α-ring CH₂	α-side chain CH₂	C+- CH₃	C+-CH₂CH₃	C+(CH₂)ₙCH₃ (n ≥ 2)	Others
4+-Pr[b]	−110							
5+-Et	−100	340.2	60.5	47.5		10.0		26.4 (β-CH₂)
6+-Me[c]								
6+-Pr	−100	329.2	56.1	60.8			13.3	26.9 (β-ring CH₂), 20.4, 22.2
6+-Bu[c]								
6+-Pent	−92	327.9	55.9	59.3			14.1	28.0 (β-ring CH₂), 32.1, 27.5, 23.0, 22.4
6+-Hex	−80	328.0	55.0	59.3			14.3	27.7 (β-ring CH₂), 31.9, 29.8, 27.0, 23.2, 22.3
6+-Hept	−79	328.1	55.8	59.3			14.0	27.8 (β-ring CH₂), 32.2, 29.8, 29.6, ca. 27,[d] 23.3, 22.2
7+-Pr	−105	331.6	58.1	62.1			12.9	28.7 (× 2), 25.8 (×2), 20.0
8+-Me[c]								
8-Et	−90	332.5	54.8 (br)[e]	51.5		12.1		37.9, ca. 36.5 (v br),[e] 27.9 (×2),
9+-Me	−100	329.3	59.4		44.8			33.2 (×2), 28.6 (×2), 27.3 (×2)
10+-Me[f]								
10-Et[f]								
10-Pr[f]								
11+-Me[f]								
11+-Et	−105	331.8 (br)[g]	54.6	54.6		12.4 (br)[g]		26.6 (br) (×4)[g]
12+-Me[f]								
12+-Pr	−106	332.0 (br)[h]	57.5	57.5			15.5	30.2 (br) (×3?),[h] 26.5 (br) (×6?),[h] 22.9
13+-Me	−89	325.5	59.8		41.5			28.4 (×2), 27.6 (×2), 24.9 (×4), 24.0 (×4)
13+-Et[j]	−86	331.1	56.5	52.5		9.8		27.4 (×4), 25.0 (×4), 24.1 (×2)
14+-Me[j]	−86	331.0	58.8		44.7			28.3 (×2), 27.4 (×2), 25.9 (×2), 25.4, 22.9 (×4)
14+-Et[k]	−81	331.5	56.2			9.7		
15+-Me	−92	327.4[l]	59.0		42.8			27.7 (×2), 28.2 (×2), 25.1 (×4), 25.4 (×4)

[a] Where useful, multiplicities have been confirmed by off-resonance decoupling experiments; ^{13}C shifts in δ ppm relative to external Me₄Si; double intensity peaks indicated as (×2), etc.; br = broad. [b] Reference 8a. [c] Reference 9. [d] Peak partially obscured. [e] Broad owing to conformational averaging; see ref 9. [f] Reference 10. [g] Most of the peaks in this cation are broad owing to the existence of at least two conformers, interconverting relatively slowly on the NMR time scale; see ref 10. [h] At low temperatures, one sees distinct line broadening, indicative of slow conformational averaging of ^{13}C sites. [j] See Figure 2 for the actual spectrum. [k] This cation was produced from the 15+-Me cation, forming an equilibrium mixture 15+-Me/14+-Et = 2.0. Only the peaks characteristic of 14+-Et are quoted. [l] In ^{13}C-methyl labeled 15+-Me, the ^{13}C+–^{13}CH₃ coupling constant is 31.1 Hz.

Table II. ^{13}C NMR Shifts for Large Ring Expansion Series[a]

```
12+-Pent[b] →  13+-Bu[c]  →  14+-Pr    ⇌  15+-Et   ⇌  16+-Me
  331.0          326.0        329.1        329.1       329.1
  13.9           13.6         13.6         9.7         42.9

12+-Hex  →  13+-Pent  →  14+-Bu   ⇌  15+-Pr[d] ⇌  16+-Et  ⇌  17+-Me
  331.1       326.0        328.6       327.3        330.2      327.7
  14.4                                 13.5         9.7        42.2

12+-Hept →  13+-Hex   →  14+-Pent ⇌  15+-Bu   ⇌  16+-Pr  ⇌  17+-Et  ⇌  18+-Me
  331.0       325.9        328.3       326.5       328.0      330.3      330.1
  14.5                                                        9.7        43.2

12+-Oct  →  13+-Hept  →  14+-Hex  ⇌  15+-Pent  ⇌  16+-Bu   ⇌  17+-Pr  ⇌  18+-Et    ⇌  19+-Me
  331.0       325.3        328.1       326.0 or     327.3 or    ...       330.1 or     329.7 or
  14.5                                 327.3        326.0                 329.7        330.1
                                                                          9.7          42.8

12+-Nonyl →  13+-Oct  →  14+-Hept                                                      20+-Me
  330.9       324.7        328.0  ----------------------------------------------------  ...
  14.6                                                                                 43.5
```

[a] Symbols, etc., as in Table I. The larger number refers to the C+ chemical shift and the smaller number to the CH₃ carbon. Assignments of the C+ chemical shifts are based partly on the sequential appearance of peaks and should be regarded as tentative in a few cases. Additional peaks can be identified, e.g., α-ring CH₂ carbons of the largest ring. [b] The α-ring and α-side chain carbons are readily identified in all of the cyclododecyl cations, occurring about 57.2 and 56.0 ppm, respectively. The higher field region consists of a fairly distinctive pattern of peaks which is similar in the various cations (see Figure 4 for an example). At least one of the side chain carbons has an unusually low field chemical shift, ca. 37.5 ppm. [c] Characteristically, the 12+-cations have the lowest field C+ shift and the 13+-cations the highest. [d] Also prepared from the 15-Pr alcohol.

thermodynamic and kinetic reasons[5] and this entity could therefore be likened to an "end knot". One could therefore *limit* (or control) expansion processes by simply limiting the length of the side chain "rope". For contraction processes, one can start with a simple methyl substituent and it should be noted that one would have no control in this case over the
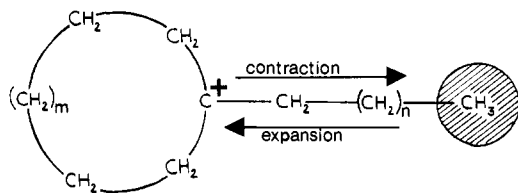
Figure 1. Schematic for general ring expansion and contraction processes in observable cycloalkyl carbocations. The C^+ center functions as a mechanistic "slip-knot" to allow the ring to contract or expand to the most stable size. The methyl group functions as an "end-knot" if the ring expansion proceeds this far.
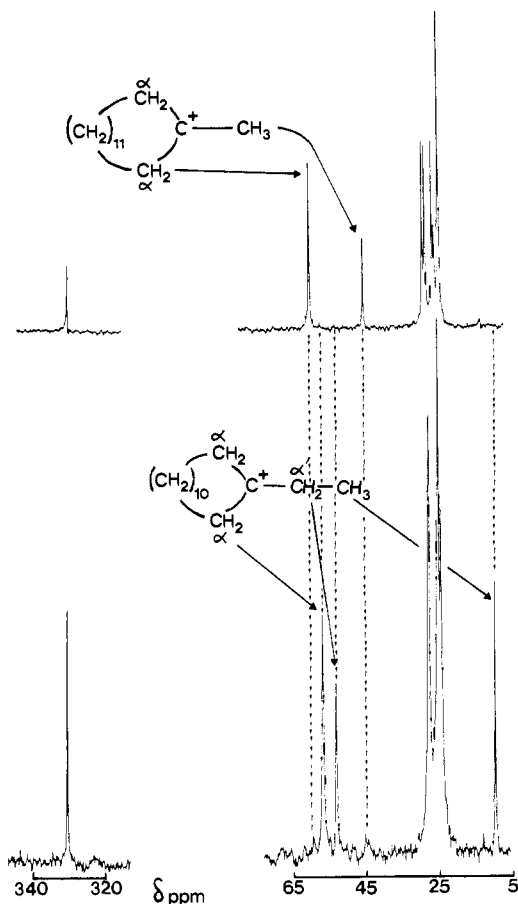

Number Of Carbons In Ring

Figure 3. Schematic summary of the ring contraction and ring expansion reactions observed in this work.

Figure 2. Lower, noise-decoupled ^{13}C NMR spectrum of the 13^+-Et cation. Upper, Noise-decoupled ^{13}C NMR spectrum of the resulting rearrangement product, the 14^+-Me cation.

number of contraction steps since these would simply involve the extrusion of a longer and longer side chain.

We therefore undertook to prepare tertiary cycloalkyl cations from C_4 (cyclobutyl) to C_{20} (cycloeicosyl), with varying linear alkyl side chain substituents (depending upon the particular circumstances), with a view to determining the feasibility and/or generality of these proposed stepwise contraction–expansion processes depicted in eq 1.

When this study commenced, it was by no means certain that one could even prepare the larger ring tertiary cycloalkyl cations,[6] let alone interconvert them. It soon became evident, however, that both these aspects were practical and we therefore extended our studies to the measurement of the kinetics involved in the expansion or contraction processes.

Results

Starting with either the tertiary cycloalkyl alcohol or chloride, depending on the particular case, one can prepare and directly observe all of the initially expected ions (i.e., those from
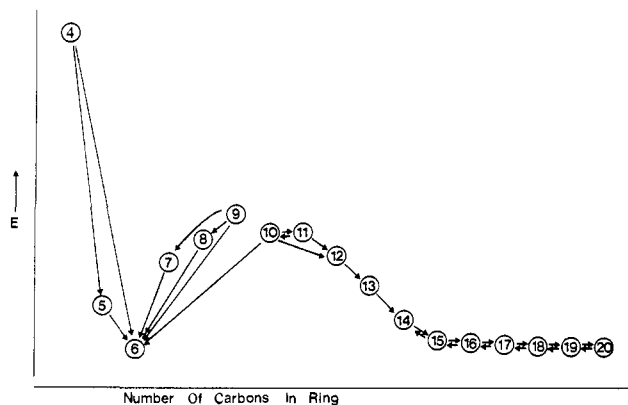
simple solvolysis), if the ion preparation is conducted at sufficiently low temperatures (-120 to -130 °C for the most unstable examples). For ring systems of greater than six carbons, ^1H NMR spectra are virtually featureless so that we have had to rely entirely on ^{13}C NMR spectroscopy both to characterize all of the initially formed ions and to detect and characterize the rearrangement products (and thus also for kinetic measurements). The structures of all of the rearrangement ions were verified by direct comparison to spectra of the authentic cation, except in some cases where the ring size was 16 carbons or greater. Even in these cases, the unique position of certain ^{13}C lines makes the assignments definitive. The ^{13}C peak positions of all of the ions involved in this study are collected together in Tables I and II.

A simple illustrative example of our approach is shown in Figure 2, where the 1-ethylcyclotridecyl (henceforth abbreviated as 13^+-Et) cation (produced directly from the alcohol) expands to 14^+-Me (purposely constrained to one step). This 14^+-Me cation spectrum shows the expected pattern of six double ^{13}C peaks and three singles,[7] with the CH_3 being unique for a ^+C-CH_3 type cation. However, this assignment is then verified by comparing the spectrum to that of the 14^+-Me cation, derived directly from the corresponding alcohol. For kinetic purposes, there are several peaks unique to each ion, e.g., α-ring CH_2, α-side-chain CH_2, and CH_3 of ethyl for the 13^+-Et cation and α-ring CH_2 and CH_3 peaks for the 14^+-Me cation.

A number of the tertiary cycloalkyl cations show interesting properties in themselves; e.g., the cyclobutyl system is unique,[8] the cyclohexyl cations have a twist-boat conformation which is more stable than the chair conformation,[9] the cyclooctyl and cyclodecyl cations show NMR line broadening due to degenerate conformational averaging[9] and the cyclodecyl system shows other peculiarities possibly attributable to transannular interactions.[10] These features have been commented on and only those aspects which relate to the rearrangements will be discussed here.

The Rearrangements. Thermodynamic Aspects. A schematic summary of the various contraction and expansion processes observed in this work is shown in Figure 3. The corresponding kinetic data are collected together in Table III. For rate comparison purposes, we shall be primarily interested in the $\Delta G^{\ddagger}$ activation barrier column.

The data in Table III exemplify the fact that all of the proposed contraction and expansion reactions can indeed be made to occur in a *multiple* rearrangement sense, in most cases quite cleanly. In retrospect, however, we have been very fortunate because there turns out to be very little temperature margin of safety. Thus the slowest rearrangements proceed at a reasonable rate at about -70 °C, but by about -50 °C, most of the larger cations (solutions) show only "baseline-noise" type

Table III. Kinetic Data for the Cation Rearrangements

rearrangement	temp, K	method[a]	k, s^{-1}	$\Delta G^{\ddagger}$ ($\pm$0.2 kcal/ mol)	comments
4^+-Pr $\rightarrow$ 5^+-Et + 6^+-Me	174	A	1.4×10^{-3}	12.3	b
5^+-Et $\rightarrow$ 6^+-Me	214	A	8.4×10^{-4}	15.4	
7^+-Pr $\rightarrow$ 6^+-Bu	185.5	A	8×10^{-4}	13.3	
8^+-Et $\rightarrow$ 6^+-Bu	201.5	A	1.3×10^{-3}	14.3	c
8^+-Me $\rightarrow$ 6^+-Pr	188	AC	3×10^{-4}	13.9	c
9^+-Me $\rightarrow$ 8^+-Et + 7^+-Pr + 6^+-Bu	168	AC	7×10^{-4}	12.1	d
10^+-Me $\rightarrow$ 6^+-Pent	211.5	A	2×10^{-3}	14.8	e
10^+-Et $\rightleftharpoons$ 11^+-Me	188	B	4×10^{-4} (K = 2.0)	13.8	f
11^+-Me $\rightleftharpoons$ 10^+-Et $\xrightarrow{k}$ 6^+-Hex	188	B	1.4×10^{-4}	14.1	f
10^+-Pr $\rightarrow$ 12^+-Me + 6^+-Hept	197	A	2×10^{-3}	13.9	g
11^+-Et $\rightarrow$ 12^+-Me + 10^+-Pr	172	B	1.5×10^{-4}	12.9	h
12^+-Pr $\rightarrow$ 13^+-Et	190	ACM	5.6×10^{-4}	13.8	
13^+-Et $\rightarrow$ 14^+-Me	201	A	2.5×10^{-3}	14.0	j
14^+-Et $\rightleftharpoons$ 15^+-Me	197.5	B	1×10^{-3} (K = 2.0)	14.1	k
12^+-R $\rightarrow$ expansions				$\sim$14–15	l

[a] See Experimental Section for details. Estimated error limits in k have only been incorporated into the $\Delta G^{\ddagger}$ values. [b] Ratio of 5^+-Et/6^+-Me is very variable and seems to be related to the temperature used in the rearrangement. [c] There is a very small concentration of the seven-membered cation present during the actual rearrangements. Small concentrations of isoalkyl side chain cations are also formed in a competitive irreversible process (see ref 12). [d] The approximate ratio of products is 8^+:7^+:6^+ = 38:47:15. [e] Note that this rearrangement could easily be stepwise since the 10^+ $\rightarrow$ 9^+ step is rate determining. [f] The rate quoted is the forward rate constant, 10^+-Et $\rightarrow$ 11^+-Me, employing a computer simulation to obtain the three rate constants for a competitive A $\rightleftharpoons$ B $\rightarrow$ C process. The 10^+ $\rightleftharpoons$ 11^+ equilibrium (K = 2.0) is reached well before the subsequent irreversible conversion to the 6^+-cation is completed. [g] The product ratio is 12^+:6^+ = 3:2. [h] The product ratio is ca. 12^+:10^+ = 3:1. There is a remarkable difference in stability between the 11^+-Me and 11^+-Et cations, relative to the 10^+-Et and 10^+-Pr cations. In the former comparison, an equilibrium, 11^+-Me/10^+-Et = 2.0, is observed, while in the latter, 11^+-Et/10^+-Pr, there is no sign of an equilibrium and K must be less than 0.05. At higher temperatures, the 10^+-Pr cation will, of course, further rearrange to give more 12^+-Me cation and some 6^+-Hept cation. Overall for 11^+-Et, expansion is preferred to contraction by a 9:1 margin. [j] See Figure 2. [k] Measured using labeled 15^+-Me cation (see Experimental Section), employing reversible first-order kinetics. [l] Complex consecutive reactions which were not analyzed in detail (see Figure 4). The 12^+ $\rightarrow$ 13^+ transformation is marginally faster than the subsequent expansions in agreement with the 12^+-Pr results in this table.

spectra indicative of a myriad of rearrangement, cleavage, or oxidative decomposition products.[11] This disappearance of the cycloalkyl cations may be autocatalytic since it seems to occur quite suddenly as one raises the temperature. Additionally, in the cyclooctyl cation contraction (and apparently only here) one sees a minor product indicative of a competing secondary-primary cation contraction process.[12]

In a thermodynamic sense (Figure 3), there are two possible fates for the cations (given sufficient side chain carbons); they either contract or expand to form cyclohexyl cations *or* expand to very large ring cations ($\geq$ 15-ring). The former result is unexceptional and is expected from ring stability considerations and the previous experimental work of Olah;[3] however, the latter result raises some interesting possibilities which will be discussed later. These two regions of stability are not connected in a kinetic or thermodynamic sense since the previously mentioned decomposition occurs at a much lower temperature than that needed to cause the ions to climb over the energy divide separating these regions (from either side). The division between contraction and expansion occurs in the ten-ring cations and can be nicely demonstrated with the 10^+-Pr cation. About 40% of this cation *contracts* to the 6^+-Hept cation and 60% *expands* to the 12^+-Me cation, these processes being irreversible under our operating conditions. The 10-ring and 11-ring cations can be forced to *only* contract by providing a methyl side chain substituent but the 11-ring clearly prefers to expand, given the choice. The 12-ring will *only* expand.

The relative ordering of the cation energies shown in Figure 3 can be directly determined for all expansion processes since, as previously explained, these can be *made* to stop after one expansion, i.e., using an ethyl side chain. Thus, 4^+ $\rightarrow$ 5^+, 5^+ $\rightarrow$ 6^+, 11^+ $\rightarrow$ 12^+, 12^+ $\rightarrow$ 13^+, and 13^+ $\rightarrow$ 14^+. In the contractions, we can be certain that 7^+ $\rightarrow$ 6^+ and that 9^+ $\rightarrow$ 8^+ but there is no direct observation for the 8^+ $\rightarrow$ 7^+ process since kinetically the eight-ring is more stable. The 10^+ $\rightarrow$ 9^+ (?)

situation is similarly unclear, also for kinetic reasons (see Table III). The 10^+ $\rightleftharpoons$ 11^+ cations and all cations with rings of 14 carbons or more exist in an equilibrium situation and one can, of course, directly determine their free-energy differences. These energy differences are dependent on the particular side chain and are discussed in the next section.

The solvolytic behavior of ring systems from 4 to 20 carbons was originally investigated by Prelog[13] and by Brown.[14] Differences in rate are mainly attributable to I-strain factors in the intermediate carbocations. The fact that one can now prepare all of these cations and observe directly the various ring interconversions opens the way for the direct thermodynamic measurements of the corresponding heats of reaction using scanning calorimetry. For example, the methylcyclobutyl cation, in both solvolysis[14] and stable ion work,[8] shows signs of being particularly unstable. A ΔH measurement of the 4^+-Et $\rightarrow$ 5^+-Me rearrangement and comparison to the known thermochemistry of the hydrocarbons should quantify this situation. Similar enthalpy measurements would also allow one to uncover the situation existing in 8^+ $\rightarrow$ 7^+ (?) and 10^+ $\rightarrow$ 9^+ (?), i.e., in the former case by measuring and comparing the ΔH change for 8^+ $\rightarrow$ 6^+ and 7^+ $\rightarrow$ 6^+.

Effect of the Side Chain on the Cation Stabilities. The Potential for a General Ring Expansion Synthesis for Very Large Ring Cations. Cycloalkyl cations up to n = 15 are obtainable from commercially available ketones. To go to larger rings, we decided to test the practicality of expanding 12-ring cations containing long alkyl side chains, making use of our lasso analogy, and the ready availability of cyclododecanone. Our suspicions were that we would obtain rather complex mixtures of ions which would be difficult to characterize. We were therefore rather surprised to find that the expansion reaction proceeds, in all of the cases studied, to give dominantly the largest possible ring, i.e., with a methyl substituent. Thus, the 12^+-Pent cation first gives mainly the 13^+-Bu cation and then
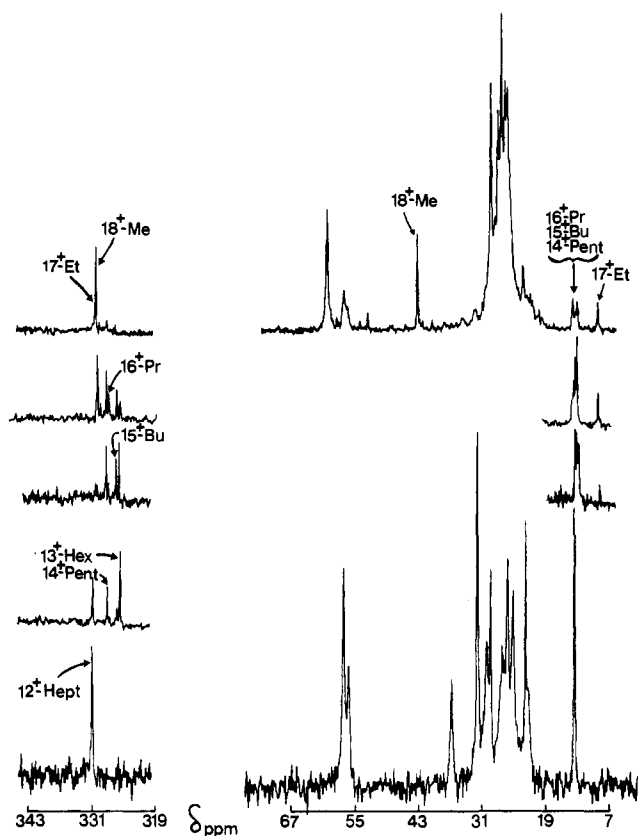
Figure 4. Lower, noise-decoupled ^{13}C NMR spectrum of the 12^+-Hept cation. Upper, noise-decoupled ^{13}C NMR spectrum of the equilibrium mixture containing predominantly the 18^+-Me cation. In the C^+ region, we show various spectra intermediate between the two shown. In the long side chain terminal methyl region, several intermediate spectra are also shown.
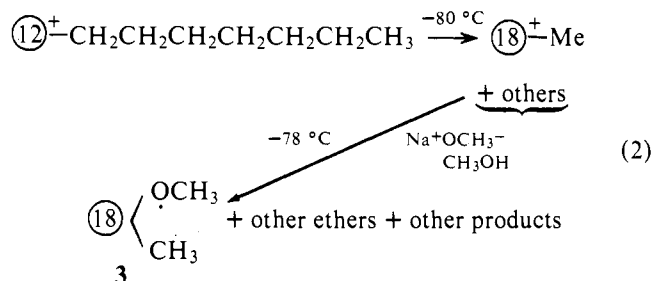
somewhat more slowly and cleanly generates the equilibrium mixture in which the 16^+-Me cation is quite dominant. This same procedure was also used to generate the 17^+-Me, 18^+-Me, 19^+-Me, and 20^+-Me cations, utilizing the appropriate 12^+-ring species. In the 17^+-Me case, we have also determined, as a check, that the 12^+-Hex and 15^+-Pr cations yield the same NMR spectrum. The spectra for the 12^+-Hept–18^+-Me case are shown in Figure 4. In this example, the expansion from the 12-membered ring is consistent with a stepwise process since fortunately one can see distinct C^+ peaks for all of the possible intermediate cations (although there is some doubt over the specific assignment). The positions of these C^+ resonances are shown in Figure 4 and the peaks assigned to the lower rings rise and fall, in sequential spectra, in a manner consistent with stepwise reactions.

In the 12^+-Octyl case, considerable experimental care was needed in order to get reproducible results, since degradation reactions are a constant hazard and finally, in the 12^+-Nonyl case, numerous attempts to obtain "clean" spectra were unsuccessful. One can obtain the 12^+-Nonyl cation very easily and cleanly, but as the solution is warmed, peaks characteristic of degradation products[15] appear simultaneously with peaks characteristic of the expanded rings. In fact, the expanded rings, once formed, seem relatively stable and the problem seems to be one of a competition at the initial 12^+-Nonyl cation stage—either expansion to relatively stable ions or further attack on the 12^+-Nonyl cation (most likely on the side chain) by the strong acid.

If the expansion reactions have gone cleanly, then the specific characterization of the ultimate and penultimate members of these various large ring cations is actually relatively easy

since both the C^+-$^{13}CH_3$ and C^+-CH_2-$^{13}CH_3$ methyl groups occupy unique positions in the ^{13}C spectrum (see Table I). However, the larger the ultimate n ring, the more $n-1$, $n-2$, $n-3$, etc., ions that are possible and, for example, in the 18^+-Me case, one expects to have at equilibrium the dominant 18^+-Me cation, the 17^+-Et cation (uniquely determined), plus 16^+-Pr, 15^+-Bu, and perhaps 14^+-Pent cations. The terminal methyl of the side chain in these latter three ions occupies a nearly identical position (see Figure 4 for an inset spectrum obtained at a time when appreciable concentrations of these "intermediate cations" are present and note the partial resolution found for the terminal CH_3 group). However, these methyls (in toto) occupy a unique position and the total concentration of all of these cations together can be approximately determined.

Quenching the 18^+-Me cation equilibrium mixture in sodium methoxide–methanol solution yields 1-methyl-1-methoxycyclooctadecane (**3**) as the major ether product (see Experimental Section), along with minor amounts of the smaller ring ethers (eq 2).

$$\underset{12}{\textcircled{12}}^{+}\text{-}CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \xrightarrow{-80\ °C} \underset{18}{\textcircled{18}}^{+}\text{-}Me$$

$$\underset{18}{\textcircled{18}}\Big\langle \begin{array}{l} OCH_3 \\ CH_3 \end{array} \quad + \text{ other ethers} + \text{ other products} \tag{2}$$

At first sight, one might conclude from these ring expansion results (i.e., favoring the largest ring) that the rings were simply becoming more stable as they become larger. However, when one looks at the concentrations of the corresponding $(n-1)^+$-Et, $(n-2)^+$-Pr, $(n-3)^+$-Bu, etc., ions (n^+-Me being the maximum size for a given number of carbons), these appear to have somewhat similar concentrations (and hence free energies).[17] One can see this quite well in the 18^+-Me cation case (Figure 4). We have previously observed a number of cases[18] where the stability of alkyl-substituted cations, in equilibrium situations, follows the hyperconjugative order, Me > Et (or n-alkyl) > i-Pr > t-Bu, and the present case seems to be (at least in part) yet another verification of this.

We conclude therefore that for ring interconversions in the 4–14 carbon cations,[19] the inherent ring strain effects are the dominant thermodynamic factor, i.e., the particular alkyl substituent is relatively unimportant. However, with rings from 15 to 20 carbons, the alkyl substituent appears to exert the dominant influence.

Kinetic Results. Activation Energy Differences. For the 5^+ → 6^+ case and for rearrangements of the large rings, e.g., 13^+ → 14^+, $14^+ \rightleftarrows 15^+$, etc., the activation energy barriers, $\Delta G^{\ddagger}$, are similar and in fact very similar to the barrier observed by Saunders and Hagen[4] for the *tert*-amyl case (see Table III). Thus, the barrier of ca. 14–15 kcal/mol appears to be typical for relatively unstrained carbocations. As the ring strain energy increases, the activation barrier generally decreases and among the least thermodynamically stable cations are the four- and nine-ring cases, which are the least stable kinetically and rearrange at a rate about 100 times faster than the "norm".

In most instances, the contraction and expansion reactions appear to occur in a stepwise manner consistent with the eq 1 mechanism. This generalization breaks down, however, in the 9^+-Me contraction and in the 4^+-Pr expansion, where 9^+-Me → 8^+-Et + 7^+-Pr + 6^+-Bu under temperature conditions where the eight- and seven-membered rings are stable. Preliminary investigations[20a] of this mechanism in the 4^+-Pr case implicate two different intermediates, one leading to the 5^+-Et

Table IV. ^{13}C NMR Characterization of the Alcohols and Chlorides[a]

alcohol	solvent	chemical shifts			
		C–O	CH$_3$	α carbons	others
4-Pr	CDCl$_3$	73.4	12.1	36.1 (×2) 42.8	16.6, 14.4
5-Et	CDCl$_3$	82.5	8.7	39.0 (×2) 33.8	23.8
6-Pr	CFCl$_3$	71.3	16.0	37.9 (×2) 45.8	26.6, 22.7 (×2), 16.6
6-Pent	CFCl$_3$	71.4	14.3	38.0 (×2) 43.3	33.2, 26.6, 23.2 (×2), 22.7 (×2)
6-Hex	CFCl$_3$	71.2	14.3	38.1 (×2) 43.5	32.5, 30.7, 26.6, 23.4, 23.2, 22.7 (×2)
6-Hept	CFCl$_3$	71.3	14.3	38.0 (×2) 43.5	32.5, 30.9, 30.0, 26.6, 23.5, 23.2, 22.7 (×2)
7-Pr	CFCl$_3$	75.2	15.0	41.8 (×2) 47.0	30.4 (×2), 23.0 (×2), 17.0
8-Et	CFCl$_3$	74.6	7.7	34.5 36.3 (×2)	28.9 (×2), 25.6, 23.0 (×2)
9-Me	CDCl$_3$	74.3	29.2	35.0 (×2)	27.1 (×2), 21.6 (×2), 19.7 (×2)
9-Me (chloride)	CFCl$_3$	74.7	32.1	37.1 (×2)	27.4 (×2), 21.0 (×2), 20.5 (×2)
11-Et	CFCl$_3$	75.6	7.5	33.6 36.2 (×2)	27.8 (×2), 26.6 (×2), 25.9 (×2), 21.8 (×2)
12-Pr	CDCl$_3$	75.1	14.6	34.4 (×2) 43.3	26.4 (×2), 26.1 (×2), 22.5 (×2), 22.0 (×2), 19.6 (×2), 16.0
12-Pr (chloride)	CFCl$_3$	78.2	14.2	37.1 (×2) 45.4	26.6 (×2), 26.2, 22.9 (×2), 22.5 (×2), 20.7 (×2), 17.5
12-Pent	CFCl$_3$	75.0	14.4	35.1 (×2) 41.6	33.3, 27.1 (×2), 26.6, 23.1 (×4), 22.7 (×2), 20.2 (×2)
12-Hex	CFCl$_3$	75.0	14.5	35.1 (×2) 41.8	32.9, 30.7, 27.3 (×2), 26.6, 23.3, 23.1 (×3), 22.9 (×2), 20.4 (×2)
12-Hept	CFCl$_3$	75.0	14.3	35.0 (×2) 41.6	32.6, 31.0, 30.1, 27.1 (×2), 26.6, 23.4, 23.1 (×3), 22.7 (×2), 20.1 (×2)
12-Octyl	CFCl$_3$	74.9	14.3	35.0 (×2) 41.6	32.5, 31.0, 30.3, 30.0, 27.0 (×2), 26.6, 23.3, 23.1 (×3), 22.6 (×2), 20.1 (×2)
12-Nonyl	CDCl$_3$	75.1	14.0	34.4 (×2) 40.9	31.8, 30.3, 29.6 (×3), 29.3, 26.4 (×2), 26.1, 22.7, 22.5 (×2), 27.1 (×2), 19.6 (×2)
13-Me	CFCl$_3$	73.0	29.6	39.8 (×2)	28.6 (×2), 27.3 (×2), 26.0 (×4), 22.0 (×2)
13-Et	CFCl$_3$	74.7	7.5	33.8 37.5 (×2)	28.6 (×2), 27.3 (×2), 26.1 (×2), 26.0 (×2), 21.6 (×2)
14-Me	CFCl$_3$	72.9	29.8	39.7 (×2)	27.2, 27.0 (×2), 26.6 (×2), 24.6 (×2), 24.2 (×2), 21.4 (×2)
15-Me	CDCl$_3$	73.0	28.9	39.7 (×2)	27.7 (×2), 26.9 (×2), 26.6 (×4), 26.3 (×2), 22.8 (×2)
15-Pr	CFCl$_3$	73.6	14.1	37.9 (×2) 43.2	27.6 (×2), 26.6 (×2), 26.4 (×4), 25.8 (×2), 21.6 (×2), 15.6

[a] In δ ppm from tetramethylsilane.

cation and one "directly" to the 6[+]-Me cation. From the product ratio changes with temperature, the intermediate leading to the 6[+]-Me cation has the lower entropy and must also have a much higher barrier for 1,2 hydride shifts. A protonated cyclopropane intermediate fits both these criteria. Similar complications of the eq 1 mechanism have also been postulated in some acyclic *tert*-alkyl cation rearrangements.[20b]

Experimental Section

Ion Preparations. These general procedures have been described.[9] For the very large carbocations, it was necessary to reduce the total weight of alcohol precursor to 100–125 mg. There appear to be two types of complications which may arise in the large carbocation studies. The first is characterized by the appearance of *tert*-butyl cation peaks (and perhaps extra "area" in the saturated CH$_2$ region) as one goes to higher temperatures. It should be emphasized that, in all cases, results can be obtained without this particular degradation and the unpredictable factors which cause this *t*-Bu[+] formation are

not well understood. However, slow addition of the alcohol to the acid during ion preparation and care in avoiding a film of acid on the upper (uncooled) portion of the NMR tube are sensible precautions. The second complication is more serious and occurs particularly in the 12[+]-Nonyl case. Two peaks appear in the C[+]–[13]CH$_3$ region and one in the C[+]–CH$_2$–[13]CH$_3$ region, together with extra C[+] peaks and others. These results might lead one to erroneously conclude that the 20[+]-Me and 19[+]-Et cations had been formed, except that the stepwise aspect is completely "wrong" in this case.

Kinetic Measurements. Two general procedures were used. (A) The carbocation solution in an NMR tube was allowed to rearrange for a time in the NMR probe at a calibrated temperature (±1 °C) and quickly cooled in a lower temperature bath, and the spectrum was recorded at a much lower temperature than the kinetics temperature. Generally about six points were obtained. (B) The kinetics and the spectra were obtained at the same temperature, taking the time as the midpoint in the spectral accumulation. These kinetics were slower and generally four to six points were obtained. The NMR equipment and operating conditions have been described.[9] In Table III, the conditions "A" refer to the (A) kinetic procedure using alcohol precursors and

1:1 FSO_3H-SbF_5 in SO_2ClF (plus SO_2F_2 in some low-temperature cases), "AC" refers to the same kinetic procedure using chloride precursors in SbF_5-SO_2ClF (sometimes with SO_2F_2), "ACM" refers to the use of chloride precursors in 1:1 FSO_3H-SbF_5 in SO_2ClF. The "B" conditions refer to the (B) kinetic procedure and these all involved alcohol precursors and 1:1 FSO_3H-SbF_5 in SO_2ClF. The error limits have been estimated from our ability to reproduce the $\Delta G^{\ddagger}$ barriers (± 0.2 kcal/mol), since the duplicate kinetics usually involve a slightly different temperature. Labeled 1-methylcyclopentadecyl cation (95% 1-$^{13}CH_3$) was prepared in order to obtain ^{13}C spectra without NOE enhancement and with a delay time between pulses. No significant differences, compared to the normal conditions, were observed so that the ^{13}C intensity vs. concentration assumptions in this work appear safe. In any case, carbons of similar multiplicity in both ions were always used in the kinetic treatment.

Preparation of Alcohol Precursors. The alcohols 1-*n*-propylcyclobutanol,[21] 1-ethylcyclopentanol,[22] 1-methyl-,[9] 1-*n*-propyl-,[23] 1-*n*-butyl-,[9] 1-*n*-pentyl-,[23] 1-*n*-hexyl- and 1-*n*-heptylcyclohexanol,[24] 1-*n*-propylcycloheptanol,[25] 1-methylcyclononanol,[14a] 1-ethylcyclodecanol and 1-*n*-propylcyclodecanol,[10] 1-methylcycloundecanol,[14a] 1-methylcyclododecanol,[26] 1-*n*-hexylcyclododecanol,[27] 1-methylcyclotridecanol,[14a] and 1-methylcyclopentadecanol[14a] have been reported. 1-Ethylcyclooctanol, bp 58 °C (0.2 mm), was prepared by the standard Grignard synthesis; 1-ethylcycloundecanol, low-melting solid, was prepared from the ketone and ethylmagnesium bromide using multiple treatments because of ketone enolization; 1-ethylcyclotridecanol, low-melting solid, by standard Grignard synthesis; 1-methylcyclotetradecanol, mp 86 °C, from the ketone and methyllithium; 1-methylcyclopentadecanol-*1*-^{13}C (95%) from the ketone and methyl Grignard-^{13}C; 1-*n*-propylcyclopentadecanol, mp 68 °C, by Grignard synthesis; 1-*n*-propyl-, mp 94 °C, 1-*n*-pentyl-, mp 69 °C, 1-*n*-heptyl-, mp 48 °C, 1-*n*-octyl-, mp 53 °C, and 1-*n*-nonylcyclododecanol, mp 40 °C, were prepared by standard Grignard syntheses, chromatographing the crude product on Florisil to separate the alcohol from the aldol condensation product of cyclododecanone, 2-[1′-(1′-hydroxycyclododecyl)]cyclododecanone, which was characterized by ^{13}C NMR and mass spectrometry. 1-Chloro-1-ethylcyclooctane, 1-chloro-1-methylcyclononane, and 1-chloro-1-propylcyclododecane were prepared in situ[9] from the alcohol. All of the alcohols were checked for purity using ^{13}C NMR spectroscopy and the results summarized in Table IV, for those not previously reported.

Quenching Experiments. The equilibrated 18^{+}-Me cation solution was cooled to about -100 °C and added to a large excess of vigorously stirred $NaOCH_3$ in methanol, held at -80 °C. After warming, the methanol was swamped with water and this aqueous solution was repeatedly extracted with ether. The combined ether extracts were dried and the ether was removed to yield an oily residue. Molecular distillation at 0.2 mm and a maximum temperature of 200 °C yielded about 65% volatile material. Gas chromatography analysis on Carbowax 20M or OV-17 showed two major peak regions; each consisted of several peaks. From GLC-MS analysis, the low retention group consist of C_{19} alkanes and alkenes.[28] The high retention group were the expected C_{20} ethers, *m/e* 296. Their GLC trace consists of a small peak followed by a large peak with indications of a trailing shoulder. The small peak shows large $M^+ - 43$ (propyl), $M^+ - 57$ (butyl), and $M^+ - 71$ ions and rather small M^+, $M^+ - 15$, and $M^+ - 29$ ions. The trailing edge is dominated by a very large $M^+ - 29$ (ethyl) base peak while the main peak shows equally dominant M^+, $M^+ - 15$ (methyl), and $M^+ - 29$ ions. Tertiary cyclic ethers

$$\textcircled{\scriptsize{n}} \hspace{-0.2cm} \Big\langle \begin{array}{c} OMe \\ R \end{array}$$
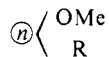
are expected to show large $M^+ - R$ fragments, particularly where R is ethyl or longer, i.e., the parent ion is much stronger in the methyl case. These results are therefore completely consistent with the cation assignments, indicating the dominant formation of 1-methyl-1-methoxycyclooctadecane.

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