value 4.176 96 × $10^{-5}$ atm/unit. The number of precision pressure gage units per cm of recorder deflection depends upon the recorder range selected.
(36) W. Garbett, D. W. Darnall, I. M. Klotz, and R. J. P. Williams, *Arch. Biochem. Biophys.*, **135**, 419 (1969).
(37) V. L. Goedken and D. H. Busch, *J. Am. Chem. Soc.*, **94**, 7355 (1972).
(38) M. C. Rakowski, M. Rycheck, and D. H. Busch, *Inorg. Chem.*, **14**, 1194 (1975).
(39) H. J. Schugar, G. R. Rossman, C. G. Barraclough, and H. B. Gray, *J. Am. Chem. Soc.*, **94**, 2683 (1972).
(40) K. S. Murray, *Coord. Chem. Rev.*, **12**, 1 (1974).
(41) The details of the correction for dimer formation are too lengthy to present here, but may be obtained on request.
(42) C. Walling and A. Goosin, *J. Am. Chem. Soc.*, **95**, 2987 (1973).
(43) C. Walling, R. C. Partch, and T. Weil, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 140 (1975).

---

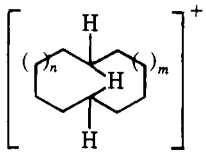
# Ring Size Limits for the Direct Observation of Hydrido-Bridged Secondary Cycloalkyl Cations. Correspondence with Chemical Reactivity Studies

**Roger P. Kirchen and Ted S. Sorensen***

*Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta T2N 1N4, Canada.* *Received November 27, 1978*

**Abstract:** The direct observation of stable hydrido-bridged cycloalkyl cations, in rings containing 8–11 carbon atoms, corresponds exactly with those cycloalkyl rings where direct transannular hydrogen shifts have been observed in reactions involving a presumed carbocation intermediate. Within this observable ion series, there are interesting variations in both the ion reactivity and in the NMR properties. For rings of 8, 9, and 11 carbons, the corresponding 1-methyl 7-, 8-, and 10-carbon tertiary ion is formed, whereas the 10-membered hydrido-bridged ion eliminates hydrogen and forms the decalyl cation. The NMR results show that decreases in the chemical shift of the two terminal hydrogens are matched by a corresponding increase in the chemical shifts of the bridging hydrogen. This behavior is consistent with theoretical models which crudely picture the bonding as a hydride ion centered between two cationic centers. The *negative* charge on the bridging hydrogen increases as the separation of the two bridged carbons is increased. Correspondingly, the terminal protons experience an increased *positive* charge.

The classic studies by Prelog and Cope and their respective co-workers[1] beginning in 1952 have established that cycloalkyl rings from $C_8$ to $C_{11}$ undergo direct transannular hydride shifts in reactions involving a carbocation intermediate. This reactivity was not observed for $C_{12}$ systems and only in a minor way for the $C_7$ case. We have recently prepared the observable $C_{10}$ cyclodecyl cation[2,3] and have suggested, based on the very unusual $^1$H NMR spectrum, that this ion possesses a $\mu$-hydrido-bridged structure **1**.

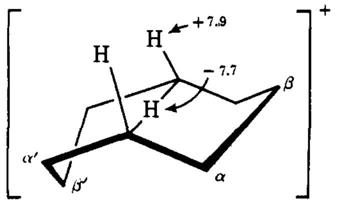


**1**, $n = m = 1$ and $n = 2$, $m = 0$[4]

Since the cyclodecyl cation transannular chemistry is not unique to this ring size, one may wonder whether hydrido bridging might also be observed in other rings.[5] The purpose of this paper is to show that, indeed, this is the case. With the complete bridged-ion series from $n = 8$ to $n = 11$ now available, one notes very interesting comparative differences in both structure and reactivity.

## Results

The most difficult cation to "observe" is the cyclooctyl member. Cyclooctyl chloride in $CFCl_3$ was added to a mixture of $SbF_5$ in $SO_2ClF$–$SO_2F_2$ at ca. −143 °C[6] (or *cis*-cyclooctene using 1:1 $SbF_5$–$FSO_3H$, same solvent), and the NMR spectrum of the resulting solution was obtained as quickly as possible (−147 °C, up to as high as −141 °C in one case). These spectra always indicated a mixture of two carbocations,[7] one being the known 1-methylcycloheptyl cation **2**.[8] The second species is characterized chemically by its very rapid conversion into **2**, $t_{1/2}$ = ca. 17 min at −142 °C, $\Delta G^{\ddagger}$ = ca. 9.3 kcal/mol. The $^{13}$C NMR spectrum consists of four lines, $\delta$ 151.7 (2 C), 50.6 (1 C), 41.3 (1 C), and 31.5 (4 C). However, the most distinctive spectral features are the characteristic very high field $^1$H signal at $\delta$ −7.7 and low field signal at $\delta$ 7.9, these having an area ratio of 1:2[9] (see Figure 1). These protons are coupled to the low field carbon peak at $\delta$ 151.7 with $J = <35$[10] and 147 ± 10 Hz, respectively. This situation is very reminiscent of that found in the cyclodecyl cation **1** and allows one to assign this ion as **3**. The $^{13}$C NMR results[11] indicate that the $\beta$ carbons are nonequivalent and this fits with the chair–boat formulation shown in **3**, a conformation similar to that previously proposed for the 1-methylcyclooctyl cation.[8] We have not attempted quenching experiments on this ion (or the $C_9$ and $C_{11}$ analogues) because of the extreme instability; how-



**3**

0002-7863/79/1501-3240$01.00/0

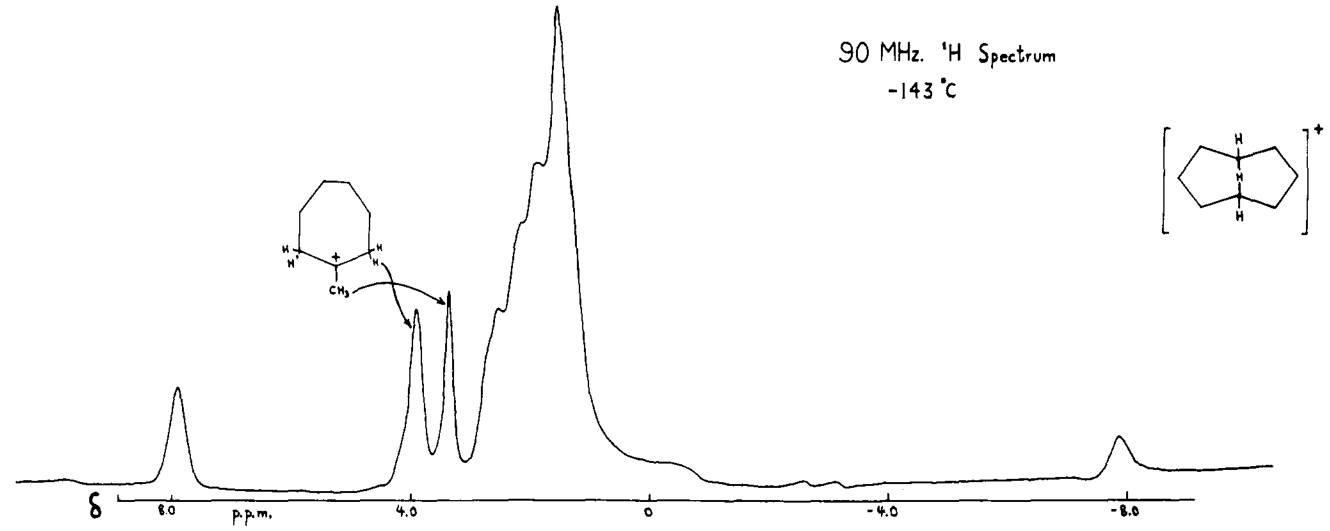
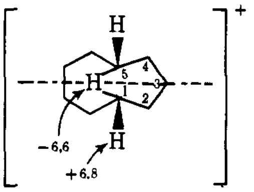


**Figure 1.** 90-MHz $^1$H NMR spectrum of approximately equal amounts of the μ-hydrido-bridged cyclooctyl cation **3** and the rearrangement product of this ion, the 1-methylcycloheptyl cation **2**.[22]

ever, the 1-methylcycloheptyl cation **2** is firmly identified as a rearrangement product and it would be hard to form this cation from any species not possessing an intact cyclooctane ring.[12]

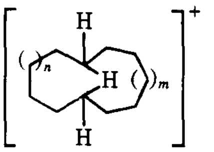
The cyclononyl cation **4** is somewhat more stable than **3**, but



**4**

shows similar NMR properties: $^{13}$C peaks at δ 137.8 (2 C) (d, $J$ = <35[10] and 148 ± 7 Hz), 46.0 (1 C), 30.5 (2 C), 25.8 (2 C), and 15.6 (2 C) (−140 °C). The characteristic $^1$H peaks are found at δ −6.6 and +6.8, area ratio 1:2.[13] As with **3**, it was not possible to obtain NMR spectra of **4** which were uncontaminated with the rearrangement ion, in this case the known 1-methylcyclooctyl cation **5**.[8] The hydrido bridging in **4** must span the 1-5 carbons and molecular model studies indicate that cis bonding at the hydrido bridge would be favored (as in **3**). However, the data do not permit one to speculate on an exact conformation, except that the cation is very likely either symmetrical or conformationally averages to give this overall symmetry (see **4**).

The cycloundecyl cation **6** is considerably more stable than **3**. The $^{13}$C NMR spectrum at −133 °C shows two low field



**6**, $n$ = 1, $m$ = 1 and/or
$n$ = 0, $m$ = 2

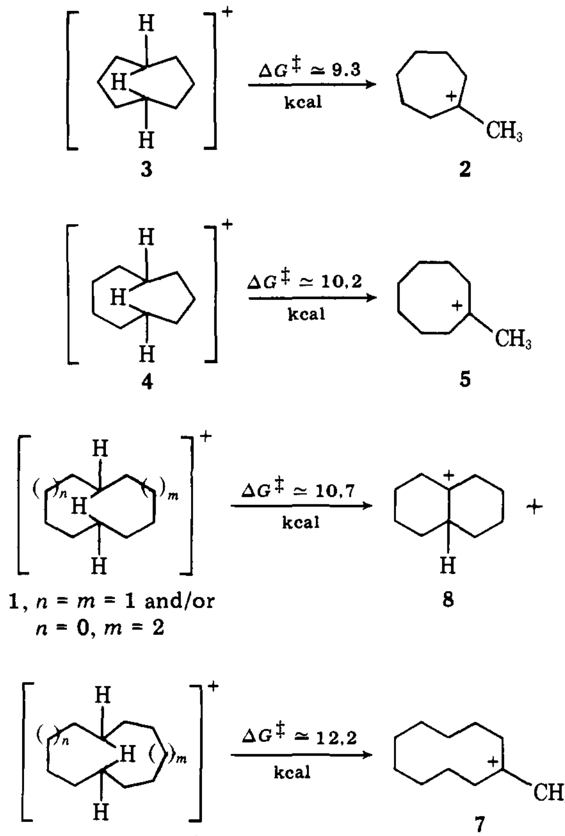
peaks at δ 151.5 and 145.6, of equal area, and an overlapping group of high field signals; the lowest field signal of this group is found at δ 42.8, area at least 2 C. In the proton spectrum at low temperature, the characteristic bridged ion signals are found at δ 6.3 and −6.0, area ratio 2:1.[14] Although it is possible that the *two* equal intensity $^{13}$C signals at δ 151.5 and 145.6 come from two conformers of the ion, a more likely explanation is that a single conformer exists in which there is no symmetry of the type depicted in structure **4**.[15] The μ-hydrido bridging could span the 1,5 or the 1,6 positions, but the latter is more consistent with the $^{13}$C NMR data, i.e., there is no obvious single intensity β carbon[4] in the region δ 46.0 or 47.8 (data of **1** and **4**). At temperatures above −130 °C, dynamic NMR line broadening is observed in both the $^1$H and $^{13}$C spectra. The $^1$H bridging signals at 6.3 and −6.0 broaden and eventually disappear as one raises the temperature (reversed on cooling). At −99 °C, a single peak appears at δ 2.1, half-width 100 Hz. By −84 °C, this has decreased to 16 Hz. The rearrangement to the 1-methylcyclodecyl cation **7**[16] becomes very rapid at this latter temperature but can be measured conventionally at lower temperatures, $\Delta G^{\ddagger}$ = 12.2 kcal/mol. The exchange process responsible for the line broadening could be caused by any one of a variety of rearrangements,[17] but $\Delta G^{\ddagger}$ will be in the range of 5-7 kcal/mol.

The addition of cycloheptyl chloride to $SbF_5$ in $SO_2ClF$/$SO_2F_2$ invariably yields the ring-contracted 1-methylcyclohexyl cation. This behavior is completely analogous to the known cyclohexyl cation-methylcyclopentyl cation rearrangement,[18] all attempts to prepare the former always yielding the latter. The cycloheptyl experiment does not relate directly to the structure of the cycloheptyl cation. However, in the absence of hydrido bridging, there is no reason why the $C_8$ and $C_9$ secondary ions **3** and **4** should not also have ring contracted, just as rapidly or more so. The circumstantial evidence, therefore, indicates that the cyclohexyl and cycloheptyl cations are reactive because they are unbridged.

Addition of cyclododecyl chloride to $SbF_5$ in $SO_2F_2$/$SO_2ClF$ gives a solution which, in contrast to the $C_8$-$C_{11}$ chlorides, shows no $^1$H NMR evidence for bridging structures, i.e., no low field or high field signals.

## Discussion

There are two features of these results which deserve comment. One is the contrast in rearrangement pathways: the cyclodecyl cation cleanly yields the decalyl cation **8** and hydrogen, while all of the others simply ring contract to a tertiary cycloalkyl cation (see Scheme I).[14] This dichotomy may relate directly to rearrangement rates, since the collapse to a tertiary ion in the case of **3** and **4** is faster than the loss of $H_2$ from **1**, Scheme I



**3** → **2**

**4** → **5**

**1**, $n = m = 1$ and/or $n = 0, m = 2$ → **8**

**6**, $n = m = 1$ and/or $n = 0, m = 2$ → **7**

**Chart I.** Comparison of Chemical Shifts of the Terminal and Bridging Hydrogens in the Various Carbocations and in a Related Diboron Analogue

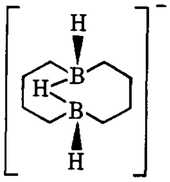
| | [H—C | —H— | C—H]$^+$ |
|---|---|---|---|
| 3 | +7.9 | −7.7 | +7.9 |
| 1 | +6.8 | −6.85 | +6.8 |
| 4 | +6.8 | −6.6 | +6.8 |
| 6 | +6.3 | −6.0 | +6.3 |
| | [H—B | —H— | B—H]$^-$ |
| 9 | +2.3 | −2.4 | +2.3 |

i.e., the different behavior in **1** could be because of an abnormally high barrier for the secondary-tertiary rearrangement. However, it is more likely that the geometry of the cyclodecyl cation uniquely favors the transition state for hydrogen loss, i.e., the transition state may already resemble the relatively strainless decalin ring system.

A second discussion point relates to a feature of the hydrido bridging, which becomes apparent if one compares the $^1$H spectra for **3**, **4**, **1**, and **6** and the related diboron anion **9**.[20] The higher the chemical shift of the bridging hydrogen, the *lower* the chemical shift of the terminal hydrogens (Chart I). This fits qualitatively with a calculated model for this hydrido bridging,[21] pictured as a hydride anion centered equidistant from two carbocation centers. Geometric constraints to the ring which might stretch the overall

$$\underbrace{\overset{\delta^+}{\mathrm{C}}-\overset{\delta^-}{\mathrm{H}}-\overset{\delta^+}{\mathrm{C}}}_{d}$$

bond distance are predicted to *increase* the positive charge on the carbons (and also on the terminal protons) in concert with an *increase* in negative charge on the μ-H. We feel that the cyclooctyl member would logically involve the longest C–C distance ($d$), and it is not unreasonable to suppose that the cycloundecyl cation distance might be the smallest.



**9**

## Experimental Section

The 1-chlorocycloalkanes[23] were prepared by addition of HCl to the alkene or by treating the alcohol, dissolved in $CFCl_3$, with $PCl_5$. Only 1-chlorocycloundecane is unreported and was prepared from the alcohol, bp 76 °C (1.5 mm). The purity of the chlorocycloalkanes was verified by $^{13}C$ NMR spectroscopy: 1-chlorocycloheptane, δ 63.0, 40.4 (×2), 29.2 (×2), 25.3 (×2); 1-chlorocyclooctane, 63.6, 36.6 (×2), 28.9 (×2), 26.4 (×2), 25.0 (×2); 1-chlorocyclononane, 63.2; 35.3 (×2), 28.3 (×2), 25.9 (×2), 23.8 (×2); 1-chlorocycloundecane, 62.2, 37.4 (×2), 27.4 (×6), 25.1 (×2). Carbocation samples were prepared directly in the NMR tubes following previous descriptions.[24] Temperature control[24] and speed of operation are crucial.[6] Due to the short lifetime of the bridged cations, sample preparations were repeated many times in order to complete the various decoupling and line-broadening studies.

**Acknowledgments.** We thank the National Research Council of Canada for generous financial support. We also thank Dr. Arvi Rauk for his stimulating suggestions and theoretical calculations.

## References and Notes

(1) (a) V. Prelog and J. G. Traynham, in "Molecular Rearrangements", Vol. 1, P. de Mayo, Ed., Interscience, New York, 1963, p 593; (b) A. C. Cope, M. M. Martin, and M. A. McKervey, *Q. Rev. Chem. Soc.*, **20**, 119 (1966).
(2) R. P. Kirchen and T. S. Sorensen, *J. Chem. Soc., Chem. Commun.*, 769 (1978).
(3) R. P. Kirchen, T. S. Sorensen, and K. Wagstaff, *J. Am. Chem. Soc.*, **100**, 6761 (1978).
(4) The major isomer of the cyclodecyl cation was previously[3] assigned a 1,6-hydrido-bridging structure, based on analogy to the 1,6-dimethyl case[2] and the fact that the decalyl cation was eventually formed. However, we were not completely happy with the pattern of the high field $^{13}C$ peaks since a ca. single intensity peak was found at δ 47.8 (plausibly the α carbons of the minor isomers). It is now clear that the β carbon of the five-membered side[11] in these bridged ions is found at abnormally low fields (see **3** and **4** data), and a 1,5-hydrido-bridged structure for **1** would now be expected to show this low field single intensity peak. Therefore, we now favor a 1,5-hydrido bridge. There are, in the NMR spectrum, two additional "minor" $^{13}C$ peaks, also indicative of "half-charged" carbons. These could be from *two* minor isomers, where the two carbons in each are internally equivalent (by symmetry or rapid conformational averaging), or *one* species where the two carbons are slightly different. One or both of these minor ions could involve 1,6-hydrido bridging.
(5) The recent paper by W. Parker and C. I. F. Watt, *J. Chem. Soc., Perkin Trans. 2*, 1647 (1975), offers good evidence for some transannular hydride participation in the transition state for solvolysis of cyclooctyl esters. A previous study had proved negative: A. A. Roberts and C. B. Anderson, *Tetrahedron Lett.*, 3883 (1969). For related work, see N. L. Allinger and S. Greenberg, *J. Am. Chem. Soc.*, **84**, 2394 (1962); A. C. Cope and D. M. Gale, *ibid.*, **85**, 3743, 3747 (1963); and L. Stehelin, J. L'homme, and G. Ourisson, *ibid.*, **93**, 1650 (1971).
(6) The temperature of the cooling bath must be carefully adjusted to prevent solidification of the solvent. Further work is needed to try to find mixtures which might remain liquid at lower temperatures, yet retain suitable solubility characteristics (ability to dissolve $(SbF_5)_n$ or $SbF_5$–$FSO_3H$ and, after reaction, to keep the resultant cation in solution). For the NMR spectra, one cannot afford to wipe the cooling bath liquid (methylcyclopentane–$N_2$ slush) from the tubes and, in these cases, an inner bath of $CF_2Cl_2$ was used, so that direct transfer to the NMR probe was possible. We have successfully experimented in the past with methods for the preparation of the cations

while the tube is in the NMR probe, but this method works only at more moderate temperatures.

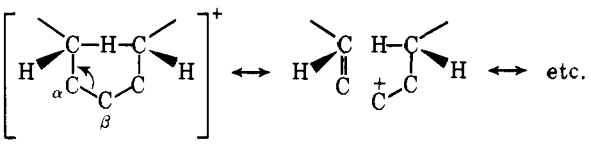
(7) In the best cases, $^{13}$C and $^{1}$H spectra were obtained showing about equal parts of **2** and **3**.

(8) R. P. Kirchen and T. S. Sorensen, *J. Am. Chem. Soc.*, **100**, 1487 (1978).

(9) From Figure 1, one notes that the intensity of the $^{1}$H signals in the $\delta$ 1–4 region (which should encompass the remaining 12 protons in **3**) is too large compared to the combined signal intensity of the bridging proton peaks. However, the two low field peaks in Figure 1 at $\delta$ 3.4 and 3.9 are from the 1-methylcycloheptyl cation **2**, and, by subtracting a similarly broadened spectrum of pure **2** from that in Figure 1, one is left with signal intensities reasonably close to that expected, i.e., 2:12:1.

(10) These were not obtained from fully coupled spectra. The 147-Hz separation was obtained by using very low power decoupling on the bridging hydrogen and vice versa for the <35-Hz measurement. This latter $\mu$-hydrido-coupled carbon peak shows indications of being a doublet, but the lines are badly overlapped and the S/N is poor. One can, however, be certain that the coupling constant is not larger than 35 Hz. For both the 147-Hz value and the <35-Hz measurement, off-resonance decoupling effects will be small but not entirely negligible. The usual cautions, in obtaining coupling constants from an (at best) ABB′XX′ spectrum, apply.

(11) We were initially very suspicious of the cyclooctyl cation $^{13}$C NMR results, since it seemed very surprising to find the $\beta$ carbons at so much lower chemical shift than the $\alpha$ carbons. However, this result has now been confirmed in a much more stable 1,5-dimethyl-$\mu$-hydrido-bridged cation (unpublished results). Carbon $C_\alpha$–$C_\beta$ hyperconjugation provides a reasonable explanation for this result.



(12) The formation of these ring-contracted tertiary carbocations probably involves a protonated cyclopropane intermediate. However, such structures cannot possibly account for the observed spectra.

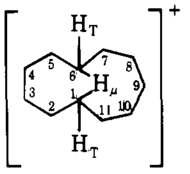
(13) The expected overall proton ratio for **4** is 2:14:1. Experimentally, the area in the $\delta$ 1–4 region is larger than this (and variable from run to run). Some of the extra area is accounted for by the 1-methylcyclooctyl cation **5** rearrangement product, and there could also be nonionized chloride present.

(14) The overall ratio in the best cases was 2:24:1, compared to the theoretical 2:18:1. This was obtained by integrating all the area in the $\delta$ 1–4 region, which would include virtually all the peaks of the rearrangement product **7**, nonionized chloride, polymer, etc., so that this result is actually quite good.

(15) This is not unreasonable. For example, the 1,6-$\mu$-hydrido-1,6-dimethylcyclodecyl cation[2] exists at low temperatures in a cis form in which the two $C^+$ carbons are equivalent only by virtue of a perpendicular $C_2$ axis. In a possible *cis*-1,6-$\mu$-hydrido-cycloundecyl cation, this axis is precluded by the unsymmetrical nature of the bridging.

(16) R. P. Kirchen and T. S. Sorensen, unpublished results.

(17) There is no evidence for the specific interchange of only the $H_T$ and $H_\mu$ protons. Perhaps the most likely event is the multiple rearrangement shown below, in which the carbon labels are assumed fixed, while the bridge "travels" around the ring in a degenerate rocking type motion. Such a degenerate process is not possible in the bridged cyclodecyl cation.



$$\begin{tikzcd}
1,6 \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, phantom, "\upharpoonleft\downharpoonright"] & 1,7 \arrow[r, phantom, "\rightleftharpoons"] & 2,7 \arrow[r, phantom, "\rightleftharpoons"] & 2,8 \arrow[r, phantom, "\rightleftharpoons"] & 3,8 \arrow[d, phantom, "\upharpoonleft\downharpoonright"] \\
11,6 \arrow[d, phantom, "\upharpoonleft\downharpoonright"] & & & & 3,9 \arrow[d, phantom, "\upharpoonleft\downharpoonright"] \\
11,5 \arrow[d, phantom, "\upharpoonleft\downharpoonright"] & & & & 4,9 \arrow[d, phantom, "\upharpoonleft\downharpoonright"] \\
10,5 \arrow[d, phantom, "\upharpoonleft\downharpoonright"] & & & & 4,10 \arrow[d, phantom, "\upharpoonleft\downharpoonright"] \\
10,4 \arrow[d, phantom, "\upharpoonleft\downharpoonright"] & & & & 5,10 \arrow[d, phantom, "\upharpoonleft\downharpoonright"] \\
9,4 \arrow[d, phantom, "\upharpoonleft\downharpoonright"] & & & & 5,11 \arrow[d, phantom, "\upharpoonleft\downharpoonright"] \\
9,3 \arrow[d, phantom, "\upharpoonleft\downharpoonright"] & & & & 6,11 \arrow[d, phantom, "\upharpoonleft\downharpoonright"] \\
8,3 \arrow[r, phantom, "\rightleftharpoons"] & 8,2 \arrow[r, phantom, "\rightleftharpoons"] & 7,2 \arrow[r, phantom, "\rightleftharpoons"] & 7,1 \arrow[r, phantom, "\rightleftharpoons"] & 6,1
\end{tikzcd}$$

(18) (a) G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lucas, *J. Am. Chem. Soc.*, **89**, 2692 (1967); (b) M. Saunders and J. Rosenfeld, *J. Am. Chem. Soc.*, **91**, 7756 (1969).

(19) These results might have been predicted: G. A. Olah, D. P. Kelly, and R. G. Johanson, *J. Am. Chem. Soc.*, **92**, 4139 (1970). Secondary cycloalkanols, with the exception of cyclodecanol, were shown to collapse to the corresponding tertiary cyclohexyl cations at −78 °C. We have since shown that the 1-methylcycloheptyl **2**, 1-methylcyclooctyl **5**, and 1-methylcyclodecyl **7** cations will ring contract, at even lower temperatures, to ultimately give cyclohexyl cations: R. P. Kirchen, T. S. Sorensen, and K. E. Wagstaff, *J. Am. Chem. Soc.*, **100**, 5134 (1978).

(20) D. J. Saturnino, M. Yamanchi, W. R. Clayton, R. W. Nelson, and S. G. Shore, *J. Am. Chem. Soc.*, **97**, 6063 (1975).

(21) A. Rauk, private communication.

(22) The Fourier transform frequency is centered just to the left of $\delta$ 0.0. Small bumps in the 0 to −4 region are due to slightly unbalanced quadrature receivers.

(23) G. Chiurdoglu, R. Fuks, and B. Tursch, *Bull. Soc. Chim. Belg.*, **67**, 191 (1957).

(24) R. P. Kirchen and T. S. Sorensen, *J. Am. Chem. Soc.*, **99**, 6687 (1977).