N-p-Nitrobenzenesulfonyltriphenylphosphinimide (14). A mixture of 0.6 g (2.6 mmol) of *N*,*N*-dichloro-*p*-nitrobenzenesulfonamide, prepared by chlorination of the sulfonamide in a procedure analogous to that for the preparation of dichloramine-T,[17] and 0.6 g (2.5 mmol) of triphenylphosphine was covered with 15 ml of carbon tetrachloride. The solution became bright red immediately. The mixture was refluxed for 15 min and then allowed to cool. The reaction mixture was never completely homogeneous during any phase of the reaction. The slightly yellow precipitate was collected by filtration and dried, 0.7 g, mp 220–225°. Recrystallization of the compound from dichloromethane–pentane gave 0.4 g (36%) of light yellow prisms, mp 229–231°. The ir spectrum in dichloromethane was very similar to that of *N*-*p*-toluenesulfonyltriphenylphosphinimide (13) with the exception of two sharp bands at 6.6 and 7.4 μ due to absorption by a nitro group. *Anal.* Calcd for $C_{24}H_{19}N_2O_4PS$: C, 62.33; H, 4.14. Found: C, 62.53; H, 4.04.

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[17] R. B. Krauss and E. Crede, *J. Amer. Chem. Soc.*, **39**, 2720 (1917).

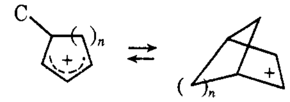
Cycloallyl–Bicycloalkyl Cation Interconversions[1]

L. Huang, K. Ranganayakulu, and T. S. Sorensen*

Contribution from The Department of Chemistry, University of Calgary, Calgary, Alberta, Canada. *Received July 8, 1972*

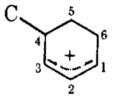
Abstract: A remarkable series of observable cation rearrangements involving the reversible interconversions of substituted cyclohexenyl and 2-bicyclo[2.2.1]heptyl (norbornyl) cations has been observed. The reactions are discussed in detail, with regard to both the thermodynamics of the reactions and their mechanisms. Two of the bicyclic cations involved in the sequence, the 3-*exo*-methyl and 3-*endo*-methyl cations **6** and **8**, provide a dramatic example of the extreme stereospecificity of the 3,2-hydride shift in tertiary norbornyl cations (rate difference $>10^5$ at 25°).

In thermochemical calculations relating to carbonium ions, chemists today have access to good data relating to (a) the stability of solution carbonium ions relative to their neutral progenitors and (b) an increasing body of data on the relative stability of isomeric gas-phase carbonium ions. There is, however, scant information relating the energies of various isomeric solution carbonium ions and, in specific cases like the $C_nH_{2n-3}^+$ cations discussed in this paper, *no* real previous information. In the position (thermodynamic stabilities) of the following equilibrium, the results are as follows

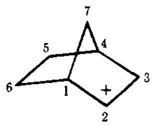


n = 1, strongly favor cycloallyl cation
n = 2, isoenergetic
n = 3, predict to favor the bicycloalkyl cation system

This paper reports an investigation of the n = 2 case: the cyclohexenyl (A) and 2-bicyclo[2.2.1]heptyl (B)



A



B

cations. Previously, we have reported[2] evidence for the 2-bicyclo[2.1.1]hexyl cation system as a high-energy intermediate in some cyclopentenyl cation rearrangements. In addition to the thermodynamic aspects, certain of the 2-bicyclo[2.2.1]heptyl cations have very interesting properties in their own right and these are fully discussed.

Results

In practice, the parent C-7 systems A and B are separated by too high a transition state barrier to allow interconversions between the two. Only when one comes to a tetramethyl-substituted case (or higher substitution) does one get facile interconversions. The following sequence (Figure 1) has been observed (the basic skeleton is outlined in each case).

Starging with cation **1**, the total sequence can be observed and one eventually ends up with an excellent yield of **10**. The further rearrangement of **10** to cyclopentenyl cations has previously been reported by Deno.[3,4] These authors actually obtained cation **10** by adding 2-methylfenchol or 2-methylborneol to sulfuric acid.[5]

The sequence can be entered at any stage and this has facilitated the determination of several of the rate constants. For example, both the **1** → **2,3,4** → **5** and the **5** → **6,7** → **8,9** reactions have to be treated as consecutive first-order processes. Generating the **2,3,4** cation mixture directly allows one to independently determine the second rate constant and also to better characterize these ions. Actually, in order to prove the structures of the various cations, each system has been independently prepared by reasonably unambiguous means. These are outlined below in Scheme I.

The cations **11** and **12** (Figure 1) were also prepared, because they seemed like possible intermediates in the main sequence and we wished to test their reactivity. Although they do enter the main sequence at the indicated points, they probably represent "dead-end" paths (*vide infra*). They were prepared from the alcohols **23** and **24**.

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[1] Presented in part at the Adelaide Symposium of the Royal Australian Chemical Institute, May 16–19, 1972.

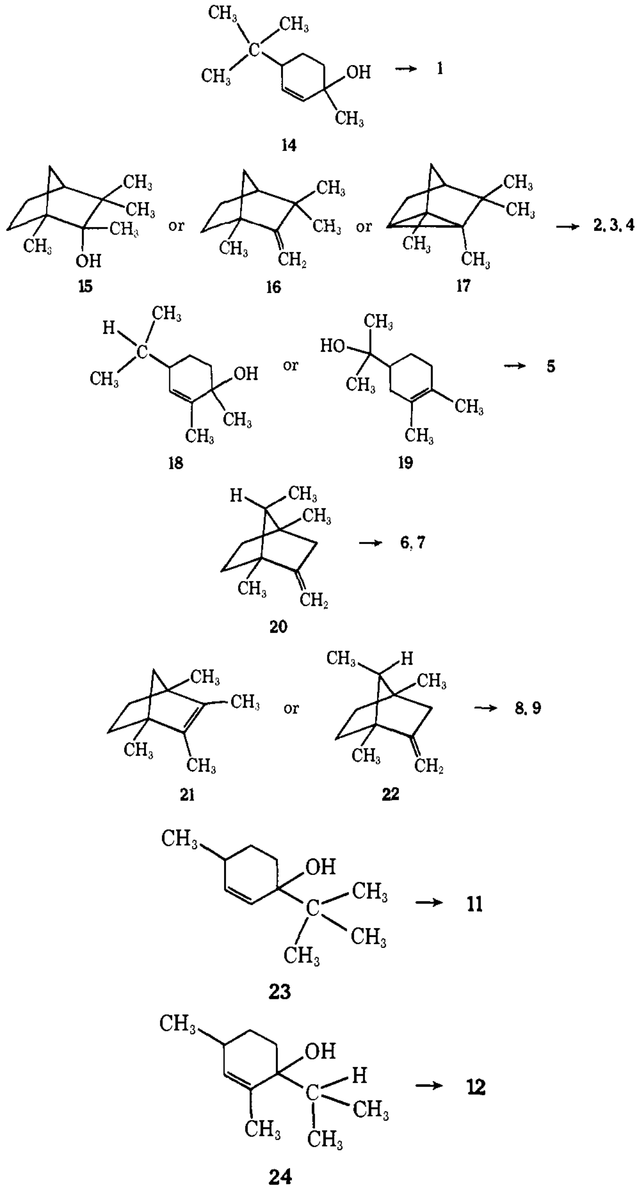
[2] T. S. Sorensen and K. Rajeswari, *J. Amer. Chem. Soc.*, **93**, 4222 (1971).

[3] N. C. Deno and J. J. Houser, *J. Amer. Chem. Soc.*, **86**, 1741 (1964).

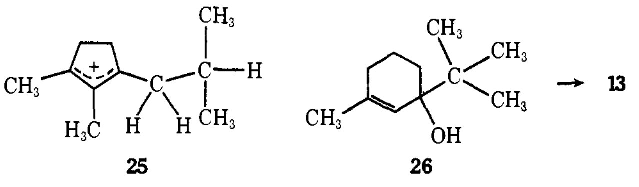
[4] N. C. Deno and R. R. Lastomirsky, *ibid.*, **90**, 4085 (1968).

[5] From our results, this is expected, since at 0° in H_2SO_4 the conversion of **2**, **3**, **4** to **5** and of **5** to **10** would be rapid.

Scheme I



Cation **13** had been prepared earlier[6] and shown to rearrange slowly in H_2SO_4 to the cyclopentenyl cation **25**. Cation **25** is the same cyclopentenyl cation as that previously obtained by Deno[3] from the rearrangement of **10** in H_2SO_4. The rearrangement of **13** to **25** is not an obvious reaction, and we have included it in Figure 1 because it seems probable that high energy intermediates produced from **13** eventually intersect the reaction sequence of Figure 1 and then fall back to the cyclopentenyl cation product, **25**, expected from this route. Cation **13** was prepared from the alcohol **26**.



The allylic alcohols were prepared, in each case, from the corresponding ketone and the appropriate alkyllithium reagent. The ketone **27**, unreported, was pre-

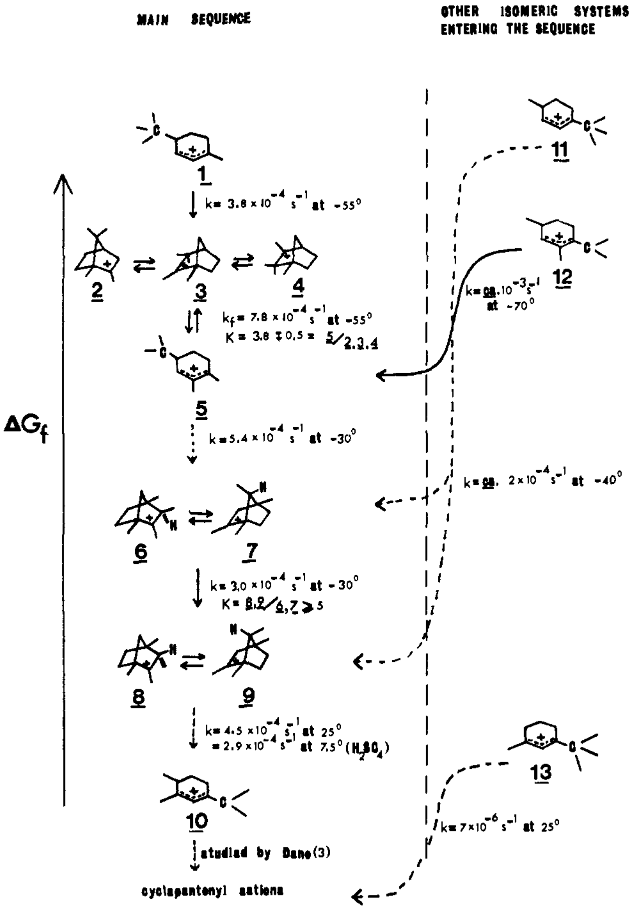
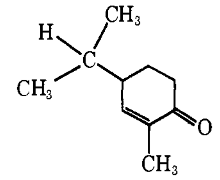


Figure 1. Sequential appearance of the cations in FSO_3H (— = methyl groups). Compounds connected by solid-line arrows can be logically (but not necessarily are) derived from the immediately less stable isomer. In the dashed-line arrows, the appearance of the products can be treated kinetically as shown, but the products are likely derived directly *via* one of the still higher energy species, present in a finite, but kinetically insignificant, concentration, because of the equilibrium nature of all of the processes. The presence of several 2-bicyclo[2.2.1]heptyl cations at each energy level is discussed in the text.



27

pared by a procedure similar to that reported for the preparation of 2,4-dimethylcyclohex-2-enone.[7] The bicyclic alcohol **15** and hydrocarbons **16** and **17** are well known.[8]

The alkenes **20**, **21**, and **22** were obtained by quenching a FSO_3H solution (−30°) of the cations **6**,**7** and **8**,**9** in aqueous base. The crude material exhibits four main peaks on glc analysis, and each of these fractions was collected by preparative glc. Each fraction, except the first, was then further purified by repeated rechromatography.

The structures assigned to ions **8** and **9** were deduced

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(6) K. A. Ananthanarayan, M.Sc. Thesis, University of Calgary, 1971.

(7) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

(8) (a) J. Bredt, *J. Prakt. Chem.*, **98**, 96 (1918); (b) S. S. Nametkin, *J. Russ. Phys.-Chem. Soc.*, **50**, 254 (1918); (c) L. Ruzicka, *Helv. Chim. Acta*, **1**, 116 (1918).

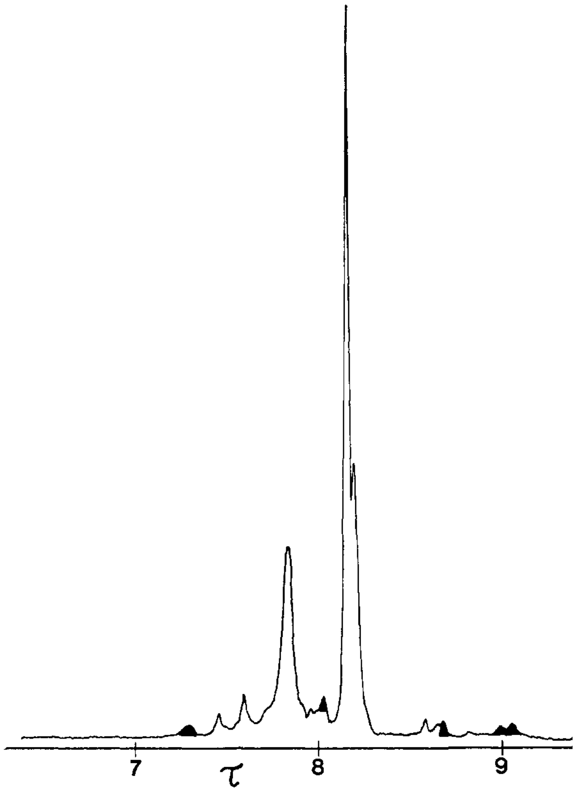
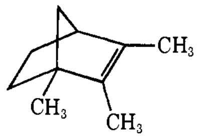


Figure 2. Nmr spectrum of cations **8,9** at -40° in 4:1 SO_2ClF–FSO_3H. The black areas are the peaks due to the presence of a small amount of cations **6,7**. The other small, high-field, peaks are unidentified. This spectrum was obtained by dissolving alkene **21** in FSO_3H. In the product obtained in the actual sequence shown in Figure 1, there are a few further, small, unidentified peaks in the high-field region.

initially from the observed nmr spectrum (see Figure 2). However, if this assignment were wrong, then the structures assigned to the expected quench products would also be wrong, and we therefore carried out an unambiguous characterization of alkene **21**. Since **21** has the expected structure, it is then possible to assign the structures of **20** and **22**.

Alkenes 21 and 22 (Glc Fractions 2 and 4). The nmr spectrum of pure **21** ($C_{11}H_{18}$) shows no peak below τ 8.0 and thus contains no alkene protons or probably even allylic protons. The spectrum is dominated by two sharp singlets at τ 8.48 and 8.825, each of six proton area, indicating two equivalent methyl groups on a double bond and two equivalent methyl groups on a saturated quaternary carbon atom. The mass spectrum is equally illuminating, the two major ions corresponding to M -28 (the retro-Diels–Alder elimination of ethylene) and M $-$ 43 (metastable at m/e 93.8), corresponding to the further loss of methyl from the methylated cyclopentadiene fragment. The major fragmentation pathway observed for methylated cyclopentadienes is the loss of methyl.[9] The mass spectral behavior of **21** is extremely similar to that of the known compounds, 1,2,3-trimethyl-2-norbornene (ϵ-fenchene) (**28**) and 1,2,4-trimethyl-2-norbornene (**29**), in which the dominant losses are also M $-$ 28 and M $-$ 43. For a compound, $C_7H_6(CH_3)_4$, the structure **21** is the only one satisfying the nmr and mass spectral data.



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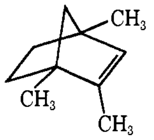

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Readdition of **21** to FSO_3H at -80° regenerates nearly pure **8,9**. This provides further evidence for the assigned stereochemistry of **6,7** and **8,9** since virtually exclusive exo protonation would be expected.[10]

Alkene **22** also regenerates the **8,9** cations. The nmr spectrum of **22** exhibits a typical $>C{=}CH_2$ pattern, two one-proton peaks at τ 5.42 and 5.55, each split into a triplet, J = 3.0 and 1.8 Hz, respectively, from long-range coupling due probably to the presence of a methylene group at C-3. The presence of a peak at τ 7.98 (2 H), which is coupled to the exocyclic methylene group, completes this assignment. The methyl groups appear as two closely spaced peaks at τ 8.99 and 9.01 and a doublet at 9.26, J = 6.8 Hz, consistent with the assigned structure.

Alkene 20 (Glc Fraction 3). This alkene could not be obtained pure in spite of repeated glc separations. Fraction 3, when added to FSO_3H, generates cations **6,7** in about 65% yield (the remainder is **8,9**). The nmr spectrum shows $>C{=}CH_2$ protons (mixture). There are two single methyl peaks at τ 8.86 and 9.02 and an unusually high-field doublet at 9.38, J = 6.8 Hz, all of about equal area, and these may represent the methyl groups of alkene **20**.[11] The $CH_3CH<$ group is placed in the C-7 (syn) position rather than C-3 (exo) because of the unusual high field position of the peak (in the shielding region of the exocyclic methylene double bond) and the presence of a peak at 8.04, appropriate for the allylic protons at C-3.

The Cations

Cycloallyl. The nmr spectra of the cycloallyl cations are mostly unexceptional[12] and the chemical shift positions are listed in Table I.

2-Bicyclo[2.2.1]heptyl. In contrast to the cycloallyl cations, these cations are extremely labile to internal rearrangements and one has mixtures at each energy level. However, the Wagner–Meerwein shifts (or the exo 3,2-methyl shifts in the case of **3** and **4**) interconverting the various isomers are so fast, even on a nmr time scale, that one can regard these as single compounds insofar as the rate constants shown in Figure 1 are concerned. We have previously discussed the ions **2**–**4** and the techniques used to quantitatively identify these.[13] The others are unreported but are a very interesting set.

The extremely simple nmr spectrum which was assigned to the cations **8,9** is shown in Figure 2. On cooling, this spectrum remains unchanged until about -95°, when both of the large peaks start to broaden. At -115°, the maximum broadening of the methyl peak (the largest) occurs, $k_{\text{coalescence}} = 270\ \text{sec}^{-1}$, $\Delta F^{\ddagger}$ = 7.3 kcal/mol. Below -115°, two broad peaks of

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[9] A. G. Harrison, P. Haynes, S. McLean, and F. Meyer, *J. Amer. Chem. Soc.*, 87, 5099 (1965).

[10] (a) S. J. Cristol, L. K. Gaston, and D. W. Johnston, *Tetrahedron Lett.*, 185 (1963). (b) H. Kwart and J. L. Nyce, *J. Amer. Chem. Soc.*, **86**, 2601 (1964).

[11] Methyl peaks are also observed at τ 8.95 and 8.97.

[12] The positions of the C-2 and C-3 protons are somewhat variable.

[13] T. S. Sorensen and K. Ranganayakulu, *Tetrahedron Lett.*, 2447 (1972).

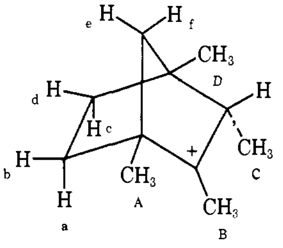
Table I. Nmr Spectra of the Cycloallyl Cations

Cation	Temp, °C, solvent	Chemical shifts[a] C-1	C-2	C-3	C-4
1	−60, FSO_3H	6.9	2.22 (d) $J = 9$	0.56 (d) $J = 9$	8.84 (*t*-Bu)
5	−40, FSO_3H	7.02	7.73	1.05 (broad)	8.880 (d) $J = 6.8$ 8.895 (d) $J = 6.8$
11	−60, FSO_3H	8.47 (*t*-Bu)	2.09 (d) $J = 9$	0.84 (d) $J = 9$	*b*
12	−80, FSO_3H	8.54[c]	7.73	1.19 (broad)	*b*
13	35, 96% H_2SO_4	8.63 (*t*-Bu)	2.27	7.15	

[a] The C-4, C-5, and C-6 protons and the isopropylmethine proton show up as broad, overlapping peaks and are of little use in characterizing individual cations. All chemical shifts are relative to internal tetramethylammonium cation, τ 6.90. *J* values in hertz. [b] The methyl doublet is obscured by the more intense isopropyl and *tert*-butyl methyl signals. [c] This peak is broad and poorly resolved, at this temperature, into the expected doublet.

equal area centered at τ 7.7 and 8.6 appear, the average of these corresponding to the chemical shift of the original large peak. It was not possible to determine what happens to the smaller peak below the coalescence temperature.

This line-broadening process must be due to a degenerate exo 3,2-hydride shift in cation **8**, in which only the C-7 methylene protons should remain unaffected.[14] The groups becoming equivalent by the exo 3,2-hydride shift are shown below.



A = D a = c
B = C b = d

The two cations **8** and **9** are being interconverted, however, by a Wagner–Meerwein shift, at an even faster rate than the 3,2 shift. This was, in fact, anticipated, since in the 1,2-dimethyl-2-norbornyl cation and in various methyl-substituted analogs, this Wagner–Meerwein shift has not been "frozen out" at temperatures as low as −130°.[13,15–17] The interconversion of **8** and **9** cannot, of course, produce any exact group equivalences. In the case where **8** and **9** are of equal energy and the related protons have similar chemical shifts, then one can have effective equivalence, and such a situation must exist in order to explain the observed spectrum. Briefly, therefore, the situation is as follows. (1) Both **8** and **9** are of *ca.* equal free energy ($K = 1$). (2) The exo 3,2-hydride shift equates pairs of methyl groups, A = D (a singlet) and B = C (a doublet with expected coupling of 3.5 Hz),[18] and from (1), A = D ≈ B = C. The accidental equivalence of the singlet and one-half of the doublet then rationalizes the observed spectrum.[19] (3) The "singlet" at τ 7.82 can be assigned in the main to the C-5 and C-6 protons, due to the approximate equivalences a = c ≈ b = d.

The nmr spectrum of cations **6** and **7** is characterized by four *separate* methyl signals at (−60°) τ 7.27, 8.04, and 8.68 and a doublet at 9.04, $J = 7.0$ Hz. Cooling the solution to −120° does not result in any slow exchange line broadening but does change the chemical shifts of the two lower field methyl groups to a marked extent. At −60°, the separation of these two peaks (δ) is 79 Hz. At −120°, the chemical shifts are τ 7.22 and 8.07 (δ 85 Hz) and at −10°, 7.31 and 8.00 (δ 69 Hz).

Briefly, therefore, the following situation exists. (1) The isomers **6** and **7** are of different free energy ($K \neq 1$), so that even though the interconversion is very rapid, one does not get the "effective equivalence" found in the **8**, **9** case. One expects changes in the chemical shifts because the relative population of the two cations, and hence the averaged chemical shift, is a function of temperature. This same behavior was observed with cations **2** and **3**, and an analysis of their temperature-dependent chemical shifts has been published.[13] (2) On an nmr time scale, the endo 3,2-hydride shift in cation **6** must be slow. (3) The predominent isomer is probably **7**.[20]

Rate Comparison of Endo and Exo 3,2-Hydride Shifts. An endo 3,2-hydride shift in cation **6** cannot have a rate constant greater than 10 sec^{-1} at −10° ($\Delta F^{\ddagger} > 14.2$

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(14) The methylene protons, C-7 in **8**, C-3 in **9**, should show up as the resultant of two individual AB patterns. It seems probable that the two small peaks at τ 7.45 and 7.59, $J = 14$ Hz, are the lower half of an averaged AB spectrum. In agreement, these peaks remain unaffected during the line broadening of the large peaks. The migrating proton, possibly obscured by the larger peaks, should change from a septet to a quartet during the process.

(15) G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *J. Amer. Chem. Soc.*, **93**, 1442 (1971).

(16) E. Huang, K. Ranganayakulu, and T. S. Sorensen, *ibid.*, **94**, 1779 (1972).

(17) E. Huang, K. Ranganayakulu and T. S. Sorensen, *ibid.*, **94**, 1780 (1972).

(18) This is derived as follows. In the rapidly equilibrating 2,3-*endo*-dimethyl-2-norbornyl cation,[17] the averaged splitting is *ca.* 4 Hz, made up by averaging an expected $CH_3CH<$ coupling of 6.5 Hz and a *ca.* 1.5-Hz long-range $>CH–C^+–CH_3$ coupling. In cation **9**, the averaged splitting can be estimated as 6.5 Hz for $CH_3–CH<$ and 0 Hz for $HC–C–CH_3$, a 3.2 Hz average. One must finally average 4 and 3.2 to get the expected value of *ca.* 3.5 Hz for the completely averaged **8**,**9** spectrum.

(19) On cooling, one should eventually observe all four methyl groups. However, when $K = 1$, then A and B have similar chemical shifts, as will C, an expected doublet, and D, based on the observed chemical shifts found for these methyl groups in related cations.[16,17] The splitting of the "single" methyl peak into two nearly equivalent pairs is further evidence for a 3,2-hydride shift since the competing process, the Wagner–Meerwein shift, would have produced a $1CH_3$ to $3CH_3$ split.

(20) From spin decoupling results, the averaged C-3 in **6**, C-7 in **7**, proton is located at *ca.* τ 7.5, which seems, from a comparison with related systems,[16,17] closer to that expected for a C-7 proton. Similarly, the methylene protons at C-7 in **6**, C-3 in **7**, which are probably buried under the lowest field methyl peak at τ 7.27, seem more appropriate for a C-3 position.

kcal/mol). Thus, in our systems, there is a minimum of 6.9 kcal/mol difference in the transition state free energies for exo and endo hydride shifts. This exceeds a predicted difference of 6 kcal/mol (the exclamation mark is redundant) made by Schleyer.[21] Recent work with the adamantyl cation[22,23] has shown up related anomalies between the "expected" and observed rates for seemingly comparable hydride shifts.

We have recently been able to measure the absolute rate of a "Wagner–Meerwein shift, 6,2-hydride shift, reverse Wagner–Meerwein shift" (WM-6,2-WM) rearrangement in several tertiary 2-norbornyl cations.[17] This reaction, of course, interconverts a 3-exo and 3-endo substituent and hence one can no longer distinguish between exo or endo 3,2-shifts in these cations. The cations **6**,**7** and **8**,**9** represent the simplest systems in which the WM-6,2-WM rearrangement does not take place, and this fact has thus allowed us to search for the endo shift at much higher temperatures than would otherwise be possible. An important conclusion therefore is the fact that endo 3,2-hydride (and probably alkyl) shifts need a much higher activation energy (>14.2 kcal/mol) than a WM-6,2-WM rearrangement (*ca.* 11 kcal/mol).[17] This result is germane to the camphenehydro cation problem[17] and to the mechanism of the longifolene–isolongifolene rearrangement.[24]

Solvent Effects on the Reaction Rates in Figure 1. Acid solvent variations are a well-defined procedure[4,25,26] for differentiating cation → cation rearrangements proceeding either by an internal reorganization (solvent independent) or through the intermediacy of neutral transition state intermediates (base catalyzed). Each rate, except **8**,**9** → **10**, was therefore measured in both FSO_3H and 4:1 SO_2ClF–FSO_3H, a stronger base.[27] The results show that if one starts with **1** or (**2**,**3**,**4**) or **5** in 4:1 SO_2ClF–FSO_3H, the rate sequence **1** → **2**,**3**,**4** → **5** is not altered significantly, but in the next step one no longer gets the sharp rate break found in pure FSO_3H between the formation of **6**, **7**, **8**, **9**, on the one hand, and **10**.

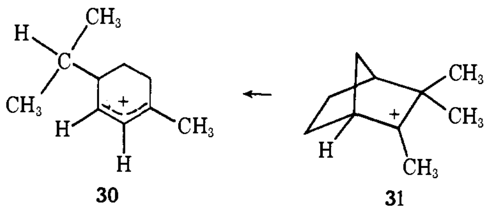
In a separate experiment, the cations **8**,**9** were prepared from the alkene **21** at 0° in 96 or 100% H_2SO_4 (also a weaker acid than FSO_3H). In this solvent, the rearrangement of **8**,**9** to **10** was clearly much faster than in FSO_3H (see Figure 1).

The conclusions are reasonably clear. (1) The precurser of cation **10** is cation **5** and this reaction is, as expected,[4,26] base catalyzed. Only when this shunt reaction is slowed down (by using a stronger acid solvent) will one see cations **6**, **7**, **8** and **9**. (2) All of the other processes are probably internal rearrangements.

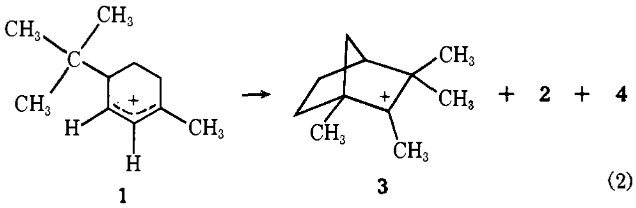
Discussion

Relative Energies of the Cations. In free energy stability terms, the cation order is: cycloallyl **1** < bicycloalkyl **2**,**3**,**4** < cycloallyl **5** < bicycloalkyl **6**,**7** < bicycloalkyl **8**,**9** < cycloallyl **10**. The stability order of the cycloallyl cations is as expected, if one looks at the alkyl substitution of the allyl portion. In terms of stability, 1,3-dialkyl substitution > 1,2-dialkyl > 1-alkyl.[28] One can estimate that cation **10** would be about 5–6 kcal/mol more stable than **1**,[29,30] so that this figure represents the total energy fall in the sequence. The energy ordering within the bicycloalkyl cations would appear to be the result of steric factors. The observed order bears a considerable resemblance to that previously observed in a trimethyl-2-norbornyl cation (fenchyl) series, where, for example, the 1,2,3-*endo*-trimethyl cation is more stable than the 3-exo analog and both are much less stable than the 1,2,4-trimethyl cation.[16] Recent combustion studies have shown that 2,3-dimethylnorbornane is *ca.* 4 kcal/mol less stable than the 1,4 isomer,[31] an indication of the decreased steric requirements of the bridgehead positions.

In comparing the bicycloalkyl and cycloallyl systems, two questions arise: (1) to what extent does the methyl substitution alter the basic comparison and (2) based on known thermochemical data, is it reasonable to find these cations to be isoenergetic? The first question is difficult to answer, but it appears that increasing methyl substitution favors the bicycloalkyl cations. Thus, the cycloallyl cation **30** is formed from the camphenehydro cation **31** (no equilibrium detected),[17,32] whereas in the corresponding tetramethyl case, the reaction occurs completely in the opposite direction (eq 1 and 2). This anomaly is probably brought about, in part, by a stabilization due to the extra 1-methyl substituent in cations **2** and **3**.



(1)



(2)

To answer the second question, one can construct the account in Table II. This comparison ignores $T\Delta S$ terms (*i.e.*, ΔG and ΔH are used interchangeably). The comparison is naive in using group equivalences for neutral hydrocarbons[33] (although the C^+ and other

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[21] P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 699 (1967).

[22] P. Vogel, M. Saunders, W. Thielecke, and P. v. R. Schleyer, *Tetrahedron Lett.*, 1429 (1971).

[23] D. M. Brouwer and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **89**, 211 (1970).

[24] J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Amer. Chem. Soc.*, **89**, 2590 (1967).

[25] T. S. Sorensen, *ibid.*, **91**, 6398 (1969).

[26] T. S. Sorensen, I. J. Miller, and C. M. Urness, *Can. J. Chem.*, **48**, 3374 (1970).

[27] The 4:1 SO_2ClF–FSO_3H acid solvent behaves as a stronger base (weaker acid) in cation → cation rearrangements which are known to proceed by a base catalysis mechanism (unpublished results from this laboratory).

[28] N. C. Deno in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1970, Chapter 18.

[29] D. M. Brouwer and J. A. Van Doorn, *Recl. Trav. Chim. Pays-Bas*, **89**, 333 (1970).

[30] K. Ranganayakulu and T. S. Sorensen, *Can. J. Chem.*, **50**, 3534 (1972).

[31] M. P. Kozina, L. P. Timofeeva, S. M. Skuratov, N. A. Belikova, E. M. Milvitskaya, and A. F. Platé, *J. Chem. Thermodyn.*, **3**, 563 (1971).

[32] Cation **30** is only one of two products formed in this reaction, but this fact has no bearing on the thermodynamic arguments being made here.

[33] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

Table II[a]

	Cycloallyl cation A	Bicycloalkyl cation B
Σ bond energies (relative)	0	−21.5
Correction for ring strain	0	+15 to 18
Allyl resonance energy	−17, −30, −33	?
Calcd difference	−10.5 to −29.5	
Obsd difference	*ca.* 0	

[a] All figures are in kcal/mol.

groups cancel). The ring strain figure is for the parent norbornane ring system.[34] The allyl resonance energy figures are literature values based on mass spectral appearance potentials[35] or theoretical calculations.[28,36–38] These values are presumably applicable to gas-phase species and should be corrected for solution comparisons. Such calculations have been attempted for alkyl cations.[35,39]

Several other factors are involved. Since an alkyl cation and an allyl cation have considerably different charge dispersion, one might have large differential solvation energies. This point does not worry us unduly since we believe this should be considered an intrinsic property of the system insofar as the data are to be applied to other solution comparisons.

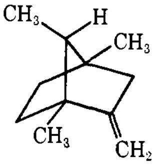
The question of a resonance energy figure for an alkyl cation is very much a matter of definition since one can incorporate this into appropriate thermochemical group equivalents. The real problem may arise when one compares quite different species, *i.e.*, allyl and alkyl cations, and then attempts to use these group equivalents.

In a practical sense, we believe that our comparison shows two things.

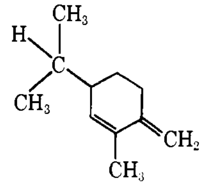
(1) The source of the bicycloalkyl cation stability, relative to the cycloallyl cation, is basically in the extra σ bond formed. A cursory examination of the system might have suggested that one was doing the impossible in going from a strainless, delocalized system to a strained, localized one.

(2) The use of thermochemical data of neutral molecules as a *convenient* way of calculating approximate carbonium ion ΔG_f values is basically unsound. Our comparison would suggest, for example, a RE value of *ca.* 0 for the allyl cation, which clashes with a considerable body of experimental evidence showing certain allyl cations to be much more stable than their unconjugated isomers.[28] Clearly, the best procedure will be to devise group equivalences appropriate for cations in solution. The calorimetric work of Arnett and Larsen[40] and the observations of isoenergetic species, as in this work, are clearly a start in this direction. Already we believe it is clear that σ bonds are strengthened much more than double bonds in going from a neutral hydrocarbon to the cation.

Cation Stabilities in a pK_a Sense. Thermochemical calculations[33] of the heat of formation of the alkene **22**



22



32

and the diene **32** lead to very similar values. There is no unique conjugate base corresponding to either of the cations **9** or **5**, but the compounds **22** and **32** should be representative as far as approximate calculations are concerned. Since **22** and **32** should be of similar energy and the corresponding cations **9** and **5** are also isoenergetic, this suggests that their pK_a values should also be similar. The pK_a's of several cyclohexenyl cations

$$\mathbf{22} + [H^+] \rightleftharpoons \mathbf{9}$$

$$\mathbf{32} + [H^+] \rightleftharpoons \mathbf{5}$$

have been measured.[41] The pK_a of the 1,3,5,5-tetramethylcyclohexenyl cation is estimated to be −3.4 compared with −7.3 for the 1,5,5-trimethylcyclohexenyl cation (which lacks a methyl group on the active allyl position). One might estimate an intermediate value of −5 to −6 for the pK_a of **5** (a 2-methyl substituent is moderately stabilizing[41]).

The bicycloalkyl cations **8** and **9** are, to our knowledge, the first purely alkyl cations (excluding cyclopropylcarbinyl systems) which are perfectly stable, in a pK_a sense, in 96% H_2SO_4. The solutions show no evidence of polymerization or nmr line broadening, suggesting that the pK_a value is well below the H_0 value of the solvent. This is perfectly consistent therefore with the calculations outlined at the beginning of this section.

Probable Mechanism of the Reactions. The reversible interconversion of cations **2** and **5** is mechanistically the most clear cut, involving two 1,2-hydride shifts[42] and a ring closure or opening by the 1–7 π-route. The 1–6 π-route leading to a 2-bicyclo[2.2.1]heptyl cation is well known,[43] but this is the first simple example, in a purely hydrocarbon system, of the 1–7 π-route.[44] This reaction is, of course, a postulated biosynthetic step, but

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(34) P. v. R. Schleyer, I. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).

(35) J. L. Franklin in "Carbonium Ions," Vol. 1, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1968, Chapter 2.

(36) J. L. Franklin and F. H. Field, *J. Amer. Chem. Soc.*, **75**, 2819 (1953).

(37) I. J. Miller, *Aust. J. Chem.*, **25**, 507 (1972).

(38) Some literature values of allyl cation resonance energy are unsuitable because they are based on a comparison to the CH_3^+ cation. Probably the most satisfactory approach is to correlate the difference in calculated resonance energies for homologous systems, *i.e.*, allyl, pentadienyl, etc., with physical data. For example, in simple HMO theory, the calculated difference in RE between allyl and pentadienyl cation is 0.64 β, which has been correlated with differences in appearance potentials.[35] This value of β can then be used to calculate absolute values of RE.

(39) D. Bethell and V. Gold, "Carbonium Ions, An Introduction," Academic Press, New York, N. Y., 1967, p 136 ff.

(40) E. M. Arnett and J. W. Larsen in ref 35, Chapter 12.

(41) N. C. Deno, J. J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Houser, *J. Amer. Chem. Soc.*, **85**, 2998 (1963).

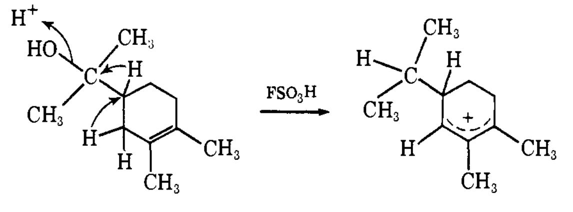
(42) We have no evidence for or against a direct 1,3-hydride shift, although this process has been shown to take place in the dimethyl isobutyl carbonium ion: D. M. Brouwer and J. A. Van Doorn, *Recl. Trav. Chim. Pays-Bas*, **88**, 573 (1969). In cations like 1, where a direct 1,3-methyl shift is excluded (or at least does not occur), the molecules are at least as reactive (obligatory double 1,2 shifts) as those where both shift possibilities could occur.

(43) (a) R. Lawton, *J. Amer. Chem. Soc.*, **83**, 2399 (1961); (b) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).

(44) See, however, (a) H. Felkin and C. Lion, *Chem. Commun.*, 60 (1968); (b) J. C. Fairlie, G. L. Hodgson, and T. Money, *ibid.*, 1196 (1969).

attempts to duplicate the reaction chemically have failed.[45]

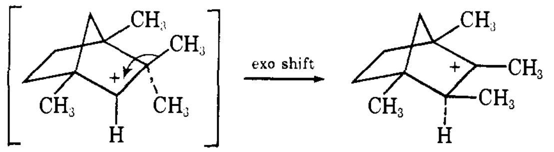
The slow step in the interconversion of **2** and **5** is probably the actual ring closure, since the alcohol **19** yields only the cation **5** on addition to FSO_3H. The transition state energy advantage obtained by generating a tertiary cationic center in the side chain, during the transformation, accounts for the apparent necessity of having either an isopropyl or a *tert*-butyl group at the C-4 position of the cycloallyl cation.



19 **5**

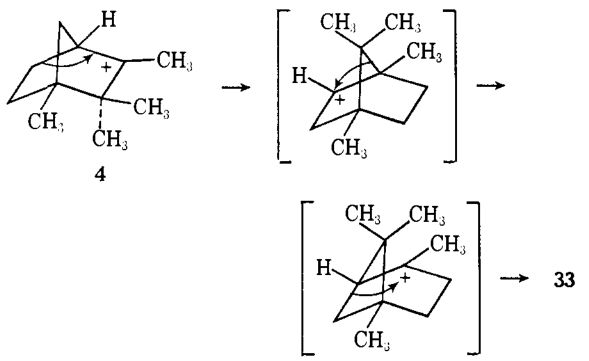
The conversion of cation **1** into **2,3,4** can be rationalized in a similar way, although further transformations must take place in the initially formed bicycloalkyl cation.

The formation of cations **6,7** probably occurs *via* cation **4**. The initial formation of the less stable 3-exo methyl isomer suggests that the last step may be eq 3.



33 **6** (3)

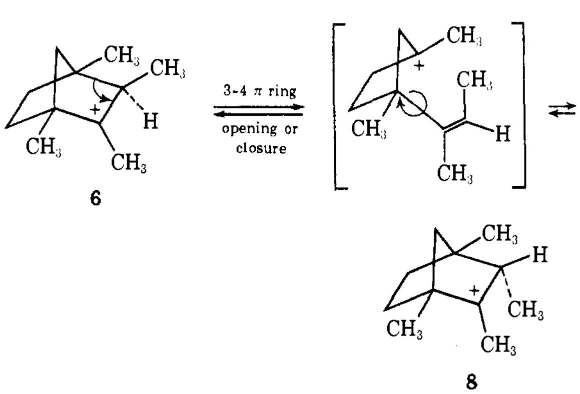
The formation of such an intermediate might be rationalized as shown in eq 4.



4 (4)

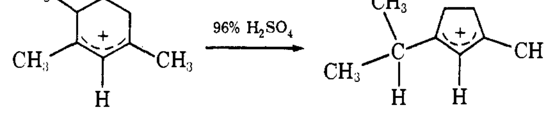
The mechanism of the **6,7** ⇄ **8,9** reaction is not obvious, but eq 5 is perhaps the most attractive possibility.

The cation **11**, from the observed reactivity, is obviously not involved as an intermediate in the reactions of **1** and, in fact, just the reverse may be true. Cation **12** rearranges completely (within the limits of the experimental error) to cation **5**, in a very fast reaction. A similar rearrangement had been observed earlier in a tetramethyl analog so this reaction was expected.[46] There is no evidence that cation **12** is part of the main sequence, but one cannot rigorously exclude the possibility.



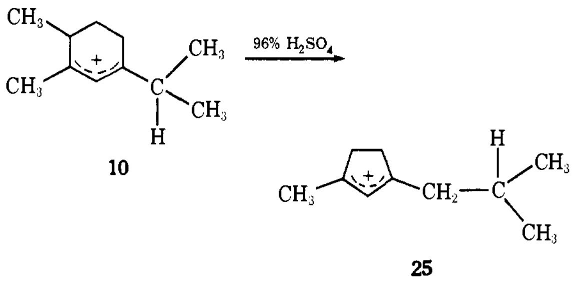
6 **8** (5)

Bicycloalkyl Cations as Intermediates in Cyloallyl Cation Rearrangements. Even though their respective ΔG_f values are similar, the bicycloalkyl cations are obviously much more susceptible to internal rearrangements, hydride shifts, etc., than are the cycloallyl cations. This suggests the possibility that 2-bicyclo[2.2.1]heptyl cations might well be the reactive intermediates in cycloallyl cation → cycloallyl cation rearrangements, even though this intermediate might be slightly less stable than both of the cycloallyl cations and hence not observed. One possible example of this has already been pointed out, *i.e.*, in the reaction of cation **13** to cation **25** (see under Results). Another case concerns some work reported several years ago by Deno and coworkers.[3,4] They showed the reactions given by eq 6 and 7. These authors were obviously concerned by this discrepancy and were able to show that the second reaction can be slowed down drastically if one uses a stronger acid (FSO_3H), in which case one also gets, in part, a second product **36**, obviously related to that found in the first reaction. However, in 96% H_2SO_4, why does not one get the cation **37** in the first reaction?



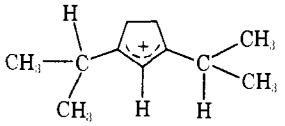
34 **35** (6)

$t_{1/2}$ = 129 hr at 25°



10 **25** (7)

$t_{1/2}$ = 63 min at 25°; this rate is acid dependent



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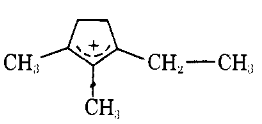

37

We suggest the mechanism shown in Scheme II, albeit incomplete in detail, for the formation of **25**.

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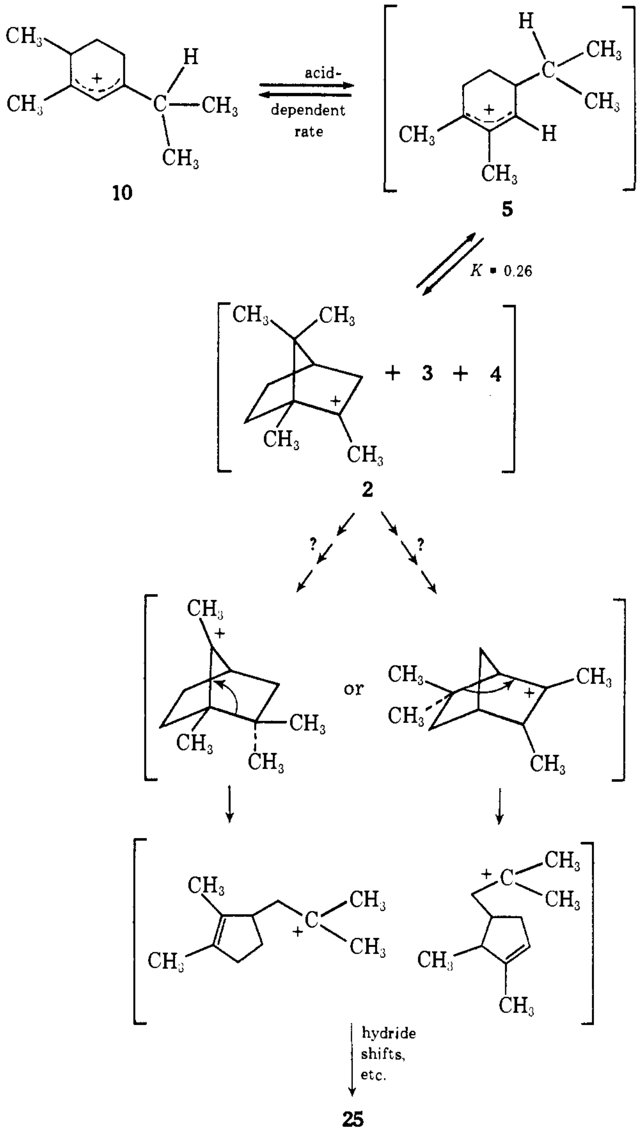
[45] (a) G. Le Ny, *C. R. Acad. Sci.*, **251**, 1526 (1960); (b) R. S. Bly and H. L. Dryden, *Chem. Ind.* (*London*), 1287 (1959); (c) C. F. Wilcox and S. S. Chibber, *J. Org. Chem.*, **27**, 2332 (1962); (d) F. Cramer and W. Rittersdorf, *Tetrahedron*, **23**, 3015 (1967).

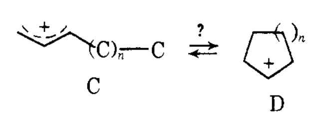
[46] K. Rajeswari and T. S. Sorensen, *Can. J. Chem.*, in press.

Scheme II



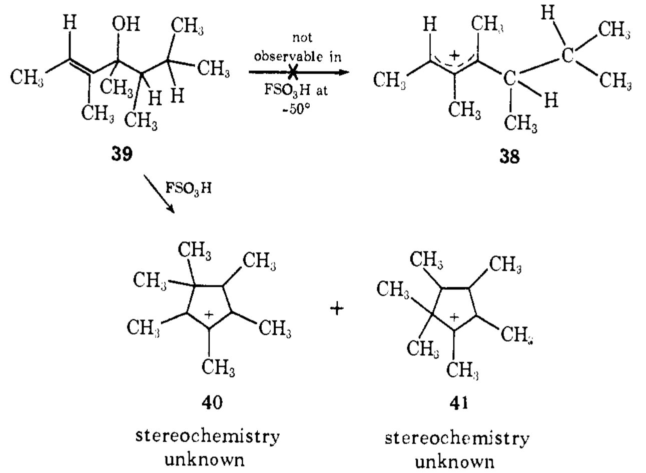
This mechanism (see preceding section) would not be open to the all methyl-substituted cation **34**.

Generalization of the Results. The generalized ion structures C and D represent the $C_nH_{2n-1}^+$ analogy to the systems studied in this paper. When $n = 1$, *i.e.*,



D = the cyclopentyl system, one should have a much less strained alkyl system than that existing in the 2-bicyclo[2.2.1]heptyl case. Therefore, other things being equal, one might expect that the C $\rightleftarrows$ D equilibrium would favor the cyclopentyl cation D by as much as 15 kcal/mol. The possibility of just the opposite behavior has, in fact, been suggested recently by Deno,[47] illustrating the need for experimental work in this area.

In the system C $\rightleftarrows$ D, for the same reasons as in the cycloallyl–bicycloalkyl case, one is forced to work with the less fundamental methyl-substituted derivatives, and in preliminary experiments[48] it has not even been possible to prepare the allylic cation **38**, starting with the allylic alcohol **39**. The nmr spectrum of the initially observed product (FSO_3H, $-50°$) is dominated by a single broad (*ca.* 7.2-Hz width at half-height) peak at τ 8.28, which is about the expected position for methyl groups in the cyclopentyl cations **40** and **41**, assuming that hydride and methyl shifts are so rapid that one gets "effective" equivalence of all of the methyl groups. Allyl cations with a terminal methyl group instead of the terminal *sec*-pentyl group are readily formed from the corresponding allylic alcohol and are perfectly stable under the same conditions as above, demonstrating that the allylic cation **38** would have been stable in a pK_a sense.



Experimental Section

All nmr spectra were measured at 100 MHz using a Varian HA-100 spectrometer. For the cations, the acid proton was used as a lock signal. Neutral compounds were measured as *ca.* 10% solutions in CCl_4 (TMS, τ 10).

Cation Preparation. The procedures used were identical with previous descriptions.[49] The nmr peaks, which are characteristic of each of the cycloallyl cations, are given in Table I. The nmr peaks observed for the bicycloalkyl system **2,3,4** have been described,[13] and those for the bicycloalkyl systems **6,7** and **8,9** are described under Results (see also Figure 2). The temperature calibration for the line-broadening experiments was accomplished by inserting a thermocouple directly into the nmr tube.

Kinetic and Equilibrium Measurements. The kinetics were carried out on nmr samples, thermostated in a cryostat, and the recorded temperatures are accurate to better than ±1°. The nmr measurements were made at a temperature much lower than the cryostat temperature. The nmr area measurements were made by either weighing peaks, measuring the height of similarly shaped peaks, or by multiplying peak heights by their width at half-height and comparing this product. All measurements were made at least twice and usually more. The experimental error based on repeat runs is within ±10%. For most of the rate studies, a nitromethane reference peak was used as a constant area to standardize the measured areas of peaks increasing or decreasing. Simple or reversible first-order rate expressions were used where appropriate. In addition, the rates of appearance of the cations **2,3,4**, and in another series, **6,7**, were measured, and this curve was compared with that expected on the basis of the independently measured rate constants using a consecutive first-order rate expression, *i.e.*, plotting B/A_0 in an $A \rightarrow B \rightarrow C$ sequence, treating the second step in each case as irreversible in order to simplify the expression. The agreement was good, except at the longer times, where the neglect of the reversible nature of the second step begins to show up as a deviation. The rearrangement of cations **8,9** to **10**, in H_2SO_4, was also followed by ultraviolet spectroscopy. The rearrangement of cation **13** to cation **25** was followed by measuring the decrease in the area of the

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(47) Reference 28, p 796.

(48) N. Chiu, unpublished results.

(49) P. H. Campbell, N. W. K. Chiu, K. Deugau, I. J. Miller, and T. S. Sorensen, *J. Amer. Chem. Soc.*, **91**, 6404 (1969).

tert-butyl peak of **13** and the increase in area of the C-2 methyl peak in **25**.[50]

1-Methyl-4-*tert*-butylcyclohex-2-en-1-ol (14). 4-*tert*-Butylcyclohex-2-en-1-one[51] (1.976 g, 0.013 mol) was dissolved in 50 ml of ether and cooled to 0°. To this solution was added dropwise 11 ml of 2.4 *M* methyllithium in ether. After the usual work-up,[52] a colorless product, bp 59–61° (0.25 mm), 1.52 g (70%), was obtained. The material solidifies below room temperature. A successful C, H analysis was not obtained, and the parent mass spectral peak was not observed because of facile dehydration. The nmr spectrum shows a mixture of two isomers, *ca.* 20:80 ratio, corresponding to the cis and trans geometrics. Peaks were observed at τ 9.12 (*tert*-butyl of major isomer), 9.08 (*tert*-butyl of minor isomer), 8.79, 4.41 (the C-2 and C-3 protons of the major isomer), and 4.31 (these protons in the minor isomer). The hydroxy proton peak and a complex region 8–9 were also present.

4-Isopropyl-2-methylcyclohex-2-en-1-one (27). This ketone was prepared from the piperidine enamine of isovaleraldehyde and ethyl vinyl ketone using a procedure identical with that reported for the synthesis of 2,4-dimethylcyclohex-2-en-1-one.[7] The yield of product (0.16 mol scale) was 65%, bp 96–100° (5 mm). *Anal.* Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.98; H, 10.40. Nmr: τ 9.03 (d, J = 6.5 Hz), 8.26 (d, J = 1.5 Hz), a complex region 7–8.5, and 3.42 (q, J = 1.5 Hz).

4-Isopropyl-1,2-dimethylcyclohex-2-en-1-ol (18). The ketone **27** (7.00 g, 0.046 mol) was dissolved in 50 ml of ether and cooled to 0°. An excess of methyllithium was added dropwise and the resulting solution was stirred at 0° for 30 min. Work-up in the usual way led to 5.48 g of the title compound, bp 43–51° (0.05 mm), yield 71%. *Anal.* Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.37; H, 11.95. The nmr spectrum shows that the product is a mixture of the cis and trans isomers. The C-1 methyl group appears at τ 8.82 in both isomers and the C-3 proton at 4.74 and 4.88, both broad, in the two isomers, ratio *ca.* 40:60.

α,α,3,4-Tetramethylcyclohex-3-ene-1-methanol (19). This alcohol was prepared from methyl 3,4-dimethylcyclohex-3-ene-1-carboxylate[53] according to the literature procedure.[54] This alcohol generates cation **5** in FSO_3H at −80° and this becomes the most convenient route to the quenched bicyclic alkenes. However, on addition to 4:1 SO_2ClF–FSO_3H at −120°, alcohol **19** yields an unidentified product, possibly a protonated ether.

1-*tert*-Butyl-4-methylcyclohex-2-en-1-ol (23). 4-Methylcyclohex-2-en-1-one was prepared according to literature procedures[55] but could not be separated from the accompanying β,γ isomer by spinning band column distillation. The mixture was therefore dissolved in ice-cold 96% H_2SO_4 (5 g/50 ml) and left for 2 hr. The H_2SO_4 solution was then added dropwise to a vigorously stirred ice-cold solution of aqueous sodium bicarbonate and ether. Work-up of the reaction mixture and distillation gave the pure α,β-unsaturated ketone (by nmr). The title alcohol was obtained by treating this ketone twice, with an intermediate work-up,[52] with an excess of *tert*-butyllithium in pentane. Two fractions were collected in 60% combined yield (6 mmol scale): (1) bp 72–74° (1 mm), and (2) bp 74–78° (1 mm). Both fractions are contaminated (by nmr analysis) with a higher boiling impurity and the first fraction is, of course, the purest. *Anal.* Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.61; H, 12.17. Nmr: τ 9.04, the *tert*-butyl group; 4.30 and 4.35, the C-2 and C-3 protons. The C-4 methyl doublet appears to be partially buried under the *tert*-butyl peak. The remaining peaks are nondescript. The cation **11** was prepared from the first fraction and is contaminated by the impurity in the alcohol, but this did not affect the characterization of **11**.

2,4-Dimethyl-1-isopropylcyclohex-2-en-1-ol (24). The title alcohol was prepared in 70% yield (0.02 mol scale) by adding isopropyllithium in pentane twice, with an intermediate work-up, to 2,4-dimethylcyclohex-2-en-1-one.[7] The product had a bp 63–66° (1 mm). *Anal.* Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.30; H, 11.42. From the nmr spectrum, the product is a mixture of the cis and trans isomers of **24**.

Recovery (Quenching) Experiments. Alcohol **19**, 10.0 g, was added to *ca.* 75 ml of FSO_3H at −80°. The resulting cation solution was then gradually warmed and aliquots were monitored by nmr analysis until the reaction sequence of Figure 1 had proceeded to the desired extent. In some cases, a mixture of **6**,**7** and **8**,**9** at −30° was quenched in ice-cold aqueous hydroxide,[56] and in others, the quench of predominantly **8**,**9** was carried out at 0°. In the large-scale experiments, the organic material was recovered in virtually quantitative yield. However, this product was a complex mixture which required glc for separation of the individual components. For preparative work, a 12 ft × $^3/_8$ in. column of 30% Carbowax 20M on Chromosorb 60–80 was used. The 0 and −30° quenches produce different proportions, but in both cases four major glc peaks were observed; at 95°, He flow rate of 40 ml/min, the retention times were 33, 45, 53, and 60 min, respectively. At 0°, the relative peak areas were *ca.* 1:3:2:1. The characterization of the last three fractions is discussed under Results. From the nmr spectrum, fraction 1 appeared to be mainly a tetramethylnortricyclene compound contaminated with alkenes showing a single proton on an internal double bond, *i.e.*, products from the elimination of a C-3 proton from cations **7** and **9**.

Miscellaneous Compounds. The alcohol **15** and the hydrocarbons **16** and **17** were purified by preparative glc and characterized by nmr spectroscopy. All have been previously reported.[8] The hydrocarbons **28** and **29** were available from previously described quenching experiments.[16]

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

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[50] This experiment, including the preparation of alcohol **26**, was carried out by Mr. K. A. Ananthanarayan.

[51] E. W. Garbisch, *J. Org. Chem.*, 30, 2109 (1965).

[52] T. S. Sorensen, *J. Amer. Chem. Soc.*, **89**, 3782 (1967).

[53] T. Inukai and M. Kasai, *J. Org. Chem.*, **30**, 3567 (1965).

[54] N. P. Sopov, *Zh. Obshch. Khim.*, **25**, 2082 (1955); *Chem. Abstr.*, **50**, 8487i (1956).

[55] W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968).

[56] T. S. Sorensen, *Can. J. Chem.*, **42**, 2768 (1964).