0.8 g of aldehyde **35** was added. A dense precipitate formed immediately. The reaction mixture was refluxed for 2 hr, cooled, diluted with 200 ml of ether, and filtered. The filter cake was washed thoroughly with ether, and the combined filtrate and washes were washed with water and dried. Removal of solvent gave 0.48 g (52%) of the clear diene: ir (neat) 3080, 2930, 2880, 1645, 1600, 1460, 1000, 910, 760, 735, 700 cm^{-1}; nmr ($CDCl_3$) δ 1.2 (3 H, s), 1.8–2.1 (2 H, m), 2.8 (2 H, t, J = 7 Hz), 4.8–6.2 (5 H, m), 7.1 (4 H, s).

Acknowledgment. The authors acknowledge their gratitude to David Larsen for preliminary studies on the synthesis of the spiroindans.

Rearrangement of Cyclopropyl-Substituted Allylic Cations. II. An Intramolecular 2 + 2 Cycloaddition

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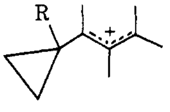
Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada. *Received July 8, 1972*

Abstract: Cyclopropyl-substituted allylic cations, in a general reaction, rearrange to give cyclohexenyl and dienylic cations. Labeling the α-cyclopropyl position with a methyl group shows that a very specific skeletal change accompanies the rearrangement. Evidence is presented to show (1) that a 2-bicyclo[3.1.0]hexyl cation is the primary rearrangement product, and (2) that the reaction is best described as an allowed ${}_{\pi}2_a + {}_{\sigma}2_a$ or ${}_{\pi}2_s + {}_{\sigma}2_a$ cycloaddition, the first example involving an allyl cation and a σ bond. An experiment designed to test the stereospecificity of the cycloaddition was carried out.

Cyclopropyl-substituted allylic cations **1** (R = H) have previously been prepared and characterized



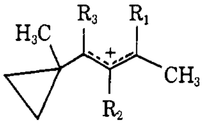
1

in situ by nmr spectroscopy.[1] Those described rearrange in the temperature range +25 to −40°, but the mechanism of this rearrangement was particularly difficult to establish because the supposed primary rearrangement products were themselves *less* kinetically stable compared with **1**. The secondary rearrangement reactions produce branching pathways so that one ends up with many products of diverse structures.

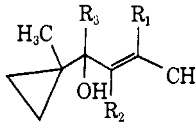
The addition of a methyl group to the α-cyclopropyl position, R = CH_3, results in two valuable advantages: (1) the rearrangement rate of **1** is greatly increased, thereby permitting one to observe the more "primitive" if not the primary product ions; and (2) the added group serves as a convenient mechanistic label.

Results and Discussion

The cyclopropyl-substituted allylic cations **2**–**5** were



2, $R_1 = R_3 = CH_3$; $R_2 = H$
3, $R_2 = R_3 = CH_3$; $R_1 = H$
4, $R_1 = R_2 = CH_3$; $R_3 = H$
5, $R_1 = R_2 = R_3 = CH_3$



6, $R_1 = R_3 = CH_3$; $R_2 = H$
7, $R_2 = R_3 = CH_3$; $R_1 = H$
8, $R_1 = R_2 = CH_3$; $R_3 = H$
9, $R_1 = R_2 = R_3 = CH_3$

studied in three solvent systems, 96% H_2SO_4, FSO_3H, or this acid diluted with SO_2ClF and in FSO_3H–SbF_5. The precursers were in each case the corresponding 3-hydroxy-3-cyclopropyl-1-propenes **6**–**9**, which were prepared from the cyclopropyl carbonyl compound and the appropriate vinyllithium reagent. Using pure FSO_3H or FSO_3H–SO_2ClF, it was possible, with care, to directly observe (*in situ*) each of the cyclopropyl-substituted allyl cations and to characterize these by nmr spectroscopy. The chemical shifts observed are listed in Table I and the features of interest in the nmr spectra are described in footnotes.

In 96% H_2SO_4, the ion preparation was carried out at 0°, and for this reason none of the cyclopropyl-substituted allylic cations were directly observed (see Table II). In 4:1 FSO_3H–SbF_5, only cations **2** and **4** were directly observed (ion preparation temperature *ca.* −80°).

Rearrangement Kinetics. Table II summarizes the observed findings. The reactions show first-order kinetics. The rate constants observed for the disappearance of the cyclopropyl-substituted allylic cations can be roughly compared with those for the corresponding α-H analogs I, R = H, and the large rate enhancement due to the α-CH_3 is shown in column six. In the only example studied, cation **2**, there appears to be only a modest rate increase in changing the solvent from pure FSO_3H to 4:1 FSO_3H–SbF_5. There is a change in product composition ratio also.

Rearrangement Products. The actual product ion composition, both in type and amount, is quite solvent dependent. The most valuable results, in terms of mechanistic investigations, are those obtained in FSO_3H or FSO_3H–SO_2ClF solvents, where one can directly observe the rearrangement process. These will therefore be discussed first.

Overall, the most striking feature of the rearrangement products is the change in the sequential methyl substitution pattern from that existing in the parent cyclopropyl-substituted allylic cations. However, the substitution pattern of the allylic portion does not ap-

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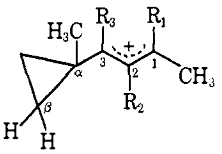
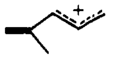
(1) T. S. Sorensen and K. Rajeswari, *J. Amer. Chem. Soc.*, **93**, 4222 (1971).

Table I. Nmr Spectra of the Cyclopropyl-Substituted Allylic Cations



Ion	Temp, °C	Chemical shifts[a] CH$_3$-1	R$_1$	R$_2$	R$_3$	α-CH$_3$	β-H[b]
2	−25	7.33	7.33	2.48[c]	7.40[d]	8.35	7.0–7.35
3	−90	7.85 (d) J = 7[e]	2.60 (q) J = 7	7.88	7.45	8.17	6.8 v br
4	−55	7.30, 7.40		7.63	1.67	8.20	6.7–7.3
5[f]	−90	7.85 (3 H), 7.91 (6 H)			7.06	8.04	6.6–7.0

[a] Relative to internal tetramethylammonium cation = τ 6.90. [b] Very broad and featureless peaks. [c] Cation **2**, like the α-H analog,[1] shows both temperature-dependent chemical shifts and a low-temperature line broadening of the R$_2$ proton (coalescence temperature *ca.* −90°) indicating the presence of both the conformers **2a** and **2b**. With a methyl group at R$_2$, cations **3**, **4**, and **5**, one does not observe either the temperature-dependent chemical shifts or line broadening, presumably because the conformer **a** is now overwhelmingly dominant.[1] [d] This peak was assigned from the observed temperature dependence of the chemical shift (τ increases as temperature decreases). This behavior is discussed in part I.[1] [e] Assigned on the basis of the R$_1$ proton splitting since this doublet is partially obscured. [f] The chemical shift positions observed for this ion are unusual, *i.e.*, the large chemical shift difference between the R$_1$, CH$_3$-1, and the R$_3$ methyl groups, a result of the abnormally low R$_3$ position and the abnormally high R$_1$ and CH$_3$-1 positions, and the somewhat low chemical shift of the α-CH$_3$ peak. These observations show that the allylic cation is *substantially* nonplanar and that the ion is probably better represented as a vinyl-substituted cyclopropyl cation. This result in this particular cation must be due to the cumulative effect of the nonbonded interactions of the vicinal methyl groups. In cation **3**, one observes the same tendencies, but to a somewhat lesser extent.


2a


2b

▬ = edge view of cyclopropane ring

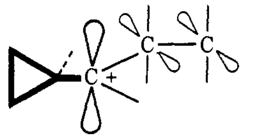


Table II. Rate of Rearrangement of the Cyclopropyl-Substituted Allylic Cations

Ion	Solvent	Temp,[a] °C	k, sec^{-1} [b]	$\Delta F^{\ddagger}$, kcal/mol	$k_{\alpha\text{-CH}_3}$[c]/$k_{\alpha\text{-H}}$
2	FSO$_3$H	−25.0	1.1×10^{-3}	17.9	3.1×10^{2}
	FSO$_3$H-SbF$_5$ (∼4:1)	−40.0	4.5×10^{-4}	17.2	
3	FSO$_3$H-SO$_2$ClF (∼1:4)	−94.8	8.1×10^{-4}	12.8	1×10^{8}
4	FSO$_3$H	−53.5	1.1×10^{-3}	15.8	
5	FSO$_3$H-SO$_2$ClF (∼1:4)	−96.0	1.8×10^{-4}	13.3	2.3×10^{4}

[a] ±1°. [b] Based on duplicate or triplicate runs in which the experimental values are within ±10% of the average result. [c] These comparisons are made at the temperature at which the α-CH$_3$ cation kinetics were run since activation energies were measured for the α-H cations,[1] but not for the α-CH$_3$ cations.

pear to change, in most cases, and is outlined in the product ions shown in Scheme I[2] (methyl = ——). The dienylic cations **10**[4] and **14**[6] were both known from unambiguous syntheses. The cyclohexenyl cation **12** was also known.[7] The remaining structures were assigned on the basis of the observed nmr spectra, which are distinctive enough to permit a definitive assignment[8] (see Table III). The relative amounts of ions

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(2) This procedure may appear to arbitrarily focus on those products with the unchanged allyl pattern. However, cation 17 can be derived from 16 by a reaction occurring as fast as the disappearance of the original cyclopropyl cation 5.[3] Similarly, if the mechanism to be proposed is correct, then the expected cyclohexenyl cation derived from 2 would be extremely unstable and 11 and 12 are not unreasonable secondary products, considering the temperature involved (−25°).

(3) K. Rajeswari and T. S. Sorensen, *Can. J. Chem.*, **50**, 2939 (1972).

(4) The ion 10, shown in brackets, was not directly observed. The cyclization reaction of 10 has, however, been well studied[5,6] and (a) it occurs at a rate considerably faster than that observed for the disappearance of 2 (thus precluding the observation of 10); (b) the two observed product ions 35 and 36 (see Appendix) are formed in the relative amounts 36/35 = 1.6, as is also observed in this work; and (c) enough is known about the mechanism of these dienylic cation cyclizations[5,6] to state confidently that only this particular pentamethyldienylic cation could have yielded the observed results.

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

(6) R. Bladek and T. S. Sorensen, *Can. J. Chem.*, **50**, 2806 (1972).

(7) N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Amer. Chem. Soc.*, **85**, 2991 (1963).

(8) This is not as difficult as might appear, given that one knows the empirical formula. For a start, cyclohexenyl and cyclopentenyl cations are easily distinguished by the coupling constants and chemical shifts, if there are protons at C-1 and C-2 of the allylic portion. For

Table III. Nmr Data for All New Ions[a]

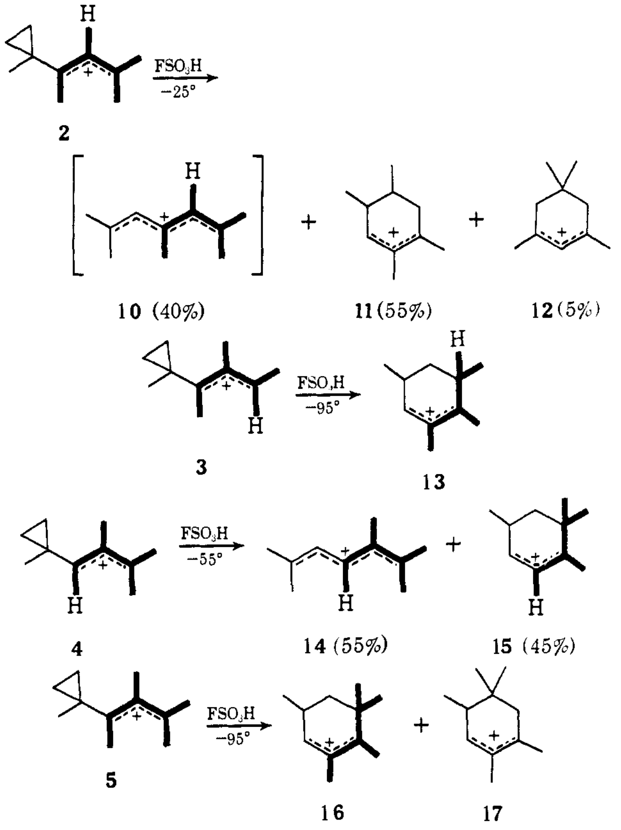
Solvent	Ion	C-1	C-2	C-3	C-4	C-5	C-6 (when present)
FSO_3H	**15**[d]	*c*	2.35[d] (d) $J = 9$	1.01 (d) $J = 9$	*c*, *e*	*c*	8.48
FSO_3H	**16**[f]	*c*	7.71[f]	1.29[f]	*c*, *e*	*c*	8.58, 8.64
FSO_3H	**17**[g]	*c*	7.71[f]	1.29[f]	*c*, *e*	8.78, 9.02	*c*
H_2SO_4	**19**[h]	7.21	7.82	7.21	*c*	8.865 (d) $J = 6.5$	*c*
H_2SO_4	**23**[i]	*c*	2.42	*c*	8.625 (d) $J = 7$	8.88	*c*
H_2SO_4	**24**[j]	*c*	2.54	*c*	8.56	8.10 (d) $J = 8$	8.565 (d) $J = 7$
FSO_3H	**40**[k]	6.86	7.69	0.17	8.84 (*t*-Bu)	*c*	
FSO_3H	**41**[l]	8.58 (*t*-Bu)	*m*	0.51	*e*	*c*	
H_2SO_4	**44**[n]	8.54 (*t*-Bu)	2.33	7.05	8.61 (d) $J = 7$	*c*	

[a] The spectra of ions **11**, **13**, **20**, and **21**, although new to this work, are reported in a separate publication.[3] [b] 1,4,6,6-Tetramethylcyclohexenyl. [c] Only those peaks which are characteristic of the particular ion (often in a mixture) are quoted. In general, C-4, C-5, and C-6 ring protons and methyl groups at C-1 and C-3 are not sharp peaks and are not very useful for specific characterization of ions where mixtures, each having these groups, are present. [d] ±0.01 ppm, b = broad, (d) = doublet, J in Hz, all peak positions relative to internal tetramethylammonium cation = τ 6.90. [e] The methyl group at C-4 could not be assigned with certainty. [f] 1,2,4,6,6-Pentamethylcyclohexenyl; these peaks in **16** and **17** overlap completely. [g] 1,2,4,5,5-Pentamethylcyclohexenyl. [h] 1,2,3,5-Tetramethylcyclohexenyl. [i] 1,3,4,5,5-Pentamethylcyclohexenyl. [j] 1,3,4,4,6-Pentamethylcyclohexenyl. [k] 1,2-Dimethyl-4-*tert*-butylcyclopentenyl. [l] 1-*tert*-Butyl-2,4-dimethylcyclopentenyl. [m] Probably buried under τ 7.69. [n] 1-*tert*-Butyl-3,4-dimethylcyclopentenyl. This ion was also prepared by an unambiguous synthesis.

16 and **17** were difficult to determine at the rearrangement temperature of **5** (*ca.* −95°) because the nmr peaks were viscosity broadened. At higher temperatures, **16** and **17** probably form an equilibrium mixture, K = **17**/**16** = 4.

In 96% H_2SO_4 solvent, at 0°, the observed products are quite different. There are two reasons for this: (1) even in FSO_3H at 0°, some of the ions initially observed at low temperatures have undergone secondary rearrangement reactions; and (2) in H_2SO_4 (a much stronger base than FSO_3H), secondary rearrangement reactions proceeding by a deprotonation–protonation mechanism are much more likely to occur and one might expect to find products with the methyl substitution pattern of the first-formed ions but with the allyl portion displaced if this yields a more stable cation. This expectation is indeed found, as shown by the series of reactions at 0° in Scheme II.

Scheme I



The cations **19**, **20**, and **23** are derivable from **13** and **16** by the deprotonation–protonation mechanism. In the same way, cation **24** is derived from **17**, and **12** can be derived from the primary cyclohexenyl cation expected from **2** (see ref 2). Cation **22**, although of a rearranged skeleton, is probably derived from **15**, since **15** can be expected, from previous work,[1] to give only **22** in the weaker acid solvents. Cation **21** is derived by a mechanism identical with that giving cation **24**.[3] It is significant that the percentage of dienylic cation product formed in H_2SO_4 is virtually the same as in the much weaker base, FSO_3H, a point to be discussed later.

Cations **12** and **22** were known.[7,9,10] The structures assigned to the remainder are based on the characteristic nmr spectra observed (Table III) and on the observed reactivity of the ions (see Appendix). Both **20**

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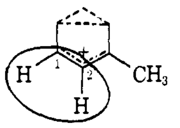
example, the partial structure i would appear as two low-field doublets



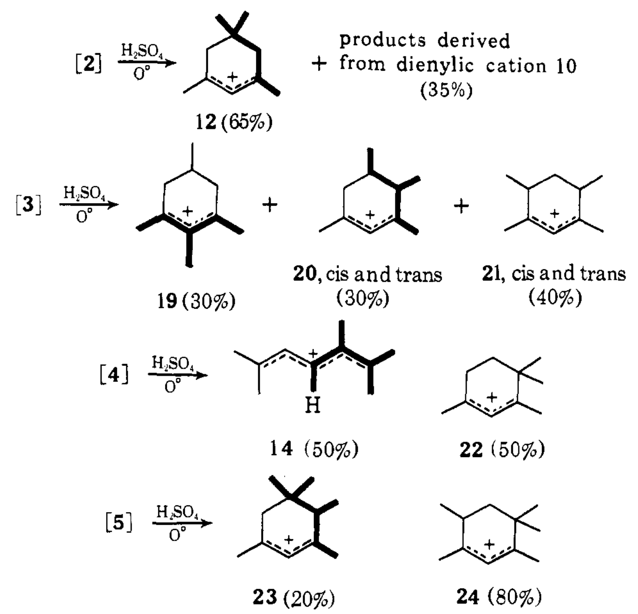
i

in both cases, but the coupling constant in the cyclopentenyl cases is about 4–5 Hz compared with 8–9 for the cyclohexenyl.[9] Furthermore, a C-1 proton resonates at about τ 0.0 in the cyclopentenyl and about τ 1.0 in the cyclohexenyl case.[9] The substitution (H or CH_3) at C-1,2 and -3 is extremely easy to establish, and one is usually left in these structure determinations with no choice of reasonable possibilities for placing the remaining methyl groups.

(9) For example, see T. S. Sorensen and K. Ranganayakulu, *J. Amer. Chem. Soc.*, 92, 6539 (1970).

(10) N. C. Deno and R. R. Lastomirsky, *Ibid.*, 90, 4085 (1968).

Scheme II

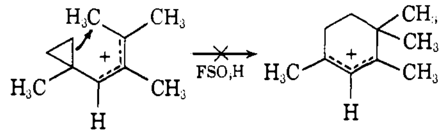


and **21** appear, from the number of methyl doublets observed, to be mixtures of both the cis and trans isomers, although exact assignments were not possible.

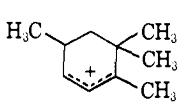
In FSO_3H-SbF_5 (4:1), the products are generally the same as in pure FSO_3H, but the dienylic cation formation is greatly enhanced; *e.g.*, with **2** and **5**, the dienylic cation accounts for 90% of the product.

Most of the primary products undergo at higher temperatures one or more further secondary reactions. These are peripheral to the discussion but are included in an Appendix for completeness.

Structural Features of the Rearrangement. For a given system, the cyclohexenyl product ion produced is by no means either the most stable (among isomers) or that produced by the most economical mechanism (in terms of bond-making and -breaking processes). For example, cation **4** would, on these grounds, have yielded **22**, instead of the observed **15**.

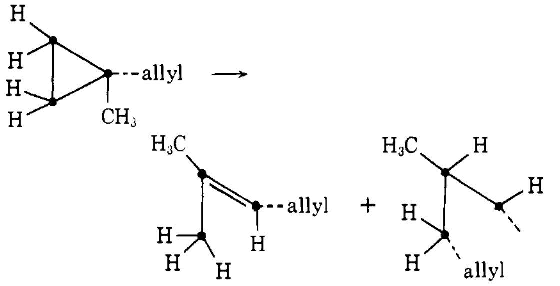


4 **22**



15

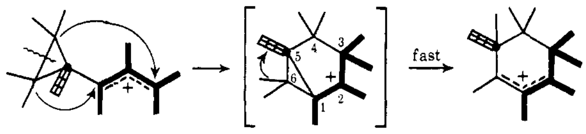
The following points are relevant, in particular, to the FSO_3H solvent rearrangement results: (1) in a majority of cases, the integrity of the original allyl portion is kept; and (2) *in both* the dienylic and cyclohexenyl cation products, the rearranged skeleton is related, even though the hydrogen substitution and the points of attachment to the original allyl portion differ (eq 1).



(1)

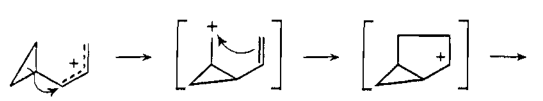
One notes, for example, *in both products*, the allyl portion *is not joined to a carbon bearing the methyl substituent.*

In part I,[1] it was suggested, partly from the preliminary results described in this paper, that the key intermediate might be a 2-bicyclo[3.1.0]hexyl cation,[11] formed by the effective addition of the terminal ends of the allyl cation across the $C_\beta-C_\beta$ bond of the cyclopropane ring (eq 2). This mechanism uniquely ratio-



(2)

nalizes the rearrangement features (*i.e.*, the "odd" repositioning of the original α-methylcyclopropyl group and the intact allyl portion) of the cyclohexenyl cations formed. One now has the additional problem of explaining the co-occurrence of dienylic cations in two of the cases studied. The actual addition might plausibly have occurred by a synchronous cycloaddition or by a two-step process; *i.e.*, the two bonds formed at different times. The latter involves an allyl cation first rearranging to a *primary* cyclopropylcarbinyl system (shown in eq 3). Although related cyclo-



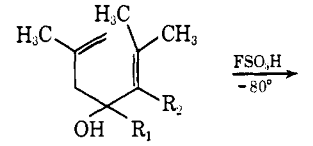
(3)

propylcarbinyl systems are stable enough for direct observation,[12] we believe that the synchronous process is more likely because: (1) in a relative energy context, such an intermediate would appear to be *much* less stable than a cyclopropylallyl system; (2) attempts to generate what would be the product of an initial cyclopropylcarbinyl rearrangement lead to different results;[13] and (3) a related rearrangement observed in

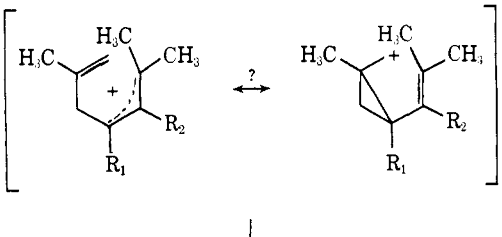
(11) G. A. Olah, G. Liang, and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 3544 (1972), have subsequently investigated the behavior of the parent system in strong acid solvents.

(12) G. A. Olah, D. P. Kelly, C. L. Jevell, and R. D. Porter, *ibid.*, **92**, 2544 (1970).

(13) For example, the following results have been observed:[14]



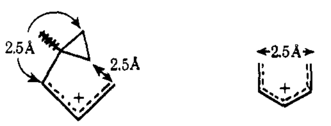
i, R_1 = H; R_2 = CH_3
ii, R_1 = CH_3; R_2 = H
iii, R_1 = R_2 = CH_3



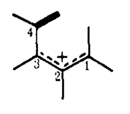
only dienylic cation **14** from i
only dienylic cation **10** from ii
cyclohexenyl cations **16** and **17** from iii

In the event that the intermediates shown above (bracketed) are formed, then the products to be expected from the corresponding (same methyl the bicyclo[3.1.0]hexenyl cations is closely analogous to the case in hand (see Discussion).

In considering a possible concerted reaction, it is worth noting that the termini of the "to be" bonded atoms in a bisected conformation are both *ca.* 2.5 Å apart, a distance virtually identical with that found in dienylic cations, previously shown[15] to undergo a stereospecific electrocyclic transformation to a cyclopentenyl cation.



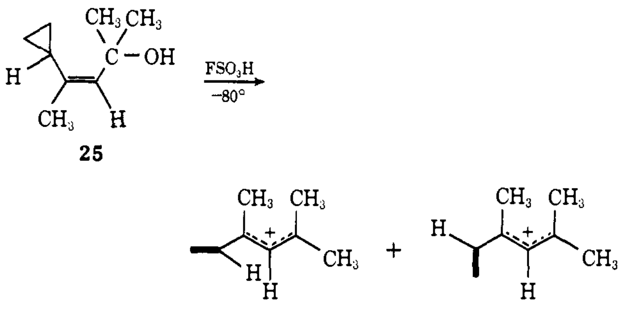
A concerted reaction presupposes the existence of the conformer shown below, designated **2Z,3Z**.[16] The most stable conformer (see footnote *c* to Table I) has the **2E,3E** configuration in all cases. The overall reaction would therefore involve two prerearrangement steps, *i.e.*, eq 4. The rate of the first process has been measured (footnote *c*, Table I) and is considerably *faster* than the rearrangement rates. The second process, **2E** ⇄ **2Z**, has also been shown to be not rate determining by our attempts to synthesize the **2Z** conformer. Thus, the alcohol **25**, when added to FSO_3H at −80°, gave only the equilibrium **2E,3E** and **2E,3Z** mixture of ion **26** (see part I for a description of **26**[1]). Therefore the k_{-2} step must be faster than the k_3 step. The rate constants (k_{obsd}) in Table II would therefore consist of the terms $k_{\text{obsd}} = k_3K_1K_2$. There is evidence to suggest that the term K_2 should be very small in a cation like **4** (eq 5), since, quite apart from the enhanced electronic overlap with a transoid (**2E,3E**) cyclopropane ring, one might estimate a steric factor of perhaps 5 kcal/mol destabilizing the **2Z** form.[18] The complexity of the k_{obsd} term makes the enhancement of k_{obsd} on methyl substitution at the C_α position more plausible since K_1 and K_2 as well as k_3 may all be affected. In any case, if the transition state for the k_3 step resembles the product, then methyl substitution at C_α would be expected to lower $\Delta F^{\ddagger}$.[19]



▬ = edge view of bisected cyclopropane ring

2Z,3Z

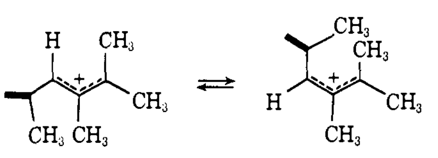
$$\begin{tikzcd} \mathbf{2E,3E} \arrow[r, shift left, "k_1"] & \mathbf{2E,3Z} \arrow[l, shift left, "\substack{k_{-1}\\(K_1)}"] \arrow[r, shift left, "k_2"] & \mathbf{2Z,3Z} \arrow[l, shift left, "\substack{k_{-2}\\(K_2)}"] \arrow[d, "k_3"] & \text{(or the reverse order)} \\ & & \text{products} & \end{tikzcd} \qquad (4)$$



25

26 2E, 3E

26 2E, 3Z



4, 2E,2E **4, 2Z,3E** (5)

Possible ${}_{\sigma}2_s + {}_{\pi}2_a$ or ${}_{\sigma}2_a + {}_{\pi}2_s$ Cycloaddition. Although one is unfortunately ignoring the extended conjugation in the system, one can treat a concerted reaction case, for simplicity, as an allowed 2 + 2 cycloaddition[20] of an allylic cation and a cyclopropane σ bond. In this section, we shall analyze the predicted stereochemistry and then describe experiments aimed at testing the predictions.

There are a total of 16 allowed cycloaddition processes. One-half of these yield a trans fused cyclopropane ring and are thus excluded. Of the remaining eight, four are enantiomorphs of the other four, in our case, since a plane of symmetry exists in the bisected conformation; *i.e.*, both β CH_2 groups are equivalent. The four allowed processes are given in Scheme III.

The main interest in our case concerns the fate of a substituent Y in the original cyclopropylallyl cation, which, depending on whether inversion occurs in the cyclopropane ring atoms or in the allyl cation portion, will yield a different stereochemistry. Unfortunately, the *initially observed* product in this transformation is not the 2-bicyclo[3.1.0]hexyl cation. The cyclohexenyl

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substitution) cyclopropylallyl systems, **4** and **2**, should have been identical. In practice (see Results) cyclohexenyl cations are also formed when **4** and 2 rearrange. It is, of course, possible that the intermediates from the alcohols i and ii are not the same as the hypothetical intermediates from a cyclopropylcarbinyl rearrangement.

The cyclohexenyl cation products from iii are virtually identical with those from the cyclopropylallyl system **5**. This can be used as evidence for an initial cyclopropylcarbinyl rearrangement in **5**, but it seems more likely to us that this contrasting behavior (*cf.* i and ii) is the result of competing ring closure and hydride shift processes, the latter dominating in the case of the intermediates from i and ii.

(14) P. Christensen, Ph.D. Thesis, The University of Calgary, 1971.

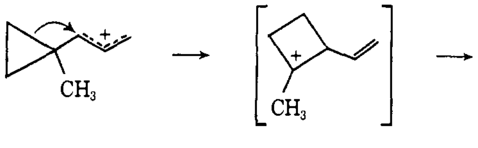
(15) P. H. Campbell, N. W. K. Chiu, K. Deugau, I. J. Miller, and T. S. Sorensen, *J. Amer. Chem. Soc.*, **91**, 6404 (1969).

(16) This conformation is only one of four possibilities for a bisected structure.[1] The cis, s-cis, etc., nomenclature is cumbersome and is best replaced by the *E*, *Z* system.[17] In the cyclopropylallyl cations, the cyclopropane ring takes priority over a proton or a methyl group at C-4. Substituents at C-1 can likewise be given either an *E* or *Z* designation, considering the allyl cation as a distinct unit.

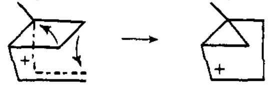
(17) IUPAC Tentative Rules for the Nomenclature of Organic Chemistry. Section E, Fundamental Stereochemistry, *J. Org. Chem.*, **35**, 2849 (1970).

(18) J. Packer, J. Vaughn, and E. Wong, *J. Amer. Chem. Soc.*, **80**, 905 (1958).

(19) Originally, the enhanced rates were assumed to be due to a mechanism in which positive charge was developed at C_α in the rearrangement, *i.e.*



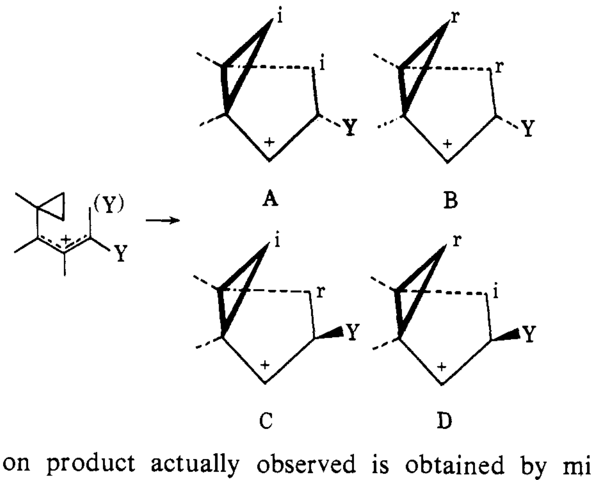
While one might conceive of a rearrangement of this intermediate into the 2-bicyclo[3.1.0]hexyl cation, such a process certainly appears less plausible than the 2 + 2 cycloaddition to be discussed in the next section.



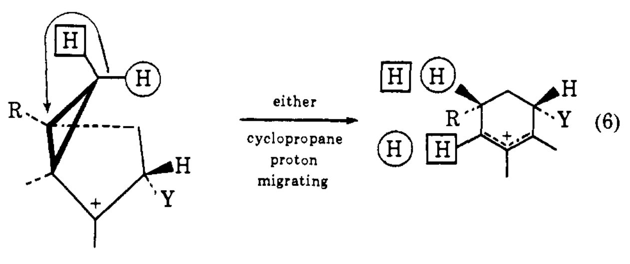
(20) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag-Chemie, Weinheim, Germany, 1970.

Scheme III

(A) $_{\sigma}2_s + _{\pi}2_a$ double inversion on σ bond, inversion of end allyl π bond
(B) $_{\sigma}2_s + _{\pi}2_a$ double retention on σ bond, inversion of end allyl π bond
(C) $_{\sigma}2_a + _{\pi}2_s$ inversion, retention on σ bond, double retention on π bond
(D) $_{\sigma}2_a + _{\pi}2_s$ retention, inversion on σ bond, double retention on π bond



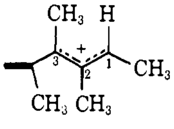
cation product actually observed is obtained by migrating a proton as shown (eq 6).



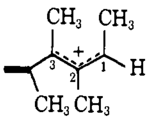
one configuration only

It would appear from steric considerations that the proton must end up on the same side of the ring as the original cyclopropane group. The original stereochemistry (R and Y) is therefore maintained, and a determination of the R, Y stereochemistry in the cyclohexenyl cation product would show where the inversion occurred.

The cyclopropyl-substituted allylic systems chosen for study were **3a** and **3b** (the corresponding 1-(*E*)-

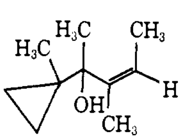


3a



3b

methyl and 1-(*Z*)-methyl substituents as Y in the general discussion). The isomer **3a** (alcohol **7**) was described in the first part of this paper. The stereoisomeric alcohol **27** was prepared from 2-(*Z*)-2-butenyllithium and methyl 1-methylcyclopropyl ketone, in 95% geometric purity (by nmr). However, addition of alcohol **27** to FSO_3H-SO_2ClF at −130° did not yield the expected cation **3b**, in marked contrast to the behavior of the isomeric alcohol **7**. The nmr spectrum of the product actually observed is approximately the same as that which one obtains on rearrangement of **3a**, *i.e.*, that assigned to the cyclohexenyl cation **13**, although the spectra are not as well resolved.[21] One must conclude therefore that the 1-(*Z*)-methyl cation **3b** rearranges at a much faster rate than **3a**, but that it yields the same product.



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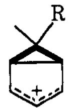
The product nmr spectrum obtained from the rearrangement of **3a** or **3b** and assigned the structure **13**, appears to be a mixture of the cis and trans isomers since a doubling[22] of the C-2 methyl signal (expected to be a sharp singlet if a single ion) was observed. Thus, it appears that inversion probably occurs in a given molecule either on the cyclopropyl or the allyl cation carbon, assuming the proposed mechanism is correct.

Comparison with Related Systems. Further Evidence for a Concerted Reaction. Examples of cycloadditions involving cyclopropane σ bonds are moderately plentiful.[24,25] There are, however, no very close ionic analogies to the reactions described in this work. Perhaps the most closely related species is the bicyclo[3.1.0]-hexenyl cation system **28**, first described by Winstein, Childs, and Sakai[26,27] and subsequently by other workers.[28,29,30] Even earlier, protonated ketone analogies had been reported by Hart.[31] The two structures are shown below in a way which emphasizes the relationship.



28

1

Cation **28** (heptamethyl-substituted) undergoes a degenerate rearrangement in which the cyclopropane moiety rotates around the ring, with the important stereochemical observation that an inner substituent R always remains "inner."[27] Although this stereospecificity is described in terms of a 1,4-sigmatropic shift, the same result is obtained by considering it as a 2 + 2 cycloaddition. Because of the constraints of this system, only the $_{\pi}2_s + _{\sigma}2_a$ process with double retention in the allyl cation and inversion of the migrating cyclo-

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(21) Attempts to generate 1-(*Z*)-methylcyclopropylallyl or 1-(*Z*)-methyl dienylic cations have produced reasonably well-resolved spectra at the low-temperature range. However, on warming, the spectra lose all resolution and very broad bands typical of polymers appear. What makes this observation unusual is the fact that qualitatively the *same* spectrum can sometimes be observed from the 1-(*E*)-methyl precursors, but in this case no subsequent polymerization occurs. A polymerization catalyst not detected by nmr must be produced in the former case.

(22) There is a faint possibility that this doubling could be due to "frozen out" *ae* and *ea* conformers of a trans **13**.[23] Unfortunately, cation **13** is not thermally stable and further rearranges rapidly at −60°,[3] precluding a test of the expected coalescence behavior of such a system.

(23) H. Hogeveen, C. J. Gaasbeek, and H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **88**, 379 (1969).

(24) P. G. Gassman and G. D. Richmond, *J. Amer. Chem. Soc.*, **92**, 2090 (1970).

(25) D. J. Pasto and A. Chen, *ibid.*, **93**, 2562 (1971).

(26) R. F. Childs, M. Sakai, and S. Winstein, *ibid.*, **90**, 7144 (1968).

(27) R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968).

(28) V. A. Koptyug, L. I. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, *Chem. Commun.*, 389 (1969).

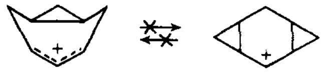
(29) R. F. Childs and B. Parrington, *ibid.*, 1541 (1970).

(30) P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Bersen, *J. Amer. Chem. Soc.*, **93**, 1551 (1971).

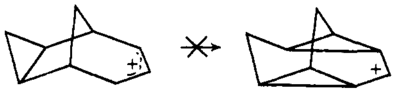
(31) H. Hart, T. R. Rodgers, and J. Griffiths, *ibid.*, **91**, 754 (1969), and earlier papers.

propane carbon is possible, giving the same stereochemical result.

There are two further systems **29**,**30** and separately **31**, solvolytically generated in the former, where a cycloaddition or cycloreversion process was *not* observed.[32,33] However, in both cases, it is sterically impossible to have a ${}_{\pi}2_s + {}_{\sigma}2_a$ or ${}_{\sigma}2_s + {}_{\pi}2_a$ process.



29 **30**



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Dienylic Cation Formation. The substitution pattern observed in these cations requires a rearrangement of the basic cyclopropylallyl skeleton before the dienylic cation formation.[34] The observed pattern is that which occurs by either (1) an initial cyclopropylcarbinyl rearrangement and subsequent hydride shifts (see ref 13) or (2) cleavage of the 3,4 bond of the 2-bicyclo[3.1.0]hexyl cation[35] leading to the same intermediate as in (1) and then the same hydride shifts. We have already commented on the problems involved in postulating an initial cyclopropylcarbinyl rearrangement of the cyclopropylallyl cations.

The fact that dienylic cation formation is enhanced in FSO_3H-SbF_5 solvent is not explained by either (1) or (2) above and the solvent may be found to be fundamentally involved in this reaction. At present, it seems futile to speculate further on the detailed mechanism.

Experimental Section

The methods used to prepare the ions and the procedures used in the rate studies are similar to those described.[1] In this work, several ions were prepared at −130°, and this was done by cooling a *ca.* 4:1 v/v $SO_2ClF-FSO_3H$ solution, already in an nmr tube, to −130° in a pentane–liquid nitrogen slush bath. Small quantities of the alcohols were then added from a long dropper to the side of the nmr tube, just above the acid solution, and this solidified mass was then mixed with the acid solution by the vigorous up and down action of a platinum spiral stirrer.

In the rate studies, temperatures were monitored using a thermocouple placed directly in the nmr tube.[6] The nmr tube transfer from the bath to the nmr probe (Varian Associates HA-100) had to be carried out as quickly as possible.

1-Methylcyclopropanecarboxylic Acid. To a stirred, 0°, solution of sodium hypobromite (from 165 g, 4.1 mol) of sodium hydroxide in 1.4 l. of water and 240 g (1.5 mol) of bromine, keeping the temperature below +10°, was added, dropwise, 49 g (0.5 mol) of methyl 1-methylcyclopropyl ketone,[36] the temperature of the mixture being kept below 5°. The solution became decolorized after 1 hr, but stirring was continued for 3 hr further. The solution was then extracted with ether (3 × 100 ml) to remove any unreacted ketone and bromoform, and these extracts were rejected. The aqueous layer was cooled in ice and acidified with 400 ml of 40% H_2SO_4; this mixture was washed with water (2 × 50 ml) and dried over $MgSO_4$. Distillation of the residue, after ether removal, through an 18-in. spinning band column (no cold water circulation in the condenser), reflux ratio 10:1, gave a product, 40 g (80%), bp 79–80° (12 mm), which solidified at room temperature, mp 31–32°, lit.[37] 29.5–32°; 60-MHz nmr (CCl_4) τ 2.4 (1 H), 8.75 (3 H), two multiplets 8.6–9.45 (4 H), analyzing for an AA′BB′ multiplet.

1-Methylcyclopropanecarboxaldehyde. The acid chloride of the above acid was prepared in 95% yield using the thionyl chloride procedure, bp 50–51° (42 mm). This, 23.7 g (0.2 mol), was dissolved in 100 ml of diglyme and added to a 1-l. three-necked flask equipped with a magnetic stirrer, low-temperature thermometer, and a separatory funnel. The flask was then cooled in a Dry Ice–acetone bath, and to the stirred solution, under nitrogen, was added 50.6 g (0.2 mol) of lithium tri-*tert*-butoxyaluminohydride, prepared by the method of Brown,[38] in 200 ml of diglyme, over a period of 1 hr. The temperature of the reaction mixture remained about −60°. After addition, the reaction mixture was allowed to warm to room temperature over a 2-hr period. The contents were then poured into crushed ice and extracted (4 × 150 ml) with ether. The combined ether layers were washed with water (50 ml) and dried over $MgSO_4$ (hydroquinone crystal added). The ether was removed through a 20-in. fractionating column and the residue distilled through a 30-in. Teflon spinning band column, reflux ratio 50:1, collecting the fraction bp 102–103° (657 mm), lit.[35] 106–108° (760 mm). The isolated yield was 5 g (30%), but the calculated yield before distillation (by nmr) was 65%. The 2,4-DNPH had mp 222–223°, lit.[39] 222.1–222.8°; 60-MHz, nmr (CCl_4) τ 1.40 (1 H), 8.75 (3 H), 8.8–9.2 (4 H), analyzing for an AA′BB′ multiplet.

2-[1-(1-Methylcyclopropyl)]-4-methyl-3-penten-2-ol (6). From 5.0 g (0.05 mol) of methyl 1-methylcyclopropyl ketone, 9.5 g (0.07 mol) of isobutenyl bromide, and 1 g (0.14 g-atom) of lithium metal, there was obtained in the usual manner[1] 5.0 g (64%) of the title alcohol: bp 77–78° (10 mm); 60-MHz nmr (CCl_4) τ 4.76 (septet, J = 1.4 Hz, 1 H), 8.15, (d, J = 1.4 Hz, 3 H), 8.29, (d, J = 1.4 Hz, 3 H), 8.78 (3 H), 8.95 (3 H), 9.0–9.9 (the cyclopropane protons and OH).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 78.37; H, 11.78.

2-[1-(1-Methylcyclopropyl)]-3-(*E*)-methyl-3-penten-2-ol (7). From 5.0 g (0.05 mol) of the above ketone, 10 g (0.07 mol) of 2-(*E*)-bromo-2-butene,[15] and 1 g (0.14 g-atom) of lithium metal, there was obtained 6.0 g (76%) of the title alcohol: bp 81–82° (12 mm); 60-MHz nmr (CCl_4) τ 4.46 (quartet of quartets, J = 7 Hz), 1.5 (1 H), 8.36 (quartet, J = 1.5 Hz, 3 H), 8.38 (d, J = 7 Hz), 3 H), 8.84 (3 H), 9.15 (3 H), 8.95–9.9 (cyclopropane protons and OH). Analysis of the τ 4.46 and 4.71 region indicated a geometric purity of at least 95%.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.45; H, 12.06.

2-[1-(1-Methylcyclopropyl)]-3-(*Z*)-methyl-3-penten-2-ol (27). This alcohol was prepared in 75% yield from the 2-(*Z*)-bromo-2-butene[15] and the ketone: bp 70–75° (12 mm); 60-MHz nmr (CCl_4) τ 4.71 (quartet, J = 7 Hz, 1 H), 8.29 (3 H), 8.87 (3 H), 8.29 (d, J = 7 Hz), 8.96 (3 H), 9.0–9.95 (m, cyclopropane protons and OH). Analysis of the τ 4.46 and 4.71 region indicated a 95% geometric purity.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.41; H, 11.64.

2-[1-(1-Methylcyclopropyl)]-3,4-dimethylpent-3-en-2-ol (9). From 5.0 g (0.05 mol) of the ketone, 8.0 g (0.05 mol) of 2-bromo-3-methyl-2-butene,[1] and 1.0 g (0.14 g-atom) of lithium metal, there was obtained 5.0 g (58%) of the title alcohol: bp 98–99° (12 mm); 60-MHz nmr (CCl_4) τ 8.10 (3 H), 8.36 (6 H), 8.91 (3 H), 9.00 (3 H), 8.6–9.9 (m, the cyclopropane protons and OH).

Anal. Calcd for $C_{10}H_{18}O$: C, 78.51; H, 11.98. Found: C, 78.99; H, 12.33.

1-[1-(1-Methylcyclopropyl)]-2,3-dimethyl-2-buten-1-ol (8). From 4.2 g (0.05 mol) of 1-methylcyclopropanecarboxaldehyde, 13.4 g (0.09 mol) of 2-bromo-3-methyl-2-butene, and 1.4 g (0.2 g-atom) of lithium metal, there was obtained 5.0 g (65%) of the title alcohol: bp 36° (0.03 mm); 60-MHz nmr (CCl_4) τ 5.54 (1 H), 7.63 (1 H, OH proton), 8.35 (b, 9 H), 9.12 (3 H), 8.6–9.9 (cyclopropane protons).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.80; H, 11.85.

Ethyl 3-(*Z*)-cyclopropyl-2-butenoate was prepared by the procedure of Jorgensen,[40] in *ca.* 90% (by glc) geometric purity after

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(32) J. B. Lambert, F. R. Koeng, and A. P. Jovanovich, *J. Org. Chem.*, 37, 374 (1972).

(33) A. F. Diaz, D. L. Harris, M. Sakai, and S. Winstein, *Tetrahedron Lett.*, 303 (1971).

(34) No evidence for the shift of a methyl group from one sp^2 center to another in a dienylic cation has even been observed. Further, such a reaction appears mechanistically improbable.

(35) This could be looked on as a cycloreversion to a double bond and an allyl cation, allowed for a ${}_{\pi}2_a + {}_{\pi}2_s$ process.[20]

(36) French Patent 1,259,995; *Chem. Abstr.*, **56**, 353*d* (1960).

(37) S. Siegal and C. G. Bergstrom, *J. Amer. Chem. Soc.*, **72**, 3816 (1950).

(38) H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5377 (1958).

(39) D. I. Schuster and J. D. Roberts, *J. Org. Chem.*, **27**, 51 (1962).

(40) M. J. Jorgensen, *J. Amer. Chem. Soc.*, **91**, 6432 (1969).

fractional distillation through an 18-in. spinning band column, bp 88–90° (14 mm).

4-(*Z*)-Cyclopropyl-2-methylpent-3-en-2-ol (25) was prepared by methyllithium addition to the above ester. This alcohol has been reported.[41]

Acknowledgment. The authors thank the National Research Council of Canada for generous financial support and Dr. A. C. Oehlschlager for a valuable discussion.

Appendix

Secondary Rearrangements. Only those processes which are unpublished and which are reasonably rapid at room temperature are shown. The rearrangement mechanisms involved have been discussed.[1] The nmr assignments are given in Table III. References are given to the rearrangement reactions which have been published.

Cation **2**

11,[3] **12**,[7] cation **10** has been shown[5,6] to give a 39:61 mixture of **32** and **33** in FSO_3H or $ClSO_3H$.

Cation **3**

FSO_3H **13**[3]

H_2SO_4 Cyclohexenyl cations **20** and **21** rearrange at 25° to give nearly pure **19**, $k \sim 4 \times 10^{-4}$ sec^{-1}.

Cation **4**

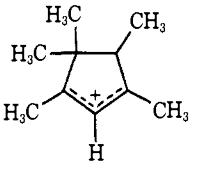
FSO_3H **14**.[6] Cation **15** forms the *tert*-butylcyclopentenyl cation **34**, $k \sim 4 \times 10^{-4}$ sec^{-1} at −37°. This cation, **34**, then rearranges to an equilibrium mixture with **35**, probably by way of the known[1,9] cyclohexenyl cation **36**, also observed in small amounts during the **34** $\rightleftarrows$ **35** equilibration. The further reactions of **34** and **35** have been described.[9] The forward rate constant **34** $\rightleftarrows$ **35** was *ca.* 9×10^{-4} sec^{-1} at −10° and *K* was *ca.* 3.

H_2SO_4 **22**.[9,10,42]

Cation **5**

FSO_3H Cations **16** and **17** eventually rearrange to the single cation **37**, $k \sim 7 \times 10^{-4}$ sec^{-1} at −52.5°. During this process, transient peaks appear, which are assigned to the cation **38**. This cation probably represents a dead-end shunt which eventually is funneled back to **37**. Cation **37** further rearranges, $k \sim 1.4 \times 10^{-4}$ sec^{-1} at −10°, to give mainly cations **39**, **40** (both known),[43,44] and **24**, although several other minor products are also formed.

H_2SO_4 Cation **24** (also formed above in FSO_3H) rapidly yields cation **41**, $k \sim 2.4 \times 10^{-3}$ sec^{-1} at 25°, while **23** much more slowly gives the known[43,44] equilibrium mixture **40** and **42**. Cation **41** also slowly yields the same pair.



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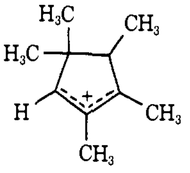

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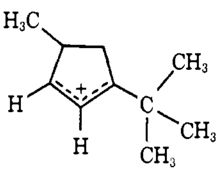

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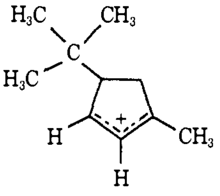

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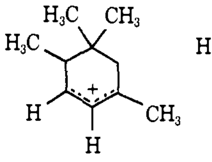

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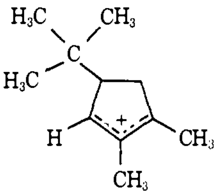

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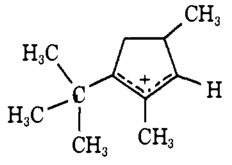

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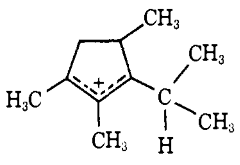

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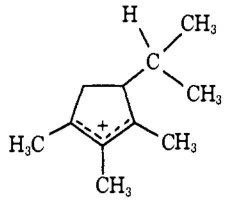

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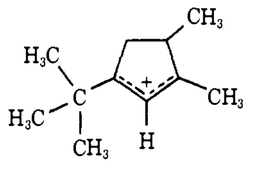

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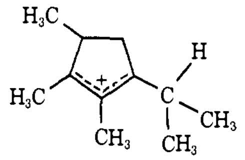

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