The temperature of the gas stream is controlled by a thermistor, mounted just below the nmr tube, which through a relay determines the rate of boiling of the N_2. The temperature of the gas stream and HFSO$_3$ solution can be monitored with suitably placed thermocouples.

In a typical experiment durene (20 mg) was dissolved in FSO$_3$H (0.5 ml) and irradiated at −90° using a thick window glass filter, cutoff 320 nm. The reaction was monitored by nmr and typically a photostationary state (60% conversion) was reached within 60 min of irradiation. After 150 min of irradiation *ca.* 18% of **7** was detected.
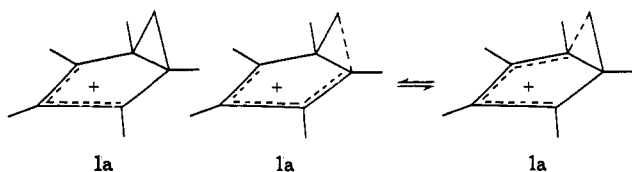
Circumambulatory Hexa- and Heptamethylbicyclo[3.1.0]hexenyl Cations

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Abstract: The low temperature photoisomerization of hepta-, **5**, and hexamethylbenzenonium ions, **6**, in HFSO$_3$ gave respectively the hepta-, **4**, and 6-*endo*-hexamethylbicyclo[3.1.0]hexenyl cations, **7**. Alternatively, **7** and its exo-isomer **10** could be obtained by protonation of the corresponding homofulvenes. These bicyclic cations were stable at low temperatures but rearranged on heating to the corresponding benzenonium ions. The rate of this isomerization was shown to be dependent upon the C$_6$ substituents. Both **4** and **10** exhibited variable temperature nmr spectra that indicated a degenerate migration of the cyclopropane around the periphery of the five-membered ring was occurring. This migration was shown to proceed by successive 1,4-shifts and not to involve the intermediacy of a bicyclo[2.1.1]hexenyl cation. A very high stereoselectivity was observed in these rearrangements, the C$_6$ substituents always remaining in the same relative positions. Thus for every 8×10^8 migrations of the cyclopropyl of **10**, less than one took place with an overall inversion of stereochemistry to give **7**. This observed stereoselectivity is that required by orbital symmetry considerations if the rearrangement proceeds by a concerted 1,4-sigmatropic shift. The barriers to these degenerate rearrangements were found to be 10.1 kcal/mol for **4**, 12.0 kcal/mol for **10**, and 17.5 kcal/mol for **7**. A consideration of the marked sensitivity of this isomerization to the nature and position of the C$_6$ substituents suggests that the transition state may be represented as a substituted cyclopentadiene-5-methyl cation in which both lobes of the formally vacant p orbital on C$_6$ are interacting symmetrically with the diene. A C$_6$ endo substituent would appear to reduce the importance of this overlap by sterically interacting with C$_2$ and C$_3$ and thus preventing C$_6$ from moving toward the diene. The isomerizations of the 2-hydroxy-1,3,4,5,6,6-hexamethylbicyclo[3.1.0]hexenyl cation were investigated and compared with the rearrangements of **4**.

The preceding paper in this series has emphasized in particular two aspects of the chemistry of the bicyclo[3.1.0]hexenyl cations, namely their structure and their relationship to the isomeric benzenonium cations.[2] An important feature of these ions is that charge delocalization involves the two external cyclopropane bonds, rather than the internal C$_1$–C$_5$ bond. For example, the nmr spectrum of the pentamethyl cation **1** showed that there was considerable leakage of positive charge onto C$_6$. Structures such as **1a** were proposed to account for the properties of this cation.

<center>

1a   **1a**   **1a**

</center>

One of the classic probes for an electron deficient carbon is to examine the effect of alkyl substitution upon its stability and reactivity. The elegant study of Swatton and Hart indeed suggested that methyl substitution at C$_6$ of these systems might have a profound effect upon their reactions.[3] These authors showed through the use of suitably deuterated materials that there was a migration of cyclopropane around at least four of the five sides of the cyclopentenyl ring of the hydroxy cation **2** (Scheme I). No such comparable reaction was detected with **1** nor with the tetramethylbicyclo[3.1.0]hexenyl ions.[4]

With the discovery of a novel photochemical route to **1** from the pentamethylbenzenonium ion, it seemed worthwhile to attempt the preparation of derivatives of **1** bearing methyl groups upon C$_6$. In this paper we report the synthesis and observation of the hexa- and heptamethylbicyclo[3.1.0]hexenyl cations.[5]

(1) (a) Address all correspondence to this author at McMaster University; (b) deceased November 23, 1969.

(2) R. F. Childs, M. Sakai, B. D. Parrington, and S. Winstein, *J. Amer. Chem. Soc.*, **96**, 6403 (1974).

(3) D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 5075 (1967).

(4) R. F. Childs and B. Parrington, *J. Chem. Soc. D*, 1540 (1970).

(5) Part of this work has appeared in preliminary form, R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7146 (1968).
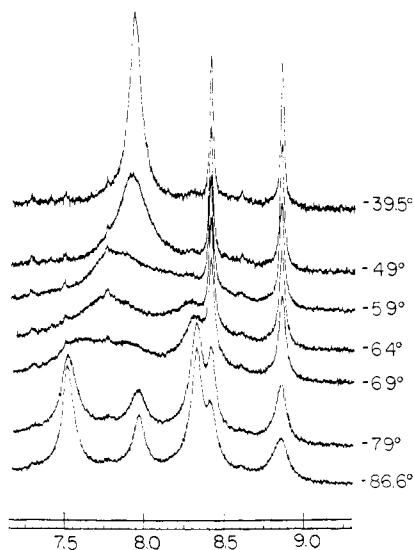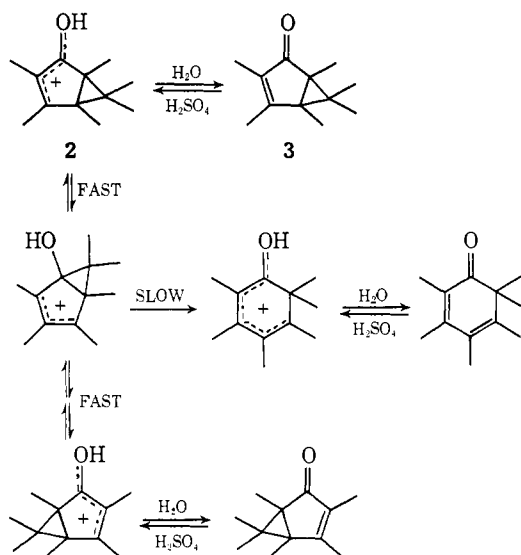
Figure 1. Variable temperature pmr spectra of 4 obtained by photoisomerization of 5.

Scheme I

Results and Discussion

Synthesis and Characterization of 4. The cation required for the photochemical preparation of **4** is the heptamethylbenzenonium ion **5**, which has been characterized by Doering, et al.[6] Protonation of the methylenecyclohexadiene derivative **6**[7] in $HFSO_3$ gave **5**, with a very similar nmr spectrum to that previously reported.[9]
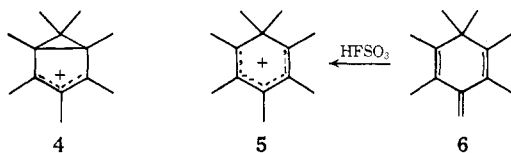
(6) W. v. E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).

(7) A. convenient route to **6** has been described.[8]

(8) H. Hart, P. M. Collins, and A. J. Waring, *J. Amer. Chem. Soc.*, **88**, 1005 (1966).

(9) The signal positions originally reported by Doering are incorrect.[8,10]

The cation **5**, which has a long wavelength absorption at 400 nm (log ϵ 4.04),[8] was irradiated at $-78°$ in $HFSO_3$. While it was quite clear from the changes occurring in the nmr spectrum that a photochemical reaction was taking place, the product had a different spectrum to that expected on the basis of **1**. The photoproduct derived from **5** exhibited a reversible temperature dependent spectrum, although the freezing point of $HFSO_3$ ($-88.98°$)[11] precluded the observation of the limiting low temperature spectrum. On warming the solution to $-9°$ a thermally irreversible isomerization took place to regenerate **5**, the rate constant for this first-order process being 2.2×10^{-4} sec^{-1} at $-9°$ ($\Delta F^{\ddagger} = 19.8$ kcal/mol).

To characterize this photoproduct it was desirable to record the limiting low temperature spectrum and to this end it was prepared in a $HFSO_3$–SO_2ClF (2:1) solution. The nmr spectrum could now be recorded over the range -110 to $-9°$. Sample spectra are shown in Figure 1. Some viscosity broadening of all the peaks is occurring at the lower temperatures. Resonances attributable to a small amount of the benzenonium ion **5** can be detected in these spectra.
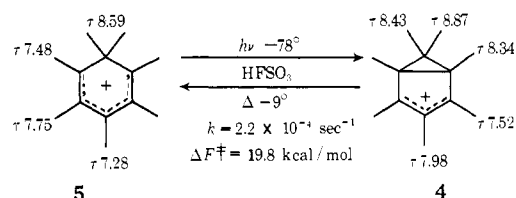
Below $-90°$ the nmr spectrum of the photoproduct is essentially frozen, no further major change occurring on cooling the sample below this point. Apart from the two high field methyl resonances the methyl signals in this frozen spectrum occur in very similar positions to those observed for **1** and are quite consistent with the formation of **4**.[2] The two resonances at τ 8.87 and 8.43 can be attributed to the C_6 methyl groups, both occurring in the region expected for similarly situated groups upon a cyclopropyl allyl cation.[12]

On warming the $HFSO_3$–SO_2ClF solution of **4** above $-90°$, the resonances attributed to the cyclopentenyl ring methyls broadened and coalesced at about $-60°$ and above this temperature became a singlet. For example, at $-39.5°$ there are only three signals observed for **4** with the ratio 15:3:3. The observed position of the averaged ring methyls is τ 7.95, which is very close to the position expected for the mean of their low temperature positions (τ 7.94). On cooling the sample, the original five-line spectrum was restored. During this averaging of the ring methyls there was no detectable change in the signals attributable to the C_6 *gem*-dimethyl group.
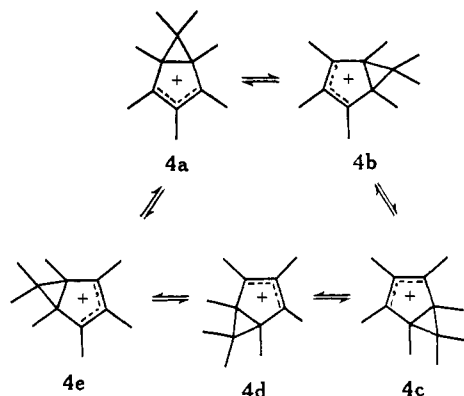
The averaging of the five cyclopentenyl methyl groups of **4** clearly means that there must be some process which has the effect of moving the cyclopropane group around the periphery of the five-membered ring, without the destruction of the cation (Scheme II). The very

(10) V. A. Koptyug, V. G. Shubin, A. I. Rezbukin, D. V. Korchagina, V. P. Tret'yakov, and E. S. Rudakov, *Dokl. Akad. Nauk SSSR*, **171**, 1109 (1966); M. Saunders in "Magnetic Resonance in Biological Systems," Pergamon Press, New York, N. Y., 1967, p 85.

(11) R. J. Gillespie and T. E. Peel, *Advan. Phys. Org. Chem.*, **9**, 1 (1971).

(12) K. E. Hine and R. F. Childs, *J. Amer. Chem. Soc.*, **93**, 2323 (1971); K. Rajeswari and T.S. Sorensen, *ibid.*, **95**, 1239 (1973).
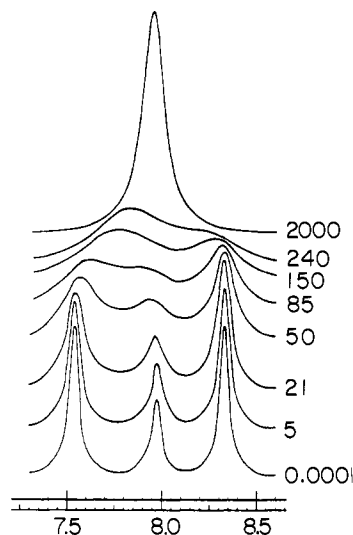
Scheme II

Figure 2. Calculated pmr spectra for the rearrangement of **4**. Only signals attributable to the five ring methyls are shown. (Rate constants are given in sec^{-1}.)

near coincidence of the observed and calculated averages of these methyls also shows that if any other bicyclic cations are involved in these reactions, they are only present to a very small extent.

Careful examination of the nmr spectrum of **4** during the onset of averaging reveals that not all the peaks of the cyclopentenyl ring methyls are broadened to the same extent. For example, at $-79°$, the peak attributable to the C_1 and C_5 methyls, at τ 8.34, is still relatively sharp compared to those of the C_2, C_4, and C_3 groups. This suggests that the migration of the cyclopropyl occurs in discrete steps, such as **4a** to **4b** or **4e** and not **4a** directly to **4d** or **4c**. Precedent for this stepwise migration of the cyclopropyl can be found in the previously discussed results of Hart.[3] A comparable, but single step migration forms one of the basic stages proposed by Zimmerman[13] in the photorearrangements of the 2,5-cyclohexadienones.

The line shapes expected for such a migration, computed using a Saunders many site nmr line-shape program[14] are shown in Figure 2. It can be seen that the calculated spectra closely mimic the ones obtained experimentally, confirming again the suggestion of the discrete stepping motion of the cyclopropane around the cyclopentenyl ring. Several good fits of the calculated and observed spectra were obtained: the spectra at $-86.6°$ corresponding to a rate of 5 sec^{-1}, $-79°$ to 21 sec^{-1}, $-69°$ to 85 sec^{-1}, $-64°$ to 150 sec^{-1}, and $-59°$ to 240 sec^{-1}. These rates correspond to a $\Delta F^{\ddagger}$ of 10.1 kcal/mol.[15,16]

It was pointed out earlier that during this degenerate cyclopropyl migration there is no averaging observed of the two C_6 methyl groups. This must mean that these two groups must retain their identity during the migration, the exo methyl remaining exo and the endo methyl remaining endo. If these were interconverting, then it would lead to a line broadening and eventually

averaging of these two signals. The half widths of the signal attributable to the *gem*-dimethyl group of **5** were compared to those of the C_6 methyl resonance of **4** (τ 8.87) at various temperatures, Table I.[18] If any

Table I. Comparison of *gem*-Dimethyl Group Half Widths of **4** and **5**

Temp, °C	**4** (τ 8.87) half width, Hz	**5** (τ 8.43) half width, Hz
-71	1.8 ± 0.1	1.8 ± 0.1
-17	1.9	1.8
-9	1.8	1.6

broadening of this resonance of **4** is occurring, it is small and is certainly less than 1 Hz. Using the slow exchange approximation,[19] a change in half width of 1 Hz would correspond to a first-order rate constant of 3 sec^{-1}. Thus the free energy barrier to interconversion of the C_6 methyls at $-9°$ is greater than 14.7 kcal/mol.

The Hexamethylbicyclo[3.1.0]hexenyl Cations. Our initial entry into these hexamethyl substituted systems was from the well-characterized hexamethylbenzenonium ion, **6**, prepared by protonation of hexamethylbenzene.[20] Irradiation of a HFSO$_3$ solution of **6** (λ_{max} 395)[21] through Pyrex at $-78°$ resulted in the formation of a single product that was identified as the bicyclic cation **7**. The nmr spectrum of **7** was quite consistent with its structure, bearing striking similarities to the other polymethylbicyclic cations discussed in this series of papers.[2] Heating the HFSO$_3$ solution of **7** to $-35°$ caused it to isomerize cleanly to **6** with a first-order rate constant of 5.2 $\times$ 10^{-4} sec^{-1} ($\Delta F^{\ddagger}$ = 17.4 kcal/mol).

(13) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962); H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); H. E. Zimmerman, D. Dopp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, **88**, 5352 (1966).

(14) M. Saunders, *Tetrahedron Lett.*, 1699 (1963).

(15) The rate constants quoted in this paper are based upon nmr spectra obtained on a 100-MHz instrument. As a result, the temperature at which averaging becomes visible and the coalescence temperatures are different from those quoted in our original communication.[5] The value of $\Delta F^{\ddagger}$ given here is more reliable in that the limiting low temperature spectrum was better defined at 100 MHz.

(16) Koptyug, *et al.*,[17] have reported a rate constant for this degenerate rearrangement of **4** at $-89°$ to be 11 sec^{-1}. The discrepancy between the two results most probably arises from errors in the measurement of the probe temperature and difficulties in obtaining the limiting low temperature spectrum.

(17) (a) I. S. Isaev, V. I. Mamatyuk, L. I. Kuzubova, T. A. Gordymova, and V. A. Koptyug, *Zh. Org. Khim.*, **6**, 2482 (1970); (b) V. A. Koptyug, L. I. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, *ibid.*, **6**, 2258 (1970).

(18) At these temperatures the rate of the degenerate methyl migration in **5** is very low.[10]
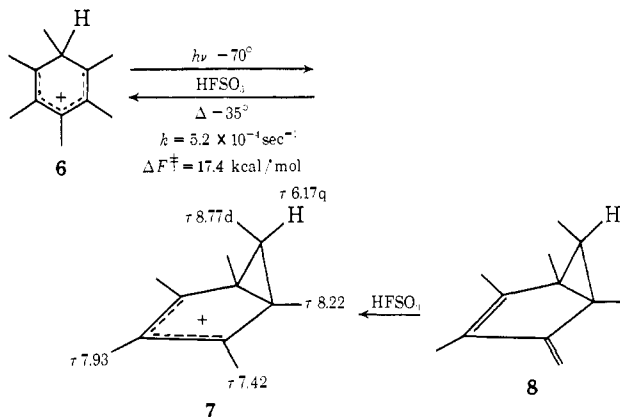
(19) For leading references see F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **89**, 760 (1967).

(20) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42**, 502 (1964).

(21) N. C. Deno, P. T. Groves, J. J. Jaruzelski, and M. N. Lugasch, *J. Amer. Chem. Soc.*, **82**, 4719 (1960).

There are two possible isomers that could result from the photochemical closure of **6**, differing by the stereochemistry of the C_6 methyl group.

Identification of **7** as the endo isomer was made by preparing the ion independently from the homofulvene **8**. This fulvene and its exo isomer have been isolated

hν −70°
HFSO₃
Δ −35°
$k = 5.2 \times 10^{-4} sec^{-1}$
$\Delta F^{\ddagger} = 17.4$ kcal/mol

6

τ 8.77 d τ 6.17 q H
τ 7.93 τ 8.22 HFSO₃ H
τ 7.42

7 **8**

and characterized by Criegee in the reaction of hexamethyl prismane with tosylic acid.[22,23] Protonation of **8** by extracting it from a CH_2Cl_2 solution into $HFSO_3$ at −78° gave **7** with an identical nmr spectrum with that obtained for the photoproduct.[24] On warming to −35° it rearranged to **6** with the same rate constant.[25]

Extraction of the homofulvene **9** into $HFSO_3$ gave the cation **10**, with an nmr spectrum that retained the

9

τ 6.78 H τ 8.59
τ 8.31
τ 8.05 +20° **6**
τ 7.40 $k = 4.7 \times 10^{-4}$
$\Delta F^{\ddagger} = 21.6$ kcal/mol

10
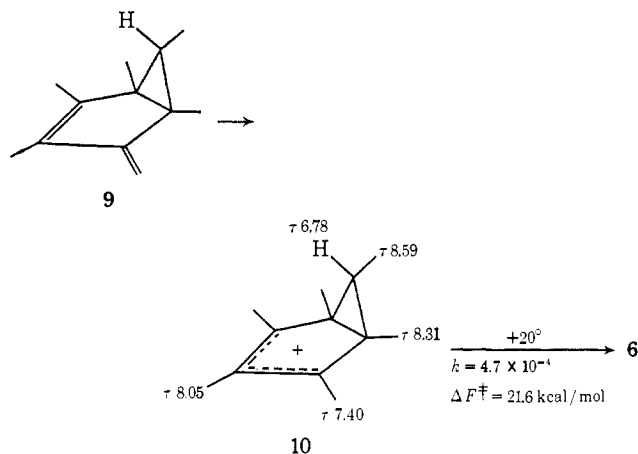
familiar cyclopentenyl pattern below −60°. It differed from **7** in the position of its C_6 methyl and proton resonance.[27]

On warming the $HFSO_3$ solution of **10** a comparable

(22) (a) R. Criegee and H. Grüner, *Angew. Chem., Int. Ed. Engl.*, **7**, 467 (1968); R. Criegee, H. Grüner, D. Schönleber, and R. Huber-*Chem. Ber.*, **103**, 3696 (1970); (b) W. Schäfer and H. Hellmann, *Angew. Chem., Int. Ed. Engl.*, **5**, 518 (1967).
(23) Additional evidence for the assignment of the exo and endo configurations of the two hydrocarbons **8** and **9** has been obtained from their ¹³C spectra; J. B. Grutzner, personal communication to S. Winstein, 1969.
(24) Generous amounts of **8** and **9** were provided by Professor R. Criegee.
(25) The same cation has been obtained by Koptyug, *et al.*,[26] by treating 1-α-chloroethylpentamethylcyclopenta-2,4-diene with Al_2Cl_6 in CH_2Cl_2.
(26) V. A. Koptyug, L. I. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, *J. Chem. Soc. D*, 389 (1969); *Zh. Org. Khim.*, **6**, 1843 (1970).
(27) It is interesting that the position of the C_6 methyl protons in **7** and **10** differ by 0.61 ppm. This is both of the same magnitude and in the same direction as the difference calculated by the semiempirical treatment of Grutzner and Jackman.[2]

averaging of the five-membered ring methyls to that described for **4** occurred. Broadening of the cyclopentenyl ring methyls took place at temperatures greater than −60°, coalescence at *ca.* −35°, and at higher temperatures they became a sharp averaged singlet (τ 7.85). Throughout this averaging the methyl doublet and proton quartet, attributable to the C_6 assemblage, remained sharp and nonaveraged. On cooling the sample the original spectrum was obtained. At no stage in the rearrangement was there any evidence for the formation of the endo cation **7**. The rate of this degenerate migration of the cyclopropyl was obtained in a similar manner to that described for the rearrangement of **4**. At −36.5° the rate constant was found to be 40 sec⁻¹ ($\Delta F^{\ddagger} = 12$ kcal/mol).[17,26]

On further heating of the solution of **10** to temperatures above 0°, an irreversible isomerization to **6** occurred. At +20° the rate constant for this unimolecular isomerization was found to be 4.7×10^{-4} sec⁻¹ ($\Delta F^{\ddagger} = 21.6$ kcal/mol).

With the observation of a degenerate cyclopropyl "merry-go-round" in **10**, the question arises as to whether a comparable reaction is occurring with the endo isomer **7**. At −35°, the temperature at which the rate of rearrangement of **7** to **6** was measured, there was no evidence for any line broadening of the cyclopentyl ring methyl signals. Even at −11.5° no broadening could be detected.

To enable slower rates of migration to be detected, the deuterated cation **7**-*d* was prepared by dissolving **8**


H
DFSO₃

8

H H
38°
$k = 2.4 \times 10^{-4}$
$\Delta F^{\ddagger} = 17.5$ kcal/mol
CH_2D CH_2D
7d **7d**
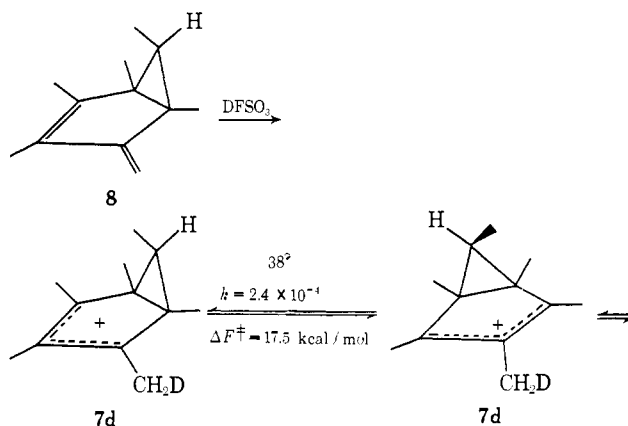
in $DFSO_3$. The structure of **7**-*d* was established by its nmr spectrum at −50° in which the resonance attributable to the **2** and **4** methyl groups had a relative intensity of 5 as compared to the other methyl signals. At −38°, a slow equilibration of the CH_2D group with the other methyl positions of the five-membered ring was observed. The first-order rate constant for this rearrangement was found to be 2.4×10^{-4} sec⁻¹ which means that the free energy barrier to migration in the endo cation **7** must be 17.5 kcal/mol.[28]

Mechanistic Consideration of the Cyclopropyl Circumambulation. Bearing in mind the observed stereospecificity, there are basically two types of mechanisms which can be advanced to account for the migration of the cyclopropyl around the periphery of the five-member ring. These are shown in Scheme III for the

(28) The observed rate constant for loss of CH_2D from the 2 and 4 positions was 3.6×10^{-4} sec⁻¹. The rate constant for migration is two-thirds of this apparent rate constant.

Scheme III
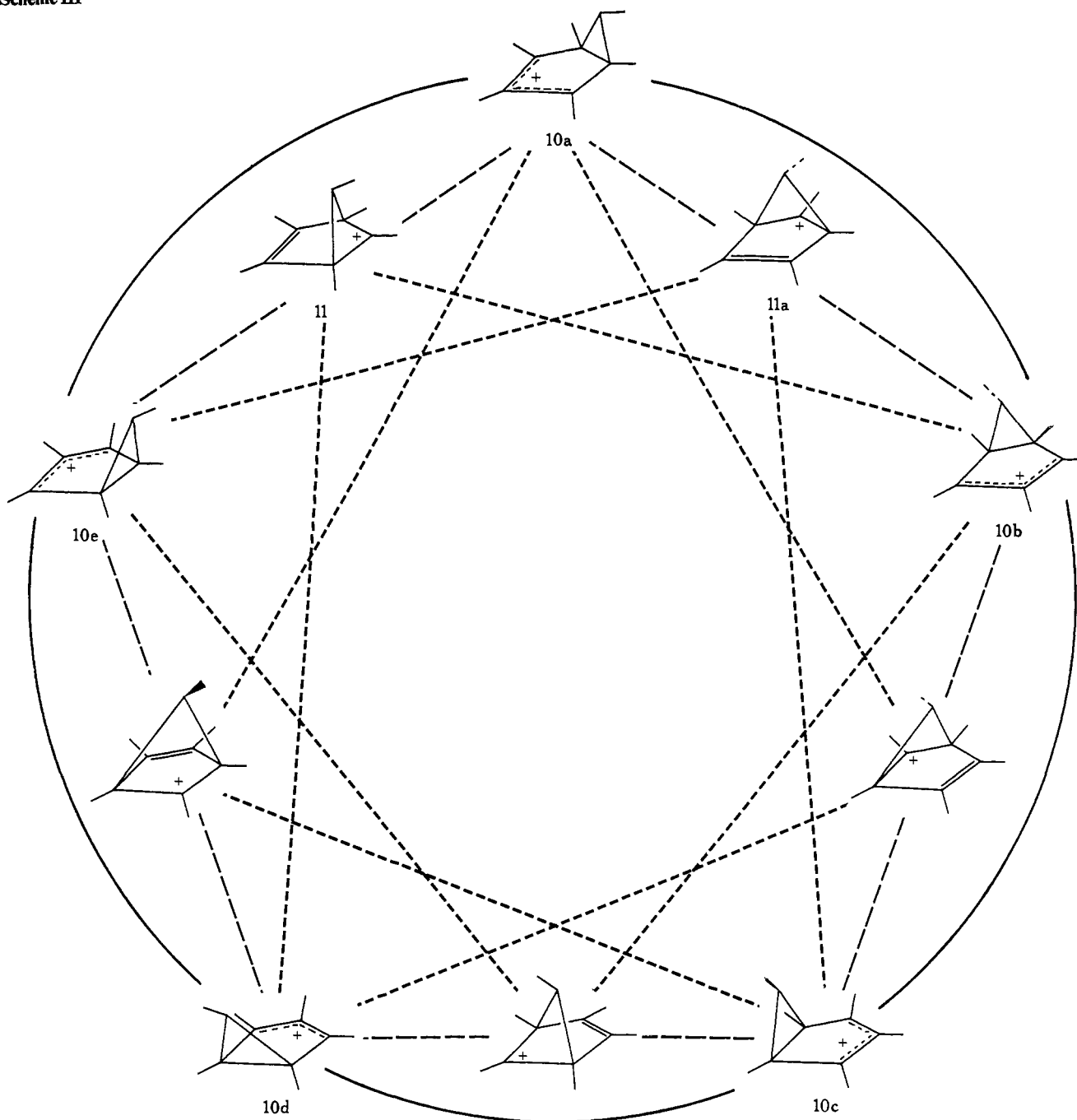
degenerate rearrangement of **10**. The first of these would involve the direct conversion of, for example, **10a** to **10b** by what can be regarded as a [1,4] suprafacial sigmatropic shift.[29] Alternatively the homoaromatic bicyclo[2.1.1]hexenyl cation, **11**, could be an intermediate in the reaction. Thus a [1,2] shift could isomerize **10a** to **11a**, which then could revert by a further [1,2] shift back to **10a** or **10b**. As Scheme III shows, two successive [1,3] shifts can also achieve a comparable movement of the cyclopropyl around the cyclopentenyl ring, again involving **11**. However, this movement does not meet the requirement of a stepwise migration demanded by the observed averaging process.[30] Precedent for these latter reaction sequences can be found in

the five carbon scrambling reactions of the 7-norbornadienyl cation.[31]

While all of these rearrangement pathways could successfully account for the observed stereospecificity, a clear distinction can be made between them as both the [1,2] and [1,3] shift mechanisms propose the intermediacy of **11**. This cation, which has been reported to be produced on the protonation of hexamethyl Dewar benzene, does not rearrange to **10** even at temperatures well above those at which the degenerate isomerization of **10** occurs.[32] As **11** had been obtained in acids other than HFSO₃, the precaution was taken of protonating

(29) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969.

(30) *Cf.* K. Schaffner, *Advan. Photochem.*, **4**, 81 (1966).

(31) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2347 (1972).

(32) (a) H. Hogeveen and H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **87**, 385, 1042 (1968); **88**, 353 (1969); (b) L. A. Paquette, G. R. Krow, J. M. Bollinger, and G. A. Olah, *J. Amer. Chem. Soc.*, **90**, 7147 (1968).

12 in this medium. In $HFSO_3$ comparable phenomena to those found in the other acid media were observed. 11 and 13 were found to interconvert at low temperatures and cleanly isomerize to 6 at $+20°$, $k = 1.03 \times 10^{-3} \sec^{-1}$ ($\Delta F^{\pm} = 21.2$ kcal/mol). No peaks attributable to 7 or 10 were observed at any stage during this isomerization.

It is apparent from these results that 11 cannot be an intermediate in the degenerate rearrangement of 10 and that the reaction proceeds by a [1,4] shift mechanism.

As Scheme III shows, the bicyclo[2.1.1]- and -[3.1.0]-hexenyl cations are very closely related. Indeed, it would seem that the isomerization of the 11–13 mixture


12
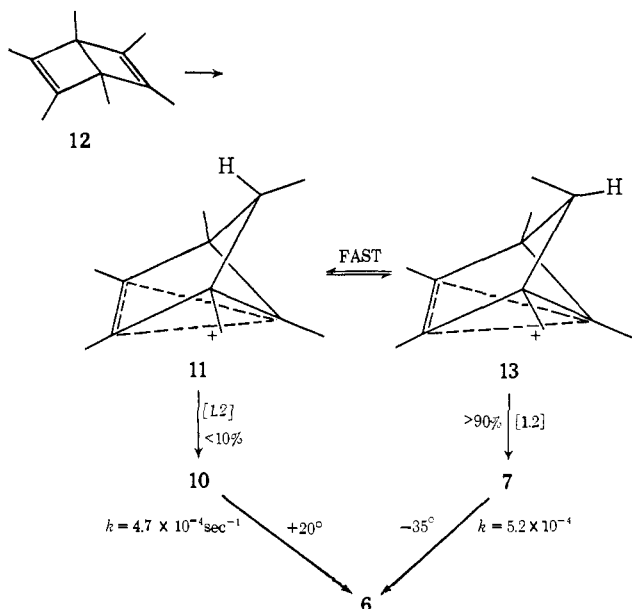
to 6 must involve either or both of the cations 7 and 10. Chemical support for this can be found in electrophilic additions to 12 which frequently produce pentamethyl-cyclopentadienylmethyl derivatives, arising presumably from capture of 7 or 10 at C_6.[33] The rearrangement of 11 by either a [1,2] or [1,3] shift would give 10, while 13 by a similar rearrangement would give only 7. However, as the rate of isomerization of 10 to 6 is slower than the observed rate of isomerization of 11–13 to 6, if 10 is an intermediate in this rearrangement then it should be capable of detection. After one half-life, less than 5% of 10 could be detected which must mean that at least 90% of the 11–13 mixture isomerizes by way of 7.[34]

(33) (a) W. Schäfer and H. Hellmann, *Angew. Chem., Int. Ed. Engl.*, 6, 518 (1967); L. A. Paquette, R. J. Haluska, M. R. Short, L. K. Read, and J. Clardy, *J. Amer. Chem. Soc.*, 94, 529 (1972); L. A. Paquette, S. A. Lang, Jr., M. R. Short, B. Parkinson, and J. Clardy, *Tetrahedron Lett.*, 3141 (1972); G. R. Krow and J. Reilly, *ibid.*, 3129, 3133 (1972); J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 91, 5970 (1969); (b) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 3197 (1972).

(34) This result would imply that the acid catalyzed formation of 9 from hexamethylprismane[22a] (HMP) does not involve the bicyclo[2.1.1]-hexenyl cations 10 and 7, for if these cations were intermediates then the production of at least some 8 would have been anticipated. However, the report that the protonation of HMP with $HFSO_3$–SbF_5 gives a mixture of 11, 13, and 6 would seem to be at variance with this conclusion.[32b] We find that the protonation of HMP in strong acids is complex. In $HFSO_3$ at $-78°$ four cations were formed: $11 + 13$ (84%); 6 (10%); 10 (6%). Diluting the $HFSO_3$ with CF_3COOH (1:1 mixture) gave $11 + 13$ (72%), 6 (9%), and 10 (19%). This marked dependence of product ratios upon acid strength can most readily be understood in terms of a competition between two possible sites of protonation, attack on the sterically less congested cyclopropane bond of HMP giving rise to 11, 13, and 6, while protonation at the cyclobutane bond resulting in the formation of 10, in what could be a concerted process.

Stereoselectivity of the [1,4] Migration. The peregrinations of the cyclopropyl in 4 and 10 could be regarded as an example of a concerted [1,4] sigmatropic shift. Such a migration in these systems is bound to be suprafacial and thus when thermally induced must involve inversion of configuration at the migrating carbon.[29] This can be readily seen by considering the highest occupied MO of the diene or diene cation radical of the transition state interacting with the cationic or radical center at C_6. Continuous bonding is only maintained if both lobes of the antisymmetric p orbital at C_6 are used. While C_6 is inverted during each migration the net effect is to slide the cyclopropane around the five-membered ring with overall maintenance of the stereochemistry at C_6.[35,37]

allowed   forbidden
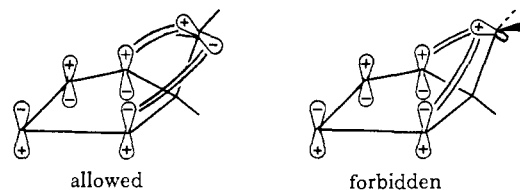
The very high degree of retention of the overall stereochemistry at C_6 during the migration of the *gem*-dimethyl group around the cyclopentenyl ring of 4 has been shown, *vide supra*. At $-9°$, the rate at which the two C_6 methyls exchange positions was shown to be less than 3 $\sec^{-1}$ ($\Delta F^{\pm} > 14.7$ kcal/mol) whereas the free energy of activation measured for the cyclopropyl migration was 10.1 kcal/mol. This means that the allowed migration is preferred by at least 4.6 kcal/mol over the "forbidden" process.

An even more striking limit may be put upon this stereoselectivity in the migration of the hexamethyl system 10. If 10 rearranged by the "forbidden" path, then the endo isomer 7 would be produced. At no time during the degenerate rearrangement of 10 was any 7 seen to build up. However, 7 has been shown to isomerize to 6 at $-35°$ and if the rate of the conversion of 10 to 7 were much slower, then 7 would not be observed but rather 6. The exo isomer 10 does indeed isomerize to 6 at $+20°$. While this isomerization may be a direct process and not involve the intermediacy of the endo cation 7, the rate of the isomerization of 10 to 7 cannot exceed the measured rate of $10 \rightarrow 6$ (Scheme IV).

The difference in free energy between the "allowed" and "forbidden" rearrangements of 10 must then be greater than or equal to $21.6 - 12.0 = 9.6$ kcal/mol. Put in terms of the difference in rate constants at $-36.5°$, the temperature at which the allowed migration has a rate constant of 40 $\sec^{-1}$, the nonallowed reaction has $k \leqslant 5 \times 10^{-8}$ $\sec^{-1}$. In other words, *the allowed*

(35) An investigation of the stereoselectivity of an analogous degenerate rearrangement of the hydroxy substituted bicyclohexenyl cations has been reported by Hart.[36a] Similar conclusions were recorded by Zimmerman, *et al.*,[36b] and Brennan and Hill[36c] for the rearrangement of the corresponding zwitterions.[30]

(36) (a) H. Hart, T. R. Rogers, and J. Griffiths, *J. Amer. Chem. Soc.*, 91, 754 (1969); (b) H. E. Zimmerman and D. S. Crumrine, *ibid.*, 90, 5612 (1968); H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, 91, 434 (1969); (c) T. M. Brennan and R. K. Hill, *ibid.*, 90, 5614 (1968).

(37) An alternative, complimentary view of this rearrangement has been suggested by Zimmerman, *et al.*[36b]

Scheme IV
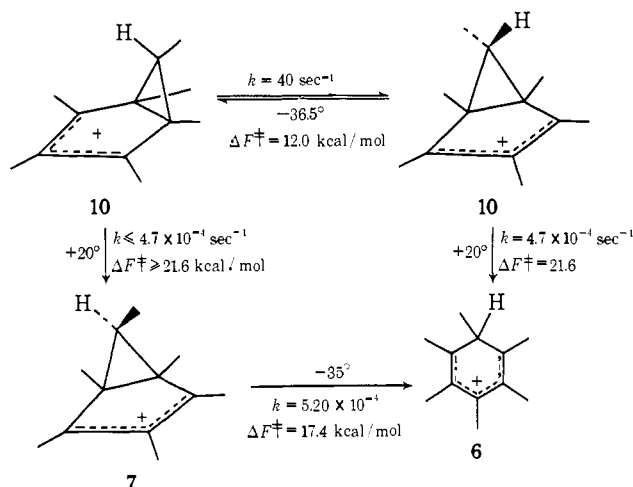
process is occurring at least 8 × 10⁸ times faster than the forbidden migration.[38]

While the large energy preference shown for the allowed reaction is impressive and could be construed as a striking validation of the concepts of orbital symmetry control, it must be pointed out that this migration is also favored by least motion.[39] The "forbidden" reaction involves a much larger twisting of the C_6 group as compared to the sliding motion of the "allowed" reaction.[40]

C_6-Substituent Effects upon the [1,4] Migration. The measured activation energies for the degenerate rearrangements of the bicyclohexenyl cations are summarized in Table II. While the competing isomerization

Table II. Energy Barriers for Cyclopropyl Migration

Cation	C_6 substituent		$\Delta F^{\ddagger}$, kcal/mol
	Exo	Endo	
4	Me	Me	10.1
10	Me	H	12.0
7	H	Me	17.5
1[a]	H	H	>13
14[b]	H	H	>18.6

[a] Reference 2. [b] 1,2,4,5-Tetramethylbicyclo[3.1.0]hexenyl cation, ref 2.

(38) It would seem that a necessary consequence of this result is that the acid-catalyzed equilibration of **8** and **9** observed by Criegee[22a] must involve a covalent intermediate such as a cyclopentadienecarbinol derivative and not occur by interconversion of the cations 7 and 10.

(39) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938); **7**, 199 (1939). For reviews of later work, S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968); O. S. Tee, *J. Amer. Chem. Soc.*, **91**, 7144 (1969).

(40) It is interesting that no comparable degenerate rearrangement has been detected in the homotropylium cation, a reaction which would involve a non-least-motion migration if symmetry were to be conserved.[41] It should be emphasized, however, that there are very large differences in the ground state properties of the $4n$ electron bicyclo-[3.1.0]hexenyl ion and the $4n + 2$ electron homotropylium cation.[42,43] The bicyclo[5.1.0]octadienyl anion does not appear to undergo a degenerate migration of the cyclopropyl even though this rearrangement could now proceed with inversion of configuration in this $4n$ electron anion.[44]

(41) J. A. Berson and J. A. Jenkins, *J. Amer. Chem. Soc.*, **94**, 8907 (1972).

(42) S. Winstein, *Chem. Soc., Spec. Publ.*, **No. 21**, 5 (1967); *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

(43) *Cf.* W. J. Hehre, *J. Amer. Chem. Soc.*, **94**, 8908 (1972); **95**, 5807 (1973).

(44) H. Kloosterziel and E. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **88**, 1373 (1969); H. Kloosterziel and G. M. Gorter-la Roy, *J. Chem. Soc. D*, 352 (1972).

of the bicyclic cations to the benzenonium ions precludes accurate measurement for several of the systems, it is quite obvious that the nature of the substituents upon C_6 have a marked effect upon the ease of this migration.

It would appear that the barrier to migration is greatly dependent upon the ability of C_6 to support a positive charge. Thus the lowest energy migration occurs with two methyl substituents upon C_6 and the highest when there are no substituents on this carbon, *e.g.*, **14**. Changes of this magnitude would strongly suggest that in the transition state for this rearrangement a considerable fraction of the positive charge is borne by the migrating carbon.[17a]

However, quite clearly another factor must be operative. The large difference in the rate of migration of the two hexamethyl systems, **10** and **7**, cannot be accounted for simply on the basis of the charge stabilizing ability of the C_6 substituents.

This large rate difference would not seem to result from differing ground state energies of the two ions **7** and **10**. Thus while a direct measure of the relative ground state stabilities of these two cations has not been achieved, the two hydrocarbons **8** and **9** can be

8 60%   **9** 40%
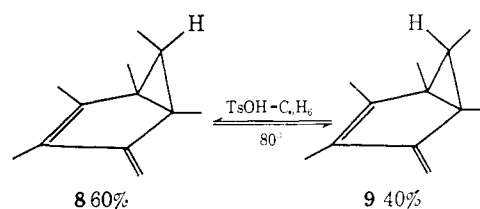
considered as reasonable models. Criegee[22a] has been able to establish a thermodynamic equilibrium between these two hydrocarbons and has found that there is little difference in energy between them.

The difference in energy required for cyclopropyl migration in **7** and **10** must then result from a difference in energy of the two transition states, represented without electron delocalization as **15a** and **15b**, respectively.

15a   **15b**
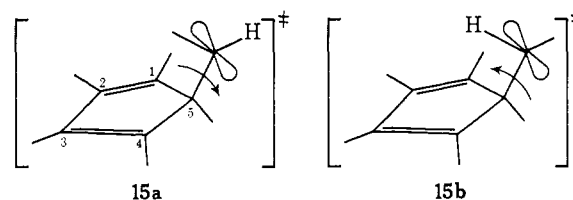
From an examination of models it would appear that one distinction between **15a** and **15b** is the ability of the formal p orbital on C_6 to interact with the diene. For effective overlap between C_6 and the diene, C_6 must lean over the five-membered ring toward the p orbitals on C_1 and C_4. The possibility for such a bending of the C_5–C_6 bond and puckering of the five-membered ring is lessened when an endo methyl group is on C_6, **15a**, as a severe interaction develops between this methyl and C_2 and C_3. No such hindrance is present in **15b** and more effective overlap could occur.

It is instructive to consider the magnitude of the energy barriers to be expected if in the transition states of migration of these ions there were no interaction of C_6 with the diene. Then not only would the migrations of **7** and **10** be expected to have the same rate but the difference in the energy barrier of the migration in **4**, **7**, **10** and **1** should be comparable in magnitude to

the energy differences found between simple tertiary, secondary, and primary carbonium ions. In similar superacid media the free energy difference between secondary and tertiary alkyl cations has been estimated to be 12–15 kcal/mol.[45] This is much larger than the difference between **4** and **10** or even **4** and **7** found in this work, Table II. Of course, alkyl substitution will affect the relative ground state energies of the bicyclo-[3.1.0]hexenyl cations but this will be very much attenuated as compared to the larger differences observed between the basic alkyl cations. It must be concluded that a full positive charge is not developed at C_6 during the migration and that there is overlap of the formally vacant p orbital at C_6 with the dienylic part of the cation. Combining this conclusion with the very high stereospecificity observed, it would seem that this overlap is occurring with both lobes of the p orbital at C_6. That is, the reaction is proceeding with continuous bonding being maintained in the manner prescribed for the symmetry allowed concerted reaction.[48]

Isomerization to Benzenonium Ions. On heating, all the bicyclohexenyl cations discussed in this paper ultimately isomerize to the corresponding benzenonium cation. The activation energies associated with these reactions are summarized in Table III.

Table III. Energy of Bicyclohexenyl to Benzenonium Cation Isomerization

Cation	Product	$\Delta F^{\pm}$, kcal/mol
4	5	19.8
7	6	17.4
10	6	21.6
1	a	17.6
14	b	17.1

_a_ Pentamethylbenzenonium cation. _b_ Durenonium cation.

The rearrangement of the bicyclo[3.1.0]hexenyl cations to the benzenonium ions would appear to involve the symmetry "forbidden" breaking of the C_1–C_5 bond.[4] The results in Table II show that the rate of isomerization is dependent upon the substitution pattern at C_6. While there will be differences in the relative thermodynamic stabilities of these sets of ions, it would seem that one of the effects of the C_6 substituent is steric in origin.

During the isomerization the exo substituent is forced to pass between the C_1 and C_5 methyl groups, both of which are effectively buttressed by the other methyls upon the five-membered ring. The activation energies associated with these rearrangements are all comparable while the exo position remains unsubstituted, e.g., **7**, **1**, and **14**. The introduction of an exo methyl group at C_6 raises the activation energy by some extra 2 kcal/mol, e.g., **4** and **10**.

(45) The tertiary/secondary cation enthalpy difference has been estimated by Saunders and Hagen[46] to be 11–15 kcal/mol, which agrees closely to the value obtained by Arnett and Larsen[47] from calorimetric data. The free energy difference was evaluated using the data of the former authors.

(46) M. Saunders and E. L. Hagen, J. Amer. Chem. Soc., **90**, 2436 (1968).

(47) E. M. Arnett and J. W. Larsen in "Carbonium Ions," Vol. 1, Interscience, New York, N. Y., 1968, p 441.

(48) Cf. S. Winstein and M. Battiste, J. Amer. Chem. Soc., **82**, 5244 (1960); L. de Vries, ibid., **82**, 5242 (1960).

The suggestion has been made that the isomerization of these ions involves the formation of the cyclopenta-dienylmethyl cation, **16**, which then undergoes a 1,2-


16
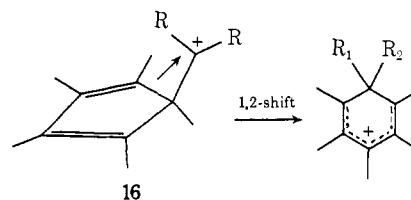
shift to give the benzenonium cation.[33b,48] If this were the case, then it would be expected that alkyl substitution at C_6 would increase and not decrease the rate of isomerization as is observed. Indeed, this seems a most unlikely pathway in view of the evidence presented in this paper concerning the role of structures such as **16** in the chemistry of the bicyclo[3.1.0]hexenyl cations.

Isomerizations of the Hydroxybicyclo[3.1.0]hexenyl Cations. The close correspondence of the reactions of the bicyclic cations described in this paper and the hexamethyl hydroxy cations, e.g., **2**, reported by Hart,[3] made it seem worthwhile to obtain more quantitative data for the isomerizations of the latter systems.

Stable solutions of **2** were readily prepared by protonation of the ketone **3** in FSO_3H at low temperatures.[49] On warming to $+10°$, **2** underwent a clean unimolecular isomerization to give the protonated dienone **17**. At higher temperatures **17** rearranged to **18**[50] (Scheme V).

Scheme V
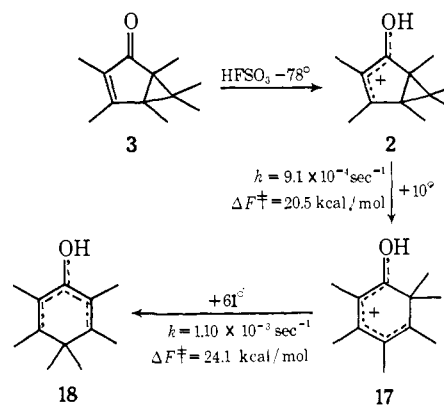
As there was no evidence in the nmr spectrum of **2** at $+10°$ of line broadening, any cyclopropyl migration that is occurring must be slow with respect to the nmr time scale. Using the deuterium labeled cation **2**-d, obtained by protonation of **3**-d, an interconversion of **2**-d and **2'**-d could be detected at temperatures above $-35°$ (Scheme VI). This was evident by the equilibration of the CD_3 label, initially at C_4 with the methyl upon C_5.

It would seem likely, as was suggested by Hart,[3] that **19** and **19'** are intermediates in the reaction. Consistent

(49) Generous quantities of these ketones were supplied by H. Hart.

(50) H. Hart and D. W. Swatton, J. Amer. Chem. Soc., **89**, 1874 (1967); V. G. Shubin, V. P. Chzhu, A. I. Rezvukin, A. A. Tabatskaya, and V. A. Koptyug, Izv. Akad. Nauk SSSR, Ser. Khim., 2365 (1967); V. G. Shubin, V. P. Chzhu, A. I. Rezvukin, and V. A. Koptyug, ibid., 2056 (1966); R. F. Childs, J. Chem. Soc. D, 946 (1969).

Scheme VI
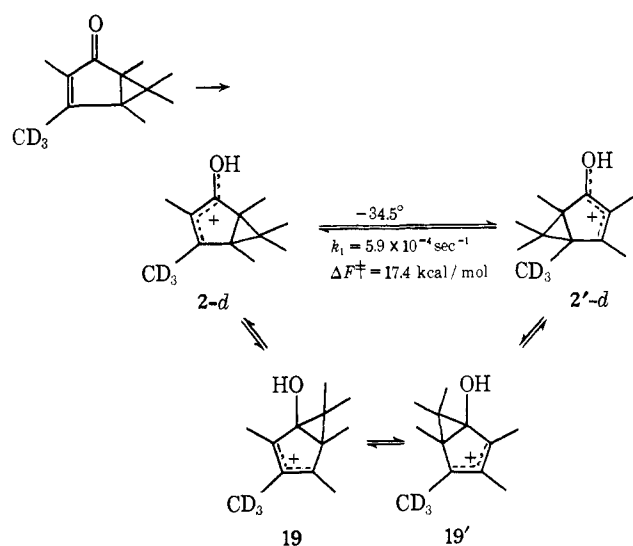
with this proposal is the considerable retardation of the rate of this degenerate rearrangement as compared to that of **4**, the system without the hydroxy group. The isomerization of **2** to **19** involves removing the stabilizing effect of the hydroxy group from the formally charged part of the system.

It is interesting that the opening of the bicyclohexenyl cation **2** to give **17** also involves the bicyclic cation **19**.[3] As **19** is only present to a very small extent at any given time, it must mean that the opening of **19** to give **17** is particularly facile. It is likely that the hydroxy group substituted upon the bridgehead position facilitates this ring opening.[51]

Preliminary photochemical experiments showed that both **17** and **18** could be rearranged to **2** when irradiated at low temperatures in HFSO$_3$. These isomerizations, which are of considerable interest in terms of the conventional solution phase photochemistry of the cyclohexadienones, have been investigated in more depth.[52]

Experimental Section

General Procedures. Nmr spectra were recorded on Varian A-60 and HA-100 spectrometers fitted with variable-temperature probes. The probe temperature was measured with methanol samples. A small but systematic difference in kinetic results was observed when different machines were used (UCLA, McMaster) which probably results from a difference in temperature measurement and control. All rates reported in this paper for the hexamethyl systems were recorded on the same machine. Protonations, rate measurements, and photochemical reactions were carried out as previously described.[2]

(51) *Cf.* R. Breslow, J. Napierski, and A. H. Schmidt, *J. Amer. Chem. Soc.*, 94, 5906 (1972).

(52) B. Parrington and R. F. Childs, *J. Chem. Soc. D*, 1581 (1970); N. Filipescu and J. W. Pavlik, *J. Amer. Chem. Soc.*, 92, 6062 (1970).