

## Penta- and Tetramethylbicyclo[3.1.0]hexenyl Cations

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**Abstract:** The protonation of 1,3,4,5-tetramethyl-2-methylenebicyclo[3.1.0]hex-3-ene with  $\text{FSO}_3\text{H}$  at  $-78^\circ$  is shown to give 1,2,3,4,5-pentamethylbicyclo[3.1.0]hexenyl cation, **5**. The structure of this cation was assigned on the basis of its nmr spectrum which indicated that the external cyclopropane bonds,  $\text{C}_1\text{--C}_6$  and  $\text{C}_5\text{--C}_6$ , were involved in charge delocalization. At  $-35^\circ$  **5** rearranged to the pentamethylbenzenonium cation, **7** ( $k = 2.2 \times 10^{-4} \text{ sec}^{-1}$ ,  $\Delta F^\ddagger = 17.6 \text{ kcal/mol}$ ). This formally symmetry forbidden thermal isomerization could be reversed photochemically; irradiation of the long wavelength absorption of **7** giving **5**. The low temperature irradiation of protonated durene, **8**, in  $\text{HFSO}_3$  gave predominantly the 1,2,4,5-tetramethylbicyclo[3.1.0]hexenyl cation, **9**, and minor amounts of protonated isodurene, **10**. At  $-31^\circ$ , **9** thermally isomerized to **8** with a first-order rate constant of  $1.46 \times 10^{-8} \text{ sec}^{-1}$ . Replacement of the  $\text{C}_6$  methylene hydrogens of **9** with deuterium did not detectably alter the rate of this thermal rearrangement to **8**. Irradiation of **10** at  $-90^\circ$  did not produce 1,2,3,5-tetramethylbicyclo[3.1.0]hexenyl cation, **11**, but led instead to the slow production of **8** and **9**. An attempted independent synthesis of **11** showed it to be thermally unstable at  $-75^\circ$  in  $\text{HFSO}_3$ , it isomerizing to **10** ( $k > 1.3 \times 10^{-2} \text{ sec}^{-1}$ ). From these results it is concluded that the preferred reaction paths for the photochemical and thermal interconversions of the benzenonium and bicyclo[3.1.0]hexenyl cations involve the making and breaking of the  $\text{C}_1\text{--C}_5$  bond in electrocyclic processes.

The bicyclohexenyl cations form a group of structurally related carbonium ions that are isomeric with the well-characterized cyclohexadienyl or benzenonium ions. Two important members of this series are the bicyclo[3.1.0]hexenyl cation, **1**, and the bicyclo[2.1.1]hexenyl cation, **2**. Despite their intrinsic interest



and frequent invocation as reaction intermediates, little is known about the chemistry of these systems.<sup>2</sup> Indeed, only recently have the parent ions **1**<sup>3</sup> and **2**<sup>4</sup> been reported.

These two cations, which are structurally related by a 1,2-alkyl shift, exhibit contrasting modes of electron delocalization. Thus **2** is an example of a nonclassically stabilized or bishomoaromatic cation and is directly comparable to the extensively studied 7-norbornenyl cation.<sup>5</sup> On the other hand, depending on the extent of delocalization of the  $\text{C}_1\text{--C}_5$  bond of the cyclopropane, **1** has the potential of being an antihomoaromatic ion.

Evidence suggesting the intermediacy of a substituted bicyclo[3.1.0]hexenyl cation was obtained several years ago in a study of pentamethylcyclopentadienylmethyl *p*-

toluenesulfonate; however, it was by no means clear how best to represent its structure.<sup>6</sup> With the hindsight afforded by the development of the concepts of homoaromaticity<sup>5</sup> and orbital symmetry,<sup>7</sup> certain of the initially suggested formulations may be rejected or modified. However, as these initial studies were completed before the general utility and power of direct observation techniques in superacids were realized, it seemed worthwhile to attempt the generation of this cation under these long lifetime conditions.

In this paper we report the successful preparation of some bicyclo[3.1.0]hexenyl cations and examine their structure and relationship to the parent benzenonium ions.<sup>8</sup>

## Results and Discussion

**The Preparation of 5.** Pentamethylcyclopentadienylmethanol (**3-OH**) was prepared by the method of deVries.<sup>9</sup> Extraction of **3-OH** from  $\text{CH}_2\text{Cl}_2$  into  $\text{FSO}_3\text{H}$  or  $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$  at  $-78^\circ$  gave a solution, the nmr spectrum of which was consistent with both ring carbon and alcohol oxygen protonation.<sup>10</sup>

The homofulvene **4**, derived from **3-OTs**, was extracted into  $\text{FSO}_3\text{H}$  from  $\text{CH}_2\text{Cl}_2$  or, better,  $\text{CHCl}_3$  to give a cation whose nmr spectrum was consistent with the bicyclo[3.1.0]hexenyl cation **5**. The assignment of the methylene group resonances was made by protonation of the dideuterio olefin **4-d**. The methyl group resonances displayed the necessary symmetry for a structure such as **5** and resonated in similar positions to those described for the corresponding methyls on a

(1) (a) University of California at Los Angeles; (b) McMaster University; (c) address all correspondence to this author at McMaster University; (d) deceased Nov 23, 1969.

(2) These cations can formally be derived from protonation of the valence tautomers of benzene, e.g., Dewar benzene, prismane, benzvalene, and fulvene.

(3) (a) J. A. Berson and N. M. Hasty, Jr., *J. Amer. Chem. Soc.*, **93**, 1549 (1971); (b) P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *ibid.*, **93**, 1551 (1971).

(4) (a) S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969); (b) S. Masamune, E. N. Cain, R. Vukov, S. Takada, and N. Nakatsuka, *J. Chem. Soc. D*, 243 (1969).

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

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

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

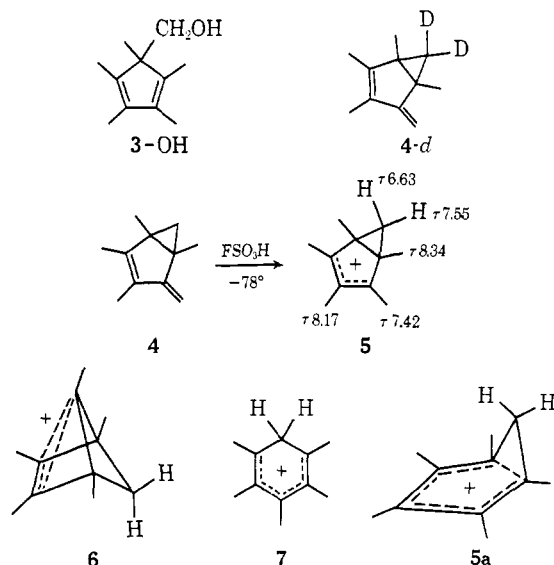
(8) Preliminary accounts of part of this work have appeared: R. F. Childs, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7144 (1968); R. F. Childs and B. D. Parrington, *J. Chem. Soc. D*, 1540 (1970).

(9) L. deVries, *J. Org. Chem.*, **25**, 1838 (1960).

(10) 5-Acylpentamethylcyclopentadienes are cleanly diprotonated in  $\text{HFSO}_3$ .<sup>11</sup>

(11) M. Zeya, Ph.D. Thesis, McMaster University, Hamilton, Ontario, 1973.

cyclopentenyl cation.<sup>12</sup> Two other isomeric cations which could have been obtained by thermal rearrangement of **5** are the bicyclo[2.1.1]hexenyl cation **6** and benzenonium ion **7**. Both of these possibilities can be



discounted. The nmr spectrum of the cation obtained upon protonation of **4** is quite different from that of authentic **7**<sup>13</sup> and from that expected for a bicyclo[2.1.1]hexenyl cation.<sup>4b, 14, 15</sup>

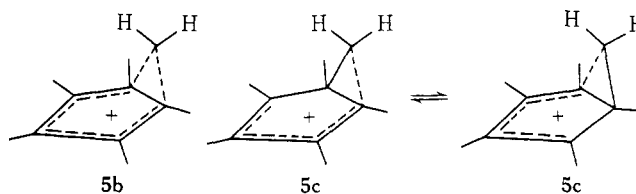
**Electron Delocalization in 5.** While the gross structure of the cation derived from **4** would seem to be **5**, the question arises as to how the cyclopropane is involved in the electron delocalization. One of the initially suggested<sup>6</sup> structures of this ion, **5a**, would now be recognized as an antihomoaromatic cation.<sup>5</sup> Such a structure containing four electrons, cyclically delocalized, would be expected to be of relatively high energy. Not only does **5a** have theoretical disadvantages but the magnitude of the geminal coupling constant observed for the  $\text{C}_6$  methylene protons of **5** ( $J_{\text{gem}} = 3 \text{ Hz}$ ) would rule against such a mode of delocalization. Involvement of the  $\text{C}_1\text{--C}_3$  bond electrons would have the effect of increasing this bond length and thus increasing the  $\text{C}_1\text{--C}_6\text{--C}_5$  bond angle. As a result, the geminal coupling constant would be expected to increase over that usually found for a cyclopropane.<sup>17, 18</sup>

While involvement of the  $\text{C}_1\text{--C}_3$  bond is not favored for **5**, the  $\text{C}_1\text{--C}_6$  and  $\text{C}_5\text{--C}_6$  cyclopropane bonds are well situated for delocalization with the allyl cation. The participation of these external cyclopropane bonds is strongly supported by the observed deshielding of the  $\text{C}_6$  methylene protons of **5** as compared to its neutral precursor, **4**.

If the structure of the ion could simply be regarded as that shown in **5**, then the only difference in the position of the methylene protons of **5**, as compared to **4**, should arise from the extra inductive and direct field effects of the allylic cation. The inductive effect of the allyl cation over two carbons will result in a  $\sim 0.3 \text{ ppm}$  down-field shift.<sup>12</sup> The magnitude of the direct field effect can be estimated with the semiempirical equation developed by Grutzner and Jackman.<sup>21</sup> Using this treatment, both of the methylene protons of **5** are predicted to be deshielded, the exo proton by  $\sim 1 \text{ ppm}$  and the endo by  $0.25 \text{ ppm}$ .<sup>22, 23</sup> Combined, the inductive and field effects cannot account for the observed deshielding of the methylene protons, and the extra *ca.*  $1.5 \text{ ppm}$  down-field shift observed for both protons must be attributable to cyclopropane involvement in **5**. The reported nucleophilic capture of **5** at  $\text{C}_6$  under solvolytic conditions supports this suggestion.<sup>6</sup>

Perhaps the simplest representation of the electron delocalization which is consistent with the observed spectrum and properties of **5** is **5b**.<sup>24</sup> Such a structure has the necessary symmetry demanded by the nmr spectrum. However, as has been pointed out by Hehre,<sup>25</sup> **5b** has a Möbius arrangement of atomic orbitals and with six electrons in the delocalized system it would be expected to be antiaromatic.

The unsymmetrical homopentadienyl formulation **5c**, would also give rise to the same spectrum, provided that there is a rapid equilibration between two such equivalent structures. Cooling a solution of **5** in  $\text{FSO}_3\text{H}\text{--}\text{SO}_2\text{ClF}$  to  $-120^\circ$  caused no detectable freezing out of the spectrum of **5c**.<sup>26</sup>



The results of a recent quantum mechanical exploration of the unsubstituted cation **1** substantiate these conclusions regarding the structure of the bicyclo[3.1.0]hexenyl cations.<sup>27</sup> While the major part of the charge was located upon  $\text{C}_2$ ,  $\text{C}_3$ , and  $\text{C}_1$ , it is interesting that there were substantial changes in the bond lengths of the

(12) (a) N. C. Deno, D. B. Boyd, J. D. Hodge, C. U. Pittman, and J. O. Turner, *J. Amer. Chem. Soc.*, **86**, 1745 (1964); T. S. Sorensen, *Can. J. Chem.*, **42**, 2768 (1964); D. M. Brouwer and J. A. Van Doorn, *Recl. Trav. Chim. Pays-Bas*, **89**, 333 (1970); (b) T. S. Sorensen, *J. Amer. Chem. Soc.*, **89**, 3782, 3794 (1967).

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

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

(15) Direct evidence against the bicyclo[2.1.1]hexenyl structures has been found with the analogous hexamethyl substituted systems.<sup>16</sup>

(16) (a) R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7146 (1968); V. A. Koptug, L. I. Kuzubova, I. S. Isaev, and V. I. Mamtyuk, *J. Chem. Soc. D*, 389 (1969); *Zh. Org. Khim.*, **6**, 1843, 2258 (1970); (b) R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **96**, 6409 (1974).

(17) P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2280 (1972).

(18) It has been suggested that evidence for the "closed" cyclopropane formulation of cations similar to **5** comes from the magnitude of the  $^{13}\text{C}_6\text{H}_2$  coupling constant.<sup>19</sup> However, the value obtained does not differ significantly from that measured for the  $^{13}\text{C}_6\text{H}_2$  coupling constant of the homotropylium ion.<sup>20</sup>

(19) I. S. Isaev, V. I. Mamtyuk, T. G. Egorova, L. I. Kuzubova, and V. A. Koptug, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2089 (1969).

(20) P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970).

(21) J. B. Grutzner, Ph.D. Thesis, Melbourne, 1967.

(22) The exo and endo protons are assigned upon the basis of these calculations. This assignment is supported by the results obtained with the hexamethyl cations.<sup>16</sup>

(23) It is interesting that the relative positions of the methylene protons in the nmr spectrum of **1** are reversed. The suggestion has been made that the low field position of the endo  $\text{C}_6$  proton in **1** may be due to an enhanced paramagnetic contribution to the ring current.

(24) Cf. H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, **91**, 434 (1969).

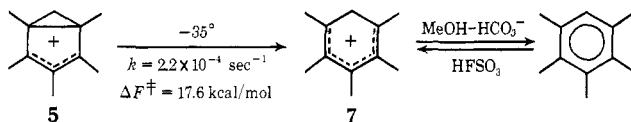
(25) W. J. Hehre, *J. Amer. Chem. Soc.*, **95**, 5807 (1973).

(26) A further doubly homoallylic structure was suggested in the original communications.<sup>6</sup> While such a structure is not in accord with the properties of **5** it is of considerable importance in the degenerate rearrangements of these systems.<sup>16</sup>

(27) W. J. Hehre, *J. Amer. Chem. Soc.*, **94**, 8900 (1972).

cyclopropane from their normal values.<sup>28</sup> A substantial lengthening of the C<sub>1</sub>-C<sub>6</sub> and C<sub>5</sub>-C<sub>6</sub> bonds and contraction of the C<sub>1</sub>-C<sub>5</sub> bond was found as would be expected for structures such as **5b** or **5c**.

**Thermal Isomerization of 5.** While FSO<sub>3</sub>H solutions of **5** were stable at low temperatures, on warming, a quantitative, unimolecular rearrangement took place to give **7**.<sup>29</sup> At -35° the first-order rate constant for this thermal isomerization was  $2.22 \times 10^{-4} \text{ sec}^{-1}$  ( $\Delta F^\ddagger = 17.6 \text{ kcal/mol}$ ). The product **7** had an identical nmr



spectrum to authentic **7** obtained by the protonation of pentamethylbenzene.<sup>13</sup> Quenching the FSO<sub>3</sub>H solution of **7** in methanol-bicarbonate at -78° gave pentamethylbenzene in good yield.

Superficially, the simplest pathway for the conversion of **5** into **7** is the electrocyclic reaction that breaks the C<sub>1</sub>-C<sub>5</sub> cyclopropane bond. While **5** and **7** are related by a disrotatory movement, such a process is symmetry forbidden in the ground state.<sup>7</sup> Indeed, the reverse reaction, the closure of a linear pentadienyl cation to cyclopentenyl ion, has been shown to proceed in a conrotatory manner.<sup>7,30</sup> Such a motion is unattainable in small cyclic systems such as the cyclohexadienyl cations.<sup>31</sup> It is not unreasonable, therefore, that there is a relatively high energy barrier observed for this isomerization which, if it proceeds by simple concerted breaking of the C<sub>1</sub>-C<sub>5</sub> bond, is forced to travel the "forbidden" pathway.

**Photochemical Conversion of 7 to 5.** As a corollary of the ground state "forbidden" interconversion of **5** and **7**, it is predicted that in the first excited state such an interconversion would involve a disrotatory motion and thus become an "allowed" process. The pentamethylbenzenonium ion, **7**, has an absorption spectrum similar to other alkylated benzenonium ions, with a long wavelength absorption at 377 nm ( $\epsilon$  9800).<sup>32</sup> A dilute solution of **7** in FSO<sub>3</sub>H contained in a regular clear-walled nmr tube was irradiated while being kept at -78° in a Dry Ice-acetone bath. The reaction was monitored by observing the nmr spectrum of the solution at temperatures below -50°.

It was found that upon irradiation of **7** the bicyclohexenyl cation **5** was produced (Figure 1). The photo-

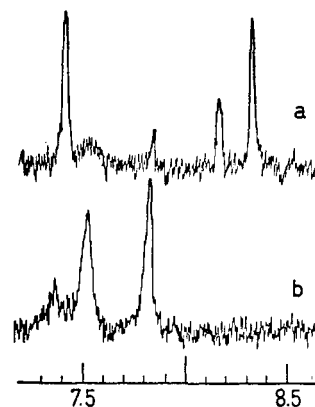


Figure 1. Pmr spectrum of **7** in FSO<sub>3</sub>H before (b) and after (a) irradiation.

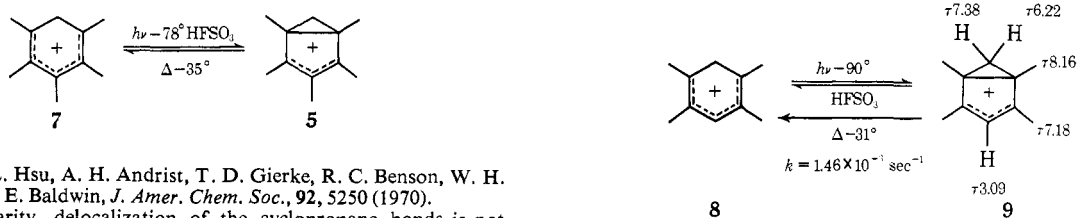
product was shown to be **5** by the identity of its nmr spectrum with that of the cation derived from **4**. Moreover, heating the FSO<sub>3</sub>H solution of the photoproduct to -35° caused it to revert to **7** with the same rate constant as that measured for authentic **5**.

The maximum conversion of **7** into **5** that was achieved was 80%. Continued irradiation after this point was reached had no effect upon the composition of the solution. No other products could be detected by nmr at any stage in the photoreaction. Comparison of signal intensities before and after irradiation with internal tetramethylammonium chloride showed that there was no loss of material occurring during the irradiation.

While the interconversions of **5** and **7** have been discussed in terms of simply making and breaking the C<sub>1</sub>-C<sub>5</sub> bond, there are alternative mechanisms that can be written.<sup>33</sup> To test for the occurrence of more deep seated skeletal rearrangements, the interconversions of the less highly substituted tetramethyl systems have been studied.

**Tetramethyl Substituted Systems.** Dissolution of durene in FSO<sub>3</sub>H at -78° gave the benzenonium cation **8**.<sup>13</sup> Irradiation of the long wavelength absorption of **8** ( $\lambda_{\text{max}}$  394 nm;  $\log \epsilon$  3.75  $\pm$  0.2), at -90°, using a Pyrex filter, gave a new cation that was stable at low temperatures.

The nmr spectrum of the product, apart from the interchange of a vinyl for a methyl resonance, was markedly similar to that of **5** and is quite consistent with the photoproduct being **9**. The methyl resonances dis-



(28) Cf. S. L. Hsu, A. H. Andrist, T. D. Gierke, R. C. Benson, W. H. Flygare, and J. E. Baldwin, *J. Amer. Chem. Soc.*, **92**, 5250 (1970).

(29) For clarity, delocalization of the cyclopropane bonds is not shown in the rest of this paper.

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

(31) G. A. Olah, R. H. Schlosberg, D. P. Kelly, and Gh. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 2546 (1970).

(32) W. I. Aalbersberg, C. J. Hoijtink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.*, 3049, 3054 (1959); D. Dalinga, E. L. Mackor, and A. A. Verrijn Stuart, *Mol. Phys.*, **1**, 123 (1958); for an excellent review of the electronic spectra of organic cations see G. A. Olah, C. U. Pittman, Jr., and M. C. R. Symons in "Carbonium Ions," Vol. I, Interscience, New York, N. Y., 1968, p 153.

(33) Cf. J. E. Baldwin and A. H. Andrist, *J. Chem. Soc. D*, 1561 (1970); J. E. Baldwin and G. D. Andrews, *J. Amer. Chem. Soc.*, **94**, 1775 (1972); G. D. Andrews, M. Davalt, and J. E. Baldwin, *ibid.*, **95**, 5046 (1973); see, however, S. McLean, D. M. Findlay, and G. I. Dmitrenko, *ibid.*, **94**, 1380 (1972); M. C. Flowers and H. M. Fry, *ibid.*, **94**, 8636 (1972); J. I. Brauman, W. E. Fameth, and M. B. D'Amore, *ibid.*, **95**, 5043 (1973).

typical position for a similarly situated proton on a cyclopropylallyl cation.<sup>34</sup>

The maximum concentration of **9** which could be obtained using a Phillips lamp and a Pyrex filter was 60%. Upon continued irradiation of this photostationary mixture at low temperatures, the slow formation of the isodurenonium cation **10** was observed.<sup>35</sup> Although the design of the photochemical equipment used did not permit accurate quantitative data to be obtained, it would appear that the formation of **10** is at least a factor of 10 slower than the photoisomerization of **8** to **9**.

The bicyclic cation **9** was stable at low temperatures in  $\text{HFSO}_3$ , but on warming it rearranged to give **8**. At  $-31^\circ$  the first-order rate constant for this isomerization was  $1.46 \times 10^{-3} \text{ sec}^{-1}$  ( $\Delta F^\ddagger = 17.1 \text{ kcal/mol}$ ). No other product was detected during this isomerization even though less than 5% of **10** could have been seen under the nmr conditions used.<sup>36</sup> Both **8** and **10**



were stable under the conditions at which this thermal isomerization took place.<sup>37</sup>

To completely define the course of these reactions, it is important to know more about the thermal and photochemical behavior of **10** and **11**. To this end the photochemistry of **10**, formed readily by the protonation of isodurene, was studied.<sup>35</sup>

The isodurenonium ion, **10**, gave no detectable products when it was irradiated at  $-90^\circ$  in  $\text{HFSO}_3$  using comparable conditions and times to those employed for the isomerization of **8**. With much longer irradiation times, a mixture of **8** and **9** was slowly produced. At no stage during the reaction was there any evidence to suggest the formation of **11**. The failure to detect **11** is at first glance surprising. One possible reason for this failure could be that **11** is thermally unstable under the conditions used for the photochemical reaction.

The bicyclic ketone **12** became available when its protonated form, **13**, was shown to be one of the major products obtained upon irradiation of protonated 2,4,6-trimethylphenol in  $\text{HFSO}_3$ .<sup>39</sup> The ketone **12** was recovered from the irradiated  $\text{FSO}_3\text{H}$  solution by quenching the acid in a methanol-bicarbonate slurry at  $-78^\circ$ .

(34) T. S. Sorensen and K. Rajeswari, *J. Amer. Chem. Soc.*, **93**, 4222 (1971); K. Rajeswari and T. S. Sorensen, *ibid.*, **95**, 1239 (1973); N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 152 (1964).

(35) D. M. Browner, E. L. Mackor, and C. MacLean, *Recl. Trav. Chim. Pays-Bas*, **84**, 1564 (1965).

(36) As 5% of **10** could have been detected,  $k$  for the isomerization of **9** to **10** must be  $< 7.3 \times 10^{-5} \text{ sec}^{-1}$ ;  $\Delta F^\ddagger > 18.6 \text{ kcal/mol}$ . An alternative route whereby **9** could isomerize to **10** is by an initial cyclopropyl migration to give **11** and then ring opening to give **10**. As **11** will be shown later to rapidly isomerize to **10** at  $-75^\circ$ , the rate limiting step in this pathway must be the cyclopropyl migration. It is then clear that the barrier to isomerization of **9** to **11** is  $> 18.6 \text{ kcal/mol}$ .

(37) At higher temperatures ( $> 0^\circ$ ), a quantitative fluorosulfonation occurred to give, after quenching in water, the appropriate tetramethylbenzenesulfonyl fluoride in high purity and yield. It is interesting that no methyl group migrations occur during this fluorosulfonation to give prehnitenesulfonyl fluoride. This contrasts markedly with the products obtained under the normal Jacobsen reaction conditions.<sup>38</sup>

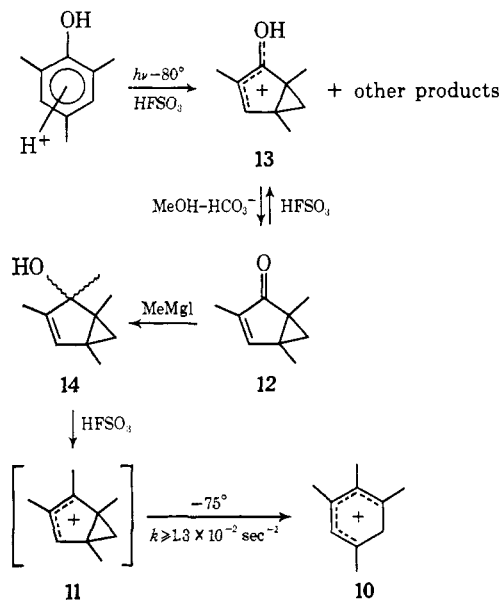
(38) L. I. Smith, *Org. React.*, **1**, 370 (1942).

(39) R. F. Childs and B. Parrington, presented at the CIC Conference, Quebec, June 1972, Abstract 67; B. D. Parrington, M.S. Thesis, McMaster University, 1971.

The spectra of **12** and its protonated form **13** are consistent with the structure indicated.

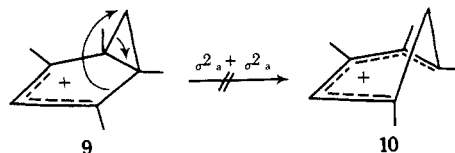
The tetramethyl alcohol(s), **14**, obtained by reaction of **12** with methylmagnesium iodide, was extracted from  $\text{CH}_2\text{Cl}_2$  into  $\text{HFSO}_3$  at  $-78^\circ$ . When the nmr spectrum was recorded at  $-75^\circ$ , 3 min after preparation of the solution, only resonances attributable to **10** could be detected. As protonation of **14** can be expected to give **11**, this cation must be thermally unstable at  $-75^\circ$  and rearrange to give **10** (Scheme I).<sup>3b</sup> An estimate of

Scheme I



the lowest value this rate constant may have can be based upon the assumption that 10% of **11** could have been detected in the first spectrum. This gives  $k \geq 1.3 \times 10^{-2} \text{ sec}^{-1}$  at  $-75^\circ$  ( $\Delta F^\ddagger < 13.1 \text{ kcal/mol}$ ) for the isomerization of **11** into **10**. This is a remarkably facile process compared to the rearrangements of related cations.<sup>3b, 16, 40</sup>

**Mechanism of the Thermal Isomerizations.** As has already been pointed out, the thermal isomerization of these bicyclo[3.1.0]hexenyl cations to the corresponding benzenonium ions by a simple electrocyclic process is formally symmetry "forbidden." However, the retention of the methyl group substitution pattern during this rearrangement requires that the  $\text{C}_1\text{-C}_5$  bond of the bicyclohexenyl cation be broken. Thus, while a  $[\sigma_2^a + \sigma_2^s]$  route is attractive in that it circumvents the forbidden electrocyclic process, such a pathway can be eliminated from consideration as it leaves the  $\text{C}_1\text{-C}_5$  bond intact.<sup>33</sup>

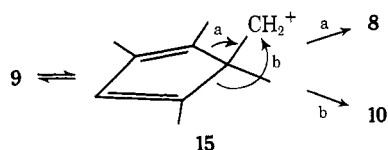


Likewise, the proposal of Hogeveen,<sup>41</sup> in which a cyclopentadienylmethyl cation is an intermediate in the ring

(40) I. S. Mamatyuk, L. I. Kuzobova, T. A. Gordymova, and V. A. Koptuyg, *Zh. Org. Khim.*, **6**, 2482 (1970).

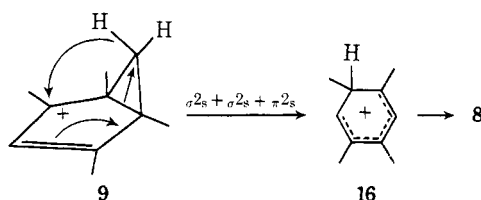
(41) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 3197 (1972).

opening rearrangement, cannot account for the exclusive breakage of the C<sub>1</sub>-C<sub>5</sub> bond. Thus for example, **15**,



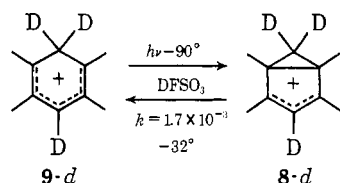
formed from **9**, could equally well undergo a 1,2-alkyl shift to give either **10** or **8**. Indeed considering the relative stabilities of the two benzenonium ions, it might be expected that **10** and not **8** would be formed.<sup>42</sup>

A reaction which satisfies both the need to break the C<sub>1</sub>-C<sub>5</sub> bond and conserve orbital symmetry is a retroene, or [ $\sigma 2_s + \sigma 2_s + \pi 2_s$ ] reaction.<sup>43</sup> The first step in this reaction sequence, which involves the transfer of the endo-C<sub>6</sub> proton to either C<sub>2</sub> or C<sub>4</sub>, would be the rate-determining one. The intermediate produced in the reaction, **16**, can rearrange to **8** by a hydride shift, a



process which is known to be extremely facile in these systems.<sup>44</sup>

Large primary kinetic isotope effects have been reported for the retroene reaction, and it would be expected that if the isomerization were proceeding *via* this pathway, a marked rate retardation would be found for the rearrangement of **9-d** as compared to **9**.<sup>45</sup> The



deuterated cation **8-d** was obtained upon solution of durene in DFSO<sub>3</sub> at  $-78^\circ$ , and this gave **9-d** upon irradiation. The nmr spectrum of **9-d** was fully consistent with its structure, no resonance attributable to the C<sub>3</sub> vinyl or C<sub>6</sub> methylene protons being detected. At  $-32^\circ$ , **9-d** rearranged to **8-d** with a first-order rate constant of  $1.7 \times 10^{-3} \text{ sec}^{-1}$ , the same, within the error limits of the experiment ( $\pm 10\%$ ), as that measured for **9**. For at least the rearrangement of **9** to **8** the retroene mechanism cannot be operative.

Thus in the absence of a viable alternative it would appear that the isomerization of these bicyclic cations to the benzenonium ions proceeds by way of the symmetry forbidden electrocyclic rearrangement.

In view of the interest recently given to "forbidden" reactions, it is instructive to note that the energy barriers

(42) E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 66 (1958).

(43) Cf. J. E. Baldwin, R. K. Pinschmidt, Jr., and A. H. Andrist, *J. Amer. Chem. Soc.*, **92**, 5249 (1970).

(44) D. M. Brouwer, C. MacLean, and E. L. Mackor, *Discuss. Faraday Soc.*, No. **39**, 121 (1965).

(45) S. McLean, C. J. Webster, and R. J. D. Rutherford, *Can. J. Chem.*, **47**, 1555 (1969); W. R. Roth and J. König, *Justus Liebigs Ann. Chem.*, **699**, 24 (1966).

associated with the rearrangements of these cationic systems are much lower than those of the corresponding neutral analogs.<sup>46</sup> The more highly strained bicyclo[2.1.0]pentenes have been reported to isomerize to the cyclopentadienes with a free energy of activation of about 25 kcal/mol.<sup>47</sup> This is 7 kcal/mol greater than the barrier found for any of the systems discussed in this paper and 5 kcal/mol higher than that reported for the rearrangement of the unsubstituted bicyclo[3.1.0]hexenyl cation.<sup>3</sup>

While it has not been possible to determine with precision the exact position of the long wavelength absorption of the bicyclo[3.1.0]hexenyl cations, it is reasonably certain that they have a maximum above 300 nm.<sup>48</sup> Thus, as would be expected for a charged system,<sup>51</sup> there is a much lower lying excited state available in these cations than exists for the comparable, neutral molecules, and this is reflected in the reduced barrier for their thermal isomerizations.<sup>52</sup>

The isomerization of the bicyclic cation **11** to benzenonium ion **10** takes place at a much lower temperature than the comparable rearrangements of the bicyclic cations **5** and **9**. There are several possible causes for the reduction in the energy barrier for the isomerization of **11** to **10**. Firstly, the position of the methyl substituents is such that the bicyclic cation **11** is thermodynamically less stable and the benzenonium ion **10** is as or more stable than the other pairs of ions discussed in this paper.<sup>42</sup> Alternatively, the unsymmetrical arrangement of the methyl groups on **11** could contribute to a reduction in the barrier for opening of the C<sub>1</sub>-C<sub>5</sub> bond.<sup>53</sup> A further possibility is that **11** isomerizes to **10** by a retroene pathway, for such a route could convert **11** directly to **9** without the intervention of a high energy intermediate as was the case for the rearrangements of either **5** or **9**.

**Mechanism of the Photochemical Isomerization.** The presumed involvement of cationic species in these photoisomerizations, made in a preliminary account of this work,<sup>8</sup> has been questioned.<sup>54</sup> The alternate suggestion advanced was that the unprotonated benzene derivative, in equilibrium with the cation, was undergoing the photorearrangement and the so formed products subsequently being protonated. Such a proposal is in accord with the recent studies on the mechanism of the photohydration of benzene in aqueous acid.<sup>3a,55</sup>

(46) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, *Accounts Chem. Res.*, **5**, 402 (1972); J. A. Berson, *ibid.*, **5**, 406 (1972).

(47) D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).

(48) It has not yet been possible to obtain a reproducible uv spectrum of these bicyclo[3.1.0]hexenyl cations. However, alkylated cyclopentenyl cations typically have a long wavelength absorption between 300 and 310 nm.<sup>49</sup> Substitution of a cyclopropyl at C<sub>1</sub> or C<sub>3</sub> of the cyclopentenyl cation causes a red shift of more than 30 nm.<sup>50</sup> A further model for these cations is protonated 1,3,4,5,6,6-hexamethylbicyclo[3.1.0]hex-3-en-2-one, which has a  $\lambda_{\text{max}}$  340 nm ( $\log \epsilon$  3.78).

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

(50) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Amer. Chem. Soc.*, **87**, 4533 (1965).

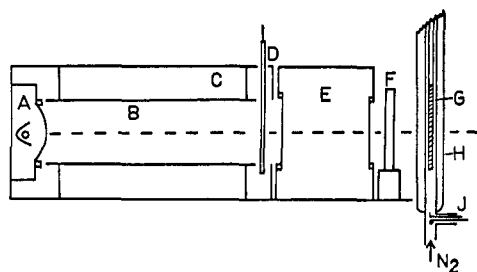
(51) M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6193 (1971).

(52) R. G. Pearson, *J. Amer. Chem. Soc.*, **94**, 8287 (1972); *Accounts Chem. Res.*, **4**, 152 (1971); J. E. Baldwin and A. H. Andrist, *J. Amer. Chem. Soc.*, **93**, 3289 (1971).

(53) R. Breslow, J. Napieriski and A. H. Schmidt, *J. Amer. Chem. Soc.*, **94**, 5908 (1972).

(54) G. Tennant, *Annu. Rep. Chem. Soc., B*, 249 (1971).

(55) L. Kaplan, D. J. Rausch, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **93**, 1549 (1971).



**Figure 2.** Schematic diagram of photolysis apparatus: (A) Phillips SP 500-W lamp for directed irradiation, water cooled; (B) polished aluminum tube; (C) light box; (D) shutter; (E) water filter, quartz windows, glass filters also included when desired; (F) cylindrical lens; (G) clear-wall nmr tube; (H) quartz dewar, unsilvered; (J) thermistor temperature controller and thermocouple.

There can be, however, little doubt with the superacid conditions employed in this work that it is the benzenonium cation which is undergoing the photoisomerization. The least basic of the aromatic hydrocarbons that has thus far been reported to photorearrange in  $\text{FSO}_3\text{H}$  is durene ( $\log k_b = -2.2$ ).<sup>42</sup> Even this hydrocarbon is essentially completely protonated in  $\text{HFSO}_3$  ( $H_0 = -15.07$ ).<sup>56</sup> Not only is the concentration of the unprotonated hydrocarbon very low, but the irradiations were carried out with light of wavelength greater than 320 nm. Under these conditions protonated durene, **5**, can readily absorb light ( $\lambda_{\text{max}}$  394 nm;  $\log \epsilon$   $3.75 \pm 0.2$ ) whereas durene has no significant absorption.<sup>57</sup> Further evidence for the cations being the photoreactive species comes from the results of a study of the heptamethylbenzenonium ion.<sup>16, 40</sup>

From the results presented above, it is quite clear that the photochemical transformation of the benzenonium ions to the bicyclo[3.1.0]hexenyl cations occurs very largely with the retention of the methyl substitution pattern. Thus, the primary photoproduct of **8** is **9**, the product of the symmetry-allowed electrocyclic reaction. It is not clear at this stage how the slow photochemical interconversion of 1,2,4,5 and 1,2,3,5 sets of tetramethyl cations are occurring.

## Experimental Section

**General Procedures.** Melting points were determined in open capillaries and are uncorrected. An Aerograph A-90-P3 instrument was used for all vpc separations. Nmr spectra were obtained on a Varian A-60 spectrometer fitted with a variable temperature probe, the probe temperature being measured with a methanol sample. A Varian C-1024 time averaging computer was used to amplify some of the cation spectra, the CAT being triggered on a generated side band of the  $\text{FSO}_3\text{H}$ . Cation solutions for nmr observation were prepared by extraction into  $\text{FSO}_3\text{H}$  or  $\text{FSO}_3\text{H}-\text{SbF}_5$  at  $-78^\circ$  from  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$  as previously described.<sup>58</sup> Chemical shifts were referred to internal  $\text{CH}_2\text{Cl}_2$  taken as  $\tau$  4.70. Cation solutions used for the photochemical experiments were prepared by direct solution of the appropriate hydrocarbon in  $\text{FSO}_3\text{H}$  at  $-78^\circ$ .

**1,2,3,4,5-Pentamethylcyclopentadienylcarbinol- $d_2$ .** Ethyl 1,2,3,4,5-pentamethylcyclopentadienylcarboxylate<sup>9</sup> (1.8 g) in anhydrous tetrahydrofuran (10 ml) was added to a stirred solution of lithium aluminum deuteride (0.5 g) in tetrahydrofuran (40 ml) at  $0^\circ$ . The mixture was stirred at room temperature for 18 hr. The excess hydride was destroyed by addition of saturated aqueous  $\text{NH}_4\text{Cl}$ ; ether (50 ml) was added and the ether layer separated. The aqueous layer was further extracted with ether ( $2 \times 25$  ml), and the com-

bined ether layers were washed with water ( $2 \times 25$  ml) and dried over  $\text{MgSO}_4$ . Removal of the ether and distillation gave the title compound as a pale yellow oil, bp  $53-55^\circ$  (0.5 mm) (1.2 g). Apart from the absence of the  $\text{CH}_2\text{OH}$  resonance ( $\tau$  6.49), the nmr spectrum was identical with the nondeuterated carbinol.

**1,2,3,4,5-Pentamethylcyclopentadienylmethyl- $d_2$  p-toluenesulfonate** was prepared using the conventional procedure from the deuterated alcohol described above.<sup>6</sup> Recrystallized from pentane at  $-17^\circ$  to give the tosylate as needles, mp  $73.5-75^\circ$ .

**1,3,4,5-Tetramethyl-2-methylenebicyclo[3.1.0]hex-3-ene-6- $d_2$  (4-d).** The above tosylate (0.9 g) was added to dry, oxygen free pyridine (5 ml) (distilled from KOH, flushed with  $\text{N}_2$  for 6 hr) at room temperature, stirred for 3 hr, and then kept at  $0^\circ$  overnight. Pentane (100 ml) was added and the pentane solution was washed with water ( $4 \times 50$  ml) and dried over  $\text{MgSO}_4$ . The pentane solution was concentrated to 3 ml and cooled to  $-17^\circ$ , and 0.2 g of the starting tosylate was collected. Further evaporation gave a yellow oil. Preparative vpc on 30%  $\gamma$ -nitro- $\gamma$ -methylpimelonitrile (2 m) gave 4-d (0.4 g). The nmr spectrum was identical with that of **4** apart from the absence of the  $\text{C}_6$  methylene resonances.

**Preparation and Protonation of 2-Hydroxy-1,2,3,5-tetramethylbicyclo[3.1.0]hex-3-ene (14).** 1,3,5-Trimethylbicyclo[3.1.0]hex-3-en-2-one<sup>39</sup> (**12**) (20 mg) in ether (1 ml) was added to  $\text{MeMgI}$  (prepared from Mg (48 mg) and  $\text{MeI}$  (350 mg)) in ether (10 ml) and stirred at room temperature for 4 hr. Saturated aqueous  $\text{NH}_4\text{Cl}$  solution (10 ml) was added and the ether layer was separated, dried over  $\text{MgSO}_4$ , and evaporated to give **14** (12 mg): nmr ( $\text{CS}_2$ )  $\tau$  9.71 and 9.59 (each 1, d,  $J = 4$  Hz, cyclopropyl H's), 8.87 (s, 6) and 8.82 (s, 3) (1,2- and 5-Me groups), 8.52 (d,  $J = 2$  Hz, 3, 3-Me), 5.37 (broad, 1, OH), and 4.66 (q,  $J = 2$  Hz, 1 vinyl H). This alcohol was protonated by extraction from  $\text{CH}_2\text{Cl}_2$  into  $\text{FSO}_3\text{H}$  at  $-78^\circ$  and observed by nmr after 3 min at  $-75^\circ$ . Only signals attributable to **10** could be detected.

**Quenches.** These were effected by pouring the  $\text{FSO}_3\text{H}$  solution at  $-78^\circ$  into a rapidly stirred suspension of sodium bicarbonate ( $\sim 2$  g) in methanol ( $\sim 15$  ml) at  $-78^\circ$ . The mixture was allowed to warm to room temperature, water (20 ml) was added, and the product was extracted into ether ( $2 \times 20$  ml). The ether extract was washed with water ( $2 \times 20$  ml) and dried over  $\text{K}_2\text{CO}_3$ . Vpc analysis using a  $\gamma$ -methyl- $\gamma$ -nitropimelonitrile column (30%, 2 m) was carried out on this dilute solution.

**Kinetic Measurements.** These were performed by monitoring the changes with time of the appropriate methyl resonances in the nmr spectrum of the rearranging cation. The probe temperature was calibrated before introduction of the cold sample and rechecked at the conclusion of the kinetic run. It was necessary to allow 3-5 min to elapse prior to recording the first spectrum. Each rate was measured at least twice. The concentration of the rearranging cation at any time was found by comparison with a nonrearranging internal standard, tetramethylammonium chloride. It was found to be accurate and more convenient to use a peak height comparison of the two peaks. Rate constants were calculated in the normal manner.<sup>59</sup>

**Photochemical Procedure.** Initially the photolyses were performed by irradiating the cation, dissolved in  $\text{FSO}_3\text{H}$ , in a clear, thin-wall nmr tube with a Bausch and Lomb 100-W medium-pressure light source. The necessary cooling was provided by placing the sample in a clear-wall Pyrex dewar containing, Dry Ice-acetone. The light was passed through the side of the vessel onto the sample. Conversion rates were low, and to see a reasonable percentage change in a realistic time ( $\sim 12$  hr) the sample size was restricted to 1-3 mg in 0.5 ml of  $\text{FSO}_3\text{H}$ . The reaction was followed by nmr, using a CAT technique to enhance the signal to noise ratio.

A diagram of the apparatus developed and used for the experiments with the tetramethyl substituted systems is shown in Figure 2. The light source is a Phillips SP 500-W super-pressure mercury lamp for directed radiation and it is so arranged in a small light box with a shutter that access can be made to the filter assembly and sample dewar while the light is operating. This facility both prolongs the lamp life (average 50 hr) and reduces the danger of exposure to the light during removal of the sample. The whole apparatus is contained in a large light box and the shutter may be operated from outside of this. The light is passed through a water filter and glass filter before being focused with a cylindrical quartz lens on the sample contained in a clear-wall nmr tube. An unsilvered quartz dewar surrounds the nmr tube and cooling is provided by passing a stream of  $\text{N}_2$ , obtained by boiling liquid  $\text{N}_2$ , through the dewar.

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

(57) G. Illuminati and J. S. Sproctor, *Gazz. Chim. Ital.*, **83**, 579 (1953).

(58) M. Brookhart, Ph.D. Thesis, University of California, Los Angeles, 1968.

(59) R. F. Childs, M. A. Brown, F. A. L. Anet, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2175 (1972).

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  $FSO_3H$  (0.5 ml) and irradiated at  $-90^\circ$  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.

**Acknowledgment.** Support of this work by the National Science Foundation and the U. S. Army Research Office (UCLA) and by the National Research Council of Canada and the Department of University Affairs (Ontario) (McMaster) is gratefully acknowledged.

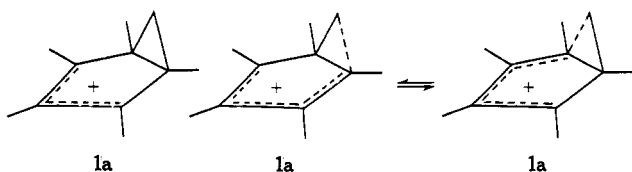
## Circumambulatory Hexa- and Heptamethylbicyclo[3.1.0]hexenyl Cations

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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  $8 \times 10^8$  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.<sup>2</sup> 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.



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

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.<sup>3</sup> 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.<sup>4</sup>

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.<sup>5</sup>

(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).