The following reaction scheme accounts for the previously mentioned formation of 1-hydronaphthyl from 1-naphthyl and for the fact that radicals were not observed in irradiated naphthalene which received the same dosage from X-rays as the samples enriched in naphthalene-1-*t* received from tritium $\beta$ radiation (60–90 Mrads).

$$RT \longrightarrow RHe^+ + \beta^- \qquad (1)$$

$$RHe^+ \longrightarrow R^+ + {}^3He \qquad (2)$$

$$R^+ + e^- \longrightarrow R\cdot\ (I) \qquad (3)$$

$$R\cdot + RH \longrightarrow RR + H\cdot \qquad (4)$$

$$H\cdot + RH \longrightarrow RH_2\cdot\ (II) \qquad (5)$$

Reaction 1 is the spontaneous radioactive decay of tritium with a half-life of 12.26 years and a maximum $\beta$ particle energy of 18.1 keV. The maximum recoil energy of 3.3 eV for the $^3$He ensures that the species formed in reaction 1 will not have its nuclear framework destroyed by the primary event. The order of, or even the separate existence of, reactions 2 and 3 are of course uncertain; however, the neutralization of ionic species would be expected in the semiconducting lattice of naphthalene. Reaction 4 can occur between neighboring naphthalene sites with relatively little displacement from the equilibrium positions. The coupling would be between positions 1 on one naphthalene and 2 on the other. The existence of reaction 5 was demonstrated by Leone and Koski in frozen alcohol solutions.[3]

We seem to have here a unique system which offers the opportunity to study free-radical reactions upon which certain geometrical constraints can be placed. Further experiments are being planned to check the hypotheses put forward in this communication and, if possible, to obtain rate constants and activation energies for the reactions occurring in the solid state.

**Acknowledgment.** This work was aided by a National Science Foundation instrument grant.

[6] Recipient of a grant from the Minnesota Mining and Manufacturing Co.

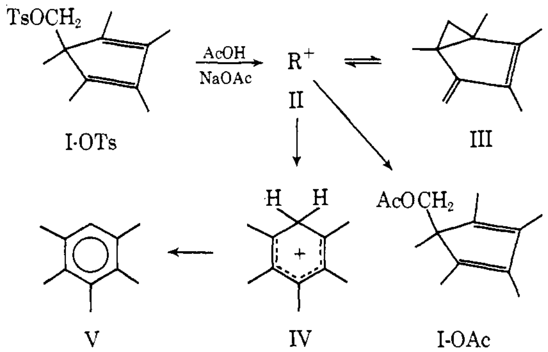
**R. V. Lloyd,[6] F. Magnotta, D. E. Wood**
*Department of Chemistry and Mellon Institute*
*Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213*
*Received October 14, 1968*

---

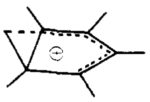
## The Observation and Behavior of the Pentamethylcyclopentadienylmethyl Cation[1,2]

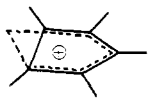
*Sir:*

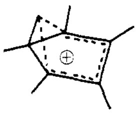
In this communication we return to the subject of the intermediate nonclassical ion or ions (II) in the solvolysis of pentamethylcyclopentadienylmethyl *p*-toluenesulfonate (I-OTs).[3] As reported some years ago,[3] acetolysis of this system is tremendously anchimerically accelerated, the product of kinetic control being nearly entirely olefin III with a very small proportion of acetate I-OAc. On standing in acetic acid solution, even under basic conditions (0.11 *M* NaOAc), olefin III adds acetic acid, and I-OAc becomes the major component of the III–I-OAc mixture. Under such conditions pentamethylbenzene (V) was not observed, no leakage from II to the pentamethylbenzenonium ion IV being detectable. Under more vigorous acidic conditions, permitting many repeated regenerations of II, pentamethylbenzene became a minor, or even a major, product.

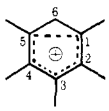


While it was clear from the former work that II was nonclassical,[3] it was not entirely clear how to represent the electron delocalization nor how many such discrete species need be written. This was illustrated[3a] with ions IIa, termed homoallylic, IIc, called doubly homoallylic,[3c] and IId, monohomocyclopentadienyl.


IIa


IIb


IIc



IId

We have now been able to observe ion II directly by nmr in $FSO_3H$ medium and to study the thermal conversion of II to IV, as well as the photochemical transformation of IV to II. The results are outlined and discussed in the present communication.

Extraction of olefin III from methylene chloride or preferably chloroform into $FSO_3H$ at low temperature[4] gives a good yield of a cation whose nmr spectrum is clearly consistent with the bicyclo[3.1.0]hexenyl structure[5] II (leaving aside the question of the degree or mode of cyclopropane involvement). In the nmr spectrum[7] the methyl group singlets appear at $\tau$ 8.34 (2 $CH_3$), 7.42 (2 $CH_3$), and 8.17 (1 $CH_3$), and the cyclopropane methylene proton doublets appear at $\tau$ 7.55 and 6.63. The latter are absent in the spectrum of the cation from protonation of the dideuterioolefin III-D. As regards electronic structure of ion II, it is impressive that the cyclopropane methylene protons are deshielded

---

[1] Research supported in part by the National Science Foundation and in part by the U. S. Army Research Office.

[2] Reported at the 12th Reaction Mechanisms Conference, Brandeis University, June 19–22, 1968.

[3] (a) S. Winstein and M. Battiste, *J. Am. Chem. Soc.*, **82**, 5244 (1960); (b) L. de Vries, *ibid.*, **82**, 5242 (1960); (c) for structure IIc we had visualized[3a] overlap between one lobe of a p or hybrid orbital on the $CH_2$ carbon atom with each of the p orbitals on the terminal carbon atoms of the butadiene system. See the following communication for a different orbital arrangement in the transition state for the degenerate "cyclopropane merry-go-round."

[4] Attempted conversion of carbinol I-OH to II in $FSO_3H$ or $FSO_3H$–$SbF_5$–$SO_2$ was unsuccessful, giving large amounts of polymer and a complex unrecognizable nmr spectrum.

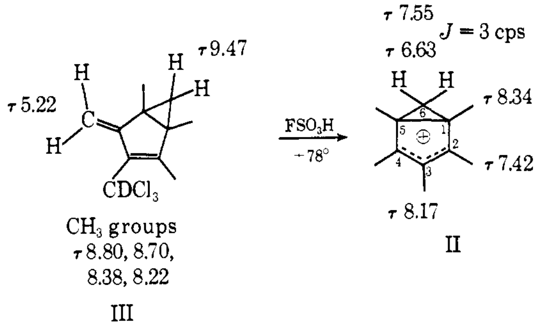
[5] The bicyclo[3.1.0]hexenyl cation seems to be a possible intermediate in many recently described reactions. Some of the products from the reaction of benzvalene and substituted benzvalenes[6a] in acidic or protic media could involve this cation. This is true also of the photochemical transformation[6b] of benzene in acidic media, although the exact timing of the protonation is not clear.[6c]

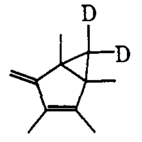
[6] (a) K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Am. Chem. Soc.*, **88**, 2881 (1966); **89**, 1031 (1967); (b) E. Farenhorst and A. F. Bickel, *Tetrahedron Letters*, 5911 (1966); (c) D. Bryce-Smith, A. Gilbert, and H. C. Longuet-Higgins, *Chem. Commun.*, 240 (1967).

[7] All chemical shifts for the cations are referred to internal $CH_2Cl_2$ taken as $\tau$ 4.70.

in the cation relative to the olefin III by some 2–3 ppm, indicating substantial involvement of the cyclopropane group in charge delocalization.[8] Another strong argument for this involvement of the cyclopropane group in carbonium ion stabilization is the very great reactivity of olefin III in reactions proceeding through a cation, *e.g.*, the easy transformation of III to I-OAc in basic AcOH solvent even at room temperature.

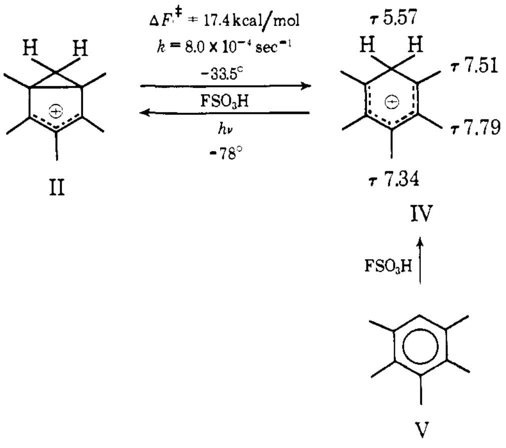
On the basis of our more recent theoretical ideas,[10a] we can reject structures IId and IIc[3c] since these are delocalized four-electron monohomo- and bishomocyclopentadienyl cations and are antihomoaromatic. While there is an argument against serious involvement of the 1,5-cyclopropane bond in electron delocalization, conditions are stereoelectronically and theoretically favorable for substantial involvement of the 1,6- and/or 5,6-cyclopropane bonds in such delocalization. Thus, symmetrical structure IIb, involving both 1,6 and 5,6 bonds, is the simplest representation which explains the nmr spectrum. Unsymmetrical structure IIa, which can be termed monohomopentadienyl,[10b] is an alternative which would also fit the observed nmr spectrum, provided there is rapid equilibration between two such equivalent structures. If such equilibration between equivalent structures IIa is actually occurring, it is not frozen out in $SO_2ClF$–$FSO_3H$ solvent at −120°, the lowest temperature at which we observed the nmr spectrum of II.





III-D

When $FSO_3H$ solutions of II are warmed, a unimolecular change of the nmr spectrum occurs, the nmr spectrum of the pentamethylbenzenonium ion[11a] IV growing in. The latter spectrum is identical with that which we obtain by protonating pentamethylbenzene (V), both in its peak positions and temperature dependence. Quenching the solution in $CH_3OH$–$NaHCO_3$ at −78° gives a good yield of V. At −33.5° the observed first-order rate constant for the thermal conversion of II to IV is $8.0 \times 10^{-4}$ $sec^{-1}$, corresponding to a $\Delta F^{\ddagger}$ of 17.4 kcal/mol.



The orbital symmetry argument employed by Woodward and Hoffmann[12] for electrocyclic reactions predicts a conrotatory course for a concerted ring opening in the thermal conversion of II to IV. Such a concerted conrotatory opening is essentially precluded in the present ring system, where the observed II → IV thermal conversion must proceed in the "forbidden" disrotatory fashion. Consistently, the thermal II → IV transformation involves a quite substantial free energy barrier of 17.4 kcal/mol.

Whereas the II $\rightleftharpoons$ IV interconversions are predicted to be conrotatory, such interconversions in the first excited state are predicted[12a] to be disrotatory and thus "allowed." Benzenonium ions show[11b] intense absorption in the uv at *ca.* 390 mμ, and thus irradiation of ion IV might be expected to lead to II. By such irradiation of solutions of IV in $FSO_3H$ at −78° in an nmr tube, conversions of IV to II of over 80% were in fact achieved in reasonable irradiation times. This photochemical reaction[13] was very clean, no other products being observed. The photochemically produced II was identical with that formed by protonation of III as regards nmr spectrum and rate constant for thermal conversion to IV.

Correlating our present findings and interpretations with the former solvolytic work,[3a] ion IIb (or equilibrating ions IIa, if this structure is in fact preferred by the system) is the intermediate in solvolysis of I-OTs giving rise to olefin III and acetate I-OAc. From the directly measured rate constant for the ring-opening conversion of II to IV it becomes clear why "leakage" from nonclassical ion II to classical benzenonium ion IV competes so poorly in the reactions of I-OTs and olefin III under solvolytic conditions. This is because the first-order rate constant for reaction of II with a solvent as nucleophilic as AcOH can be expected to exceed

---

(8) An attempt was made to calculate the downfield shift of the two cyclopropane methylene protons due to the direct field effect of the positive charge, using a semiempirical equation developed by Grutzner and Jackman.[9] The predicted deshielding is *ca.* 1 ppm for the "outside" proton and *ca.* 0.25 ppm for the "inside" one. Since the inductive effect is quite small over two C–C bonds, the residual deshielding of *ca.* 1.5 ppm is to be attributed to cyclopropane involvement in charge delocalization.

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

(10) (a) S. Winstein, Special Publication No. 21, The Chemical Society, London, 1967, p 5; (b) R. J. Piccolini and S. Winstein, *Tetrahedron Suppl.*, **2**, 423 (1963).

(11) (a) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42**, 502 (1964); (b) G. A. Olah, C. V. Pittman, Jr., and M. C. R. Symons in G. A. Olah and P. von R. Schleyer, "Carbonium Ions," Vol. 1, Interscience Publishers, New York, N. Y., 1968, p 183.

(12) (a) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); (b) see R. B. Woodward, Special Publication No. 21, The Chemical Society, London, 1967, p 217; for the conrotatory closure of protonated dicyclohexenyl ketone.

(13) Such photochemical transformations of carbonium ions are relatively new and promise to be important. van Tamelen[14] has recently studied the photolysis of some particularly stable cations, trapping the products in a nucleophilic medium.

(14) E. E. van Tamelen, *et al.*, *J. Am. Chem. Soc.*, **90**, 1372 (1968).

$8 \times 10^{-4}$ sec$^{-1}$, the value of the rate constant for II → IV (−33.5°), by at least a few powers of ten.[10a]

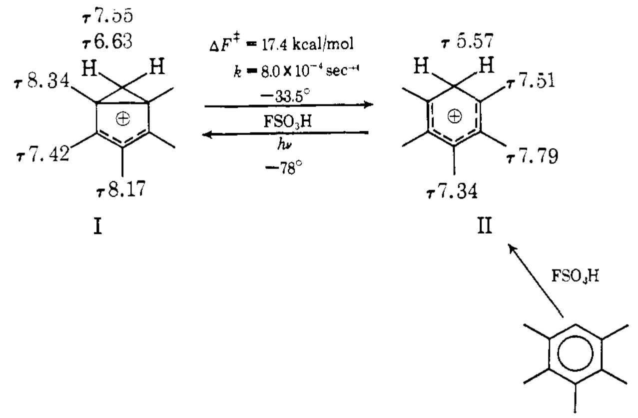
**R. F. Childs, M. Sakai, S. Winstein**
*Contribution No. 2275, Department of Chemistry*
*University of California, Los Angeles, California 90024*

*Received July 29, 1968*

## Ring Opening and Fivefold Degenerate Scrambling in Hexa- and Heptamethylbicyclo[3.1.0]hexenyl Cations[1,2]

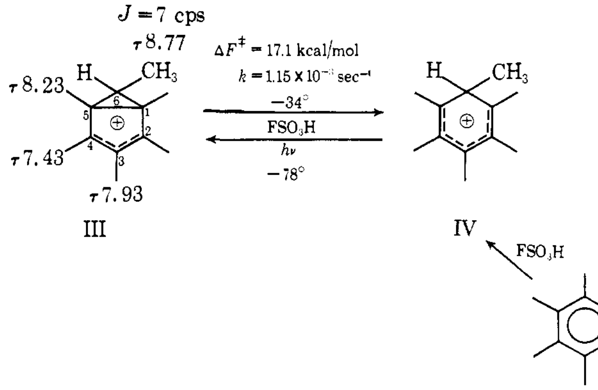
*Sir:*

In the preceding communication[3] we reported the direct observation of the pentamethylbicyclo[3.1.0]hexenyl cation I in $FSO_3H$ by nmr, the rate of its ring-opening conversion to benzenonium ion II, and its photochemical synthesis from II. The photochemical route provides a very clean and efficient way to generate ions such as I, and we have applied it in the study of the hexamethyl and heptamethyl analogs of I. The results of this study are outlined and discussed in the present communication.

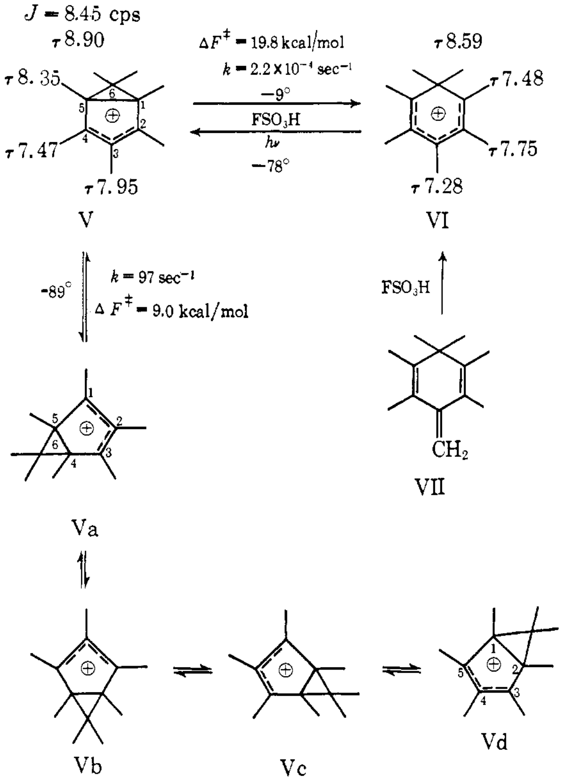


Protonation of hexamethylbenzene in $FSO_3H$ and irradiation of the hexamethylbenzenonium ion[4] IV at −78° gives rise to the hexamethylbicyclo[3.1.0]hexenyl cation III very cleanly. The nmr spectrum[5] of III is very similar to that of I,[3] and no other products are observed. There are two conceivable stereoisomers from the IV → III ring closure, one with an "inside" and the other with an "outside" 6-$CH_3$ group. However, essentially only one of these is apparently produced in the present work, judging by the fact that only one sharp doublet at $\tau$ 8.77 is observed for the 6-$CH_3$ group in III. It is not possible from the present evidence to state unequivocally which isomer is produced from IV.[6]

When the $FSO_3H$ solution of III is warmed to −34°, a clean first-order reversion to the hexamethylbenzenonium ion IV occurs with a rate constant of $1.15 \times 10^{-3}$ sec$^{-1}$, the $\Delta F^{\ddagger}$ value being 17.1 kcal/mol. After 5 min at 0°, only ion IV is observed in the nmr.



Doering[9] first prepared the heptamethylbenzenonium ion VI, and for the present study it was conveniently prepared by one of his methods, namely protonation of hydrocarbon VII in $FSO_3H$. Irradiation of the resulting solution of VI at −78° caused a clean transformation to the heptamethylbicyclo[3.1.0]hexenyl cation V. When this solution was warmed to −9° a smooth reversal to the heptamethylbenzenonium ion VI occurred with a first-order rate constant of $2.2 \times 10^{-4}$ sec$^{-1}$, $\Delta F^{\ddagger}$ being 19.8 kcal/mol.



The heptamethylbicyclo[3.1.0]hexenyl cation V displays a temperature-dependent nmr spectrum, and to permit lower temperature observations cation V was produced photochemically in a 2:1 $SO_2ClF$–$FSO_3H$ mixture. In this solvent the nmr spectrum of V could

---

[1] Research supported by the National Science Foundation.

[2] Reported at the 12th Reaction Mechanisms Conference, Brandeis University, June 19–22, 1968.

[3] R. F. Childs, M. Sakai, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 7144 (1968).

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

[5] Chemical shifts of the cations are referred to internal $CH_2Cl_2$ taken as $\tau$ 4.70. The signal for the $C_6$ proton in III was not detected, probably being obscured under the hexamethylbenzenonium ion signal.

[6] At least some of the products of reported electrophilic additions to hexamethyl Dewar benzene[7a] and hexamethylprismane[7b] may well be related to ion III. The protonation (HF–$BF_3$) of hexamethyl Dewar benzene is reported[8] to give a bicyclo[2.1.1]hexenyl cation which isomerizes relatively slowly (compared to III) with a rate constant of $1.03 \times 10^{-3}$ at 20° ($\Delta F^{\ddagger}$ = 21.2 kcal/mol) to IV, probably[8] *via* the bicyclo[3.1.0]hexenyl cation III.

[7] (a) W. Schäfer and H. Hellman, *Angew. Chem. Intern. Ed. Engl.*, **6**, 518 (1967); L. A. Paquette and G. R. Krow, *Tetrahedron Letters*, 2139 (1968); (b) R. Criegee and H. Grüner, *Angew. Chem.*, **80**, 447 (1968).

[8] H. Hogeveen and H. C. Volger, *Rec. Trav. Chim.*, **87**, 385 (1968).

[9] W. von E. Doering, *et al.*, *Tetrahedron*, **4**, 178 (1958).