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

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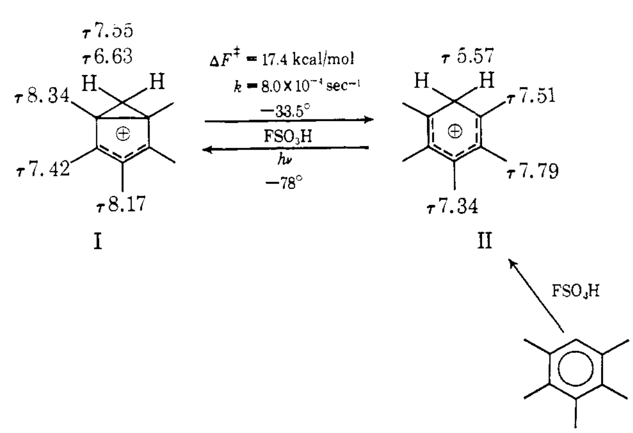
Ring Opening and Fivefold Degenerate Scrambling in Hexa- and Heptamethylbicyclo[3.1.0]hexenyl Cations[1,2]

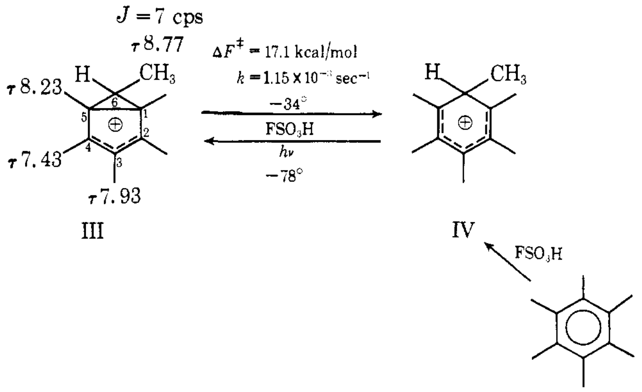
Sir:

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.

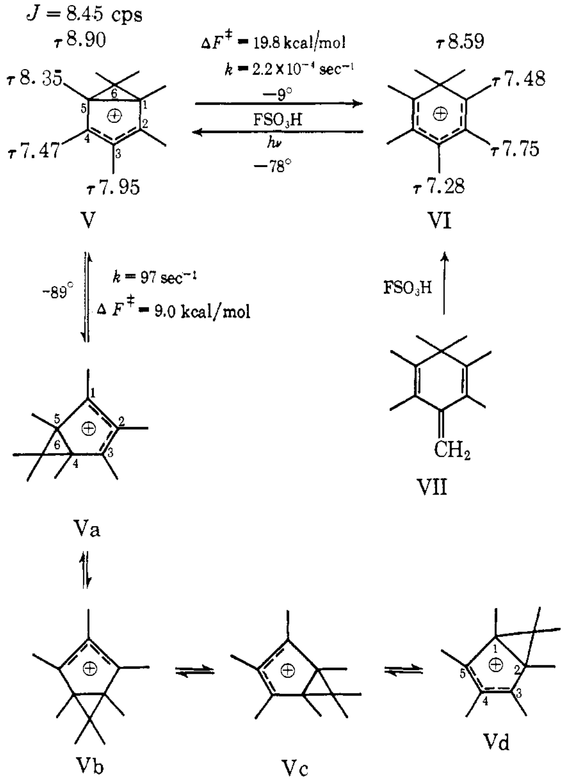


Protonation of hexamethylbenzene in FSO_3H and irradiation of the hexamethylbenzenonium ion[4] IV at −78° gives rise to the hexamethylbicyclo[3.1.0]hexenyl cation III very cleanly. The nmr spectrum[5] of III is very similar to that of I,[3] and no other products are observed. There are two conceivable 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 τ 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 1.15×10^{-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 2.2×10^{-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

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[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 τ 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 1.03×10^{-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).

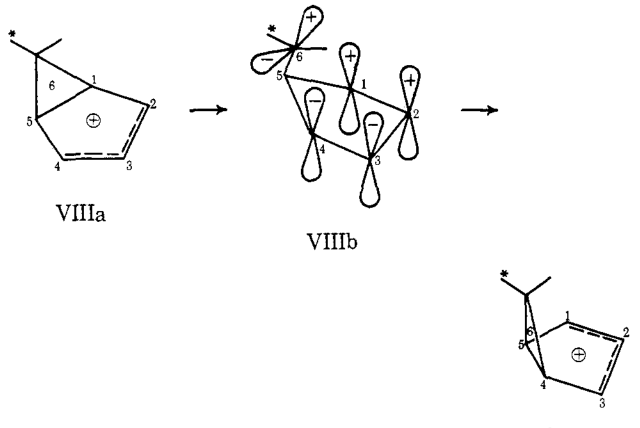
[8] H. Hogeveen and H. C. Volger, *Rec. Trav. Chim.*, **87**, 385 (1968).

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

be recorded over the temperature range −110 to −9°. Below −100° the spectrum of V is very similar to those for I and III. As the temperature is raised the signals for the five methyl groups on the cyclopentenyl ring broaden, coalesce at *ca.* −87°, and become a sharp statistically averaged singlet (τ 7.90) at higher temperature (*e.g.*, −48°). While at higher temperatures these five CH_3 groups are averaging, the two CH_3 groups on the cyclopropane methylene carbon atom C_6 remain distinct and show no sign of averaging up to −9°.

The observed fivefold degenerate scrambling in V apparently involves migration of the cyclopropyl methylene carbon atom C_6 around the five-membered cyclopentenyl ring, thus equilibrating structures V, Va, Vb, Vc, and Vd.[10] Using a Saunders many-site nmr line-shape program,[11] line shapes for the three types of averaging CH_3 groups (C_1, C_2, and C_3) were calculated and plotted for a range of different rate constants. In this way a rate constant of 97 sec^{-1} at −89° was obtained for the shift of C_6 from one site to the next. This corresponds to a $\Delta F^{\ddagger}$ of 9.0 kcal/mol.

The key step in the fivefold degenerate rearrangement of V is best viewed as a concerted sigmatropic 1,4 shift of C_6 which, in the present ring system, must be suprafacial.[12] Viewing the transition state as involving a C_6 cationic or radical center interacting with a butadiene or butadiene cation radical system, respectively, the orbital symmetry of the highest occupied MO in the butadiene portion is as indicated in VIIIb. This predicts that C_6 employs both lobes of an antisymmetric p orbital, as in VIIIb, and is thus inverted in each shift. On this basis, the "outside" CH_3 group on C_6 (the starred CH_3 group in VIII) should remain "outside" and the "inside" CH_3 group should remain "inside" during the fivefold degenerate rearrangement, as is indicated in VIIIa → VIIIc. This is just what is observed, the two C_6 methyl groups maintaining their identities even when the other five methyl groups are averaging very rapidly.



VIIIa

VIIIb

VIIIc

How strictly the "allowed" stereochemistry is obeyed in the fivefold degenerate rearrangement of V may be judged from an estimated upper limit to the rate constant for averaging the two C_6 methyl groups. From the fact that no significant broadening (<1 cps) of the C_6 methyl signals could be detected up to a temperature of −9°, an upper limit of 3 sec^{-1} at −9° can be placed on the rate constant for exchange between "inside" and "outside" CH_3 groups, corresponding to a $\Delta F^{\ddagger}$ greater than 14.7 kcal/mol for the "forbidden" process. The $\Delta\Delta F^{\ddagger}$ between "allowed" and "forbidden" processes is thus greater than 5.7 kcal/mol. At −9° the "allowed" process is more than 50,000 times faster than the "nonallowed" one, providing a striking validation of the Woodward–Hoffmann selection rules for sigmatropic migrations.[13]

It is interesting that the rate of the fivefold degenerate rearrangement of the bicyclo[3.10]hexenyl cations is very sensitive to the state of substitution of the cyclopropane C_6 carbon atom, being unobservable for cations I and III on the nmr time scale. From line-width considerations it is clear that the rate constant for such rearrangements in I and III is less than 5 sec^{-1} at −34°, $\Delta F^{\ddagger}$ being greater than 13.0 kcal/mol and at least 4.0 kcal/mol greater than in the case of V. At −34°, the effect of changing the migrating C_6 from secondary to tertiary is to increase the rate of migration by at least a factor of 5×10^3. This is probably an indication that the migrating carbon atom bears considerable positive charge in the transition state.[14]

The $\Delta F^{\ddagger}$ values for ring-opening conversion of ions I, III, and V to the corresponding benzenonium ions, 17.4, 17.1, and 19.8 kcal/mol, respectively, do not exhibit a definite trend with the degree of substitution of C_6. With changing steric factors as well as the extent of cyclopropyl involvement in stabilization of the bicyclohexenyl cation, and with only one configuration of III yet available, it is difficult to draw any definite conclusions.

(10) Such a degenerate rearrangement in bicyclo[3.1.0]hexenyl cations has been anticipated by D. W. Swatton and H. Hart, *J. Am. Chem. Soc.*, **89**, 5075 (1967), who observed slow cyclopropyl migration in some hydroxy-substituted bicyclohexenyl cations.

(11) M. Saunders, *Tetrahedron Letters*, 1699 (1963).

(12) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

(13) An electronically analogous 1,3-carbon migration in the thermal transformation of a bicyclo[3.2.0]heptene derivative to its [2.2.1] isomer has been shown by J. Berson (*Accounts Chem. Res.*, **1**, 152 (1968)) to involve a highly specific suprafacial inversion of the migrating carbon.

(14) It is interesting that the fivefold degenerate rearrangement of V is very much faster than are 1,2-methyl shifts around the six-membered ring of VI. For the latter rearrangement Saunders[15] has observed an energy of activation of 15.2 kcal/mol, with log A = 12.3 sec^{-1}. For the least substituted bicyclohexenyl cation, I, however, the fivefold degenerate rearrangement will probably prove to be slower than is the rearrangement of VI.

(15) M. Saunders, "Magnetic Resonance in Biological Systems," Pergamon Press, New York, N. Y., 1967, p 85.

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The Protonation of Hexamethyl Dewar Benzene and Hexamethylprismane in $FSO_3H–SbF_5–SO_2$

Sir:

We have conducted an nmr investigation on hexamethyl Dewar benzene (**1**) and hexamethylprismane (**2**) in fluorosulfuric acid–antimony pentafluoride ("magic acid"(1)) solution in an effort to derive spectral information on the nature of the cationic species present under such conditions. These highly strained hydrocarbons were selected because of their relationship to

(1) E. M. Arnett and J. W. Larsen, *Chem. Eng. News*, **46**, 36 (Feb 26, 1967); G. A. Olah and R. H. Schlosberg, *J. Am. Chem. Soc.*, **90**, 2726 (1968).