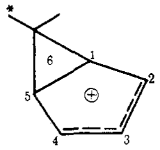
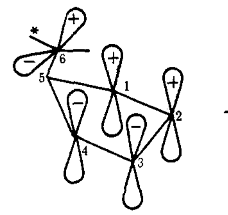
be recorded over the temperature range −110 to −9°. Below −100° the spectrum of V is very similar to those for I and III. As the temperature is raised the signals for the five methyl groups on the cyclopentenyl ring broaden, coalesce at *ca.* −87°, and become a sharp statistically averaged singlet (τ 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.

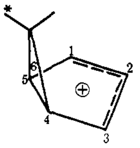
The key step in the fivefold degenerate rearrangement of V is best viewed as a concerted sigmatropic 1,4 shift of C_6 which, in the present ring system, must be suprafacial.[12] Viewing the transition state as involving a C_6 cationic or radical center interacting with a butadiene or butadiene cation 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.

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[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

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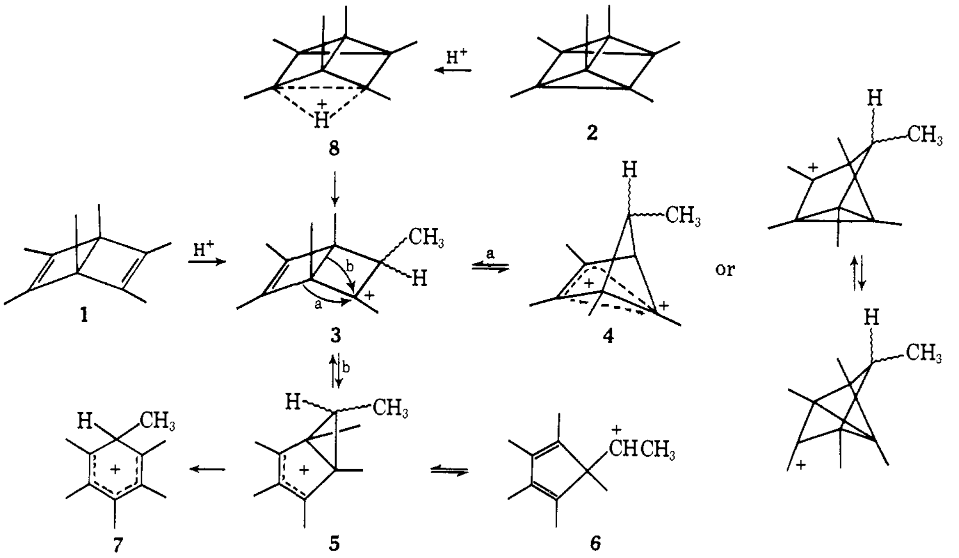
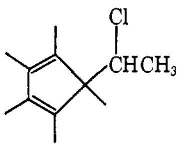
[1] E. M. Arnett and J. W. Larsen, *Chem. Eng. News*, **46**, 36 (Feb 26, 1967); G. A. Olah and R. H. Schlosberg, *J. Am. Chem. Soc.*, **90**, 2726 (1968).



several interesting carbonium ions (**3**–**8**) a number of which have actually been trapped in the course of recent studies. For example, addition of HCl to CH_2Cl_2 solutions of **1** leads primarily to **9**;[2] some **10** is also present in minor quantity.[3] When **1** is treated with chlorosulfonyl isocyanate, adduct **11** is obtained;[4] in contrast, reaction with ethyl N-sulfonylcarbamate gives **12**.[5] Analogously, reaction of prismane **2** with 4-phenyl-1,2,4-triazoline-3,5-dione in strongly polar solvents provides a number of addition products formally derived from several of these cations.[6,7]



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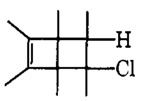

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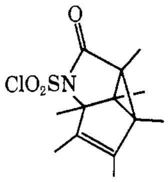

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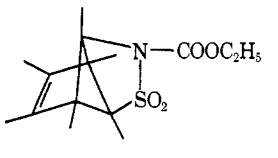
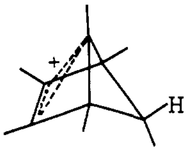
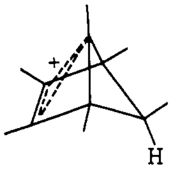


12

Addition of **1** to a 1:1 mixture of antimony pentafluoride–fluorosulfuric acid diluted with an equal volume of sulfur dioxide at −78° gave a nearly quantitative yield of two cations present in an approximate ratio of 75:25. The predominant cation displays methyl group singlets at δ 1.31 (3 H), 1.57 (6 H), and 2.01 (6 H), together with a methyl doublet (J = 6.5 Hz) at 0.67 and a one-proton quartet (J = 6.5 Hz) at 3.05.[8] The corresponding peaks in the minor cation appear at δ 1.35 (3 H), 1.45 (6 H), 2.03 (6 H), and 1.44 (doublet, J = 6.5 Hz); the low concentration of this cation precluded direct observation of the tertiary proton quartet. These spectra were seen to be temperature dependent, an observation which clearly demonstrated the propensity of these cations for interconversion at higher temperatures. This temperature dependence has been attributed to rapid interconversion of the isomeric bicyclo[2.1.1]hexenyl cations i and ii (presumably by alkyl shifts[9]).



i



ii

An identical result was obtained by dissolving **1** in fluorosulfuric acid diluted with an equal volume of sulfur dioxide at −78°. Again under these conditions there was no detectable formation of the hexamethylbenzenonium ion (**7**).[10]

The dissolution of hexamethylprismane (**2**) in these media at −78° proved to be vigorously exothermic. The resulting spectra were identical with those obtained from **1** with the exception that a significant concentration of cation **7** was present in solution. This result would obtain if the heat liberated in dissolving hydrocarbon **2** were sufficient to cause partial conversion to hexamethylbenzene. This interpretation is reasonable in view of the strain embodied in **2** (82 kcal/mol) and its well-established thermal lability.[6]

The stereoisomeric carbonium ions of structure **3** have been ruled out for the two observable cations on the basis of symmetry; unless coincidence is at play, no two methyl groups in these structures are expected to exhibit the same chemical shift. Structure **6** is also incongruent with the spectral data, particularly because no absorption characteristic of four vinylic methyl groups is seen.

Inasmuch as our spectra differ substantially from that observed by Childs and Winstein[11] for the hexamethyl-

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(2) L. A. Paquette and G. R. Krow, *Tetrahedron Letters*, 2139 (1968).

(3) W. Schäfer and H. Hellmann, *Angew Chem.*, **79**, 566 (1967); *Angew. Chem. Intern. Ed. Engl.*, **6**, 518 (1967).

(4) L. A. Paquette, *Tetrahedron Letters*, 2133 (1968).

(5) G. M. Atkins, Jr., and E. M. Burgess, *J. Am. Chem. Soc.*, **90**, 4744 (1968).

(6) (a) D. M. Lemal and J. P. Lokensgard, *ibid.*, **88**, 5934 (1966); (b) D. M. Lemal, private communication.

(7) For additional recent work in this area, see: (a) R. Criegee and H. Grüner, *Angew. Chem.*, **80**, 447 (1968); (b) H. Hogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967).

(8) All chemical shifts for the cations are referred to external tetramethylsilane.

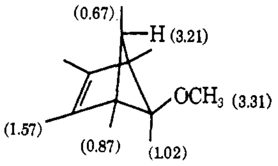
(9) H. Hogeveen and H. C. Volger, *Rec. Trav. Chim.*, **87**, 385 (1968).

(10) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42**, 502 (1964); G. A. Olah, *J. Am. Chem. Soc.*, **87**, 1103 (1965), and references given therein.

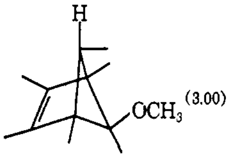
(11) R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968).

bicyclo[3.1.0]hexenyl cation **5**,[12] it likewise becomes possible to remove this structure from consideration.

The nmr spectra are entirely consistent, however, with the bicyclo[2.1.1]hexenyl cation structure **4** of which there exist two possible stereoisomers, one with a "quasiaxial" and the other with a "quasiequatorial" methyl group (relative to the cyclobutane ring). Corroborative evidence was obtained when the cold FSO_3H-SbF_5-SO_3 solution of **4** was quenched at −78° with excess sodium methoxide in methanol under conditions of rapid magnetic stirring. There was produced in 76% over-all yield the two methyl ethers **13** and **14** in a ratio of 75:25, respectively. These isomers proved to be difficult to separate and purify because of their high reactivity.[13] Careful fractional recrystallization of the mixture from methanol at low temperatures, however, ultimately resulted in the isolation of the major product, mp 44–45°, in 10–15% yield; on the basis of its nmr spectrum (δ values, CCl_4, internal TMS), this isomer has been assigned structure **13**. We have so far been unable to isolate a pure sample of **14**, and the indicated structural assignment must be considered tentative. Although it has not proven possible from the present data to state unequivocally which isomer of **4** predominates in the strongly acidic medium, the cation corresponding to isomer **13** seems most likely, particularly since the quenching is expected to be kinetically controlled under the conditions employed. The stereochemistry of the methoxyl groups in **13** and **14** follows from the customary steric considerations given to related ions.



13



14

Previously, the bicyclo[2.1.1]hexene system has proven very elusive; only recently has the first number of the series been described.[14] Should such quenching reactions prove to be general in nature, facile synthetic entry to a variety of bicyclo[2.1.1]hexene derivatives would be available.

Earlier work suggests implicitly that structures of types **3**–**7** constitute a set of $C_{12}H_{18}R^+$ cations[15] which exist on a single potential energy surface.[2–7] The various isomers are accessible by either thermal[2–7] or photochemical means.[11] The present findings [Dewar benzene and prismane routes] denote that the bicyclo[2.1.1]hexenyl cation (**4**) may be an energy minimum (with respect to the various cations) in strongly acidic media. Irradiation of **7** at −78° in FSO_3H gives **5**. Both **4** and **5** are subject to clean first-order conversion to **7**, but at greatly differing rates [for **4**, $k = 10.3 \times 10^{-4}$ sec^{-1} at 20.5° in HF–BF_3 solution;[7b,16] for **5**, $k = 1.15 \times 10^{-3}$ sec^{-1} at −34° in FSO_3H[11]]. Because **4** rearranges more slowly than **5**, it is not possible to examine the thermal interconvertibility of these cations by this technique. Nevertheless, the isomerization of **4** to **7** is perhaps best rationalized as proceeding *via* cation **5**.

Acknowledgment. The authors wish to thank Professor David Lemal for a generous gift of hexamethylprismane, and the Petroleum Research Fund administered by the American Chemical Society, for partial support of this work.

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(12) Protonation of **1** in neat FSO_3H [the solvent system used by Childs and Winstein;[11] shifts referred to internal CH_2Cl_2 (τ 4.70)] gives rise to an identical spectrum. The chemical shift values seen in FSO_3H–SbF_5–SO_3 solution [this work; reference point is capillary TMS (τ 10.00)] are approximately 0.15 ppm higher than the same values in FSO_3H (S. Winstein, personal communication).

(13) Silica gel chromatography converts **14** to hexamethylbenzene and partially transforms **13** into unidentified products. Both isomers readily add a second mole of methanol, and if the quenching is done in a methanol-potassium carbonate suspension without rapid stirring a dimethanol addition compound is produced to the extent of approximately 70%. We have not yet been able to assign a structure to this material.

(14) J. Meinwald and F. Uno, *J. Am. Chem. Soc.*, **90**, 800 (1968); F. T. Bond and L. Scerbo, *Tetrahedron Letters*, 2789 (1968).

(15) R need not necessarily be a proton but may also be a different electrophilic moiety.

(16) This rate is not significantly altered in FSO_3H (S. Winstein, personal communication).

(17) Considered as Stable Carbonium Ions. LXXVIII.

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Received August 13, 1968

Photochemical Transformations of 2-Methoxyazabullvalene[1,2]

Sir:

Interest in the ground- and excited-state properties of molecules with fluctuating bonds is at an all-time high. However, in spite of the relatively numerous accounts of photochemical routes to bullvalene,[3] semibullvalene,[4] and their derivatives, only in the case of bullvalene has more extensive photolysis of such a system been examined.[5] In this communication we wish to report our study of the photochemical transformations of 2-methoxyazabullvalene (**1**)[3e,6] under conditions of direct irradiation.

On exposure of methanol or tetrahydrofuran solutions of **1** to an unfiltered 450-W Hanovia lamp for 15 hr, a number of photoproducts result (Table I). The duration of the experiments was dictated by the fact that certain of the photoproducts were also unstable to ultraviolet light; under the stated conditions, the yields of the various components appeared to be maximized. Separation of the compounds was achieved by preparative-scale vpc separation at 160° on a 10-ft column

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(1) Unsaturated Heterocyclic Systems. XLVII. For the previous paper in this series, see I. C. Paul, S. M. Johnson, L. A. Paquette, J. H. Barrett, and R. J. Haluska, *J. Am. Chem. Soc.*, **90**, 5023 (1968).

(2) Partial support of this research by the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

(3) For example, see (a) G. Schröder, *Angew. Chem.*, **75**, 722 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 481 (1963); (b) G. Schröder, *Ber.*, **97**, 3140 (1964); (c) W. von E. Doering and J. W. Rosenthal, *Tetrahedron Letters*, 349 (1967); (e) L. A. Paquette and T. J. Barton, *J. Am. Chem. Soc.*, **89**, 5480 (1967).

(4) (a) H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (c) J. P. N. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967); (d) R. S. H. Liu, *J. Am. Chem. Soc.*, **90**, 215 (1968).

(5) M. Jones, Jr., *ibid.*, **89**, 4236 (1967).

(6) L. A. Paquette, T. J. Barton, and E. B. Whipple, *ibid.*, **89**, 5481 (1967).