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Rearrangement of Nonamethylbicyclo[3.2.1]octa-3,6-dien-2-yl Cation to the Corresponding [3.3.0] Cation

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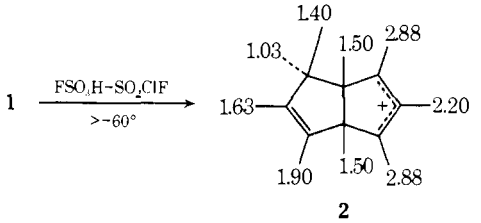
Abstract: The title ion **1**, which in FSO_3H-SO_2ClF undergoes rapid degenerate rearrangements below −60°, rearranges irreversibly above that temperature to the 1,2,3,4,5,6,7,8,8-nonamethylbicyclo[3.3.0]octa-3,6-dien-2-yl ion, **2**. The mechanism involves a cyclopropylcarbinyl–cyclopropylcarbinyl type of rearrangement (A → D); labeling experiments eliminate an alternative mechanism involving a 1,2-methyl shift. Ion **2** incorporates deuterium on standing in trifluoroacetic acid-*d*. Eventually all nine methyls become labeled, but they do so at different rates, and a mechanistic scheme is suggested to account for the results. These studies delineate preferred paths for carbonium ions which have several alternatives for rearrangement; attention is drawn to the importance of bishomoantiaromaticity as a factor in these rearrangements.

In a previous paper[1] we described two rapid degenerate rearrangements which the nonamethylbicyclo[3.2.1]octa-3,6-dien-2-yl cation (**1**) undergoes below −60° in FSO_3H-SO_2ClF. The faster of these is a circumambulatory process which is NMR-observable; the three carbons which bear methyl groups 1, 5, 8, and 8′ circumambulate about the five carbons which bear methyls 2, 3, 4, 6, and 7 in such a manner that these five methyls equilibrate, as do methyls 8 and 8′, but methyls 1 and 5 remain unique. The slower process, detected only by deuterium labeling studies, equilibrates methyls 1 through 7, and methyls 8 and 8′; it is most simply rationalized via a 1,2-bridge shift. Both processes are illustrated in Scheme I. Circumambulation has a $\Delta H^{\ddagger}$ of 7.4 kcal/mol, whereas the $\Delta H^{\ddagger}$ for bridge shift is somewhat higher, but less than 17.8 kcal/mol.

On standing in FSO_3H-SO_2ClF at or above −60°, ion **1** rearranges to the [3.3.0] ion **2**. In this paper we discuss in detail the mechanism of this rearrangement.[2]



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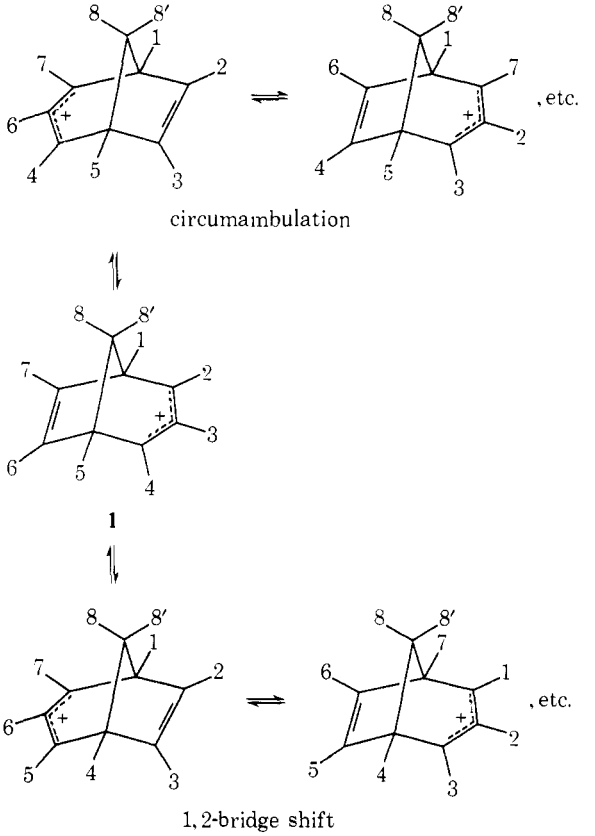
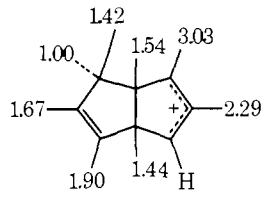
Scheme I



Results and Discussion

Structure of Ion 2. Because of the circumambulatory process, the ^1H NMR spectrum of **1** at −60° or above consists of only three peaks, a sharp singlet at δ 1.27 due to equilibrating methyls 8 and 8′, a sharp singlet at δ 1.52 due to methyls 1 and 5, and a broad singlet at δ 2.20 due to equilibrating methyls 2, 3, 4, 6, and 7. Gradually, with a rate constant of $1.9 \pm 0.2 \times 10^{-4}$ sec^{-1} at −52°, this spectrum is replaced by one with seven peaks, assigned as shown in

the structure of **2**. The spectrum is similar to those already assigned[3] to the closely related ions **3** and **4**.[4] We believe



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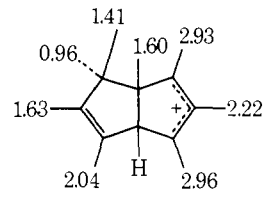

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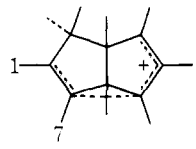
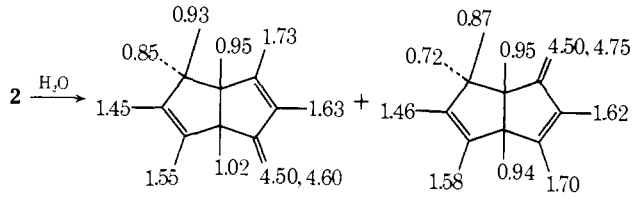
that the structures of these ions are best represented as shown, and that a structure involving charge delocalization to the double bond, such as **2′** is not important, because if it



2′

were, one would expect the C-1 methyl to appear at lower field than the C-7 methyl, whereas the opposite is observed.

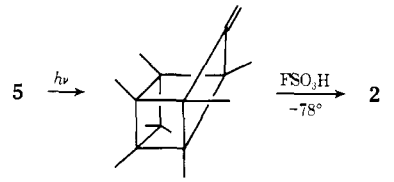
Structure **2** was confirmed by quenching studies. When solutions of **2** were added to an ice slurry of sodium hydroxide, two hydrocarbons were obtained to which we assign structures **5** and **6**; the former usually predominated,



5 **6**

though the ratio of **5**:**6** varied with the quenching conditions. The ^{1}H NMR spectra of **5** and **6**, shown on the structures, were similar to one another. Each showed four aliphatic methyl singlets, four homoallylically coupled vinyl methyls, and two vinyl protons. Dissolution of either **5** or **6** in FSO_3H or trifluoroacetic acid (TFA) gave identical solutions of **2**, which was stable in TFA up to +50°.

The structures of **5** and **6** were confirmed by their photoisomerization.[5] Each gave a different, less saturated photoisomer, and these behaved differently from one another on protonation in strong acid. Compounds **7** and **8** correspond in structure to the $_\pi2 + _\pi2$ cycloaddition products of the two endocyclic double bonds in **5** and **6** respectively.



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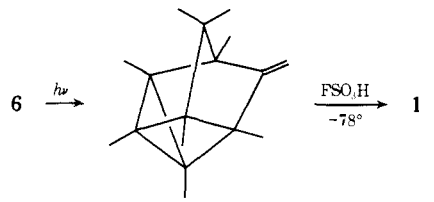

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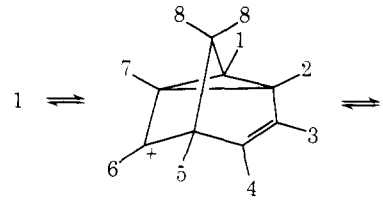
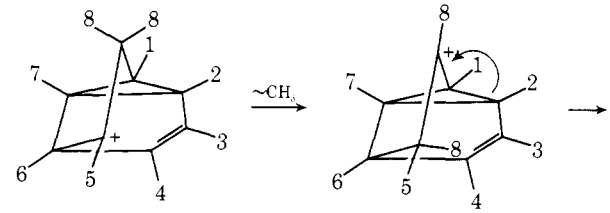
Mechanism for the Isomerization of 1 to 2. Interaction between the π electrons of the double bond and the allylic cation in **1** should have a destabilizing effect since the ion is incipiently bishomoantiaromatic.[6] In other terms, **1** is a pericyclic cation of the $(2^+,2^0)$ mode;[7] consequently, it is not surprising that **1** is thermally unstable relative to **2**, which can be regarded as a simple allyl cation. This factor, as well as relief of strain, may contribute to the driving force for the facile isomerization of **1** to **2**.

There are at least two plausible mechanisms for the rearrangement. One involves a methyl migration, as shown in Scheme II. Ion A is the intermediate required to rationalize

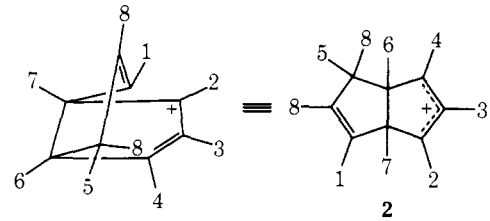
Scheme II (Methyl Migration)



A



B **C**



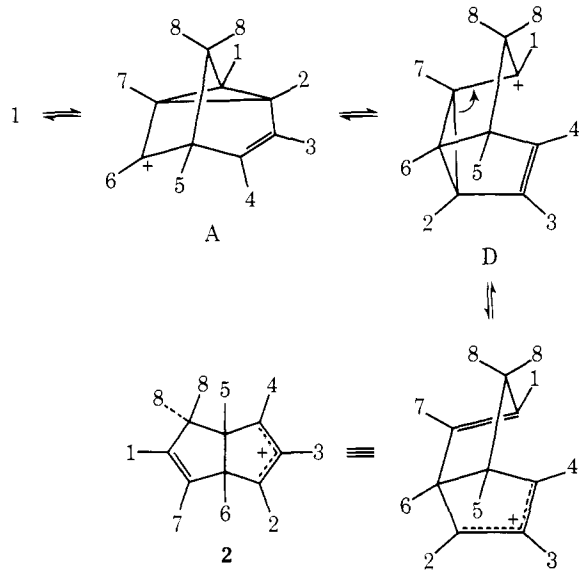
2

the observed circumambulation in **1**.[1] By a process which would require a higher activation energy than circumambulation, A could rearrange to B (a 1,2-vinyl shift, which presumably would proceed via a dicyclopropylcarbinyl cation). A 1,2-methyl shift would then give C which, by ring-opening, could give **2** with the methyls (from **1**) located as shown on the structure of **2** in Scheme II. This scheme was tested by deuterium labeling.

Rearrangement of **1** labeled with 3/7 deuterium in methyls 1-7[1] gave **2** in which the two NMR signals at δ 1.03 and 1.40 showed no reduction in area (i.e., represented 6 H) relative to the remaining methyl signals. Consequently, the *gem*-dimethyl group in **1** must have remained intact throughout the rearrangement, and Scheme II, or any other mechanism involving a 1,2-methyl shift, can be unequivocally discarded.[8]

A mechanism which does not involve a methyl shift is shown in Scheme III. A cyclopropylcarbinyl-cyclopropylcarbinyl type rearrangement could convert A to D. This might occur in one step, as shown (formally a 1,3-shift; break the C-1–C-2 bond and make the C-2–C-6 bond), or by two successive 1,2-shifts (break C-2–C-7 and make C-2–C-6 to form a cyclobutyl cation, then break C-1–C-2 and make C-2–C-7 to form D). We believe that Scheme III represents the correct mechanism for the conversion of **1** to **2** in FSO_3H. It is not absolutely necessary, however, that the classical ion D represent a minimum on the energy surface, though D is useful in helping to follow the rearrangement course. We will return later to a discussion of why Scheme

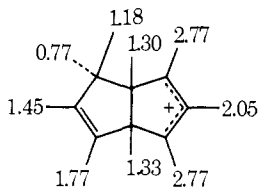
Scheme III



III represents an energetically more favorable path for converting **1** to **2** than does Scheme II.

To gain further insight into the rearrangement, and in particular to examine the possible reversibility of steps in these schemes, we studied the incorporation of deuterium into the methyl groups of ion **2** in deuterated trifluoroacetic acid (TFA).

Deuterium Incorporation in Ion 2. The ^{1}H NMR spectrum of **2** is slightly different in TFA from what it is in FSO_3H; the chemical shifts are shown on the structure. The entire spectrum is shifted upfield, the shift ranging from 0.11 ppm for the methyls at the terminus of the allyl cation to about 0.24 ppm for the *gem*-dimethyls.

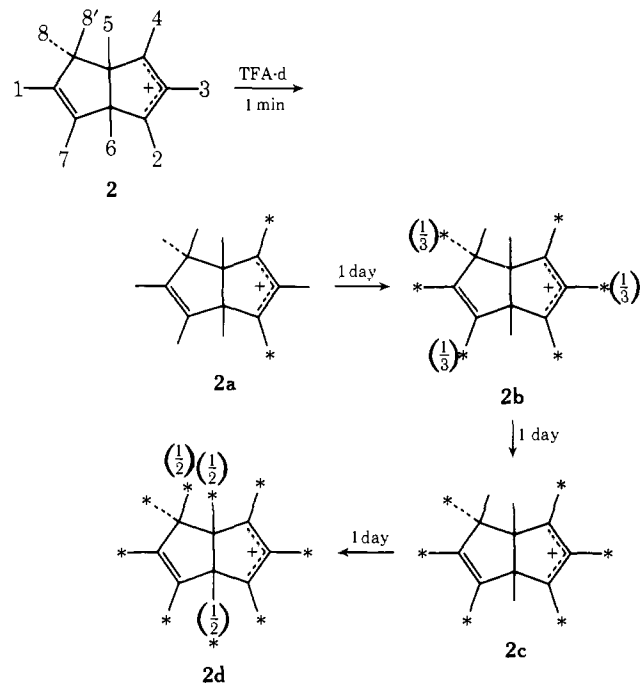


2 (in TFA)

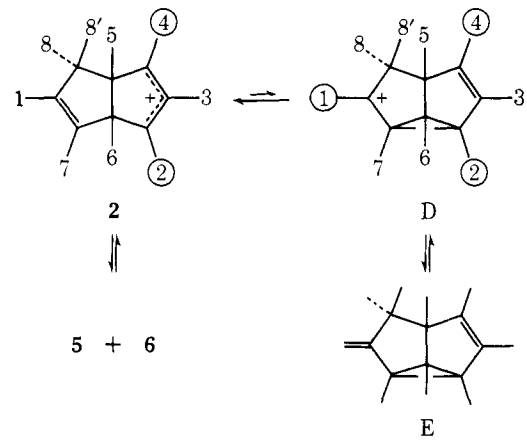
A mixture of **5** and **6** was dissolved in excess TFA-*d* at room temperature. Its ^{1}H NMR spectrum, taken about 1 min after mixing, was identical with that shown for **2** except that the signal at δ 2.77 was totally absent. After 1 day at room temperature, the peaks at δ 2.77 and 1.45 were absent, and those at δ 0.77, 1.77, and 2.05 were reduced in area by about one-third relative to the remaining peaks. One additional day gave a spectrum with only three peaks, at δ 1.18, 1.30, and 1.33. After a third day, even these peaks were reduced in area by about 50%; this was verified by quenching the solution and dissolving the resulting labeled **5** and **6** in ordinary TFA. This procedure immediately regenerated the peak at δ 2.77 to full intensity and permitted this peak to serve as an internal reference for integrating the peaks at δ 1.18, 1.30, and 1.33.

The exchange results are summarized in Scheme IV, with the numbering in Scheme III retained except for the distinction between methyls 8 and 8′. Three features of these experiments are apparent: (a) ion **2** is stable for long time periods in TFA at room temperature, but unlike FSO_3H, the medium must be sufficiently basic to permit equilibration of carbocations with their corresponding alkenes; (b) the methyls exchange deuterium at different rates, but some are grouped together with approximately equal exchange rates; and (c) eventually *all* methyl protons, even

Scheme IV



Scheme V



those of the *gem*-dimethyl group, exchange with the solvent. It is clear that although the conversion of **1** to **2** in FSO_3H does not involve methyl shifts, the incorporation of deuterium into every methyl group of **2** in TFA-*d* requires such shifts.

The essentially instantaneous exchange of the C-2 and C-4 methyls shows that in TFA **2** is rapidly and reversibly in equilibrium with trienes **5** and **6**. The next methyl to exchange completely is at C-1. This can be rationalized by some reversibility from **2** to D and proton loss from the C-1 methyl. If D is a discrete intermediate, the equilibrium between **2** and D must be very largely on the side of **2** since deuterium incorporation at methyl **1** was slow at room temperature, and in FSO_3H, **2** is formed rapidly from **1** (via D) even at −50°. The first two steps of deuterium incorporation into **2** are therefore rationalized by Scheme V; the exchanged methyls are circled.

Alternatively, one could explain the results in terms of a single ion, **2**, from which proton removal at the C-2 and C-4 methyls (to give **5** and **6**) is fast, but from which proton removal at the C-1 methyl (to give E) is relatively slow. It is not possible, from our data, to distinguish between these two ways of viewing the deuterium exchange.

Next to exchange is a group of three methyls, those at

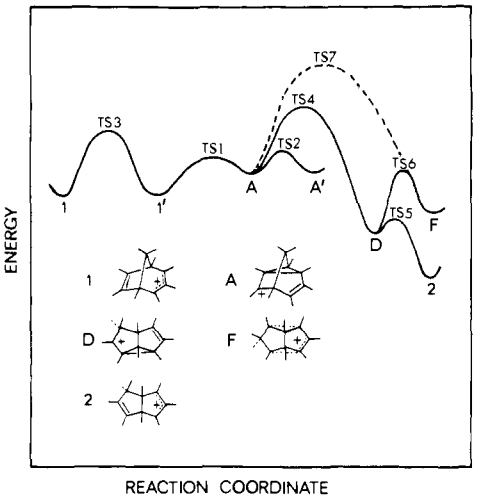


Figure 1. Energy diagram for the rearrangements of **1** and the deuterium exchange of **2**.

C-3, C-7, and C-8 [the C-3 and C-7 methyls are unequivocally assigned from their chemical shifts (δ 2.05 and 1.77, respectively); the other signal to exchange, at δ 0.77, must be assigned to one of the *gem*-dimethyls, and we believe by analogy with ions **3** and **4** that it is the "endo" methyl]. To effect this exchange, some rearrangement of ion **2** or D is necessary. We are forced to conclude that the next lowest energy path for ion D (or ion **2**) in TFA is not reversion to ion A (Scheme III), for if it were, the C-6 methyl (or all the methyls except 8 and 8′, because of circumambulation and 1,2-bridge shifts) would be next after the C-1 methyl to exchange.

A mechanism which allows the observed exchange involves a stereospecific 1,2-methyl shift to give ion F (Scheme VI); this ion has a symmetry plane, and equilibration with alkenes G and H would exchange protons at the C-3, C-7, and C-8 methyls.

Finally, we must account for the slowest exchange which is observed, i.e., at the C-5, C-6, and C-8′ methyls. Either of two mechanisms is in principle possible. A process might be devised which places a positive charge at those framework carbons, so that exchange via the corresponding alkenes becomes possible. Alternatively, a process which allows those methyls to become equivalent to others which have already undergone hydrogen–deuterium exchange would suffice. We believe that the latter process prevails, and that the final exchange is due to some equilibration of **2** with **1** over a long time period in TFA at room temperature. This would, through rapid circumambulation[9] and 1,2-bridge shifts, eventually result in complete hydrogen–deuterium exchange in **2**. The return from **2** to **1** (via D and A, Scheme III) must have a higher activation energy than the 1,2-methyl shift (D → F, Scheme VI), since exchange via the latter process is observed first.[17]

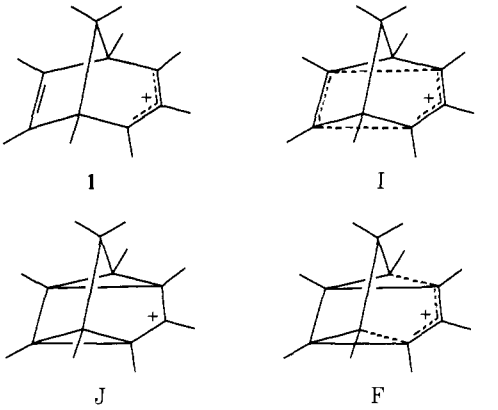
Mechanistic Summary. Figure 1 is an energy diagram which summarizes our mechanistic speculations regarding the degenerate rearrangements of **1** (circumambulation and 1,2-bridge shifts) and the rearrangement of **1** to **2** in FSO_3H at low temperatures (<−40°), as well as the mechanism for deuterium incorporation into **2** in TFA at room temperature. The diagram only shows the various carbocations and omits, for simplicity, the alkenes which must equilibrate with them to accomplish deuterium exchange. Ions A and D are represented as discrete intermediates, in order to better visualize each of the various processes. However, A and D can also be regarded as minor contributors to structures **1** and **2**, respectively, without altering in a major way the reaction mechanisms that are involved.

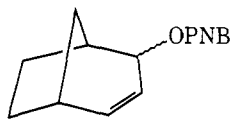
The lowest energy process ($\Delta H^{\ddagger}$ = 7.4 kcal/mol, the energy difference between **1** and TS2) is circumambulation illustrated in Scheme I and discussed previously[1] in detail. The next lowest energy process (with $\Delta H^{\ddagger}$ somewhere between 7.4 and 17.8 kcal/mol, the energy difference between **1** and TS3) is the 1,2-bridge shift[1] (Scheme I), which converts **1** directly to its mirror image **1′**. Both of these degenerate rearrangements of **1** are rapid below −50° in FSO_3H. At a somewhat higher temperature, in the same solvent, **1** is converted to **2**. The $\Delta H^{\ddagger}$ for this process, 17.8 kcal/mol, is the energy difference between **1** and TS4; this is the transition state for the 1,3-cyclopropylcarbinyl–cyclopropylcarbinyl shift (A → D) represented in Scheme III. In FSO_3H at −50° product **2** is formed without methyl migration. If D is a discrete intermediate, then the reaction proceeds from D exclusively (to the limits of NMR detection) via TS5 to **2**, and avoids TS6 which involves a 1,2-methyl shift. Under these reaction conditions (FSO_3H, <−40°), the conversion of **1** to **2** is essentially irreversible.

Deuterium exchange in **2** was carried out under quite different reaction conditions from those used to form **2** from **1**, i.e., TFA at room temperature. Initial exchange (C-2 and C-4 methyls) occurs from **2**, and the next fastest exchange (C-1 methyl) occurs from D (Scheme V). The next observed exchange (C-3, C-7, and C-8 methyls, Scheme VI) requires a methyl shift. The transition state for this process (TS6) must therefore have a lower energy then TS4, which must be achieved for return of **2** to **1**. The energy difference between TS4 and TS6 cannot be very large, however, since some exchange at C-5, C-6, and C-8′ begins before exchange at C-3, C-7, and C-8 is complete.

Finally, it is instructive to consider why methyl migration (Scheme II) does not occur during the rearrangement of **1** and **2** in FSO_3H. One will note, for example, that ion C in Scheme II is identical with ion D, and in fact that ion B is one of several possible resonance contributors to ion F. The question resolves to why approach to F is better from D (TS6, Figure 1) than it is from A (TS7, Figure 1). One possible answer is that the system tends to avoid intermediates with antiaromatic (more correctly, bishomo*anti*aromatic) structures.

Consider the exceptional propensity of **1** toward rearrangement. Symmetric interaction of the π electrons of the double bond with the allyl cation leads to a bishomo*anti*aromatic system, as expressed in structure I. One might expect such an interaction to exert a destabilizing effect on cation **1**. This effect has been seen in the strong rate-retarding effect of the additional double bond on the solvolysis rate of *p*-nitrobenzoates **9** and **10**, k_{rel} **9**/**10** being 235.[10] Analogous to **1**, the bicyclo[3.2.0]heptadienyl cation (**11**) is unstable and rearranges with great facility to the 7-norborna-





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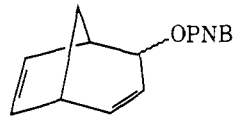

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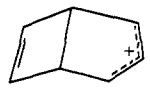
dienyl cation.[11] The accelerating effect of the *second* cyclopropane ring is small relative to that of the *first* cyclopropane ring in the solvolysis of quadricyclyl derivatives **12**.[12,13] Once again bishomoantiaromaticity, as expressed in structure K (analogous to I), is probably an important contributing factor to these effects.



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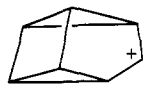

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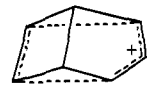


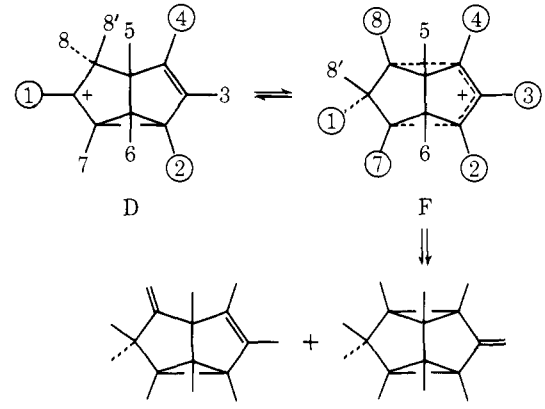
K

This concept of avoidance of bishomoantiaromatic structures is helpful in rationalizing the preferred and rejected paths in the rearrangements of **1** and **2**. The NMR spectrum of **1** at low temperatures shows that it has the allylic structure,[1] and that at best, A is only a very minor contributor to the structure. However, the rearrangements of **1** (except for the bridge shift) proceed via A, in which the double bond and allylic moieties of **1** interact asymmetrically. Circumambulation, which equilibrates A with its mirror image A′, is the process with the lowest activation energy. The options open to A aside from circumambulation are only two: cyclopropylcarbinyl rearrangement (Scheme III) to D via TS4 or a 1,2-vinyl shift (Scheme II) to give B (or F) via TS-7. We believe that the latter process is avoided because TS7 has bishomoantiaromatic character; that is, the transition state for the vinyl shift is similar to I (in classical terms, it would involve the dicyclopropylcarbinyl ion J, but approached along a reaction coordinate in which the charge is delocalized as shown in I, not F). Consequently, A rearranges to D, then **2**.

Geometric restrictions prevent a symmetric interaction between the double bond and the allyl moiety in **2**; it suffers no antiaromatic destabilization and, being also a cyclopentenyl (rather than cyclohexenyl) cation, is very much more stable than **1**.[14]

In the reverse process (**2** → **1**, observed via deuterium exchange), the first ion formed from **2** will be D, which then has only two pertinent[15] options for rearrangement: cyclopropylcarbinyl rearrangement directly back to A (and **1**), or a 1,2-methyl shift to give F. The experimental results show that the methyl shift was preferred. We believe that the approach to F is easier from D than from A because it does not involve an antiaromatic transition state.[16] This is easily seen by comparing the structures of D and F as they are drawn in Scheme VI. Consequently, one does observe the 1,2-methyl shift under the less acidic and higher temperature conditions used in the exchange studies. Our results are consistent with the notion that in the dicyclopropylcarbinyl cation J, charge delocalization into the cyclopropyl bonds which are not directly joined to one another (structure F) will be more important than charge delocalization into the cyclopropyl bonds which are directly joined to one another (structure I) as a consequence of bishomoantiaromatic destabilization in the latter instance. We hope to be able to test this suggestion by more direct experimentation.

Scheme VI



Experimental Section

NMR spectra of neutral compounds were obtained on a Varian Associates T-60 spectrometer, usually in CCl_4 using tetramethylsilane (Me_4Si) as an internal reference. Carbocation spectra were obtained on a Varian Associates A56-60 or HA-100 spectrometer equipped with a variable-temperature probe; the solvent was FSO_3H-SO_2ClF (ca. 1:5) or CF_3CO_2H(D), with either $(CH_3)_4NBF_4$ (δ 3.13) or CH_2Cl_2 (δ 5.30) as internal standards. The temperature control was calibrated with a methanol standard and is accurate to ±0.5°.

Ir spectra were measured on a Unicam SP-200 spectrometer and were calibrated against polystyrene. Uv spectra were measured in 95% ethanol using a Unicam SP-800 spectrometer. Mass spectra were obtained at 70 eV on a Hitachi Perkin-Elmer RMU-6 spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich., and by Clark Microanalytical Laboratories, Urbana, Ill. Melting points are uncorrected.

Rearrangement of 1 to 2. A solution of **1** in 250 μl of FSO_3H-SO_2ClF (1:4) was prepared at −78° from 30 mg of 1,2,3,4,5,6,7,7,8-nonamethyltetracyclo[3.3.0.$0^{2,8}$.$0^{3,6}$]octan-4-ol, as described previously.[1] The solution was warmed to −52° and the changes in the ^1H NMR spectrum were monitored with time. Peaks at δ 1.27 (6 H), 1.52 (6 H), and 2.20 (15 H) were gradually replaced by peaks at δ 2.88 (6 H), 2.20 (3 H), 1.90 (3 H), 1.63 (3 H), 1.50 (6 H), 1.40 (3 H), and 1.03 (3 H), all assigned (see text) to ion **2**. The reaction rate was followed both by disappearance of certain peaks (e.g., δ 1.27) in the ^1H NMR spectrum of **1** and the appearance of certain peaks (e.g., δ 2.88) in the ^1H NMR spectrum of **2**. The first-order rate constants (sec^{-1}) given are the average of at least four runs at each temperature: $k \times 10^4$ (°C) = 25 ± 1 (−36), 11 ± 1 (−41.5), 5.8 ± 0.3 (−45), 4.7 ± 0.3 (−46), 3.6 ± 0.1 (−47.5), 1.9 ± 0.2 (−52), 1.3 ± 0.1 (−53), 0.91 ± 0.04 (−55); Eyring parameters at −45°, $\Delta F^{\ddagger}$ = 16.6 kcal/mol, $\Delta S^{\ddagger}$ = +3.5 eu/mol, $\Delta H^{\ddagger}$ = 17.4 kcal/mol.

1,2,3,5,6,7,8,8-Octamethyl-4-methylenebicyclo[3.3.0]octa-2,6-diene (5) and 1,3,4,5,6,7,8,8-octamethyl-2-methylenebicyclo[3.3.0]octa-3,6-diene (6). On a preparative scale, the preparation of **5** and **6** was carried out as follows. To approximately 5 ml of TFA was added, with stirring at room temperature, 500 mg of 1,2,3,4,5,6,7,7,8-nonamethyltetracyclo[3.3.0.$0^{2,8}$.$0^{3,6}$]octan-4-ol.[1] The resulting solution was dropped into an ice slurry of aqueous sodium hydroxide, which was then extracted with methylene chloride. The extract was washed with water and dried (Na_2SO_4), and the solvent was removed under reduced pressure to leave 430 mg of a pale yellow oil shown by vpc to be a 3:2 mixture of **5**:**6**. The mixture was separated by preparation VPC (10 ft × ¼ in. column, 20% FFAP on Chromosorb W, 160°, 100 ml/min He). A similar mixture of **5** and **6** was obtained when FSO_3H-SO_2ClF solutions of **2** (vide supra) were quenched in base; when such solutions were quenched in ice water, then neutralized, the ratio of **5**:**6** was 2:1. Partial interconversion of **5** and **6** occurs thermally (1,5-H shift) under the VPC conditions used to isolate them.

The first VPC peak (ret time 9 min) was due to **6**: ir (CCl_4) 1625 (m), 870 (s) cm^{-1}; uv (ethanol) 247 nm (ϵ 14200); mass spectrum (70 eV) *m/e* (rel intensity) 230 (31), 216 (18), 215 (100), 200 (28), 187 (11), 186 (9), 185 (19), 173 (42), 159 (18), 119 (11); ^1H NMR (CCl_4), see structure; all peaks were singlets except those at δ 1.46, 1.58, 1.62, and 1.70, which were homoallylically coupled quartets, $J \simeq 1$ Hz; the peaks at δ 1.58 and 1.62 were partially superimposed.

Anal. Calcd for $C_{17}H_{26}$: C, 88.62; H, 11.38. Found: C, 88.68; H, 11.27.

The second VPC peak (ret time 10 min) was due to the major product **5**; ir (CCl_4) 1620 (m), 870 (s) cm^{-1}; uv (ethanol) 244 nm (ϵ 17100); mass spectrum, identical with that of **6**; ^1H NMR (CCl_4), see structure; all peaks were singlets except at δ 1.45, 1.55, 1.63, and 1.73, which were homoallylically coupled quartets, $J \simeq 1$ Hz.

Anal. Calcd for $C_{17}H_{26}$: C, 88.62; H, 11.38. Found: C, 88.68; H, 11.27.

Solutions of either **5** or **6** or mixtures thereof in FSO_3H-SO_2ClF or TFA at room temperature gave ^1H NMR spectra indistinguishable from those of **2** prepared from **1** in the same solvents.

Rearrangement of Labeled 1. A solution of **1** containing 3/7 CD_3 (4/7 CH_3) at methyls 1, 2, 3, 4, 5, 6, and 7, but CH_3 at methyls 8 and 8′ (prepared as described in ref 1), in FSO_3H-SO_2ClF (1:4) was maintained at −45° until rearrangement to **2** was complete. The ^1H NMR spectrum was identical with that of unlabeled **2** (see structure) except that the peak areas were as follows: δ 2.88 (3.4 H), 2.20 (1.7 H), 1.90 (1.7 H), 1.63 (1.7 H), 1.50 (3.4 H), 1.40 (3 H), 1.03 (3 H).

Deuterium Incorporation in 2. A mixture of **5** and **6** (40 mg) was placed in an NMR tube and 0.4 ml TFA-*d* was added at room temperature. The ^1H NMR spectrum, taken within 1 min, was identical with that shown on the structure of **2** (see text) except that the lowest field peak, δ 2.77, was absent. After 1 day at room temperature, the peaks at δ 2.77 and 1.45 were absent, and those at δ 0.77, 1.77, and 2.05 were reduced to only 50% of the area of the remaining peaks. After one more day, the spectrum consisted of only three peaks, approximately equal in area, at δ 1.18, 1.30, and 1.33. After a third day, the remaining peaks were reduced in area by about 50%; that is, the solution was quenched in ice and extracted with methylene chloride, and the resulting mixture of labeled **5** and **6** was dissolved in TFA at room temperature. The ^1H NMR spectrum of this solution, obtained within a few minutes, had peaks at δ 2.77 (6 H) and at δ 1.18, 1.30, and 1.33 (1.5 H each).

Irradiation of 5. A solution containing 100 mg of **5** in 8 ml of ether was degassed and irradiated in a quartz test tube through a Vycor filter (Hanovia 450-W lamp). The reaction was monitored by VPC (5 ft × 0.125 in. column, 15% Carbowax 20M on Chromosorb W, 110°, 30 ml/min N_2). The peak due to **5** (ret time 16 min) gradually decreased in area as a new peak appeared (ret time 2.5 min). After 24 hr of irradiation, the solvent was removed in vacuo to leave a pale yellow oil which consisted (^1H NMR) of 80% product (**7**) and 20% starting material (**5**). Purification of 7 was accomplished by VPC (5 ft × 0.25 in. column, 20% FFAP on Chromosorb W, 110°, 100 ml/min He), although some **7** reverted to **5** during this process. The retention time of **7** was 9 min; it was collected as colorless crystals (sublimes); ir (CCl_4) 1678 (m), 875 (m) cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 230 (11), 216 (19), 215 (100), 200 (44), 185 (38), 173 (77); ^1H NMR (CCl_4) δ 0.63 (3 H, s), 0.83 (3 H, s), 0.89 (6 H, s), 0.91 (6 H, s), 0.97 (3 H, s), 1.07 (3 H, s), 4.15 (1 H, s), 4.22 (1 H, s).

Anal. Calcd for $C_{17}H_{26}$: C, 88.62; H, 11.38. Found: C, 88.54; H, 11.20.

A solution of **7** (20 mg) in FSO_3H-SO_2ClF (1:4, 0.4 ml) at −78° gave a ^1H NMR spectrum identical with that of authentic **2**.

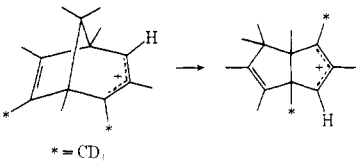
Irradiation of 6. A solution containing 50 mg of **6** in 8 ml of ether in a quartz test tube was degassed and irradiated through a Vycor filter (Hanovia 450-W medium-pressure lamp). The reaction was monitored by VPC (5 ft × 0.125 in. column, 15% Carbowax 20M on Chromosorb W, 110°, 30 ml/min N_2); the peak due to starting material (ret time 12.5 min) was gradually replaced by the product peak (ret time 3 min). After 24 hr, the ether was removed in vacuo to leave pale yellow crystals which NMR showed to be mainly one product. Purification by VPC (5 ft × 0.25 in. column, 20% FFAP on Chromosorb W, 110°, 100 ml/min He) gave pure **8** (mp 213–214°, sublimes), ret time 10 min; ir (CCl_4) 1670 (s), 890 (s) cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 230 (15), 216 (20), 215 (100), 200 (26), 185 (23), 173 (48), 161 (13), 159 (19); ^1H NMR (CCl_4) δ 0.33 (3 H, s), 0.65 (3 H, s), 0.82 (6 H, s), 0.92 (3 H, s), 0.93 (3 H, s), 0.97 (3 H, s), 0.98 (3 H, s), 4.12 (2 H, s).

Anal. Calcd for $C_{17}H_{26}$: C, 88.62; H, 11.38. Found: C, 88.70; H, 11.33. Solutions of **8** in FSO_3H-SO_2ClF gave quantitative yields of ion **1**.[1]

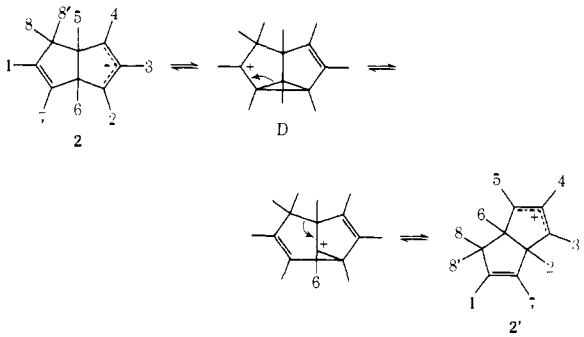
Acknowledgment. Support of this research by the National Science Foundation is gratefully acknowledged.

References and Notes

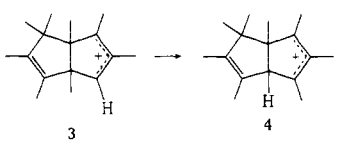
(1) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **97**, 2459 (1975).
(2) For a preliminary account, see M. Kuzuya and H. Hart, *Tetrahedron Lett.*, 3891 (1973).
(3) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **96**, 6436 (1974).
(4) The accidental degeneracy of the bridgehead methyls in **2** was resolved when the ion was prepared in trifluoroacetic acid; see Experimental Section.
(5) For a preliminary account of these irradiations, see H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **96**, 3709 (1974).
(6) R. D. Breslow, *Angew. Chem., Int. Ed. Engl.*, 7, 565 (1968).
(7) M. J. Goldstein and R. Hoffmann, *J. Am. Chem. Soc.*, **93**, 6193 (1971).
(8) The generality of this conclusion has been reinforced by the observation that



H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, following paper in this issue.
(9) In the accompanying paper we show that in a closely related ion circumambulation can occur rapidly at room temperature in a weakly acidic aqueous acetone medium.
(10) A. F. Diaz, M. Sakai, and S. Winstein, *J. Am. Chem. Soc.*, **92**, 7477 (1970).
(11) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6350 (1967).
(12) H. G. Richey, Jr., and N. C. Buckley, *J. Am. Chem. Soc.*, **85**, 3057 (1963); for a review, see P. R. Story and B. C. Clark, Jr., in "Carbonium Ions", Vol. 3, G. A. Olah and P. V. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., (1972), p 1007.
(13) L. M. Loew and C. F. Wilcox, *J. Am. Chem. Soc.*, **97**, 2296 (1975).
(14) For a review of allyl cations, see N. C. Deno in "Carbonium Ions", Vol. 2, Wiley-Interscience, New York, N.Y., 1970, p 783.
(15) A circumambulatory process, in which the three-carbon bridge moves around the five-membered ring is also possible:



This process did not occur, for if it had, methyls 3, 5 (and possibly 6) would have been next to exchange deuterium, after methyl 1 (whereas in fact methyls 3, 7, and 8 were next to exchange). However, this process (one step, at least) has been observed[3] in the case of the less stable ion **3**. However, the process is complex since **3** gave another product in addition to **4**[9]; also **4** lost a proton in preference to further circumambulation.



(16) For an analogous discussion of the idea that the energy barrier to the formation of an ion depends on the direction of approach, see M. Geisel, C. A. Grob, W. Santi, and W. Tschudi, *Tetrahedron Lett.*, 4311 (1972).
(17) It is always possible that we have overlooked an alternative mechanism for explaining our exchange results. Although none has been found by us or the referees, Dr. Clair J. Collins (a referee of this paper) has suggested that a computer-assisted approach outlined by him and his coworkers [*J. Am. Chem. Soc.*, **95**, 4766 (1973); **96**, 2514, 2524 (1974)] might disclose alternate pathways, if any, and we agree.