Circumambulation, Bridge Shifts, and Cyclopropylcarbinyl Rearrangements in Bicyclo[3.2.1]octadienyl Carbocations

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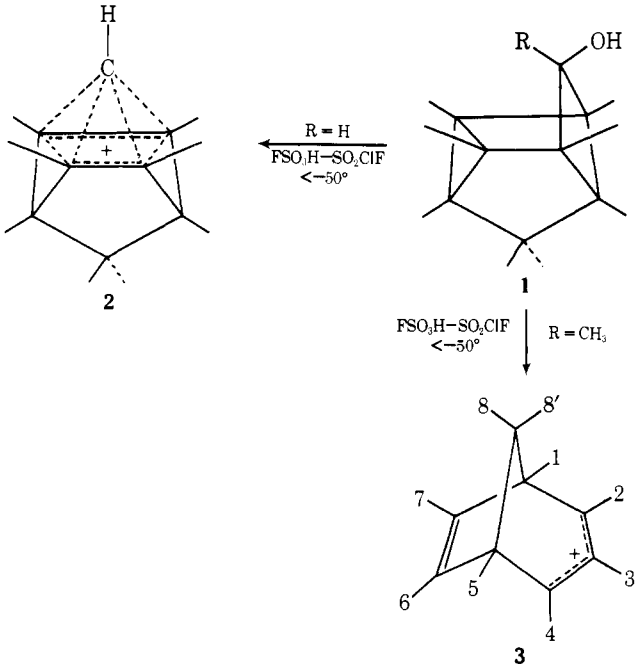
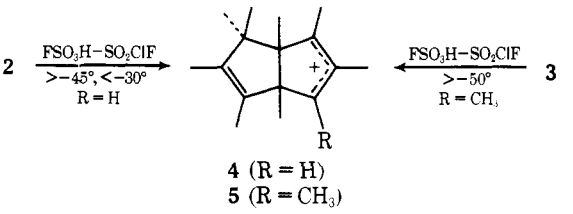
Abstract: Ionization of the secondary alcohols **6x** and/or **6n** in FSO_3H-SO_2ClF below −50° gave the allylic ion **8** in which the proton originally at C-2 (and the carbon to which it was attached) had rearranged to position 3. The mechanism (Scheme IV) was shown by labeling experiments to involve a circumambulatory carbon skeleton rearrangement; an alternative 1,2-bridge shift mechanism is unequivocally excluded. Thus similar treatment of **6**-d_6 (CD_3 groups at C-4 and C-6, separated by a bridgehead carbon) with acid gave **8**-d_6 (CD_3 groups adjacent, at C-6 and C-7). Treatment of **6x** with a trace of acid in aqueous acetone gave tricyclic hydrocarbon **10; 6n** was recovered unchanged from similar treatment. Therefore **6x** ionizes with participation of the remote, not the allylic double bond. Slightly stronger acid converts both epimers of **6** to the seemingly unrearranged bicyclic triene **11.** However, labeling results disclose the even under these mild conditions circumambulatory rearrangements occur (Scheme II), rapidly interconverting ion D with its enantiomer D′. Thus dehydration of either **6**-d_3 (C-4 CD_3) or **6**-d_3' (C-6 CD_3) gave **11** with label scrambled between the exocyclic methylene protons and the methyl at C-7. At or above −50° in FSO_3H-SO_2ClF cation **8** rearranges to ion **12,** in which the proton-bearing carbon is in a bridgehead position, and to the bicyclo[3.3.0]octadienyl cation **4**. The mechanism (Scheme V) involves first a reversal of the circumambulatory scheme by which **8** was formed, to give ion **E** which then either undergoes a 1,2-bridge shift to give **12** or a 1,3-cyclopropylcarbinyl shift to give **4**. This mechanism is also supported by the unique labeling pattern of **4**-d_6 derived from **8**-d_6. Ion **12** was also prepared more directly. Rearrangement of the secondary bicyclo[2.2.2]octadienol **17** in acidic aqueous acetone gave the methylene bicyclo[3.2.1]octadienes **14** and **15** which, in FSO_3H-SO_2ClF at <−50°, gave **12.** The NMR spectrum of **12** (Figure 1) showed remarkable changes over the temperature range −88 to −33°, which show that a circumambulatory type of process occurs (Scheme VI) with a marked preference for bridging remote from the bridgehead proton (tertiary bridging). At lowest temperatures, an oscillatory motion occurs, but as the temperature is raised circumambulation through alternate tertiary and secondary bridging becomes possible. Finally, FSO_3H-SO_2ClF solutions of **12** held at >−45° slowly rearrange to ion **4** (Scheme V). Our results show that the processes of circumambulation, 1,2-bridge shifts, and 1,3-cyclopropylcarbinyl shifts in bicyclo[3.2.1]octadienyl cations (Scheme VII) require increasingly higher activation energies, in that sequence. We suggest that antiaromaticity is a factor in the remarkable reactivity of these ions. Finally, it is certain that bicyclo[3.2.1]octadienyl ions are not intermediates in the rearrangement of the pyramidal cation **2** to cation **4**.

Ionization of the tetracyclic alcohols **1** proceeds differently depending on whether R = H or CH_3. When R = H, the first formed ion is the pyramidal cation **2**; the favorably located cyclopropane bond participates in the ionization.[1,2] When R = CH_3, analogous participation does not occur. Instead, the cyclobutane ring contracts, leading to cation **3**.[3] Possible reasons for these differences have been discussed.[3] Cation **2** is stable below −50°; its NMR spectrum was unchanged from −50 to −120° and gave no evidence of any dynamic processes occurring in that temperature range. In contrast, cation **3** was shown to be undergoing two different types of rapid dynamic degenerate rearrangements. The faster of these, circumambulation, equilibrates methyls 2, 3, 4, 6, and 7 and methyls 8 and 8′, but leaves methyls 1 and 5 unique. The slower process (but still fast at −50°) is a 1,2-bridge shift which equilibrates methyls 1-7 and methyls 8 and 8′.[3]



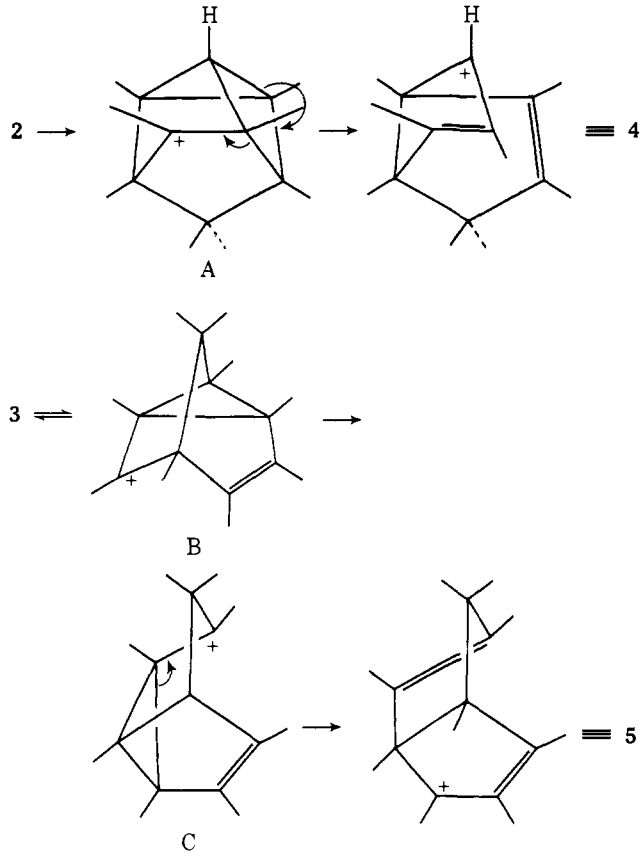
Above −50°, ions **2** and **3** rearrange to the allylic ions **4** and **5**. We have proposed two different mechanisms for



4 (R = H)
5 (R = CH_3)

these isomerizations. With **2**, the rearrangement involves collapse of the classical ion A readily derived from **2**. With **3**, the preferred path involves the cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement of B to C which can then collapse to **5**.[5,6] These reaction paths were delineated in part by deuterium labeling.

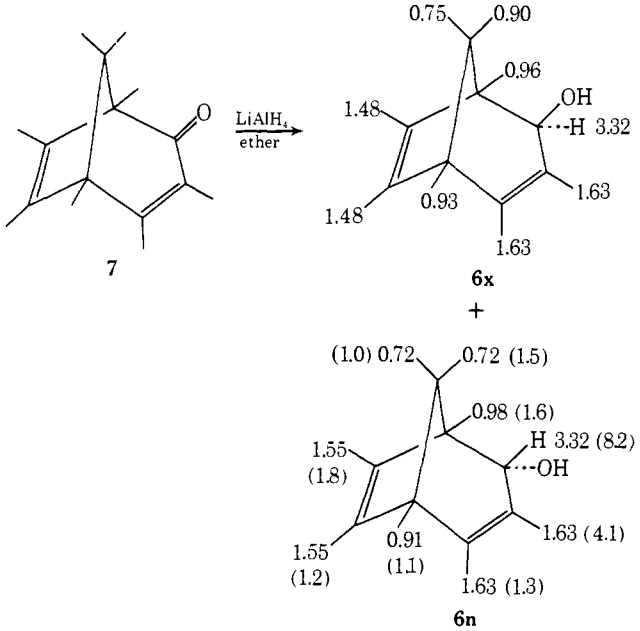
The formation of similar products (**4** and **5**) from **2** and **3** led us to consider the possibility that ions of the type **3**, with one methyl group replaced by H, might be undetected intermediates in the isomerization of **2** to **4**. Accordingly, we synthesized several such possible intermediates by direct routes and studied their rearrangements in strong acids. These studies, reported here, confirm the previously pro-



posed[1] direct mechanism for the rearrangement of **2** to **4**. But more important, they considerably enhance our understanding of degenerate rearrangements of the type observed with ion **3**. Our starting point was the synthesis and ionization of alcohols **6x** and **6n.**

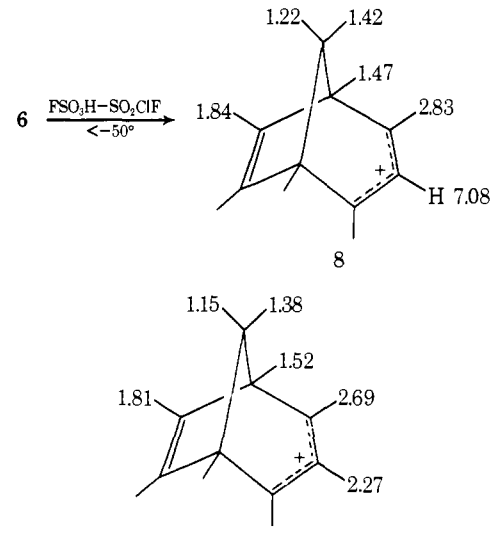
Results and Discussion

Synthesis and Ionization of 6. Reduction of **7**[1] with lithium aluminum hydride gave a 45:55 mixture of the epimeric alcohols **6x** and **6n.** It was not possible to isolate **6x** pure

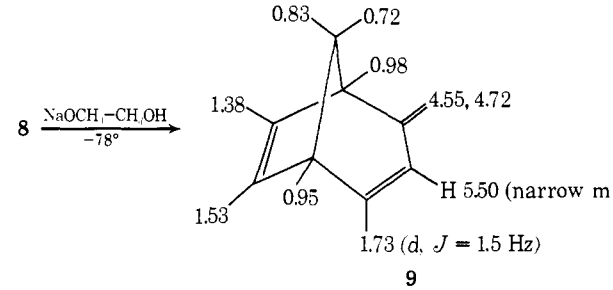


owing to its facile dehydration (vide infra), but **6n** was obtained crystalline (mp 59–60°) by purification of the epimeric mixture. Configurations are assigned on the vast difference in ease of ionization, and on the difference in chemical shifts of the *gem*-dimethyls on the one-carbon bridge.[7]

Ionization of the epimeric mixture of **6** in FSO_3H–SO_2ClF (1:4) at low temperatures gave a simple NMR spectrum which can be attributed to a single carbocation. At −60° the spectrum consisted of six singlets with areas and chemical shifts consistent with structure **8**. The spectrum of **3** (at −90°) is shown for comparison.[8] The symmetry of the spectrum and the chemical shifts eliminate any other position for the single hydrogen.[9]



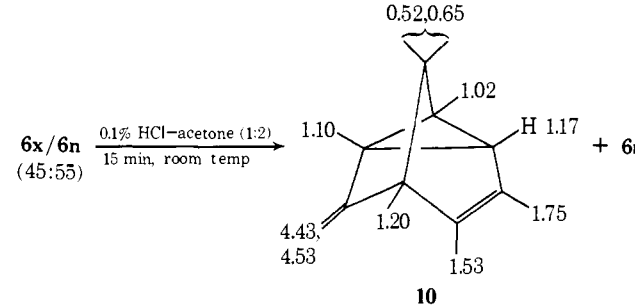
The structure of **8** was confirmed by quenching (excess $NaOCH_3$ in methanol, −78°), which afforded the hydrocarbon **9** in nearly quantitative yield. The structure of **9** follows from its spectral properties, including decoupling of the ^1H NMR spectrum, and from its photoisomerization.[9]



We will return later (vide infra) to the question of the rearrangement of **8** to **4** and consider first the mechanism by which **8** is formed from **6.**

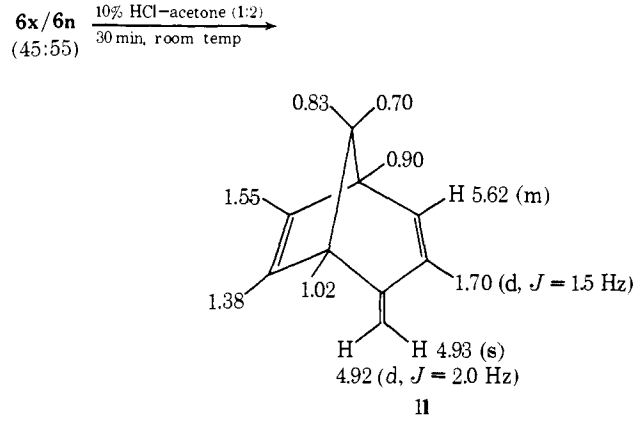
Mechanism of the Ionization of 6. It is obvious from their structures, that the ionization of **6** to **8** in FSO_3H is accompanied by rearrangement. To elucidate the rearrangement mechanism, we allowed the protonation of **6** to occur under less acidic and more nucleophilic conditions.

Under very mild conditions, **6x** was converted to **10**,[10] whereas **6n** was recovered unchanged. The yield of **10** from



6x was essentially quantitative, and separate exposure of pure **6n** to these conditions gave 100% recovery of starting material, although with longer reaction times some **10** was formed from **6n.**

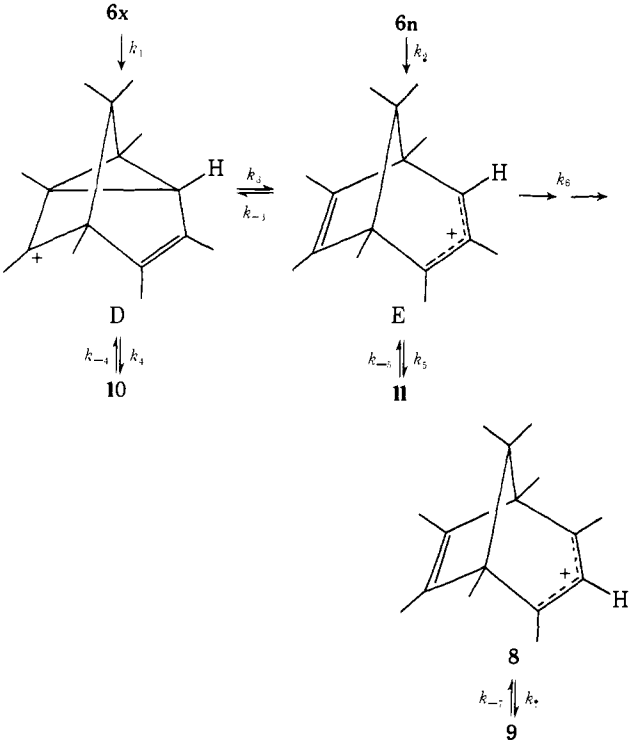
An increase in the acid strength converted both **6x** and **6n** almost quantitatively to **11.**[11] Separate exposure of **10** to



identical reaction conditions also gave a quantitative yield of **11.**[12] Prolonged treatment of **6** under these conditions (36 hr) gave a mixture of **11** (78%) and **9** (22%).

It is evident from these results that carbocation precursors of **10, 11,** and **9** are formed in that sequence when **6** is protonated. One possible scheme which rationalizes these results is shown (Scheme I). Clearly $k_1 > k_2$ because the

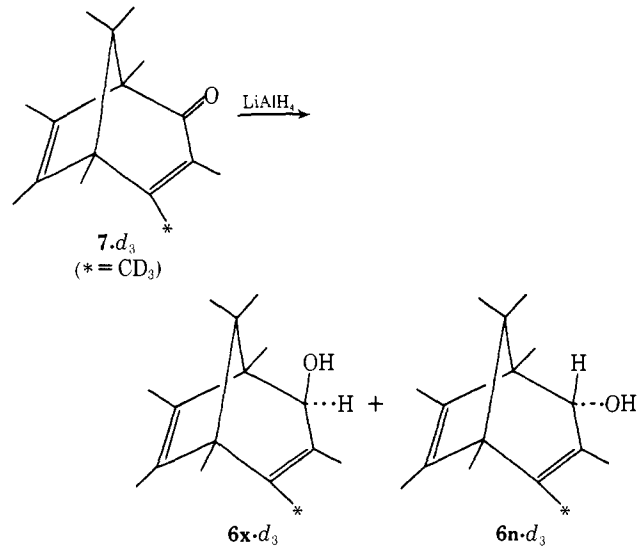
Scheme I



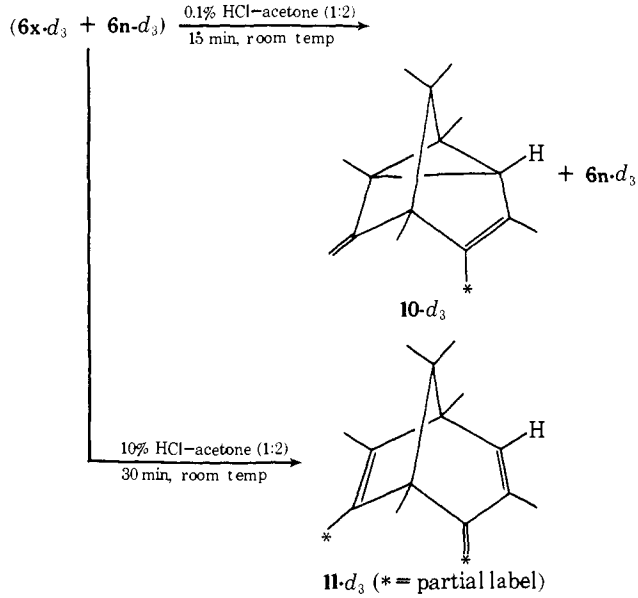
double bond is suitably disposed to participate in the ionization of the exo alcohol, leading directly to ion D. Such participation is not possible with the endo alcohol, which presumably first gives ion E. However, D and E must be in equilibrium, because some **10** is formed from **6n;** for example, exposure of a 45:55 mixture of **6x:6n** to 2% HCl in acetone (1:2) for 30 min at room temperature gave 75% of **10** and 25% of **11.**[12] We believe that D and E represent equilibrating ions, and not resonance contributors to a single species. Symmetric delocalization of the charge in E from the allylic moiety to the double bond should be energetically disfavored because it leads to a bishomo*anti*-aromatic species.[13,14] Less than symmetric delocalization is more plausible, but it will be shown in the next part of this paper that D undergoes further rearrangements, and that D and E are best treated as distinct species. If the equilibration of D and E is rapid compared with proton loss, then our results suggest that **10** is a product of kinetic control, whereas **11** is the thermodynamically more stable product of proton loss. Finally, the rearrangement of E to **8** is a multistep process whose mechanism will be considered in greater detail below. But first we must describe some labeling results which show that even the left-hand portion of Scheme I is oversimplified.

Label Scrambling and the Mechanism for the Formation of 11 from 6. One can easily imagine several different mechanisms for the rearrangement of E to **8.** For example, two 1,2-shifts of the one-carbon bridge would suffice. But our prior experience[3] that such rearrangements in **3** are slow relative to circumambulatory type rearrangements suggested that some deuterium labeling experiments might be enlightening.

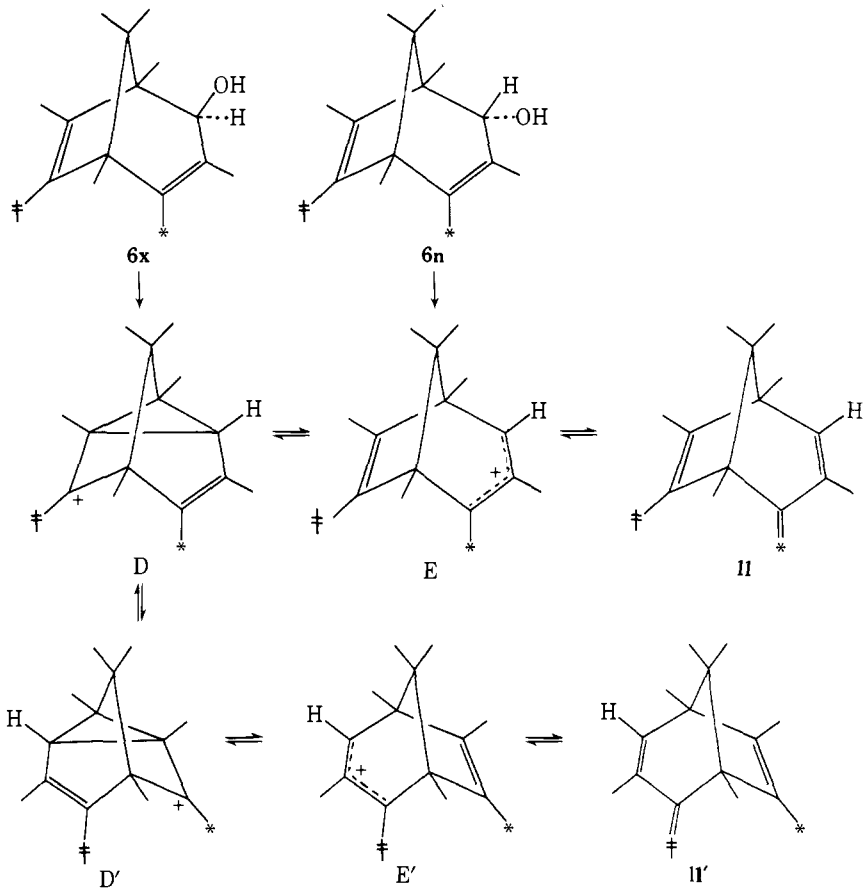
Reduction of **7**-d_3[1] gave a mixture of the correspondingly labeled **6x** and **6n.**[15] Very mild treatment of the mixture



with acid gave labeled **10** and recovered **6n**-d_3 as expected.[16] More vigorous conditions converted the alcohols to la-

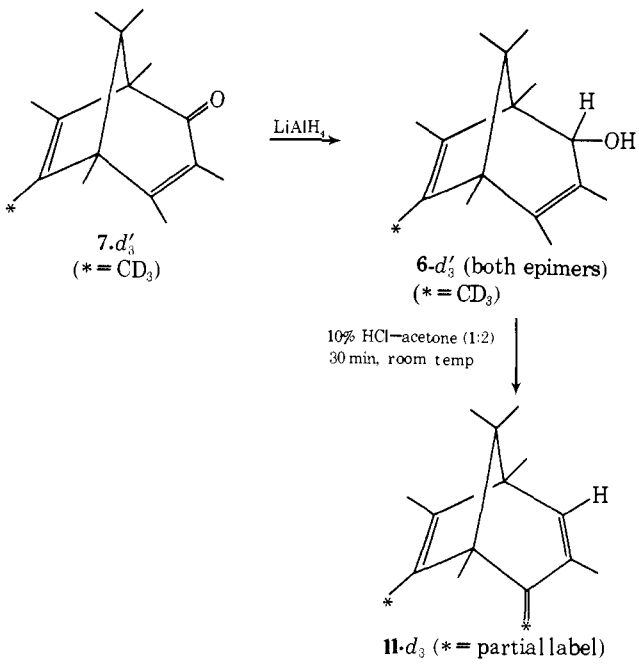


Scheme II

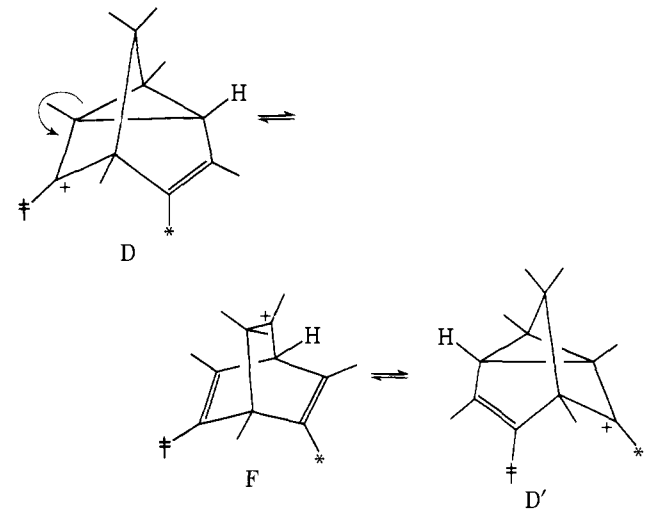


beled **11**. *Contrary to expectation from Scheme I, 50% of the label appeared in one of the allylic methyl groups* (see structure); if no additional rearrangements were involved, all of the label should have appeared in the methylene group.[17]

Label scrambling in the formation of **11** from **6** was confirmed by starting with the label in the other position. Reduction of **7**-d'_3 with lithium aluminum hydride gave a mixture of the correspondingly labeled epimeric alcohols which, on exposure to the appropriate acidic conditions, gave **11** with scrambled label, as shown.[17]



Scheme III

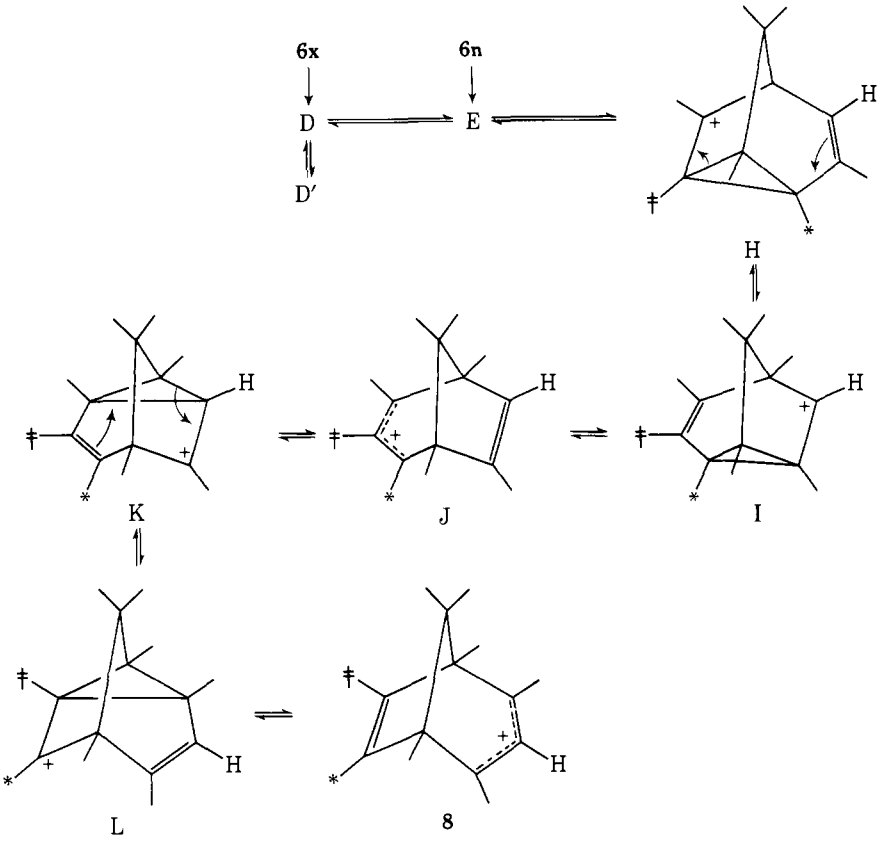


Equilibration of the two allylic methyl groups (at C-4 and C-6) in **6** during its dehydration to **11** suggests that either a symmetric intermediate or enantiomeric intermediates are involved. Scheme II represents the minimal expansion of Scheme I which is necessary to rationalize the scrambling of label in **11**.

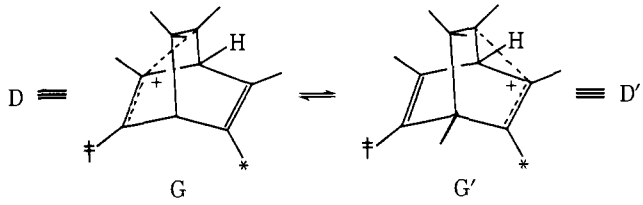
Ionization of **6x** or **6n** leads directly to D or E, respectively, and these ions equilibrate rapidly if the medium is sufficiently acidic.[18] Also fast, under these conditions, must be the equilibration of D with its enantiomer[19] D′. This is the step which is essential to account for the label scrambling. By symmetry, D′ and E′ must equilibrate rapidly, resulting in a 50:50 mixture of **11** and **11′**.

The interconversion of D and D′ involves the same type of mechanism which was required to account for "cir-

Scheme IV



cumambulation" in cation **3**.[3] Possible steps, using classical ion structures, are shown in Scheme III. The reaction proceeds via the symmetric [/2/2] cation F. Alternatively, D and D′ may be represented by the corresponding delocalized structures G and G′, in which case F might be regarded



as representing the transition state for their interconversion. It is known from our work[3] on ion **3** that such processes are rapid ($\Delta H^{\ddagger}$ = 7.4 kcal/mol, $k^{-80°}$ = 31 sec^{-1}) in FSO_3H; the present work shows that this type of rearrangement can be rapid even in acidic aqueous acetone.

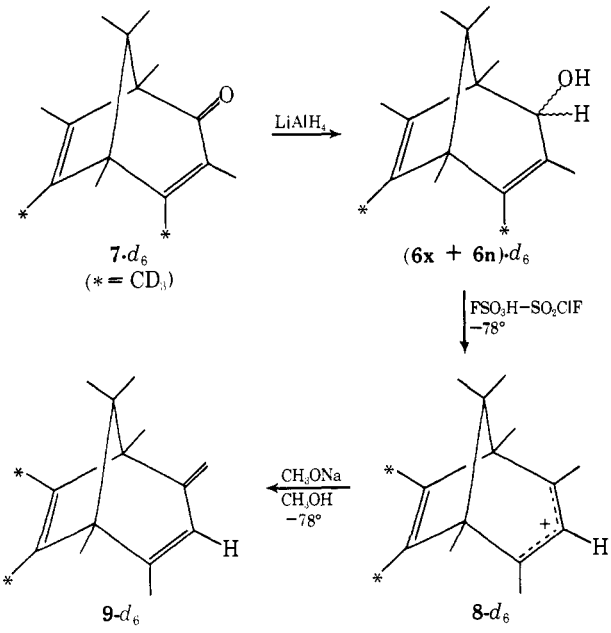
Mechanism for the Formation of Ion 8 from 6. An extention of Scheme II provides a mechanism for the formation of carbocation **8** (and hydrocarbon **9**) as the observed ionization product of alcohols **6** in FSO_3H-SO_2ClF. It involves circumambulatory-type rearrangements analogous to the equilibration of D with D′ and is shown in Scheme IV. Allylic ion E can close to form a cyclopropylcarbinyl cation in two ways, either at the "back" to form D (as shown in Scheme II) or at the "front" to form H (Scheme IV). Whereas the cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement of D only results in its enantiomer D′, similar rearrangement of H gives a new ion I. Since I can open to J, in which both termini of the allylic ion are tertiary (whereas in E one of the termini is secondary), the rearrangement of E to J can be regarded as energetically favorable. Ion J can either reclose to I, or close at the "back" to give K; this ion can rearrange to L which opens to the observed symmetric ion **8**.

Several features of Scheme IV deserve scrutiny. The scheme involves the successive rearrangement of three closely related allylic ions, E → J → **8**. It is easy to see why J and **8** are more stable than E (tertiary vs. secondary), but it is less obvious why **8** is more stable than J. Several factors may be involved. In J three methyls on the allylic moiety are eclipsed, whereas in **8** this strain is relieved by having a hydrogen in the middle. Also, the double bond in J is trisubstituted, whereas in **8** it is tetrasubstituted. At any rate, once conditions were sufficiently acidic to permit the rearrangement of E, it went all the way to **8**, and we could not intercept any of the intermediates.

Scheme IV also involves three very similar circumambulatory-type rearrangements (D ⇌ D′, H ⇌ I, K ⇌ L). We know from label scrambling (vide supra) that the first of these is rapidly reversible. The others have been written as reversible, and evidence for this reversibility will be presented below. Finally, each line in Scheme IV represents an allylic ion and the cyclopropylcarbinyl ions with which they might equilibrate. In the first line (D, E, H), the allylic ion is secondary at one terminus; in the second line (I, J, K), one of the cyclopropylcarbinyl ions is tertiary. Consequently the entire process should be energetically favorable, with **8** as the thermodynamic energy well, as observed.

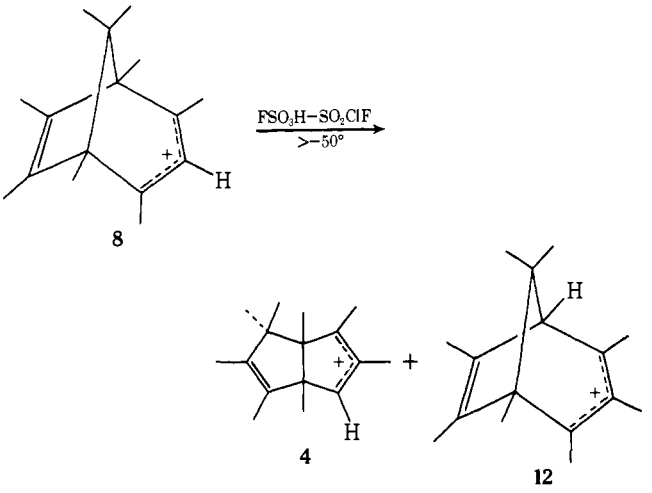
An Experimental Test of Scheme IV. As shown on the structures, Scheme IV contains a labeling prediction which we have tested. Ketone **7**-d_6[20] was reduced with lithium aluminum hydride to give a mixture of **6x**-d_6 and **6n**-d_6. When this alcohol mixture was treated with FSO_3H-SO_2ClF at −78°, the resulting **8**-d_6 had an NMR spectrum identical with that of unlabeled **8** except that the six-proton peak at δ 1.84 due to the methyls on the double bond was absent. This result was confirmed by quenching the solution to give **9**-d_6 in which the peaks at δ 1.38 and 1.53 assigned to the methyls on the two-carbon bridge were absent.

Since the label is 1,3- in the starting alcohols and 1,2- in the resulting ion **8**, a sequence of direct 1,2-bridge shifts (E



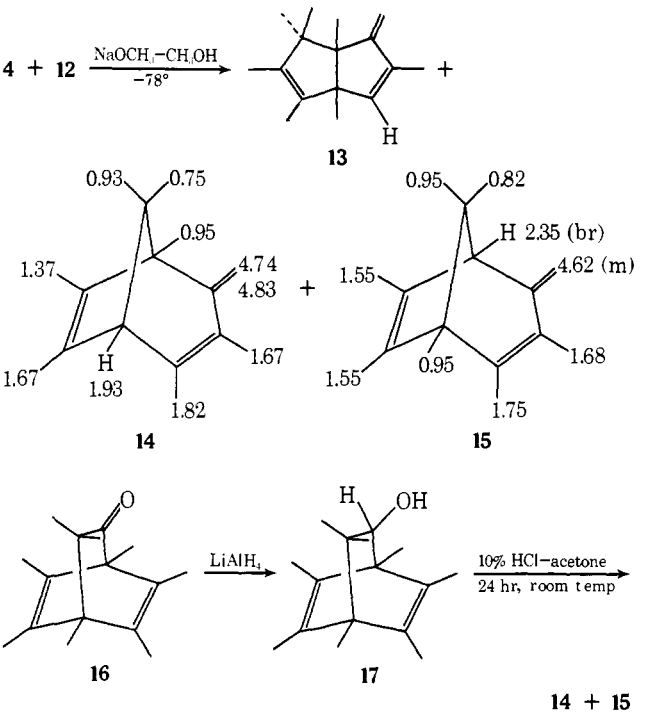
→ J → **8**) is unequivocally excluded as the path from **6** to **8**.[22]

Further Rearrangements of Cation 8. When solutions of cation **8** in FSO_3H-SO_2ClF (1:4) were allowed to stand at −50° or above for an extended time, **8** rearranged to **4** and another ion to which we assign structure **12**. The product

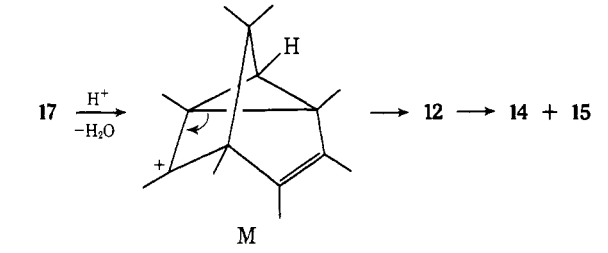


ratio was ca. 3:2 and remained constant throughout the rearrangement, suggesting competetive rather than successive processes. Ion **4** could be identified directly from its NMR spectrum, which was identical with that of **4** produced by the rearrangement of the pyramidal cation **2**. The identification was confirmed by isolation of the known quenching product **13**.[1] Two other hydrocarbons were isolated from the quenching experiment, assigned structures **14** and **15**. Compounds **14** and **15** were identified by their spectral properties and by independent synthesis (vide infra). In particular, their uv and NMR spectra were similar to those of **9**, **11**, and other closely related compounds,[3,9,23] but the third nonmethyl proton was clearly at a bridgehead rather than a vinyl position.

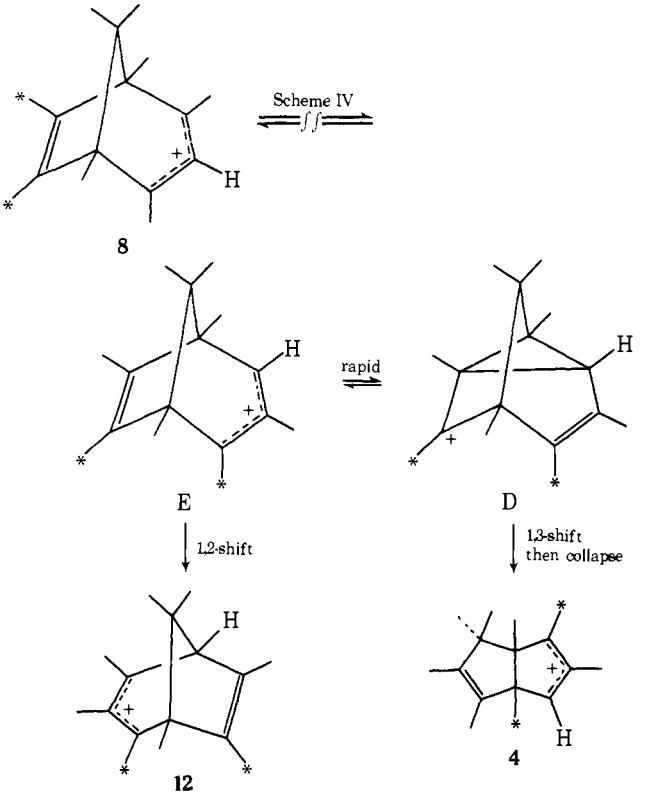
Trienes **14** and **15** were synthesized independently in the following way. Reduction of **16**[1,24] gave **17** which under carefully controlled acidic conditions was dehydrated to a 7:3 mixture of **14** and **15** in about 90% yield.[25] Ionization of **17** presumably proceeds with double bond participation to give M, which under these mild and nucleophilic conditions



does not rearrange further, but opens to **12** and loses a proton to give **14** and **15**.

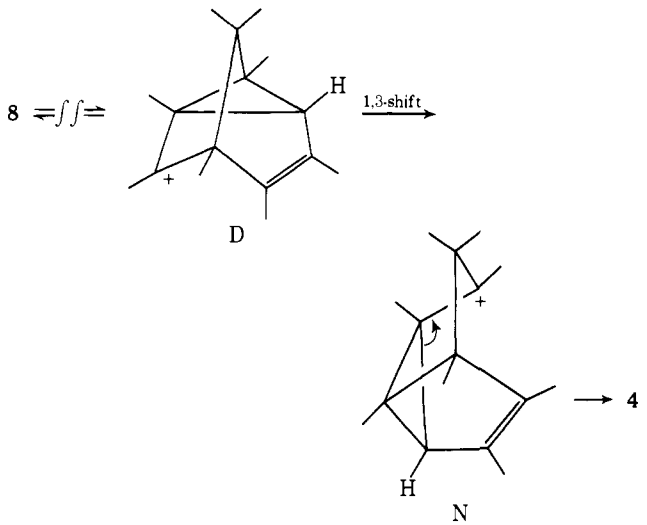


Scheme V

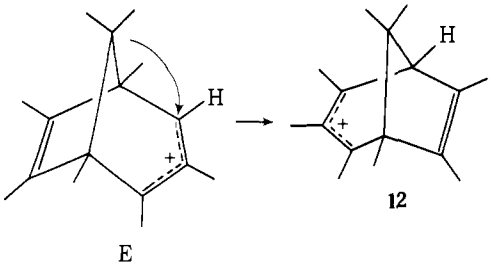


Solutions of either **14** or **15** in FSO_3H-SO_2ClF at −78° gave identical NMR spectra (due to ion **12**); furthermore, this spectrum, together with the known[1] spectrum of **4**, accounts for virtually all of the lines observed in solutions of rearranged **8**. Consequently we conclude that **8** rearranges almost exclusively to a mixture of **4** and **12**.

Mechanism for the Rearrangement of 8 to 4 and 12. If the rearrangement of **8** to a [3.3.0] cation were entirely analogous to the rearrangement of **3** (→ B → C → **5**), then the rearrangement product would have the proton on the central carbon of the allyl cation and not at the terminus remote from the *gem*-dimethyl group as observed (in **4**). The only cyclopropylcarbinyl ion of type B (but with one methyl replaced by H) which can rearrange directly to **4** is ion D (Schemes II and IV). Consequently one attractive possible mechanism for the formation of **4** from **8** is to proceed backward from **8** to D in Scheme IV; D may then rearrange to **4** via N as shown.



The fact that the ratio of **4**/**12** remained constant throughout the rearrangement of **8** suggests that they are formed from common or rapidly equilibrating intermediates. Since D and E have been shown to equilibrate rapidly even under milder conditions than those used to rearrange **8** to **4** and **12**, it would be reasonable to propose that **12** arises from a 1,2-bridge shift rearrangement of E.

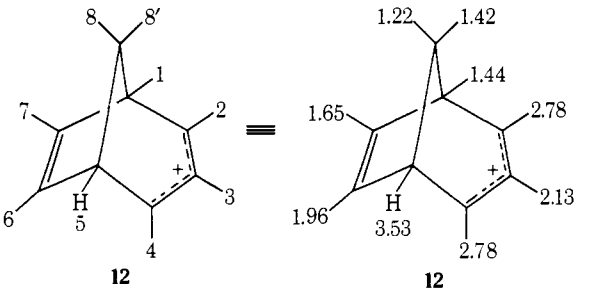


The proposed mechanism for rearrangement of **8** to **4** and **12** is summarized in Scheme V. This mechanism is subject to a labeling test as suggested by the asterisks in the scheme. In fact, when **8**-d_6, labeled as shown, was allowed to rearrange, the resulting **4**-d_6 was labeled precisely as shown in Scheme V. This remarkable result lends great credence to the proposed mechanism. It especially supports the complete reversibility of all the steps in Scheme IV. An alternative scheme for the formation of E (and D and **4**) from **8** is a sequence of two 1,2-bridge shifts. Although this mechanism would be far more economical in number of steps than the reversal of Scheme IV, it can be conclusively ruled out by the labeling result (it would require **4** to be labeled at the two bridgehead methyls).

Although the labeling pattern in **4**-d_6 obtained from **8**-d_6 was exactly as expected from Scheme V, *the labeling pattern in the resulting* **12**-d_6 *was not.* In **12**-d_6, the label was *equally* distributed in all methyls except the *gem*-dimethyl group! The only reasonable conclusion (since label integrity was maintained in **4** and therefore presumably in D and E) is that label scrambling occurs rapidly in ion **12** under the conditions of its formation from **8**. We therefore decided to study that possibility directly by preparing **12** under milder conditions from its triene precursors (**14** and **15**).

Degenerate Rearrangements in Ion 12. Solutions of **12** in FSO_3H-SO_2ClF (1:4) at low temperatures were prepared from **14** and/or **15**. Quenching of such solutions with $NaOCH_3$-CH_3OH gave a mixture of **14** and **15** (approximately 3:1). The quenching results were the same at −78 or −35°, despite the fact that over this temperature range the NMR spectrum of **12** in the strongly acidic solvent underwent some rather drastic changes. Therefore **12** must undergo degenerate rearrangements under these experimental conditions. Selected spectra at different temperatures are shown in Figure 1.

The NMR changes can be summarized as follows. At the lowest temperature (−88°), the spectrum corresponds to the chemical shifts shown on the structure.[26] The C-2 and C-4 methyls coincidentally have the same chemical shift (δ 2.78). The lone proton is clearly at a bridgehead position (δ 3.53). Also noteworthy is the appreciable chemical shift difference between the two allylic methyls (δ 1.65, 1.96).



As the temperature is raised, the peaks at δ 1.22 and 1.42 due to methyls 8 and 8′ broaden, coalesce (at −77°), then sharpen to a singlet at δ 1.32 which, though quite sharp at −54°, continues to sharpen as the temperature is raised to −33°. Over this entire temperature range, the signals due to the bridgehead proton (δ 3.53) and methyl (δ 1.44) continue to remain sharp and unique.[27] The latter result is reminiscent of the degenerate circumambulation process observed with **3**,[3] described in the first paragraph of this paper.

Other changes which occur are more remarkable. The signal at δ 2.78 remains unique, but gradually shrinks in relative area (beginning at about −76°) from 6 H to 4 H. The peaks at δ 1.65, 1.96, and 2.13 broaden early; at −76°, the δ 1.96 and 2.13 peaks have coalesced, and at slightly higher temperatures the peak at δ 1.65 has also merged. At −64°, an averaging peak at δ 1.97 begins to sharpen, and another averaging peak barely emerges at δ 2.41. These peaks continue to sharpen as the temperature is raised further. At −33°, the NMR spectrum of **2**[28] consists of six sharp signals, at δ 3.53 (1 H), 2.78 (4 H), 2.41 (5.3 H), 1.97 (5.7 H), 1.48 (3 H, and 1.32 (6 H). The fractional areas, as well as the chemical shifts of the averaging peaks, must be rationalized mechanistically. The situation is analogous to, but considerably more complex than, the circumambulatory mechanism for the results can be rationalized with the help of Scheme VI. All of the intermediates in this scheme are analogous to those in Schemes I-V.

The "tertiary" bridging path should be preferred over the

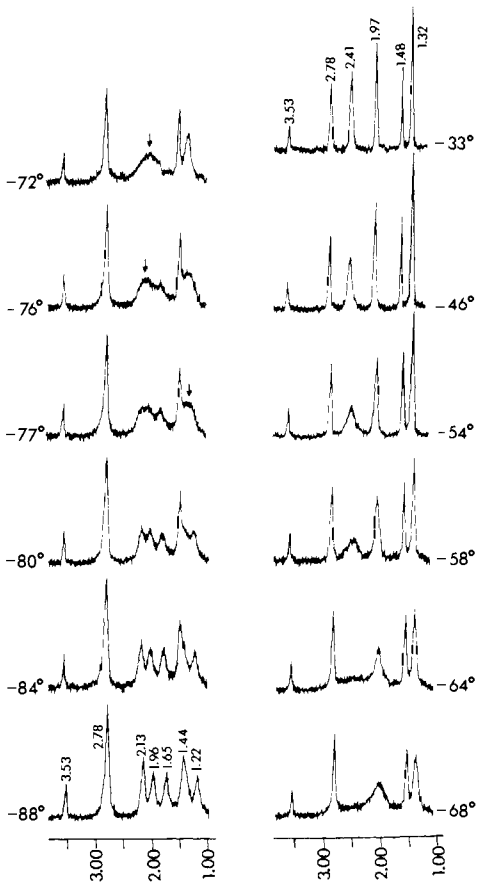


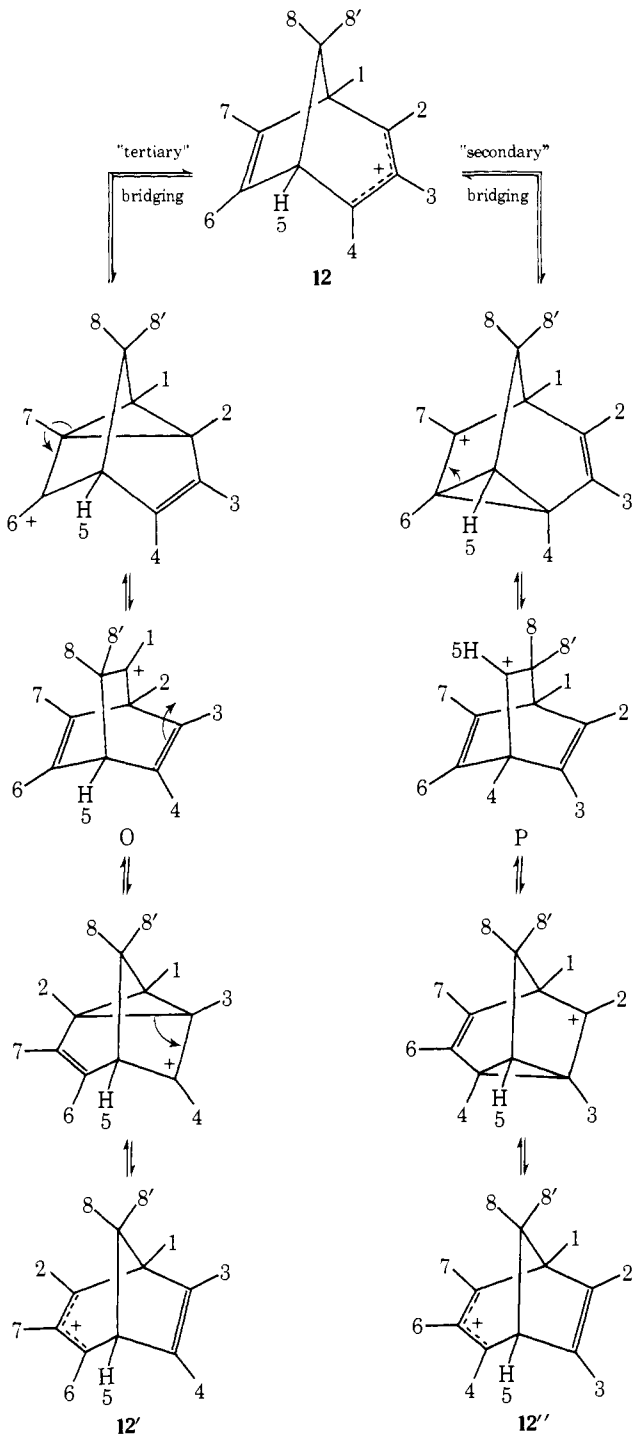
Figure 1. The proton NMR spectrum of cation **12** in FSO_3H–SO_2ClF in the temperature range −88 to −33°.

"secondary" bridging path because it proceeds entirely through tertiary rather than secondary ions (compare O and P). It is instructive to consider the expected NMR changes if "tertiary" bridging occurred exclusively. Ion **12** would equilibrate only with **12′**. In this event, methyl 1 and bridgehead proton 5 would remain unique, as observed. One of the methyls (methyl 2) at the allyl cation termini would remain unchanged, but the other (methyl 4) would equilibrate with methyl 6. Thus the area of the peak at δ 2.78 should shrink from 6 H to 3 H (it did shrink in area, but only to 4 H) and a new 6 H peak should appear at δ 2.37 [(1.96 + 2.78)/2] (a new peak did appear, but slightly shifted to δ 2.41 and with area only 5.3 H). Methyls 3 and 7 should also average to a 6 H peak at δ 1.89 [(2.13 + 1.65)/2] (a new peak did appear, but shifted downfield to δ 1.97 and with area 5.7 H). Finally, methyls 8 and 8′ should equilibrate as observed (δ 1.32, 6 H).

The above analysis shows that the "left" portion of Scheme VI (**12** ⇌ **12′**) comes close to explaining the NMR spectral changes observed between −88 and −33° in ion **12**. But it is not the whole story. If it were, the ratio of peak areas at δ 2.78, 2.41, and 1.97 should be 3:6:6 instead of the observed 4:5.3:5.7 and two of the peaks should have slightly different chemical shifts. One is therefore obliged to also consider the possibility of "secondary" bridging as shown in the right-hand portion of Scheme VI (**12** ⇌ **12″**).[29] It could, for example, explain why the δ 2.78 peak has an enhanced area (4 H rather than 3 H), because the C-4 methyl in this part of the scheme maintains its identity. Presumably this equilibration path is slower than the "tertiary" bridging process and only becomes important when the temperature is raised.

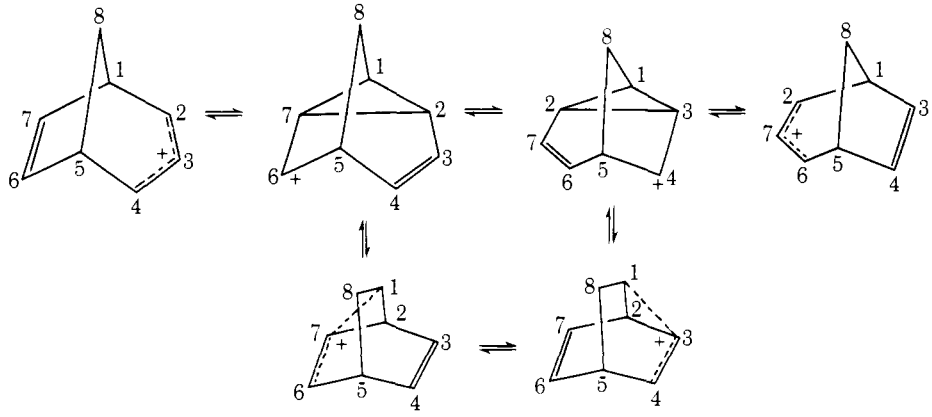
Double irradiation experiments (DISST)[30] gave very different results as the temperature was varied. At −85°, irradiation at δ 2.78 (C-2 and C-4) caused a reduction in area only of the peak at δ 1.96 (C-6), and irradiation at δ 2.13 (C-3) caused a similar area reduction only of the peak at δ 1.65 (C-7). Thus at this temperature, only C-3/C-7 exchange and C-4/C-6 exchange occur (C-2 remains unique throughout as described above). At −40°, however, irradiation of any one of the three peaks at δ 2.78, 2.41, and 1.97 caused an area reduction in the other two, showing that at the higher temperature all five methyls (C-2,3,4,6,7) are exchanging. These results are most easily rationalized if, at the lower temperature only, "tertiary" bridging is important, but at the higher temperature both types of bridging shown in Scheme VI contribute to the exchange process. The low-field chemical shift of the C-6 methyl in **12** (δ

Scheme VI

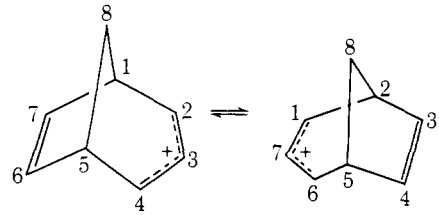


Scheme VII

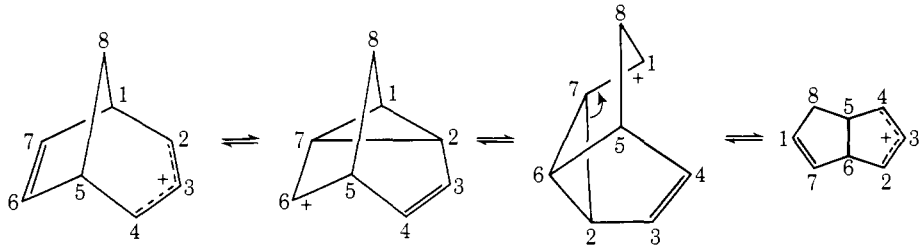
(a) Circumambulation



(b) 1,2-Bridge Shift

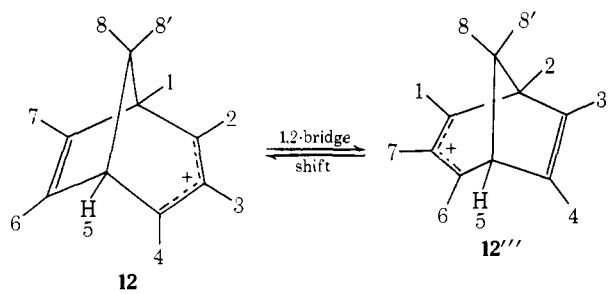


(c) 1,3-Cyclopropylcarbinyl Shift



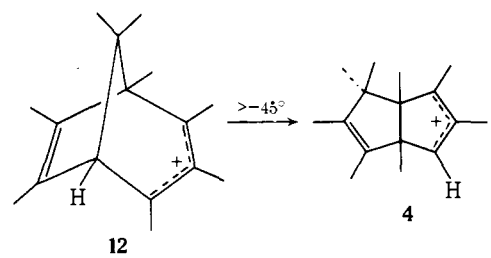
1.96) relative to that of the C-7 methyl (δ 1.65) is perhaps in part a reflection of this preferred tertiary bridging at low temperatures.

Finally, we must return to the deuterium exchange result (vide supra) that **8**-d_6 gave **12** in which the label was scrambled in *all six* methyl groups (all but methyls 8 and 8′). Scheme VI does not provide a mechanism for getting label into the bridgehead methyl (C-1). We conclude that **12** must also undergo 1,2-bridge shifts (**12** ⇌ **12‴**), but that this process is slower than either of the processes in Scheme VI; consequently, it escapes NMR detection but is observed by deuterium label. This behavior is entirely analogous to that of **3**.[3]



12 **12‴**

Skeletal Rearrangement of Ion 12. When a solution of **12** in FSO_3H-SO_2ClF (1:4) was maintained at −45° for several hours, the NMR spectrum (Figure 1) gradually changed to that of the known cation **4**. The first-order rate constant for the disappearance of **12** was $4.4 \pm 0.2 \times 10^{-5}$ sec^{-1} at −42°.[31] It seems most likely that this rearrangement occurs via a reversal of the paths shown in Scheme V (i.e., **12** → E → D → **4**).[32]



12 **4**

General Mechanistic Conclusions. The present work (on ions **8, 12,** D, and E) reinforces conclusions[3] based only on studies of ion **3**, that there are three distinct types of rearrangements which these ions undergo. They are, *in order of increasing activation energy,* (a) circumambulation, (b) 1,2-bridge shift, and (c) a 1,3-cyclopropylcarbinyl rearrangement. These rearrangements are illustrated in Scheme VII. The first two types equilibrate bicyclo[3.2.1]octa-3,6-dien-2-yl cations, and the third type results in rearrangement of these ions to bicyclo[3.3.0]octa-3,6-dien-2-yl cations.

Examples from the present study which support Scheme VII are the following. Ions D or E (derived from **6x** or **6n,** respectively) rearrange to **8** by the circumambulation mechanism and *not* by successive 1,2-bridge shifts, as proved by deuterium labeling experiments (see Schemes II

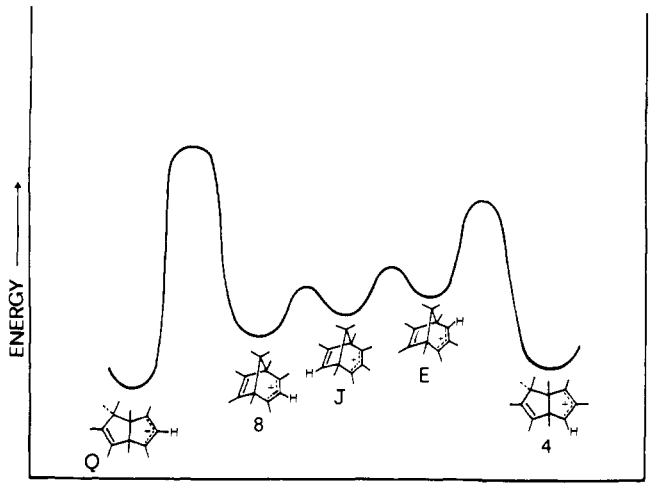


Figure 2. Schematic energy diagram for interconverting (by circumambulation; Scheme IV) cations **8**, J, and E and two (of the three possible) bicyclo[3.3.0]octadienyl cations to which they might rearrange.

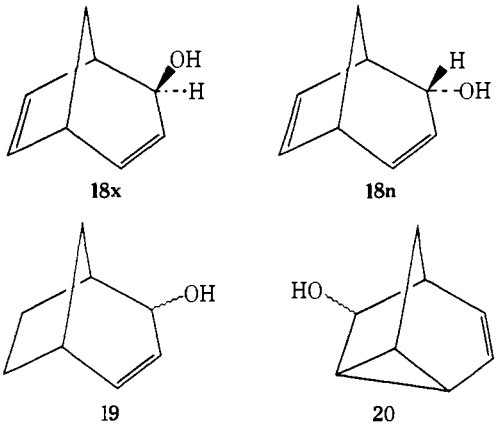
and IV). Only at higher temperatures do 1,2-bridge shifts (**8** → **12**) or 1,3-cyclopropylcarbinyl shifts (**8** → **4**) occur. Similarly, circumambulation (NMR observed) of **12** occurred faster than 1,2-bridge shifts (observed by deuterium scrambling), and the slowest reaction was a 1,3-cyclopropylcarbinyl shift (**12** → D → **4**).

The presence of a single hydrogen on the otherwise permethylated bicyclo[3.2.1]octa-5,6-dien-2-yl cation allows us to make several other observations about the relative energies of competing carbonium ion processes. For example, E → D is favored over E → H (Schemes I, II, and IV); that is, label equilibration via D was faster than isomerization of E (via H) to **8**. The preference may be due either to the unequal charge distribution at the termini of the allylic system in E (preferential reaction occurring at the least substituted carbon), or it may be due to a preference for a transition state leading to the most (D) rather than least (H) substituted double bond.

Another conclusion we may draw is that the stability of the ions in Scheme IV is E < J < **8**.[33] Reasons for this order have already been offered (vide supra). We call attention to the fact that rearrangements of a group of equilibrating ions such as these proceed by transition states which are most related structurally to the *least* stable of these ions. For example, thermal rearrangement of **8** → **12** proceeds via a transition state structurally related to E, not **8**. Rearrangement of **8** → **4** also proceeds through a transition state structurally related to E (→ D → **4**). And the rearrangement of **12** to **4** occurs similarly (**12** → E → D → **4**). It seems as if the minimum energy path involves a series of steps, each with a small energy increment, rather than one step with a large activation energy. Consider, for example, the rearrangement of **8** to **4**. An energy diagram is shown in Figure 2. The observed product **4** has a structure most closely related to that of E, the *least* stable of the equilibrating group (**8**, J, E); ion Q, for example, which could be formed from **8** by a mechanistic scheme exactly analogous to the formation of **4** from E, is not observed, even though it might actually be expected to be somewhat more stable than **4** (compare **8** and E).[34] We see no obvious reason why the barrier of **8** → Q is so much higher than that of E → **4**, though from the experimental observations it must be. Our observation that rearrangements from a series of equilibrating ions occur via a transition state that is structurally related to the least stable member of the group may be a consequence of the fact that as the temperature is raised the population of the least stable member (in Figure 2, ion E) is increased; if only one transition state is accessible to the assemblage (**8**, J, E), it will resemble the highest energy precursor.

Finally, we answer the question posed at the beginning of this paper. It is clear that if the rearrangement of the pyramidal ion **2** to **4** proceeded via ions such as **8**, this ion would have been detectable and would also have produced not only **4** but **12** under the conditions of the rearrangement of **2** to **4**. We conclude, therefore, that the rearrangement of **2** to **4** is a direct process as previously proposed, and does *not* involve bicyclo[3.2.1]octa-5,6-dien-2-yl cations as intermediates.

Comparison with the Nonmethylated System. The solvolysis rates and products of the *p*-nitrobenzoates (PNB) of **18x** and **18n**, the nonmethylated analogs of **6x** and **6n**, were



studied by Winstein.[35] There was an appreciable rate decrease on going from **19** to **18** because of the 6,7-double bond; derivatives of **19** solvolyzed 235 times faster than those of **18** under comparable conditions. This rate retardation was considered larger than could be attributed solely to the inductive effect of the vinyl group, and antiaromaticity of the intermediate cation was thought to also be a factor. The products from **18**-OPNB in 60% aqueous acetone were mainly the alcohols of **18**-OH; each pure epimeric *p*-nitrobenzoate gave a mixture of epimeric alcohols, with a preference for configurational retention. Small amounts of rearranged alcohols **20** were also formed.

There was no evidence in these solvolysis studies for carbon skeletal scrambling as observed by us for the methyl-substituted analogs (e.g., **6** → **8** or **12**). Nor can one tell (no distinguishing experiments were performed) whether **20** is formed from **18** via a symmetric intermediate or through participation of the 6,7-double bond (as, for example, in the formation of **10** from **6x**). However, unlike the present work where **6x** solvolyzed considerably faster than **6n**, the exo-endo rate ratio for the PNB's of **18** was nearly unity.

No studies of the ionization of **18** under stable ion (superacid) conditions have been reported, and our own efforts[36] along these lines indicate that the system has a high propensity for polymer formation. It seems unlikely that the unsubstituted system will exhibit the intricate rearrangements described here for the highly methylated system. It remains to be seen just how far and from what positions one can strip the system of substituents and still have it undergo circumambulation, bridge shifts, or cyclopropylcarbinyl rearrangements.

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. Decoupling experiments

were done on the T-60 or an HA-100 spectrometer. 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. 1:4), sometimes with added methylene chloride or CD_2Cl_2 at the lowest temperatures; either $(CH_3)_4NBF_4$ (δ 3.13) or CH_2Cl_2 (δ 5.30) was used as an internal reference. The temperature control was calibrated with a methanol standard sample 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 were uncorrected.

***exo*- and *endo*-1,3,4,5,6,7,8,8-Octamethylbicyclo[3.2.1]octa-3,6-dien-2-ol (6x,6n) and 6-Methylene-1,3,4,5,7,8,8-heptamethyltricyclo[3.2.1.$0^{2,7}$]octene (10).** To a suspension of 70 mg of $LiAlH_4$ in 10 ml of anhydrous ether at 0–5° was added dropwise with stirring a solution of 1,3,4,5,6,7,8,8-octamethylbicyclo[3.2.1]octa-3,6-dien-2-one (**7**)[1] (1.0 g) in 20 ml of anhydrous ether. The mixture was stirred for 3 hr at room temperature. Excess hydride was destroyed with water, the ether layer and extracts were washed with saturated sodium chloride solution and dried ($MgSO_4$), and the solvent was evaporated to give a pale yellow oil (**6x:6n,** 45:55 by NMR) in virtually quantitative yield. Attempts to separate the epimeric mixture by TLC or fractional crystallization failed. Vapor phase chromatography (VPC; 5 ft × 0.25 in. column, 20% FFAP on Chromosorb W, 120°, 100 ml/min of He) gave two major peaks, retention times 15 and 36 min. The product with the shorter retention time was a colorless oil identified as **10:** ir (CCl_4) 1650 (m), 1600 (w), 1450–1470 (br), 1390 (m), 1370 (m), 1075 (m), 903 (m), 885 (s) cm^{-1}; uv (ethanol) 242 nm (sh, ϵ 3100); NMR (CCl_4), see structure. The five highest field methyl peaks were sharp singlets, as was the 1 H peak at δ 1.17; the signals at δ 1.53 and 1.75 showed homoallylic coupling (3 H, q, $J \simeq 1.0$ Hz), and the vinyl proton peaks were singlets. Mass spectrum (70 eV) *m/e* (rel intensity) 216 (32), 202 (22), 201 (100), 186 (30), 171 (25), 159 (49), 148 (20), 147 (23), 145 (17), 133 (20).

Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.85; H, 11.19.

The product responsible for the second VPC peak (36 min) was collected as colorless crystals, mp 59–60°. It is assigned structure **6n:** ir (CCl_4) 3500 cm^{-1}; NMR (CCl_4) see structure. All peaks were sharp singlets except for the 1 H peak at δ 3.32, which was broad. Mass spectrum (70 eV) *m/e* (rel intensity) 216 (30), 202 (28), 201 (200), 186 (29), 173 (15), 171 (25), 159 (53), 148 (20), 147 (25), 145 (17), 133 (33), 105 (26), 99 (37).

Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.92; H, 11.15.

Subtraction of the NMR spectrum of **6n** from that of the crude product mixture before VPC allowed the assignment of the NMR spectrum of **6x** shown on its structure.

Preparation and Quenching of Cation 8. 2-Methylene-1,4,5,6,7,8,8-heptamethylbicyclo[3.2.1]octa-3,6-diene (9). The general procedure we have used to obtain carbocation solutions in FSO_3H–SO_2ClF has been previously described in detail[1] and was used throughout the present work. From 40 mg of **6** (45:55 epimeric mixture) in 250 μl of FSO_3H–SO_2ClF (1:4) there was obtained at −78° a navy blue solution of carbocation **8**. The NMR spectrum consisted of six sharp singlets at δ 1.22, 1.42, 1.47, 1.84, 2.83, and 7.08 with relative areas 3:3:6:6:6:1. The spectrum showed no new peaks over the temperature range −60 to −120°, although below −90° there was considerable line broadening and some overlap of the three highest field signals.

The solution of **8** prepared as above was added dropwise but quickly at −78° to a vigorously stirred suspension containing excess sodium methoxide in methanol. The resulting suspension was slowly warmed to room temperature, then concentrated to dryness under reduced pressure. Water was added, and the mixture was extracted thoroughly with ether. Combined ether layers were washed with saturated sodium chloride solution and dried ($MgSO_4$). Evaporation left a pale yellow oil which, by NMR, consisted only of **9**, formed in essentially quantitative yield. Purification by VPC (10 ft × 0.25 in. column, 20% FFAP on Chromosorb W, 155°, 100 ml/min of He, ret time 9.5 min) gave **9** as a colorless oil: ir (CCl_4) 1635 (w), 1600 (m), 1450–1475 (m, br), 1425 (w), 1395 (s), 1380 (sh), 1075 (m), 900 (s) cm^{-1}; uv (ethanol) 243 nm (ϵ 13000); mass spectrum (70 eV) *m/e* (rel intensity) 216 (19), 201 (100), 186 (34), 171 (22), 159 (50), 147 (17), 145 (12), 133 (10), 91 (14); NMR (CCl_4), see structure; the peaks at δ 1.38 and 1.53 were homoallylically coupled quartets, J = 1.5 Hz, peaks at δ 1.73 and 5.50 were split as shown on the structure, all other peaks were singlets. Double irradiation at δ 5.50 caused collapse to a singlet of the doublet at δ 1.73.

Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.84; H, 11.21.

Treatment of 6x and 6n with Hydrochloric Acid and Aqueous Acetone. (a) With 0.1% HCl. A solution of **6x** and **6n** (50 mg, 45:55) in 0.5 ml of 0.1% hydrochloric acid diluted with 1 ml of acetone was allowed to stand for 15 min at room temperature. The mixture was diluted with water and extracted with methylene chloride. The combined extracts were washed with 5% sodium bicarbonate and then water and dried (Na_2SO_4). The residue after evaporation of the solvent was separated by preparative TLC (2.0 mm silica gel on glass, methylene chloride eluent) to give recovered **6n** (R_f 0.28) and **10** (R_f 0.70) is essentially quantitative yield. Each product had an NMR spectrum identical with the products obtained by VPC purification of a **6x–6n** mixture as described above.

(b) With 10% HCl. To 4 ml of acetone containing 80 mg of **6x** and **6n** (45:55) was added 2 ml of 10% hydrochloric acid, and the mixture was allowed to stand at room temperature for 30 min. The mixture was then diluted with water and extracted with methylene chloride (3 × 20 ml). Combined methylene chloride layers were washed with 5% sodium carbonate solution and then water and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave **2-methylene-1,3,5,6,7,8,8-heptamethylbicyclo[3.2.1]octa-3,6-diene (11)** as a pale yellow oil in nearly quantitative yield. Purification by VPC (10 ft × 0.25 in. column, 20% FFAP on Chromosorb W, 155°, 100 ml/min of He, ret time 8 min) gave **11** as a colorless oil: ir (CCl_4) 1600 (m), 1465 (m), 1455 (s), 1395 (s), 1380 (sh), 905 (s) cm^{-1}; uv (ethanol) 244 nm (ϵ 12400); mass spectrum (70 eV) *m/e* (rel intensity) 216 (30), 202 (20), 201 (100), 186 (33), 171 (27), 159 (55); NMR (CCl_4), see structure. The peaks at δ 1.38 and 1.55 were homoallylically coupled quartets, J = 1.0 Hz; other peaks were singlets or split as shown on the structure. Double irradiation of the peak at δ 5.62 caused collapse to singlets of the peaks at δ 1.70 and 4.92.

Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.85; H, 11.19.

(c) Other Conditions. Similar experiments, all at room temperature, using 40 mg of a mixture of **6x** and **6x,** 1 ml of aqueous hydrochloric acid of a designated concentration, and 2 ml of acetone gave the following results: **0.1% HCl for 1 hr,** 35% **6n,** 60% **10,** 5% **11: 0.5% HCl for 15 min,** 27% **6n,** 65% **10,** 8% **11; 2% HCl for 30 min,** trace of **6n,** 75% **10,** 25% **11; 10% HCl for 36 hr,** 78% **11,** 22% **9**. In each case, products were identified by VPC retention times and NMR spectra.

Treatment of 10 with Hydrochloric Acid and Aqueous Acetone. To 2 ml of acetone containing 40 mg of **10** was added 1 ml of 10% hydrochloric acid, and the mixture was allowed to stand at room temperature for 30 min. Work-up as above gave a nearly quantitative yield of **11,** identified by NMR.

Preparation of Deuterium Labeled 6. The preparation of several types of deuterium labeled **7** has been described. These include **7**-d_3[1] (C-4 CD_3) and **7**-d_6 (ref 3, footnote 6; C-4 and C-6 CD_3). Reduction of these ketones with $LiAlH_4$ as described for the reduction of unlabeled **7** gave labeled **6**. From **7**-d_3, the resulting mixture of **6x** and **6n** had an NMR spectrum identical with that of unlabeled material except that the signal at δ 1.63 was reduced in area from 6 H to 3 H. Similarly, from **7**-d_6, the NMR spectrum of the resulting **6x** had peaks at δ 1.63 and 1.48 reduced in area from 6 H to 3 H, and the resulting **6n** showed analogous reduction of peaks at δ 1.63 and 1.55. Another type of labeled **7** previously described[1] had 50% label at the C-3 and C-7 methyls and 100% label in the C-4 methyl. In the present work, this sample of labeled **7** was converted to **7**-d_9 which was fully labeled at the C-4 and C-6 methyls and 50% labeled at the C-3 and C-7 methyls by using the same procedure (ref 3, footnote 6) used to prepare **7**-d_6 from **7**-d_3. Reduction of this **7**-d_9 gave **6x** whose NMR spectrum had the signals at δ 1.63 and 1.48 reduced in area to 1.5 H and **6n** whose sig-

nals at δ 1.63 and 1.55 were similarly reduced. Finally, **7**-d_3' (C-6 CD_3) was prepared from **7**-d_6 by back exchange of protons into the C-4 methyl group using $NaOCH_3$–CH_3OH and following the same procedure[1] used to prepare **7**-d_3. Reduction of **7**-d_3' gave **6**-d_3' whose NMR peaks for the exo and endo isomers at δ 1.48 and 1.55, respectively, were reduced in area from 6 H to 3 H.

Treatment of Deuterium Labeled 6x and 6n with Hydrochloric Acid and Aqueous Acetone. The procedures were as described for unlabeled material. From a mixture of **6x**-d_3 and **6n**-d_3 (C-4 CD_3), 0.1% HCl, 15 min at room temperature, there was obtained **10**-d_3 whose NMR spectrum was identical with that of unlabeled **10** except that the signal at δ 1.53 was absent and that at δ 1.75 sharpened to a singlet. Also, **6n**-d_3 was recovered from this experiment. When a similar mixture of **6x**-d_3 and **6n**-d_3 was treated with 10% HCl, 30 min at room temperature, there was obtained in nearly quantitative yield **11**-d_3 whose NMR spectrum was identical with that of unlabeled **11** except that the peak at δ 1.38 was reduced in area from 3 H to 1.5 H and the peaks at δ 4.92 and 4.93 were reduced in area from 2 H to 1.5 H. Treatment of **6**-d_3' (C-6 CD_3) in the same way with 10% HCl gave identically labeled **11**-d_3.

Preparation and Quenching of 8-d_6. The same procedure was used as described above for the preparation and quenching of unlabeled **8**. A solution containing 40 mg of **6x**-d_6 and **6n**-d_6 (45:55; C-4 and C-6 CD_3) in 250 μl. of FSO_3H-SO_2ClF (1:4) at −78° gave an NMR spectrum identical with that of unlabeled **8** except that the peak at δ 1.84 was absent. When the solution was quenched at −78° with $NaOCH_3$–CH_3OH, there was obtained an essentially quantitative yield of **9**-d_6 whose NMR spectrum was identical with that of unlabeled **9** except that the peaks at δ 1.38 and 1.53 were absent. Solutions of **8**-d_6 prepared as just described showed no change in distribution of label even after 72 hr at −78°.

Rearrangement of 8 to 4 and 12. A solution of **8** in FSO_3H–SO_2ClF prepared at −78° as described above was held at −51° for several hours, and the reaction was monitored by NMR. Peaks due to **8** disappeared with a first-order rate constant 1.8×10^{-4} sec^{-1}. Simultaneously, two new sets of peaks appeared with a constant area ratio of 3:2. One set of peaks could be assigned to the previously known[1] ion **4**. The other set of peaks coincided with those shown in Figure 1 for ion **12**. When rearrangement was essentially complete, the mixture was cooled to −78° and quenched at that temperature with excess $NaOCH_3$ suspended in CH_3OH. The usual work-up (as described for the quenching of **8**) gave three hydrocarbons, **13, 14,** and **15.** Compound **13** was already known[1] and was identified by NMR comparison. Compounds **14** and **15** were identical (NMR) with authentic samples prepared as described below. The ratio of **13** to (**14** + **15**) was 3:2; the ratio of **14:15** varied depending on the quenching technique, but **14** usually predominated.

1,3,3,4,5,6,7,8-Octamethylbicyclo[2.2.2]octa-5,7-dien-2-ol (17). A solution containing 2 g of 1,3,3,4,5,6,7,8-octamethylbicyclo[2.2.2]octa-5,7-dien-2-one (**16**)[1,24] in 100 ml of anhydrous ether was treated with excess lithium aluminum hydride for 6 hr at room temperature, then worked up in the conventional manner to afford 1.8 g (90%) of **17** as a nearly colorless oil: ir (neat) 3500 (m, br), 1480 (sh), 1460 (s, br), 1395 (s), 1370 (m), 1250 (m), 1160 (m), 1125 (w), 1105 (m), 1050 (s, br), 1015 (s), 975 (m), 920 (w), 900 (w), 875 (w), 800 (s, br) cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 234 (1), 201 (2), 162 (46), 147 (100), 121 (24), 119 (74), 117 (77); NMR (CCl_4) δ 0.67 (3 H, s, C-3 methyl syn to OH), 0.78 (3 H, s, C-3 methyl anti to OH), 1.24 (3 H, s, C-4 methyl), 1.35 (3 H, s, C-1 methyl), 1.62 (6 H, s, C-6 and C-5 methyls), 1.64 (6 H, s, C-8 and C-7 methyls), 2.82 (1 H, s, C-2 proton). The relative europium shifts of the signals in the order given were 5.0, 2.0, 1.7, 4.5, 1.8 and 1.0, 2.3 and 1.8, 9.5. The OH proton was not located. We were unable to get a satisfactory analysis on this compound although the results fit moderately with expectation for a hydrate of **17** (Anal. Calcd for $C_{16}H_{26}O \cdot H_2O$: C, 76.19; H, 11.10. Found: C, 76.16; H, 10.54). The dehydration products of **17** (i.e., **14** and **15**) gave satisfactory analyses.

Dehydration of 17. 2-Methylene-1,3,4,6,7,8,8-heptamethylbicyclo[3.2.1]octa-3,6-diene (14) and 2-Methylene-3,4,5,6,7,8,8-heptamethylbicyclo[3.2.1]octa-3,6-diene (15). To a solution containing 400 mg of **17** in 20 ml of acetone was added 10 ml of 10% hydrochloric acid, and the mixture was allowed to stir at room temperature for 24 hr. The resulting solution was diluted with water and extracted with methylene chloride (3 × 50 ml). Combined methylene chloride layers were washed with 5% sodium bicarbonate solution, water, and dried (Na_2SO_4). Removal of the methylene chloride under reduced pressure gave 320 mg (86%) of a mixture of **14** and **15** (ratio 7:3 by NMR) as a pale yellow oil contaminated with about 5% of hexamethylbenzene (identified by NMR). Separation and purification was accomplished by VPC (10 ft × 0.25 in. column, 20% FFAP on Chromosorb W, 150°, 100 m/min of He) to give **14** and **15** as colorless oils, retention times 7 and 8 min, respectively. For **14:** ir (neat), 1630 (w), 1600 (m), 1480 (sh, m), 1450 (s), 1395 (s), 1375 (sh, m), 1335 (w), 1300 (w), 1100 (m), 900 (s) cm^{-1}; uv (ethanol) 244 nm (ε 13700); mass spectrum (70 eV) *m/e* (rel intensity) 216 (38), 202 (18), 201 (100), 186 (36), 173 (17), 172 (13), 171 (25), 159 (49); NMR (CCl_4) see structure; peaks at δ 1.37, 1.67, and 1.82 were homoallylically coupled quartets, J = 1.0 Hz.

Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.93; H, 11.05. For **15:** ir (neat), 1645 (w), 1620 (w), 1600 (w), 895 (s) cm^{-1}; uv (ethanol) 245 nm (ε 12,500); mass spectrum (70 eV) *m/e* (rel intensity) same as **14;** it should be pointed out that the 70-eV mass spectra of **9, 10, 11, 14,** and **15** are virtually identical, with only slight intensity differences that are probably due to experimental variation. NMR (CCl_4) see structure; the peaks at δ 1.68 and 1.75 are homoallylically coupled quartets, J = 1.0 Hz; other peaks are singlets except as indicated on the structure.

Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.93; H, 11.05.

If the dehydration procedure given here is not followed carefully, yields of **14** and **15** may decrease sharply, and considerable amounts of pentamethyl- and hexamethylbenzene (PMB and HMB, respectively) will be obtained. For example, if concentrated HCl replaces 10% HCl in the above procedure, dehydration is more rapid (complete in 30 min). However, only 45% of the product was **14** and **15,** the remainder being 45% PMB and 10% HMB. Ionization of **17** in FSO_3H–SO_2ClF at −78° followed by quenching with $NaOCH_3$–CH_3OH by the usual procedure gave a complex product mixture from which **14, 15,** PMB, and HMB were isolated.

Preparation of Ion 12. Solutions of ion **12** in FSO_3H–SO_2ClF were prepared from either **14** or **15** or mixtures thereof just as described for the preparation of **8.** The NMR spectrum was measured every few degrees over the temperature range −88 to −33°. Twelve (of the 24 spectra obtained) are shown in Figure 1. See text for a discussion of the spectral changes, for double irradiation results, and for quenching results.

Rearrangement of Ion 8-d_6 to Labeled 4 and 12. Solutions of **8**-d_6 in FSO_3H–SO_2ClF at −78°, prepared as described above, were warmed to −50° and allowed to rearrange to labeled **4** and **12** as described above for the rearrangement of unlabeled **8.** In the resulting solution, the peaks at δ 3.03 and 1.44 in ion **4**[1] were absent. The solution was cooled to −78° and quenched in $NaOCH_3$–CH_3OH in the usual manner. The resulting **13** lacked the vinyl proton signals at δ 4.59 and 4.86, and the methyl signal at δ 0.92 was reduced in area from 6 H to 3 H (see ref 1 for the NMR spectrum of unlabeled **13**). The resulting **14** and **15** had NMR spectra with slightly reduced areas (approximately 30%) in all signals except the bridgehead protons and the *gem*-dimethyl group.

Rearrangement of 12 to 4. A solution of **12** in FSO_3H–SO_2ClF (prepared at −78° from a mixture of **14** and **15,** as described above) was kept at −42°; peaks due to **12** gradually disappeared and those due to **4** appeared, with a first-order rate constant of 4.4 ± 0.2 × 10^{-5} sec^{-1}. The reaction was followed only to 35% completion, because subsequent rearrangements of **4** (already described[1]) began to complicate the spectrum. Cooling to −78° and quenching gave only **13, 14,** and **15.**

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

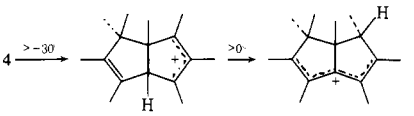
References and Notes

(1) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **96**, 6436 (1974).
(2) Ion **2** belongs to a growing class of pyramidal carbocations whose existence was predicted by R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971), and by W-D. Stohrer and R. Hoffmann, *J. Am. Chem. Soc.*, **94**, 1661 (1972); for specific examples see, in addition to ref 1, (a) S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *ibid.*, **94**, 8956 (1972); (b) S. Masamune, M. Sakai, A. V. Kemp-Jones, H. Ona, A. Venot, and T. Nakashima,

Angew. Chem., Int. Ed. Engl., **12**, 769 (1973); H. Hogeveen and P. W. Kwant, *J. Am. Chem. Soc.*, **96**, 2208 (1974); A. V. Kemp-Jones, N. Nakamura, and S. Masamune, *J. Chem. Soc., Chem. Commun.*, 109 (1974); H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **97**, 2450 (1975).

(3) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **97**, 2459 (1975).

(4) Ion **5** is stable to +50°; ion **4**, on the other hand, rearranges as follows:



The mechanisms of these rearrangements have been discussed.[1]

(5) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, preceding paper in this issue.

(6) Throughout this paper, observable ions or compounds are designated by Arabic numbers, whereas proposed intermediates are lettered.

(7) All chemical shifts are in parts per million (δ) from tetramethylsilane (Me_4Si). Numbers in parentheses are the relative extents to which these signals are shifted downfield by Eu(fod)$_3$ shift reagent; see R. E. Rondeau and R. E. Sievers, *J. Am. Chem. Soc.*, **93**, 1522 (1971), and D. R. Kelsey, *ibid.*, **94**, 1764 (1972).

(8) The assignment of the *gem*-dimethyl signals in the one-carbon bridge is arbitrary.

(9) The chemical shift is consistent with location of the hydrogen at the middle of an allylic ion; see H. Hart and M. Kuzuya, *Tetrahedron Lett.*, 1913 (1974).

(10) The structure of **10** follows from its spectral properties and reactions. It showed only two vinyl protons and two vinyl methyl groups in the NMR (contrast with three of these groups in **9** and **11**), and only a weak shoulder at 242 nm (contrast with intense maxima at about 245 nm in **9** and **11**). Labeling experiments support the NMR assignment shown on the structure.

(11) The structure of **11** follows from its spectral properties and reactions. Its uv and NMR spectra match very closely those of **9**. The largest difference in the ^{1}H NMR spectrum is the lower field position of the exocyclic methylene protons in **11**. Double irradiation clarified the relationships between coupled protons and in particular established the long range coupling (2.0 Hz) between two of the vinyl protons. Labeling experiments support the NMR assignment shown in the structure.

(12) See the Experimental Section for additional results of this type.

(13) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

(14) R. D. Breslow, *Angew. Chem., Int. Ed. Engl.*, 7, 565 (1968).

(15) The peak at δ 1.63 in each alcohol was reduced in area to 3 H and sharpened.

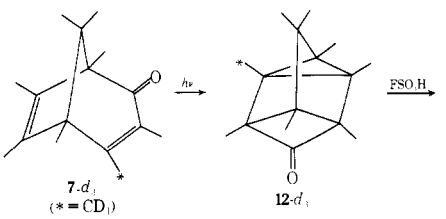
(16) The peak at δ 1.53 was absent in **10**-d_3, and the peak at δ 1.75 sharpened to a singlet.

(17) The peak at δ 1.38 was reduced in area from 3 H to 1.5 H, corresponding to 50% of the original label. The methylene protons at δ 4.92, 4.93, however, were only about 25% labeled. Apparently some of the label "washes out" of this position.

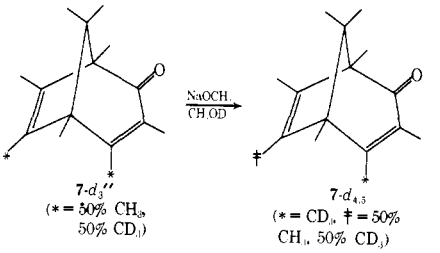
(18) If not, as in the ionization of **6x** in 0.1% acid, D loses a proton to the medium and no label scramble occurs. However, the acidity required to produce E from **6x** is sufficient to equilibrate D with E.

(19) In the labeling experiments with trideuterated precursors, D and D′ are not strictly enantiomers, but with unlabeled or hexadeuterated (vide infra) precursors, they are.

(20) Ketone **7**-d_3 was irradiated to the labeled tetracyclic ketone **12**-d_3[21] which, on treatment with FSO_3H–SO_2ClF at −78°, gave **7**-d_3'' with the label scrambled. This was exchanged with $NaOCH_3$–CH_3OD to give **7**-$d_{4,5}$, and the sequence was repeated several times to give **7**-d_6.



7-d_3 (* = CD_3) **12**-d_3



7-d_3'' (* = 50% CH_3, 50% CD_3) **7**-$d_{4,5}$ (* = CD_3, ‡ = 50% CH_3, 50% CD_3)

(21) H. Hart and G. M. Love, *J. Am. Chem. Soc.*, **93**, 6266 (1971).

(22) We cannot strictly rule out a rearrangement of E to J via cyclopropylcarbinyl intermediates as shown in Scheme IV, followed by rearrangement of J to **8** via a 1,2-bridge shift. It seems unlikely, however, that two mechanistic paths would intervene under identical conditions. We will show (vide infra) that 1,2-bridge shifts can occur in this system, but require a higher temperature.

(23) H. Hart and M. Kuzuya, *Tetrahedron Lett.*, 1969 (1974).

(24) H. Hart and G. M. Love, *J. Am. Chem. Soc.*, **93**, 6264 (1971).

(25) Stronger acid (see Experimental Section for details) gives in addition to **14** and **15** appreciable amounts of pentamethyl- and hexamethylbenzene. Even under the conditions shown, about 5% of aromatic products are formed.

(26) The spectrum shows some temperature broadening, resulting in overlap of the C-1 and C-8′ methyl signals; at −82° the separation of these signals, and especially the sharpening of the C-1 signal,becomes clearer.

(27) The chemical shift of the bridgehead methyl moves slightly downfield, from about δ 1.44 to 1.48.

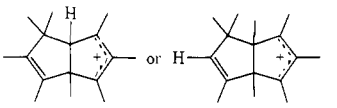
(28) Recall that quenching still gives only **14** and **15**.

(29) The scheme must, of course, be continued to include "secondary" bridging in **12′** and "tertiary" bridging in **12″**, etc.

(30) Double irradiation spin saturation transfer (DISST) has been applied to other dynamic carbonium ion systems; see E. Huang, K. Ranganayakulu, and T. A. Sorensen, *J. Am. Chem. Soc.*, **94**, 1779, 1781 (1972); also, see ref 3.

(31) The reaction was only followed to 35% completion because the reaction was so slow that known[1] subsequent rearrangements of **4** began to occur, and they complicated the NMR spectrum.

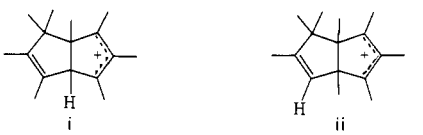
(32) Direct rearrangement of **12** via a cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement of the first formed intermediates in Scheme VI would have given



These products were not observed, although they would be expected to be stable if formed.

(33) Actually, ion J has not been detected nor has the system been entered, yet, at that point. However, the relative stabilities of E < **8** is clear, and it is not possible mechanistically to go from E to **8** via a circumambulation mechanism without passing through J (a more direct 1,2-bridge shift route is ruled out by the labeling results).

(34) Similarly, neither i nor ii, plausible rearrangement products of J, was observed.



i ii

(35) A. F. Diaz, M. Sakai, and S. Winstein, *J. Am. Chem. Soc.*, **92**, 7477 (1970).

(36) Unpublished results with E. M. Shih.