Effect of a Methyl Substituent at the Apical Carbon on the Stability of a Bishomo Pyramidal Carbocation and the Degenerate Rearrangements of the Nonamethylbicyclo[3.2.1]octa-3,6-dien-2-yl Cation

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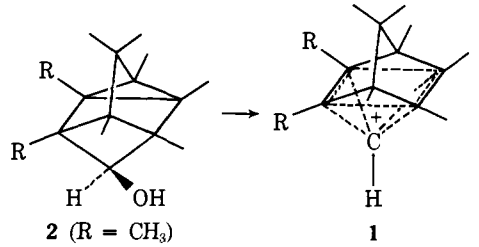
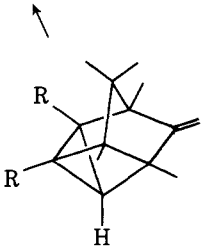
Abstract: The tetracyclic alcohol **8** (1,2,3,4,5,6,7,7,8-nonamethyltetracyclo[3.3.0.0^{2,8}.0^{3,6}]octan-4-ol) and tetracyclic alkenes **9** (4-methylene-1,2,3,5,6,7,7,8-octamethyltetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane and **10** (2-methylene-1,3,4,5,6,7,8,8-octamethyltetracyclo[3.3.0.0.^{3,7}.0^{4,6}]octane), on treatment with FSO_3H–SO_2ClF at temperatures as low as −125°, did not give the expected nonamethyl bishomo $(CH)_5^+$-type pyramidal cation **7**. Instead, the product was the nonamethylbicyclo[3.2.1]octa-3,6-dien-2-yl cation **11**. On quenching, **11** gave triene **14** (2-methylene-1,3,4,5,6,7,8,8-octamethylbicyclo[3.2.1]octa-3,6-diene), from which **11** could be regenerated in FSO_3H–SO_2ClF at <−50°. In strong acid, cation **11** underwent two types of degenerate rearrangements. The faster of these [k(−80°) 31.1 sec^{-1}, $\Delta F^{\ddagger}$ 10.2 kcal/mol, $\Delta S^{\ddagger}$ −14.5 eu/mol, $\Delta H^{\ddagger}$ 7.4 kcal/mol] was detected by changes in the NMR spectrum of **11** between −100 and −50° in FSO_3H–SO_2ClF. It equilibrates the two methyls at C-8 and the methyls at C-2, 3, 4, 6, and 7 but leaves the methyls at C-1 and 5 unique. A circumambulation mechanism (Schemes I and II) accounts for the results. The slower degenerate rearrangement of **11** ($\Delta H^{\ddagger}$ >7.4 but <17.8 kcal/mol) was concealed from NMR detection but was established by deuterium-labeling experiments. It equilibrates the two methyls at C-8 and all the methyls at C-1 through C-7. A 1,2-bridge shift (**11** ⇄ **11′**) accounts for the results. The facile degenerate rearrangements of **11** prevented mechanistic labeling studies of the ionization of **8, 9,** and **10** to **11** under stable-ion conditions. But under nonequilibrating conditions (HCl in aqueous acetone), it was shown by deuterium labeling that **8** is dehydrated to **14** (via **11**) by a contraction of the cyclobutane ring, i.e., cyclobutyl → cyclopropylcarbinyl rearrangement, Scheme IV. A similar path is involved for the rearrangement of **10** to **14.** No evidence for the pyramidal cation **7** as an intermediate in these rearrangements could be found. Apparently replacement of the apical hydrogen in the pyramidal cation **1** by a methyl group facilitates the cyclobutyl → cyclopropylcarbinyl rearrangement more than it stabilizes the pyramidal structure.

In previous papers, we described the preparation of pyramidal carbocation **1**[1] and its diphenyl analog **4**[2] from either alcohol (**2** and **5**) or hydrocarbon precursors (**3** and **6**). The effect of phenyl-for-methyl substitution was to destabilize the ion; whereas **1** was readily prepared at −78° in FSO_3H–SO_2ClF and was stable up to about −50° before it underwent an irreversible rearrangement, **4** rearranged similarly at −100° and could only be prepared by treating its precursors with FSO_3H–SO_2ClF at temperature well below −100°. Other evidence for phenyl destabilization and the reasons for it have been discussed.[2]

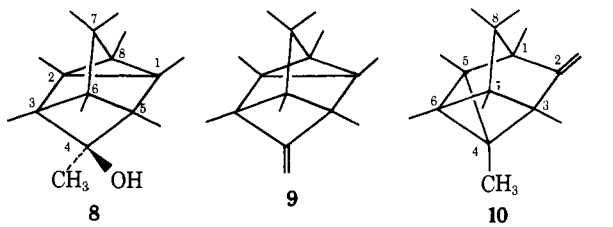


2 (R = CH_3)
5 (R = Ph)
1
4

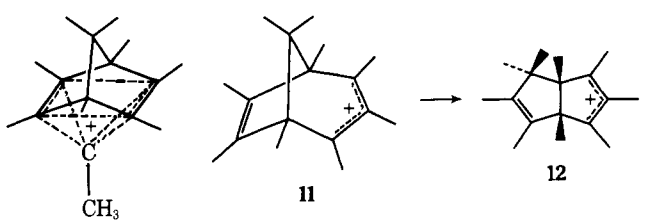


3 (R = CH_3)
6 (R = Ph)

In the present paper, we describe what happened when we tried to prepare the nonamethyl analog of **1** (i.e., **7**) in which the proton attached to the apical carbon of the pyramid is replaced by a methyl group. In fact, we were unable to prepare **7.** Three obvious precursors, **8–10,** gave instead the bicyclic allylic ion **11.** However, ion **11** exhibited quite remarkable behavior in that it underwent two distinct and independent types of degenerate rearrangements, as well as a skeletal rearrangement to **12.** We discuss here in detail the mechanisms of the degenerate rearrangements, as well as the mechanism by which **11** is formed from its various precursors.[3] We defer to a separate paper consideration of the skeletal rearrangement to **12.**



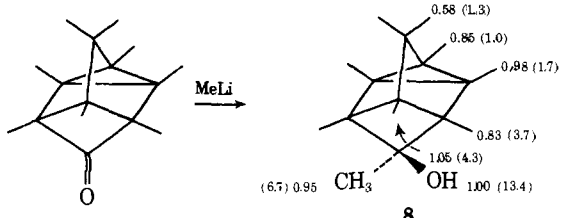
8 **9** **10**



7 **11** **12**

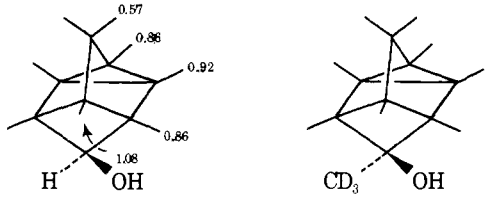
Results and Discussion

Synthesis and Reactions of 8. Treatment of ketone **13**[1,4] with methyllithium afforded a single crystalline alcohol in 85% yield, assigned structure **8**. The NMR assignments

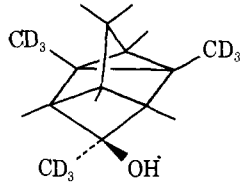


13 **8**

shown on the structure[5] are based on comparison with the corresponding secondary alcohol **2**,[1] as well as on peak areas, deuterium labeling, and Eu-shift slopes. Treatment of **13** with CD_3MgI afforded **8'**, whose NMR spectrum



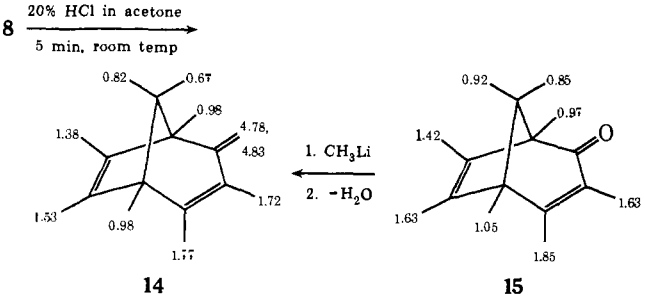
2 **8**



8''

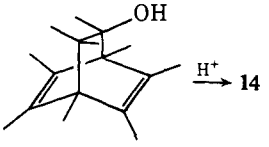
lacked the singlet at δ 0.95, thus assigning that three-proton singlet to the C-4 methyl group. The two remaining three-proton singlets (C-6 and C-8) were easily distinguished by their Eu-shift slopes. For mechanistic reasons (vide infra) it was also necessary to synthesize[6] **8''**; its NMR spectrum lacked the signals at δ 0.95 and 0.98. Thus the six-proton singlet at δ 0.98 was assigned to C-1 and C-2. The six-proton singlets due to C-3 and C-5 and C-7 were then readily distinguished by their chemical- and Eu-shift slope differences. The much larger Eu-shift slope of the C-6 methyl (slope 4.3) than those of the C-1 and C-2 methyls (slope 1.7) is only consistent with the assigned stereochemistry at C-4.

It became apparent very quickly that, in all processes which involve ionization at C-4, the chemistry of the tertiary alcohol **8** is entirely different from that of the secondary alcohol **2**. For example, whereas treatment of **2** with hydrochloric or trifluoroacetic acid gave the corresponding secondary chloride or trifluoroacetate with retention of configuration and maintenance of the integrity of the tetracyclic structure, similar reactions with **8** gave the bicyclic triene **14** in quantitative yield. The structure of **14** was apparent from its spectral properties and its independent synthesis by reaction of the known[1,4] ketone **15** with methyllithium.[7]



14 **15**

Hydrocarbon **14** was also obtained when solutions of the tertiary alcohol **16** (obtained from the corresponding ketone[1] and methyllithium) were passed over silica gel or treated with acid.



16

The presumed immediate precursor of **14** in these rearrangements is the symmetric allylic bicyclic carbocation **11**. In order to study more directly how **8**, with its tetracyclic structure, ionizes to give a product derived from the bicyclic cation **11**, we decided to examine the reaction under stable-ion conditions (i.e., in strong acid).

The Lower Energy Degenerate Rearrangement of Carbocation 11. Circumambulation. Treatment of **8** with FSO_3H–SO_2ClF (1:4) at −78° gave deep-blue solutions with the rather ill-defined NMR spectrum shown in Figure 1. Yet when such solutions were quenched ($NaOCH_3$–CH_3OH),

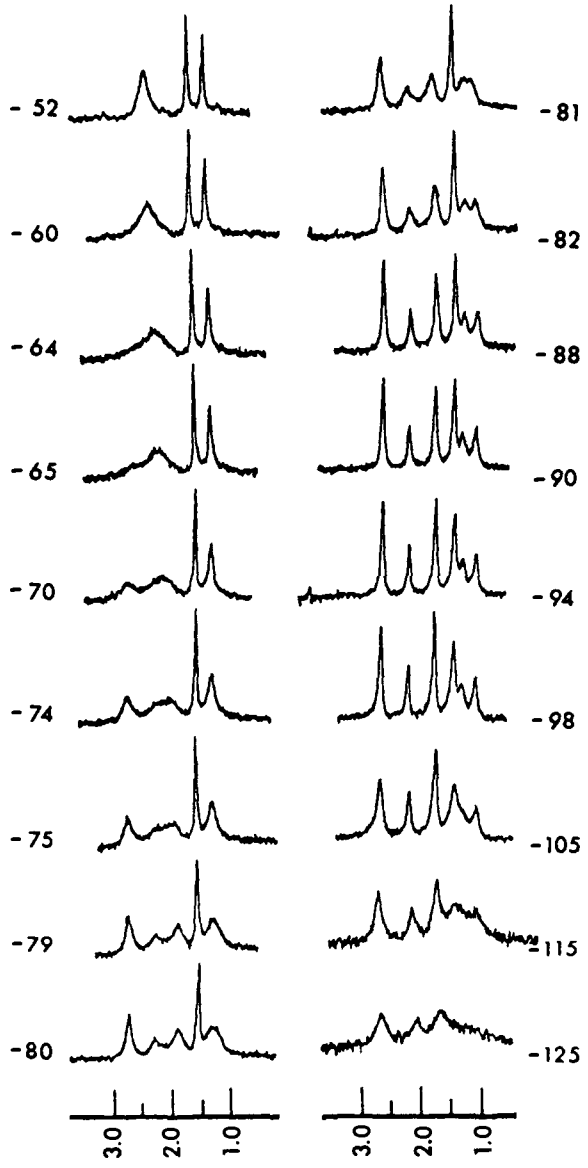
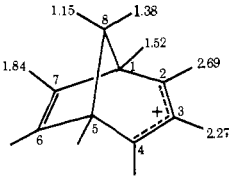


Figure 1. The temperature-dependent ^1H NMR spectrum of **11** in FSO_3H–SO_2ClF (ca. 1:4). In the −90° spectrum, peaks from low to high field are assigned as follows: peak 1 (methyls 2 + 4), 2 (3), 3 (6 + 7), 4 (1 + 5), 5 and 6 (8 and 8').

hydrocarbon **14** was obtained in quantitative yield and, when **14** was returned to FSO_3H-SO_2ClF, the same spectrum was obtained. Thus it seemed likely from the chemical evidence that, despite the seemingly ambiguous NMR spectrum, the species in solution was carbocation **11.** When the



11

temperature was lowered to −90°, an NMR spectrum[9] consistent with the C_s symmetry of **11** was obtained. It had three six-proton singlets and three three-proton singlets, assigned as shown on the structure (the only arbitrary feature of the assignment is at C-8, where we cannot say with certainty whether the lowest field methyl is syn or anti to the positively charged bridge). The C_{2v} structure **7,** which should show only four NMR peaks, is eliminated, and we could obtain no evidence for its formation from **8** even at temperatures as low as −125°.[10]

The changes which occur in the NMR spectrum of **11** as the temperature is raised from ca. −100 to −50° (Figure 1) can be summarized as follows. At −80°, the signals due to the two methyl groups at C-8 have coalesced, and those due to the methyls at C-(2 + 4), C-3, and C-(6 + 7) have broadened. At −74°, the signals due to the C-3 and C-(6 + 7) methyls have coalesced, but the C-(2 + 4) signal is still discrete; at −64°, the peaks due to all five of these methyl groups have coalesced and, at higher temperatures, this signal gradually sharpens. Throughout the entire temperature range, the peak due to the C-(1 + 5) methyls has remained sharp so that at −52° the spectrum consists of three signals: a sharp singlet at δ 1.27 (C-8 methyls), a sharp singlet at δ 1.52 [C-(1 + 5) methyls], and a broad singlet at δ 2.27 [C-(2 + 3 + 4 + 6 + 7) methyls]. These changes are completely reversible and are observed regardless of whether one starts with **8** or **14.** If the solutions are warmed above −50° or are held at that temperature for some time, an irreversible change occurs which will be discussed in a separate paper.

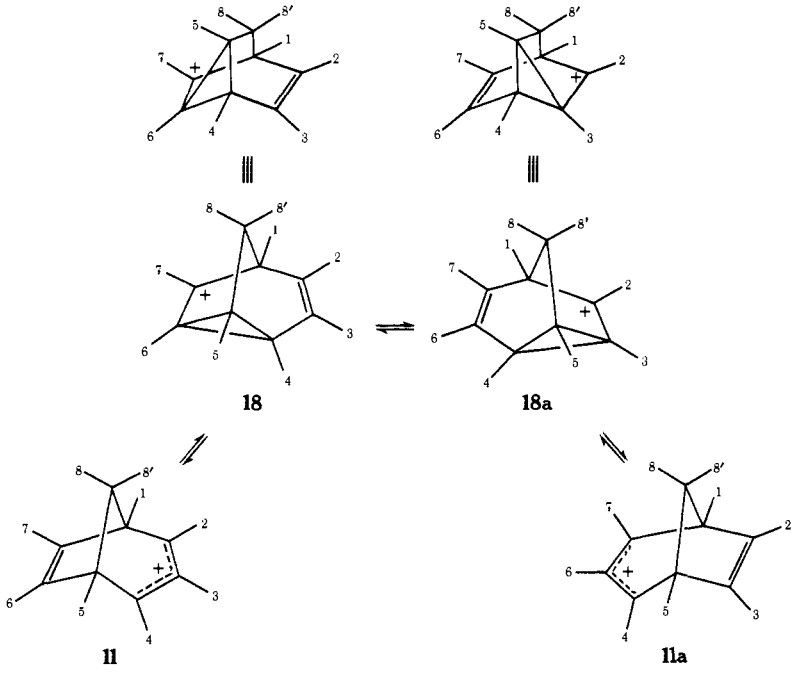
Irradiation[11] at 100 MHz and −80° of any one of the signals at δ 1.84, 2.27, or 2.69 caused a reduction in area of the other two signals. This observation provides confirmatory evidence that these methyls (C-2, 3, 4, 6, and 7) must be equilibrating chemically. But in each of these experiments, the signal at δ 1.52 remained sharp and undiminished in area, confirming that the methyls which give rise to the latter signal (bridgehead methyls C-1 and 5) do not equilibrate, on the NMR time scale, with the methyls at C-2, 3, 4, 6, and 7.

A mechanistic scheme which will rationalize the spectral changes shown in Figure 1 must equilibrate the C-8 methyls, and must equilibrate the C-2, 3, 4, 6, and 7 methyls (3, 6, and 7 slightly faster than 2 and 4), but must leave the C-1 and 5 methyls unique. Scheme I shows one step in such a mechanism (**11** ⇄ **11a**). Methyls 8 and 8′ exchange places, and methyls 2, 3, 4, 6, and 7 have become equivalent, whereas methyls 1 and 5 maintain their unique bridgehead positions. Although methyl 4 has equilibrated with 2, 3, 6, and 7, it will be noted that methyl 4 has the same location (terminus of the allyl cation) in **11** and **11a.** Since **11** has C_s symmetry, the same observation applies to methyl 2 if migration occurs in the opposite sense (Scheme II, structure **11b**). Only if the process is repeated at least once (Scheme II), do the C-2 and 4 methyls find themselves in a different magnetic environment. Consequently this mechanism explains why the peaks corresponding to the C-3 and C-(6 + 7) methyls coalesce first, and that the peak due to the C-(2 + 4) methyls merges with these only at a somewhat higher temperature.

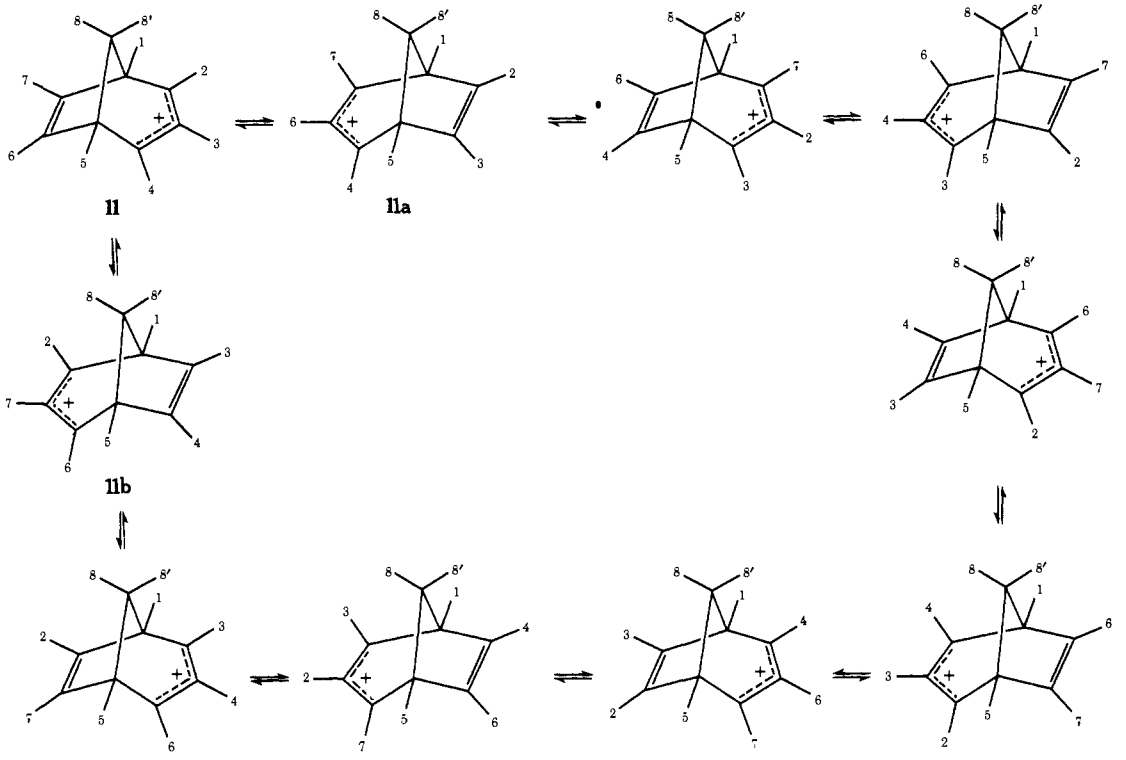
If the process in Scheme I is repeated, equilibration occurs between ten unique but equivalent structures (Scheme II). In this process, the three-carbon group bearing the C-1, 8, and 5 methyls circumambulates around the five-carbon framework, the clockwise (if viewed from the top) sequence 2-3-4-6-7 being maintained in all ten structures.

A related circumambulatory process was postulated several years ago by Winstein and coworkers[12] to rationalize their NMR observations of the 7-norbornadienyl cation **19.** The 7-norbornadienyl cation was found to undergo two distinct equilibrating processes, circumambulation and bridge flipping. In the former process, the "bound" vinyl group (C-2, C-3) maintains its identity but circumambulates

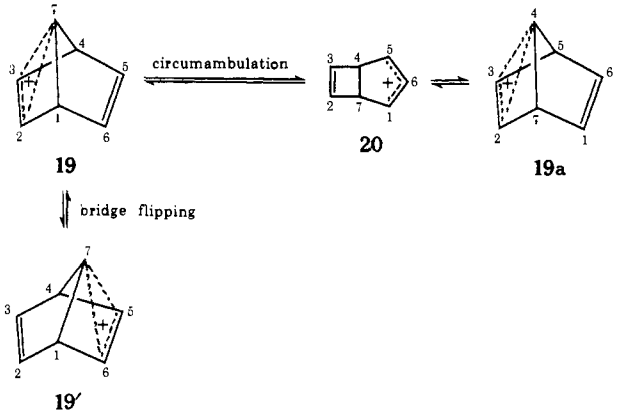
Scheme I



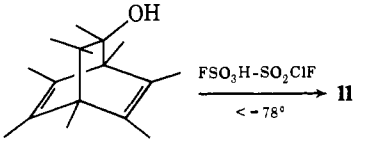
Scheme II



about the five-membered ring (shown by deuterium labeling). The suggested mechanism involved a shift of C-2 from C-1 to C-7 (or C-3 from C-4 to C-7) to form the bicyclo[3.2.0]heptadienyl ion **20.** Ion **20** could not be observed by NMR, even when appropriate precursors were added to FSO_3H at −78°; it rearranged rapidly to **19,** the equilibrium constant for **20** ⇄ **19** being at least 7000 under those conditions. Bridge flipping (**19** ⇄ **19'**) was found to have an activation energy at least 3 kcal/mol higher than that for circumambulation.[13]



The converse relationship between Winstein's results with the 7-norbornadienyl cation **19** and our own results on the bicyclo[3.2.1]octadienyl cation **11** is worth examining. The allylic ion **11** whose circumambulation we observe corresponds in structure to the intermediate **20** proposed, but not observed, by Winstein. The intermediate ion **18** which we propose, but do not observe, corresponds to the 7-norbornadienyl ion **19** whose circumambulation was observed by Winstein. The latter relationship can be better appreciated if ion **18** is written in the form of the bridged structure **18'** ⇄ **18a'** (corresponding to **18** and **18a,** Scheme I). The conversion of **18'** to **18a'** then is the equivalent of the bridge-flipping process. Ion **18** could not be observed directly; attempts to enter the system at this point, using the tertiary alcohol **16,** led only to ion **11.**



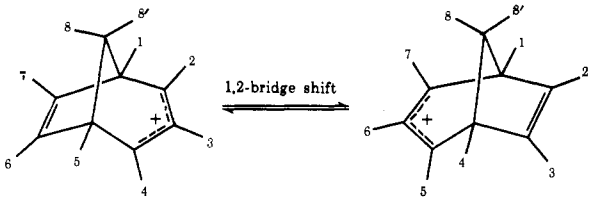
To summarize the comparison, in the bicyclo*octa*dienyl systems, we observe the allylic ion **11** and postulate the bridged ion **18** as a higher energy intermediate to account mechanistically for the observed circumambulation. In the bicyclo*hepta*dienyl system, Winstein et al. observed the bridged ion **19** and postulate the allylic ion **20** as a higher energy intermediate to rationalize the observed circumambulation. Several factors probably contribute to the reversal in energy of the two types of ions as the ring sizes are altered. Replacement of the zero-carbon bridge in **20** by a one-carbon bridge, as in **11,** should decrease ring strain and lead to a net stabilization of the allylic ion. In contrast, the off-center bridging in ion **18',** as compared with the symmetric overlap of the double bond with C-7 in the 7-norbornadienyl cation, should result in a net destabilization of **18** relative to **19.** Both of these effects work to reverse the relative energies of the ions, as depicted in Figure 2.

The activation parameters for the circumambulation of **11** were measured by studying the line shapes of the signals for the C-8 methyl signals as a function of temperature.[14] The rate constant at −80° was 31.1 sec^{-1}, with $\Delta F^{\ddagger}$ 10.2 kcal/mol, $\Delta S^{\ddagger}$ −14.5 eu/mol, and $\Delta H^{\ddagger}$ 7.4 kcal/mol. We regard the activation energy for bridge flipping (**18'** ⇄ **18a'**) to be very small, the major energy barrier to circu-

mambulation being the rearrangement of **11** to **18.** Consequently it is not surprising that, if one enters the system at **18** (that is, **16** + FSO_3H-SO_2ClF), rearrangement to **11** is essentially instantaneous and complete.

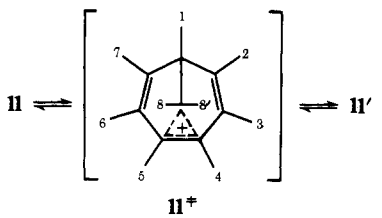
The Higher Energy Degenerate Rearrangement of Carbocation 11. 1,2-Bridge Shifts. The NMR results shown in Figure 1 definitely exclude a 1,2-bridge shift as an NMR-observable process for ion **11,** because this process would not only equilibrate the 8 and 8′ methyls but would also equilibrate *all* the methyls at C-1 through C-7. The spectra in Figure 1 show that the methyls at C-1 and C-5 remain distinct.

This result was surprising, because there is no obvious reason why the interconversion **11** ⇄ **11′**, etc. should not be



11 **11′**

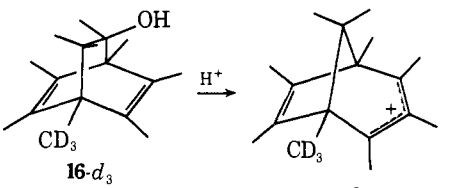
a facile process with a rather low activation barrier. One could imagine it to proceed via the attractive symmetric transition state **11**‡. To test the possibility that such a pro-



11‡

cess was indeed going on but was concealed from NMR detection, we performed the following labeling experiments.

Alcohol **16**-d_3[15] would be expected to ionize with a 1,2 shift to give bridgehead labeled **11**-d_3. If circumambulation



16-d_3 **11**-d_3

were the *only* degenerate rearrangement of ion **11,** one would expect to see an NMR spectrum in FSO_3H-SO_2ClF identical with those in Figure 1 except that the peak at δ 1.52 due to the C-(1 + 5) methyls would be reduced in area by 50%. In fact, the observed spectrum did *not* show such an area decrease but was nearly identical with those in Figure 1. Yet the deuterium was not lost by exchange with the solvent, as shown by a mass spectrum of the resulting **14**-d_3 obtained after quenching, and also by the independent observation that **11** underwent no deuterium incorporation within the limits of NMR detection, on standing in FSO_3D-SO_2ClF at −78° for 3 days. We concluded from these experiments that another intramolecular exchange process must be going on.[16] Another labeling experiment established with certainty that this additional exchange process was the anticipated 1,2-bridge shift.[17]

Treatment of the labeled[6] tetracyclic alcohol **8″** with acid would be expected, by any reasonable mechanism, to first give **11** which is *not* labeled in either bridgehead position. For example, one plausible route from **8** to **11** is via the bridged ion **18′** as shown. This mechanism places CD_3 groups at C-2, 4, and 6 of ion **11.**

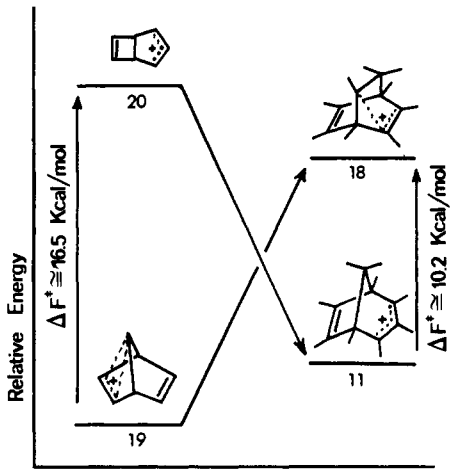
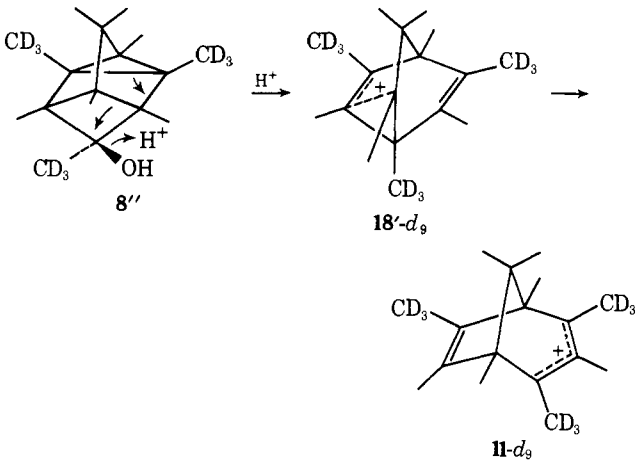
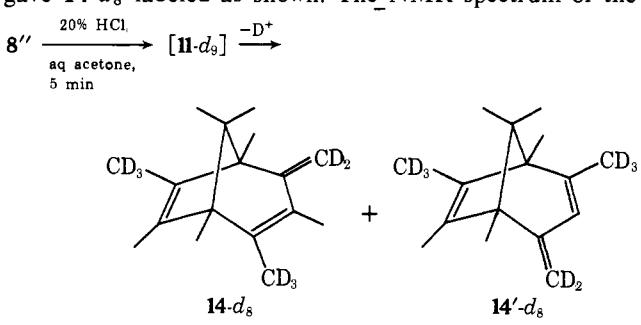


Figure 2. Relative energies of bicyclic and allylic bridged ions. Ion **11** is less strained than ion **20,** whereas charge delocalization (bridging) is more extensive in ion **19** than in ion **18.**



8″ **18′**-d_9 **11**-d_9

This expectation was confirmed experimentally by generating **11**-d_9 from **8″** under nonequilibrating conditions. Thus treatment of **8″** with 20% HCl in aqueous acetone gave **14**-d_8 labeled as shown. The NMR spectrum of the



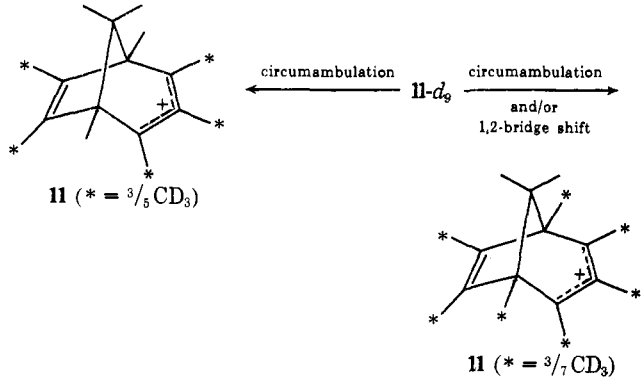
14-d_8 **14′**-d_8

isolated **14** showed that the methyls at C-6 and C-7 were approximately 50% labeled. Some of the label at the C-2 methylene and C-4 methyl was washed out by exchange with the solvent, and each of these positions was approximately 25% labeled. But no label appeared in any other positions; particularly, the area of the signal at δ 0.98 due to the bridgehead methyls was exactly equal to the sum of the areas for the *gem*-dimethyl peaks (δ 0.67 and 0.82). Thus rearrangement of **8″** to **11**-d_9 under nonequilibrating conditions puts no label whatever in the bridgehead positions.

If ion **11**-d_9 were to be prepared from **8″** under equilibrating conditions, and if the only degenerate rearrangement process were circumambulation, one would expect each methyl at C-2, 3, 4, 6, and 7 to be 3/5 labeled. On the other hand, if a bridge shift were to occur, deuterium would also be present in the bridgehead methyl signals (3/7 la-

Table I. A Comparison of the Observed Label Distribution in Ion 11 Derived from 8'' with Predictions for Degenerate Circumambulation and Bridge Shifts

Process	Expected areas of proton NMR signals (1 + 5)	(2 + 4)	(6 + 7)	(3)	(8)	(9)
Circumambulation	6	2.4	2.4	1.2	3	3
Bridge shift	3.4	3.4	3.4	1.7	3	3
Observed	3.4	3.4	3.4	1.7	3	3



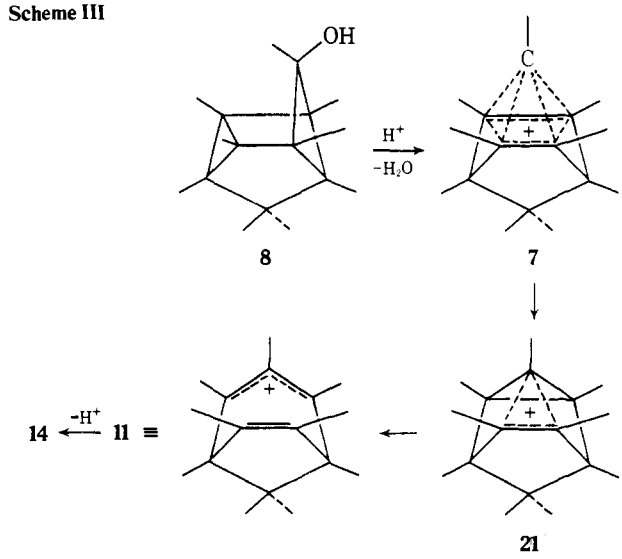
beled). The results obtained experimentally when **8''** was treated at low temperatures with FSO_3–SO_2ClF are compared in Table I with each theoretical prediction. The agreement with the bridge-shift prediction is excellent; particularly diagnostic is the observation that the peak for the C-(1 + 5) methyls had the same area as the peaks for the C-(2 + 4) and C-(6 + 7) methyls, showing that the bridgehead methyls had incorporated the label.

We conclude that, under equilibrating conditions (FSO_3H), ion **11** does in fact undergo rapid 1,2-bridge shifts (**11** ⇄ **11'**, etc.), but that the rate of these shifts is appreciably less than the degenerate circumambulatory rearrangement. We were unable to measure a rate constant for the bridge shift. Up to −50°, there was no indication (Figure 1) in the NMR spectrum of **11** that the C-(1 + 5) methyl peak was broadening or merging with the signal due to methyls at C-(2 + 3 + 4 + 6 + 7). At temperatures above −50°, or in solutions of **11** maintained at that temperature for some time, the skeletal rearrangement of **11** to **12** occurred. Consequently the bridge shift remained concealed from NMR detection and could only be recognized through the labeling results. It is possible to estimate from the DISST study[11] that the bridge shift must be at least 30 times slower than the circumambulatory process. The activation energy for the bridge shift must lie somewhere between the activation energy for circumambulation (7.4 kcal/mol) and that for the skeletal rearrangement of **11** to **12** (17.8 kcal/mol).[18]

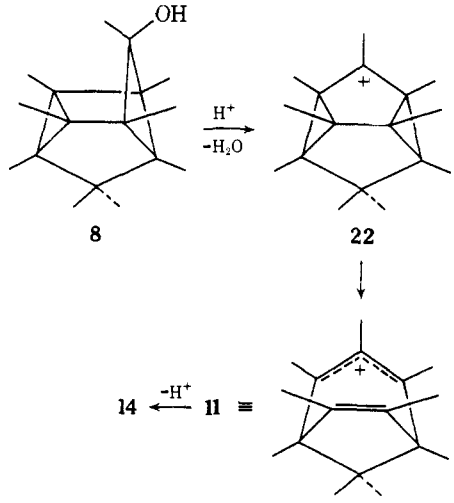
Is the Pyramidal Ion 7 an Intermediate in the Formation of 11 from 8 and Other Precursors? We next address the question of the mechanism by which the bicyclo[3.2.1]octadienyl cation **11** is formed from its tetracyclic precursor, alcohol **8**. Two different mechanisms were considered as likely alternatives (Schemes III and IV). In Scheme III, the first step involves participation by the cyclopropane bond to form pyramidal cation **7**. This is, in fact, the ionization path followed by the secondary alcohols **2** and **5**.[1,2] Ion **21** can be regarded as a discrete species or as one of the resonance contributors to **7**; ring opening of this cyclopropyl cation to allyl cation **11** should be rapid.[19] In Scheme IV, the first step involves contraction of the cyclobutane ring (i.e., cyclobutyl → cyclopropylcarbinyl rearrangement); subsequent or simultaneous ring opening of **22** leads to **11**.[20]

One can in principle distinguish between these two mechanisms by labeling experiments. For example, if the C-4

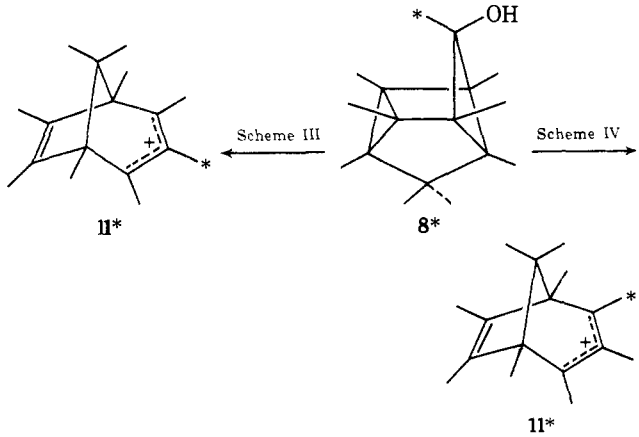
Scheme III



Scheme IV



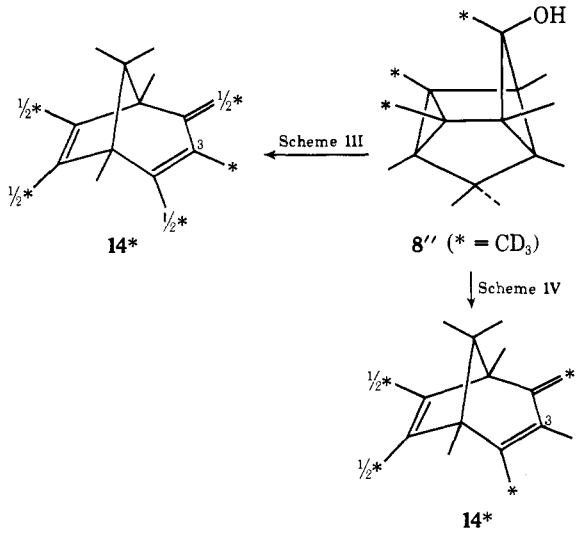
methyl group of **8** were labeled (CD_3), the label would end up in different positions in the resulting **11***. In practice,



however, this approach is invalidated under stable-ion conditions by the rapid degenerate rearrangements of **11**, which we have described in detail. Consequently our experiments had to be confined to conditions under which **11** would be trapped (as **14**) more rapidly than it underwent circumambulation or bridge shifts. Under such conditions, our experiments show that cyclobutane ring contraction (Scheme IV) is the correct mechanism.[22]

One experiment of this type has already been described. Treatment of **8''** with acid in aqueous acetone gave a 50:50 mixture of **14**-d_8 and **14'**-d_8. This result is consistent with

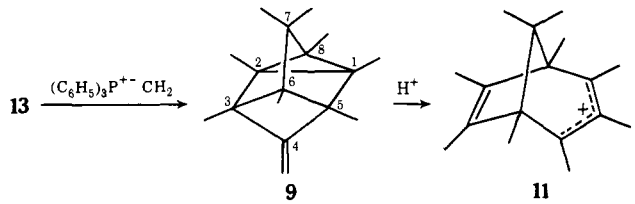
Scheme IV but does not fit the labeling expectation from Scheme III. If Scheme III were correct, the methyl at C-3 in the resulting **14*** should be fully labeled whereas, if



14* **8''** (* = CD_3) **14***

Scheme IV were correct, this methyl group should contain no deuterium, as observed. *We conclude that the pyramidal ion* **7** *is not an intermediate in the formation of* **11** from **8.**

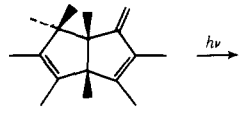
There are other possible synthetic approaches to **7,** two of which we have explored. The Wittig reaction on ketone **13**



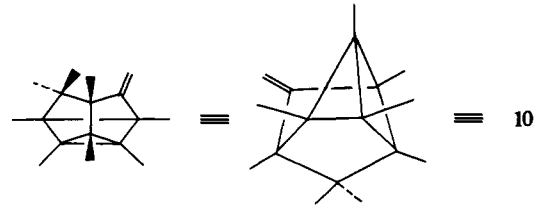
9 **11**

afforded the corresponding methylene compound **9.**[23] Treatment of **9** with FSO_3H–SO_2ClF at low temperatures gave only ion **11.** Consequently both the σ (from **8**) and π (from **9**) routes for generating a positive charge at C-4 of the fully methylated tetracyclic framework lead to contraction of the cyclobutane ring (Scheme IV) and formation of the allylic ion **11.**

With the hope of entering the system at a point which initially might favor the formation of the pyramidal ion **7** by placing positive charge on a carbon at the base of the pyramid, we studied the protonation of **10.** This hydrocarbon was obtained by irradiation of **25,** one of the two trienes



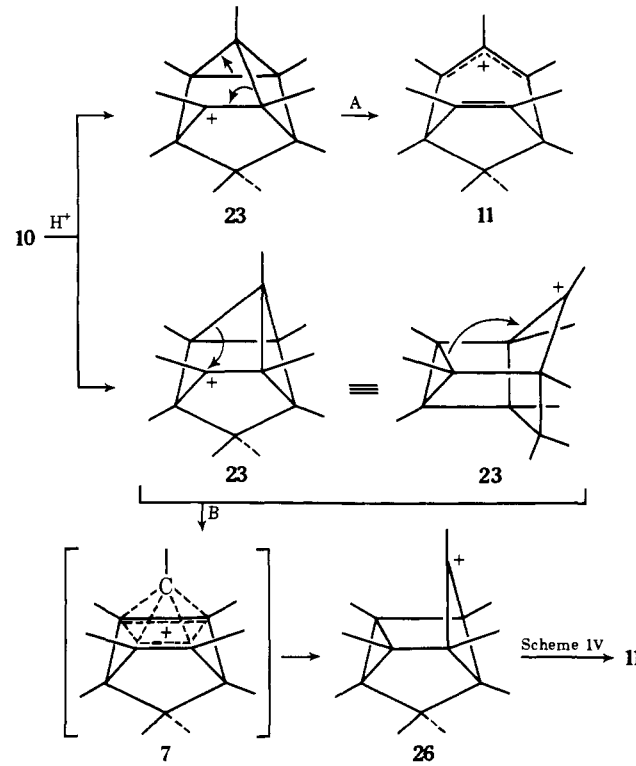
25



10

obtained on quenching ion **12,** the thermal rearrangement product of **11.**[24] There was precedent for our hope since protonation of the analogous hydrocarbons **3** and **6** readily gave the corresponding pyramidal carbocations (**1** and **4,** respectively). However, when **10** was protonated in FSO_3H–SO_2ClF at −125°, the resulting solution had the same navy-blue color characteristic of solutions of **11,** and the NMR spectrum (at −110°) was identical with that of **11**

Scheme V

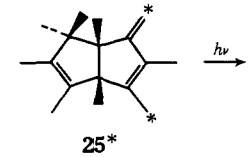


23 **11** **23** **23** **7** **26**

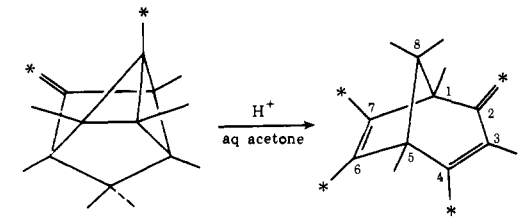
prepared from apparently more direct precursors (**8, 9,** or **14**).

There are two distinguishable routes by which **10,** on protonation, may rearrange to **11.** They are variants, in a sense, of the mechanisms shown in Schemes III and IV and may be expressed as shown in Scheme V (using classical ions for simplicity). The first-formed ion **23** may be considered as one of four equivalent resonance contributors to the pyramidal ion **7.** It can rearrange by opening the four-membered and three-membered rings (path A) or, through β-cyclopropyl participation, by placing the positive charge on the four-membered ring (path B) in the latter case to give the same ion **26** which is more directly formed from **8** or **9.** This ion was shown (vide supra) to rearrange to **11** by cyclobutane ring contraction (Scheme IV). A labeling experiment was performed to distinguish between these alternatives.

Labeled **25** was prepared and irradiated to give **10*** labeled as shown. Treatment of **10*** with 10% HCl in aqueous



25*



10* **14***

acetone at room temperature gave labeled **14.** The expectation for path A would be that the methyl at C-3 should be fully labeled, and the methyls at C-6 and C-7 should be one-third labeled. The expectation for path B would be that the methylene and C-4 methyl should be two-thirds labeled, and the methyls at C-6 and C-7 should be one-sixth labeled. Because of some exchange with the solvent during the rearrangement of **10** to **14,** the observed NMR integration did

not fit either of these expectations ideally, but it clearly ruled out path A; the C-3 methyl was not labeled at all, and the methylene and C-4 methyl were extensively labeled.

The ionization starting from **10** is completely different from that which starts from **8** or **9**. The initially formed ion from **10** is, in a classical sense, a tertiary cyclopentyl ion which, unlike the tertiary cyclobutyl ion from **8** or **9**, will not undergo facile ring contraction. Furthermore, it is one of four equivalent classical contributors to the pyramidal ion **7**, and we have already shown that β-cyclopropyl participation occurs readily in analogous ionizations (**3** → **1**; **6** → **4**).[1,2] Consequently, the pyramidal ion must be an intermediate or transition state along path B. The fact that we could not observe it, even at −125°, is a question of lifetime. Finally, in view of the results with **10** which show that **7** is unstable relative to rearrangement to **26** and **11**, it is unreasonable on energetic grounds for the pyramidal ion to be an intermediate in the ionizations proceeding from **8** or **9**.

The answer to the question posed in the title of this section is that we can find no evidence for the pyramidal cation **7** as a stable intermediate in these ionizations. Apparently, replacement of the apical hydrogen in the well-established pyramidal ion **1** by a methyl group, or presumably any electron donor which would increase the amount of positive charge on the apical carbon atom, facilitates cyclobutane ring contraction very much more than it stabilizes the pyramidal structure. Consequently three likely precursors of the pyramidal ion **7** lead instead to the bicyclo[3.2.1]octadienyl ion **11**, and labeling experiments show that, in all cases, this occurs by a mechanism which involves a cyclobutyl → cyclopropylcarbinyl rearrangement.[25]

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 on a Varian Associates 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. 1:5), sometimes with added methylene chloride or CD_2Cl_2, particularly for temperatures below −100°; either $(CH_3)_4NBF_4$ (δ 3.13) or CH_2Cl_2 (δ 5.30) was used as an internal standard. 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 are uncorrected.

1,2,3,4,5,6,7,7,8-Nonamethyltetracyclo[3.3.0.0^{2,8}.0^{3,6}]octan-4-ol (8). To 20 ml of ether containing 0.22 g (0.01 mol) of methyllithium was added dropwise at 0° a solution of 1.0 g (4.3 mmol) of 1,2,3,5,6,7,7,8-octamethyltetracyclo[3.3.0.0^{2,8}.0^{3,6}]octan-4-one (**13**)[1,4] in 10 ml of ether. The mixture was allowed to warm and was stirred at room temperature overnight. Following the slow addition of water (10 ml), the ether layer, combined with ether extracts, was washed with saturated sodium chloride solution and dried ($MgSO_4$). Removal of the ether under reduced pressure gave 0.9 g (85%) of **8** as colorless crystals (sublimes). This material was sufficiently pure for synthetic use but, for spectral and analytical data, a sample was purified by vapor-phase chromatography (VPC) using a 5 ft × 0.25 in. column, 20% FFAP on Chromosorb W, 170°, 100 ml of He/min, retention time 9 min: ir (KBr) 3450 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 248 (2), 233 (12), 230 (18), 216 (10), 215 (50), 205 (12), 200 (15), 187 (7), 185 (9), 177 (7), 173 (18), 163 (33), 162 (61), 151 (58), 147 (100), 137 (14), 136 (86), 135 (25), 124 (25), 113 (33), 91 (13); NMR (CCl_4),[5] see structure.

Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.14; H, 11.45.

4-Methyl-d_3-1,2,3,5,6,7,7,8-octamethyltetracyclo[3.3.0.0^{2,8}.0^{3,6}]octan-4-ol (8′). The procedure was analogous to that used to prepare **8**, except that CD_3MgI, prepared from 2 g of CD_3I and 360 mg of magnesium, was used in place of methyllithium. The NMR spectrum of the resulting **8′** was identical with that of **8** except that the three-proton singlet at δ 0.95 was absent.

1,2,4-Trimethyl-d_3-3,5,6,7,7,8-hexamethyltetracyclo[3.3.0.0^{2,8}.0^{3,6}]octan-4-ol (8″). The procedure for introducing a CD_3 group at C-1 of **13** has already been described.[1] The resulting **13′** (see footnote 6 for the structure) prepared from 2.0 g of **15′** was dissolved in SO_2ClF at −78° and dropped with stirring into 2 ml of FSO_3H at that temperature. After 5 min, the resulting well-stirred solution was quenched with an ice–water slurry and extracted with methylene chloride. The methylene chloride solution was washed with 5% sodium carbonate, then with water, and dried (Na_2SO_4). Removal of the solvent in vacuo left a yellow oil whose NMR spectrum was identical with that of unlabeled **15** except that the peak at δ 1.85 (C-4 methyl) was reduced in area to 1.5 H, and that at δ 1.63 (C-3 and C-6 methyls) was reduced in area to 4.5 H. This oil was a 50:50 mixture[6] of **15′** and **15″**. This mixture was subjected to the same procedure (exchange with $NaOCH_3$–CH_3OD, irradiation to form the tetracyclic ketone, then treatment with FSO_3H to reform the dienone), and the cycle was repeated four times. In this way, 0.5 g (overall yield 25%) of 1,2-dimethyl-d_3-3,5,6,7,7,8-hexamethyltetracyclo[3.3.0.0^{2,8}.0^{3,6}]octan-4-one (**13″**) was obtained whose NMR spectrum was identical with that of unlabeled **13** except that the six-proton peak at δ 1.04 was absent (since several peaks in unlabeled **13** come very close to one another,[4] the label position was verified using Eu-shift reagent).

In the manner described for the preparation of **8′**, 200 mg of **13″** was allowed to react with CD_3MgI prepared from 400 mg of CD_3I and 72 mg of magnesium in 20 ml of anhydrous ether. The product (180 mg, 85%) consisted of colorless crystals of **8″** whose NMR spectrum was identical with that of unlabeled **8** except that the peaks at δ 0.95 (3 H, C-4 methyl) and 0.98 (6 H, C-1 and C-2 methyls) were absent.

2-Methylene-1,3,4,5,6,7,8,8-octamethylbicyclo[3.2.1]octa-3,6-diene (14). To an ether solution (20 ml) containing 110 mg of methyllithium (3 ml of commercial 1 *M* solution) was added dropwise, at 0°, a solution containing 500 mg of **15**.[1,26] The mixture was allowed to warm to room temperature and was stirred overnight. To effect dehydration of the expected tertiary alcohol, 10 ml of 10% aqueous hydrochloric acid was added dropwise with stirring. The ether layer, combined with ether washings, was washed with saturated sodium chloride solution and dried ($MgSO_4$). Removal of the ether under reduced pressure gave 450 mg (90%) of **14** as a colorless oil. Purification was effected by VPC (5 ft × 0.25 in. column, 20% FFAP on Chromosorb W, 100 ml of He/min, 170°, retention time 6.5 min): ir (CCl_4) 1610 (w), 1600 (m), 900 (s); uv (ethanol) 247 nm (ϵ 13,800); mass spectrum (70 eV) *m/e* (rel intensity) 230 (35), 216 (18), 215 (100), 200 (28), 187 (11), 186 (8), 185 (18), 173 (35), 161 (17), 159 (14), 119 (10); NMR (CCl_4) see structure; the peaks at δ 1.38, 1.53, 1.72, and 1.77 were all quartets; J = ca. 1 Hz because of homoallylic coupling; other signals were singlets.

Anal. Calcd for $C_{17}H_{26}$: C, 88.62; H, 11.38. Found: C, 88.58; H, 11.27.

Reaction of 8 and 8″ with Hydrochloric Acid. A solution containing 40 mg of **8** in 1 ml of 20% aqueous hydrochloric acid diluted with 2 ml of acetone was allowed to stand at room temperature for 5 min. The mixture was diluted with water and extracted with methylene chloride. This extract was washed with 5% sodium carbonate and water and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave a pale-yellow oil whose NMR spectrum was identical with that of authentic **14.**

If **8″** was used in place of **8** in the above procedure, the resulting labeled **14** had an NMR spectrum identical with that of unlabeled **14** except that the peaks at δ 1.38 and 1.53 (C-6 and C-7 methyls) were reduced in area to ca. 1.5 H each. The peaks at δ 1.77 (C-4 methyl) and 4.78, 4.83 (vinyl protons) were also reduced in area to about 1.5, 0.75, and 0.75 H, respectively. The product is considered to be a 50:50 mixture of **14**-d_8 and **14′**-d_8 with some back exchange at the C-4 methyl and vinyl protons.

1,2,3,4,5,6,7,8,8-Nonamethylbicyclo[2.2.2]octa-2.5-dien-7-ol

(**16**). To an ether solution (30 ml) containing 0.33 g of methyllithium was added dropwise, at 0° with stirring, a solution of 1.5 g of 1,2,3,4,5,6,8,8-octamethylbicyclo[2.2.2]octa-2,5-dien-7-one.[1,26] The mixture was allowed to warm to room temperature and stir overnight. Water was added slowly to hydrolyze the excess methyllithium. The ether layer, combined with washings, was washed with saturated sodium chloride and dried ($MgSO_4$). Removal of the ether under reduced pressure gave 1.30 g (81%) of **16** as colorless crystals, mp 81–82°. Further purification by VPC was not possible because of bridge cleavage (to hexamethylbenzene): ir (KBr) 3550 (br, OH) cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 248 (2), 162 (50), 147 (100), 104 (62), 76 (57); NMR (CCl_4)[5] δ 0.70 (2.4), 0.73 (1.8), 0.85 (5.1), 1.30 (1.0), 1.35 (2.4), 1.62 (1.5), 1.62 (1.2), 1.68 (1.0). All peaks were three-proton singlets in the europium-shifted spectrum except that at δ 1.68, which integrated for six protons.

Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.12; H, 11.40.

4-Methyl-d_3-1,2,3,5,6,8,8-heptamethylbicyclo[2.2.2]octa-2,5-dien-7-one. A mixture of 1.0 g of 5-methyl-d_3-2,3,4,6,6-pentamethyl-2,4-cyclohexadienone[27] and 0.60 g of 2-butyne was heated at 220° in a thick-walled sealed glass tube for 3 days, then worked up as previously described[1,26] to give 0.90 g (70%) of the desired bicyclic ketone as a pale-yellow oil which crystallized on chilling to nearly colorless crystals. Its NMR spectrum was identical with that of the unlabeled ketone[26] except that the singlet at δ 1.35 due to the C-4 methyl was absent.

4-Methyl-d_3-1,2,3,5,6,7,8,8-octamethylbicyclo[2.2.2]octa-2,5-dien-7-ol (16-d_3). The procedure was analogous to that given for **16**. From 320 mg of 4-methyl-d_3-1,2,3,5,6,8,8-heptamethylbicyclo[2.2.2]octa-2,5-dien-7-one, there was obtained 180 mg (84%) of **16**-d_3 whose NMR spectrum was identical with that of authentic **16** except that the singlet at δ 1.30 was absent.

Reaction of 16 and 16-d_3 with Hydrochloric Acid. A solution of **16** (20 mg) in 0.5 ml of 0.1% hydrochloric acid diluted in 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 water and dried (Na_2SO_4). The pale-yellow oil obtained by concentration of the methylene chloride under reduced pressure had an NMR spectrum identical with that of **14**. When **16**-d_3 was used in place of **16**, the resulting **14**-d_3[17] had an NMR spectrum identical with that of **14** except that the peak at δ 0.98 (C-1 and C-5 methyls) integrated for only 3 H.

Nonamethylbicyclo[3.2.1]octa-3,6-dien-2-yl Cation (11). Approximately 50 μl. of FSO_3H was placed in a 5-mm diameter NMR tube, cooled to −78°, and approximately 200 μl. of SO_2ClF was condensed above the acid. A methylene chloride solution containing 30 mg of the precursor to **11** (i.e., **8**, **9**, **10**, **14** or **16**) was placed in the tube above the SO_2ClF layer and allowed to stand at −78° for 5 min. About 50 μl. of methylene chloride was used for all precursors except **8**, whose lower solubility required 100 μl. of solvent. For studies of the temperature-dependent NMR spectrum of **11**, CD_2Cl_2 was used in place of CH_2Cl_2 since the latter freezes at −97°. The contents of the NMR tube were then mixed using a "super-mixer" (Matheson Scientific, Catalog No. 60100-05) to give a navy-blue solution of cation **11**. For its NMR spectrum, see the structure in the text and Figure 1. Spectra from all precursors were identical except with **16**, which showed some minor contaminant peaks, probably due to cleavage of the C-7,C-8 bridge.

A slight modification of the above procedure was used to study the protonation of **10** at −125°. FSO_3H (50 μl.) and SO_2ClF (200 μl.) were well mixed at −78° using the "super mixer", a thin-glass stirring rod was inserted in the NMR tube, and the solution was cooled to − 125 ± 5° (liquid nitrogen–pentane slurry). Approximately 50 μl. of SO_2ClF was condensed on the mixture's surface, a solution of 22 mg of **10** in 50 μl. of CD_2Cl_2 was added and, after the contents were thoroughly cooled to −125°, they were mixed with the stirring rod. The navy-blue color of **11** was immediately apparent. This procedure had been successful in preparing **4**,[2] which is only stable below −100°.

A solution of **11** prepared from **8** as described above was quenched by dropping it quickly into a suspension of excess sodium methoxide in methanol at −78°. The resulting suspension was slowly warmed to room temperature. The residue obtained by concentrating the methanol under reduced pressure was treated with water and extracted thoroughly with ether. Combined ether layers were washed with saturated sodium chloride and dried ($MgSO_4$). Removal of the ether under reduced pressure gave as the sole product **14**, identical in all respects with an authentic sample.

Treatment of **16**-d_3 with FSO_3H–SO_2ClF at −78° as described above gave a solution of **11**-d_3 whose NMR spectrum was nearly identical with that of **11**, the peaks assigned to the C-1 through C-7 methyls being only slightly and uniformly reduced in area (about 10–15%) relative to the peaks assigned to the C-8 methyls. A mass spectrum of the resulting **14**-d_3 obtained on quenching this solution showed that the label was still present (M^+ 233).

Treatment of **8**″ with FSO_3H–SO_2ClF at −78° as described above gave a solution of **11**-d_9 whose NMR spectrum was identical with the temperature-dependent spectra shown in Figure 1 except that the peaks assigned to the C-1 through C-7 methyls were reduced in area by ca. 3/7 relative to the peaks due to the C-8 *gem*-dimethyl group. When this solution was quenched with excess $NaOCH_3$–CH_3OH at −78° and worked up as described above, the resulting **14**-d_8 had an NMR spectrum identical with that of authentic **14** with the following exceptions: the peaks at δ 0.98, 1.38, 1.53, 1.72, and 1.77 were reduced in area by 3/7 relative to the peaks at δ 0.82 and 0.67, the peaks at δ 4.78 and 4.83 were also reduced, by about 1/7 (possibly some of the label was washed out during quenching), and all the allylic methyl peaks (δ 1.38, 1.53, 1.72, 1.77) were now fairly sharp and showed no homoallylic coupling.

4-Methylene-1,2,3,5,6,7,7,8-octamethyltetracyclo[3.3.0.0^{2,8},0^{3,6}]octane (9).[23] Ketone **13**[1,4] (232 mg, 1 mmol) was stirred for 3 days at room temperature with a fourfold excess of methylene triphenylphosphorane prepared by stirring 168 mg of 57% sodium hydride (96 mg of NaH) in 1.2 ml of dimethyl sulfoxide (DMSO) with 1.57 g of triphenylmethylphosphonium bromide in 2.0 ml of DMSO. The reaction mixture was poured into water and extracted with benzene. Combined benzene extracts were washed thoroughly with water and dried (Na_2SO_4). Removal of the benzene under reduced pressure gave a nearly quantitative yield of **9** which was purified by VPC (5 ft × 0.25 in. column, 20% FFAP on Chromosorb W, 100 ml of He/min, 120°, retention time 5 min): ir (CCl_4) 1675 (m), 870 (s) cm^{-1}; uv (ethanol) only end absorption; mass spectrum (70 eV) *m/e* (rel intensity) 230 (15), 215 (100), 200 (34), 185 (32), 173 (49), 149 (23); NMR (CCl_4) δ 0.68 (s, 6 H, C-7 methyls), 0.73 (s, 3 H, C-6 methyl), 0.90 [s, 12 H, C-(1 + 2 + 3 + 5) methyls], 0.93 (s, 3 H, C-8 methyl), 4.15 (s, 2 H, vinyl).

Anal. Calcd for $C_{17}H_{26}$: C, 88.62; H, 11.38. Found: C, 88.51; H, 11.09.

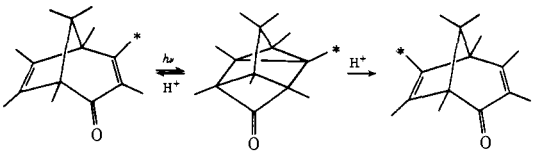
Reaction of 10-d_5 with Hydrochloric Acid. 4-Methyl-d_3-2-methylene-d_2-1,3,5,6,7,8,8-heptamethyltetracyclo[3.3.0.0^{3,7}.0^{4,6}]octane (**10**-d_5) was prepared by irradiation of **25**-d_5.[28] The latter, in turn, was prepared from unlabeled **25**[24] by reaction with CF_3CO_2D at room temperature for 5 min.[29] The C-4 methyl in the resulting **10**-d_5 was fully labeled, and the methylene group was about 50% labeled. A solution containing 40 mg of **10**-d_5 in 1 ml of 10% aqueous hydrochloric acid diluted with 2 ml of acetone was allowed to stand at room temperature for 1 hr. Work-up as in the reaction of **8** with hydrochloric acid gave a nearly quantitative yield of labeled **14** whose NMR spectrum was identical with that of unlabeled **14** except that the peak at δ 1.77 (C-4 methyl) was decreased in area to less than 50% of that for the other allylic methyls (δ 1.38, 1.53, and 1.72). The vinyl proton signal (δ 4.78, 4.83) was also noticeably reduced in area. The signal at δ 1.72 had its full intensity relative to the aliphatic methyl signals.

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

References and Notes

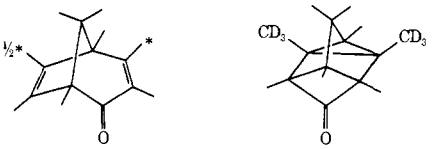
(1) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **96**, 6436 (1974); for preliminary report, see H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **94**, 8958 (1972).
(2) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, preceding paper.
(3) For preliminary accounts for portions of this work, see (a) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **95**, 4096 (1973); (b) M. Kuzuya and H. Hart, *Tetrahedron Lett.*, 3887 (1973).
(4) H. Hart and G. M. Love, *J. Am. Chem. Soc.*, **93**, 6266 (1971).
(5) 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); D. R. Kelsey, ibid., **94**, 1764 (1972).

(6) Label was introduced at C-1 and C-2 by irradiating labeled ketone **15′** to give **13′** which, on treatment with strong acid, rearranged to a 50:50 mixture of **15′** and **15″**. This mixture was treated with $NaOCH_3$–CH_3OD



15′ (* = CD_3) 13′ 15″

to give **15‴**, and the above cycle was repeated several times to give **13‴** which then was treated with CD_3MgI to give **8″**.



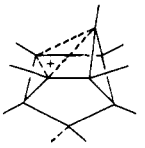
15‴ (* = CD_3) 13″

(7) The NMR assignments shown on structure **14** follow from a comparison of chemical shifts with those of related compounds such as **15** (whose assignments have been firmly established)[2] and analogous [3.2.1] hydrocarbons with a methyl substituent at various positions replaced by a hydrogen,[8] as well as by consistency with numerous deuterium-labeling experiments to be described. The only arbitrary assignment is that of the C-8 methyls, where the signal at highest field (δ 0.67) is ascribed to the methyl group syn to the three-carbon bridge (more extended π system; in ketone **15**, this assignment is confirmed by Eu-shift data).

(8) H. Hart and M. Kuzuya, unpublished observations.

(9) N. C. Deno in "Carbonium Ions", Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1970, p 796; see also K. Rajeswari and T. S. Sorensen, *J. Am. Chem. Soc.*, **95**, 1239 (1973), and *Can. J. Chem.*, **50**, 1293 (1972).

(10) Other structures with C_s symmetry, such as **17** or **21**, are readily eliminated by the chemical-shift data and quenching results.



17

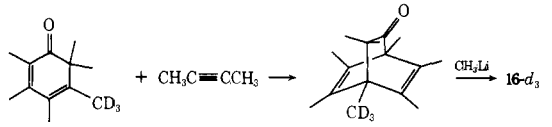
(11) The double irradiation spin saturation transfer (DISST) technique has been applied to other carbonium ions; see E. Huang, K. Ranganayakulu, and T. A. Sorensen, *J. Am. Chem. Soc.*, **94**, 1179, 1781 (1972).

(12) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6350 (1967).

(13) Bridge flipping could, however, be made the lower energy process by appropriate substitution (CH_3, Ph, OCH_3) at C-7; M. Brookhart, R. K. Lustgarten, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6352, 6354 (1967).

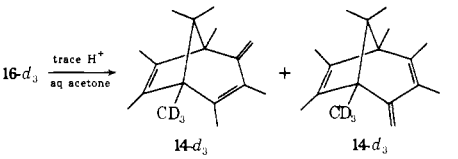
(14) The NMR pattern was compared at five temperatures (from −57 to −88°) with theoretical curves for cyclohexane-d_{11}; F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1969, p 188.

(15) Synthesized as follows:



(16) If this process were the anticipated 1,2-bridge shift, then the 3 deuteriums would be equilibrated with 18 protons, and one would expect the signals at δ 1.52, 1.84, and 2.69 to be reduced in area by $^2/_7$ and that at δ 2.27 to be reduced in area by $^1/_7$ relative to the internal reference of the C-8 methyls (δ 1.15 and 1.38). The ratios of the areas of the peaks due to C-(1 + 5), C-(2 + 4), C-(6 + 7), and C-3 were the same as they were in unlabeled **11**, and they were all decreased somewhat relative to the C-8 methyls, but the accuracy of the measured areas was not sufficient to say that the area reduction was exactly the $^1/_7$ or $^2/_7$ expected for 1,2-bridge shifts.

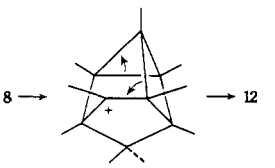
(17) When **16**-d_3 was treated with just a trace of acid (0.1% HCl in aqueous acetone, room temperature, 15 min), the product was an equimolar mixture of the two bridgehead-labeled **14**-d_3's. Consequently under



these conditions, it is possible to capture **11**-d_3 before it has an opportunity to undergo either circumambulation or 1,2-bridge shifts.

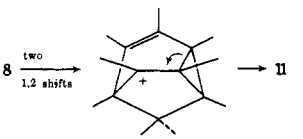
(18) M. Kuzuya and H. Hart, *Tetrahedron Lett.*, 3891 (1973).

(19) One could express the mechanism in Scheme III in classical ion terms as follows:



23

(20) The conversion of **22** to **11** in a concerted manner is actually a ground-state forbidden process,[21] suggesting perhaps that the first step involves direct formation of **24**.



24 (≡ 18)

(21) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970, p 65.

(22) We cannot, however, distinguish between the various timing alternatives implicit in either of these mechanisms.[19,20]

(23) H. Hart and M. Kuzuya, *Tetrahedron Lett.*, 1909 (1974).

(24) H. Hart and M. Kuzuya, *Tetrahedron Lett.*, 3891 (1973).

(25) This type of ring contraction is facile even in the simplest case, i.e., the 1-methylcyclobutyl cation; M. Saunders and J. Rosenfeld, *J. Am. Chem. Soc.*, **92**, 2548 (1970); G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, ibid., **94**, 146 (1972). For a general discussion, see K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1972, p 1295.

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

(27) H. Hart, P. M. Collins, and A. J. Waring, *J. Am. Chem. Soc.*, **88**, 1005 (1966).

(28) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **96**, 3709 (1974).

(29) Detailed procedures for these reactions will be presented in a more appropriate setting; i.e., in the full papers to be based on references 24 and 28.