solvent was evaporated. The remaining oil was analyzed by nmr. Integration of the signals of the vinylic protons was repeated several times, and the average value was used for calculating k_{isom}. Another part of the mixture was potentiometrically titrated with silver nitrate. Rate coefficients were calculated by using a regression program.

Stabilities of 4-E and 4-Z. Control experiments on the stability

of a 80:20 mixture of **4-E** and **4-Z** showed that no change in the relative intensities of the signals for the vinylic protons was observed after 48 hr at 10° in chloroform or in AcOH-NaOAc.
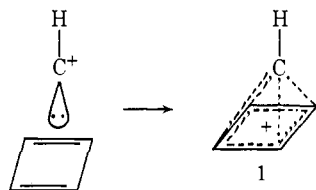
Preparation and Reactions of a Bis-Homo-(CH)₅⁺-Type Carbocation

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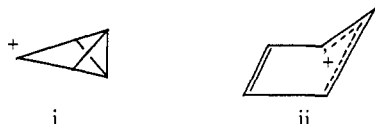
Abstract: The pyramidal carbocation **7** was formed in two ways, either by ionization of secondary alcohol **9** in FSO₃H-SO₂ClF (1:4) or by protonation of the alkene **43** in the same solvent, both at temperatures below −40°. The symmetry of the pmr and cmr spectra of **7** was consistent with the pyramidal structure and was not perturbed at temperatures as low as −120°; therefore, if the ion has the classical structure **18′′**, equilibration between equivalent structures must be rapid at −120°. Although spectra show that the positive charge resides mainly at the "basal" carbon atoms, ion **7** is quenched exclusively at the apical position, giving either **9** (with water) or **16** (with methanol). Between −45 and −30°, **7** rearranges to **24**, whose structure was proved by quenching in methanol to give **25** which thermally eliminated methanol to give the triene **26**. The mechanism of the rearrangement of **7** to **24** was elucidated by deuterium labeling (*i.e.*, **7′** → **24′**); kinetic studies show that $\Delta F^{\pm}$ for the process is 16.7 kcal/mol. Above −30° and below 0° ion **24** rearranges to **35** whose structure was proved by quenching in methanol to give **36** which thermally eliminated methanol to give the trienes **37, 38,** and **39**. The mechanism of the rearrangement of **24** to **35**, established by deuterium labeling, involves a succession of 1,2-shifts of one five-membered ring with respect to the other (circumambulation). Treatment of alcohol **9** with trifluoroacetic acid above 10° gave the pentadienyl cation **42**, whose structure was established by quenching to a mixture of **37, 38,** and **39**. Labeling experiments establish the mechanistic sequence **9** → **7** → **24** → **35** → **37** → **42** for this series of rearrangements. Protonation of **37** in FSO₃H at −78° gives mainly **35** but in TFA at room temperature gives **42**. Irradiation of **26** in ether through Vycor gave **43** which, in addition to being a suitable precursor of **7**, gave the secondary chloride **13** or trifluoroacetate **17** with hydrochloric acid or TFA, respectively. The same chloride and trifluoroacetate were obtained from **9**, and deuterium labeling experiments show that during the latter process the relative positions of the three- and four-membered rings interchange, presumably *via* a symmetric intermediate such as **7**.

Stohrer and Hoffmann[1] made the imaginative suggestion that the most stable structure for the (CH)₅⁺ cation is the square pyramid **1**.[2] In a formal sense, **1**

could be formed by bringing protonated carbon (HC:⁺) toward the center of a face of square cyclobutadiene. The symmetries of the cyclobutadiene and sp-hybridized CH⁺ orbitals are correct for stabilizing this six-electron system. Experimental evidence for a disubstituted **1** with a methyl group at the apex and at one "basal" carbon has appeared.[5]

Various homologs of **1** can be envisioned; **2–6** are

and phenyl substituents are predicted[3c] to stabilize both **1** and ii.

iii iv v

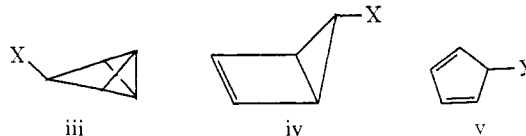(1) W-D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972).

(2) This prediction arose from extended Hückel calculations on the cation i by examining the energy of the system as the central bicyclobutane bond is stretched. More recent calculations using the CNDO[3a] or MINDO/3[3b] methods indicate that the monocyclic nonplanar allyl cation ii also constitutes an energy minimum on the (CH)₅⁺ surface, but there is some disagreement as to which, **1** or ii, has the lower energy. The calculations do indicate that iii and iv are preferred precursors of **1** whereas ionization of v would most likely lead to ii.[4] Methyl


i ii

(3) (a) H. Kollmar, H. O. Smith, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 5834 (1973); (b) M. J. S. Dewar and R. C. Haddon, *ibid.*, **95**, 5836 (1973); (c) W. J. Hehre and P. v. R. Schleyer, *ibid.*, **95**, 5837 (1973).

(4) For experimental evidence, see R. Breslow and J. M. Hoffmann, Jr., *J. Amer. Chem. Soc.*, **94**, 2110 (1972); M. Saunders, R. Berger, A. Jaffe, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffmann, Jr., C. Perchonock, E. Wasserman, R. S. Hutton, and V. J. Kuck, *ibid.*, **95**, 3017 (1973).

(5) S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *J. Amer. Chem. Soc.*, **94**, 8956 (1972).

examples.[6] The larger ring sizes should stabilize 2–6 relative to 1, but this effect may be counteracted by


2   3   4

5   6
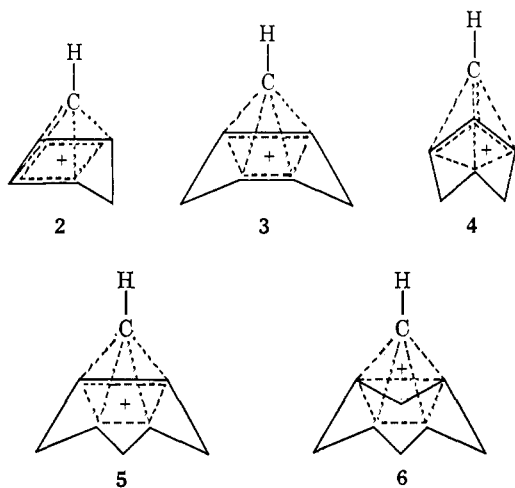
decreased orbital overlap which the larger internuclear distances may engender. We wish to present here a full account of the preparation by two routes of the pyramidal octamethyl cation 7, a derivative of the

7
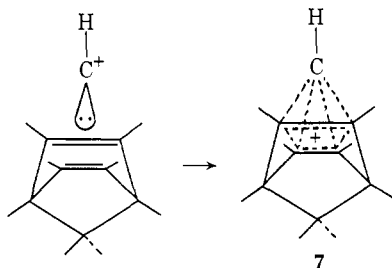
system represented by 3.[7,8] This ion can be viewed as having been derived formally from HC:+ and octa-

(6) In general, interaction of HC:+ with any system containing two interacting double bonds (or a double bond and a cyclopropane bond, etc.) could lead to some energy minimum, as in 1. Thus 3 can be imagined as arising from HC:+ and boat 1,4-cyclohexadiene. Antiaromatic systems will be stabilized by such an interaction. A striking example is the recent synthesis of the remarkably stable dication vi,

vi
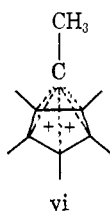
which can be viewed as arising from (CH₃)C:+ and the flat, antiaromatic pentamethylcyclopentadiene cation. H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 1665 (1973); *J. Amer. Chem. Soc.*, **96**, 2208 (1974). Analogously, tetrahedrane can be viewed as the covalent representation of the product from HC:+ and the antiaromatic cyclopropenyl anion. Indeed, since the interaction of HC:+ with the antiaromatic moiety to form species such as vi, 1, or tetrahedrane involves, in the simplest Hückel model, stabilization of highest occupied degenerate orbitals which are bonding, nonbonding, and antibonding, respectively, one might expect that the stability order of the resulting species will be (CH)₆²⁺ > (CH)₅⁺ > (CH)₄ (tetrahedrane). The observed relative stabilities of vi and dimethyl-1 are consistent with this prediction, though the different degree of methyl substitution in the two ions undoubtedly also contributes to their stability difference. The validity of these theoretical arguments is being explored.

(7) Preliminary accounts of portions of this work have appeared: (a) H. Hart and M. Kuzuya, *J. Amer. Chem. Soc.*, **94**, 8958 (1972); (b) *Tetrahedron Lett.*, 4123 (1973).

(8) A preliminary account of the preparation of 3 has appeared: S. Masamune, M. Sakai, A. V. Kamp-Jones, H. Ona, A. Venot, and T. Nakashima, *Angew. Chem., Int. Ed. Engl.*, **12**, 769 (1973); see also R. K. Lustgarten, *J. Amer. Chem. Soc.*, **94**, 7602 (1972).

methylnorbornadiene; the molecular orbital arguments for its stability are analogous to those for 1. We also describe here the reaction of 7 with nucleophiles, the unimolecular rearrangement of 7, and a number of other related carbonium ion and photochemical transformations. The starting point for our studies was the tetracyclic alcohol 9.

Results and Discussion

Synthesis and Pmr Assignments of Alcohol 9. The sole reduction product of the tetracyclic ketone 8[9] is the crystalline exo-alcohol 9. Jones oxidation of 9

8   9
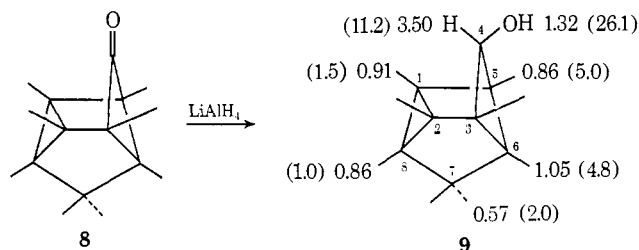
gave 8, showing that no skeletal rearrangement had occurred during the reduction. The pmr assignments shown on the structure[10] were made in the following way. The spectrum consisted of singlets at δ 0.57 (6 H), 0.86 (9 H), 0.91 (6 H), 1.05 (3 H), 1.32 (1 H, exchangeable with D₂O), and 3.50 (1 H). Reduction with lithium aluminum deuteride gave a product lacking the signal at δ 3.50. With shift reagent, the signal at δ 0.86 split into two singlets, one of which (6 H) moved downfield much farther than the other (3 H). The three six-proton peaks were not split by shift reagent, consistent with the symmetry of 9.

The distinction between the six-proton peaks at δ 0.86 and 0.91 was made on the basis of the following labeling experiments. Treatment of ketone 10[9] with NaOCH₃ in CH₃OD gave the trideuterioketone 10′ which, on irradiation, gave the labeled tetracyclic ketone 8′. Reduction of 8′ gave the secondary alcohol 9′ in which the

10   10′

8′   9′
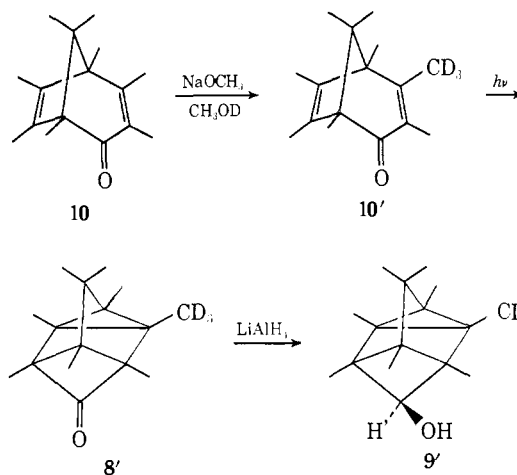
singlet at δ 0.91 was reduced in area to three protons. Consequently this signal must be due to the methyls at C1 and C2.

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

(10) All chemical shifts are in parts per million (δ) from tetramethylsilane (TMS). Numbers in parentheses are the relative extents to which these signals are shifted downfield by Eu(fod)₃[11,12] shift reagent.

(11) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).

(12) D. R. Kelsey, *J. Amer. Chem. Soc.*, **94**, 1764 (1972).

Hart, Kuzuya | A Bis-Homo-(CH)₄⁺-Type Carbocation

The labeled dienone **11**,[13] on treatment with 2-butyne, gave **12** which rearranged in acid to **10''**, in which the label was equally distributed between the C3 and C7 methyl groups. Irradiation of **10''** gave **8''** which was reduced to **9''**, in which the peak at δ 0.86 was reduced
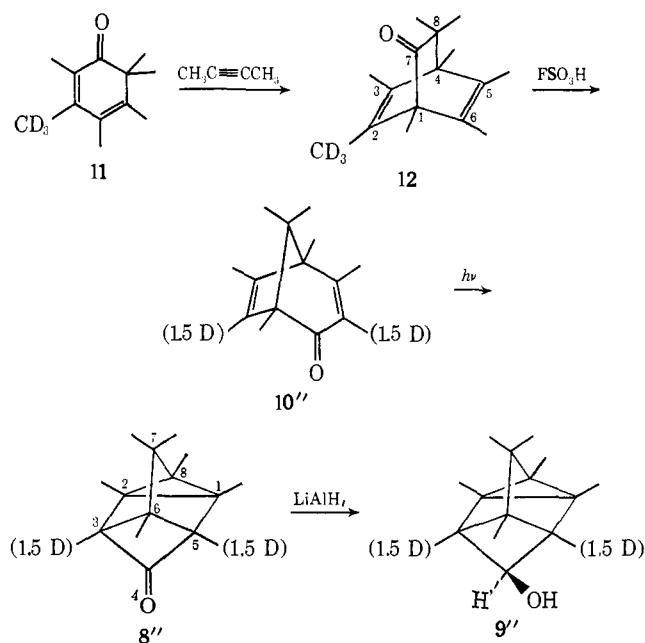
in area to six protons; this peak split into two three-proton peaks with shift reagent. Consequently this signal must correspond to the methyls at C3 and C5 (and to one of the bridgehead methyls at C6 or C8). This result also requires that the six-proton peak at δ 0.57 be assigned to the methyls at C7, an assignment which is consistent with its position at highest field.

The large shift on adding Eu(fod)₃ of the signal at δ 1.05 compared with that for the three-proton singlet at δ 0.86 and the large shift of the six-proton singlet at δ 0.86 compared with that at δ 0.91 require that the hydroxyl group be assigned the exo configuration, as shown in **9**.

Reactions of 9. When alcohol **9** was treated with anhydrous hydrogen chloride in ether for 5 min at 0° (or in acetone with concentrated HCl for 15 min at room temperature), it was converted in high yield to the crystalline chloride **13**, mp 235–237°. The chemical
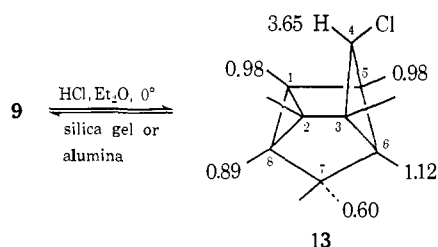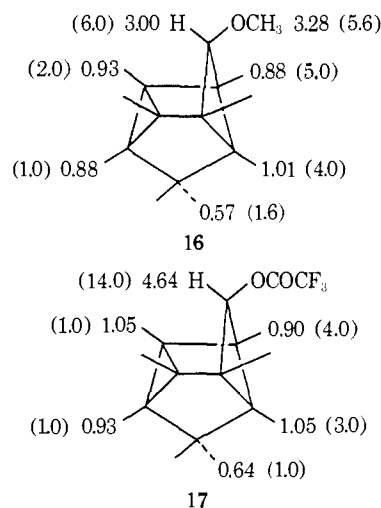

shifts of the C1, C2 and C3, C5 methyls were coincidentally identical. The different three-proton signals at δ 0.89 and 1.12 rule out possible rearranged structures such as **14** or **15**. Chromatography of **13** on silica gel

(13) H. Hart, P. M. Collins, and A. J. Waring, *J. Amer. Chem. Soc.*, **88**, 1005 (1966).
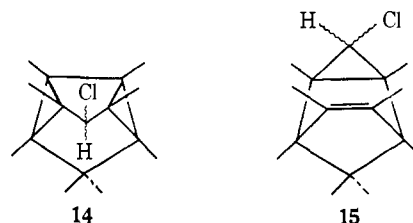
or alumina gave **9** suggesting, together with the symmetry of the pmr spectrum, that the carbon skeletons of **9** and **13** are identical. The very close parallel between the chemical shifts of corresponding methyls (and the secondary hydrogen) in **9** and **13** strongly suggests that their configurations are identical; that is, the conversion of **9** → **13** most probably proceeds with retention of configuration.

Two other reactions indicate that displacements in this system occur with retention of configuration. Treatment of **13** at room temperature for 3 hr with methanol containing a trace of sodium methoxide gave the crystalline ether **16**, mp 147–148°. Comparison of the chemical shifts and the europium shift values of **9** and **16** clearly shows that they have the same configura-


tions. The same conclusion applies to the trifluoroacetate **17**, obtained as an oil by treating a carbon tetrachloride solution of **9** for 1 min at room temperature with a little trifluoroacetic acid.

Retention of configuration in these three displacements and lack of rearrangement to the dicyclopropylcarbinyl system (see **14**) could be rationalized by invoking a carbonium ion **18** which is stabilized by interaction with the electrons of the C1–C2 cyclopropane bond. The analogy with the trishomocyclopropenyl cation **19**[14] is obvious. Indeed, the rigid framework of

(14) S. Winstein, J. Sonnenberg, and L. deVries, *J. Amer. Chem. Soc.*, **81**, 6523 (1959); even more closely related are the ions
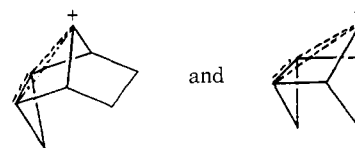
H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); S. Masamune, R. Vukov, M. J. Bennett, and J. Purdham, *ibid.*, **94**, 8239 (1972).
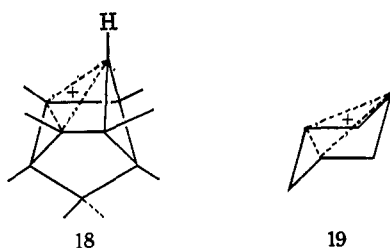
18 is ideally suited to such participation.[15] However, the situation might not be quite as simple as this, and if one considers the classical structures which might contribute to **18**, it becomes obvious that a simple mechanism is available for interchanging the relative positions of the three- and four-membered rings. To
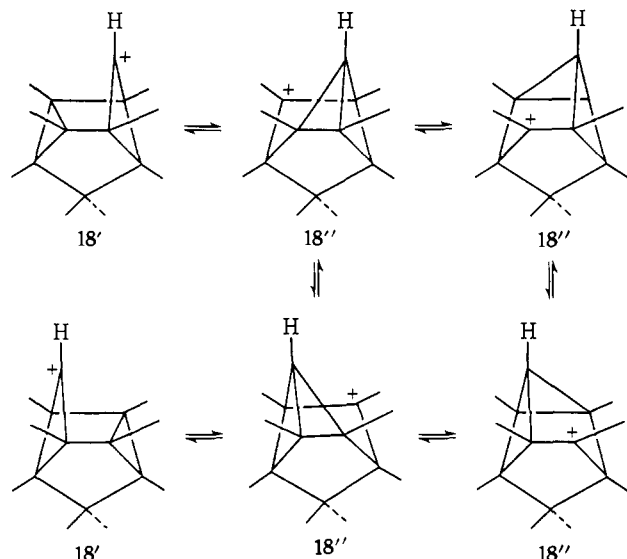
test this possibility, several labeling experiments were performed.

Treatment of **9'** with trifluoroacetic acid gave **17'**, in which the areas of the peaks at δ 0.90 and 1.05 were reduced to 4.5 H each (using shift reagent to separate out the C6 methyl in the latter case). A similar experiment with the chloride could not be directly informative

17' (* = 1.5 D)
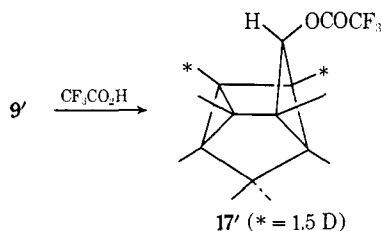
because of the coincidental identity of the chemical shifts of the C1, C2 and C3, C5 methyl signals in **13**. Shift reagent could not be used with **13**. However, when **9'** was converted to the chloride and the resulting chloride was reconverted to the alcohol by chromatography on alumina, the resulting alcohol had the deuterium equally distributed between the C1, C2 and C3, C5 positions. Completely analogous results were obtained, both for the trifluoroacetate and for the chloride, starting with the label in the other position (*i.e.*, using **9''**).

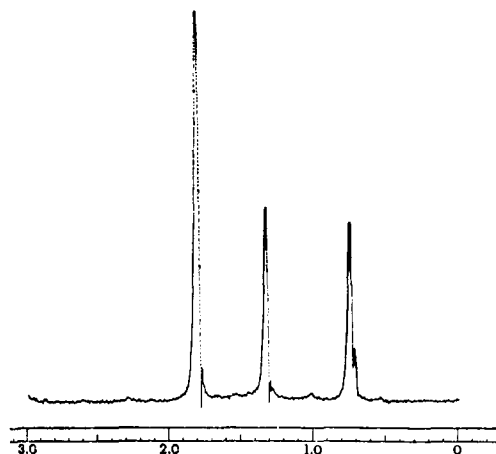(15) C. G. Biefeld, H. A. Eick, and H. Hart, *Tetrahedron Lett.*, 4507 (1973).

It was clear from these labeling experiments that the conversion of **9** to **13** or **17** involved intermediates which permit the equilibration of C1 and C2 with C3 and C5, and of C6 with C8. Clearly **18** is insufficient for this purpose, but equilibration of **18** with its enantiomer *via* contributors such as **18'** and **18''** (either as contributors to a resonance hybrid or as equilibrating classical ions) would provide one possible explanation. Alternatively, there might be a single intermediate, the pyramidal C_{2v} cation **7**. To examine the latter possibility, we decided to study the reactions under stable ion conditions (in strong acid).

Ionization of 9 in FSO_3H-SO_2ClF. Solutions of **9** in FSO_3H-SO_2ClF (*ca.* 1:4 v/v) at $-78°$ gave the simple pmr spectrum shown in Figure 1. The spectrum did not change over the temperature range -50 to $-120°$. It consisted of four sharp singlets[16] at δ 1.80, 1.33, 0.77, and 0.75 with relative areas 12:6:6:1. This spectrum is entirely consistent with the C_{2v} symmetry of **7**. The four methyl groups attached to the carbons at the base of the pyramid appear at lowest field, as would be expected from MO calculations on the analogous **1**; a large fraction of the positive charge resides on the "basal" carbon atoms. The methine proton appears at highest field, as a consequence of the rather large p component to the carbon–carbon bonds of the apical carbon (analogous to a cyclopropane proton).[17,18] The peaks at δ 1.33 and 0.77 are assigned respectively to the bridgehead and gem methyls; these assignments are based on the expected relative chemical shifts of the two types of methyl groups.

The observed pmr spectrum (Figure 1) of the cation derived from **9** is also consistent with what would be expected from a set of rapidly equilibrating classical ions of the type **18''**. If this were the case, the equilibration would have to be rapid at $-120°$ on the nmr time scale;

(16) The reference was the tetramethylammonium ion, δ 3.13.

(17) One could also view the orbital array in 7 (or 1) as analogous to a 6π aromatic system. Thus there is a similarity between 1 and the stable metallic complexes of cyclobutadiene. Consequently, the apical proton is in a sense sitting in the shielding region above the center of an electron cloud.

(18) The assignment of the δ 0.75 peak to the methine proton was verified by preparing the apically deuterated cation (**8** was reduced with lithium aluminum deuteride, and the resulting alcohol was dissolved in FSO_3H-SO_2ClF); its spectrum was identical with that of 7 except for the absence of the peak (shoulder) at δ 0.75. This result also shows that the apical proton does not undergo exchange with FSO_3H.
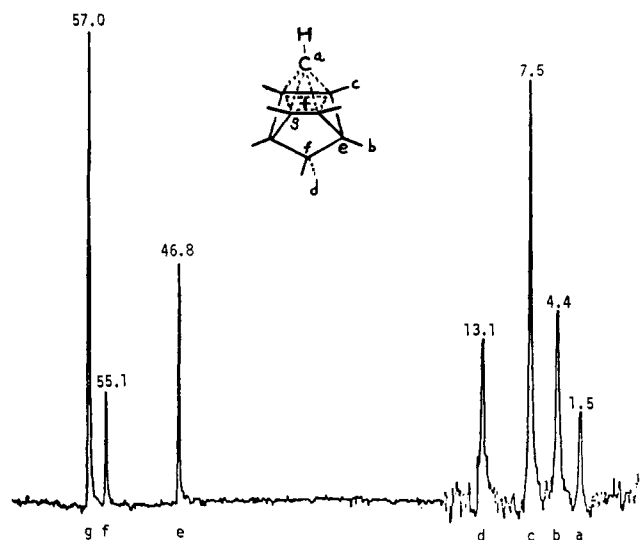
Figure 2. The ^{13}C nmr spectrum of a solution of 9 in FSO_3H–SO_2-ClF (*ca.* 1:4) at $-80°$; chemical shifts are in δ from TMS. Because of an instrument display change, intensities of the three low-field peaks should not be compared with those of the four high-field peaks.

further, there would have to be some rationale for the special stability of these tertiary β-cyclopropylethyl cations. Although the single structure **7** provides a more economical and in our view more satisfactory rationale of the data, the pmr spectrum alone cannot provide an unequivocal choice between these two alternatives.

To obtain more information on this point, the ^{13}C nmr spectrum of the ion was determined. It is shown in Figure 2. The spectrum consisted of seven peaks as expected for an ion with structure **7**. The three low-field peaks remained sharp in an off-resonance spectrum, showing that they belong to the carbon framework. All the peaks are readily assigned from their intensities (see Figure 2). Consistent with the pmr spectrum, the carbon atoms at the "base" of the pyramid, where most of the positive charge is located, appeared at lowest field (δ 57.0) and the "apical" carbon appeared at highest field (δ 1.5). It is curious that, among the proton-substituted group of carbon atoms, the four methyl carbons at the "base" of the pyramid do not appear at lowest field, although the protons attached to these methyls appear at lowest field in the proton spectrum. Strain and hybridization effects, and possibly a ring current, are factors which may influence these ^{13}C shifts.

The chemical shift of the "apical" carbon is not consistent with what might be expected if the ion consisted of equilibrating structures **18''**. The hydrocarbon **18a**


18a
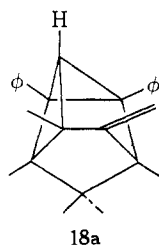
serves as a possible model for **18''** (details for its preparation will be described elsewhere); we find that

the apical carbon here appears at δ 39.5 (*cf.* δ 1.5 in **7**). Consequently we believe that the bonding of the "apical" carbon in the ion must be unusual and prefer the symmetric structure **7** to the equilibrating ion structure **18''**. Although absolute magnitudes of shifts differ, the ^{13}C spectrum of **7** is similar to that recently reported for **3**.[8]

One can imagine three plausible quenching products of nucleophilic attack on **7**. Reaction at the apical
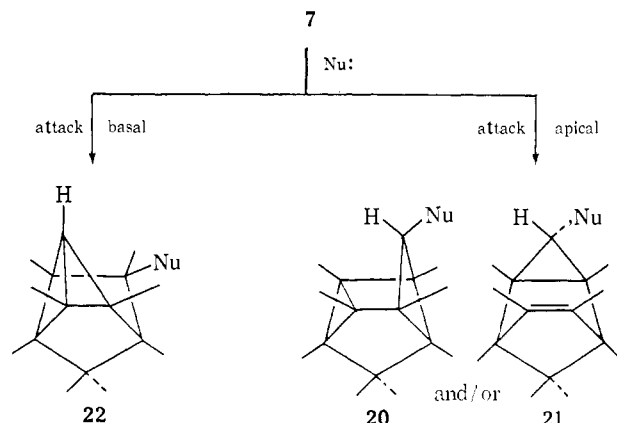
carbon could give either **20** or **21**, whereas reaction at a basal position would give **22**. In fact, when solutions of **7** were quenched at $-78°$ with a suspension of sodium carbonate in pentane, followed by hydrolysis, the product was **9** (**20**, Nu = OH). Similar quenching with sodium methoxide in methanol gave a nearly quantitative yield of **16** (**20**, Nu = OCH_3). Thus **7** reacts with nucleophiles exclusively at the apical carbon, although the nmr spectra show that the positive charge is predominantly at the basal positions. This result is to be contrasted with those reported[8] for the closely related ion **3**, which combines with nucleophiles solely at a basal position to give **23**. The difference between
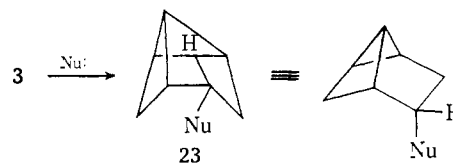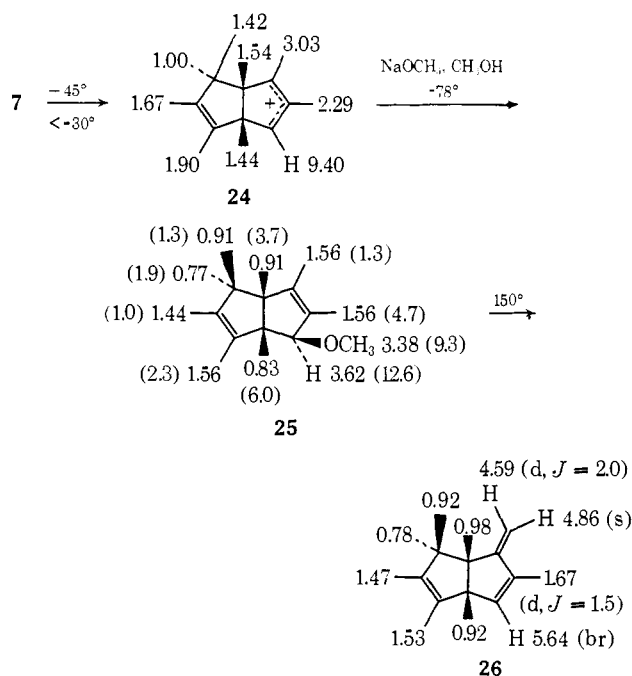

3 and **7** in reactions with nucleophiles probably arises because the basal positions in **7** are tertiary; approach of the nucleophile is hindered by the methyl groups—not only by those on the basal carbons but by those at the bridgehead positions as well. Consequently, reaction with nucleophiles occurs at the less hindered, secondary apical carbon. It is noteworthy that even in the presence of rather strong base (sodium methoxide in methanol) no elimination (for example to **43**, *vide infra*) occurs.

One can rationalize the formation of **20** in preference to **21** by considering the process to be the microscopic reverse of their ionizations. One would expect the solvolysis of **20**, which undoubtedly proceeds with participation of the three-membered ring,[19] to be very much more rapid than the solvolysis of a comparable derivative of the cyclopropyl–Nu **21**;[20] conversely, if one starts from the ion, **20** should be formed with a lower activation energy than **21**.

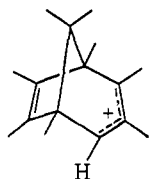(19) R. M. Coates and K. Yano, *Tetrahedron Lett.*, 2289 (1972).
(20) W. Kirmse and F. Scheidt, *Angew. Chem., Int. Ed. Engl.*, 10, 263 (1971).

The Thermal Rearrangement of 7. When solutions of 7 in FSO_3H-SO_2ClF were warmed above $-50°$, new bands appeared in the pmr spectrum as a consequence of the isomerization of 7 to other carbonium ions. When the temperature was carefully controlled at $-45°$, the first of these processes could be isolated from others which ensued at higher temperatures. The simple pmr spectrum of 7 (Figure 1) changed to one with eight three-proton singlets for the eight methyl groups, each of which became unique, and a low-field singlet for the remaining proton. The new ion is assigned structure 24, based on its pmr spectrum and on that of the quenching product. The low field proton at δ 9.40 is characteristic of allylic cations with a terminal proton.[21] The two low-field methyl signals, δ 3.03 and 2.29, are typical of methyl groups attached to the end and middle, respectively, of an allyl ion.[21] Two other methyls (δ 1.90, 1.67) were clearly vinylic, and the remainder were aliphatic.[22] We will return later to the mechanism by which 24 is formed from 7.

After ion 24 was fully formed from 7 (at $-45°$) its FSO_3H-SO_2ClF solution was cooled to $-78°$ and quenched with methanol to give the ether 25 as a pale yellow oil. The ether was not purified but on gas chromatography eliminated methanol to give a single triene, 26. The moiety

in the triene was clearly demonstrated by a decoupling experiment. Irradiation of 26 at the δ 5.64 peak caused the collapse into singlets of the methyl doublet at δ 1.67 and vinyl doublet at δ 4.59. The structure of 26 was also confirmed by its photoisomerization (*vide infra*).

The position of the methoxyl group in 25 was clear from the pmr spectrum; in particular, the single proton at δ 3.62 indicated that methanol reacted at the secondary, rather than the tertiary, terminus of the allylic cation 24. If the converse were true, this proton would have appeared in the vinyl region. Although one might expect maximum positive charge at the tertiary end of 24, the secondary end would be less sterically hindered, therefore more readily attacked by a nucleophile. Further conversions of 24 and 26 involve them in a web of reactions which cannot be rationalized by alternative structures.

A labeling experiment disclosed features of the path by which 7 rearranges to 24. Dienone 10'' was treated with sodium methoxide and deuteriomethanol to give 10''', which, on irradiation and reduction, gave 9'''.
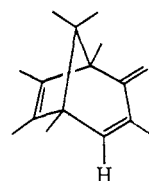

(21) N. C. Deno in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 796. See also K. Rajeswari and T. S. Sorensen, *J. Amer. Chem. Soc.*, **95**, 1239 (1973), and K. Rajeswari and T. S. Sorensen, *Can. J. Chem.*, **50**, 1293 (1972), for further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

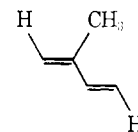(22) The pmr spectrum could also be consistent with that of the [3.2.1] cation

this structure was clearly eliminated by studying the protonation of the corresponding triene

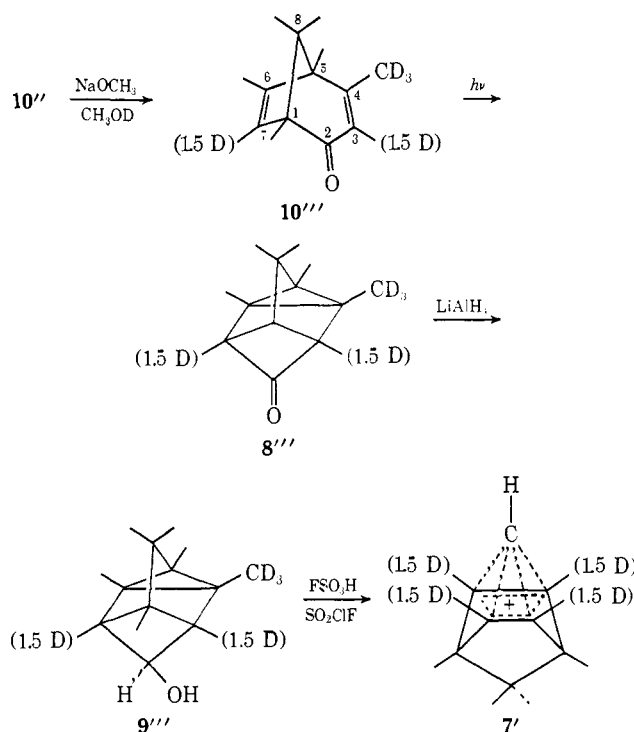these results will be described in detail in a separate paper.

The pyramidal ion 7' formed from 9''' had an identical pmr spectrum with that of 7 except that the peak at δ 1.80 was reduced from 12 protons to six, consistent with

Scheme I
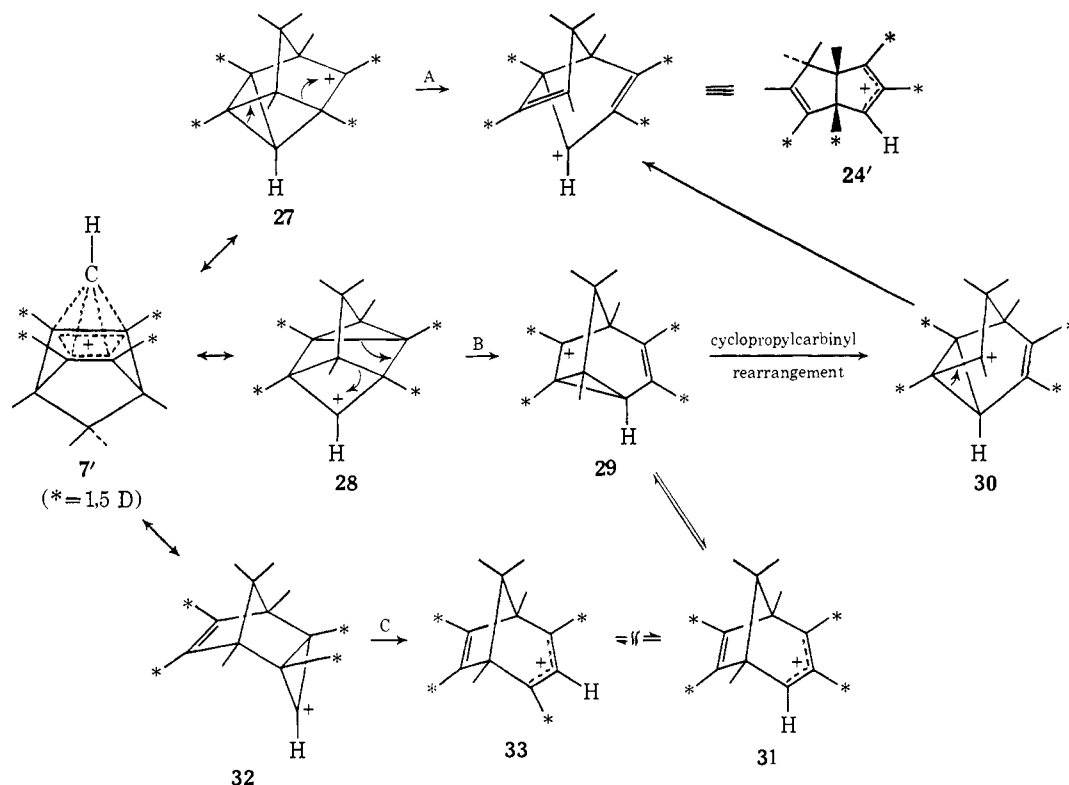
50% labeling of the four basal methyl groups. When 7' was allowed to rearrange at −45°, the resulting 24'
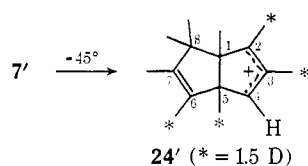
showed a 50% diminution in the areas of four methyl signals, at δ 1.44, 1.90, 2.29, and 3.03. Methanol quenching of 24' gave 25' whose pmr spectrum was different from that of 25 only by reduction of the peak at δ 0.83 to *ca.* 1.5 protons, and that at δ 1.56 to *ca.* 4.5 protons. Vapor phase chromatography of 25' converted it to 26' whose pmr spectrum was identical with that of 26 except that the peak at δ 0.92 was reduced to 4.5 protons, those at δ 1.53 and 1.67 were reduced to 1.5 protons each, and the vinyl signals at δ 4.59 and 4.86 integrated for *ca.* 0.5 proton each. These labeling results require a certain relationship between the pmr assignments in structures 24, 25, and 26 which are, in fact, satisfied by the assignments shown on the structures.

How can one rationalize the label result 7' → 24'? Several plausible mechanisms can be imagined, each of which is most easily followed by proceeding from one of the classical structures which contribute to 7. These mechanisms are shown in Scheme I. Structure 27 is one of four equivalent contributors to 7 which is tertiary, with the positive charge on one of the "basal" carbon atoms (see structures 18''). Bond reorganization as shown in path A leads directly to 24'.

Structure 28 is the contributor to 7 with the positive charge at the apical carbon (see structures 18 or 18'). Bond reorganization *via* path B could give 29 which, after a cyclopropylcarbinyl rearrangement to 30, could

lead to 24'. One might also expect 29 to be in equilibrium with the allylic ion 31.

Structure 32 could also conceivably contribute to the pyramidal ion 7 (compare iv as a precursor of 1, footnote 2). Presumably 32 could easily open (path C) to 33. We have shown previously[23-25] that the exceedingly rapid rearrangements in ions of the type 33 (particularly, replace H by CH_3 in 33) can equilibrate methyl groups in the two-carbon and three-carbon bridges of such bicyclo[3.2.1]octadien-2-yl cations (either by a circumambulatory process or a 1,2-bridge shift process[24]). Consequently, interconversion of 33 and 31 is conceivable; 31 could then produce 24' (*via* 29 and 30).

We have performed a number of experiments which conclusively eliminate paths B and C. Details will be presented later in a separate paper, since they are best understood after our experiments on circumambulatory processes and 1,2-bridge shifts, which up to now have only appeared in preliminary communications,[23-25] are reported in full. However, the sense of the results can be briefly mentioned here. A direct synthetic route to 31 and 33 from the corresponding alcohols gave solutions which, although they did produce 24, also gave other products which were not observed in the rearrangement of 7.

Actually the rearrangement of 7 to 24 *via* path A may occur in one step as shown in Scheme I (27 → 24'; this reaction may also be formally represented as a $_\sigma 2_s$ + $_\sigma 2_s$ process) or in two steps. The two-step path involves an initial expansion of the four-membered ring in 27, to give 34, which can then rearrange to 24' as shown.

(23) H. Hart and M. Kuzuya, *J. Amer. Chem. Soc.*, 95, 4096 (1973).
(24) M. Kuzuya and H. Hart, *Tetrahedron Lett.*, 3887 (1973).
(25) M. Kuzuya and H. Hart, *Tetrahedron Lett.*, 3891 (1973); see also erratum, p 4206.

27

34

24'
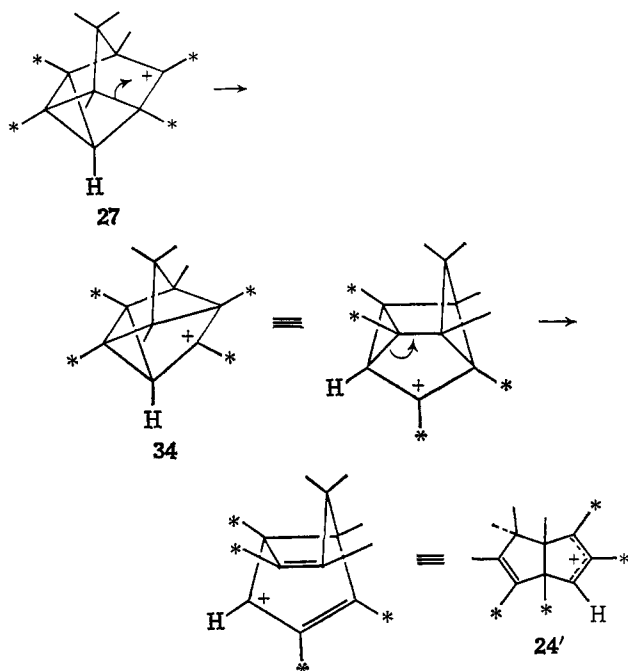
Ion **34**, when presented by the delocalized structure **34'**, bears some resemblance to the barbaralyl or tetrahydro-

34'

barbaralyl cations.[26] The only difference between the two routes from **27** to **24'** is whether or not a Wagner–Meerwein 1,2-shift occurs prior to the formation of the allylic cation.[27] Present data do not allow a distinction between these alternatives.

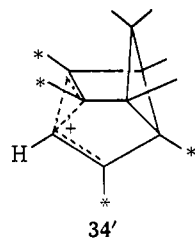The kinetics for the rearrangement of **7** to **24** were easily measured over the temperature range −55 to −39°, the conversion being followed by monitoring changes in the pmr spectrum. Rate data are given in the Experimental Section; $k(-48°)$ was $(3.1 \pm 0.1) \times 10^{-4}$ sec^{-1}. A linear Arrhenius plot gave the following activation parameters: $\Delta F^{\ddagger} = 16.7$ kcal/mol, $\Delta S^{\ddagger} = -2.8$ eu/mol, $\Delta H^{\ddagger} = 16.1$ kcal/mol.

**Further Rearrangements of 24.** As mentioned in the previous section, the rearrangement of **7** to **24** in FSO₃H–SO₂ClF occurs cleanly in the temperature range −55 to −39°; above the upper temperature limit, **24** undergoes further rearrangements. At −30° rearrangement to a new cation **35** is quite rapid.[28]

(26) P. Ahlberg, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4454 (1970).
(27) That is
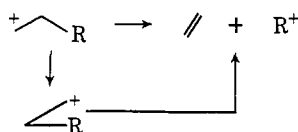
The structure of **35** is assigned from its pmr spectrum, quenching products, and further reactions. The two methyl signals at δ 2.93 and 2.96 and the methyl signal at δ 2.22 are typical for methyl substituents attached to an allyl cation in a five-membered ring,[21] and the low field position of the methine proton is consistent with

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39
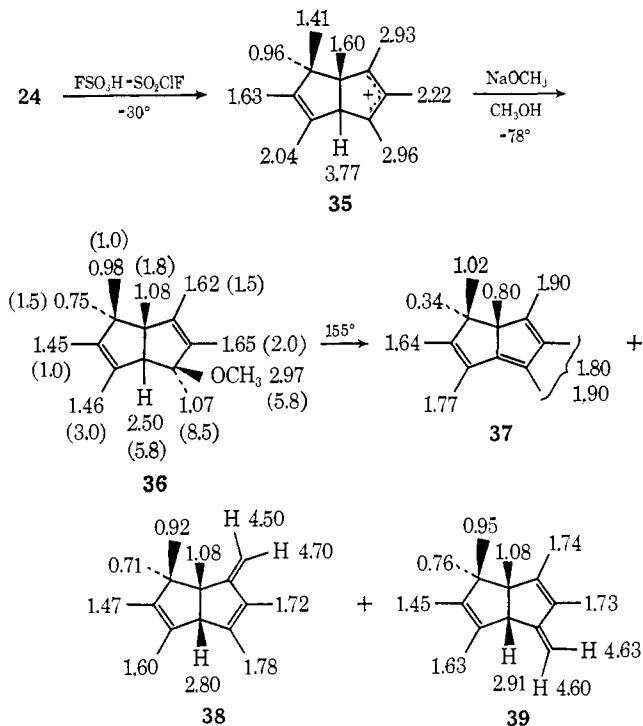
its location adjacent to an allyl cation and a double bond. This proton is also located from the pmr spectrum of the methanol quenching product **36** (*vide infra*). The remainder of the spectrum indicated two allylic methyls (δ 1.63 and 2.04) and three aliphatic methyls (δ 0.96, 1.41, and 1.60). These assignments are made as a consequence of labeling experiments (rearrangement of **24'**) to be described below.

Solutions of **35**, when cooled to −78° and quenched at that temperature with sodium methoxide in methanol, gave a single methyl ether assigned structure **36**. The europium shift data on **36** locate the tertiary methyl group (δ 1.07, rel slope 8.5) and the methine hydrogen (δ 2.50, rel slope 5.8) close to the methoxyl group, whereas the gem-dimethyl group must be remote from that function.[29] Other signals in **36** are assigned on the

(28) Although **35** is formed in yields ≧90%, another cation
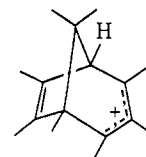
is formed concurrently, in yields up to *ca.* 10%. It also rearranges, but slowly, to **24**, then **35**. Data regarding bicyclo[3.2.1]octadien-2-yl cations related to the present study will be reported separately (*vide supra*).

(29) That is, structures vii, viii, and ix are clearly eliminated for the quenching product.

vii

viii

ix
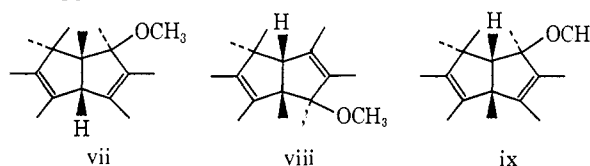
basis of chemical shift and europium slopes. The formation of a single product is probably a consequence of attack on **35** at the least hindered position (*i.e.*, exo and at the allyl terminus remote from the gem-dimethyl group).

Injection of the pale yellow oil **36** in a gas chromatograph gave three trienes, **37** and **39** as a consequence of 1,2-elimination of methanol and **38** as a consequence of 1,4-elimination. It was a simple matter to distinguish **37** from the other two trienes, since this hydrocarbon had λ_{max}^{EtOH} 304 nm, whereas each of the other trienes had a maximum at 244 nm. Further, the pmr spectrum of **37** showed no vinyl protons, just five allylic and three aliphatic methyl signals (see structure).

A distinction between **38** and **39** was difficult to make on the basis of their spectra, which were nearly identical. However labeling experiments to be described below and photolysis experiments to be discussed in a separate publication permit the assignments shown.

Rearrangement of **24'** gave the labeled ion **35'** whose pmr spectrum differed from that of **35** only in that the areas of the peaks corresponding to one terminal methyl

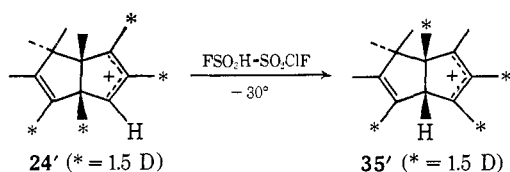and the central methyl attached to the allylic cation (δ 2.96 and 2.22), one allylic methyl (δ 2.04) and one aliphatic methyl (δ 1.60) were reduced to 1.5 H each. From this result, without assuming the assignments indicated in structure **35'**, one can immediately rule out mechanisms which scramble methyl groups randomly, as well as a methyl shift mechanism such as **24'** → **35''**; if the latter mechanism were operative, all three methyl
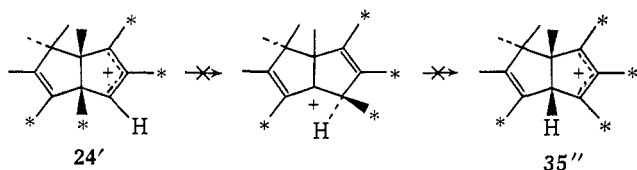
substituents on the allylic cation (*i.e.*, the three methyls at lowest field) would have been labeled.

When **35'** was quenched with methanol, the resulting **36'** had reduced methyl signals (1.5 H) at δ 1.07, 1.08, 1.46, and 1.65. Since the assignments in **36** were already clear, **36'** must have the label distributed as shown.
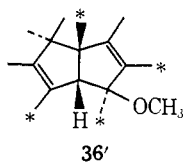
Consequently the label in the carbonium ion must be as shown by the asterisks in structure **35'**. Pyrolysis of **36'** gave **37'**, **38'**, and **39'**, with the label necessarily
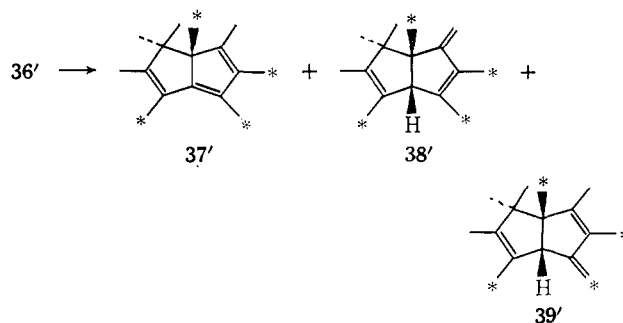
distributed as shown. In **37'**, three allylic methyls (δ 1.77, 1.80, and 1.90) and one aliphatic methyl (δ 0.80) had reduced (1.5 H) signals, consistent with expectation. Furthermore, these results permit us to distinguish between **38** and **39**. In one of these pyrolysis products, the signals of three allylic methyl positions (δ 1.60, 1.72, and 1.78) and one aliphatic methyl position (δ 1.08) were reduced in area to 1.5 H each, whereas in the other product the peak for the two vinyl protons (δ 4.60 and 4.63) was diminished to half its natural area, as were two allylic methyl peaks (δ 1.63 and 1.73) and one aliphatic methyl peak (δ 1.08). Clearly the former product must have structure **38** and the latter **39**.[30,31]

The mechanism for the rearrangement of **24'** and **35'** involves a succession of 1,2-shifts of one five-membered ring with respect to the other. These can proceed *via* the cyclopropylcarbinyl ion **40** and the bicyclo[3.2.1]-octadien-8-yl cation **41** (possibly stabilized by the 6,7-
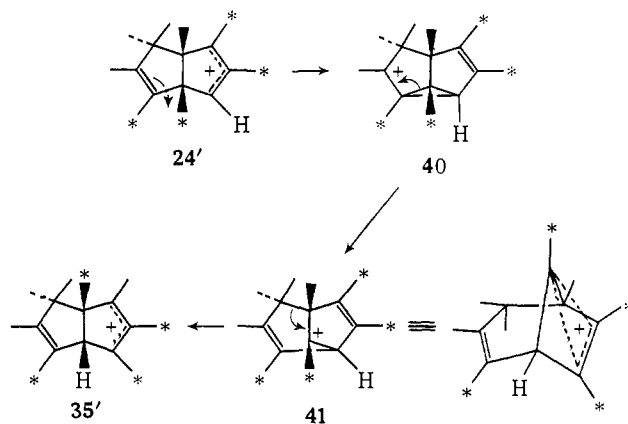
double bond). The reaction stops after one migration and does not continue the circumambulatory process because the next series of analogous shifts would place the positive charge on the secondary carbon atom.

Further Reactions of 35. Cation **35** was stable up to about 0° in FSO_3H-SO_2ClF. However, if such solutions were permitted to remain at 0° or above for an extended time, their pmr spectra slowly changed, indicative of further rearrangement. In this solvent the spectral changes were rather messy and not easily interpreted, and it soon became apparent that further re-

(30) The assignments of chemical shifts to the gem-methyl groups in **24–26** and **35–39** are made on the basis that the endo methyl lies over the π-system of the adjacent five-membered ring and consequently will be shielded by it and appear at highest field.

(31) Pmr assignments shown in structure **38** are unequivocal except for the peaks at δ 1.60, 1.72, and 1.78, which are assigned their relative positions by chemical shift comparison with many other compounds in this series; this applies also to the assignment of the relative positions of the peaks at δ 1.45 and 1.74, and also of those at δ 1.63 and 1.73, in structure **39**.

arrangements of **35** rested on removal of the methine proton and reprotonation at another site. Consequently we switched to trifluoroacetic acid (TFA), a more basic solvent than FSO_3H and therefore a solvent in which such proton transfers would be more facile.

When the tetracyclic alcohol **9** was added to TFA at $-10°$ (no reaction) and the resulting solution was slowly warmed to $10°$ and maintained at that temperature for 30 min, a new ion was formed[32] with four methyl signals below δ 2.1, but none as low as δ 2.9–3.0 expected (see **24** and **35**) for methyls at the terminus of an allyl cation. These observations suggested that charge in the new ion was more delocalized, and we assign it structure **42**.[33] The products obtained when solutions of **42** were quenched with ice-cold aqueous

$$9 \xrightarrow[\text{several steps}]{\text{TFA}} \text{42} \xrightarrow[\text{quench}]{OH^-} 37 + 38 + 39$$
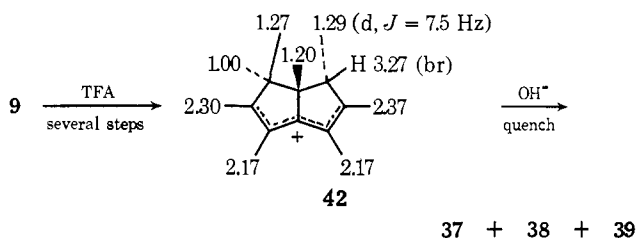
sodium hydroxide were the same three trienes (**37–39**) isolated by pyrolysis of **36**.[34] Solutions of **42** in TFA did not rearrange further (2 hr of reflux with no change in the pmr spectrum).

We propose that **42** is formed from **9** via the following sequence: $9 \rightarrow 7 \rightarrow 24 \rightarrow 35 \rightarrow 37 \rightarrow 42$. The observation that **42** is formed more readily in TFA than in FSO_3H supports the proposal that the last steps involve a deprotonation–reprotonation step with a neutral intermediate, **37**. Several experiments were performed to test this mechanism.
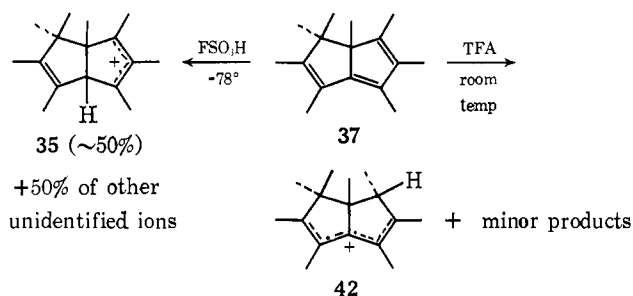
Triene **37** is protonated differently in FSO_3H and in TFA. At $-78°$ in FSO_3H protonation occurs predominantly at the unsubstituted ring junction to give

(32) The reaction was monitored by pmr; the same ion was formed immediately at room temperature but was slightly more contaminated with minor impurities.

(33) The only other alternative (in view of the quenching results) is x; this structure is excluded because of the symmetry in the chemical shifts of the four lowest field methyl signals and also from the results
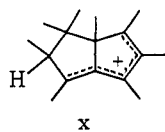
of the labeling experiments. The geometry of the methine proton in **42** is assumed. The ring skeleton is slightly cup-shaped (see also **37**) and protonation might be expected to occur from the exo face.

35 in about 50% yield. However, considerable amounts of other ions are also formed, possibly the epimer of **35** as well as products from protonation at other positions. Presumably the reaction is under kinetic control, with the major product arising from protonation at the least hindered position. In contrast, protonation of **37** at room temperature in TFA gives almost entirely **42**, presumably the product of thermodynamic control, with only very minor amounts of other ions being formed.

Deuterium labeling experiments support the proposed mechanism. For example, treatment of secondary alcohol **9** with TFA-d gave, after 5 min, **42** lacking signals at δ 1.29 (doublet) and 2.37, and with the signal at δ 2.17 reduced in area to three protons; the broad peak at δ 3.27 was also absent. When such solutions were allowed to stand at room temperature for 48 hr, the signal at δ 2.30 also gradually disappeared, but the spectrum remained otherwise unaltered. We interpret these results as shown in Scheme II. The first [3.3.0]-

Scheme II
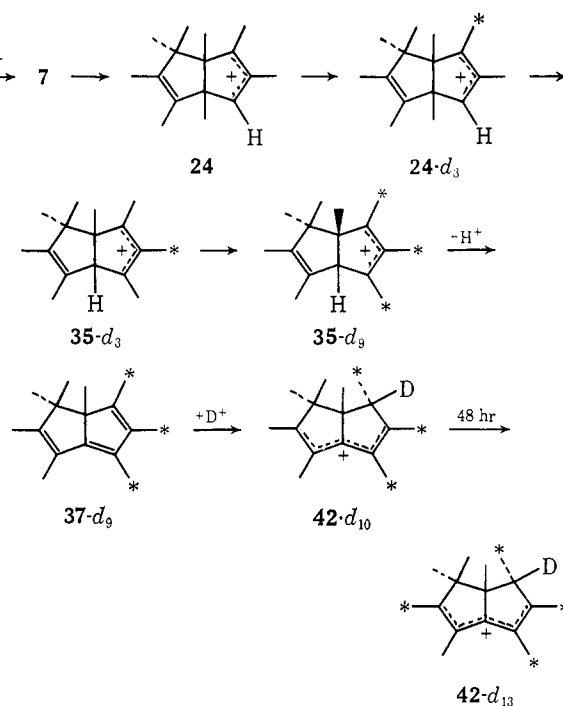
octadienyl ion, **24**, rapidly exchanges the protons on the methyl at the terminus of the allyl cation to give **24**-d_3. Rearrangement gives **35**-d_3 which rapidly exchanges an additional six protons to give **35**-d_9 which, through deprotonation and reprotonation, gives **42**-d_{10}. All of these exchanges are extremely rapid, and the **42** which is formed from **9** and TFA-d has completely exchanged ten protons for deuterium. The final ex-

(34) The predominant product was **37**, the methine proton being most easily lost. Trienes xi and xii were not detected. It is possible that **38** and **39** were formed as thermal rearrangement products of **37**.
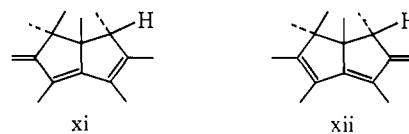
change which occurs very slowly (to give **42**-d_{13}) presumably involves xi as an intermediate.

A second labeling experiment supports this scheme. Ketone **8'''** was reduced with lithium aluminum deuteride to give **9''''** which, on treatment with TFA for 5 min at room temperature, gave **42**-d_3 in which the signals at δ 1.20 and 2.17 integrated for only 1.5 and 4.5 protons each, respectively. This result is rationalized as shown in Scheme III. Rearrangement

Scheme III
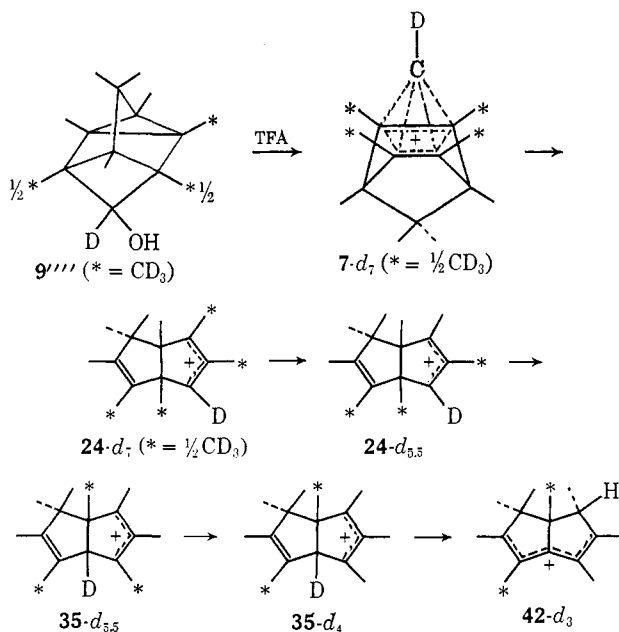
to **24**-d_7 is followed by washing out of the deuterium at the terminus of the allylic cation to give **24**-$d_{5.5}$. Rearrangement to **35**-$d_{5.5}$ is followed by a second similar wash-out to give **35**-d_4. Dedeuteration and reprotonation results in the loss of still another deuterium to give the observed product, **42**-d_3.

Finally, a solution of **42** in TFA was diluted with excess TFA-d so that the resulting solution contained about 80% TFA-d. After 48 hr at room temperature the spectrum of **42** showed the nearly complete loss of signals at δ 2.30, 2.37, and 3.27 and the doublet at δ 1.29 sharpened to a singlet. After an additional 2 weeks, the signal at δ 1.29 had disappeared and the peak at δ 2.17 was reduced in area to three protons. These results are rationalized as follows

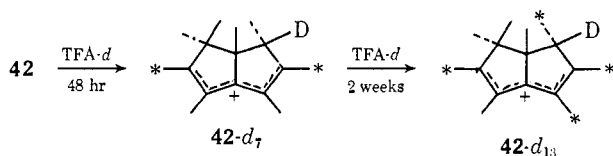Deprotonation and deuteration through the neutral trienes **37**, xi, and xii result in exchange of seven protons to give **42**-d_7. The further exchange of six more protons must arise through a reversible equilibrium between **42** and **35**.

These deuterium labeling results, which resulted in the preparation of four uniquely labeled samples of **42** (d_3, d_7, d_{10}, and d_{13} (the latter by two routes)), are diffi-

cult to rationalize *via* any other scheme than that shown. Consequently the mechanistic path **9** → **7** → **24** → **35** → **37** → **42** seems established.

An Alternate Synthesis of the Pyramidal Ion 7. In addition to compounds with structure **20** (*i.e.*, **9**), compounds with structures **21** or **22** might also serve as precursors to the pyramidal ion **7**. We have not yet synthesized **21**, but we have prepared the alkene which corresponds to **22** (*i.e.*, **43**) and find that it does in fact give **7** on protonation in strong acid.

Irradiation of an ether solution of triene **26** through Vycor gave a single crystalline photoisomer, mp 124–126°, to which we assign structure **43**.[35] The presence
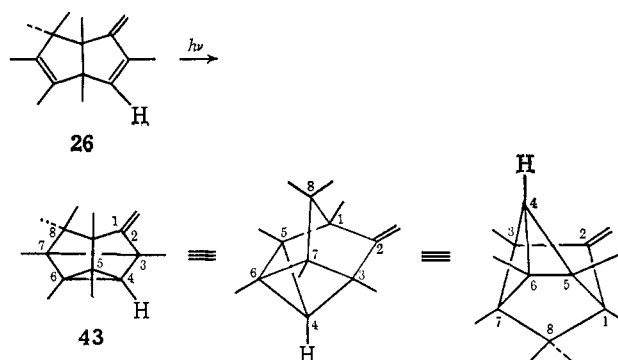
of two vinyl protons (δ 4.12) and the absence of any allylic methyl groups (no methyl signal below δ 1.10) immediately eliminate structures **44** and **45**, conceivable
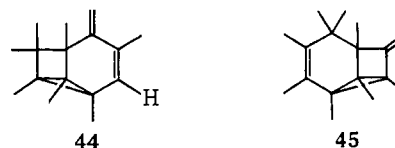
products of a di-π-methane rearrangement. The pmr spectrum of **43** is assigned as shown in the structure.
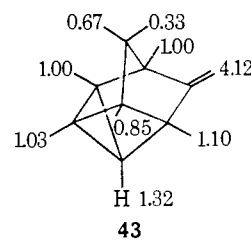
Models show that one methyl at C8 lies directly over the double bond and should be strongly shielded (δ 0.33). Irradiation of **26'** (obtained from **24'**; *vide supra*) gave **43'** in which the signals at δ 4.12, 1.10, 1.03,
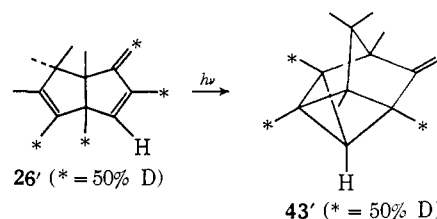
(35) Although this appears to be a 2π + 2π conversion, the actual mechanism is more complex. We defer any discussion of the mechanism for this conversion, since we have irradiated a number of olefins in the bicyclo[3.3.0]octyl and related systems, and their photochemical behavior is best considered in a separate paper dealing only with that subject. See H. Hart and M. Kuzuya, *J. Amer. Chem. Soc.*, **96**, 3709 (1974).

and 1.00 were reduced in area to 1, 1.5, 1.5, and 4.5 protons, respectively. Label should appear in the vinyl protons and in the methyl signals at C3, C5, and C6. These results require the following assignments of the methyl signals in **43**: C1, C7 = 0.85 or 1.00; C3, C5, C6 = 1.00, 1.03, or 1.10; C8 = 0.33 and 0.67. The assignments were further refined to those shown in structure **43** by comparison with the C4-methyl analog of **43**.[36]

The structure of **43** is proved by its conversion in high yield by treatment with HCl in acetone to the secondary chloride **13** and by its analogous conversion in trifluoracetic acid to the secondary trifluoroacetate **17**. Finally, a solution of **43** in FSO_3H-SO_2ClF at
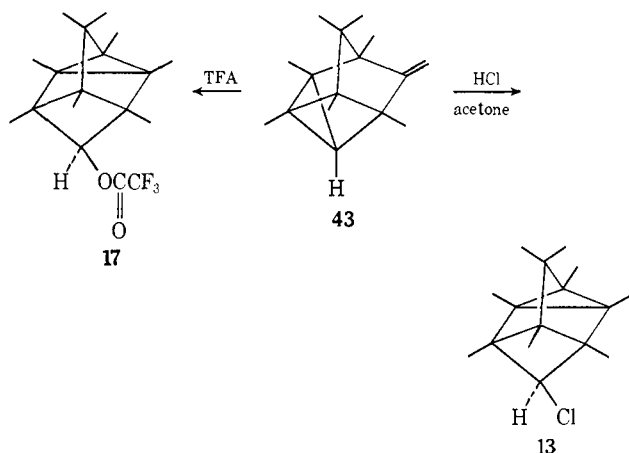
−78° gave a pmr spectrum identical with that of the pyramidal cation **7**. The reactions in this cyclical synthesis are summarized as follows
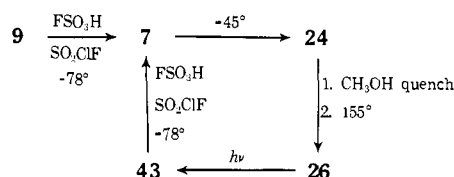
The formation of **7** from **43** represents the first synthesis of a pyramidal cation by a route other than solvolysis.

Experimental Section

General Procedures. Pmr spectra of neutral compounds were obtained on a Varian Associates T-60 spectrometer, usually in CCl_4 using TMS as an internal reference. Some decoupling experiments were done on a Varian Associates HA-100 spectrometer. Spectra of carbonium ions were obtained on a Varian Associates A56-60 spectrometer equipped with a variable temperature probe; the solvent was FSO_3H-SO_2ClF (1:4) and either $(CH_3)_4NBF_4$ (δ 3.13) or CH_2Cl_2 (δ 5.30) were used as internal standards.[10] The pmr temperature control was calibrated using a methanol standard sample before and after each measurement. Temperatures are accurate to ±0.5° of the stated values. Cmr spectra were obtained on a Varian XL-100 or a Bruker-90 spectrometer. We thank Dr. Philip Westerman and Professor George Olah (Case Western Reserve University) and Dr. Richard Schoening and Professor O. Gansow (Michigan State University) for assistance in obtaining the ^{13}C spectra.

Ir spectra were measured on a Unicam SP-200 spectrophotometer. Uv spectra were measured in 95% ethanol using a Unicam SP-800

(36) Samples of the C4-methyl analog of **43** have been prepared with deuterium label either at C4, at C7, or at C3 + C6 + the high-field methyl at C8 (H. Hart and M. Kuzuya, unpublished results). Comparison of chemical shifts of the two compounds permits a complete assignment, the only possible ambiguity being the relative assignments of the C3 and C6 methyls; we assign the lowest field of these signals to the methyl nearest the double bond.

spectrophotometer. 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. Preparative gas chromatographic separations were made using a Varian Aerograph "Autoprep" Model A-700, using 20% FFAP on Chromosorb W. Melting points are uncorrected.

1,2,3,5,6,7,7,8-Octamethyltetracyclo[3.3.0.0^{2,8}.0^{3,6}]octan-4-ol (9). To a suspension containing 70 mg of $LiAlH_4$ in 10 ml of anhydrous ether at 0° was added dropwise with stirring a solution of 1.0 g of 1,2,3,5,6,7,7,8-octamethyltetracyclo[3.3.0.0^{2,8}.0^{3,6}]octan-4-one (**8**)[9] in 20 ml of anhydrous ether, and the mixture was stirred for 6 hr at room temperature. Water was added dropwise with cooling. The ether layer, combined with ether washings of the aqueous layer, was washed with saturated sodium chloride solution and dried ($MgSO_4$). The residual solid obtained by removing the ether under reduced pressure was washed with cold petroleum ether (30–60°) to give 0.90 g (90%) of **9** as colorless crystals which sublime, rather than melt. Samples were further purified by vpc on a 5 ft × 0.25 in. column: 20% FFAP on Chromosorb W, 160°, 100 ml/min of He, retention time 10 min. Ir (KBr pellet) ν_{O-H} 3500 cm^{-1}; mass spectrum (70 eV) m/e 234 (M$^+$), 201 (base); pmr (see structure), the signal at δ 1.32 disappeared when the sample was shaken with D_2O.

Anal. Calcd for $C_{16}H_{26}O$: C, 82.05; H, 11.11. Found: C, 81.95; H, 11.16.

Similar reduction of **8** with lithium aluminum deuteride gave **9** with deuterium at C4; the pmr spectrum lacked the signal at δ 3.50.

Oxidation of 9. To a solution containing 200 mg of **9** in 5 ml of acetone at 0° was added dropwise 0.5 ml of Jones' reagent[37] and the mixture was allowed to stand for 2 hr at room temperature. Addition of sodium bisulfite solution was followed by extraction with ether (3 × 15 ml). Combined ether layers were washed with saturated sodium chloride solution, dried ($MgSO_4$), and evaporated to give 160 mg (80%) of **8**, identified by comparing its pmr spectrum with that of an authentic sample.

1,3,4,5,6,7,8,8-Octamethylbicyclo[3.2.1]octa-3,6-dien-2-one (10). The procedure given here is superior to that using trifluoroacetic acid described previously,[38] since TFA gives mixtures of **10** with various double bond isomers, which are difficult to separate on a preparative scale, whereas FSO_3H gives nearly pure **10**. A three-necked flask was modified by having a narrow exit tube at the base that followed the curve of the flask to the top, and was then bent down in a U-shape. To approximately 5 ml of fluorosulfonic acid placed in the flask, swept with dry nitrogen and cooled to −78°, was added dropwise a solution of 4.5 g of 1,2,3,4,5,6,8,8-octamethyl-bicyclo[2.2.2]octa-2,5-dien-7-one[38] in 15 ml of methylene chloride. The mixture was stirred at −30 to −35° for 3 hr. The resulting brown solution was forced by nitrogen pressure out the exit tube into a very vigorously stirred slurry of ice and water. The color was immediately discharged to pale yellow. The methylene chloride layer, combined with methylene chloride washings of the aqueous layer, was washed with sodium carbonate solution and water and dried (Na_2SO_4). Removal of the solvent gave 3.8 g (85%) of **10** as a pale yellow oil. Its pmr spectrum was essentially identical, without further purification, with that reported previously.[38]

4-Methyl-d_3-1,3,5,6,7,8,8-heptamethylbicyclo[3.2.1]octa-3,6-dien-2-one (10′). A solution of **10** (2.0 g) in 20 ml of CH_3OD containing 100 mg of $NaOCH_3$ was refluxed overnight. After removal of the excess methanol (*in vacuo*) the solid residue was treated with water and extracted with methylene chloride. The organic layer was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure to give an essentially quantitative yield of **10′**, whose pmr spectrum differed from that of **10**[38] by lacking the allylic methyl signal at δ 1.85 (due to the C4 methyl).

1-Methyl-d_3-2,3,5,6,7,8-heptamethyltetracyclo[3.3.0.0^{2,8}.0^{3,6}]octan-4-one (8′). A 1% solution of **10′** in ether was irradiated in ether solution through a Pyrex filter using a Hanovia 450-W lamp. The reaction, followed by vpc, was complete in 15 min. Removal of the ether under reduced pressure gave pale yellow crystals of **8′**, whose pmr spectrum was identical with that of authentic **8**[38] except that the peak at δ 1.04 (C1 and C2 methyls) was reduced in area from 6 H to 3 H. The yield was over 90%.

1-Methyl-d_3-2,3,5,6,7,8-heptamethyltetracyclo[3.3.0.0^{2,8}.0^{3,6}]octan-4-ol (9′). Ketone **8′** (200 mg) was allowed to react with lithium aluminum hydride (15 mg) in ether (10 ml) as described for the

(37) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

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

preparation of unlabeled 9. Work-up gave 170 mg (85%) of 9' as colorless crystals. Its pmr spectrum was identical with that of 9 except that the singlet at δ 0.91 (C1 and C2 methyls) was reduced in area from 6 H to 3 H.

2-Methyl-d_3-1,3,4,5,6,8,8-heptamethylbicyclo[2.2.2]octa-2,5-dien-7-one (12). A mixture of 5.0 g of 3-methyl-d_3-2,4,5,6,6-pentamethyl-2,4-cyclohexadienone (11)[13] and 2 equiv of 2-butyne were heated in a thick-walled sealed glass tube at 200–230° for 3 days. Excess 2-butyne was allowed to evaporate from the cooled reaction mixture, and the viscous residue was chromatographed over silica gel (EM reagent, Silica-gel 60, <230 mesh) using methylene chloride as eluent, to give 5.5 g (85%) of 12 as a pale yellow oil which crystallized on being chilled, mp 45°. The pmr spectrum of the unlabeled ketone corresponding to 12, inadvertently omitted from ref 38, consisted of the following: δ 0.82 (s, 6 H, C8 methyls), 1.30 (s, 3 H, C1 methyl), 1.35 (s, 3 H, C4 methyl), 1.67 (m, 6 H, C2 and C6 methyls), and 1.73 (m, 6 H, C3 and C5 methyls). In the pmr spectrum of 12 the peak at δ 1.67 was reduced in area from 6 H to 3 H, and the peak at δ 1.73 was somewhat sharpened.

3,7-Dimethyl-$d_{1.5},d_{1.5}$-1,4,5,6,8,8-hexamethylbicyclo[3.2.1]octa-3,6-dien-2-one (10''). A solution of 5.0 g of 12 in 15 ml of methylene chloride was treated with 5 ml of FSO₃H at −30 to −35°, as in the preparation of 10, to give 4.5 g (90%) of 10'' as a pale yellow oil. Its pmr spectrum was identical with that of authentic 10[38] except that the peak at δ 1.63 (C3 and C6 methyls) was reduced in area from 6 H to 4.5 H, and the peak at δ 1.42 (C7 methyl) was reduced from 3 H to 1.5 H.

3,5-Dimethyl-$d_{1.5},d_{1.5}$-1,2,6,7,7,8-hexamethyltetracyclo[3.3.0.0²,⁸.0³,⁶]octan-4-one (8''). A solution of 10'' in ether was irradiated through Pyrex as in the preparation of 8', to give over 90% yield of 8'' which had a pmr spectrum identical with that of 8[9] except that the singlet at δ 1.01 integrated for 3 H instead of 6 H.

3,5-Dimethyl-$d_{1.5},d_{1.5}$-1,2,6,7,7,8-hexamethyltetracyclo[3.3.0.0²,⁸.0³,⁶]octan-4-ol (9''). A solution of 200 mg of 8'' in 5 ml of ether was reduced with 15 mg of lithium aluminum hydride, as in the preparation of 9, to give 170 mg (85%) of 9'' as colorless crystals. Its pmr spectrum was identical with that of authentic 9 except that the peak at δ 0.86 (C3, C5, and C8 methyls) was reduced in area from 9 H to 6 H.

4-Chloro-1,2,3,5,6,7,7,8-octamethyltetracyclo[3.3.0.0²,⁸.0³,⁶]octane (13). Procedure A. A solution of 200 mg of 9 in 20 ml of anhydrous ether was saturated, at 0°, with anhydrous hydrogen chloride. After 5 min at 0°, the solution was poured very slowly into a slurry of ice and water. The ether layer, combined with ether washings of the aqueous layer, was washed with 5% sodium bicarbonate solution then with saturated sodium chloride solution and dried (MgSO₄). The pale yellow solid residue obtained by evaporation of the ether under reduced pressure was washed with small amounts of cold methanol to give 150 mg (72%) of 13 as colorless crystals, mp 235–237° (sublimes). Further purification was accomplished by vpc using a 10 ft × 0.25 in. column: 20% FFAP on Chromosorb W, 100 ml/min of He, 160°, retention time 9 min. The product gave a positive Beilstein test. Mass spectrum (70 eV) m/e 252 (M⁺), 253 (30% of M⁺), 254 (37% of M⁺), 201 (base peak); pmr (see structure).

Anal. Calcd for C₁₆H₂₅Cl: C, 76.04; H, 9.90. Found: C, 76.20; H, 9.87. If the ether solution was allowed to stand for 3 hr at 0° before work-up, the pmr spectrum of the product showed the presence (approximately 50%) of another product thought to arise from opening the cyclopropane ring. It was isolated by vpc and is tentatively assigned the structure 4-chloro-2-methylene-1,3,5,6,7,7,-8-heptamethyltricyclo[3.2.1.0³,⁶]octane (positive Beilstein test): pmr δ 0.52 (s, 3 H), 0.70 (s, 3 H), 0.75 (d, 3 H, J = 7.0 Hz), 0.83 (s, 3 H), 1.00 (s, 3 H), 1.07 (s, 3 H), 1.12 (s, 3 H), 2.02 (q, 1 H, J = 7.0 Hz), 3.78 (s, 1 H), 4.72 (s, 1 H), 4.93 (s, 1 H).

Procedure B. This procedure is preferred if contamination with the isomer just described is to be avoided. To a solution containing 100 mg of 9 in 5 ml of acetone was added 2.5 ml of concentrated hydrochloric acid, and the mixture was allowed to stand at room temperature for 15 min. The mixture was diluted with water and extracted (three times) with methylene chloride. The combined extracts were washed with aqueous sodium bicarbonate then with water and dried (Na₂SO₄). Removal of the methylene chloride gave pale yellow crystals which were washed with small amounts of cold methanol to give 94 mg (87%) of 13, identical (mp, ir, pmr) with the product prepared by procedure A. Chromatography of 13 on silica gel or alumina with methylene chloride as eluent afforded pure 9.

Treatment of 9' according to procedure A gave labeled 13 which, after chromatography on alumina, gave labeled 9 whose pmr spec-

trum was identical with that of unlabeled 9 except that the peak at δ 0.91 was reduced in area from 6 H to 4.5 H and the peak at δ 0.86 was reduced in area from 9 H to 7.5 H. Europium shift experiments separated the latter peak into a 4.5 H peak (C3 and C5) and a 3 H peak (C8).

4-Methoxy-1,2,3,5,6,7,7,8-octamethyltetracyclo[3.3.0.0²,⁸.0³,⁶]octane (16). A solution of 13 (70 mg) in 5 ml of methanol containing a trace of sodium methoxide was allowed to stand at room temperature for 3 hr. The reaction mixture was concentrated to dryness under reduced pressure. Water (10 ml) was added to the residue and the whole mixture was extracted with ether. Combined ether extracts were washed with saturated sodium chloride solution and dried (MgSO₄). Removal of the solvent under reduced pressure gave 58 mg (84%) of 16 as colorless crystals which were further purified by vpc, 10 ft × 0.25 in. column, 20% FFAP on Chromosorb W, 100 ml/min of He, 160°, ret time 5 min, to give colorless crystals, mp 147–148° (sublimes). Mass spectrum (70 eV) m/e: 248 (M⁺), 201 (base peak); pmr (see structure).

Anal. Calcd for C₁₇H₂₈O: C, 82.20; H, 11.36. Found: C, 82.30; H, 11.34.

1,2,3,5,6,7,7,8-Octamethyltetracyclo[3.3.0.0²,⁸.0³,⁶]-4-octyl Trifluoroacetate (17). In an nmr tube, 300 μl of trifluoroacetic acid was added (syringe) to a solution of 30 mg of 9 in 700 μl of carbon tetrachloride, and the mixture was shaken. Within 1 min the pmr spectrum showed that the starting material was consumed. The mixture was poured onto ice and extracted with methylene chloride. Combined methylene chloride extracts were washed with 10% sodium bicarbonate solution then water and dried (Na₂SO₄). Removal of the solvent under reduced pressure gave 38 mg (90%) of 17 as a pale yellow oil. Purification by vpc, 5 ft × 0.25 in. column, 20% FFAP on Chromosorb W, 100 ml/min of He, 160°, ret time 6 min, gave 17 as a colorless oil. Ir (neat) 1780 cm⁻¹ (C=O); mass spectrum (70 eV) m/e 330 (M⁺), 201 (base peak); pmr (see structure).

Anal. Calcd for C₁₈H₂₅O₂F₃: C, 65.44; H, 7.58. Found: C, 65.59, H, 7.59.

Treatment of 9' with trifluoroacetic acid following the procedure just described gave 17', whose pmr spectrum was identical with that of 17 except that the areas of the singlets at δ 0.90 and 1.05 were reduced from 6 H and 9 H to 4.5 H and 7.5 H, respectively. Shift reagent resolved the latter to two peaks of 4.5 H and 3 H.

Ionization of 9 in FSO₃H–SO₂ClF. Preparation of 7. The following procedure is general for the preparation of carbonium ions described in this paper.

Small Scale (Nmr). A proton nmr tube was marked by pencil in advance at volumes of 50 and 250 μl. About 50 μl of FSO₃H was placed in the nmr tube which was cooled to −78°. Under a nitrogen atmosphere, about 200 μl of SO₂ClF was condensed in the nmr tube, above the FSO₃H. Finally, 50 μl of a methylene chloride solution containing 40 mg of 9 was added using a syringe, and the contents were kept at −78° for 5 min. The contents were then mixed using a "super mixer" (Matheson Scientific, Cat. No. 601-0005) to give a reddish orange solution of 7. Appropriately larger amounts were used for the cmr than for the pmr spectra. The pmr and cmr spectra are shown in Figures 1 and 2, respectively.

Preparative Scale. The apparatus is shown in Figure 3. We are indebted to Professor D. G. Farnum and Dr. A. Wolf for advice. Approximately 1 ml of FSO₃H was placed in the 10-ml modified flask and cooled to −78° under a N₂ atmosphere. Compound 9 (200 mg) was placed in the cooled (−78°) jacketed dropping funnel and sufficient SO₂ClF was condensed in the funnel until 9 was completely dissolved. After about 10 min the solution was added dropwise, with stirring, to the FSO₃H at −78° to give a reddish orange solution of 7. Additional SO₂ClF was condensed in the funnel, then added to the flask, to rinse out the remaining 9. In quenching studies, the solution was forced by nitrogen pressure out the bottom of the flask into the quenching mixture.

Quenching Ion 7. With Water. A solution of 7 prepared from 200 mg of 9 in FSO₃H–SO₂ClF at −78°, as described, was added quickly but dropwise at −78° to a vigorously stirred suspension of excess sodium carbonate in 100 ml of pentane. The mixture was stirred vigorously for 1 hr at −78°. On warming to 0°, water was added dropwise until the color was discharged. After an additional 15 min of stirring, the pentane layer, combined with washings, was washed with water and dried (MgSO₄). Removal of the pentane under reduced pressure gave 180 mg of a yellow oil. The crude product was submitted to preparative thin layer chromatography (silica gel, methylene chloride eluent) to give 120 mg (60%) of pure 9 (ir, pmr).

With Methanol. A solution of 7 prepared from 40 mg of 9 in FSO₃H–SO₂ClF at −78°, as described, was quickly added to a

suspension of excess sodium methoxide in methanol at −78°. The resulting suspension was slowly warmed to room temperature. The residue obtained by removal of the methanol under vacuum was treated with water and extracted (three times) with ether. Combined ether extracts were washed with saturated sodium chloride solution and dried (MgSO₄), and the solvent was removed under reduced pressure. The residue, formed in nearly quantitative yield, was essentially pure **16** (pmr).

4-Methoxy-1,2,3,5,6,7,8,8-octamethylbicyclo[3.3.0]octa-2,6-diene (25) and 2-methylene-1,3,5,6,7,8,8-heptamethylbicyclo[3.3.0]octa-3,6-diene (26). The reddish yellow solution of **7** prepared from 40 mg of **9** in FSO₃H–SO₂ClF was allowed to stand at −45° for 2 hr. The reaction was monitored by pmr, and at the end of this time the reddish violet solution had the pmr spectrum indicated on structure **24**. The solution was cooled to −78° and added to a suspension of excess sodium methoxide in methanol kept at −78°. The suspension was slowly warmed to room temperature and concentrated to dryness under reduced pressure. The solid residue was treated with cold water and extracted fully with ether. Combined extracts were washed with saturated sodium chloride solution and dried (MgSO₄), and the ether was removed under reduced pressure to give a nearly quantitative yield of **25** as a pale yellow oil. Its pmr spectrum is shown in the structure. Injection of **25** in a 10 ft × 0.25 in. vpc column, 20% FFAP on Chromosorb W, 100 ml/min of He, 160°, ret time 15 min, gave **26** as the sole product. Ir (neat) 1635 (w), 1620 (m), 885 (s); uv (EtOH) λ_{max} 241 nm (ϵ 12,000); mass spectrum (70 eV) m/e 216 (M⁺), 201 (base); pmr see structure; the peaks at δ 1.47 and 1.53 were homoallylically coupled quartets, $J = 1$ Hz. Double irradiation of the peak at δ 5.64 caused collapse into singlets of the doublets at δ 1.67 and 4.59.

Anal. Calcd for C₁₆H₂₄: C, 88.82; H, 11.18. Found: C, 88.97; H, 11.17.

4-Methyl-d_3-3,7-dimethyl-$d_{1.5}$,$d_{1.5}$-1,5,6,8,8-pentamethylbicyclo[3.-2.1]octa-3,6-dien-2-one (10′′′). Labeled ketone **10′′** (1.0 g) was refluxed overnight in 10 ml of CH₃OD containing 50 mg of sodium methoxide. Work-up as in the preparation of **10′** gave 0.9 g (90%) of **10′′′** as a pale yellow oil. Its pmr spectrum was identical with that of **10**[38] except that the peak at δ 1.85 (C4 methyl) was absent, that at δ 1.63 (C3 and C6 methyls) was reduced in area from 6 H to 4.5 H, and that at δ 1.42 (C7 methyl) was reduced in area from 3 H to 1.5 H.

1-Methyl-d_3-3,5-dimethyl-$d_{1.5}$,$d_{1.5}$-2,6,7,7,8-pentamethyltetracyclo-[3.3.0.0²,⁸.0³,⁶]octan-4-one (8′′′). Irradiation of **10′′′** in ether as in the preparation of **8′** gave **8′′′** whose pmr spectrum was identical with that of **8**[9] except that the singlets at δ 1.01 (C3 and C5 methyls) and 1.04 (C1 and C2 methyls) were reduced in area from 6 H to 3 H.

1-Methyl-d_3-3,5-dimethyl-$d_{1.5}$,$d_{1.5}$-2,6,7,7,8-pentamethyltetracyclo-[3.3.0.0²,⁸.0³,⁶]octan-4-ol (9′′′). Reaction of **8′′′** (500 mg) with lithium aluminum hydride (35 mg) in anhydrous ether (15 ml), according to the procedure for the preparation of **9**, gave 460 mg (92%) of **9′′′** as colorless crystals. Its pmr spectrum was identical with that of **9** except that the peak at δ 0.91 (C1 and C2 methyls) was reduced in area from 6 H to 3 H and the peak at δ 0.86 (C3, C5 and C8 methyls) was reduced from 9 H to 6 H.

Preparation of 7′. Treatment of **9′′′** with FSO₃H–SO₂ClF (1:4) at −78° as in the preparation of **7** gave **7′** whose pmr spectrum differed from that of **7** only in that the peak at δ 1.80 was reduced in area from 12 H to 6 H.

4-Methoxy-2,3,5,6-tetramethyl-$d_{1.5}$,$d_{1.5}$,$d_{1.5}$,$d_{1.5}$-1,7,8,8-tetramethyl-bicyclo[3.3.0]octa-2,6-diene (25′) and 2-methylene-d_2-3,5,6-trimeth-yl-$d_{1.5}$,$d_{1.5}$,$d_{1.5}$-1,7,8,8-tetramethylbicyclo[3.3.0]octa-3,6-diene (26′). Following the same procedure as described for the preparation of **24** from **7**, 40 mg of **9′′′** was allowed to rearrange in FSO₃H–SO₂ClF at −45°. The resulting **24′** had a pmr spectrum identical with that of **24** except that the peaks at δ 1.44, 1.90, 2.29, and 3.03 were reduced in area from 3 H to 1.5 H each. Quenching with methanol, as in the preparation of **25**, gave a nearly quantitative yield of **25′** whose pmr spectrum was identical with that of **25** except that δ 0.83 (C5 methyl) was reduced in area from 3 H to 1.5 H, and that at δ 1.56 (C2, C3, and C6 methyls) was reduced in area from 9 H to 4.5 H. The entire sample of **25′** was injected in the gas chromatograph, as in the preparation of **26**, to give **26′** as a colorless oil. Its pmr spectrum was identical with that of **26** except that the peak at δ 0.92 (C5 and C8 methyls) was reduced in area from 6 H to 4.5 H, the peaks at δ 1.53 (C6 methyl) and 1.67 (C3 methyl) were reduced from 3 H to 1.5 H each, and the peaks at δ 4.59 and 4.86 (vinyl protons) were reduced from 1 H to *ca.* 0.5 H each.

Kinetics of the Rearrangement of 7 to 24. The reaction was followed by the disappearance of the combined signals at δ 0.77 and 0.75 in **7** (7 H), since **24** has no peaks in this region, and also by the
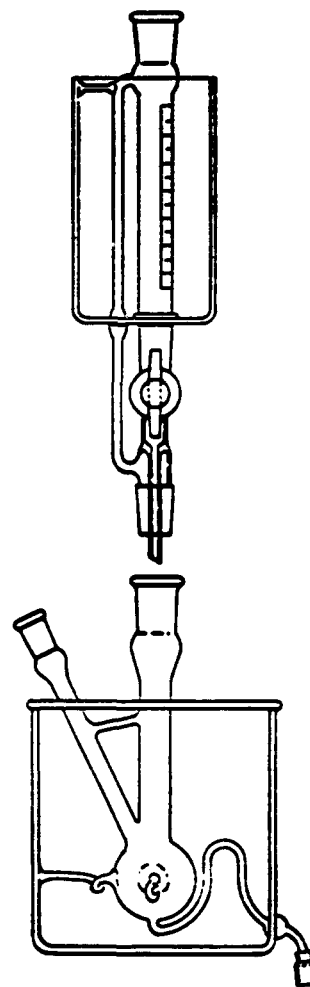

Figure 3. Apparatus used for the preparation of carbonium ion solutions.

appearance of the peak at δ 3.03 (3 H) in **24**. Reactions were followed to about 75% completion. The kinetics were strictly first order, and each rate constant is the average of at least four runs. The kinetic data are shown in Table I. The data gave a linear

Table I

t, °C	$10^4 k$, sec⁻¹	t, °C	$10^4 k$, sec⁻¹
−39.0	11 ± 2	−48.0	3.1 ± 0.1
−42.5	6.95 ± 0.5	−51.0	1.65 ± 0.2
−45.5	4.4 ± 0.4	−55.0	0.82 ± 0.02

Arrhenius plot, from which the activation parameters (at −48°) quoted in the text were calculated.

4-Methoxy-1,2,3,4,6,7,8,8-octamethylbicyclo[3.3.0]octa-2,6-diene (36). A solution of **7** prepared from 120 mg of **9** was allowed to rearrange at −35 to −30°, the reaction being followed by pmr. Almost immediate rearrangement to **24** (see experimental on kinetics) was followed by further rapid rearrangement (15–30 min) to about 90% **35** and 10% of a minor product.[28] The kinetics of the rearrangement **24** → **35** could not be followed accurately because of interference in the pmr spectrum by the minor product. The pmr spectrum of **35** is shown in the structure. When rearrangement was complete, the solution was cooled to −78° and quenched in methanol containing excess sodium methoxide at −78°, as described for **24**. The resulting suspension was slowly warmed to room temperature and concentrated to dryness under reduced pressure. Cold water was added to the solid residue, and the whole extracted with ether. Combined ether extracts were washed with saturated sodium chloride solution, dried (MgSO₄), and evaporated under reduced pressure to give **36** as a pale yellow oil, along

with small amounts of contaminating hydrocarbons. The pmr spectrum of **36** (see structure) was deduced from this mixture; the ether was not further purified.

Trienes 37, 38, and 39. The methyl ether **36**, prepared as just described, was injected in a 10 ft × 0.25 in. column, 20% FFAP on Chromosorb W, 100 ml/min of He, 155°, to give three major products. In different runs the ratios varied, since the trienes seemed to be thermally interconvertible. However, the yields were usually **39** > **38** > **37**. 1,2,3,4,6,7,8,8-Octamethylbicyclo[3.3.0]octa-2,4,6-triene (**37**): retention time 8.5 min; ir (CCl₄) 1640 (w), 1610 (w) cm⁻¹; mass spectrum (70 eV) m/e 216 (M⁺), 201 (base); uv (ethanol) 304 nm (ε 8100); pmr (see structure) the signals at δ 1.64 and 1.77 showed small homoallylic coupling (J ≅ 1 Hz); the signal at δ 1.80 was similarly split. 2-Methylene-1,3,4,6,7,8,8-heptamethylbicyclo-[3.3.0]octa-3,6-diene (**38**): retention time 10 min; ir (CCl₄) 1625 (m), 875 (s) cm⁻¹; mass spectrum (70 eV) m/e 216 (M⁺), 201 (base); uv (ethanol) 244 nm (ε 15,000); pmr (see structure) the peaks at δ 1.47 and 1.60 were homoallylically coupled quartets, J ≅ 1 Hz, as were the peaks at δ 1.72 and 1.78. 4-Methylene-1,2,3,6,7,8,8-heptamethylbicyclo[3.3.0]octa-2,6-diene (**39**): retention time 11 min; ir (CCl₄) 1620 (m), 870 (m) cm⁻¹; mass spectrum (70 eV) m/e 216 (M⁺), 201 (base); uv (ethanol) 244 nm (ε 16,400); pmr (see structure) the peaks at δ 1.45 and 1.63 were homoallylically coupled quartets, J ≅ 1 Hz, as were those at δ 1.73 and 1.74. The peaks at 2.91, 4.60 and 4.63 were narrow multiplets.

Labeled 35′–39′. The experiments were carried out as in the preparation of **35–39** but starting with 120 mg of **9′′′**. The pmr spectra were as follows: **35′** identical with **35** except that the peaks at δ 1.60, 2.04, 2.22, and 2.96 were reduced in area to 1.5 H each; **36′**, identical with **36**, except that the peaks at δ 1.07, 1.08, 1.46, and 1.65 were reduced in area to 1.5 H each; **37′**, identical with **37** except that the peaks at δ 0.80, 1.77, and 1.80 were reduced to 1.5 H each and that at δ 1.90 was reduced to 4.5 H; **38′**, identical with that of **38** except that the peaks at δ 1.08, 1.60, 1.72, and 1.78 were reduced in area to 1.5 H each; **39′**, identical with that of **39** except that the peaks at 1.08, 1.63, and 1.73 were reduced to 1.5 H each and the peaks at δ 4.60 and 4.63 were reduced to 0.5 H each.

Ion 42. A solution of 120 mg of **9** in 1.2 ml of trifluoroacetic acid prepared at −10° was slowly allowed to warm. At 10° the pmr spectrum began to change, and after 30 min at that temperature the changes were complete to give the pmr spectrum shown on structure **42**. No further change occurred in the pmr spectrum, even when the solution was refluxed for 2 hr. Solutions of **42** could also be prepared by dissolving **9** in TFA at room temperature, but the pmr spectrum showed the presence of minor impurities. When solutions of **42** prepared as described were quenched in a slurry of ice in 10% sodium hydroxide solution, extracted with ether, dried (MgSO₄), and evaporated, and the residue was subjected to vpc (10 ft × 0.25 in. column, 20% FFAP on Chromosorb W, 100 ml/min of He, 155°), trienes **37**, **38**, and **39** were the sole products, identified by ir and pmr with the same trienes obtained from **36** (*vide supra*). The relative amounts were **37** ≫ **38** > **39**.³⁹ Solutions of **37**, **38**, or **39** in trifluoroacetic acid at room temperature also gave ion **42** (pmr). However, solutions of **37** in FSO₃H–SO₂ClF 1:4 at −78° gave a pmr spectrum corresponding to 50% **35** plus additional peaks due to other ions.
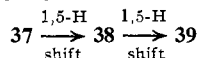
Variously Deuterated 42. Alcohol **9** (120 mg) was dissolved in 1.2 ml of CF₃CO₂D at room temperature, and the pmr spectrum was taken within 5 min. The spectrum was identical with that of **42** except that it lacked the signals at δ 1.29 (d, 3 H), 2.37 (3 H), and 3.27 (m, 1 H) and that at δ 2.17 was reduced in area from 6 H to 3 H. After 4 hr, the signal at δ 2.30 was also gone, and the spectrum consisted of only four equal signals at δ 1.00, 1.20, 1.27, and 2.17 (**42**-d₁₃).

Ketone **8′′′** (50 mg) was reduced with lithium aluminum deuteride, as in the preparation of **9**, to give **9′′′′′**, whose pmr spectrum differed from that of **9** in that the peak at δ 0.86 was reduced in area from 9 H to 6 H, that at δ 0.91 was reduced from 6 H to 3 H, and that at δ 3.50 (1 H) was absent. Alcohol **9′′′′′** (40 mg) was dissolved in 400 μl of TFA at room temperature, and the pmr spectrum was taken within 5 min. It was identical with that of **42** except that the singlet at δ 1.20 was reduced in area from 3 H to 1.5 H, and that at δ 2.17 was reduced from 6 H to 4.5 H (**42**-d₃).

A solution of **42** prepared from 50 mg of **9** in 50 μl of TFA at room temperature was diluted with 200 μl of CF₃CO₂D. After 48 hr at room temperature the pmr spectrum was identical with that of **42** except that the signals at δ 2.30, 2.37, and 3.27 were absent, and the doublet centered at δ 1.29 became a singlet (3 H) (**42**-d₇). After 2 weeks at room temperature, the peak at δ 1.29 was virtually gone and that at δ 2.17 was reduced in area from 6 H to just over 3 H (**42**-d₁₃).

2-Methylene-1,3,5,6,7,8,8-heptamethyltetracyclo[3.3.0.0³,⁷.0⁴,⁶]octane (43). A solution of **26** (100 mg) in 8 ml of anhydrous ether, in a quartz test tube, was deoxygenated by passing through a stream of dry nitrogen for 5 min. The contents were sealed with a serum cap and irradiated with a Hanovia 450-W lamp through a Vycor filter. The reaction was monitored by vpc (Varian Aerograph, Model 1400, fid) using a 5 ft × ¹/₈ in. column, 10% OV-1 on Chromosorb W 60–80, 30 ml/min of N₂ at 140°; the peak due to starting material (ret time 11 min) was gradually replaced by a product peak at 5.5 min. Reaction was complete in 5 hr. Removal of the ether under vacuum gave 100 mg (∼100%) of **43** as pale yellow crystals. Purification by preparative vpc (5 ft × 0.25 in. column, 20% FFAP on Chromosorb, 100 ml/min of He, 110°, ret. time 9 min) gave colorless crystals, mp 124–126° (sublimes). Ir (CCl₄) 1670 (m), 890 (s) cm⁻¹; mass spectrum (70 eV) m/e 216 (M⁺), 201 (base); pmr (see structure).

Similar irradiation of **26′** (50 mg) in ether (4 ml) gave a nearly quantitative yield of **43′** whose pmr spectrum was identical with that of **43** except that the peak at δ 1.00 was reduced in area from 6 H to 4.5 H, the peaks at δ 1.03 and 1.10 were reduced in area from 3 H to 1.5 H, and the vinyl proton peaks at δ 4.12 were reduced in area from 2 H to 1 H.

Conversion of 43 to 13, 17, and 7. A solution of 20 mg of **43** in 1 ml of acetone was treated with hydrochloric acid as in procedure B for the preparation of **13** from **9**. There was obtained 18 mg (80%) of **13** as pale yellow crystals, identified by pmr.

In an nmr tube, 15 mg of **43** in about 300 μl of CCl₄ was treated with 100 μl of TFA (as in the preparation of **17** from **9**). There was obtained on work-up 12 mg (78%) of **17** as a pale yellow oil, identified by its pmr spectrum.

A solution of **43** (40 mg) in FSO₃H–SO₂ClF (1:4) at −78° was prepared in a manner similar to the preparation of **7** from **9**. The resulting solution had an identical pmr spectrum to that obtained from **9**.

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(39) It seems likely that the initial deprotonation product of **42** is **37**, the product formed in greatest yield. Neither **38** nor **39** can arise directly in this manner. They may be derived from **37** by 1,5-hydrogen shifts. If so, the sequence would be

$$\mathbf{37} \xrightarrow[\text{shift}]{\text{1,5-H}} \mathbf{38} \xrightarrow[\text{shift}]{\text{1,5-H}} \mathbf{39}$$

accounting for the relative yields. Separate experiments show that these thermal rearrangements occur.