Rearrangements of Longifolene through Stable Carbonium Ions. Preparation of Novel C_{15} Hexahydronaphthalenes[1a]

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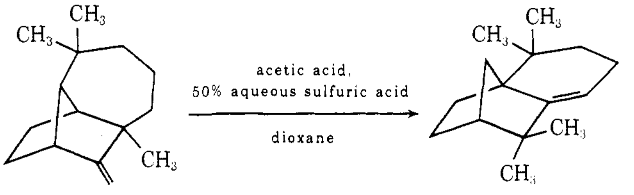
Abstract: Longifolene rearranges in fluorosulfonic acid to stable carbonium ions which give good yields of some new C_{15} hexahydronaphthalenes on quenching. By choice of the temperature at which the stable carbonium ion is formed, the structure of the product can be controlled. Below −40° the major product is 75% of a 1:1 mixture of 1,1-dimethyl-7-isopropyl-1,2,3,5,6,7-hexahydronaphthalene (**15**) and 1,1-dimethyl-7-isopropyl-1,2,3,4,5,6-hexahydronaphthalene (**16**), at 0° it is **16** (64%), and at 25° it is 1,1-dimethyl-6-isopropyl-1,2,3,7,8a-hexahydronaphthalene (**18**) (61%). Other minor products are also identified.

Acid-catalyzed rearrangements have been in the armory of the synthetic organic chemist from the beginning. They have been effective in part because the transient nature of the carbonium ion[2] intermediate limits the number of exits from it and permits equilibrium to become established among a limited number of products. In fact, when the carbonium ion is permitted to escape by too many paths, complex product mixtures are obtained since the products are often comparable in energy content or are formed in a number of competitive, irreversible reactions. The use of carbonium ion stabilizing solvents to alter the course of these reactions attracted us since the carbonium ion would have time to explore many internal escape paths, but would be blocked from proceeding to neutral products. Since electronic energy differences in carbonium ions would be magnified compared to those in neutral molecules, an equilibrium among a limited number of stable carbonium ions might be established. Irreversible quenching could then provide new products.

The rearrangements of terpenes in acidic media have been the source of extensive and at times intriguing research endeavors[4] for a long time. While systems of varying acidities were used to promote the structural changes of these compounds, the cations were present as long-lived, stable species in only a few cases. Since the competitive processes of elimination and solvent capture are minimized in the weakly basic fluorosulfonic acid, it was thought that the metastable carbonium ions initially formed in this medium might rearrange to carbonium ions of greater stability *via* intermediates not accessible to cations having shorter lifetimes.

Such a dependence of the mode of rearrangement on the acidity of the reaction medium has been observed in the rearrangements of the sesquiterpene hydrocarbon longifolene. Longifolene **1** rearranged to isolongifolene **2** and a mixture of tricyclic acetates when it was treated with a mixture of acetic acid and 50% aqueous sulfuric acid in dioxane.[5]



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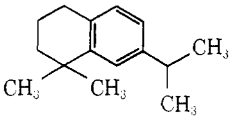
In the presence of the strong Lewis acid boron trifluoride–etherate, longifolene isomerized over a 14-hr period to a mixture of isomeric monoolefins and the aromatic hydrocarbon **3**.[6]



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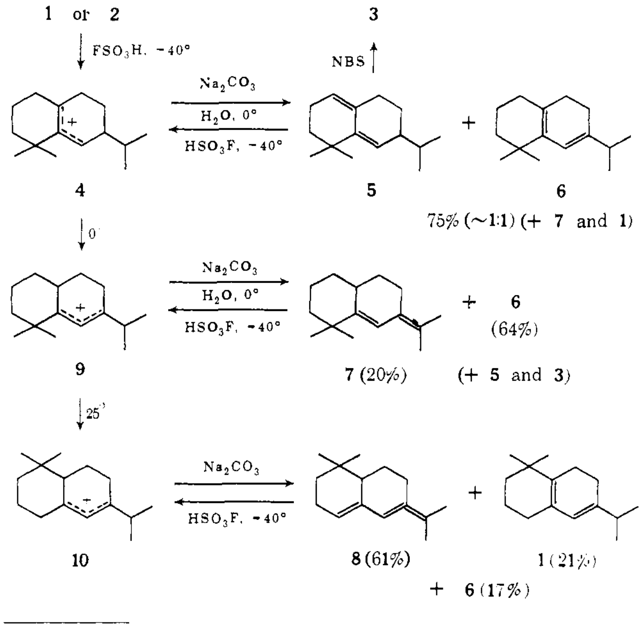
Work from this laboratory has demonstrated that longifolene undergoes a series of rearrangements when solutions in fluorosulfonic acid are warmed from −78 to 25°. A variety of products was obtained by quench-

Scheme I. Cations and Quenching Products Obtained from Longifolene in Fluorosulfonic Acid



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[1] (a) A preliminary account: D. G. Farnum and G. Mehta, *Chem. Commun.*, 1643 (1968). Abstracted in part from the Ph.D. Thesis of R. A. Mader, Michigan State University, 1972. The work was supported by the National Science Foundation under Grants GP 10734 and 27994. (b) Dow Chemical Company Summer Fellow, 1972.

[2] We prefer the term "carbonium ion" to the suggested "carbenium ion"[3] for reasons detailed in the Appendix.

[3] G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

[4] G. Ourisson, *Proc. Chem. Soc., London*, 294 (1964).

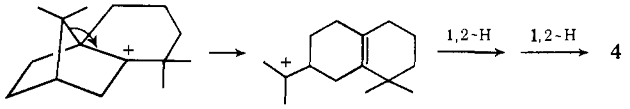
[5] J. Prahlad, R. Ranghanathan, U. Nayak, T. Santhanakrishnan, and S. Dev, *Tetrahedron Lett.*, 417 (1964).

[6] S. C. Bisarya, U. R. Nayak, and S. Dev, *Tetrahedron Lett.*, 2323 (1964).

ing the cation mixtures which were present at different temperatures in this range (Scheme I).[7] This work is discussed in more detail here.

Results

The −40° Cation and Its Quenching Products. When solutions of longifolene in fluorosulfonic acid were kept below −40° (see Experimental Section), they exhibited a reasonably clean proton nmr spectrum with a broad singlet signal at τ 0.78 corresponding to a terminal hydrogen of a cyclohexenyl cation, a sharp singlet at 8.63 for the *gem*-dimethyl, and a doublet (J = 6 Hz) at 8.86 for the isopropyl group. These data were consistent with the reasonable structure **4** for the cation, mechanistically accessible by the following transformation of cation **12**, suggested as an intermediate in the interconversion of longifolene and isolongifolene.[8]



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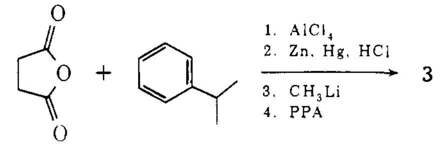
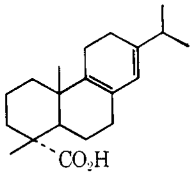
Further confirmation of the carbon skeleton of the cation came from the quenching products obtained by careful destruction of the cation solution in aqueous sodium carbonate at 0° (see Experimental Section). A 90% yield of a light yellow oil containing more than 80% of a 1 : 1 mixture of hexahydronaphthalenes **5** and **6** was obtained.[9] The mixture could be separated by preparative gas chromatography or by column chromatography. The structure **5** was easily deduced from the spectra (λ_{max} 241 (calcd, 245 nm); nmr τ 4.48 (1 H, s) and 4.70 (1 H, m), terminal dienylic hydrogens, 8.97, 9.00 (each 3 H, s), nonequivalent geminal dimethyl group, 9.10, 9.13 (each 3 H, d, J = 6 Hz) diastereotopic isopropyl methyls) and conversion to the aromatic hydrocarbon **3** by *N*-bromosuccinimide (NBS) in boiling carbon tetrachloride. The aromatic hydrocarbon (spectra in Experimental Section) was conveniently prepared for comparison as follows.



Structure **6** was more difficult to establish since the compound did not cleanly dehydrogenate to **3**, and its ultraviolet spectrum was anomalous (found λ_{max} 263 (calcd 275 nm)). However, the nmr spectrum (τ 4.38 (1 H, s), dienylic hydrogen, 8.05 (4 H, s) cyclohexadiene methylenes, 8.98 (6 H, d, J = 7 Hz), magnetically equivalent isopropyl methyls, and 9.02 (6 H, s) magnetically equivalent *gem*-dimethyls) was consistent with structure **6**, and palustric acid (**13**), with a similar chromophore, showed a similarly anomalous ultraviolet spectrum (266 nm[10]). Most convincing, although



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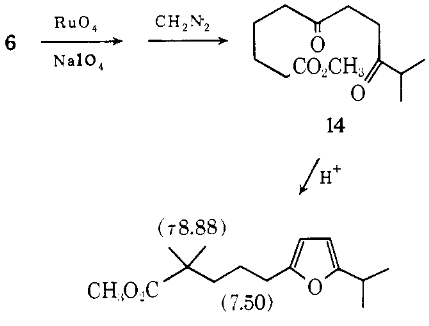
attempted degradation of **6** by ozonolysis gave a complex mixture from which nothing was identified, oxidation with ruthenium tetroxide–sodium metaperiodate[11] followed by diazomethane esterification gave the diketo ester **14** (60%) which gave furan **15** (56%) on acid-catalyzed dehydration.



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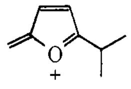
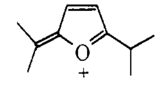
The structures of **14** and **15** were evident from their chemical relationship and spectroscopic properties (see Experimental Section), but it is probably worth noting the basis for placement of the *gem*-dimethyl group in view of its later migration (see below). The nmr spectrum of furan **15** clearly established the presence of an isopropyl group directly attached to the furan ring, since the methine septet appeared at low field (τ 7.20). The remaining low field two hydrogen multiplet (τ 7.50) could have been a methylene group α to either the furan, or conceivably the ester. That is, the *gem*-dimethyl and furan α-methylene groups in **15** might have been interchanged. However, the mass spectrum of **15** showed its base peak at m/e 123, the mass of fragment **15a**, and no peak at m/e 151, the mass of fragment **15b**.



15a m/e 123



15b m/e 151

Upon solution in fluorosulfonic acid at −40°, diene **5** regenerated the −40° cation **4**.

The 0° Cation and Its Quenching Products. When solutions of cation **4** in fluorosulfonic acid were warmed to 0° for a time, the nmr spectrum underwent an irreversible change. The new spectrum was consistent with the structure **9** for the 0° cation[12] (τ 2.23 (1 H, s), central hydrogen of an allyl cation, 8.50 (6 H, s), degenerate *gem*-methyls, 8.47 (6 H, d, J = 6 Hz), isopropyl methyls). Note that both the *gem*-dimethyl and the isopropyl resonances moved downfield by comparison with the −40° cation (**4**) consistent with their placement at the terminal carbon atoms of the allyl cation. Confirmation of the carbon skeleton of cation **9** was obtained by quenching the solution in the usual

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[7] D. G. Farnum and G. Mehta, *Chem. Commun.*, 1643 (1968).

[8] J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Amer. Chem. Soc.*, **89**, 2590 (1967).

[9] In the earlier work[7] **6** was not observed as a product from quenching the −40° cation. Product ratios were also somewhat different. This may in part be due to the difficulty in reproducing the quenching conditions. Our present quenching techniques give more reproducible results.

[10] A. W. Burgstahler and L. R. Worden, *J. Amer. Chem. Soc.*, **86**, 96 (1964).

[11] S. W. Pelletier, K. N. Iyer, and C. W. J. Chang, *J. Org. Chem.*, **35**, 3535 (1970).

[12] A small amount (<10%) of the −40° cation **14** was still present at equilibrium as evidenced by a small peak at τ 0.78.

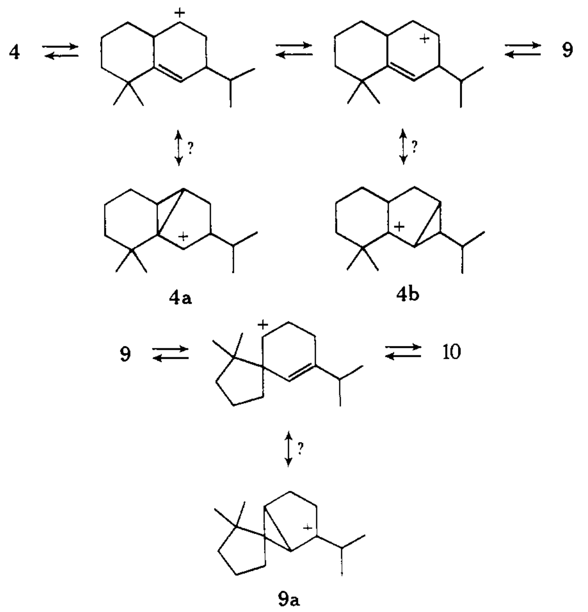
way to give a mixture of hydrocarbons in 97% crude yield containing **6** (64%), **5** (9%), **3** (2%), and a new hydrocarbon **7** (20%). Column chromatography afforded a pure sample of **7** which was characterized by its spectra (especially the ultraviolet: λ_{max} 248 (calcd, 250 nm); nmr τ 3.83 (1 H, br s), vinyl hydrogen, 8.27, 8.32 (each 3 H, s), nonequivalent vinyl methyls, 8.88, 8.95 (each 3 H, s), nonequivalent quaternary methyls, and no isopropyl group), and by its conversion to aromatic hydrocarbon **3** with NBS. Both **6** and **7** regenerated the 0° cation **9**[12] on solution in fluorosulfonic acid at −40°.

The 25° Cation and Its Quenching Products. When solutions of the 0° cation **9** are warmed to 25° for 24 hr or 50° for 1 hr, a second irreversible change takes place in the nmr spectrum. The presence of a new cation similar in substitution to cation **9** is revealed by a peak at τ 2.35 (1 H, s) for the central hydrogen on a tetrasubstituted allyl cation. The *gem*-methyls are no longer equivalent and are further from the cationic center (higher field singlet resonances at τ 8.75 and 9.02), while the isopropyl group is nearly the same (τ 8.50, d, J = 6 Hz).[13] The proposed structure **10** for this new cation was confirmed by formation of an 80% yield of quenching products consisting of **8** (61%) and **11** (21%) (hydrocarbon **6** was also obtained (17%), presumably from the cation **9** present at equilibrium). Both **8** and **11** dehydrogenated easily to the aromatic hydrocarbon **16** which was easily identified by the characteristic nmr (AB quartet centered at τ 3.05, $\Delta\tau$ 0.3 ppm, J = 8 Hz; overlapping doublet, τ 3.22, J = 3 Hz) and ir pattern (2000–1650, 895, 825 cm^{-1}) for a 1,2,4-trisubstituted aromatic, and the near identity of the remainder of its nmr spectrum with its isomer **3**. The spectra of **8** were also well accommodated by its proposed structure. Thus, the nmr showed the terminal and central hydrogens on the diene at τ 4.28 (1 H, s) and 4.70 (1 H, m), the isopropyl at 8.98 (6 H, d, J = 6 Hz), and the nonequivalent *gem*-methyls at 9.03 and 9.23 (each 3 H, s). The ultraviolet maximum at 240 nm was satisfyingly identical with the expected value. Although the nmr spectrum of **11** was well in accord with the proposed structure (it was nearly identical with that of **6** except for a small shift of the vinyl hydrogen resonance to τ 4.68, and showed the cyclohexadiene methylenes as a moderately sharp singlet resonance at τ 8.05), the ultraviolet absorption at 250 nm (ϵ 6100) required some explanation (calcd, 275 nm). It seemed possible that the bulk of the *gem*-dimethyl might introduce a still greater twisting than that present in **6** and palustric acid (**11**) and result in an even greater hypsochromic shift.[14]

Interpretation

Although the courses of these rearrangements of longifolene in fluorosulfonic acid are for the most part mechanistically unexceptional, and our main point is that the rearrangements can be controlled in a synthetically useful way, there are a few features that elicit interpretive comments. First, it is noteworthy that although the several cations are only slightly different in structure, the energetic differences (though less than a few kilocalories) are sufficient to ensure synthetically satisfactory predominance of one cation at equilibrium. This is especially interesting in cations **9** and **10**, which differ from one another only in the placement of the *gem*-dimethyl. A second related point is that the various mechanistic routes available for rearrangement of longifolene to cation **4**, cation **4** to cation **9**, and cation **9** to cation **10** are sufficiently different in activation energy to permit the use of temperature control as an on–off switch. Both of these features illustrate our premise that energy differences are enhanced in cations.

The temperatures at which the rearrangements take place suggest they have activation energies in the range of 15–20 kcal/mol, which is about the same as that found by Saunders[15] for rearrangements of tertiary carbonium ions proceeding through secondary carbonium ions, and secondary carbonium ions proceeding through primary carbonium ions.[16] We are surprised at the ease of the rearrangements of cations **4** → **9** and **9** → **10**, since normally they involve an uphill climb from a conjugated, highly substituted allyl cation to an unconjugated tertiary cation in the case of **4**, and to a secondary cation in the case of **9** as indicated below.[17]



It is for these reasons that we suggest the activation energy for the rearrangements may be lowered by contributions from structures such as **4a**, **4b**, and **9a** to the transition state.

We finally note that although the rearrangement of **9** to **10** bears a formal resemblance to the dienol–benzene

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(13) Some 20% of the isomeric cation **9** was always present at equilibrium as shown by its nmr resonance at τ 2.23.

(14) We could not find any suitable model compounds in the literature although we looked for sesquiterpenes that might be more flexible than palustric acid.

(15) (a) M. Saunders, E. L. Hagen, and J. Rosenfeld, *J. Amer. Chem. Soc.*, **90**, 6882 (1968); (b) M. Saunders and E. L. Hagen, *ibid.*, **90**, 2436 (1968).

(16) Saunders suggests[15a] that rearrangements of secondary ions may proceed through protonated cyclopropanes rather than primary carbonium ions since the activation energies (15–18 kcal) seem lower than expected.

(17) The alternative direct 1,4-hydride shift mechanism is considered unlikely since a suprafacial shift is orbital symmetry forbidden[18] while an antarafacial shift is too contorted. Proton elimination to form a diene and readdition to give the isomeric cation is not likely since exchange of deuterium in cyclohexenyl cations even in 94% D_2SO_4 is too slow[19] to account for the observed rearrangement rates.

(18) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(19) N. C. Deno, N. Friedman, J. D. Hodge, and J. J. Houser, *J. Amer. Chem. Soc.*, **85**, 2995 (1963).

and dienone–phenol rearrangements,[20] we are not aware of a report of its operation in other systems. It seems likely that the conditions of long carbonium lifetime were salubrious to its operation here.[21]

Experimental Section

General. All melting points were taken on a Thomas-Hoover apparatus. Infrared spectra were recorded as neat films on a Perkin-Elmer 237B spectrophotometer, and ultraviolet spectra in methanol solutions on a Unicam SP800 spectrophotometer. Nuclear magnetic resonance spectra were taken on Varian T-60 and HA-100 spectrometers. Tetramethylammonium tetrafluoroborate (τ 6.87[22]) was used as an internal standard for all carbonium ion spectra, and tetramethylsilane was used as an internal standard for all other spectra. An Hitachi RM-U6 spectrometer was used to obtain all mass spectra.

Preparation and Quenching of Stable Carbocations in Fluorosulfonic Acid. General Procedure. In the preparative experiments the carbocations were prepared by adding 10% solutions of the natural products in fluorotrichloromethane dropwise to a well-stirred solution of fluorosulfonic acid which had been cooled to −78°. The resultant carbocation solutions were 10% with respect to the organic cation. After the solution had been warmed to the desired temperature it was cooled back to −78°, and added dropwise to a mixture of hexane and aqueous sodium carbonate which was cooled in an ice bath and agitated with a Vibromix stirrer. The apparatus used for this operation is shown in Figure 1. This addition was accomplished by replacing the nitrogen egress tube with a stopper and gently forcing the carbonium ion solutions through the insulated glass tube with a positive nitrogen pressure. The hexane extract and washings from the quenching solution were dried over anhydrous sodium sulfate and evaporated to dryness at the aspirator. The residual oils were analyzed by gas chromatography (gc) on an F&M 700 using a 6 ft × 0.25 in. column of 5% Carbowax 20M on Chromosorb G, at 150° unless otherwise noted. Preparative gc separations employed a 9.5 ft × $^3/_8$ in. column of 20% Carbowax 20M on Chromosorb P at 170°.

The −40° Cation and Its Quenching Products. Following the general procedure above, either longifolene or isolongifolene afforded carbocation solutions which, if kept below −40°, gave nmr resonances at τ 0.78 (broad singlet, area 1), 8.63 (singlet, area ~6), and 8.86 (doublet, J = 6 Hz, area ~6). There was additional complex, broad absorption from 6.4 to 8.5, but the spectrum showed no additional peaks below 6.5 other than solvent and the 0.78 resonance.

In preparative quenching studies 1.0 g of longifolene yielded 0.90 g (90%) of a light yellow oil which resolved into four main components on gc analysis. The first of these (38% by gc), **6** (bp 126–128° (9.5 mm); n^{30}D 1.5083), showed the following spectroscopic properties: ir 1660 cm^{-1}; uv $\lambda_{max}^{CH_3OH}$ 263 nm (ϵ 11,100); nmr τ (CCl_4) 4.38 (1 H, br, s), 8.05 (4 H, s), 8.98 (6 H, d, J = 7 Hz), 9.02 (6 H, s); mass spectrum *m/e* (rel intensity) 204 (M^+, 81), 189 (100). The material was prone to discolor and become viscous on standing so reliable combustion analyses were not obtained The second component (38% by gc), **5** (bp 101–103° (5 mm), n^{30}D 1.5110), showed the following spectroscopic properties: ir 1590, 862 cm^{-1}; uv $\lambda_{max}^{CH_3OH}$ 241 nm (ϵ 22,000); nmr τ (CCl_4) 4.48 (1 H, br s), 4.70 (1 H, m), 8.97 (3 H, s), 9.00 (3 H, s) 9.10 (3 H, d, J = 6 Hz), 9.13 (3 H, d, J = 6 Hz); mass spectrum *m/e* 204. The third component (6%), **3**, could also be obtained from **5** and **6** by dehydrogenation with NBS. Its properties are reported below. The fourth component (12%), **7**, was obtained in higher yield from the 0° cation. Its properties are also reported below.

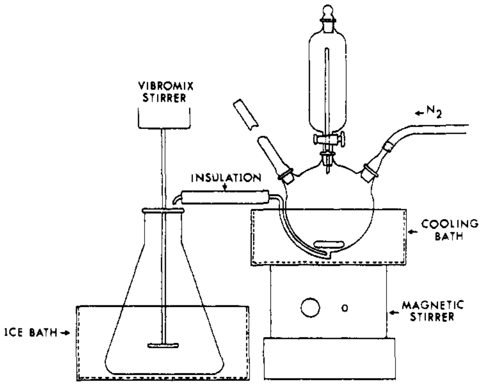

Figure 1. Apparatus used for preparative carbonium ion experiments.

The 0° Cation and Its Quenching Products. Following the general procedure above, longifolene in fluorosulfonic acid was warmed to 0° for 1 hr and then cooled to −78°. The nmr spectrum below 0° showed resonances at τ 2.23 (1 H, br s), 0.78 (very weak, <0.1 H, br s), 8.47 (~6 H, d, J = 6 Hz), and 8.50 (6 H, s). Other than the solvent peak and the usual broad absorption from τ 6.5 to 8.5, the spectrum was quite clean.

In preparative quenching experiments, 1.0 g of longifolene yielded a light yellow oil (0.97 g, 97%) which resolved into four main components on gc. The first of these (64%) was identical in spectroscopic properties with **6** obtained above. The second (9%) was similarly identical with **5** obtained above. The third (2%) was identical in retention time with **3** obtained above. The fourth (20%) was identical in retention time and spectroscopic properties with **7** obtained above (bp 80–81° (0.5 mm), n^{30}D 1.5041): ir 1650, 885, 870 cm^{-1}; uv $\lambda_{max}^{O_2H_5OH}$ 248 (ϵ 17,000); nmr τ (CCl_4) 3.83 (1 H, br s), 8.27 (3 H, br s), 8.32 (3 H, br s), 8.88 (3 H, s), 8.95 (3 H, s); mass spectrum *m/e* 204.

The 25° Cation and Its Quenching Products. Heating solutions of longifolene in fluorosulfonic acid obtained as above to 25° for 24 hr or 50° for 1 hr gave dark yellow solutions with nmrr esonances at τ 2.35 (1 H, br s), 2.23 (~0.2 H, br s), 8.50 (~6 H, d, J = 6 Hz), 8.75 (~3 H, s), and 9.02 (~3 H, s).[23] Once again the remainder of the spectrum was quite clean in the low-field region.

In a preparative quenching experiment 1.0 g of longifolene yielded a dark brown oil (0.80 g, 80%) which resolved into three major components on gc analysis (140°). These were separated by preparative gc (200°) into **6** (17%), and two new hydrocarbons, **11** (21%) and **8** (61%), in order of elution. The first of these (**11**) showed the following spectroscopic properties: ir 1600 cm^{-1}; uv $\lambda_{max}^{CH_3OH}$ 250 nm (ϵ 6100) (275, slight shoulder, 3050); nmr τ (CCl_4) 4.68 (1 H, br s), 8.05 (4 H, br s), 9.00 (6 H, d, J = 7 Hz), 9.02 (6 H, s); mass spectrum *m/e* (rel intensity) 240 (M^+, 30), 202 ($M - H_2$, 25), 189 ($M - CH_3$, 100), 187 ($M - CH_3 - H_2$, 93). The second (**8**) showed the following spectroscopic properties: ir 1640, 893 cm^{-1}; uv $\lambda_{max}^{C_2H_5OH}$ 240 nm (ϵ 18,400); nmr τ 4.28 (1 H, s), 4.70 (1 H, m), 8.98 (6 H, d, J = 6 Hz), 9.03 and 9.23 (each 3 H, s); mass spectrum *m/e* 204.

Dehydrogenation of Dienes. For all dehydrogenation experiments the following procedure was used: a mixture of the diene (*ca.* 200 mg) and *N*-bromosuccinimide (*ca.* 175 mg) in carbon tetrachloride (10 ml) was boiled under reflux for 30 min. The reaction mixture was cooled and filtered, and the filtrate was concentrated under vacuum and distilled in a short-path distillation apparatus to give the colorless oily product as indicated below.

From **5** or **7** there was obtained *ca.* 160 mg (80%) of **13**: ir 1920, 1800, 1630, 1580, 1500 cm^{-1}; nmr τ (CCl_4) 2.95 (1 H, s), 3.18 (2 H, s), 7.05–7.50 (3 H, m), 8.75 (6 H, s), 8.80 (6 H, d, J = 6 Hz); mass spectrum *m/e* 202.

From **8** or **11** there was obtained **16**: ir 1900, 1780, 1620, 1570, 1500 cm^{-1}; nmr τ (CCl_4) AB quartet centered at 3.05 (2 H, $\Delta\tau$ 0.3 ppm, J_{AB} = 8 Hz, J_{BC} ~ 3 Hz), overlapping doublet centered at 3.22 (1 H, J ~ 3 Hz), 7.00–7.50 (3 H, m), 8.77 (6 H, s), 8.82 (6 H, d, J ~ 6 Hz); mass spectrum *m/e* 202.

Preparation of 5-(4-Isopropylphenyl)-2-methyl-2-pentanol. A

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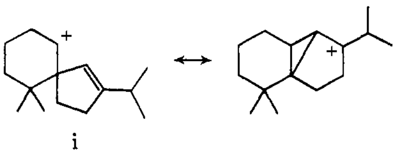
[20] R. H. Shapiro in "Steroid Reactions," C. Djerassi, Ed., Holden-Day, San Francisco, Calif., 1963, Chapter 9.

[21] The rearrangement of **9** to **10** might also take place through cation i. We choose **9a** only by analogy and for its efficiency, and have no convincing arguments against i.

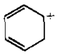
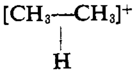
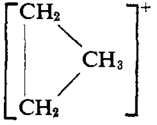
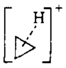
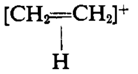
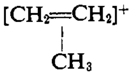
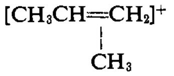
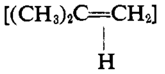
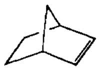
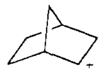
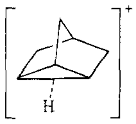


i

[22] D. G. Farnum, M. A. T. Heybey, and B. Webster, *J. Amer. Chem. Soc.*, **86**, 673 (1964).

[23] Because of the mixture of cations present, areas were only very approximate.

Table I. Some Current and Suggested Names for Some Common Carbocations

Neutral molecule		Cation	
Structure	Name	Structure	Name
$(CH_3)_2NH$	Dimethylam*ine*	$(CH_3)_2NH_2^+$	Dimethylammonium
$(CH_3)_2O$	Dimethyl ox*ide*	$(CH_3)_2OH^+$	Dimethyloxonium
$(CH_3)_2S$	Dimethyl sulf*ide*	$(CH_3)_2SH^+$	Dimethylsulfonium
$(CH_3)_2SO$	Dimethyl sulfox*ide*	$(CH_3)_3SO^+$	Trimethyloxosulfonium or trimethylsulfoxonium
CH_3Br	Methyl brom*ide*	$(CH_3)_2Br^+$	Dimethylbromonium
$(CH_3)_2C:$	Dimethylcarb*ene*	$(CH_3)_2CH^+$	Dimethylcarbonium
$CH_2{=}CH_2$	Ethen*e*	$CH_3{}^+CH_2$	Ethenonium
$(CH_3)_2C{=}CH_2$	2-Methylpropen*e*	$(CH_3)_3C^+$	2-Methyl-2-propenonium
	Cyclopropen*e*		Cyclopropenonium (or cyclopropyl cation)
	Benzen*e*		Benzenonium
CH_4	Meth*ane*	CH_5^+	Methonium
CH_3CH_3	Eth*ane*	 $\underset{\mathrm{H}}{\underset{\vert}{[\mathrm{CH_3{-}CH_3}]^+}}$	C-Ethonium
		$[CH_3CH_4]^+$	H-Ethonium
	Cycloprop*ane*		H-Cycloproponium
			C-Cycloproponium
$CH_2{=}CH_2$	Ethen*e*	 $\underset{\mathrm{H}}{\underset{\vert}{[\mathrm{CH_2{=}CH_2}]^+}}$	π-Ethenonium
		 $\underset{\mathrm{CH_3}}{\underset{\vert}{[\mathrm{CH_2{=}CH_2}]^+}}$	π-Methylethenonium
$CH_3CH{=}CH_2$	Propen*e*	 $[\mathrm{CH_3CH{=}}\underset{\mathrm{CH_3}}{\underset{\vert}{\mathrm{CH_2}}}]^+$	π-Methylpropenonium
$(CH_3)_2C{=}CH_2$	2-Methylpropen*e*	 $[\mathrm{(CH_3)_2C{=}}\underset{\mathrm{H}}{\underset{\vert}{\mathrm{CH_2}}}]$	2-Methyl-π-propenonium
	Bicyclo[2.2.1]hepten*e* or norbornen*e*		Bicyclo[2.2.1]heptenonium or norbornenonium or norbornyl cation[a]
	Tricyclo[2.2.1.0^{2,6}]hept*ane* or nortricyclen*e*		$C^{(1,2)}$-Tricyclo[2.2.1.0^{2,6}]heptonium or $C^{(1,2)}$-nortricyclonium[a]
			$H^{(1)}$-Tricyclo[2.2.1.0^{2,6}]heptonium or $H^{(1)}$-nortricyclonium[a]

[a] These last three entries are all carbocations. The first is a carbonium ion; the last two are alkonium ions.

solution of methyl-4-(*p*-isopropylphenyl)butyrate (440 mg) (obtained by treating the acid[24] with excess diazomethane) in 20 ml of ether was stirred under nitrogen. Methyllithium (2 ml of 2.4 *M* solution) in ether was added. After the solution was stirred at room temperature for 1 hr, water was added cautiously. The ether layer was removed and the aqueous phase extracted with ether. The solvent was removed and the product was evaporatively distilled at 60° (~0.4 mm) to give 321 mg (73%) of an oil: ir 3450, 1525 cm^{-1}; nmr τ (CCl_4) 3.00 (4 H, s), 8.82 (6 H, d, J = 6 Hz), 8.90 (6 H, s); *m/e* (rel intensity) 202 (4, M − H_2O), 187 (4, M − H_2O − CH_3).

Preparation of 1,1-Dimethyl-7-isopropyl-1,2,3,4-tetrahydronaphthalene (13). The carbinol obtained above (238 mg) was added to poly(phosphoric acid) (4.0 g). The mixture was heated to 100° for 30 min and cooled to room temperature, and ice-water was added. The product was extracted with hexane and the extract was chromatographed on activity II alumina (10 × 1 cm column). The column was eluted with 50 ml of hexane, and the eluate was evaporatively distilled to give 153 mg (10%) of an oil whose spectroscopic properties were identical with those reported above for 3 obtained by dehydrogenation of 5.

Ruthenium Tetroxide–Sodium Metaperiodate Oxidation[11] of 16. Preparation of Methyl-6,9-diketo-2,2,10-trimethylundecanoate (14). To a suspension of ruthenium dioxide (K & K, 50 mg) in 25 ml of acetone was added a solution of sodium metaperiodate (500 mg) in 10 ml of water. The mixture was stirred for 30 min, and a solution of 16 (200 mg, 1 mmol) in 15 ml of acetone was added dropwise. The yellow suspension was stirred for 10 hr while fractions of a solution of 2.0 g of sodium metaperiodate in 1:2 water–acetone were added at 2-hr intervals. Isopropyl alcohol (10 ml) and Norit A (2 g, to aid in the removal of ruthenium dioxide) were added, and the mixture was stirred for 15 min. The mixture was then filtered, and the residue was washed with copious amounts of acetone. The acetone and isopropyl alcohol were removed under reduced pressure, and the aqueous residue was extracted with three 50-ml portions of ether. The ether extracts were combined and treated with excess diazomethane. The solvent was removed to give 198 mg (74%) of a yellow oil of which 85% was contained in one peak on gc analysis. An analytical sample was obtained by preparative tlc on alumina eluted with 2:1 ether–hexane: ir 1710 and 1735

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[24] L. I. Smith and C.-P. Lo, *J. Amer. Chem. Soc.*, 70, 2209 (1948).

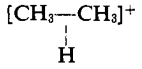
cm^{-1}; nmr τ (CCl_4) 6.40 (3 H, s), 8.87 (6 H, s), 8.92 (6 H, d, J = 7 Hz); *m/e* (rel intensity) 270 (M^+, 2), 252 (8 M − H_2O).

Acid-Catalyzed Cyclization of 14. Formation of 2-Isopropyl-5-(4-carbomethoxy-4-methylpentyl)furan (15). A solution of **14** (262 mg, 0.98 mmol) and *p*-toluenesulfonic acid (100 mg) in 30 ml of benzene was placed in a flask equipped with a Dean-Stark trap. The solution was heated to reflux for 30 min. The reaction mixture was cooled to room temperature, and 20 ml of 10% sodium carbonate solution was added. The benzene layer was removed, and the aqueous phase was extracted twice with 30 ml of ether. The benzene and ether extracts were combined, washed with saturated potassium chloride, and dried over anhydrous sodium sulfate. Removal of the solvent gave 234 mg of a dark oil which was chromatographed on activity II alumina. Elution with 1:4 ether–hexane gave 134 mg (56%) of nearly pure **15**. Preparative gc (235°, 10 ft × 0.38 in. column of 20% SE-30 on Chromosorb P) afforded an analytical sample: ir 1735, 1570 and 780 cm^{-1}; uv $\lambda_{max}^{CH_3OH}$ 223 nm (ϵ 7000); nmr τ (CCl_4) 4.28 (2 H, s), 6.46 (3 H, s), 7.20 (1 H, sept, J = 7 Hz), 7.50 (2 H, m), 8.80 (6 H, d, J = 7 Hz), 8.88 (6 H, s); *m/e* (rel intensity) 252 (M^+, 96), 237 (95, M − CH_3).

Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.16; H, 9.78.

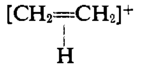
Appendix

As a result of his extensive work on carbocations in strong acid media, and his discovery of pentacoordinated cations such as CH_5^+, Olah has suggested replacement of the term "carbonium ion" with "carbenium ion" for trivalent carbocations, reserving the carbonium ion term for the pentavalent species.[3] Although we find the "carbocation" term very attractive, and intend to use it, and we agree with the need for a new term to describe pentavalent carbocations, we prefer to retain the term "carbonium ion" for trivalent carbocations for the following reasons. We feel that changing a well-established nomenclature should be done only if it proves to be unwieldy by comparison with its replacement, or is clearly logically inconsistent in essentials, or is ambiguous, or is unable to accommodate new structures. None of these criteria seem to us to apply to the term "carbonium ion" when properly used. We find it at least as "wieldy" as the alternative carbenium ion system proposed by Olah. It has been claimed that the term is logically inconsistent in that it does not reserve the "onium" suffix for the highest valence state of the ion as is done with other ions, and suggests an analogy with other onium ions which is not present.[3] However, in practice the "onium" suffix has *not* been reserved for the highest valence state, as the two species trimethylsulfonium, $(CH_3)_3S^+$, and trimethyloxosulfonium, $(CH_3)_3S^+O$, clearly show. In fact, the term "onium" reduced to its basic implication seems to imply a species formed by coordination of a cationic center with a free electron pair of a neutral species, *i.e.*, $N: + A^+ \rightarrow [NA]^+$ (see Table I). Seen from this perspective, combination of a cationic center with a carbene to give a carbonium ion (perhaps carbenonium ion would be a more accurate term, but carbonium ion is unambiguous and less awkward) is clearly analogous to combination with an amine to give an ammonium ion (see Table I). The objection has also been raised that, according to IUPAC rules, addition of a proton to carbene should give a carbenium ion in the same way that addition of a proton to ethene gives an ethenium ion. We are not convinced that carbene need be treated in the same way as "ethene" (nor are we in fact convinced that the rule is a good one or has been or will be followed in practice). In short, the logic of nomenclature is, and should be, a "loose" logic which adapts to perspective. Concerning the ambiguity of the carbonium ion nomenclature, it does not seem to us to be ambiguous when properly used. Once CH_3^+ is named either "carbonium ion" or "methyl cation" other trivalent carbocations can be named as derivatives of it or as cations of the parent organic radical. Although it is a bit unusual, we see no difficulty in practice in using the term "carbonium ion" as a general name for trivalent carbocations as well as a formal designation for the parent member of the series, methyl cation. In fact, the term "carbene" has been used in the same way without undue complications. Some unfortunate early confusion resulted in misnomers such as "benzylcarbonium ion" instead of either "phenylcarbonium ion" or "benzyl cation" for $C_6H_5CH_2^+$. Certainly not all trivalent carbocations can be named as derivatives of carbonium ion conveniently, but this does not warrant replacing such a useful system. We finally consider whether the current nomenclature is able to accommodate new structures, in particular pentavalent carbocations like CH_5^+. We submit that a simple extension of the implication of the "onium" suffix is all that is necessary. When any cation can be considered as formed by the combination of a neutral species and a cationic one, it can be named by dropping any unnecessary suffix from the name of the neutral species and adding "-onium ion." Thus "alkanes" become "alkanonium" or, more simply, "alkonium" ions, "alkenes" become "alkenonium ions," "cycloalkanes" become "cycloalkonium ions," "benzene" becomes "benzenonium" (or perhaps benzonium) ion, etc. In many cases the names, especially for the pentacoordinate carbocations, are the same as those suggested by Olah, *e.g.*, CH_5^+ = methonium ion, $(CH_2)_3H^+$ = cycloproponium ion. It will still be necessary to designate the site of protonation where this is other than through a two-electron σ bond to carbon, but this can easily be done following and extrapolating Olah's suggestions, *e.g.*



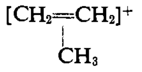
$$[CH_3\underset{\underset{H}{|}}{—}CH_3]^+$$

is C-ethonium, $CH_3CH_4^+$ = H-ethonium, $CH_3CH_2^+$ = ethenonium



$$[CH_2\underset{\underset{H}{|}}{=}CH_2]^+$$

is π-ethenonium, and



$$[CH_2\underset{\underset{CH_3}{|}}{=}CH_2]^+$$

is π-methylethenonium. A number of cations are named in Table I, not in order to develop a comprehensive system, but rather to illustrate the feasibility and consistency of this minimal and, we believe, essentially sufficient extension of current practice. The suffixes dropped in the name of the neutral molecule are italicized.