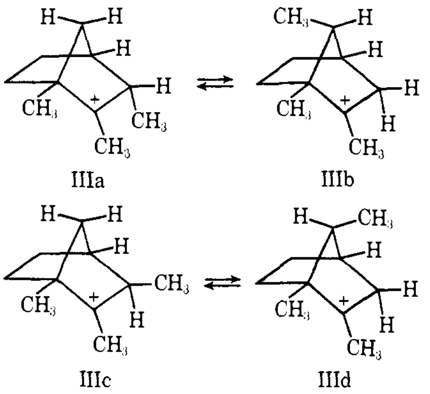
Carbonium Ion Rearrangements in the Fenchyl Series

Sir:

The dehydration of α-fenchol by various acidic catalysts has been an extensively studied reaction[1] and presently five different fenchenes (α → ζ) and cyclofenchene have been characterized. Although the carbonium ion rearrangements relating these fenchenes are well known,[2] little is known concerning the relative thermodynamic stability of the various carbonium ions or the kinetics of the rearrangements relating the ions.

Addition of α-fenchene (7,7-dimethyl-2-methylenenorbornane), β-fenchene (5,5-dimethyl-2-methylenenorbornane), or cyclofenchene, but not α-fenchol,[3] to 4:1 $SO_2ClF-FSO_3H$ at −130° yields a solution which contains, by nmr,[4] an equilibrium mixture of the cations I and II (Scheme I). The equilibrium constant is close to one and the value of k_1 (Scheme I) was estimated[5] to be 1 sec^{-1} at −78° ($\Delta F^{\ddagger}$ *ca.* 11.2 kcal/mol). On warming to −92°, I $\rightleftarrows$ II disappear completely forming III, with a rate constant k_2 of 5.1 ± 0.2 × 10^{-4} sec^{-1} ($\Delta F^{\ddagger}$ = 13.1 kcal/mol). Like the 1,2-dimethyl-2-norbornyl cation,[6] it has not been possible to observe the individual isomers IIIa and IIIb in the nmr spectra, since the Wagner–Meerwein rearrangements interconverting the two are still very rapid at −130°. Ion III further exists in two geometric forms, the equilibrium favoring the endo-anti pair IIIa–IIIb (K = 6.3 ± 0.3). At −15.0°, ion III rearranges to the "ultimate rearrangement" product of this bicyclo[2.2.1]heptyl series, ion IV, with a rate constant k_3 of 1.1 × 10^{-3} sec^{-1} ($\Delta F^{\ddagger}$ = 18.5 kcal/mol). The WM shift in this cation is also rapid on the nmr time scale at −130°. The final product is the allylic cation V, formed at 25.0° with a rate constant k_4 of 3.2 ± 0.2 × 10^{-4} sec^{-1} ($\Delta F^{\ddagger}$ = 22.2 kcal/mol). The formation of this cation from α-fenchol in sulfuric acid solvent was first reported by Deno and Houser.[7]

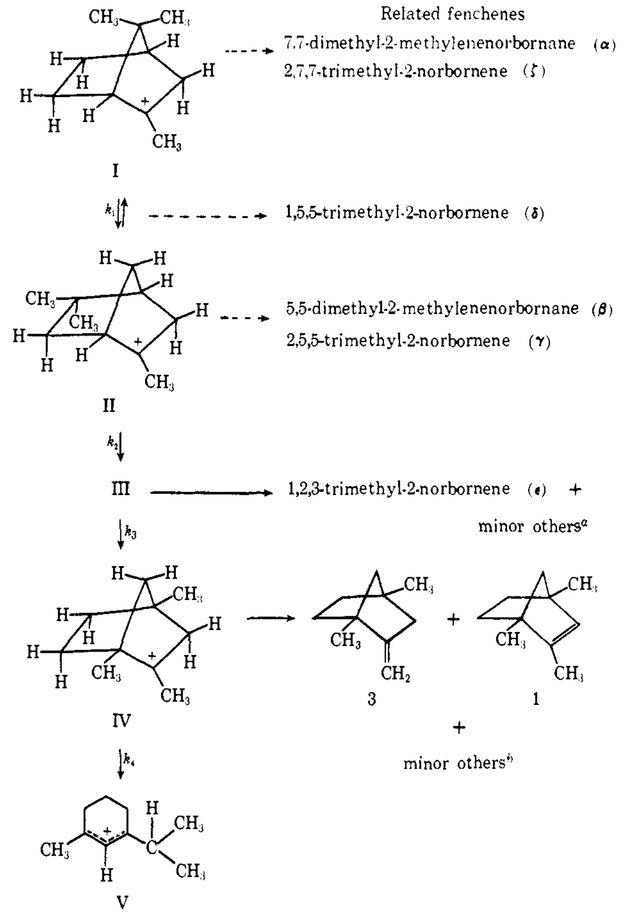


IIIa IIIb

IIIc IIId

In this work, recovery experiments (*i.e.*, quenching the ion solution in aqueous base) have been performed on ions III and IV yielding the results shown in Scheme I. The known products of the acid-catalyzed dehydration of α-fenchol stop at ion III derived compounds and it is apparent that k_3 is too slow to be of significance in the reactions previously studied. The two new "fenchenes" derived from IV have been isolated in a pure form and characterized by physical and chemical means.

Scheme I



[a] Exocyclic compounds derived from IIIa–d. Only one of these compounds could be isolated pure. A small amount of IV-derived products were also present. Pure 1,2,3-trimethyl-2-norbornene in acid gives only the IIIa–IIIb ions initially. [b] At least two further fenchenes are formed in small amounts and their structures is under investigation. All these compounds can be used to regenerate IV.

From the signal-to-noise ratio of the nmr spectra concerned, the difference in free energy between cations I $\rightleftarrows$ II and IV at 25° must be at least 4 kcal/mol. This is in excellent agreement with recent combustion results of Kozina, *et al.*,[8] who have shown that *trans*-2,3-dimethylnorbornane is *ca.* 4 kcal/mol less stable than the 1,4 isomer.

It is also possible that 1-methyl substituents are favored for electronic reasons since the 2,4-dimethyl-2-norbornyl cation rearranges[5] to the 1,2 isomer (K >

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(1) Reviewed in "Rodd's Chemistry of Carbon Compounds," 2nd ed, S. Coffey, Ed., Elsevier, Amsterdam, 1969, part II, pp 243–249.

(2) W. Hückel and D. Volkmann, *Ann. Chem.*, **664**, 31 (1963).

(3) This endo alcohol and others are simply protonated at this temperature and heterolysis of the C—O bond does not occur rapidly until the temperature reaches about −40°.

(4) The peaks for the two ions are so similar in chemical shift that one is unable to assign the peaks in detail. The gross features are, however, consistent with these structures.

(5) See part II of this series: E. Huang, K. Ranganayakulu, and T. S. Sorensen, *J. Amer. Chem. Soc.*, **94**, 1780 (1972).

(6) G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *ibid.*, **93**, 1442 (1971).

(7) N. C. Deno and J. J. Houser, *ibid.*, **86**, 1741 (1964).

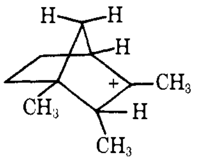
(8) M. P. Kozina, L. P. Timofeeva, S. M. Skuratov, N. A. Belikova, E. M. Milvitskaya, and A. F. Platé, *J. Chem. Therm.*, **3**, 563 (1971). We thank a referee for calling attention to this.

Table I. Nmr Chemical-Shift Positions[a] of the Carbonium Ions

Ion	Description
I and II	At −95°, 5.26 (d, J = 7 Hz), 5.34 (d, J = 7 Hz), the C-1 protons of the two ions; 6.12 and 6.34 (broad), the C-6 exo protons; 6.59, the C-2 methyl protons of both isomers; 6.79, probably the C-3 protons; 8.69 and 8.94, the nonequivalent *gem*-dimethyl groups of one isomer and 8.69 and 8.87, these same groups in the other isomer
IIIa ⇄ IIIb	At −40°,[b] 6.945, C-6 exo proton of IIIa (C-6 endo of IIIb); 7.300, probably C-4 proton; 7.49 (from decoupling experiments), C-3 proton of IIIa (C-7 of IIIb); 7.695, C-2 methyl protons of IIIa (C-1 of IIIb); 7.795, C-1 methyl protons of IIIa (C-2 of IIIb); 8.480 (d, J = 6.0 Hz), C-3 methyl protons of IIIa (C-7 of IIIb); 8.1–8.4, C-5 exo and endo protons[c]
IIIc ⇄ IIId	At −40°,[b] 7.655, C-1 methyl group of IIIc (C-2 of IIId); 7.97, C-2 methyl group of isomer IIIc (C-1 of isomer IIId); 7.55 (from decoupling experiments), C-3 proton of IIIc (C-7 of IIId); 8.95 (d, J = 7.2 Hz), C-3 methyl protons of IIIc (C-7 of IIId)[c]
IV	7.00 (very broad), averaged C-6 exo and endo protons; an AB pair centered at 7.51 and 7.72 (J = 15.0 Hz), the averaged C-3 exo-C-7 syn and C-3 endo-C-7 anti protons; 7.612, averaged C-1 and C-2 methyl protons; 8.415 (t, J = 6.0 Hz), this coupling with C-6 protons confirmed by double irradiation, the averaged C-5 exo and endo protons; 8.556, the C-4 methyl protons
V	2.36, C-2 proton; 6.82 (t, J = 6.0 Hz), the methylene protons at C-4 and C-6; 7.14, C-1 methyl protons; 7.68 (q, J = 6.0 Hz), the C-5 protons; 8.595 (d, J = 7 Hz), the isopropyl methyl protons[c]

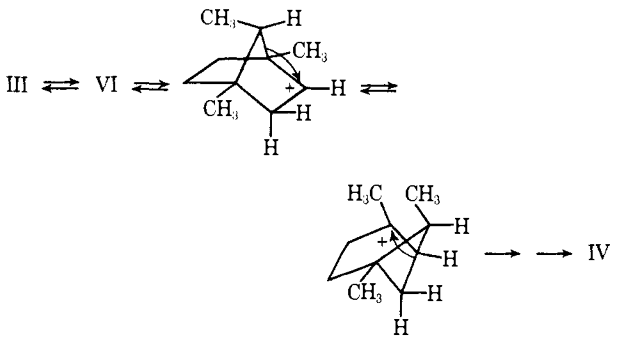
[a] In τ (parts per million) relative to internal tetramethylammonium cation; τ 6.90 in this and the following paper. [b] The chemical shifts are very temperature dependent, showing that the proportions of IIIa and IIIb or IIIc and IIId are changing with temperature. This is, of course, expected if the equilibrium constants are something other than unity. [c] Only peaks which could be assigned with reasonable certainty are included in the table. There are, in addition, broad absorptions in the regions expected for the protons not included in the table.

10) and ions such as III exist predominantly in the forms indicated, in spite of the easy accessibility of cation VI.



VI

The order in which the ions appear in the rearrangements is not an indication of sequential reactions since each step is certainly reversible. We believe, for example, that ion V is actually derived from I. The mechanism of the ion III → IV rearrangement is the only one not reasonably obvious and may involve a bicyclo[3.1.1]heptyl cation intermediate.



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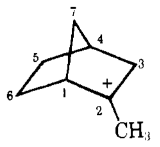
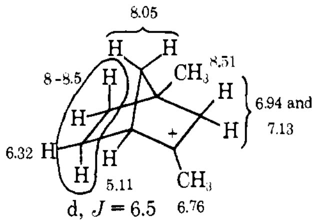
Observable Degenerate Rearrangements in 2-Methyl-2-norbornyl and Related Cations

Sir:

The 2-methyl-2-norbornyl cation I and 2,4-dimethyl-2-norbornyl cation II, in acidic solvents,[1] show nmr spectra at −80° appropriate for the static structures, but, at higher temperatures, line broadening is readily apparent. The results are complementary. In I, the C-1 proton doublet broadens above −80°[2] and the high-field peaks for the C-5, C-6-endo, and C-7 protons also broaden in a nondescript manner. The C-2 methyl peak remains unchanged and the C-6-exo peak becomes *less* broad. Beyond the coalescence temperature, the high-field region resembles an AB quartet and a coalesced peak (τ 6.71) develops under the C-2 methyl group (confirmed using 2-CD$_3$ derivative). Double irradiation spin saturation transfer (DISST) experiments[6,7] show that the C-1 proton is exchanging with a complex peak centered at *ca.* τ 8.30, assigned to the C-6-endo proton.



I



II

Cation II was prepared from 1,4-dimethyl-2-*endo*-norbornanol and is unreported. As the temperature is raised, the C-1 proton peak broadens but *both* methyl peaks *and* the C-6-exo proton peak remain nearly unchanged. The C-3-exo and endo proton peaks coalesce. DISST experiments at temperatures (−60°) where line broadening is just observable, in the region

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(1) For example, FSO$_3$H, FSO$_3$H–SO$_2$ClF, SbF$_5$–SO$_2$, FSO$_3$H–SbF$_5$. The rearrangement rates are virtually identical.

(2) The spectrum of I at −95° has been published by Olah, *et al.*[3,4] Their assignments were based on the earlier work of Farnum and Mehta[5] on the 2-phenyl analog. Our results show that the C-6-endo and a C-5 proton assignment should be interchanged. Olah, *et al.*, have referred vaguely to nmr line broadening for I but the results described, particularly in the later paper, are quite contrary to our own.

(3) G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3958 (1969).

(4) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970).

(5) D. G. Farnum and G. Mehta, *ibid.*, **91**, 3256 (1969).

(6) S. Forsén and R. A. Hoffman, *J. Chem. Phys.*, **39**, 2892 (1963).

(7) F. A. L. Anet and A. J. R. Bourns, *J. Amer. Chem. Soc.*, **89**, 760 (1967).