on a 6-ft. × 0.25-in. column of 10% Dow 710-on-Chromosorb-P at 200° and 200 cc. He/min. The mass spectrum at 8–10 e.v. showed the composition: 73.3% of d_6, 23.1% of d_5, 3.2% of d_4, and 0.4% of d_3.. The combustion analysis (by the falling drop method) gave 5.65 atoms of deuterium per molecule. The integrated intensity of the methyl p.m.r. signal, 6.36 methyl protons per molecule relative to 6.0 aromatic protons, showed that all of the deuterium atoms were distributed among the methyl groups. The chemical shifts are: aromatic multiplet at τ 2.87, methyl singlet at τ 8.11; optical rotations: α^{26} 0.0 ± 0.02° (c 5.0, isooctane, l 2) at 589, 435, and 365 mμ; α^{24} 0.0 ± 0.02° (c 3.1, chloroform, l 2) at 589 and 435 mμ; α^{25} 0.00 ± 0.01° (c 5.0, isooctane, l 0.5) between 350 and 275 mμ; $\alpha < 0.0005°$ (above 230 mμ (c 0.0176, isooctane, l 0.0108).[36]

Acknowledgments.—It is a pleasure to acknowledge the many fruitful and stimulating discussions with Dr. Clair J. Collins, Oak Ridge National Laboratory, and Dr. Max Wolfsberg, Brookhaven National Laboratory.

(36) This measurement was kindly performed for us by Dr. J. J. Duffield, Applied Physics Corp., using a Cary Model 60 spectropolarimeter.

[CONTRIBUTION FROM THE COLLEGE OF SCIENCE, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNA.]

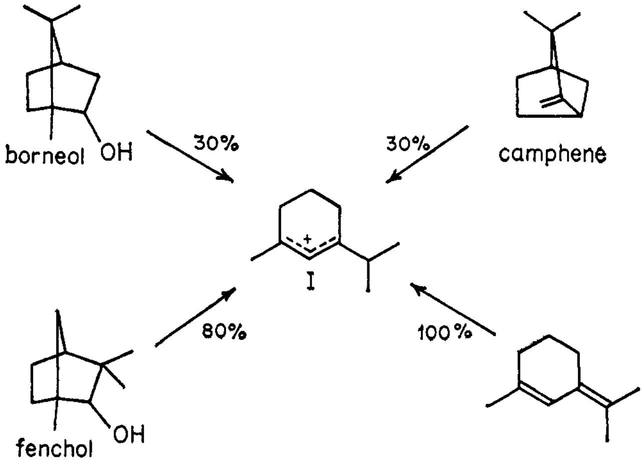
Carbonium Ions. XIV. The Opening of Bicyclic Alcohols to Cyclohexenyl Cations and the Further Conversion to Cyclopentenyl Cations

BY N. C. DENO AND JOHN J. HOUSER

RECEIVED DECEMBER 6, 1963

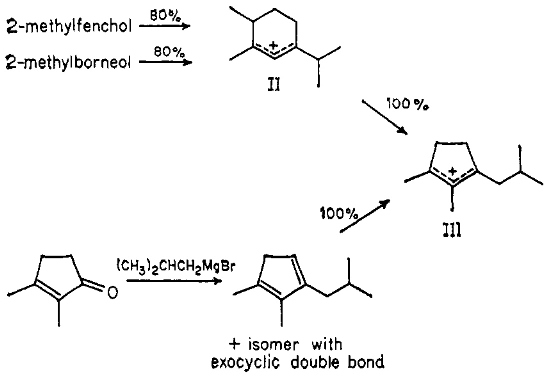
Fenchol and borneol open to the 1-isopropyl-3-methylcyclohexenyl cation in 96% H_2SO_4. 2-Methylfenchol and 2-methylborneol open to the 1-isopropyl-3,4-dimethylcyclohexenyl cation, which subsequently rearranges to the 1-isobutyl-2,3-dimethylcyclopentenyl cation. Similar reactions occur with 2,3,3-trimethylborneol, 2-phenylborneol, and 2-phenylfenchol. The yields are generally over 80% and the reactions are of synthetic value.

The following conversions are complete within minutes in 96% H_2SO_4.



The n.m.r. spectrum of I (Table I) is in exact accord both with the areas calculated for structure I and with the characteristic band positions established for cyclohexenyl cations.[1] In 96% H_2SO_4 at 25°, the half-time for conversion of fenchol to I is 4.6 min. in 10^{-5} M solution and 4.0 min. in 10^{-4} M solution. The rates exhibit first-order kinetics over the entire course of the reaction. The half-time for conversion in 82% H_2SO_4 is 5 min.

The following reactions, homologous to the above, introduce as an added feature an interesting collapse of a cyclohexenyl cation to a cyclopentenyl cation. The half-life for the conversion of II to III at 25° is 63 min. in 96% H_2SO_4 and 7 min. in 83% H_2SO_4. The n.m.r. spectrum of II appears in Table I and that of III is presented in Fig. 1. As pointed out by a referee, methylfenchyl and methylbornyl cations should rapidly interconvert and give the same yield of II and this was found.



The structure of III can be deduced from the n.m.r. spectrum (Fig. 1) alone. However, the assignment was confirmed by an independent synthesis of III, using the more conventional route shown in the above diagram.

A similar collapse of a cyclohexenyl cation to a cyclopentenyl cation probably takes place when 1,2,3,3,7,7-hexamethylbicyclo[2.2.1]heptan-2-ol (IV), trimethylborneol, is added to 96% H_2SO_4. After 35 days, product VI is present which has only CH_3 at C-2. In the interim, three intermediate cations with only H at C-2 can be recognized by the appearance and disappearance of n.m.r. bands at 7.43, 7.48, and 7.62 p.p.m. At 67 sec. after addition, 7.43 predominates and this must be a cyclohexenyl cation because of its ultraviolet absorption maximum at 320 mμ. At 500 sec., all three are nearly equal. At 7000 sec., 7.62 is strongly dominant. The 7.62 band also dominates at 20 hr. and is provisionally identified as V on the basis of the n.m.r. spectrum (Fig. 2) and the λ_{max} at 296 mμ, typical of highly alkylated cyclopentenyl cations.

The final product VI is a cyclopentenyl cation as shown by λ_{max} at 302 mμ. The n.m.r. spectrum (Fig. 3) is provisionally interpreted as a mixture of the general structure shown in Fig. 3. The two CH_3 groups at C-4 and C-5 are interpreted to be partly on each carbon and partly on a single carbon.

---

(1) N. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).

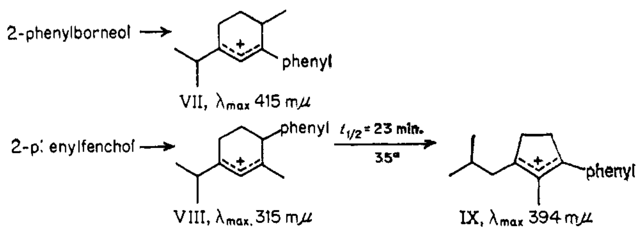
Table I

N.m.r. Spectra of Cyclohexenyl Cations

Substituent	Position of bands,[a] H on: Phenyl	C-2	C-4 and C-6	CH of *i*-Pr group	CH₃ on C-3	C-5	CH₃ of *i*-Pr group	CH₃ on C-4 (or C-6)	Relative areas, exptl.
1-Isopropyl-3-methyl (I)	.....	7.60	3.16[b]	[c]	2.84	2.07[d]	1.35[e]	..	0.9:3.8:2.9:2.0:6
1-Isopropyl-3,4-dimethyl (II)	.....	7.58	3.20[f]	[c]	2.85	2.13[g]	1.38[e]	1.41[e]	1.0:2.0:2.9:6 + 3
1-Phenyl-3-methyl	7.1–8.1	[h]	3.52[b] 3.09[b]	...	2.78	2.17[d]	..	..	7.0[i]:2.1:2.1:3:2.3
1-Phenyl-3-isopropyl-6-methyl (VII)	7.6–8.4	[h]	3.5–4.0 2.9–3.2	[j]	..	1.9–2.3	1.38[e]	1.41[e]	6.9[i]:~1:3.0:1.8:6 + 3
1-Isopropyl-3-methyl-4-phenyl (VIII)	7.32[k] 7.13[l]	7.73	3.20	[c]	2.58	2.26[g]	1.36[e]	..	3.1:1.9:0.9:3:3.1:1.9:6.0

[a] Positions are in p.p.m. relative (and downfield) to tetramethylsilane. The method of calibration is given in ref. 1. [b] Triplet, J = 6.0 c.p.s. [c] Recognition prevented because of broadening and splitting. [d] Quintet, J = 6.0 c.p.s. [e] Doublet, J = 6.6 c.p.s. [f] Footnote b, applied to the H on C-6. [g] Center of a multiplet. [h] Included in the phenyl H. [i] The structure would require 6 rather than 7. [j] This H is interpreted to be included in the area of the 2.9–3.2 band. [k] Center of *ortho* and *para* H multiplet. [l] Center of *meta* H multiplet.

2-Phenylborneol and 2-phenylfenchol ring open as shown below. The initial ring opening is complete



within minutes in 96% H_2SO_4. The n.m.r. spectra for VII and VIII appear in Table I and serve to identify the ions. The n.m.r. spectrum of 1-phenyl-3-methylcyclohexenyl cation is included for reference. The n.m.r. spectrum of IX is presented in Fig. 4 and the interpretation is regarded as provisional.

The band of the C-2 methyl in IX is at 2.44 p.p.m. This was lower than that of other cyclopentenyl cations, and it was suspected that this was due to paramagnetic currents in the neighboring phenyl at C-1. This suspicion was confirmed when it was found that 1-phenyl-2,3-dimethylcyclopentenyl cation, formed *via* a conventional Grignard synthesis, also had the 2.44 position for the C-2 methyl. The complete n.m.r. spectrum is shown in Fig. 5.

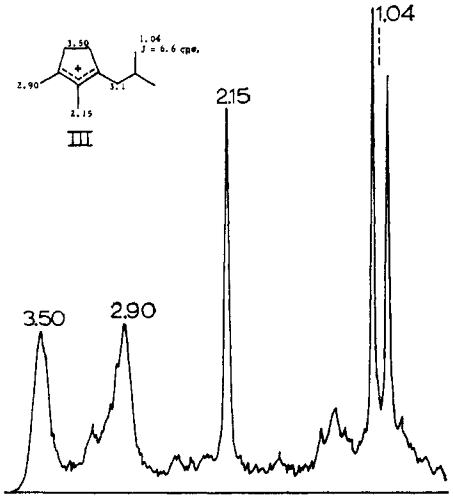


Fig. 1.—N.m.r. spectrum of III in 96% H_2SO_4 formed by adding 2-methylfenchol or 2-methylborneol to 96% H_2SO_4.

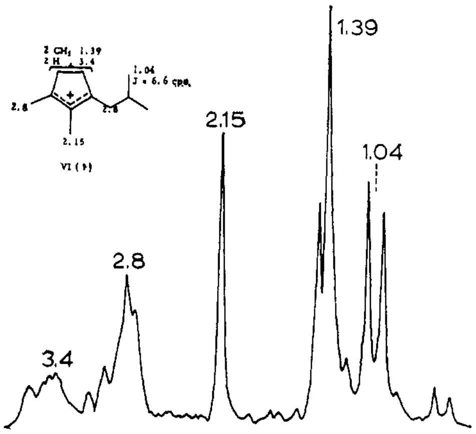


Fig. 3.—N.m.r. spectrum of VI in 96% H_2SO_4.

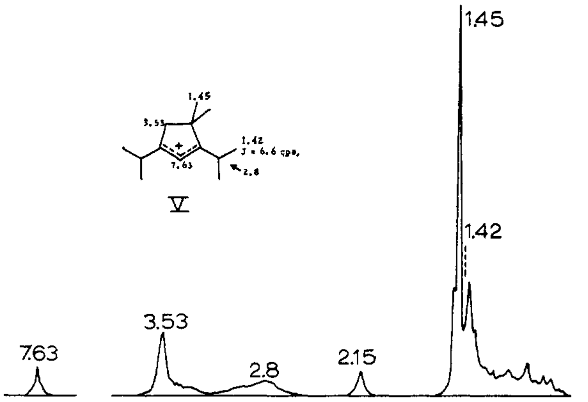


Fig. 2.—N.m.r. spectrum of V in 96% H_2SO_4 formed by adding 2,3,3-trimethylborneol (IV) to 96% H_2SO_4.

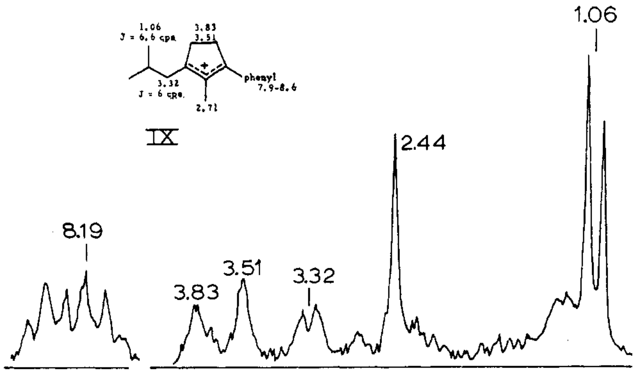


Fig. 4.—N.m.r. spectrum of IX in 96% H_2SO_4.

The high yields of these conversions and the ability generally to recover dienes from alkenyl cations by rapid dispersal techniques[1] means that these reaction are synthetic routes to highly alkylated cyclohexadienes and cyclopentadienes.

The results with 2-phenylborneol show that our supposed observations on the phenylbornyl cation[2] were in fact observations on VII. A similar conclusion probably holds for the other supposed arylbornyl cations in ref. 2. However, a series of arylnorbornyl cations,[3,4] the anisylnorbornyl cation in particular,[5] the 2,6-diarylnorbornyl cations,[6] and the anisylcamphenilyl cation,[7] do not appear to ring open but remain in solution in 96% H_2SO_4 as the arylbicycloalkyl cations. The n.m.r. spectrum of a solution of norborneol in 96% H_2SO_4 is interpreted as that of norbornyl hydrogen sulfate in which 1,2-alkyl shift is rapid enough to lead to hybrid n.m.r. bands.[8] 2-Methylnorborneol gave a featureless n.m.r. spectrum in 96% H_2SO_4.

Two closely related ring openings have been studied recently. Addition of camphorquinone to oleum produces 4-isopropenyl-2-methyl-1,3-cyclohexanedione.[9] Addition of fenchone to 96% H_2SO_4 at 80–100° produces 3,4-dimethylacetophenone.[10,11]

Experimental

The n.m.r. spectra were recorded on a Varian A-60 instrument. The usual rapid dispersal precautions[1] were employed in introducing the alcohols or dienes into the 96% H_2SO_4 although this was not always necessary. $(CH_3)_4N^+Cl^-$ was used as an internal standard and the n.m.r. bands are expressed in p.p.m. downfield and relative to $(CH_3)_4Si$.

The substituted borneols and fenchols were made by addition of RMgBr or RLi to the appropriate ketones. It is not known whether the OH group was *exo* or *endo* in the products and for the purposes of this study it makes little difference, since either isomer would produce the same intermediate carbonium ions. The yields were estimated from the n.m.r. spectra using the areas of the bands of the cations relative to the area of any featureless background.

2-Methylborneol has been reported.[12] The yield is low in a single treatment because part of the camphor simply donates a proton to the CH_3MgBr and is thus regenerated on hydrolysis. A more complete conversion was effected by two successive treatments of the initial reaction mixture (containing camphor plus 2-methylborneol) with excess CH_3MgBr. The camphor impurity still remaining was removed by formation of the oxime and fractional sublimation of the 2-methylborneol from the camphor oxime. In the preparation of 2-methylfenchol,[12] the fenchone impurity was similarly removed by conversion to the oxime and fractional distillation.

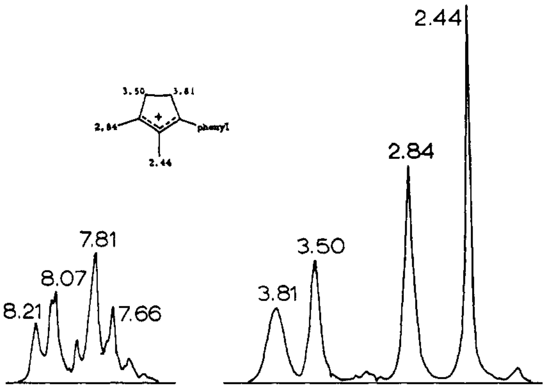


Fig. 5.—N.m.r. spectrum of 1-phenyl-2,3-dimethylcyclopentenyl cation in 96% H_2SO_4.

The preparation of 2-phenylborneol[13] and 2-phenylfenchol[14] have been reported.

1,2,3,3,7,7-Hexamethylbicyclo[2.2.1]heptan-2-ol (2,3,3-Trimethylborneol) (IV).—3,3-Dimethylcamphor was prepared by exhaustive methylation of camphor.[15] Treatment with a 10-fold excess of CH_3Li in ether for 6 days produced a crude product which was steam distilled twice and then sublimed at 20 mm. The m.p. of 111–131° suggests that the product was a mixture of the *endo* and *exo* isomers of IV.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.75; H, 12.35.

1-Isobutyl-2,3-dimethylcyclopentenyl Cation (III).—Cyclohexyl levulinate was prepared as described.[16] A benzene solution of 0.83 mole of CH_3CH_2MgBr was added to 0.64 mole of cyclohexyl levulinate in benzene at 0°. The yield of the lactone of 4-hydroxy-4-methylcaproic acid was 45%. The improved yield over that reported,[16] 30%, is apparently due to using an excess of the CH_3CH_2MgBr. The lactone was converted to 2,3-dimethylcyclopent-2-en-1-one as described.[16]

This ketone was treated with excess $(CH_3)_2CHCH_2MgBr$ in ether and hydrolyzed with aqueous NH_4Cl. The product was flash distilled at 20 mm. and then vacuum distilled. The product, b.p. 80–86° at 18 mm., was a mixture of dienes based on the infrared and n.m.r. spectra.

Anal. Calcd. for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.95; H, 12.00.

Addition of the diene mixture to 96% H_2SO_4 produced III quantitatively. The n.m.r. spectrum (Fig. 1) was identical with the n.m.r. spectrum of III when it was produced either from 2-methylborneol or 2-methylfenchol.

1-Phenyl-2,3-dimethylcyclopentenyl Cation.—The product from the addition of C_6H_5MgBr to 2,3-dimethylcyclopent-2-en-1-on was distilled and added to 96% H_2SO_4 to produce the n.m.r. spectrum in Fig. 5.

Acknowledgment.—We are grateful to the National Science Foundation for providing funds both to support this research and to aid in the purchase of the Varian A-60 n.m.r. spectrometer.

---

(2) N. Deno, P. T. Groves, J. J. Jaruzelski, and M. N. Lugasch, *J. Am. Chem. Soc.*, **82**, 4719 (1960).

(3) N. Deno, P. von R. Schleyer, and D. C. Kleinfelter, *Tetrahedron Letters*, 414 (1961).

(4) H. G. Richey, Jr., unpublished n.m.r. spectra.

(5) N. Deno, J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, **85**, 2999 (1963).

(6) P. von R. Schleyer, D. Kleinfelter, and H. G. Richey, Jr., *ibid.*, **85**, 4801 (1963).

(7) P. D. Bartlett, C. E. Dills, and H. G. Richey, Jr., *ibid.*, **82**, 5414 (1960).

(8) G. Fraenkel, unpublished results, Ohio State University.

(9) T. A. Spencer and M. D. Newton, *Tetrahedron Letters*, 1019 (1962).

(10) D. S. Noyce, *J. Am. Chem. Soc.*, **72**, 924 (1950).

(11) R. P. Lutz and J. D. Roberts, *ibid.*, **84**, 3715 (1962).

(12) N. Zelinsky, *Ber.*, **34**, 2883 (1901).

(13) S. S. Nametkin, A. A. Kichkina, and D. N. Kursanov, *J. prakt. Chem.*, **124**, 144 (1930); N. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

(14) A. N. Nesmeyanov, V. A. Sazonova, and R. B. Materikova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 988 (1955); *Chem. Abstr.*, **50**, 11,284 (1956).

(15) A. Haller and E. Bauer, *Ann. chim.*, [9] **8**, 117 (1917); A. Haller and J. Louvrier, *ibid.*, [9] **9**, 190 (1918); F. Reinartz and K. Meessen, *Ber.*, **72**, 1 (1939).

(16) R. L. Frank, R. Armstrong, J. Kwiatek, and H. A. Price, *J. Am. Chem. Soc.*, **70**, 1379 (1948).