

ratio 65:1 and the n.m.r. spectrum which showed a methyl doublet at 0.82 and 0.90 and a complex multiplet with maxima at 1.59 and 1.73. The ratio of the areas of the doublet to multiplet was 5.9:10 (calcd. 6:10).

Equation 3.—The n.m.r. spectrum of the 1,3,5-trimethylcyclohexenyl cation exhibited a band at 7.52 (the H on C₂), broad absorption maximizing at 2.50 and 3.14 (the H on C₄ and C₆), a narrower band at 2.83 (the CH₃ on C₁ and C₃), and a doublet with $J = 6.0$ c.p.s. at 1.15 (the CH₃ on C₅). The relative areas were 1:~11:6.0:~3 in accord with 1:10:6:3, calculated from the structure. The lone H at C₅ was not resolved.

The gas chromatogram of the C₉-alkanes showed three peaks in the area ratios of 20:15:1. The n.m.r. spectrum, shown in Fig. 1, can be interpreted as due to comparable amounts of the two isomeric 1,3,5-trimethylcyclohexanes. The n^{26}_D of 1.4245 is in further accord.

Equation 4.—The products of the reaction at the high dilution used were entirely soluble in the 96% H₂SO₄. The cyclopentenyl cation was provisionally identified on the basis of λ_{max} at 292 m μ , which is the same as that for the homologous 1,2,3,4,4-pentamethylcyclopentenyl cation.⁷ The extinction coefficient was 9100 when calculated on the basis of 1 mole of cation forming from 2 moles of the trimethylcyclohexanol.

Equation 5.—The n.m.r. spectrum of both pentamethylcyclopentenyl cations were known as well as the rate of rearrangement of the 1,3,4,4,5- to the 1,2,3,4,4-isomer.⁸ This added help to identification was needed because the remaining area was not entirely featureless, there being several well-resolved but as yet unidentified bands.

The gas chromatogram of the C₁₀-alkanes showed four peaks in the ratios 9:8:2:1.

Equation 6.—The products were entirely soluble in the H₂SO₄ and it is presumed that this is a result of sulfonation of the phenyl ring of the alkane fraction. The n.m.r. spectrum of 1-phenyl-3,5,5-trimethylcyclohexenyl cation was known.⁹ The bands at 2.60, 2.77, and 3.26 were far from any other bands and their areas were used to estimate the per cent yield.

Preparation of Reactants.—The alcohols and alkenes were prepared by addition of RMgBr to the appropriate ketones. The compounds are well known and bibliographies of their preparations appear in "Beilstein" and/or Faraday's "Encyclopedia of Hydrocarbons."

Acknowledgment.—We are grateful to the National Science Foundation for providing funds both to support

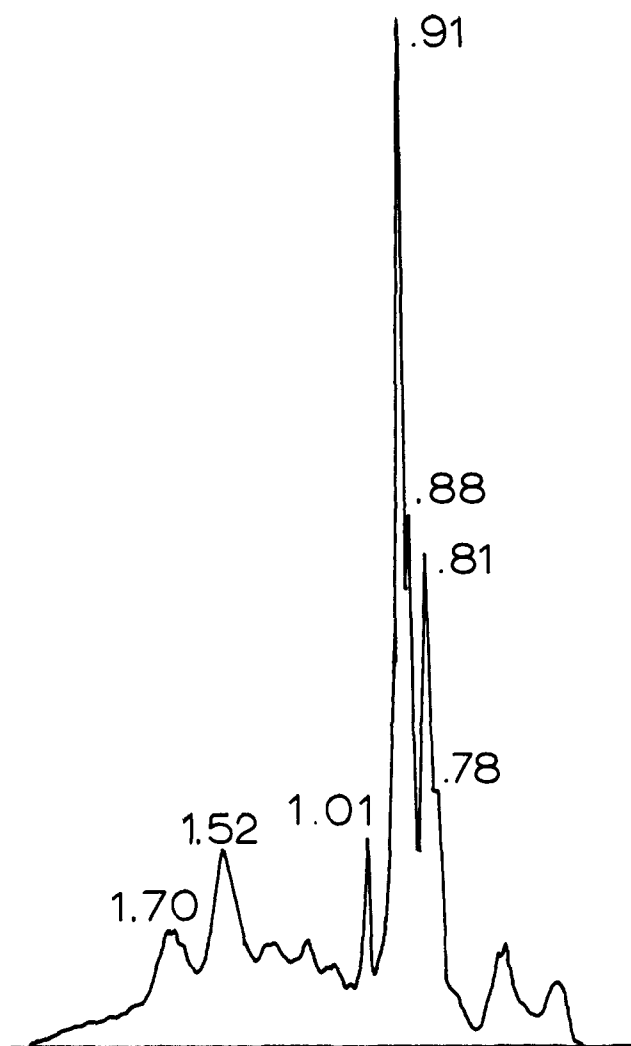


Fig. 1.—N.m.r. spectrum of the C₉-alkanes from eq. 3.

this research and to aid in the purchase of the Varian A-60 n.m.r. spectrometer.

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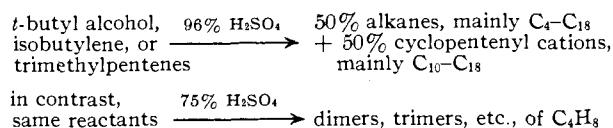
Carbonium Ions. XVI. The Fate of the *t*-Butyl Cation in 96% H₂SO₄

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1-Butanol, 2-butanol, *t*-butyl alcohol, or 2,2,4-trimethylpentenes all produce the same products in 96% H₂SO₄, but at different rates. These products are 50% H₂SO₄-insoluble alkanes and ~50% H₂SO₄-soluble cyclopentenyl cations. The yield of alkanes >C₁₈ is 12%. Of the dienes recovered from the cyclopentenyl cations, the over-all yield from the reactants is 30–42%. The fraction >C₁₈ is only 11%. About 2% over-all yield is identified with reasonable confidence as the 1,2,3,4,4-pentamethylcyclopentenyl cation (I), a C₁₀-cation. The remainder are dominantly 1,2-dimethyl-3-alkylcyclopentenyl cations of C₈–C₁₈. The possibility of identifying the H₂SO₄-soluble products had not been previously appreciated because conventional drowning procedures lead to polymeric dienes which are artifacts of the drowning procedure.

In the complex reactions of *t*-butyl alcohol with 96% H₂SO₄, the following partial elucidation has been achieved.



This over-all disproportionation resembles the simple disproportionations of certain cycloalkanols, reported

in the preceding paper, except that a fantastic maze of alkylations and rearrangements have been combined with the hydride transfers.

Addition of 100 g. of 2,2,4-trimethylpentenes to 500 ml. of 96% H₂SO₄ produced 50 g. of alkanes which were insoluble in the H₂SO₄ and about 50 g. of an H₂SO₄-soluble product, which was a mixture of cyclopentenyl cations.

Alkanes.—For the H₂SO₄-insoluble product, the absence of C=C absorption in the infrared spectrum,

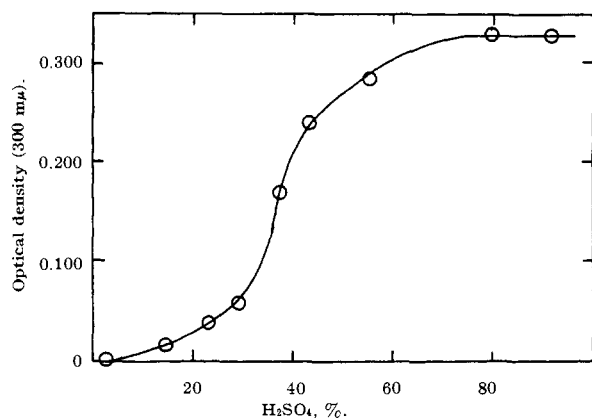


Fig. 1.—Shift of equilibrium from cyclopentenyl cations (formed by addition of *t*-butyl alcohol to 96% H_2SO_4) to dienes on dilution of the H_2SO_4 solution. The experimental points have been corrected for the effects of dilution alone.

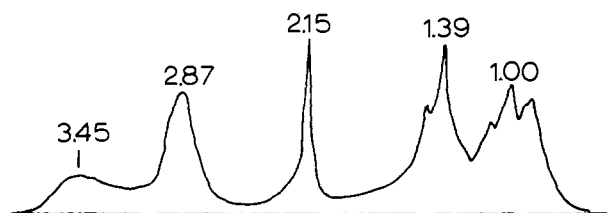


Fig. 2.—N.m.r. spectrum of the H_2SO_4 solution formed by addition of 2,2,4-trimethylpentenes to 96% H_2SO_4 .

the absence of vinylic hydrogens in the n.m.r. (nuclear magnetic resonance) spectrum, and the insolubility and inertness to 96% H_2SO_4 all serve to identify the products as a mixture of saturated hydrocarbons. Distillation through a spinning-band column gave the following weights and boiling points: 1.0 g., 31–36°; 0.25 g., 59–60°; 0.38 g., 72–75°; 1.35 g., 97–103°; 3.35 g., 118–141°; 2.60 g., 143–160°; 3.85 g., 163–179°; 4.40 g., 181–193°; 3.85 g., 200–220°; 4.40 g., 220–231°; 5.65 g., 231–250°; 5.65 g., 250–260°; and 12.3 g. of residue. The b.p.'s indicate that the carbon content ranges principally from C_5 – C_{18} . A small C_4 -fraction was also present. The C_5 -cut, b.p. 31–36°, was shown to be 2-methylbutane by the identity of the infrared and n.m.r. spectra with authentic spectra.

Properties of the Mixture of Cyclopentenyl Cations.—Several properties of the H_2SO_4 solution, obtained directly from reaction, identified the H_2SO_4 -soluble product as predominantly 1,2-dimethyl-3-alkylcyclopentenyl cations with varying substituents on C_4 and C_5 and varying RCH_2 - for the alkyl group. The λ_{max} at 302 $m\mu$ is characteristic of highly alkylated cyclopentenyl cations.¹ The ultraviolet spectra of variously diluted samples of the H_2SO_4 solution generated the curve shown in Fig. 1 after correction for the dilution. This equilibrium curve, and particularly the half-formation of cation at 35% H_2SO_4 , is characteristic of the 1,3-dialkylcyclopentenyl cations and is distinct from such curves for 1,3-dialkylcyclohexenyl cation or linear alkenyl cations of the $R_2=CH=CR_2^+$ type, which exhibit half-formations at ~50% and ~75% H_2SO_4 .¹ Less alkylated allylic cation systems would not have been chemically stable.¹

The n.m.r. spectrum of the H_2SO_4 solution (Fig. 2) showed a broad band centering at 3.45 p.p.m. (rela-

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

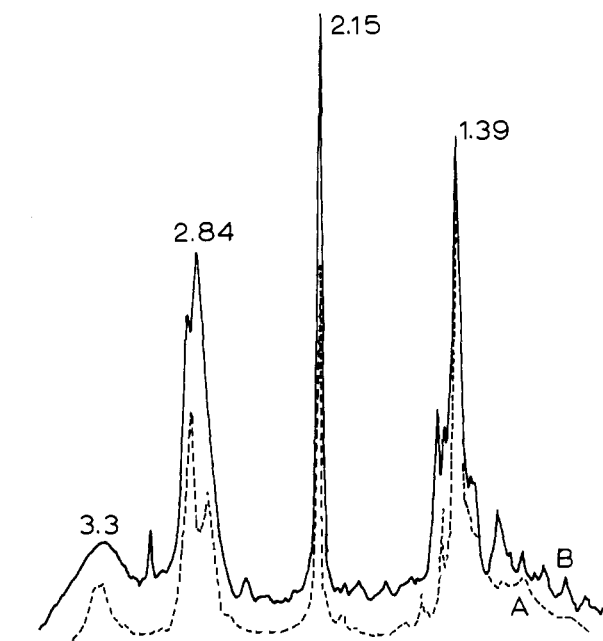


Fig. 3.—(A) N.m.r. spectrum of the 1,2,3,4,4-pentamethylcyclopentenyl cation (I) in H_2SO_4 . (B) N.m.r. spectrum of a H_2SO_4 solution of the cyclopentenyl cations derived from the dienes of b.p. 55–60° at 20 mm. which were obtained from the trimethylpentenes.

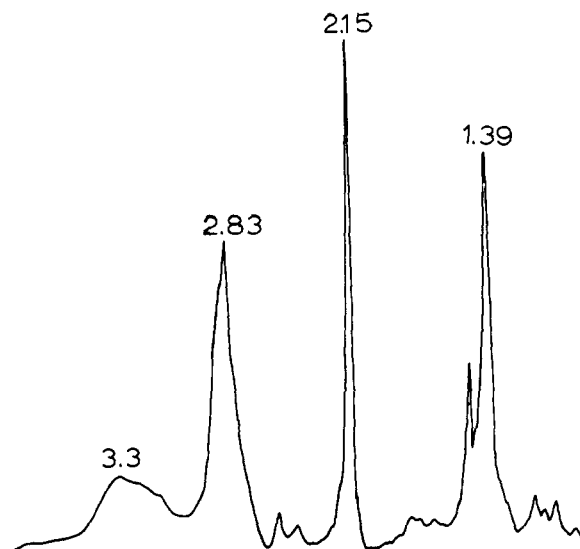


Fig. 4.—N.m.r. spectrum of a H_2SO_4 solution of the cyclopentenyl cations derived from the dienes of b.p. 55–75° at 20 mm. which were obtained from 2-butanol.

tive to Me_4Si and at lower field), typical of H attached to C_4 or C_5 of cyclopentenyl cations; a moderately broad band at 2.87, characteristic of CH_3 or RCH_2 - groups at C_1 and C_3 ; and an unusually narrow band at 2.15, which is highly characteristic of CH_3 on C_2 .² Both position and shape of the bands are characteristic. The relative area of the bands at 2.87 and 2.15 was 2.0:1 and this combined with their positions is evidence for the methyl groups at C_1 and C_2 and either CH_3 or RCH_2 - at C_3 .

1-Butanol, 2-Butanol, and *t*-Butyl Alcohol.—*t*-Butyl alcohol in 96% H_2SO_4 gives 50% alkanes and 50% cyclopentenyl cations. In 1 *M* solution the reaction is complete in minutes. The b.p. range of the alkanes

(2) N. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *ibid.*, **85**, 2991 (1963).

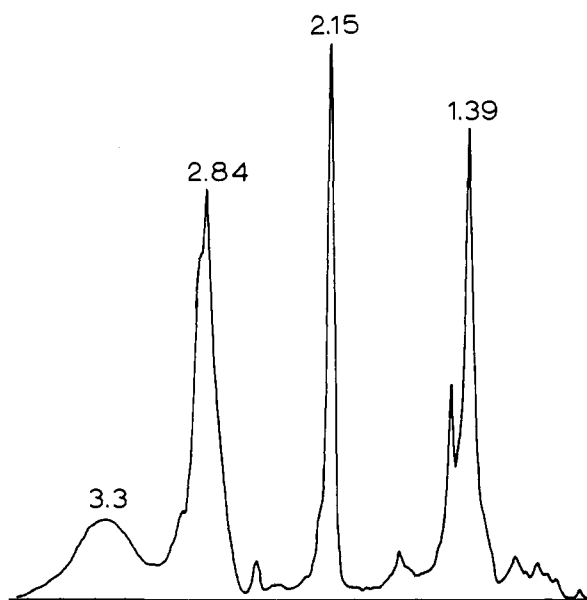


Fig. 5.—N.m.r. spectrum of a H₂SO₄ solution of the cyclopentenyl cations derived from the dienes of b.p. 55–75° at 20 mm. which were obtained from 1-butanol.

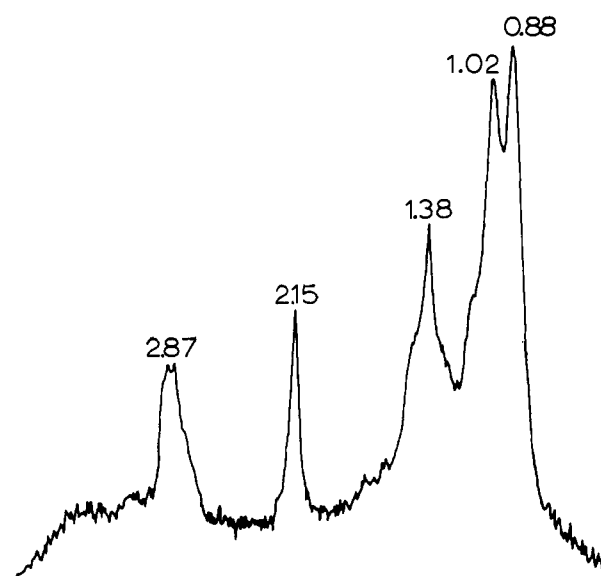


Fig. 7.—N.m.r. spectrum of a H₂SO₄ solution of the cyclopentenyl cations derived from the dienes of b.p. 150–165° at 20 mm. which were obtained from the trimethylpentenes.

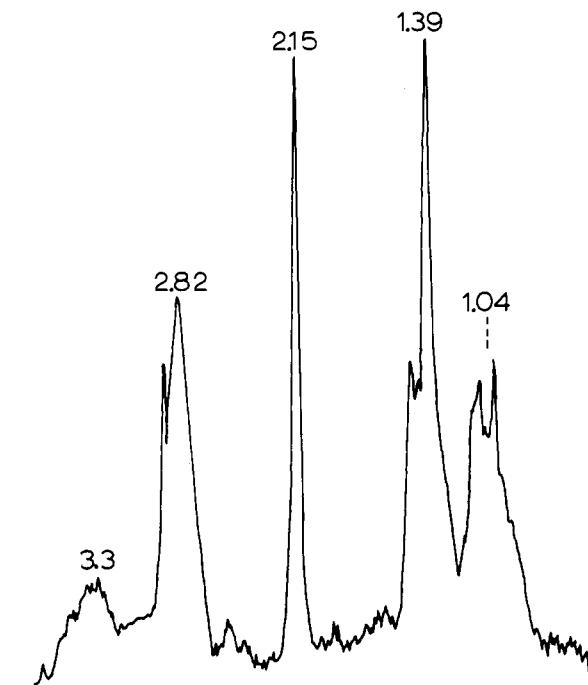


Fig. 6.—N.m.r. spectrum of a H₂SO₄ solution of the cyclopentenyl cations derived from the dienes of b.p. 100–110° at 20 mm. which were obtained from the trimethylpentenes.

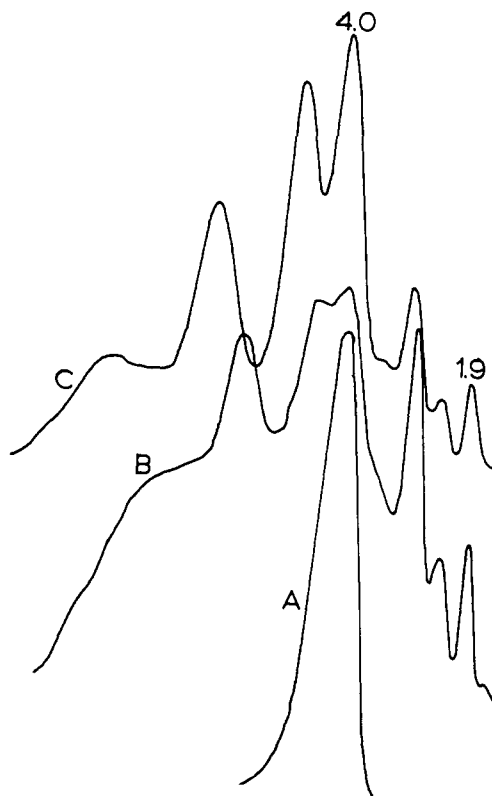


Fig. 8.—Gas chromatograms of (A) the dienes derived from an authentic sample of I, (B) the dienes of b.p. 55–75° (at 20 mm.) formed from 2-butanol, and (C) the dienes of b.p. 55–75° (at 20 mm.) formed from 1-butanol. The stationary phase was Apiezon J on a Gas-Chrom R support with helium as the carrier gas. The column temperature was 180°. The numbers 1.9 and 4.0 are the retention times in minutes.

and the n.m.r. and ultraviolet spectra of the mixed cyclopentenyl cations were similar to those observed for the products from the trimethylpentenes. Further comparison was abandoned upon finding that even 1-butanol and 2-butanol gave the same products.

After 5 weeks at 25° in 500 ml. of 96% H₂SO₄, 132 g. of 1-butanol (equivalent to 100 g. of C₄H₈) produced 30 g. of alkanes and 36 g. of dienes, recovered by the usual rapid dispersal of the H₂SO₄ solution into 10% aqueous NaOH. Similarly, 132 g. of 2-butanol gave 40 g. of alkanes and 34 g. of dienes.

Figures 3, 4, and 5 show the n.m.r. spectra of the cyclopentenyl cations produced by dissolving the lowest boiling diene fraction (55–75° at 20 mm.) from 1-butanol, 2-butanol, and the trimethylpentenes into 96%

H₂SO₄. The spectra are all virtually identical. Figures 6 and 7 show the n.m.r. spectra of cyclopentenyl cations derived from two of the higher boiling fractions. Figures 6 and 7 are actually from dienes derived from the trimethylpentenes but could have served equally well for dienes of the same b.p. derived from 1-butanol or 2-butanol because there was no significant difference. Similar equivalence was found for the n.m.r. spectra of

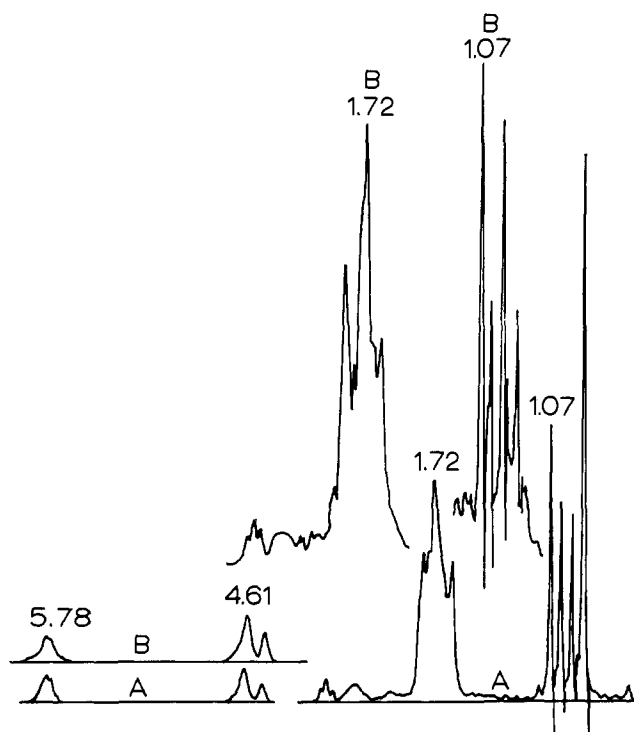


Fig. 9.—(A) N.m.r. spectrum of the dienes derived from I (b.p. 52–53° at 20 mm.). (B) N.m.r. spectrum of the dienes (b.p. 55–60° at 20 mm.) formed from trimethylpentenes. The solvent is CCl_4 .

the cyclopentenyl cations formed from all diene fractions.

Figure 8 shows the vapor phase chromatogram of the dienes (b.p. 55–75° at 20 mm.) from 1-butanol and 2-butanol. The close similarity further supports the conclusion that the same cyclopentenyl cations are produced.

Kinetics of Cyclopentenyl Cation Formation.—Dilute solutions (10^{-4} to 10^{-6} M) of *t*-butyl alcohol in 96% H_2SO_4 produce the same λ_{max} and extinction coefficients as the more concentrated solutions though at much slower rates. Extensive kinetic studies³ show that the ~ 300 μm absorption forms in the early stages (0–20% completion) by a process that is kinetically second order in *t*-butyl alcohol concentration and this alone refutes any claim that the absorption is due to the *t*-butyl cation.

Identification of the Individual Cyclopentenyl Cations.—The n.m.r. spectra in Fig. 3, 6, and 7 differ in that as the molecular weight increases, the bands in the 0.5–1.5 region increase, showing the addition of hydrogens on carbons farther removed from the allylic system than either the α - or β -positions. The bands of the hydrogens on the α - and β -carbons stay much the same, showing that a central unit is maintained throughout the range of cyclopentenyl cations produced.

Figures 3, 4, and 5 show that the dienes of b.p. 55–75° at 20 mm. produce an n.m.r. spectrum in 96% H_2SO_4

(3) Ph.D. Thesis, J. D. Hodge, Pennsylvania State University, 1962.

that is very close to that of the 1,2,3,4,4-pentamethylcyclopentenyl cation (I).^{2,4} The n.m.r. spectra of the dienes, Fig. 9, is also similar to that of the dienes recovered from authentic I. The C and H analysis of the 55–60° diene fraction also suggested a $\text{C}_{10}\text{H}_{16}$ formula (Calcd.: C, 88.15; H, 11.85. Found: C, 88.27; H, 11.52). These observations alone would lead to the conclusion that Fig. 3–5 were all of the same cation, I, and Fig. 9 portrayed two samples of a similar diene mixture, derived from I.

However, a gas chromatogram of the sample of diene from authentic I exhibited a single unresolved band, Fig. 8 (despite the apparent presence of four dienes as evidenced by four different *gem*-dimethyl bands at 1.07, 1.01, 0.95, and 0.89 p.p.m. in the n.m.r. spectrum), whereas the dienes of b.p. 55–75° (at 20 mm.) from 1-butanol, 2-butanol, and trimethylpentenes exhibit a series of bands, Fig. 8. One of these bands does coincide with the authentic diene band so that there is a reasonably reliable identification of about 25% of this diene fraction as dienes arising from I. The adjoining bands are probably those of higher and lower homologs. The explanation for the similarity of the n.m.r. spectra in Fig. 3–5 is that the immediate homologs of I would give average n.m.r. spectra similar to that of I.

One other point of difference was that the authentic dienes from I boiled sharply at 52–53° at 20 mm.

The only other identification that can be suggested at this time is that the n.m.r. spectrum in Fig. 6 is in reasonable accord with structure II. A spectrum closely resembling Fig. 6 (and provisionally identified as partially due to II) was generated from 2,3,3-trimethylborneol (a C_{13}) on standing for 2 months in 96% H_2SO_4 as reported in a preceding paper, part XIV.



Conclusions.—It is astonishing that the carbon framework of the products and the number of carbons bear so little relation to that of the reactants. A fantastic maze of alkylation–dealkylation, rearrangements, and hydride transfers must be involved. Also surprising is the dominance of cyclopentenyl cations, although this was perhaps foretold by the greater stability of such cyclopentenyl cations relative to other alkenyl cations.¹

Previous Related Work.—The work reported herein contrasts with the reaction of tertiary alcohols in 75% H_2SO_4 where only olefin polymers are found.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.

(4) N. Deno, N. Friedman, J. D. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, **85**, 2995 (1963).

(5) F. C. Whitmore and co-workers, *ibid.*, **63**, 756, 1460, 2035, 2197, 2200 (1941); and **67**, 2158 (1945).