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

Carbonium Ions. XV. The Disproportionation of Cycloalkyl Cations to Cycloalkenyl Cations and Cycloalkanes

BY N. C. DENO AND CHARLES U. PITTMAN, JR.

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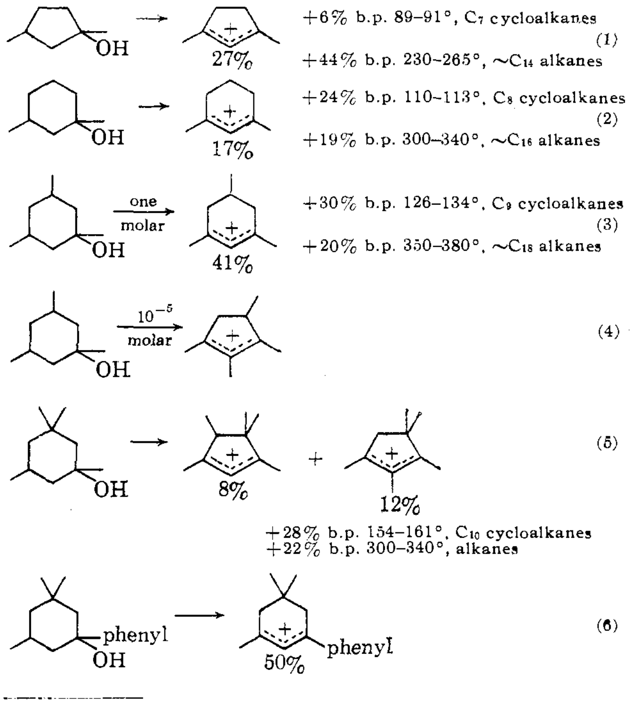
Tertiary aliphatic alcohols form alkyl cations in 96% H_2SO_4. These abstract hydride from their equilibrating alkenes to produce 1 mole of alkane and 1 mole of alkenyl cation. By choosing alcohols of the same carbon skeleton as stable alkenyl cations, the simple disproportionation can sometimes be observed. More generally, the disproportionation is accompanied by rearrangement and/or alkylation–dealkylation.

In 1884, Friedel and Crafts recognized alkanes in the products derived from *t*-amyl chloride plus $AlCl_3$.[1] The oxidation–reduction nature of this reaction was first expressed by Ipatieff.[2] Conventional drowning procedures led to complex mixtures of polyenes which defied characterization of the individual components, although the gross properties of the mixture suggested that cyclopentadiene units were involved.[3,4]

With the understanding gained in the direct studies of alkenyl cations,[5–7] it became a relatively easy matter to choose alcohols of carbon skeletons which would exhibit simple disproportionation of the alcohol (or alkene) to 1 mole of alkanes and 1 mole of alkenyl cations. The following diagram summarizes some of the best examples. All of these reactions were conducted in 96% H_2SO_4 at 25° and the reactions were all complete within minutes.



In eq. 1, 2, 3, and 5, the alkenes gave the same products as the alcohols and, presumably, this is generally true.

The rearrangements in eq. 4 and 5 must take place *before* the hydride transfer because the cyclohexenyl cations that would have been produced by the simple hydride transfer (1,3,5-trimethyl and 1,3,5,5-tetramethyl) are both stable in 96% H_2SO_4. The difference in behavior of 1,3,5-trimethylcyclohexanol in 1 *M* and in 10^{-5} *M* solution (eq. 3 and 4) reflects the fact that the disproportionation is a hydride transfer reaction with kinetics that are second order in alcohol concentration, whereas the rearrangement is kinetically first order in alcohol concentration.

The identification of the products is given in the Experimental.

Experimental

The general procedure was to stir the alcohol with 96% H_2SO_4 at 25° for 1 hr. In most cases, two layers immediately formed. The upper one was composed of saturated alkanes and this was removed, washed, and distilled. The identification as a mixture of alkanes was based on the insolubility and inertness to H_2SO_4, the absence of C=C bands in the infrared spectra, and the absence of vinylic hydrogen in the n.m.r. spectra.

The lower layer was a solution of the alkenyl cations in 96% H_2SO_4. Direct examination by n.m.r. and ultraviolet spectroscopy was sufficient to identify the monomeric alkenyl cations. The position of the n.m.r. bands are expressed in p.p.m. downfield and relative to $(CH_3)_4Si$ and were calibrated using the secondary standard $(CH_3)_4N^+Cl^-$.

Equation 1.—The n.m.r. spectrum of the 1,3-dimethylcyclopentenyl cation was known.[5] Its bands accounted for 54% of the total area and were superimposed in sharp contrast to the featureless background. This background comprised the other 46% of the area and was concentrated in the 0.5–1.5 p.p.m. range.

The H_2SO_4-insoluble product was entirely composed of a monomeric C_7-alkane, b.p. 89–91°, and an alkane, b.p. 230–265°, which is about the b.p. expected for the dimeric C_{14}-alkanes. The n.m.r. spectrum of the C_7-alkane consisted of a methyl doublet at 0.93 and 1.02 and a complex multiplet centering at 1.77 p.p.m. The ratio of the areas of the doublet to the multiplet was 6.0:8.0 in accord with a 1,3-dimethylcyclopentane structure. A gas chromatogram (SE-30 on Chromosorb W) showed two peaks in the ratio 9:1, suggesting that one of the isomers (*cis* or *trans*) was predominantly formed. The 1,3-dimethylcyclopentane identification was further confirmed by the $n^{28}D$ of 1.4013 which is in the range expected.

Equation 2.—The n.m.r. spectrum of the 1,3-dimethylcyclohexenyl cation exhibited a band at 7.40 (the H on C_2), a broad unresolved band at 2.9–3.3 (the H on C_4 and C_6), a band at 2.82 (the CH_3 on C_1 and C_3), and a poorly resolved multiplet at 2.16 (the H on C_5). The relative areas were 0.84:~4:6:~2 in accord with the calculated 1:4:6:2. The band positions (and shapes) were as expected from precedent.[5]

The infrared spectrum of the C_8-alkane was identical with that of *cis*-1,3-dimethylcyclohexane (published in reports of American Petroleum Institute Project 44). This identification was supported by the gas chromatogram which showed two peaks in the

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[1] M. C. Friedel and J. M. Crafts, *Ann. chim.*, [6] **1**, 451 (1884).

[2] V. N. Ipatieff and C. B. Linn, U. S. Patent 2,421,946; *Chem. Abstr.*, **41**, 5296 (1947); V. N. Ipatieff, R. E. Schaad, and W. B. Shanley in "The Science of Petroleum," Vol. V, Part II, Oxford University Press, New York, N. Y., 1953, pp. 14 and 15.

[3] H. S. Bloch, U. S. Patents 2,476,955; 2,477,038; 2,514,533; and 2,603,629.

[4] S. Miron and R. J. Lee, *Ind. Eng. Chem.*, **54**, 287 (1962).

[5] 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).

[6] N. Deno, N. Friedman, J. D. Hodge, and J. J. Houser, *ibid.*, **85**, 2995 (1963).

[7] N. Deno, J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Houser, *ibid.*, **85**, 2998 (1963).

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 C_2), broad absorption maximizing at 2.50 and 3.14 (the H on C_4 and C_6), a narrower band at 2.83 (the CH_3 on C_1 and C_3), and a doublet with J = 6.0 c.p.s. at 1.15 (the CH_3 on C_5). The relative areas were 1:~11:6.0:~3 in accord with 1:10:6:3, calculated from the structure. The lone H at C_5 was not resolved.

The gas chromatogram of the C_9-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% H_2SO_4. The cyclopentenyl cation was provisionally identified on the basis of λ_{max} at 292 mμ, 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.[6] 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 C_{10}-alkanes showed four peaks in the ratios 9:8:2:1.

Equation 6.—The products were entirely soluble in the H_2SO_4 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.[5] 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."

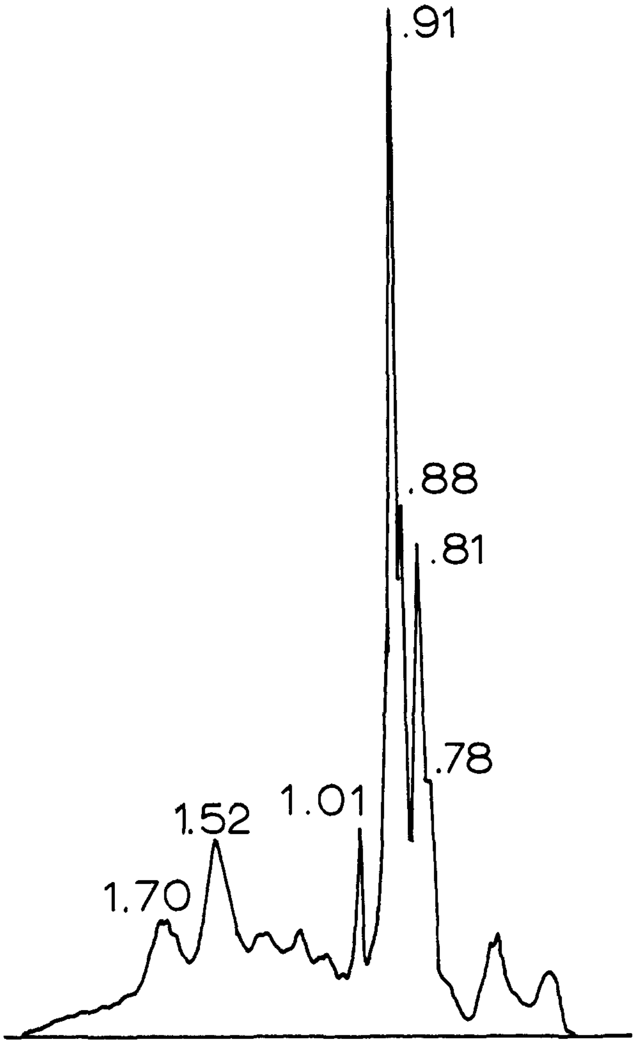

Fig. 1.—N.m.r. spectrum of the C_9-alkanes from eq. 3.

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Carbonium Ions. XVI. The Fate of the *t*-Butyl Cation in 96% H_2SO_4

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1-Butanol, 2-butanol, *t*-butyl alcohol, or 2,2,4-trimethylpentenes all produce the same products in 96% H_2SO_4, but at different rates. These products are 50% H_2SO_4-insoluble alkanes and ~50% H_2SO_4-soluble cyclopentenyl cations. The yield of alkanes $>C_{18}$ is 12%. Of the dienes recovered from the cyclopentenyl cations, the over-all yield from the reactants is 30–42%. The fraction $>C_{18}$ is only 11%. About 2% over-all yield is identified with reasonable confidence as the 1,2,3,4,4-pentamethylcyclopentenyl cation (I), a C_{10}-cation. The remainder are dominantly 1,2-dimethyl-3-alkylcyclopentenyl cations of C_8–C_{18}. The possibility of identifying the H_2SO_4-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% H_2SO_4, the following partial elucidation has been achieved.

$$\begin{array}{l}\textit{t}\text{-butyl alcohol,} \\ \text{isobutylene, or} \\ \text{trimethylpentenes}\end{array} \xrightarrow{96\%\ H_2SO_4} \begin{array}{l}\text{50\% alkanes, mainly } C_4\text{–}C_{18} \\ +\ \text{50\% cyclopentenyl cations,} \\ \text{mainly } C_{10}\text{–}C_{18}\end{array}$$

$$\begin{array}{l}\text{in contrast,} \\ \text{same reactants}\end{array} \xrightarrow{75\%\ H_2SO_4} \text{dimers, trimers, etc., of } C_4H_8$$

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% H_2SO_4 produced 50 g. of alkanes which were *insoluble* in the H_2SO_4 and about 50 g. of an H_2SO_4-*soluble* product, which was a mixture of cyclopentenyl cations.

Alkanes.—For the H_2SO_4-insoluble product, the absence of C=C absorption in the infrared spectrum,