[Contribution from the Ipatieff High-Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University, and The Universal Oil Products Company]

Studies in the Terpene Series. I. Dehydration of Alcohols in the Terpene Series Under Pressure and in the Presence of Dilute Aqueous Salt Solutions

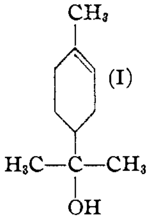
By V. N. Ipatieff and Herman Pines

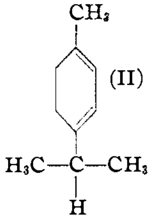
In the study of the dehydration of alcohols by means of salts, it was shown[1] that dilute aqueous solutions of acids or acid-acting salts act as catalysts for the conversion of alcohols to the corresponding olefinic hydrocarbons; water alone or aqueous solutions of potassium or sodium chloride have no catalytic effect upon the dehydration of alcohols.

This paper deals with the action of dilute aqueous solutions of magnesium chloride, under pressure and at elevated temperatures, upon the dehydration of terpineol, 1,8-*p*-menthanediol, dihydroterpineol, menthol, isoborneol and borneol. It was found that these alcohols, with the exception of borneol, undergo dehydration when heated at 230° for two to three hours under pressure and in the presence of equal volumes of 1 to 2% aqueous solution of magnesium chloride.

The choice of this catalyst was governed by the very small amount of side reaction that occurs in its presence.

Terpineol (I) undergoes dehydration to hydrocarbons boiling between 171 and 189°, the product consisting of α-terpinene (II), dipentene (III), and a terpene of unknown structure.


(I)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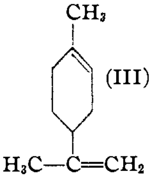
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The unidentified terpene forms a tetrabromide consisting of tetragonal prisms melting at 96° (Fig. 1). Crystals of tetrabromide of dipentene, which are in the form of hexagonal prisms, melt at 124–125° (Fig. 2), while α-terpinene yields a liquid tetrabromide.

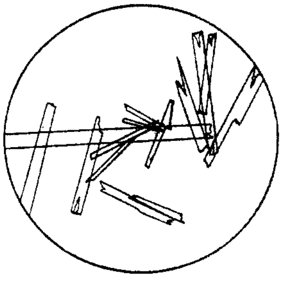


Fig. 1.—Crystals of the tetrabromide of unidentified terpene (magnification × 100).

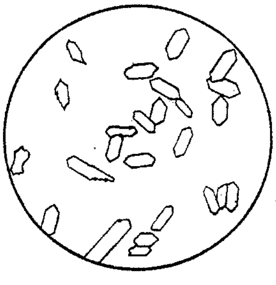
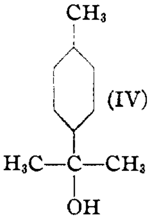


Fig. 2.—Crystals of the tetrabromide of dipentene (magnification × 24).

The dehydration of the terpineol was effected without isomerization of the six-membered ring to a five-membered ring. This was demonstrated by hydrogenating the product to the cycloparaffin and dehydrogenating the latter by means of platinized alumina to the corresponding aromatic, which was identified as paracymene. The dehydrogenation was complete.

1,8-*p*-Menthanediol (1-methyl-4-isopropylcyclohexanediol-1,8) yields the same dehydration products as terpineol.

Dihydroterpineol (IV) on dehydration yields a mixture of V and VI.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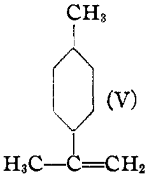
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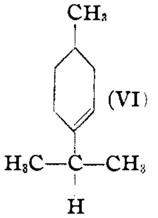
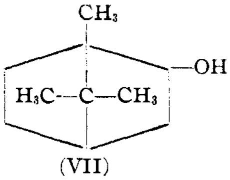
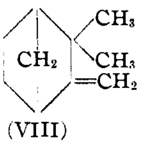

(VI)

The presence of VI, 4-methyl-1-isopropyl-1-cyclohexene, was demonstrated by preparing a solid nitrosochloride.

Menthol undergoes dehydration to a hydrocarbon material which is mainly 2-methyl-5-isopropyl-1-cyclohexene (rather than VI), since it does not form a solid nitrosochloride.

Isoborneol (VII) reacts in the presence of dilute solutions of magnesium chloride at 240° to form camphene (VIII), which melts at 50°; the latter on hydrogenation forms isocamphane (IX), which melts at 62°. A small amount of a liquid isomer is also formed during the dehydration.


(VII)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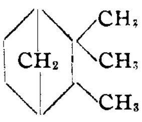
(IX)

Borneol is more stable toward dehydration than is isoborneol, and the temperature required to effect it ranges from 285 to 295°. The reaction product, as in the case of isoborneol, consists of camphene and a liquid isomer, the yield of the latter increasing with the increase of the temperature of dehydration. The two compounds can be separated by cooling the mixture to 0° and

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[1] V. N. Ipatieff and G. S. Monroe, in publication.

filtering it; the liquid isomer freezes at −15°. Both the solid and the liquid isomers obtained from either borneol or isoborneol form an addition product with hydrogen chloride, which melts at 150° and corresponds to isobornyl chloride. The formation of the latter from camphene is due to the fact that camphene hydrochloride, which is the primary product of the reaction, undergoes isomerization, under the experimental conditions used, to a more stable isobornyl chloride.[2]

On hydrogenation, the solid isomer forms isocamphane, while the liquid isomer yields a dicyclic hydrocarbon which according to physical constants corresponds to isobornylane.

Experimental Part

Dehydration of Terpineol.—Two hundred grams of terpineol, m. p. 35°, and 200 cc. of water containing 8 g. of magnesium chloride hexahydrate were placed in an 850-cc. rotating autoclave and heated at 230° for two hours. The maximum pressure registered was 70 atm. From two runs, 314 g. of water-insoluble product was obtained having the following boiling ranges: (a) 171–184°, 79%, $n^{22}D$ 1.4782; (b) 184–189°, 11%, $n^{22}D$ 1.4827; (c) higher boiling products, 10%. The first two fractions were redistilled on a high-efficiency column and yielded the following products: (1) 171–173°, $n^{20}D$ 1.4739, 8.2%; (2) 174–175°, 1.4772, 15.7%; (3) 179–181.5°, 1.4828, 12%; (4) 181.5–183.5°, 1.4849, 11.5%; (5) 183–186°, 1.4891, 7.3%.

Nitrosite.—A concentrated aqueous solution containing 2.5 g. of sodium nitrite was added to a mixture of 5 g. of the terpenes boiling between 171 and 173° and 11 g. of 20% aqueous acetic acid solution. A crystalline compound which melted at 156–157° and corresponded to α-terpinene nitrosite was obtained.

Maleic Anhydride Addition Product.—A mixture of 10 g. of terpenes boiling between 171 and 173°, 10 g. of benzene, and 7 g. of maleic anhydride was refluxed for two hours. The product was steam-distilled in order to remove the benzene and the unreacted terpenes. The product remaining in the flask was washed several times with water to remove maleic acid. It was then extracted with ether and treated with a dilute sodium hydroxide solution. On evaporation of the ether a maleic acid anhydride addition product of α-terpinene remained which after recrystallization melted at 64–65°.

Anal.[3] Calcd. for $C_{14}H_{18}O_3$: C, 71.79; H, 7.69. Found: C, 71.69; H, 7.50.

The sodium hydroxide extract was concentrated and acidified with hydrochloric acid. A precipitate was formed which corresponded to the addition product of maleic acid with α-terpinene. On recrystallization from dilute ethanol it melted at 127–128°.

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.66; H, 7.94. Found: C, 67.67; H, 7.68.

The same dibasic acid was obtained by hydrolysis of the anhydride with hot dilute alkali.

Bromination.—The various fractions were brominated according to the following procedure: Four grams of hydrocarbons was dissolved in 14 cc. of a solvent consisting of equal volumes of ethanol and ether. The solution was cooled to 0° and bromine was added dropwise until an orange color persisted. The tetrabromides obtained were crystallized from ethanol. The solid tetrabromide mixture obtained from various fractions had the following melting points: fraction boiling at 171–173°, melting point of tetrabromides, 124.5–125; 174–175, 124–124.5; 179–181.5, 124–125; 181–183.5, 113–116; 183.5–186, 116–118. In addition to the crystalline tetrabromides in each case, a liquid tetrabromide was obtained which corresponded to the tetrabromide of α-terpinene.

A microscopic examination of the crystalline tetrabromides showed that they consist of two types of crystals: (a) hexagonal prisms, the only crystals obtained from fractions boiling below 180°, melting at 124–125° and corresponding to dipentene tetrabromide; (b) prisms of unknown constitution melting at 95° in admixture with crystals of dipentene tetrabromide and obtained by bromination of hydrocarbons boiling above 180°. The two types of crystals can be separated by careful fractional crystallization. The analysis showed that the various solid tetrabromides correspond to $C_{10}H_{16}Br_4$.

Dehydration of 1,8-*p*-Menthanediol.—The experimental conditions were the same as for terpineol. From 200 g. of 1,8-*p*-menthanediol, 141 g. of hydrocarbons was obtained, which distilled as follows: (1) 176–178°, $n^{20}D$ 1.4746, 29%; (2) 178–181°, 1.4782, 29%; (3) 181–182°, 1.4802, 5%; (4) 182–183°, 1.4825, 29%; (5) 183–185°, 1.4854, 5%.

Fraction 1 yielded a nitrosite melting at 155–156° and corresponding to α-terpinene; the higher-boiling products yielded no solid nitrosates. The first three cuts on bromination formed tetrabromide, melting at 124–125° and corresponding to that of dipentene. The higher-boiling fractions yielded a crystalline tetrabromide in the form of prisms melting at 95–97°.

Dehydration of Dihydroterpineol.—Dihydroterpineol was obtained by hydrogenating terpineol at 60–70° under 100 atm. of hydrogen pressure in the presence of a nickel-kieselguhr catalyst.[4] The dihydroterpineol distilled at 69° under 5 mm.

The dehydration of dihydroterpineol was carried out at 230–240° with the same quantities of material as in the case of menthol (see below). The liquid product distilled as follows: (1) 173.5–174°, $n^{20}D$ 1.4570, 18%; (2) 174°, $n^{20}D$ 1.4573, 22%; (3) 174–174.5°, $n^{20}D$ 1.4581, 21%; (4) 174.5–177°, 20%; (5) 177–180°, 11%.

The **nitrosochloride** of Fraction 2 melted at 130–131°, corresponding to that of 4-methyl-1-isopropyl-1-cyclohexene (inactive *p*-menthene).

Dehydration of Menthol.—A mixture of 100 g. of menthol, 100 cc. of water, and 6 g. of magnesium chloride hexahydrate was heated under pressure at 310–320° for two hours. Eighty-seven grams of hydrocarbons corresponding to menthenes was obtained, which distilled as follows: (1) 167–168°, $n^{20}D$ 1.4503, 40%; (2) 168–169°, $n^{20}D$ 1.4507, 41%; (3) 169–172°; $n^{20}D$ 1.4537, 14%.

Fractions 1 and 2 did not yield a solid nitrosochloride.

Dehydration of Isoborneol.—The dehydration was carried out at 250° under conditions described for terpineol. Seventy grams of isoborneol yielded 57 g. of hydrocarbons, which distilled as follows: (1) 156–160°, 78%; (2) 160–166°, 13%. The first fractions melted at 50° and consisted of almost pure camphene. Fraction 2 solidified at 0° and contained a small amount of a liquid isomer.

The camphene melting at 50° was hydrogenated at 60° under 100 atm. of initial hydrogen pressure in the presence of nickel-kieselguhr catalyst. The isocamphane formed melted at 61–62° and distilled at 164–165°; $[\alpha]^{20}D$ −10.8°.

The camphene dissolved in ether–alcohol solution was treated with anhydrous hydrogen chloride; a solid melting at 150° and corresponding to isobornyl chloride was obtained.

Dehydration of Borneol.—In order that dehydration might be insured, it was necessary to heat the borneol for about three to five hours at 280–290°. The resulting hydrocarbon, which was liquid, distilled as follows: (1) 156–158°, 44%; (2) 158–159°, 22%; (3) 159–162°, 20%. The first two fractions were composed mainly of camphene, which melted at 49–50°. The third fraction was composed of camphene and a liquid isomer.

The solid camphene present in Fraction 3 was separated from the liquid isomer. The latter, distilling at 159–161°,

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[2] H. Meerwein and K. Van Emster, *Ber.*, **53**, 1815 (1920); **55**, 2500 (1922).

[3] Microanalyses were made by Dr. T. S. Ma of the University of Chicago.

[4] V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **26**, 1838 (1934).

was hydrogenated under pressure at 70–80°; the resulting product, which reacted mildly with a nitrating mixture, was treated with 15% fuming sulfuric acid in order to remove any traces of olefins. The hydrogenated product after purification distilled at 163–165°; m. p. −18°, $n^{20}{}_D$ 1.4577; $d^{20}{}_4$ 0.8613.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found: C, 86.87; H, 12.77.

This compound corresponds to isobornylane.

Summary

Terpineol, 1,8-*p*-menthanediol, dihydroterpineol, menthol. borneol and isoborneol were dehydrated under pressure in the presence of dilute aqueous solutions of magnesium chloride at temperatures ranging from 230 to 320°.

Terpineol and 1,8-*p*-menthanediol on dehydration yielded dipentene, α-terpinene, and small amounts of an unknown terpene, which formed a characteristic solid tetrabromide.

4-Methyl-1-isopropyl-1-cyclohexene was obtained from the dehydration of dihydroterpineol.

Menthol on dehydration formed a compound corresponding to 2-methyl-5-isopropyl-1-cyclohexene.

Isoborneol dehydrated to camphene, while borneol formed a mixture consisting of camphene and a liquid isomer of camphene.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Direct Aromatic Amination: A New Reaction of Hydroxylamine-O-sulfonic Acid[1]

BY R. N. KELLER AND PETER A. S. SMITH

Introduction

In 1924 Karl Schmidt[2] converted benzene directly to aniline, and carbonyl compounds to substituted amides, by reaction with hydrazoic acid in the presence of sulfuric acid. Sommer, Schulz and Nassau[3] aminated primary amines to hydrazines by means of hydroxylamine-O-sulfonic acid ($H_2N\text{-}O\text{-}SO_3H$).[4] In both instances these reactions were explained on the basis of the intermediate formation of the radical NH. Specht, Browne and Sherk[6] have shown the close relationship between the two aminating agents by preparing hydroxylamine-O-sulfonic acid from hydrazoic acid and fuming sulfuric acid. They explained this on the basis of the intermediate formation of NH_2^+. Since NH can be expected to have a proton affinity, and Schmidt's reaction took place under strongly acid conditions, it appears preferable to formulate his intermediate as NH_2^+ also. The reaction of Sommer, Schulz and Nassau takes place in alkaline solution, and NH as such may actually be the intermediate.

The work of Schmidt prompted the investigation of the mechanism of the decomposition of hydrazoic acid.[7,8,9] The decomposition was found to be unimolecular, and could best be explained by assuming that $HN_3 = N_2 + NH$ is the rate-determining step. Gleu,[7] using ultraviolet light to decompose aqueous hydrazoic acid, found one-third of the nitrogen in solution as hydroxylamine, which is very similar to the finding of Schmidt that the decomposition of hydrazoic acid by sulfuric acid also yields hydroxylamine.

Tolmachev[10] has identified the bands of NH in the spectra obtained by exploding hydrazoic acid.

The assumption that NH or NH_2^+ is the intermediate in all these reactions leads to the expectation that the amination of aromatic nuclei would be accomplished by reaction with hydroxylamine-O-sulfonic acid, and with hydrazoic acid under the action of ultraviolet light. Our experiments have confirmed this expectation.

Experimental[11]

Hydroxylamine-O-sulfonic acid was prepared according to Sommer, Schulz and Nassau[3] from redistilled chlorosulfonic acid and hydroxylammonium sulfate. Most of the aminations were run with the material thus obtained without further purification; in a few cases, purified[5] HSA[4] was used, but the increase in yield was a few per cent. at most. All other chemicals were of reagent quality or the equivalent.

HSA by itself is stable toward aromatic hydrocarbons. This is to be expected if its reactivity is due to the formation of NH, because the pure acid does not decompose below its melting point, 210°. A mixture of the acid with

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(1) From the Doctoral dissertation of Peter A. S. Smith.

(2) K. F. Schmidt, *Ber.*, **57**, 704 (1924).

(3) F. Sommer, O. F. Schulz and M. Nassau, *Z. anorg. allgem. Chem.*, **147**, 142 (1925).

(4) The compound H_2NOSO_3H has been referred to in *Chemical Abstracts* by no less than five different names, often without cross reference. No single name seems to have been accepted by more than one author. We propose to use the name "hydroxylamine-O-sulfonic acid,"[5] which we consider more appropriate than names containing the prefix "per." It also conforms to the current *Chemical Abstracts'* nomenclature for hydroxylamine derivatives (*cf.* the well-known "hydroxylamine-N-sulfonic acid," $HSO_3\text{-}NH\text{-}OH$). In some places in this paper the abbreviation HSA will be used.

(5) *Cf.* P. Baumgarten and H. Erbe, *Ber.*, **71**, 2603 (1938).

(6) H. E. M. Specht, A. W. Browne and K. W. Sherk, THIS JOURNAL, **61**, 1083 (1939).

(7) K. Gleu, *Ber.*, **61**, 702 (1928).

(8) A. O. Beckmann and R. G. Dickinson, THIS JOURNAL, **52**, 124 (1930).

(9) R. Meyer and H. J. Schumacher, *Z. physik. Chem.*, **A170**, 33 (1934).

(10) Y. M. Tolmachev, *J. Phys. Chem.* (U. S. S. R.), **14**, 615 (1940).

(11) All temperatures given for melting points are corrected.