[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, AND UNIVERSAL OIL PRODUCTS COMPANY]

# Dehydration of 2-Methyl-2,4-pentanediol and 4-Methyl-x-penten-2-ol Under Pressure and in the Presence of Dilute Aqueous Salt Solutions

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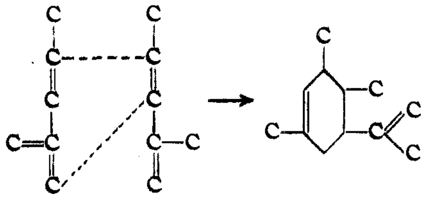
As a continuation of the study of the dehydration of alcohols by means of dilute aqueous solutions of acids or acid-acting salts,[1,2] 2-methyl-2,4-pentanediol and 4-methyl-x-penten-2-ol were submitted to the action of dilute aqueous ferric chloride and magnesium chloride solutions. The reactions were carried out under pressure and at temperatures of 145–250°. It was found that the reaction was more complex than in the case of aliphatic or terpenic alcohols. The complexity of the reaction was due partly to the fact that 2-methyl-1,3- and 4-methyl-1,3-pentadiene were formed, which, under the conditions of reaction, underwent polymerization. The main products of the reaction were methylpentadienes, and the dimers of the dienes. The methylpentadienes consisted of a mixture composed of 85% of 2-methyl-1,3-pentadiene and 15% of 4-methyl-1,3-pentadiene, as determined by the method of Bachman and Goebel.[3] The dimeric methylpentadienes consisted of 1,3,5-trimethyl-5-isopropenyl-1-cyclohexene which yielded a crystalline product melting at 118° when treated with nitrosyl chloride. The constitution of the dimer was determined by means of hydrogenation, which produced cyclic hydrocarbons as determined by physical constants and elementary analysis. On dehydrogenation the dimer yielded a tetra-substituted benzene, which on oxidation was converted to 1,2,3,5-benzenetetracarboxylic acid. The dimer was probably formed by Diels–Alder condensation:

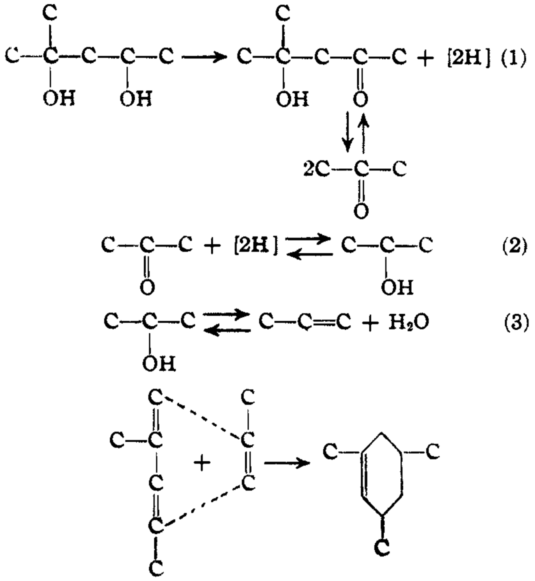


The hydrocarbons distilling within the boiling range of the dimers of methylpentadiene contained about 10–12% of aromatic hydrocarbons formed probably from the dimer by a hydrogen transfer reaction.[4]

The aromatic hydrocarbons were detected by selective hydrogenation whereby only the olefinic hydrocarbons underwent hydrogenation while the aromatic remained unchanged.

Among the products of reaction a small amount of hydrocarbons which corresponded to 1,3,5-trimethyl-1-cyclohexene was found. This hydrocarbon was admixed with alcohols. The hydrocarbon after being hydrogenated to 1,3,5-trimethylcyclohexane and separated from the alcohol, was converted by means of dehydrogenation to mesitylene, identified by means of its tribromo and trinitro derivatives.

The formation of the trimethylcyclohexene was probably due to the interaction of methylpentadiene with propene according to the equations



The partial dehydrogenation of methylpentanediol to the diacetone alcohol might have been initiated by a hydrogen transfer reaction; the olefins being the hydrogen acceptor. The acetone formed by equation 1 acts then as a hydrogen acceptor while the glycol acts as a hydrogen donor; a similar type of reaction was described in a previous paper.[5] The dehydration of isopropyl alcohol to propylene was reported by Ipatieff and Monroe.[2] It was found that by treating 2-methyl-2,4-pentanediol with propylene a large yield of 1,3,5-trimethyl-1-cyclohexene was obtained.[6] In addition to the above-mentioned hydrocarbons, the reaction product contained unsaturated ethers boiling at about 135–140°, the structure of which was not determined.

The treatment of 4-methyl-x-penten-2-ol with dilute salt solutions gave the same type of compounds as 2-methyl-2,4-pentanediol and, there-

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[1] V. N. Ipatieff and H. Pines, THIS JOURNAL, 66, 1120 (1944).

[2] V. N. Ipatieff and G. S. Monroe, *ibid.*, 66, 1627 (1944).

[3] G. B. Bachman and C. G. Goebel, *ibid.*, 64, 787 (1942).

[4] V. N. Ipatieff, H. Pines and R. C. Olberg, *ibid.*, 67, 694 (1945).

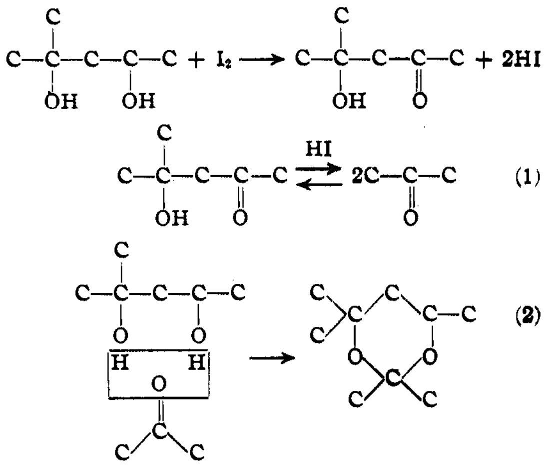
[5] R. C. Olberg, H. Pines and V. N. Ipatieff, *ibid.*, 66, 1096 (1944).

[6] H. Pines and V. N. Ipatieff, unpublished work.

fore, no details of the identification of the products will be given under "Experimental Part."

The crude 4-methyl-x-penten-2-ol[7] was prepared by the dehydration of 2-methyl-2,4-pentanediol by means of iodine. On distillation, 4-methyl-x-penten-2-ol was separated. The position of the hydroxy group in this carbinol was determined by hydrogenating it to the corresponding saturated alcohol and identifying it by preparing the 3,5-dinitrobenzoate.

The 4-methyl-x-penten-2-ol fraction contained a compound boiling at 139–141° which did not react with metallic sodium, reacted violently with a nitrating mixture, and was soluble in dilute sulfuric acid. According to the elementary analysis, physical constants, and chemical behavior, the compound corresponded to 2,2,4,4,6-pentamethyl-1,3-dioxane. This dioxane was probably formed as follows: part of the 2-methyl-2,4-pentanediol in the presence of iodine might have undergone oxidation to diacetone alcohol, which depolymerized to acetone, and the latter underwent condensation with the unreacted methylpentanediol. The reaction can be presented as follows



## Experimental Part

2-Methyl-2,4-pentanediol or 4-methyl-x-penten-2-ol was heated in a rotating autoclave with an equal volume of dilute ferric chloride and magnesium chloride solutions. The product resulting from this reaction was composed of two layers; the upper which consisted mainly of hydrocarbons was separated, washed, and distilled. The experimental results obtained are summarized in Table I.

The reaction products from experiments 3 and 4 were combined and distilled; the distillation curve is given in Fig. 1. The water layer contained practically no organic material.

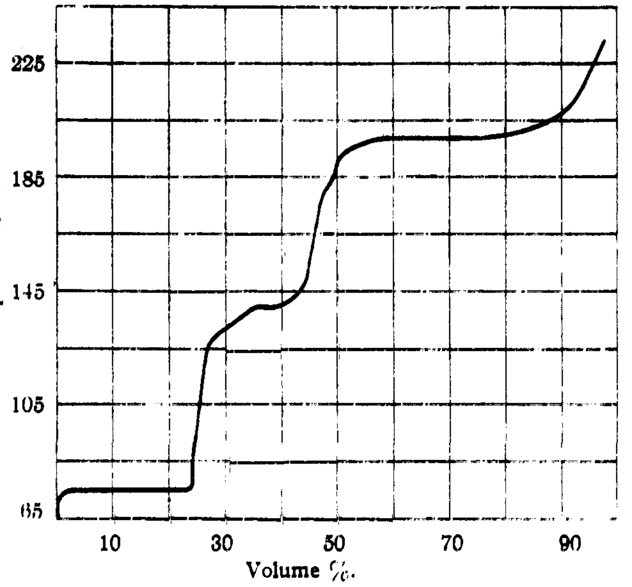


Fig. 1.—Distillation of the product obtained from the treatment of 2-methyl-2,4-pentanediol with aqueous ferric chloride solution.

**Fraction b. p. 75–75.7°.**—This fraction represented 24% by weight of the total product. It absorbed, on hydrogenation under pressure at 80°, two moles of hydrogen per one mole of hydrocarbon, thereby indicating two double bonds per molecule. The dienes which were analyzed by means of maleic anhydride (Bachman and Goebel method[8]) consisted of 15% of 2-methyl-2,4-pentadiene and 85% of 2-methyl-1,3-pentadiene. The latter yielded, with maleic anhydride, a solid adduct melting at 150–151°.

TABLE I

| Experiment number | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Material charged | 2-Methyl-2,4-pentanediol | | | | 4-Methyl-x-penten-2-ol | | |
| Material charged, amt. g. | 70 | 70 | 120 | 163 | 209 | 209 | 210 |
| Catalyst | $FeCl_3 \cdot 6H_2O$ | | | | | $MgCl_2 \cdot 6H_2O$ | |
| Catalyst, g. | 2.5 | 2.5 | 4.0 | 5.0 | 6.0 | 10 | 10 |
| Water, g. | 70 | 75 | 130 | 183 | 250 | 250 | 250 |
| Temperature, °C. | 145 | 165 | 190 | 190 | 210 | 208 | 250 |
| Duration of heating, hrs. | 1.5 | 1.4 | 1.3 | 1.1 | 2.0 | 2.0 | 1.5 |
| Max. press. at working temp., atm. | 22 | 29 | 25 | 25 | 27 | 28 | 60 |
| Capacity of autoclave, cc. | 450 | 450 | 850 | 850 | 850 | 850 | 850 |
| Charging material reacted, % | 73 | 83 | 94 | ... | 70 | 26 | 75 |
| Mole % of the material reacted converted to: | | | | | | | |
| Methylpentadienes | 30 | 12 | 26 | 20 | 10 | | 17 |
| Dimers | 35 | 40 | 34 | 33 | 32 | | 47 |
| Higher polymers | 14 | 31 | 13 | 26 | 30 | | 25 |

**Fraction 135–140°.**—The material was stable toward ammoniacal silver nitrate and toward sodium, indicating the absence of aldehydes and alcohols. *Anal.*[8] Calcd. for $C_9H_{14}O$: C, 78.26; H, 10.15. Found: C, 77.73; H, 10.81.

Eight grams of the product was dissolved in 10 cc. of pentane and hydrogenated at 70° in the presence of a nickel-kieselguhr catalyst[9] and at initial hydrogen pressure of 100 atmospheres. From the drop in the pressure of hydrogen it was calculated that two moles of hydrogen were absorbed per 1 mole of the product. The hydrogenated material distilled at 131–138° and did not react with metallic sodium; it corresponded to an ether, the structure of which

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(7) The carbinol was kindly furnished by Dr. C. L. Thomas of The Universal Oil Products Laboratories.

(8) Microanalyses were made by Dr. T. S. Ma, University of Chicago.

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

was not studied. *Anal.* Calcd. for $C_9H_{18}O$: C, 76.00; H, 12.76. Found: C, 76.94; H, 12.61; $n^{20}\mathrm{D}$ 1.4160.

**Fraction 143–145°.**—This fraction constituted 7% of the total product. *Anal.* Found: C, 82.71; H, 12.13; $n^{20}\mathrm{D}$ 1.4426. The product was hydrogenated in the presence of a nickel–kieselguhr catalyst at 68° and at initial hydrogen pressure of 100 atmospheres. After hydrogenation, it was stable toward permanganate solution but reacted with sodium, indicating the presence of alcohols. The latter were removed from the hydrocarbons by means of sulfuric acid. The resulting product was refluxed over sodium and distilled at 144–148°. *Anal.* Calcd. for $C_9H_{18}$: C, 85.63; H, 14.37. Found: C, 85.39; H, 14.94; $n^{20}\mathrm{D}$ 1.4182.

This material was dehydrogenated by passing it over platinized alumina at 250°.[10] An aromatic hydrocarbon was obtained which on nitration yielded a solid which melted at 238° and corresponded to trinitromesitylene. A mixed melting point with a synthetic sample did not show a depression.

Fraction 198–200°.—*Anal.* Calcd. for $C_{12}H_{20}$: C, 87.80; H, 12.20. Found: C, 88.30; H, 11.70.

The *nitroso chloride* of this hydrocarbon, prepared by the usual method using amyl nitrite and concentrated hydrochloric acid, melted at 117–118°. *Anal.* Calcd. for $C_{12}H_{20}NOCl$: $N_2$, 6.20. Found: $N_2$, 6.48.

**Hydrogenation.**—Sixteen grams of the hydrocarbon boiling at 198–200° dissolved in 20 cc. of pentane was hydrogenated at 46° in the presence of a nickel–kieselguhr catalyst and under initial hydrogen pressure of 74 atmospheres, measured at 28°.

1.75 moles of hydrogen was absorbed per 1 mole of product charged. The hydrogenated material did not contain any olefins as determined by means of dilute potassium permanganate solution. It reacted, however, with nitrating mixture (1 vol. of 72% $HNO_3$ and 2 vols. of 96% $H_2SO_4$) indicating the presence of aromatics. The latter amounting to about 10–12% were removed by treating the hydrogenated product with sulfuric acid containing 15% $SO_3$. The aromatic-free hydrocarbon distilled at 198–202°, $n^{20}\mathrm{D}$ 1.4460. *Anal.* Calcd. for $C_{12}H_{24}$: C, 85.63; H, 14.37. Found C, 85.92; H, 13.72.

**Dehydrogenation.**—Twelve grams of the hydrogenated product was dehydrogenated by passing it over platinized alumina at 300°. According to the hydrogen liberated 84% of the material underwent dehydrogenation to the corresponding aromatic hydrocarbons, which distilled at 225–228°, $n^{20}\mathrm{D}$ 1.5179.

**Oxidation.**—Six-tenths of a gram of the dehydrogenated product was oxidized at 135° with 40 cc. of a 25% concentration of nitric acid.[9] A solid was separated which melted at 246–248°; it corresponded to 1,2,3,5-benzenetetracarboxylic acid. *Anal.* Calcd. for $C_{10}H_6O_8$: C, 47.24; H, 2.33. Found: C, 47.10; H, 2.82.

**Isolation of Tetramethyldioxane.**—The crude carbinol was prepared by Dr. C. L. Thomas by the dehydration of 2-methyl-2,4-pentanediol. The product of the reaction of 68.5 moles of 2-methyl-2,4-pentanediol with 10 g. of iodine consisted of the following:

| Products obtained | Yield, mole % |
|---|---|
| Methylpentadienes | 66.0 |
| Methylpentenol | 29.2 |
| 2,2,4,4,6-Pentamethyl-1,3-dioxane | 1.5 |
| Polymers | 3.3 |

The methylpentenol fraction contained a compound boiling at 139–141°, $n^{20}\mathrm{D}$ 1.4195, which did not react with sodium but reacted with a 2% aqueous solution of potassium permanganate. On hydrogenation at 60° under 60 atmospheres of pressure in the presence of a nickel–kieselguhr catalyst, this material absorbed 0.3 mole of hydrogen per 1 mole of product charged. The material obtained from hydrogenation was stable toward a dilute permanganate solution but reacted violently with a nitrating mixture; it did not react with metallic sodium. The material, because of the presence of some hydrocarbons, was only partly soluble in a 50% solution of sulfuric acid from which it was separated by dilution with water. The acid-soluble product distilled at 139–140°. *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.36; H, 11.47. Found: C, 67.70; H, 11.16; $n^{20}\mathrm{D}$ 1.4196.

The product corresponds to 2,2,4,4,6-pentamethyl-1,3-dioxane.

## Summary

2-Methyl-2,4-pentanediol and 4-methyl-x-penten-2-ol were heated under pressure with dilute aqueous ferric chloride and magnesium chloride solutions.

Among the products resulting from this reaction certain hydrocarbons were identified: 2-methyl-1,3- and 4-methyl-1,3-pentadiene, 1,3,5-trimethylcyclohexene and 1,3,5-trimethyl-5-isopropenyl-1-cyclohexene.

A compound corresponding to 2,2,4,4,6-pentamethyl-1,3-dioxane in a yield of 2% was found among the products resulting from the dehydration of 2-methyl-pentanediol with iodine.

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[10] H. Pines, A. V. Grosse and V. N. Ipatieff, This Journal, **61**, 640 (1939).