

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE DEHYDRATION OF 2,3,4-TRIMETHYLPENTANOL-3¹

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The dehydration of this alcohol was prompted by interest in the isomers of diisobutylene² and in rearrangements accompanying the dehydration of relatively simple carbinols.³ In this case no rearrangement was detected. 2,3,4-Trimethylpentanol-3, when dehydrated with a trace of iodine, gave a mixture of the normal dehydration products, 3-methyl-2-isopropylbutene-1 and 2,3,4-trimethylpentene-2 in the ratio 1:2. Their structures were determined by ozonolysis.

Experimental

Diisopropyl ketone was prepared in 85% yield by oxidizing 2,4-dimethylpentanol-3 (Eastman Practical) in 200-g. lots with 235 g. of potassium dichromate and 340 g. of sulfuric acid in 2 liters of water with stirring at 40° for twenty-two hours. The ketone was collected at 122–127° (739 mm.), n_D^{20} 1.3998. The ketone was treated with methylmagnesium chloride according to Stas⁴ to give 2,3,4-trimethylpentanol-3 in 76% yield. The product was fractionated through column A (38 × 1.5 cm. total condensation, variable take-off packed column⁵). After the removal of the ether, twelve fractions and a residue of 4 cc. were obtained: Fractions 1–6, 36 cc., b. p. 66° (72 mm.) to 69° (39 mm.), n_D^{20} 1.4029 to 1.4218; fractions 7–12, 189 cc., b. p. 72° (40 mm.) to 66° (25 mm.), n_D^{20} 1.4318 to 1.4342. The main product (fractions 9–12) boiled at 75–77° (40 mm.) and had n_D^{20} 1.4341 to 1.4343.

The carbinol (130 g. from fractions 9–12) was dehydrated by refluxing with a crystal of iodine under a 90 × 2 cm. column provided with a water separator at its top. The product was distilled rapidly through column A to remove any unchanged carbinol, was then dried over 3 g. of sodium and carefully fractionated through a 90-cm. partial condensation column.⁶ Twelve fractions and a residue of 10 cc. were obtained: Fractions 1–3, 15 cc., n_D^{20} 1.4083, Cottrell b. p. 101.9° (741 mm.); fractions 11–12, 25 cc., n_D^{20} 1.4263, Cottrell b. p. 114.3° (739 mm.). The intermediate fractions amounted to 34 cc. and had n_D^{20} 1.4105 to 1.4261.

Nine grams of fractions 1–3 was ozonized and decomposed according to the technique of Church.⁷ The water layer of the distillate gave a strong test for formaldehyde with resorcinol.⁸ The oily layer, amounting to 5 cc., was dried with 1 g. of potassium carbonate. It then had n_D^{20} 1.4007. Its 2,4-dinitrophenylhydrazone prepared by

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² Whitmore and Wrenn, *THIS JOURNAL*, **53**, 3156 (1931); Whitmore and Church, *ibid.*, **54**, 3710 (1932).

³ Whitmore, *ibid.*, **54**, 3274 (1932); Whitmore and Laughlin, *ibid.*, **54**, 4011 (1932).

⁴ Stas, *Bull. soc. chim. Belg.*, **35**, 379 (1926).

⁵ Cf. Whitmore and Lux, *THIS JOURNAL*, **54**, 3448 (1932).

⁶ "Johnston Column," Whitmore and Lux, *ibid.*, **54**, 3453 (1932).

⁷ Whitmore and Church, *ibid.*, **54**, 3710 (1932).

⁸ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., 1st edition, Vol. I, p. 24.

Allen's second method⁹ and crystallized twice from absolute alcohol melted at 88°. A known sample prepared from diisopropyl ketone (n_D^{20} 1.3998) melted at 85–86°. A mixture melted at 87°. Thus the lower boiling olefin is 3-methyl-2-isopropylbutene-1.

Nineteen grams of fractions 10–12 was ozonized and decomposed. A small amount of solid ozonide was formed. The water layer gave a slight test for formaldehyde. The water layer was distilled through column A. To the first 5 cc. of distillate was added 0.4 cc. of benzaldehyde (freshly prepared from the bisulfite compound), 2 cc. of alcohol and 0.5 cc. of 10% sodium hydroxide solution. The mixture was boiled and evaporated to dryness on the steam-bath. The product was washed with hot water and the residue was crystallized from alcohol, m. p. 109°. A sample of dibenzylideneacetone prepared from acetone in the usual way¹⁰ melted at 108–109°; mixture, m. p. 108–109°. The oily layer (17 cc.) from the decomposition of the ozonide was fractionated through a 25 × 1 cm. indented partial condensation column at 727 mm. Five fractions were obtained boiling from 48 to 92° and having n_D^{20} 1.3693 to 1.3927. A small residue decomposed violently, apparently due to the presence of unchanged ozonide. Fraction 5 gave a 2,4-dinitrophenylhydrazone, m. p. 119°. The known derivative prepared from methyl isopropyl ketone (n_D^{20} 1.3898) melted at 116–117°; mixture, m. p. 118°. Thus the higher boiling olefin is 2,3,4-trimethylpentene-2.

Summary

1. The dehydration of 2,3,4-trimethylpentanol-3 with iodine gives the normal dehydration products with about twice as much dehydration from the tertiary hydrogen atoms as from those of the methyl group.

2. 3-Methyl-2-isopropylbutene-1 and 2,3,4-trimethylpentene-2 have been obtained and identified by ozonolysis.

⁹ Allen, THIS JOURNAL, 52, 2955 (1930).

¹⁰ Mulliken, Ref. 8, p. 148.

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THE COMPOSITION AND POSSIBLE CONSTITUTION OF SEVERAL SULFUR DYES¹

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The facts that the majority of the sulfur dyes cannot be obtained in crystal form and that in most cases they form colloidal solutions have made investigation of their constitutions exceedingly difficult. However, the thiazine nature of the black and blue dyes has been established by the collection of a plethora of data from various sources.² The full structural formula of only one of the sulfur dyes, *Immedial Reinblau*, which forms a

¹ The material in this article is extracted from a dissertation submitted by W. Norton Jones, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Johns Hopkins University, June, 1932.

² Lange, "Die Schwefelfarbstoffe, ihre Herstellung und Verwendung," Verlag Otto Spamer, Leipzig, 1921, pp. 20.