hindrance involved and only in part to the insolubility of the ketones in the aqueous solutions used.

URBANA, ILLINOIS

RECEIVED APRIL 10, 1933
PUBLISHED AUGUST 5, 1933

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

The Dehydration of Capryl Alcohol

BY FRANK C. WHITMORE AND JOHN M. HERNDON[1]

In a recent paper[2] it is reported that octanol-2 was "transformed by elimination of water into octene." Following the same procedure octanol-1 was dehydrated and in describing the product it is stated that "it is to be expected that this is octene-1." The results showed "that the two octene preparations notwithstanding the great difference between the starting materials had practically the same characteristics. Further, the unsaturation of both preparations approaches the theoretical value." Because of the present interest in molecular rearrangements in this Laboratory[3] and in view of some related work on the dehydration of capryl alcohol, this paper is presented. Highly purified capryl alcohol (octanol-2) has been dehydrated and the resulting products have been ozonized with the conclusion that they consist of octene-2 and octene-1, the former predominating. Octene-1 has been prepared and purified. From the constants of octene-1 and octene-2[4] it appears that the material obtained by Waterman and teNuyl from octanol-1 was a mixture of octene-2 and octene-1 rather than pure octene-1.

Experimental

Purification of Capryl Alcohol.—This alcohol was purified by careful distillation through an adiabatic packed column,[5] 8.3 meters high and 7.6 cm. in diameter.

Physical constants of pure octanol-2: b. p. 177.3° (731 mm.) (Cottrell): n^{20}_{D} 1.4260; d^{20}_{4} 0.817. This material gave no precipitate with sodium bisulfite solution even on long standing.

Dehydration of Capryl Alcohol.—In a 3-liter flask, provided with a 25 × 2 cm. packed column[6] of the total condensation, adjustable take-off type, was placed 250 cc. of phosphoric acid (sp. gr. 1.7). The flask was heated in an oil-bath to 235°. Five moles (650 g.) of the pure capryl alcohol was added dropwise. The water and olefin were distilled through the column and collected during four hours. The oily layer, carefully separated from the aqueous portion of the distillate, was fractionated through

---

(1) Presented in partial fulfilment of the requirements for the Ph.D. degree.

(2) Waterman and teNuyl, *Rec. trav. chim.*, **51**, 533 (1932).

(3) See THIS JOURNAL, **54**, 3279 (1932).

(4) Constants for octene-2 kindly given by C. E. Boord.

(5) The construction and operation of this column have been described in detail by Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932). The capryl alcohol was supplied by the Rohm and Haas Co. of Philadelphia, Pa.

(6) See THIS JOURNAL, **54**, 3451 (1932).

a 75 × 2.1 cm. column (same type as the 25 × 2 cm. column) at 738 mm. with a reflux ratio of 25:1. Distillation A gave eleven fractions (total 483 g.) from 115–123.7° with n_D^{20} 1.4020 to 1.4139; residue 42 g., n_D^{20} 1.4213. The important fractions were A4–9, 378 g., 121.5–123.0°, n_D^{20} 1.4134 to 1.4137.

Ozonolysis of Fraction A9.—The 60 g. (0.53 mole) in 300 cc. of low boiling hydrocarbon was ozonized at −10° during eighteen hours.[7] Removal of the solvent under vacuum gave 77 g. of colorless liquid ozonide. Decomposition of the ozonide gave 44 g. of oil and 190 cc. of aqueous layer. Qualitative tests for formaldehyde with Schryver's[8] reagent and 1% aqueous resorcinol were obtained. The hydrogen peroxide method showed 3.4 g. of formaldehyde in the aqueous products. The absorption apparatus[6] consisted of three tubes each holding 100 cc. of dry ether. Upon completion of the steam distillation, the absorption apparatus was removed and the ether dried over 20 g. of anhydrous sodium sulfate. A stream of dry ammonia was then passed through the clear ether solution with the formation of 3.8 g. of crystalline acetaldehyde-ammonia, m. p. 88.5–90°, mixed m. p. 88–89°. The oily products were distilled through a 68 × 1.1 cm. glass, indented, adiabatic (electrically heated), total condensation adjustable take-off column[5] under reduced pressure. Distillation B gave eight fractions (total 39 g.) from 47° (123 mm.) to 60° (8 mm.), n_D^{20} 1.3890 to 1.4182; residue, 0.8 g., n_D^{20} 1.4475. Fractions B3–6 (22.7 g.), n_D^{20} 1.4027 to 1.4040, were nearly pure hexaldehyde, while fractions B7–8 (9.5 g.), n_D^{20} 1.4101 to 1.4182, contained heptaldehyde.

Oxidation of Hexaldehyde.—Fraction B4 was oxidized with sodium dichromate and sulfuric acid. The oil collected as a distillate had the characteristic odor of *n*-caproic acid. It was converted to the amide which after recrystallization from ethyl acetate, melted at 97.6–98.5°; mixed m. p. 98–99°. The ozonolysis products consisted of formaldehyde, acetaldehyde, hexaldehyde and heptaldehyde, thus proving the olefin to be a mixture of octene–1 and octene–2.

Additional Purification of Octenes.—Fractions A6–7 were combined and refluxed with sodium for 110 hours. The yellow precipitate was removed at twelve-hour intervals. The purified olefin was then distilled through the 68 × 1.1 cm. column at 732 mm. using a reflux ratio of 20:1, to give three fractions with b. p., wt. and n_D^{20} as follows: C1, 119.5–121°, 3 g., 1.4130; C2, 121–122°, 18 g., 1.4135; C3, 122–122.5°, 58 g., 1.4137, d_4^{20} 0.7197.

Ozonolysis of Fraction C3.—A solution of 28 g. of fraction C3 in 200 cc. of solvent was ozonized at −10° during ten hours in the usual way. Removal of the solvent under reduced pressure left 40 g. of colorless ozonide which was decomposed as usual. The oily portion of the distillate, amounting to 16 g., was distilled through the 68 × 1.1 cm. column, under reduced pressure to give seven fractions (total 13 g.) from 64° (110 mm.) to 85° (23 mm.) and n_D^{20} 1.3975 to 1.4120; residue, 1 g., n_D^{20} 1.4307. Fractions D2–6 (11 g.) contained hexaldehyde while fraction D7 (1 g.) contained heptaldehyde. The aqueous portions were combined and qualitative tests for formaldehyde with Schryver's reagent and 1% resorcinol were obtained. The hydrogen peroxide method showed 1.48 g. of formaldehyde to be present in the aqueous portion. The acetaldehyde-ammonia amounted to 1.6 g.

Preparation of Octene-1.—The procedure for the preparation of octene-1 has been reported[9] previously. In the present case an ethereal solution of allyl bromide cooled to 0° was vigorously stirred during the addition of filtered *n*-amyl Grignard solution. The reaction mixture was treated in the usual manner and the olefin obtained was dis-

---

[7] For details of ozonization and hydrolysis of ozonides see Whitmore and Church, THIS JOURNAL, **54**, 3712 (1932).

[8] Schryver, *J. Chem. Soc.*, **98**, II, 357 (1910).

[9] Compare Kirrmann, *Bull. soc. chim.*, [4] **39**, 990 (1926); Wilkinson, *J. Chem. Soc.*, 3057 (1931).

tilled through a 90 × 1.5 cm. column.[6] The portion collected at 115–120° (744 mm.), n_D^{20} 1.4086–1.4090, was diluted with ether and cooled to −12°. Bromine was added dropwise. The dibromide purified by distillation was slowly added to a warm mixture of zinc dust and alcohol. The reaction mixture was diluted with a large volume of water and steam distilled. The regenerated olefin was separated from the aqueous portion of the distillate and dried over 5 g. of anhydrous potassium carbonate. The oil was distilled through the 68 × 1.1 cm. column at 739 mm. using a reflux ratio of 20:1, to give six fractions (59 g.) from 118.5 to 119.8°, n_D^{20} 1.4079 to 1.4089; residue, 4 g., n_D^{20} 1.4205. The chief fractions with b. p., wt. and n_D^{20} were E3, 119°, 12 g., 1.4083; E4, 119–119.5°, 16 g., 1.4087; E5, 119.5–119.8°, 14 g., 1.4088.

Ozonolysis of Fractions E3 and 4.—The combined 28 g. of olefin, d_4^{20} 0.7154, was ozonized and treated like fraction C3. The oily portion of the decomposition products amounting to 23.5 g. was distilled through the 68 × 1.1 cm. column, under reduced pressure to give five fractions (21 g.) from 80° (70 mm.) to 73° (43 mm.), n_D^{20} 1.4100 to 1.4120; residue, 1.3 g., n_D^{20} 1.4322. The important fractions with b. p., wt. and n_D^{20} were: F1, 80° (70 mm.), 1.6 g., 1.4100 and F4, 69° (45 mm.), 7.8 g., 1.4118. Fraction F1 would contain any hexaldehyde if present. A portion of this fraction was converted into the 2,4-dinitrophenylhydrazone. Recrystallization of the derivative finally brought the m. p. to 104°.

M. p. of 2,4-dinitrophenylhydrazone of hexaldehyde 104°
M. p. of 2,4-dinitrophenylhydrazone of heptaldehyde 106.5°
M. p. of derivative from F1 mixed with that of hexaldehyde 93–94°
M. p. of derivative from F1 mixed with that of heptaldehyde 105°

Thus no hexaldehyde was found. The aqueous portions were combined and qualitative tests for formaldehyde with Schryver's reagent and 1% aqueous resorcinol were obtained. The hydrogen peroxide method showed 5.5 g. of formaldehyde to be present in the aqueous portions. No acetaldehyde ammonia was found.

An examination of the constants of the materials ozonized, Fractions A9 and C3, and the material obtained by Waterman from octanol-1 shows that the constants for these mixtures lie between those for the pure octene-1 Fraction E4, b. p. 119–119.5° (739 mm.), n_D^{20} 1.4087, d_4^{20} 0.715, MR_D 38.7 and for pure octene-2,[4] b. p. 124.1–124.7° (745 mm.), n_D^{20} 1.4149, d_4^{20} 0.722, MR_D 38.9.

Summary

1. Very pure capryl alcohol (octanol-2) has been obtained by careful fractional distillation.

2. The dehydration products of octanol-2 consist of a mixture of octene-1 and octene-2 in the ratio 1:4 approximately.

3. The dehydration of octanol-1 involves a rearrangement and the product is a mixture of octene-1 and octene-2 in the ratio 2:1 approximately.

STATE COLLEGE, PENNSYLVANIA

RECEIVED APRIL 10, 1933
PUBLISHED AUGUST 5, 1933