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

The Separation of Primary Active Amyl Alcohol from Fusel Oil by Distillation

By FRANK C. WHITMORE AND J. HARRIS OLEWINE

Fusel oil, regardless of its origin, generally consists of primary active amyl alcohol $CH_3CH_2CH(CH_3)CH_2OH$, and isoamyl alcohol $(CH_3)_2CHCH_2CH_2OH$. These two alcohols, boiling at 128° and 130.5°, respectively, had never before been separated effectively by distillation alone.

Klages and Sautter[1] obtained active amyl alcohol in 42–61% purity by distillation of fusel oil from beet sugar molasses. Votocek and Vesely[2] isolated the active alcohol in only 46% purity by the distillation of fusel oil obtained from molasses. Since the completion of the present study (1936), Brauns has reported such a successful separation.[3] In this paper, the fractionation of fusel oil to give primary active amyl alcohol of approximately 95% purity, is described. The separation necessitated the use of very efficient columns.[4,5]

Experimental

The fusel oil used was a refined product[6] obtained in the fermentation of cane molasses, $\alpha^{33}D$ −0.69°. Prior to fractionation, it was dried at 0° for forty-eight hours with anhydrous sodium sulfate.

Preliminary Fractionation.—In a series of trial fractionations, two packed columns of metal construction were used. One column was 27 feet (7.9 meters) long and 3 inches (7.6 cm.) in diameter with a capacity of 13 gallons (49 liters), the other column was 52 feet (15.4 meters) long and $3/4$ inch (1.9 cm.) in diameter with a capacity of 1.5 gallons (5.7 liters). The construction and operation of

(1) Klages and Sautter, Ber., **37**, 649 (1904).

(2) Votocek and Vesely, ibid., **47**, 1515 (1914).

(3) Brauns, J. Research Nat. Bur. Standards, **18**, 315–31 (1937).

(4) Fenske, Quiggle and Tongberg, Ind. Eng. Chem., **24**, 408 (1932).

(5) Fenske, Tongberg, Quiggle and Cryder, ibid., **28**, 644 (1936).

(6) Obtained from the U. S. Industrial Chemical Company, Baltimore, Maryland.

these columns already has been described in detail.[4] In one preliminary fractionation, 40 liters of the refined fusel oil was first distilled in the 27-foot (7.9-m.) column and the best intermediate fractions therefrom were then twice redistilled in the 52-foot (15.4-m.) column. Approximately 0.6 liter of primary active amyl alcohol was obtained, b. p. 128° (760 mm.), $n^{20}D$ 1.4111, having an average observed rotation of $\alpha^{33}D$ −4.27° in a 1-dm. tube. The maximum rotation included in this average value was −4.34°, specific rotation $[\alpha]^{33}D$ −5.32°. Based on −5.9° as the specific rotation of pure primary active amyl alcohol, the alcohol thus obtained was approximately 90% pure.

Isolation of Primary Active Amyl Alcohol.—The design and efficiency of the distillation equipment used in this fractionation had been described previously.[5] The column was of nickel construction with a height of packed section of 38 feet (11.4 meters) and having a distilling capacity of 12 liters. When tested with n-heptane and methylcyclohexane and operating at a velocity of 3.4 liters per hour at the top of the tower, the column had the equivalent of 101 theoretical plates.

Four fractionations were made using a total of 35.2 liters of fusel oil. The following describes a typical run. A charge of 10 liters of fusel oil was refluxed for twelve hours to bring the column to equilibrium, after which the distillate was collected at a rate of approx. 70 cc. per hour during a period of continuous operation for eight and one-half days. This rate enabled an average reflux ratio of 30:1 to be maintained and to give at 760 mm.: Fractions 1–13, 1310 cc., b. p. (Cottrell) 107.8–117.4°, $n^{20}D$ 1.3835–1.4000; 14–17, 450 cc., 119.6–128.7°, 1.4025–1.4102, obsd. rotation (1-dm. tube) $\alpha^{27}D$ −0.72 to −3.81°; 18–42, 3300 cc., 129.3–130.8°, 1.4101–1.4069, −3.49 to 0.00°; 43–62, 3973 cc., 130.8–131°, 1.4069; residue, 725 cc.

The cuts of the four fractionations having the highest concentration of active alcohol were combined (8209 cc.) and refractionated through the nickel column during seven days to give: Fractions 1–7, 625 cc., b. p. 125.1–127.9° (760 mm.), $n^{20}D$ 1.4003–1.4110, $\alpha^{18}D$ −0.41 to −4.90; 8–22, 1310 cc., 127.7–128.5°, 1.4110, −4.91 to −4.93°,

d^{23}_4 0.8169–0.8137; 23–34, 1465 cc., 128.5–129.8°, 1.4110–1.4103, −4.92 to −4.12°, 0.8137–0.8130; 35–44, 1210 cc., 129.7–131.0°, 1.4097–1.4070, −3.55 to −0.70°, 0.8130.

Fractions 8–34 are primary active amyl alcohol of high rotatory power. The maximum observed rotation for the best fraction was α^{28}D −4.93°; specific rotation $[\alpha]^{28}$D −6.04°. The constants (average) of the primary active amyl alcohol are: b. p. 128–129° (760 mm.), n^{20}D 1.4109, d^{20}_4 0.8189, $d^{27.5}_4$ (calcd.) 0.813, $\alpha^{27.5}$D −4.77°, $[\alpha]^{27.5}$D −5.86° (1-dm. tube). The rotation of an aliquot sample was kindly checked by Levene,[7] who reports $\alpha^{25}_{5875.6}$

(7) Dr. P. A. Levene, Rockefeller Institute of Medical Research, New York City, private communication.

−9.186 ± 0.003° (2-dm. tube), and Wallis,[8] who reports $\alpha^{24.5}_{5893}$ −4.52° (1-dm. tube).

Summary

Primary active amyl alcohol having a high optical purity can be separated from fusel oil by a laboratory distillation process. The physical constants are reported.

(8) Dr. E. S. Wallis, Princeton University.
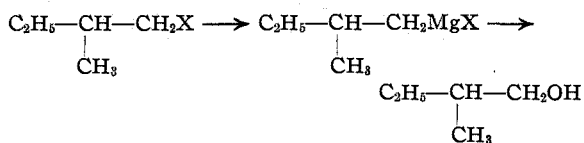
STATE COLLEGE, PENNA.   RECEIVED JULY 11, 1938

The Primary Active Amyl Halides

BY FRANK C. WHITMORE AND J. HARRIS OLEWINE

The separation of approximately 95% pure primary active amyl alcohol by fractionation of fusel oil has been described in the preceding paper.[1] Disagreement concerning the optical purity of the halides prepared from this alcohol exists in the literature.[2] In the present work, the preparation and properties of the active halides are reported. The chief objective of the study was the determination of the amount of racemization on conversion to the Grignard reagent and then to the alcohol.

$$C_2H_5—\underset{\underset{CH_3}{|}}{CH}—CH_2X \longrightarrow C_2H_5—\underset{\underset{CH_3}{|}}{CH}—CH_2MgX \longrightarrow$$
$$C_2H_5—\underset{\underset{CH_3}{|}}{CH}—CH_2OH$$

The action of thionyl chloride on primary active amyl alcohol in pyridine gave the corresponding chloride in 77% yield, specific rotation $[\alpha]^{28.5}$D +1.66°. Treatment of the alcohol with phosphorus tribromide produced the active halide in 29% yield, $[\alpha]^{29}$D +3.75°. These values agree closely with those of Brauns[2] but are lower than those of Marckwald.[3] The iodide, $[\alpha]^{28}$D +4.84°, was prepared in 17.5% yield by conversion of the alcohol to the benzoate and treatment with magnesium iodide. The low value for the rotation indicated racemization.

Conversion of the chloride and bromide to the Grignard reagents, and treatment with oxygen regenerated the active amyl alcohol with a total racemization not greater than 10% for the four reactions. Similar treatment of the iodide gave no active amyl alcohol. This reaction will be investigated further.

Experimental

Preparation of Primary Active Amyl Chloride.—The method of Clark and Streight[4] was used in a series of one mole preparations. Addition of 2 moles of thionyl chloride to a solution of one mole of primary active amyl alcohol in one mole of dry pyridine gave the crude chloride. Purification in the usual fashion and fractionation with an efficient column, 75 × 2 cm.,[5] packed with 4-mm. single-turn glass helices,[6] gave a 77% yield of primary active amyl chloride, b. p. (Cottrell) 50.5–51° (140 mm.), n^{20}D 1.4125, d^{20}_4 0.8852, $[\alpha]^{28.5}$D +1.66°.

Preparation of Primary Active Amyl Bromide.—The method of Jones[2] was used. The crude product from the addition of 0.37 mole of phosphorus tribromide to one mole of primary active amyl alcohol at 5–15° was purified and fractionated to give a 29% yield of active amyl bromide, b. p. 69.6° (140 mm.), n^{20}D 1.4450, d^{20}_4 1.2239, $[\alpha]^{29}$D +3.75°.

Preparation of Primary Active Amyl Iodide.—The halide was prepared by the action of magnesium iodide on active amyl benzoate.[7] Treatment of 1.5 moles of primary active amyl alcohol with 2 moles of benzoyl chloride gave an 80% yield of the benzoate, b. p. (Cottrell) 140.2° (20 mm.), n^{20}D 1.4948, d^{20}_4 0.9913, α^{28}D +6.09° (1-dm. tube). Magnesium iodide was prepared from magnesium and iodine in dry ether. Refluxing of a solution of 1.5 moles of

(1) Whitmore and Olewine, THIS JOURNAL, **60**, 2569 (1938).

(2) Le Bel, Bull. soc. chim., **25**, 546 (1876); Marckwald, Ber., **37**, 1046 (1904); Klages and Sautter, ibid., **37**, 649 (1904); Neuberg and Federer, ibid., **38**, 1248 (1905); Jones, J. Chem. Soc., **87**, 138 (1905); Hardin and Sikorsky, J. chim. phys., **6**, 179–211 (1908); McKenzie and Clough, J. Chem. Soc., **103**, 690 (1913); Brauns, J. Research Nat. Bur. Standards, **18**, 315–31 (1937).

(3) Marckwald, Ber., **37**, 1038 (1904); **42**, 1583 (1909).

(4) Clark and Streight, Trans. Roy. Soc. Can., **23**, 77 (1929).

(5) Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

(6) Wilson, Parker and Laughlin, ibid., **55**, 2795 (1933).

(7) Zal'kind, J. Russ. Phys.-Chem. Soc., **46**, 692 (1914); Gomberg and Bachmann, THIS JOURNAL, **50**, 2762 (1928).