

d^{25}_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^{26}_D –4.93°; specific rotation $[\alpha]^{26}_D$ –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 $\alpha^{25}_{875.6}$

(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 $\alpha^{24.5}_{898}$ –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.

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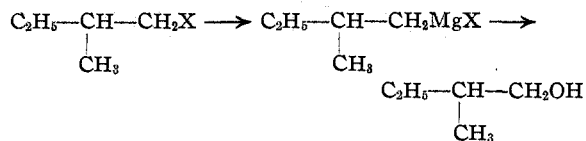
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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

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.



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 Brauns² 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.

(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); Neuberger 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 (1913).

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

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 Streight⁴ 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 Jones² 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

(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).

	Average values for original primary active amyl alcohol to make the		Average values for regenerated primary active amyl alcohol obtained from the	
	Chloride	Bromide	Chloride	Bromide
B. p., °C. (20 mm.)	50.1	50.1	50.1	50.1
n_D^{20}	1.4109	1.4109	1.4109	1.4109
d_4^{20}	0.81876	0.81846	0.81842	0.81829
d_4	0.813 ^{27.5}	0.813 ^{27.5}	0.796 ²⁸	0.795 ²⁷
α_D	-4.8 ^{27.5}	-4.8 ^{27.5}	-4.28 ²⁶	-4.48 ²⁷
$[\alpha]_D$	-5.9 ^{27.5}	-5.9 ^{27.5}	-5.38 ²⁸	-5.63 ²⁷

magnesium iodide and one mole of the ester in 500 cc. of ether for two weeks gave 126.5 g. of crude iodide and much resin formation. Fractionation of the crude product gave 17.5% of primary active amyl iodide, b. p. (Cottrell) 47.1° (20 mm.), n_D^{20} 1.4969, d_4^{20} 1.5227, $[\alpha]_D^{20}$ +4.84°.

Regeneration of Primary Active Amyl Alcohol from the Corresponding Chloride and Bromide.—The primary active amyl chloride and bromide were converted into the Grignard compounds in 83 and 76% yields, respectively. Treatment of the Grignard compounds with oxygen at 0° and decomposition of the complex with water regenerated the primary active amyl alcohol. A comparison of the constants for the regenerated alcohol with those of the original alcohol is given.

A similar attempt to regenerate the active alcohol from primary active amyl iodide failed.

Summary

1. The preparation and physical constants of the primary active amyl chloride, bromide and iodide are reported.

2. Primary active amyl alcohol can be regenerated from the corresponding chloride or bromide by conversion to the Grignard compound and treatment with oxygen. The iodide cannot be used for the conversion.

3. The total racemization in the steps alcohol → bromide or chloride → Grignard reagent → alcohol is not over 10%.

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The Nonanes. 2-Methyloctane, 3-Ethylheptane, 2,3-Dimethylheptane and 2,2,4,4-Tetramethylpentane¹

BY FRANK C. WHITMORE AND HARRIET A. SOUTHGATE

The present work was undertaken because of the interest in this Laboratory in petroleum hydrocarbons, in rearrangements in the aliphatic series, in the limitations of typical aliphatic reactions and in the relation of structure to physical properties of aliphatic compounds.

Theoretically, thirty-five structurally isomeric nonanes are possible. Twelve were known when the present work was started, namely, *n*-nonane, the three monomethyloctanes, 2,4-, 2,5-, 2,6- and 3,3-dimethylheptanes, 4-ethylheptane, 2,3,5- and 2,2,5-trimethylhexanes, and 3,3-diethylpentane. The scattered and incomplete data on the physical properties of these eleven nonanes indicate that regularities exist similar to those found in the hexanes, heptanes and octanes.

Three new nonanes, 3-ethylheptane, 2,3-dimethylheptane and the most highly branched nonane, 2,2,4,4-tetramethylpentane, have been synthesized in the present study. Since the data

on 2-methyloctane are meager,² this compound also was prepared.

The 2,2,4,4-tetramethylpentane was obtained in poor yield from 2,2,4-trimethyl-4-bromopentane or the corresponding chloride with dimethylzinc. The main course of the latter reaction involved the removal of halogen acid to form the known diisobutylenes. This agrees with results obtained by S. N. Wrenn of this Laboratory on the action of a variety of alkaline agents with these halides. The other three nonanes were obtained by dehydration of the tertiary alcohols, 2-methyl-2-octanol, 3-ethyl-3-heptanol, and 2,3-dimethyl-3-heptanol by Hibbert's³ iodine method and hydrogenating the olefin mixtures at high pressure using a nickel catalyst supported on alumina.

The reactions involved in these syntheses are not ones which are accompanied by rearrange-

(2) Späth, *Monatsh.*, **34**, 1965 (1913); Richards and Shipley, *This Journal*, **41**, 2002 (1919); Dobjranski and Chessin, *Chem. Zentr.*, **101**, I, 2662 (1930).

(3) Hibbert, *This Journal*, **37**, 1748 (1915).

(1) Original manuscript received April 23, 1934.