chloropentane was made alkaline with sodium carbonate and the liberated ketone was distilled. The semicarbazone prepared from this melted at 122–123.5°. A mixture with the known semicarbazone of 2-hexanone of m. p. 124–125° melted at 122.5–124°.

Identification of 2-Ethyl-1-chlorobutane (A).—Fraction 7 of the hexanols from Distillation D (described under 3-chlorohexane) gave the α-naphthylurethan of 2-ethyl-1-butanol, m. p. and mixed m. p. 63–64°.

Fraction 43 of the mixed chlorides from Distillation B, 13.5 g., b. p. 76.5–77.5° (160 mm.), $n^{20}\mathrm{D}$ 1.4198, was shaken with 50 cc. of normal aqueous silver nitrate solution for three hours at room temperature to remove secondary and tertiary halides. The organic material was distilled from the mixture, separated, washed with carbonate solution, dried and fractionated. Treatment of the Grignard reagent with phenyl isocyanate gave crystals melting at 80.5–81.5°. Mixture with a known sample of β-ethylvaleranilide of m. p. 83–84° melted at 80.5–82.5°. The known specimen was prepared in the same way from a sample of 2-ethyl-1-chlorobutane made by the action of thionyl chloride on the carbinol.

Anal. Calcd. for $C_{13}H_{19}NO$: N, 6.84. Found: N, 6.93.

The other fractions were studied without obtaining any evidence for the presence of chlorides other than the seven identified.

Treatment of 2-Ethyl-1-chlorobutane with Zinc Chloride in Hydrochloric Acid.—One mole, 120.5 g., of 2-ethyl-1-chlorobutane, $n^{20}\mathrm{D}$ 1.4228–30, prepared by the action of thionyl chloride and pyridine on 2-ethyl-1-butanol, was stirred vigorously with a solution of 1.25 moles, 171 g., of fused zinc chloride in 2 moles, 202 g., of concentrated hydrochloric acid at 79–87° for seven hours. The halide layer was separated, washed with water and carbonate solution, dried and fractionated. The yield of chlorohexanes recovered was 108.6 g., or 90.0% of the starting material. The yield of unchanged 2-ethyl-1-chlorobutane was 86.1 g.; this is 71.4% of the starting material and 79.2% of the recovered halides. The remainder was rearranged hexyl chlorides.

Approximation of the Percentage of Individual Hexyl Chlorides Present.—Only a rough estimate, based on fractionation data, can be given. 3-Methyl-3-chloropentane (D), present in 35–40% yield, was the most abundant isomer. 2-Chlorohexane (C), 2-methyl-2-chloropentane (F) and 3-methyl-2-chloropentane (E) were present in 5–10%; the remaining isomers, 1–5% each. It is quite possible that other hexyl chlorides, present in smaller quantities, were not identified.

Summary

1. 2-Ethyl-1-chlorobutane is produced by the action of thionyl chloride and pyridine on 2-ethyl-1-butanol without any detectable rearrangement.

2. The action of zinc chloride in hydrochloric acid solution on 2-ethyl-1-butanol gives at least seven different chlorohexanes, namely, 3-methyl-3-chloropentane, 2-methyl-2-chloropentane, 3-methyl-2-chloropentane, 4-methyl-2-chloropentane, 3-chlorohexane, 2-chlorohexane, and 2-ethyl-1-chlorobutane.

3. At least the major part of the rearrangements occurred during the formation of the chlorides.

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

Preparation and Properties of 2- and 3-Chloropentanes

BY FRANK C. WHITMORE AND F. A. KARNATZ

Much work has been done on the secondary chlorides and bromides of *n*-pentane.[1] In the present study, it was found that both 2-pentanol and 3-pentanol gave mixtures of 2- and 3-chloropentanes even with as mild treatment as the action of hydrogen chloride gas at room temperature. The amount of rearrangement was considerably less with 2-pentanol.

In order to obtain pure samples of 2- and 3-chloropentanes for the determination of physical constants, it was necessary to use thionyl chloride in the presence of pyridine.[2] There is evidence[3] that this reaction gives least rearrangement. Samples of the two chlorides were obtained, the properties of which showed a maximum difference; namely, for 2-chloropentane, $n^{20}\mathrm{D}$ 1.4069 and d^{20}_{4} 0.8695, and for 3-chloropentane, $n^{20}\mathrm{D}$

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(1) Wagner and Saizew. *Ann.*, **179**, 321 (1875); Przewalski, *J. Russ. Phys.-Chem. Soc.*, **41**, 464–469 (1909); Clough and Johns, *Ind. Eng. Chem.*, **15**, 1032 (1923); Norris and Taylor, THIS JOURNAL, **46**, 753 (1924); Grignard and Ono, *Bull. soc. chim.*, [4] **39**, 1589 (1926); Norris and Reuter, THIS JOURNAL, **49**, 2630 (1927); Sherrill, Otto and Pickett, *ibid.*, **51**, 3027 (1929); Sherrill, Baldwin and Haas, *ibid.*, **51**, 3036 (1929); Ayres, *Ind. Eng. Chem.*, **21**, 899 (1929); Boord and Soday, THIS JOURNAL, **55**, 3296 (1933); Tabern and Volwiler, *ibid.*, **56**, 1139 (1934); Shonle, *ibid.*, **56**, 2490 (1934); Hass and Weber, *Ber.*, **67**, 974 (1934); Underwood and Gale, THIS JOURNAL, **56**, 2118 (1934); Lauer and Stodola, *ibid.*, **56**, 1215 (1934); Hass, McBee and Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935); Hass and Weber, *Ind. Eng. Chem., Anal. Ed.*, **7**, 231 (1935).

(2) (a) Darzens, *Compt. rend.*, **152**, 1314 (1911); (b) Clark and Streight, *Trans. Roy. Soc. Can.*, **23**, 77 (1929).

(3) McKenzie and Clough, *J. Chem. Soc.*, **103**, 687 (1913); Gilman and Harris, *Rec. trav. chim.*, **50**, 1052 (1931); Kirner, THIS JOURNAL, **50**, 1958 (1928); Ref. 2a; also, unpublished work in this Laboratory.

1.4104 and d^{20}_4 0.8795. The boiling points, 96.8 and 97.8°, are too close together to be of any significance as criteria of purity.

The stability of the chlorides to heat was established by heating samples of them in sealed tubes to 100° for forty-eight hours without obtaining any significant change in refractive index. However, it was found that either chloride could be isomerized to an equilibrium mixture of the two by shaking it with $ZnCl_2$–HCl solution at room temperature for seventy-two hours. The composition of this mixture was about 80% 2-chloropentane.

The physical constants determined were

	2-Chloropentane	3-Chloropentane
B. p., Cottrell, 760 mm., °C.	96.84–96.88	97.76–97.82
Freezing points, °C.	−137–139	−105–106
Density, d^{20}_4	0.8695	0.8795
Refractive index, n^{20}D	1.4069	1.4104
Viscosities at 20°, centistoke	0.5672	0.5845

Experimental

Preparation of 3-Chloropentane.—A solution of 1 mole, 88 g., of 3-pentanol, b. p. 114.5–114.9° (730 mm.), n^{20}D 1.4100, prepared from methyl formate and ethylmagnesium bromide, in 1.1 mole, 87 g., of dry pyridine, b. p. 113.3–114.5° (735 mm.), was treated with 1.3 moles, 154.8 g., of thionyl chloride (Eastman Kodak Co.), in the cold, over a period of fifty minutes. A heavy white precipitate formed. When addition was complete the ice-bath was removed, and after an hour the flask was warmed in a water-bath from 30 to 53° during two hours to drive off sulfur dioxide.

The reaction mixture, present as two brown layers, was poured on 200 g. of ice, and the layers were separated. The halide layer was washed with 10% sodium carbonate solution and dried. Fractionation at 731 mm. through a total condensation type column, 1.5 × 66 cm., packed with glass helices[4] gave a 46% yield of 3-chloropentane, b. p. 96°, n^{20}D 1.4104, d^{20}_4 0.8795. These values were checked in two similar runs.

Preparation of 2-Chloropentane.—The same procedure was used as for 3-pentanol. The 2-pentanol, 0.50 mole, b. p. 117.9–118.5° (739 mm.), n^{20}D 1.4058, was prepared by the method of Sherrill, Baldwin and Haas.[1] The yield of 2-chloropentane, b. p. 95° (729 mm.), n^{20}D 1.4068, was 28%. More non-volatile material was formed than with the 3-compounds.

Treatment of 3-Pentanol with Hydrogen Chloride.—The following is a description of a typical run. One mole, 88 g., of synthetic 3-pentanol, n^{20}D 1.4100, b. p. 114.7–115.5° (734 mm.), and 10 g. of concentrated hydrochloric acid were saturated with hydrogen chloride at 0°; 25 g. was absorbed. After six weeks at room temperature, the solution was resaturated with hydrogen chloride at 0°; 17.5 g. was absorbed. After standing for an additional fourteen weeks, the layers were separated.

The colorless halide layer, washed with 10% sodium carbonate solution, dried first with sodium sulfate and then with potassium carbonate, was fractionated at 300 mm. to give an 84% yield of 2- and 3-chloropentanes, b. p. 69–69.3°, n^{20}D 1.4092–1.4096. The constancy of the boiling point assured the absence of any compounds other than 2- and 3-chloropentanes. Judging from the refractive indices, the proportions were about 75% of the 3-chloro and 25% of the 2-chloro compounds.

A mixture of about this composition was obtained also in runs in which 0.01 mole of aluminum chloride, zinc chloride, or ferric chloride was added to the solution. The effect of these salts in this amount on the rate of the reaction was negligible.

Attempted Purification of 3-Chloropentane by Fractionation.—The best fractions from six runs of synthetic 3-pentanol with hydrogen chloride in sealed bottles, n^{20}D above 1.4094, comprising 300 g., were combined and fractionated very carefully through column N[5] at atmospheric pressure. The time of the distillation was thirty-one and one-half hours. The refractive index of the product rose gradually as the fractionation proceeded but the highest value reached was 1.4100. This indicates that the isolation by distillation of *pure* 3-chloropentane from a mixture with 2-chloropentane is practically impossible.

Treatment of 3-Pentanol with $ZnCl_2$–HCl Solution.—An improved form[6] of the method of Lucas[7] was used. A solution of 2.2 moles, 300 g., of fused zinc chloride in 2.2 moles, 223 g., of concentrated hydrochloric acid was prepared in an ice-bath. This solution was put in a 500-cc. three-necked flask fitted with a stirrer, dropping funnel and thermometer dipping into the solution. The flask was cooled in an ice–salt bath. One mole, 88 g., of synthetic 3-pentanol, n^{20}D 1.4100, b. p. 114.3–114.7° (730 mm.), was added over a period of thirty minutes. After the mixture had been stirred for six hours, the dropping funnel was replaced with a gas inlet tube leading to the bottom of the flask, and a stream of hydrogen chloride was passed in with stirring for eight and one-half hours. The temperature of the mixture was kept below −1° throughout the reaction.

The halide layer was separated, washed with water and then with 10% sodium carbonate solution, and dried. Fractionation at 300 mm. gave an 81% yield of chloropentanes, b. p. 68.5–68.7° (300 mm.), n^{20}D 1.4086–1.4093.

Treatment of 2-Pentanol with Hydrogen Chloride.—A sample of synthetic 2-pentanol, b. p. 117.3–118.3° (739 mm.), n^{20}D 1.4056, was treated with hydrogen chloride at room temperature according to the procedure described for 3-pentanol. The product was fractionated at 738 mm. to give 8 fractions, b. p. 95–95.5°. n^{20}D 1.4068–1.4071, d^{20}_4 0.8696–0.8705. The yield of chloropentanes was 78.4%. The gradual changes in refractive index and density values show the presence of 3-chloropentane in 5–8% yield.

Identification of the Chlorides.—Samples of the chlorides were converted to the Grignard reagents and these

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[4] Wilson, Parker and Laughlin, THIS JOURNAL, **55**, 2795 (1933).

[5] Laughlin, Nash and Whitmore, *ibid.*, **56**, 1396 (1934).

[6] Developed by W. H. James of this Laboratory.

[7] Lucas, THIS JOURNAL, **51**, 248 (1929).

were treated with phenyl isocyanate. The derivative obtained from 3-chloropentane was identified as diethylacetanilide, m. p. and mixed m. p., 125–128°. The derivative obtained from 2-chloropentane was methyl-*n*-propylacetanilide, m. p. and mixed m. p. 94–96°.

Stability toward Heat.—Samples of the two chlorides were heated in sealed tubes at 100° for forty-eight hours. No change in refractive index was noted for either 2- or 3-chloropentane.

Isomerization of Chlorides with $ZnCl_2$–HCl Solution.—A sample of 0.2 mole, 21.3 g., of 2-chloropentane, n^{20}_{D} 1.4069, was shaken with a solution of 0.4 mole, 54.5 g., of fused zinc chloride in 0.4 mole, 40.5 g., of concentrated hydrochloric acid for twenty-four hours at room temperature (26–28°). The layers were separated, and the halide was washed with water, dried, and fractionated to give: nos. 1–3, 15.5 g., 95.5–96° (732 mm.), n^{20}_{D} 1.4076; no. 4, 1.5 g.; residue, 1.4089. Fractions 1–3 were combined and shaken with the same $ZnCl_2$–HCl solution for an additional forty-eight hours. The halide was separated, washed, dried, and distilled as before. The product had an index of 1.4076.

A sample of 0.2 mole, 21.3 g., of 3-chloropentane, n^{20}_{D} 1.40965, was treated according to the same procedure. At the end of the full seventy-two hours, the chlorides had an index of 1.4077.

Judging from the refractive index of the equilibrium mixture obtained from either isomer, its composition is roughly 80% 2-chloropentane.

Determination of Physical Constants.—Refractive indices were measured with a Valentine precision refractometer (Abbe type) calibrated by the Bureau of Standards. Densities were determined with a 4-cc. pycnometer, using a constant temperature bath held within ±0.03 of 20.00°.

The Cottrell boiling points were found using 20-cc. samples of the pure chlorides and a copper–copel thermocouple in the apparatus at the Petroleum Refining Laboratory of The Pennsylvania State College.[8] The 2-chloropentane, n^{20}_{D} 1.40690 and d^{20}_{4} 0.8695, gave the following boiling points at 760 mm.:

Initial—96.84° 20% off—96.88°
5% off—96.84° 40% off—96.88°

The 3-chloropentane, n^{20}_{D} 1.41035 and d^{20}_{4} 0.8795, gave these boiling points at 760 mm.:

Initial—97.76° 20% off—97.82°
5% off—97.76° 40% off—97.82°

The freezing points were determined by cooling samples of the pure chlorides with liquid air. Great difficulty was encountered due to persistent supercooling of the compounds. This trouble was about equally bad whether a simple outfit consisting of a jacketed test tube, wire loop stirrer, and chromel–copel thermocouple or a more refined apparatus[9] at the Petroleum Refining Laboratory was used. The best values are −105–106° for 3-chloropentane and −137–139° for 2-chloropentane.

The viscosities were measured at 20.00° in a microviscometer which used a 3-cc. sample and had a constant of 59040 sec./stoke.[10] Pure samples of the 2- and 3-chloropentanes were used having n^{20}_{D} 1.40690, d^{20}_{4} 0.8695, and n^{20}_{D} 1.41035, d^{20}_{4} 0.8795, respectively. The values obtained, 0.5672 and 0.5845 centistoke, respectively, were checked within 0.1%.

Summary

1. Pure samples of the 2- and 3-chloropentanes were made by the action of thionyl chloride and pyridine on the corresponding alcohols.

2. Various physical constants of these chlorides were determined.

3. The chlorides were found to be stable to heat, but were isomerized to an equilibrium mixture by long shaking with $ZnCl_2$–HCl solution at room temperature.

4. Mixtures of the chlorides were obtained in all cases of the treatment of the carbinols with hydrogen chloride.

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(8) Quiggle, Tongberg and Fenske, *Ind. Eng. Chem., Anal. Ed.*, **6**, 466 (1934).

(9) To be described elsewhere.

(10) Calibrated by R. Sobatzki of this Laboratory.