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

The Preparation of Chlorides from Certain Aliphatic Branched Chain Secondary Carbinols[1,2]

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It has long been known that carbinols containing a grouping R_3C–CHOH– fail to give the corresponding halide when the hydroxyl is replaced. Instead, a rearrangement occurs. Thus pinacolyl alcohol gives a tertiary chloride in at least 90% yield,[3] $Me_3CCHOHMe \longrightarrow Me_2CXCHMe_2$. In spite of nearly seventy years[2] (note 2) of study of the replacement of the hydroxyl in methylisopropylcarbinol, the course of the reaction and its products are still not clear. This condition induced the present study of two types of aliphatic secondary carbinols (1) with a fork next to the carbinol group and (2) with the fork farther removed. Even under the mildest conditions the first gave almost entirely the tertiary chloride formed by shift of the tertiary hydrogen atom adjacent to the carbinol group; thus $(CH_3)_2CHCHOHCH_3 \longrightarrow (CH_3)_2CXCH_2CH_3$. The stability recently proven for the secondary chloride[2] indicates that the tertiary chloride is formed during the replacement of hydroxyl and not through the secondary chloride as an intermediate either by direct shift of chlorine or by loss and addition of hydrogen chloride as have been suggested by the earlier workers.[2] At room temperature, without a catalyst, the second type of carbinol gave no detectable rearrangement with hydrogen chloride. Thus a secondary hydrogen does not shift appreciably under these mild conditions.

The chlorides were distilled under reduced pressure below 30° to avoid any thermal change in the products. *Thus any rearrangement which took place occurred during the replacement of hydroxyl and not by a shift of the chlorine after the replacement.* The rearrangements observed with the halides themselves take place at much higher temperatures (above 200°).[4]

In the present study, methylisopropylcarbinol has been treated with (1) zinc chloride and hydrochloric acid (Lucas) at 0°, (2) thionyl chloride and pyridine at 20°, (3) phosphorus pentachloride at 20°, (4) phosphorus trichloride at 0°, and (5) hydrogen chloride below 20° for ten weeks. The phosphorus trichloride gave only a phosphite. The other methods gave *t*-amyl chloride with only traces of material which might contain the secondary chloride. The low temperature treatment with hydrogen chloride repeatedly gave yields of over 90% of *t*-amyl chloride. This method was adopted as standard procedure with the other alcohols studied. In this way ethylisopropylcarbinol, *n*-propylisopropylcarbinol and diisopropylcarbinol gave the tertiary chlorides, dimethyl-*n*-propyl-, dimethyl-*n*-butyl- and dimethylisobutylcarbinyl chlorides, respectively. In each case the crude chloride was distilled below 30° to avoid the suspicion of temperature effects. Similarly methylisobutylcarbinol, methylisoamylcarbinol and methylneopentylcarbinol (2,2-dimethylpentanol-4) were converted to chlorides. In each case the product was the secondary chloride formed by simple replacement of hydroxyl by chlorine. No trace of tertiary chloride was detected in any of the compounds having the fork not adjacent to the carbinol group.

Experimental

Conversion of Methylisopropylcarbinol to *t*-Amyl Chloride.—Isopropyl alcohol (Petrohol supplied by Stanco, Inc.) was converted to the chloride by $ZnCl_2 \cdot HCl$ treatment in 75% yield; b. p. 33–36° (737 mm.), n^{20}_D 1.377. Nine moles of the chloride was converted to the Grignard reagent using 1.7 liters of ether; yield 90%. Treatment with acetaldehyde and fractionation of the product through a packed column, 2.2 × 85 cm.,[5] gave the desired carbinol; yield 56%, b. p. 110–111° (727 mm.), n^{20}_D 1.4090, d^{20}_4 0.818.

1. **By Zinc Chloride–Hydrochloric Acid Mixture.**—To a cooled solution of 546 g. of fused zinc chloride and 335 cc. of concd. hydrochloric acid, saturated with hydrogen chloride gas, and cooled to −10° by dry ice, was added 176 g. (2 moles) of methylisopropylcarbinol with mechanical stirring. After two hours, hydrogen chloride gas was introduced in a slow stream. Soon the mixture solidified. After standing overnight, the mixture was allowed to melt and was saturated with hydrogen chloride gas below 0°. After a total time of twenty-four hours, the chloride layer was separated and dried with 50 g. of anhydrous sodium sulfate and freed from excess hydrogen chloride by dry nitrogen; yield, 172 g. (80%).

The chloride was distilled under reduced pressure through a column with a partial condenser. Between

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[1] Original manuscript received April 3, 1934.

[2] *Cf.* Whitmore and Johnston, THIS JOURNAL, **55**, 5020 (1933).

[3] Whitmore and Rothrock, *ibid.*, **55**, 1106 (1933).

[4] Faworsky, *Ann.*, **354**, 325–89 (1907); Michael and Zeidler, *ibid.*, **385**, 227–92 (1911).

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

the column and pump were placed a manometer, a spiral trap cooled with dry ice, a 12-liter bottle to minimize changes in pressure and an adjustable leak for controlling the pressure. During a typical distillation the partial condenser was kept at about 3° with mechanically circulated ice water, the temperature in the flask was 25–26° and in the room 28–30°. Reflux from the partial condenser was kept at about 200 drops per minute. Fractions were taken every thirty minutes. The fractions, pressures (mm.), wts., g. and n^{20}_{D} were as follows: 1, (35), 3.5, 1.4049; 2, (32), 8.8, 1.4051; 3–10, (31), 127.0, 1.4052; 11, (29), 6.0, 1.4053; 12, (24), 13.4, 1.4060; residue, 2.0, 1.4340. The main fractions boiled at 84–84.5° (734 mm.). A sample hydrolyzed with distilled water[6] for thirty minutes, and titrated by the Volhard method showed 95% hydrolysis. A known sample of *t*-amyl chloride, b. p. 51° (238 mm.), n^{20}_{D} 1.4055 showed the following percentages of hydrolysis at fifteen, thirty and sixty minutes, 88.6, 94.9 and 95.4. Thus the product of the action of zinc chloride and hydrochloric acid with methylisopropylcarbinol was *t*-amyl chloride. No product having the properties of secondary isoamyl chloride, b. p. 91.9° (736 mm.), n^{20}_{D} 1.4095, was obtained.

2. **By Thionyl Chloride.**—A mixture of 103 g. of dry pyridine (b. p. 112–120°) and 88 g. (1 mole) of the carbinol cooled to 0° was treated during four hours with vigorous stirring with 143 g. (1.2 moles) of thionyl chloride. The mixture was stirred for three hours at room temperature. The top layer was decanted. The bottom layer consisted of a crystalline solid and a viscous oil. The top layer was diluted with low boiling hydrocarbon (b. p. 0–30°)[7] and washed with sodium bicarbonate solution and water until neutral. After drying over 10 g. of calcium chloride the solvent was removed at 300 mm. pressure and the residue was fractionated through a 1.4 × 50 cm. column of the type used in this Laboratory.[5] The temperature was 27–23° and the pressure 90–55 mm. Most of the fractions had n^{20}_{D} 1.4050–1.4060. The yield was 73%. A sample treated with water[6] showed 92% hydrolysis.

3. **With Phosphorus Pentachloride.**—To 214 g. (1.05 mole) of phosphorus pentachloride and 200 cc. of 0–30° hydrocarbon[7] cooled to 0° was added with stirring during two hours 88 g. (1 mole) of the carbinol. After stirring for three and one-half hours the evolution of hydrogen chloride had ceased. Two 50-g. portions of cracked ice were added. The chloride layer was washed and dried as usual and distilled to a 76% yield of crude chloride. This was distilled at 27–24° and 95–60 mm. to give mainly a product with n^{20}_{D} 1.4069 which was 83% hydrolyzed by cold water.[6] A Michael determination for secondary and tertiary halides gave 84%. Attempts to prove the presence of secondary isoamyl chloride failed.

5. **With Hydrogen Chloride.**—The pure carbinol was saturated with dry hydrogen chloride gas at 0° and sealed in pressure bottles. After four weeks at about 20° the bottles were opened and again saturated at 0°. After six weeks more, the chloride layer showed no further increase. It was separated, dried and distilled as usual at low pressure. Four runs with a total of 580 g. of carbinol absorbed 264 g. of hydrogen chloride and gave 676 g. of crude chloride, yield 97%. Distillation of 305 g. of the chloride at 25–26° and 33–28 mm. gave fractions with wts. (g.) and n^{20}_{D} as follows: 3–6, 83, 1.4051; 7–12, 111, 1.4053; 16–19, 42, 1.4058; 20, 14, 1.4069; residue, 13, 1.4410. Analyses for tertiary chloride and for tertiary and secondary chloride[6] on the fractions gave the values, 7, 95.6% tertiary; 18, 82% tertiary, 86.5% tertiary and secondary; 100.2% total amyl chloride (Carius); 20, 33.4% tertiary; 44.9% tertiary and secondary. The possible presence of traces of secondary and primary chlorides in the later fractions is being further investigated.

Conversion of Ethylisopropylcarbinol to Dimethyl-*n*-propylcarbinyl Chloride.[8]—The carbinol was prepared from isopropylmagnesium chloride and propionaldehyde in 52% yield, b. p. 125–126° (742 mm.), n^{20}_{D} 1.4170, d^{20}_{4} 0.824.[9] From 404 g. of the carbinol and hydrogen chloride was obtained 430 g. of crude chloride, 89% yield. This was distilled at reduced pressure with the water in the partial condenser at 12–13° and the heating bath at 39–42°. Fractionation of 410 g. of the chloride gave a 68% yield of material, b. p. (Cottrell) 110–111° dec. (734 mm.), n^{20}_{D} 1.4125–1.4130, d^{20}_{4} 0.863. These properties correspond to those of dimethyl-*n*-propylcarbinyl chloride.[10]

The structure of the chloride was proved further by conversion to the Grignard compound, treatment with oxygen[5] and conversion in 48% yield[11] to dimethyl-*n*-propylcarbinol, b. p. 93.5° (265 mm.); (Cottrell), 119.5–120.5° (738 mm.), n^{20}_{D} 1.4103, d^{20}_{4} 0.808. These properties correspond to the values in the literature.

When saturated with hydrogen chloride gas for fifteen minutes the carbinol was converted back to the chloride, thus confirming its tertiary nature.

Conversion of *n*-Propylisopropylcarbinol to Dimethyl-*n*-butylcarbinyl Chloride.—The carbinol was prepared from *n*-butyraldehyde, b. p. 72–74°, n^{20}_{D} 1.379 (from Butalyde supplied by Commercial Solvents Corp.), and isopropylmagnesium chloride in 62% yield, b. p. 144–145° (734 mm.), n^{20}_{D} 1.4213, d^{20}_{4} 0.822.[8] A total of 435 g. of the carbinol was saturated with dry hydrogen chloride at 0° as usual. The crude chloride was dried and distilled at 3 mm. pressure. Fractionation of 476 g. gave an 80% yield of chloride, b. p. (Cottrell) 133° dec. (734 mm.), n^{20}_{D} 1.4200–1.4210, d^{20}_{4} 0.863. These agree with the properties of dimethyl-*n*-butylcarbinyl chloride.[12]

The structure of the chloride was confirmed by conversion to dimethyl-*n*-butylcarbinol through the Grignard reagent.[5] A half-mole run gave a 42% yield of carbinol, b. p. 110° (250 mm.) 139.5–140.5° (741 mm.) (Cottrell), n^{20}_{D} 1.4173, d^{20}_{4} 0.813.[12] The residue of n^{20}_{D} 1.4400 amounted to only 3 g. The carbinol was changed to the chloride by hydrogen chloride gas at 0°.

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[6] Michael and Leupold, *Ann.*, **379**, 294 (1911).

[7] From the Viking Corporation, Charleston, W. Va.

[8] Grigorowitch and Pawlow, *J. Chem. Soc.*, **64**, I, 124 (1893), claim to have obtained the secondary chloride by means of phosphorus pentachloride. Van Risseghem, *Bull. soc. chim. Belg.*, **32**, 144–150 (1923), has reported the secondary chloride as a by-product of the action of chlorine with 2-methylpentene-2.

[9] *Cf.* Pickard and Kenyon, *J. Chem. Soc.*, **101**, 628 (1912).

[10] *Cf.* Schreiner, *J. prakt. Chem.*, [2], **82**, 294 (1910).

[11] The low yields of carbinols from the tertiary chlorides are due to olefin formation as indicated in the lower fractions. *Cf.* Whitmore and Badertscher, THIS JOURNAL, **55**, 1559 (1933).

[12] Whitmore and Woodburn, *ibid.*, **55**, 363 (1933).

Conversion of Diisopropylcarbinol to Dimethylisobutylcarbinyl Chloride.—The carbinol was kindly supplied by the du Pont Ammonia Department. It was fractionated through a 2.2 × 90 cm. column; b. p. 137–8° (738 mm.), n^{20}_D 1.4246, d^{20}_4 0.831.[12] The carbinol (464 g.) absorbed hydrogen chloride gas more slowly than the other carbinols studied. At first a pale purple color was formed. This gradually changed to brownish yellow. Reaction was complete in ten weeks at 20° and the yield of chloride was quantitative. It was distilled at 3 mm. to give 272 g. of chloride, b. p. (Cottrell) 127–128° dec. (733 mm.), n^{20}_D 1.4180, d^{20}_4 0.861. These properties correspond to dimethylisobutylcarbinyl chloride.[11] The identity was confirmed by conversion of the chloride, in 32% yield,[13] to dimethylisobutylcarbinol, b. p. (Cottrell) 130–131° (738 mm.), n^{20}_D 1.4166, d^{20}_4 0.811.[14] Treatment of fraction 7 with hydrogen chloride at 0° gave the tertiary chloride. No color appeared.

Conversion of Methylisobutylcarbinol to its Chloride.[15]—The carbinol was made in 42% yield from isobutylmagnesium bromide and acetaldehyde: b. p. 129.5° (734 mm.), n^{20}_D 1.4111, d^{20}_4 0.807.[16] Treatment of 408 g. of the carbinol with dry hydrogen chloride in the usual way for eighteen weeks gave 398 g. of crude chloride, 82% yield. Fractionation and refractionation gave methylisobutylcarbinyl chloride, b. p. (Cottrell) 111–112° (733 mm.) n^{20}_D 1.4113, d^{20}_4 0.861. The identity was substantiated further by conversion to the carbinol in 62% yield through the Grignard reagent.[5] The methylisobutylcarbinol was identified by b. p. 68° (64 mm.), n^{20}_D 1.4112 and conversion to the α-naphthylurethan, m. p. and mixed m. p. 96–97°.

Conversion of Methylisoamylcarbinol to its Chloride.—The carbinol was prepared in 65% yield from acetaldehyde and isoamylmagnesium chloride; b. p. 150.5–151° (742 mm.), n^{20}_D 1.4180, d^{20}_4 0.814. In the usual way hydrogen chloride gas was passed into 464 g. of the carbinol. After six weeks the chloride was separated and treated as usual. The partial condenser was kept at 14–15° and the heating bath at 50–52°. Fractionation gave a 90% yield of chloride, b. p. 138° dec. (735 mm.), d^{20}_4 0.863. Conversion of the chloride through the Grignard reagent and oxygen gave methylisoamylcarbinol in 60% yield, b. p. 151–152° (736 mm.), n^{20}_D 1.4180, α-naphthylurethan, m. p. and mixed m. p. 84–85°.

Conversion of Methylneopentylcarbinol to its Chloride.—The carbinol was prepared in 64% yield by reduction of methyl neopentyl ketone,[17] b. p. 136.5° (738 mm.), n^{20}_D 1.4180. The carbinol (36 g.) saturated with hydrogen chloride and allowed to stand for eight weeks gave a 90% yield of chloride which was distilled through a 1.1 × 70 cm. column[5] to give mainly methylneopentylcarbinyl chloride, b. p. 93° (250 mm.), n^{20}_D 1.4180; d^{20}_4 0.855. Only 2 g. of low boiling material was obtained. The chloride was converted to the carbinol in the usual way and the latter was converted to the α-naphthylurethan, m. p. 83°, mixed m. p. 84°.

Summary

1. It has not been possible to convert methylisopropylcarbinol to the corresponding secondary chloride.
2. Four secondary carbinols having tertiary hydrogen atoms alpha to the carbinol group gave tertiary chlorides on treatment with hydrogen chloride at room temperature.
3. Three secondary carbinols having no branch in the alpha position reacted normally without rearrangement to give the secondary chlorides.

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(13) The yield of olefins was 30%, the higher boiling material only 2.5 g.

(14) *Cf.* deGraef, *Bull. soc. chim. Belg.*, **40**, 315 (1931).

(15) This chloride has been obtained by Levene and Mikeska, *J. Biol. Chem.*, **65**, 509 (1925), and by Maass and Sivertz, THIS JOURNAL, **47**, 2883 (1925). The iodide has been made by Umnova, *J. Russ. Phys.-Chem. Soc.*, **42**, 1530–1543.

(16) Vavon, *Compt. rend.*, **155**, 287 (1912).

(17) Whitmore and Homeyer, THIS JOURNAL, **55**, 4194 (1933).

STATE COLLEGE, PENNA. RECEIVED JULY 9, 1938

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

Tertiary Butyl Chloride from Tertiary Amyl Chloride and Hydrogen Fluoride

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Bockemüller[1] states that alkyl chlorides, bromides and iodides are only slightly soluble in anhydrous hydrogen fluoride and that no reaction takes place when the alkyl halides are mixed with hydrogen fluoride. In the gaseous state at higher temperatures, and in the presence of a metallic fluoride catalyst, the alkyl halide will undergo double decomposition with hydrogen fluoride, yielding an alkyl fluoride. No investigations of the action of hydrogen fluoride on tertiary chlorides, bromides, or iodides, were found in the literature. The present study was started to fill this gap.

There have been obtained 10–17% yields of *t*-butyl chloride by treating *t*-amyl chloride with an equimolal quantity of anhydrous hydrogen fluoride at 0°. Besides the *t*-butyl chloride, there was also obtained a mixture probably containing hexyl, heptyl, decyl or undecyl (possibly both), and pentadecyl chlorides.

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(1) Bockemüller, Sammlung chemischer und chemisch-technischer Vortrage, 1936.