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

Secondary Isoamyl Chloride, 3-Chloro-2-methylbutane

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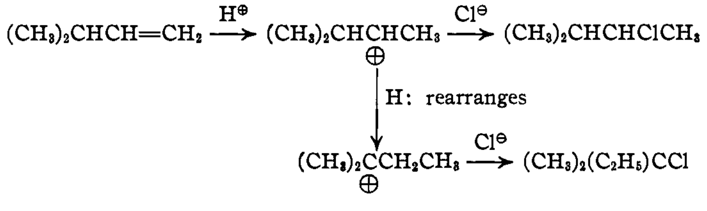
In the many preparations of this chloride,[2] it has invariably been accompanied by *tert*-amyl chloride. The implied or stated assumption has been that the secondary chloride was first formed and then rearranged to the tertiary chloride. Indeed, in the most recent work, Waterman states that the secondary chloride is unstable at its boiling point at atmospheric pressure. Other investigations in this Laboratory indicated that the secondary chloride should be stable and that the tertiary chloride was not formed by way of the secondary chloride.[3] The present study has confirmed these points. Hydrogen chloride was added to isopropylethylene at room temperature without any added catalyst according to the technique of Kharasch,[4] whereby peroxides and moisture are excluded. A 90% yield of an equimolecular mixture of secondary isoamyl chloride and tertiary amyl chloride resulted. The tertiary chloride was removed by hydrolysis with water at room temperature and the residual secondary chloride was dried and distilled at reduced pressure below 26°. The purified chloride was stable to long heating at 100°. Its structure was proved by conversion to methylisopropylcarbinol through the Grignard reaction.[5]

The course of the addition of hydrogen chloride to isopropylethylene, according to the working hypothesis used in this Laboratory,[3] would be as follows:



$$\begin{tikzcd}
\mathrm{(CH_3)_2CHCH{=}CH_2} \arrow[r, "\mathrm{H}^{\oplus}"] & \mathrm{(CH_3)_2CH\underset{\oplus}{C}HCH_3} \arrow[r, "\mathrm{Cl}^{\ominus}"] \arrow[d, "\mathrm{H}:\ \text{rearranges}"] & \mathrm{(CH_3)_2CHCHClCH_3} \\
& \mathrm{(CH_3)_2\underset{\oplus}{C}CH_2CH_3} \arrow[r, "\mathrm{Cl}^{\ominus}"] & \mathrm{(CH_3)_2(C_2H_5)CCl}
\end{tikzcd}$$

It is notable that the "positive fragment" which undergoes rearrangement is not formed by the removal of an atom or group with a complete octet of electrons,[3] but is *formed by the addition of a proton to one carbon of the*

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(2) Wurtz, *Ann.*, **129**, 368 (1864); Schorlemmer, *Ber.*, **7**, 1793 (1874); Wischnegradsky, *Ann.*, **190**, 328 (1878); Mayberry and Hudson, *Am. Chem. J.*, **19**, 243 (1897); Ipatiew and Dechanow, *Chem. Zentr.*, II, 691 (1904); Michael and Zeidler, *Ann.*, **385**, 227–292 (1911); Sabatier and Mailhe, *Compt. rend.*, **156**, 658 (1913); *ibid.*, **169**, 124 (1919); Aschan, *Chem. Abs.*, **14**, 3654 (1920); Ayres, *Ind. Eng. Chem.*, **21**, 899 (1929); Pratesi, *Atti. Accad. Lincei*, **13**, 779 (1931); Piotrowski and Winkler, *J. Inst. Pet. Techn.*, **17**, 225–240 (1931); Leenderste, Tulleners and Waterman, *Rec. trav. chim.*, **52**, 515 (1933).

(3) Whitmore, THIS JOURNAL, **54**, 3274–3283 (1932); Fleming and Whitmore, *ibid.*, **54**, 3460 (1932); **55**, 4161 (1933).

(4) Kharasch and Mayo, *ibid.*, **55**, 2493 (1933).

(5) Whitmore and Lux, *ibid.*, **54**, 3448 (1932).

ethylenic linkage leaving the other carbon with only six electrons.[6] Several other cases of this phenomenon are being studied in this Laboratory.

Experimental

The Addition of Hydrogen Chloride to Isopropyl Ethylene.—The technique of Kharasch[4] was used. A typical run follows: isopropylethylene, b. p. 20–21° (745 mm.), from the dehydration of isoamyl alcohol over alumina, purified by treatment with sulfuric acid according to Wischnegradsky,[2] and dry hydrogen chloride were sealed in a Pyrex tube 60 × 3.1 cm. with 3-mm. wall. After seven weeks (optimum time not determined) in the dark at room temperature, the tube was opened with the proper precautions and the excess hydrogen chloride determined by allowing it to escape into scrubbing towers. Dissolved hydrogen chloride was removed by passing a stream of dry nitrogen through the chloride mixture cooled in an ice–salt bath. From 33 g. (0.47 mole) of isopropylethylene 44 g. (0.41 mole) of amyl chlorides was obtained; yield, 88%. There was an excess of 16 g. (0.44 mole) of hydrogen chloride.

Analysis of the Reaction Mixture.—The crude chloride mixture had n^{20}_D 1.4060 and d^{20}_4 0.866. Carius determinations showed 98.0–98.6% amyl chlorides.

A determination for tertiary chloride according to the method of Michael and Zeidler[2] was made by hydrolyzing a sample with a known quantity of water at room temperature. It was 48–48.5% hydrolyzed in one-half hour. Pure tertiary amyl chloride under the same conditions was 95% hydrolyzed.

Hydrolysis of the crude chloride with an excess of 0.1*N* silver nitrate for three hours at room temperature indicated only 56–57% tertiary and secondary chlorides. Hydrolysis during sixteen hours with silver nitrate gave 68–69%, and during sixty hours 95% secondary and tertiary. Primary isoamyl chloride under the latter conditions reacted only 3–4%. Therefore, the reaction mixture contained approximately equal amounts of the tertiary and secondary amyl chlorides.

Isolation of the Pure Secondary Isoamyl Chloride.—The reaction mixture was freed from tertiary amyl chloride by repeated hydrolyses with water until the wash water no longer gave a test for the chloride ion. The chloride was then dried over anhydrous sodium sulfate in the refrigerator.

Distillation was carried out at reduced pressure in a total condensing, indented, Pyrex Vigreux column 68 × 1.1 cm. the condenser and fraction cutter of which were cooled by circulating ice water. A spiral glass trap in a freezing mixture, an automatic pressure regulator, and a water pump completed the set up.

Fraction	Temp., °C.	n^{20}_D	Wt., g.	Press., mm.	Reflux ratio
Initial	23.4			60	
1	25.0	1.4080	3.5	60	15:1
2	25.4	1.4095	6.5	60	15:1
3	25.7	1.4095	13.5	60	20:1
4	25.8	1.4092	4.5	60	10:1
5	In trap	1.4075	5		
6	Residue		0.5		

In spite of the precautions for cooling the distillate about 20% of the original charge was lost during the fractionation.

Fraction 3 had d^{20}_4 0.878, MR_D 30.03, calcd. 30.16.

Fractions 2–4 were combined and distilled from a modified Cottrell b. p. apparatus. The initial b. p. was 91.8° and after 80% had been distilled off the b. p. was 91.9° (736

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(6) *Cf.* Lowry, *J. Chem. Soc.*, **123**, 3006 (1923).

mm.). No hydrogen chloride could be detected either by wet litmus paper or by odor. The pure chloride had a sweet odor similar to that of the other amyl chlorides.

Proof of the Structure of the Secondary Chloride.—Since Whitmore and Lux[5] have shown that there is no rearrangement during the conversion of an aliphatic halide to the corresponding alcohol by the Grignard reaction, this method was used to determine the structure of the secondary chloride.

To 1.2 g. (0.05 mole) of fine magnesium turnings with a crystal of iodine in a 200-cc. round-bottomed three-necked flask fitted with a stirrer, dropping funnel, and reflux condenser was added 5 g. (0.05 mole) of the dried secondary chloride (after removal of the tertiary chloride but without distillation) diluted with 10 cc. of dry ether after starting the reaction with 2–3 cc. of this mixture. No difficulty was encountered. The reaction mixture was allowed to stand overnight and treated with dry oxygen in the cold. The addition product was decomposed with ice and ammonium chloride in the usual manner, the aqueous layer extracted with 25 cc. of ether, the ether extracts dried with 1 g. of potassium carbonate, and the ether removed through the Vigreux column described above. Without further purification this carbinol gave an α-naphthyl urethan, m. p. 108–110° after three crystallizations from petroleum ether. The α-naphthyl urethan of a known sample of methylisopropylcarbinol had m. p. 111–112°, mixed m. p. 110–111°.

The 3,5-dinitrobenzoate was also prepared. It melted at 74–75° after three crystallizations from dilute ethyl alcohol. The 3,5-dinitrobenzoate of methylisopropylcarbinol had a m. p. 76°; mixed m. p. 74–75°.

Stability of the Secondary Chloride.—Four grams of the crude secondary chloride was heated in a sealed tube in live steam at atmospheric pressure for twenty-four hours. At the end of that time the chloride had become slightly yellow, but there was no odor of hydrogen chloride. A Grignard reaction was run as before, but considerable difficulty was experienced in starting the reaction. After treatment with oxygen and isolation of the carbinol as above, the 3,5-dinitrobenzoate of methylisopropylcarbinol was obtained, m. p. and mixed m. p. 74–75°.

Summary

1. Secondary isoamyl chloride, 3-chloro-2-methylbutane, has been prepared in pure form.

2. This chloride is stable at its boiling point at atmospheric pressure, stable at 100° for twenty-four hours, and stable to water at room temperature.

3. A new type of rearrangement resulting from addition to an olefinic linkage is indicated.

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