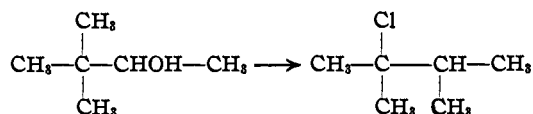


[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Pinacolyl Chloride from the Chlorination of Neohexane

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Compounds of the type R_3CCHXR' were unknown prior to the present work. Several attempts have been made to prepare the simplest member of the series, pinacolyl chloride, from pinacolyl alcohol.¹ In each case, the product obtained was dimethylisopropylcarbinyl chloride.²



Earlier workers therefore assumed pinacolyl chloride to be unstable, rearranging to give the tertiary chloride. In the present study, chlorination of neohexane, 2,2-dimethylbutane, gave 11% of the desired chloride, $(\text{CH}_3)_3\text{CCHClCH}_3$, which proved to be a stable secondary chloride. Refluxing and distillation at atmospheric pressure gave no change. With silver nitrate it behaved as a typical secondary alkyl chloride. It reacted with magnesium to give a Grignard reagent which was converted to a stable chloromercuri derivative. The relation of the preparation and properties of pinacolyl chloride to the rearrangement studies of this Laboratory is similar to that of neopentyl chloride.³

Neohexane was prepared from *t*-amyl chloride and methylmagnesium chloride. Chlorination gave, together with pinacolyl chloride, a good yield of *t*-amylcarbinyl chloride and some neopentylcarbinyl chloride.

Experimental

Preparation of Neohexane.—Methylmagnesium chloride was prepared from gaseous methyl chloride, 122 g. (5 moles) of magnesium and 1600 cc. of dry di-*n*-butyl ether.

(1) Friedel and Silva, *Jahresber.*, 340 (1873); Couturier, *Ann. chim.*, [6] 26, 433-501 (1892); Delacré, *Chem. Zentr.*, 77, II, 498 (1906).

(2) Whitmore and Rothrock, *THIS JOURNAL*, 55, 1106 (1933).

(3) *Ibid.*, 54, 3460 (1932); 55, 3403, 4161 (1933).

Addition of 610 cc. (5 moles) of *t*-amyl chloride in 1 liter of di-*n*-butyl ether was conducted at 50° for eight hours. Decomposition with ice and distillation of the ether layer gave impure hydrocarbon, b. p. 37-50°. Treatment with concd. sulfuric acid and refractionation produced pure neohexane in 36-39% yield, b. p. 49.5° (740 mm.), n_D^{20} 1.3688.

Chlorination of Neohexane.—Chlorine was added to neohexane at salt-ice temperature until approximately half of the hydrocarbon had reacted. The excess hydrocarbon was removed by distillation. The yield of neohexyl chlorides was 67%. Higher chlorides appeared in only small amount.

Fractionation of Neohexyl Chlorides.—A 28-plate total condensation variable take-off column having a section of 262 × 1.2 cm. packed with glass helices was used. Fraction 1, 66.5 g., b. p. 109-110° (734 mm.), n_D^{20} 1.4180, was pinacolyl chloride, identified by addition of oxygen to the Grignard compound⁴ to give pinacolyl alcohol; phenylurethan, m. p. and mixed m. p. 78.5-79.5°. The constants for refractionated pinacolyl chloride are: b. p. (Cottrell) 109.9° (734 mm.), f. p. -0.9°, n_D^{20} 1.4181, d_4^{20} 0.8767. Fraction 2, 130.2 g., b. p. 113.5-115°, n_D^{20} 1.4190, was largely *t*-amylcarbinyl chloride with a little neopentylcarbinyl chloride.

Preparation of Pinacolylmercuric Chloride.—The method of Marvel was used.⁵ Recrystallization from dilute ethyl alcohol gave m. p. 88.5-90°. *Anal.*⁶ Calcd. for $\text{C}_6\text{H}_{13}\text{HgCl}$: Hg, 62.5. Found: Hg, 63.3.

Summary

1. Neohexane was prepared in 36-39% yield from *t*-amyl chloride and methylmagnesium chloride.

2. Chlorination of neohexane gave 11% of pinacolyl chloride. *t*-Amylcarbinyl chloride and neopentylcarbinyl chloride were the chief products.

3. The preparation and stability of pinacolyl chloride accord with other work on molecular rearrangements.

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

(5) Marvel, Gauerke and Hill, *ibid.*, 47, 3009 (1925).

(6) Whitmore and Sobatzki, *ibid.*, 55, 1131 (1933).