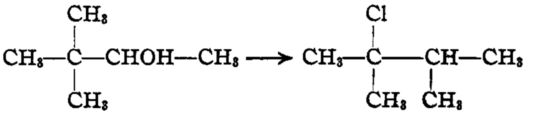
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Pinacolyl Chloride from the Chlorination of Neohexane

BY FRANK C. WHITMORE, H. I. BERNSTEIN AND L. W. MIXON

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]



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CHOH-CH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{Cl}{C}}-\underset{CH_3}{CH}-CH_3$$

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, $(CH_3)_3CCHClCH_3$, 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. 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.), $n^{20}{}_D$ 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.), $n^{20}{}_D$ 1.4180, was pinacolyl chloride, identified by addition of oxygen to the Grignard compound[4] 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°, $n^{20}{}_D$ 1.4181, $d^{20}{}_4$ 0.8767. Fraction 2, 130.2 g., b. p. 113.5–115°, $n^{20}{}_D$ 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 $C_6H_{13}HgCl$: 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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(1) Friedel and Silva, *Jahresber.*, 340 (1873); Couturier, *Ann. chim.*, [6] **26**, 433–501 (1892); Delacre, *Chem. Zentr.*, **77**, **II**, 498 (1906).

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

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

(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).