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

Preparation and Properties of Neopentyl Chloride in Relation to Molecular Rearrangements[1]

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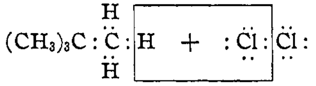
Tissier[3] and Richard[4] prepared what appeared to be neopentyl chloride. The former stated that the monochloride obtained by the chlorination of neopentane was identical with that obtained from neopentyl alcohol and dry hydrogen chloride and that it decomposed on distillation. It has recently been found in this Laboratory that neopentyl chloride cannot be prepared from the alcohol.[5] In the present study it has been found that neopentyl chloride, formed by the chlorination of neopentane, is stable at 200° for long periods of time and is extraordinarily inactive, giving none of the ordinary reactions of alkyl halides except the formation of a Grignard reagent. Through that reaction and the action of phenyl isocyanate, it has been converted to *tert*-butylacetanilide, thus showing that it forms a Grignard reagent without rearrangement.[6]

The failure to obtain neopentyl chloride from neopentyl alcohol and its successful preparation from neopentane by chlorination illustrate again the instability of the "positive" neopentyl group and the stability of the same group when "negative."[7] The latter also confirms the common conception that chlorination involves the entrance of "positive" chlorine into the molecule. Thus the formation of neopentyl chloride may be represented electronically as involving the change:



$$(CH_3)_3C:\overset{H}{\underset{H}{\ddot{\underset{\cdot\cdot}{C}}}}:\boxed{H \;+\; :\ddot{\underset{\cdot\cdot}{Cl}}:}\ddot{\underset{\cdot\cdot}{Cl}}:$$

in which the neopentyl group is not deprived of any of its electrons. The stability and inactivity of neopentyl chloride are strong indications of the tenacity with which the neopentyl group holds its electrons. The "electronegativity" of this group is being studied in a variety of ways in this Laboratory.

Experimental

Chlorination of Neopentane.—The reaction of neopentane and chlorine in direct sunlight at room temperature is extremely vigorous, much heat is evolved and there is some charring. With the light of a 1000-watt tungsten lamp, the chlorination takes place more slowly.

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(1) *Cf.* THIS JOURNAL, **54**, 3460 (1932); **55**, 3403 (1933).

(2) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(3) Tissier, *Ann. chim. phys.*, [6] **29**, 344 (1893).

(4) Richard, *ibid.*, [8] **21**, 323 (1910).

(5) Whitmore and Rothrock, THIS JOURNAL, **54**, 3431 (1932).

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

(7) *Cf.* Whitmore and Homeyer, *ibid.*, **54**, 3436 (1932).

Neopentane was chlorinated by passing chlorine over the surface of the hydrocarbon at 0° in diffused daylight. After distillation of a small sample of the crude chloride had shown it to be stable, the main fraction was distilled at atmospheric pressure through a precision column.[6] *No tertiary amyl chloride was formed during the chlorination or the distillation.*

Pure neopentyl chloride has the following physical constants: d_4^{20} 0.866; n_D^{20} 1.4042; f. p. −20 ± 1°; mol. ref. 30.01, calcd. 30.06; b. p. (Cottrell) 84.4° (760 mm.), 83.9° (750 mm.), 83.5° (740 mm.).

Reactivity of Neopentyl Chloride

Formation of Grignard Reagent.—Neopentyl chloride in dilute ether solution reacts slowly with magnesium. The product with phenyl isocyanate gives an anilide, m. p. 125–126°. A known sample of *tert*-butylacetanilide had m. p. 131° and mixed m. p. 126–128°, showing that the conversion of the chloride to the Grignard reagent involved no rearrangement. The Grignard solution with mercuric chloride gives neopentylmercuric chloride, m. p. 116.5–117°.[8]

Magnesium without Solvent.—*n*-Amyl chloride reacts completely with magnesium in eighteen hours at 200°, whereas neopentyl chloride was recovered unchanged after seventy hours under the same conditions.

Silver Acetate in Ether.—Contrary to the results of Tissier,[3] neopentyl chloride failed to react when heated for six hours at 40° and twelve hours at 60°.

Other Reagents.—While *n*-amyl chloride reacts completely with alcoholic potash in one hour at 100°, neopentyl chloride remained unchanged at the end of twenty hours under the same conditions. The chloride failed to react with cuprous cyanide in a sealed tube at 90° during two hundred hours. While *n*-amyl chloride reacts with potassium iodide in acetone to the extent of about 33%, neopentyl chloride gives no reaction under the same conditions.[9] The chloride failed to react with potassium acetate in absolute ethyl alcohol at 125° during thirty hours. Neither *n*-amyl nor neopentyl chloride reacted appreciably with diphenylmercury at 125° during seventeen hours. The former reacted slightly more than the latter when heated at 200°.

The other neopentyl halides are being prepared and studied in this Laboratory.

Summary

1. Neopentyl chloride has been obtained by direct chlorination of the corresponding hydrocarbon.

2. The physical constants of this chloride have been determined.

3. Neopentyl chloride has been found to be very stable and inactive chemically. The Grignard reagent has been formed.

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(8) This substance was prepared by E. L. Wittle of this Laboratory.

(9) This reaction is being studied by F. W. Herman.