

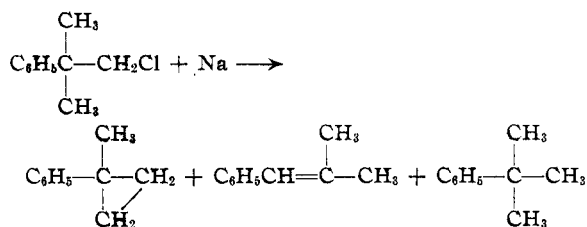
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Formation of Cyclopropanes from Monohalides. IV.¹ Some Reactions of 1-Chloro-2-methyl-2-phenylpropane (Neophyl Chloride)BY FRANK C. WHITMORE, CYRUS A. WEISGERBER² AND A. C. SHABICA, JR.³

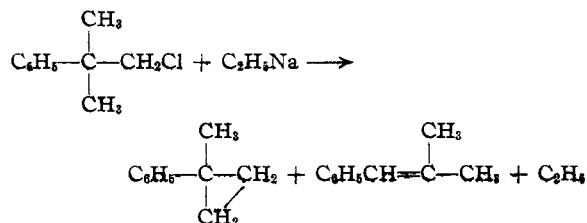
The easy availability of neophyl chloride $\text{C}_6\text{H}_5\text{-}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{-CH}_2\text{Cl}$ in contrast to that of neopentyl chloride $\text{CH}_3\text{-}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{-CH}_2\text{Cl}$ makes this compound a natural choice for further study of the neopentyl system.

Neophyl chloride was prepared in 68% yield from benzene and methallyl chloride in the presence of concentrated sulfuric acid.

Neophyl chloride does not react rapidly with sodium below 90°. It is thus considerably *less reactive with sodium* than is neopentyl chloride.⁴ At this temperature and with a molar ratio of chloride to sodium of five to one the following reaction occurred

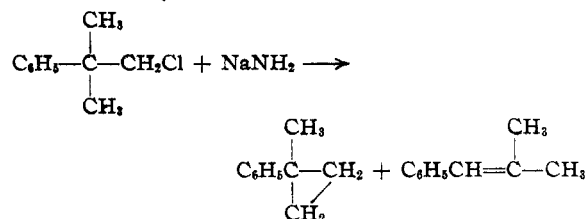


The reaction of neophyl chloride with ethylsodium in pentane at -10 to 20° gave products similar to those obtained in the above Wurtz reaction. With ethylsodium and neopentyl chloride under these conditions there was essentially no reaction.¹ Thus neophyl chloride is *more reactive with ethylsodium* than is neopentyl chloride.



The relation between the Wurtz reaction and the

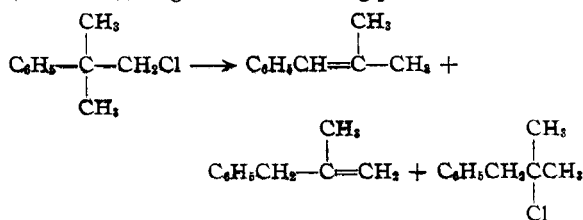
reaction of neophyl chloride with ethylsodium is apparent. In the Wurtz reaction the amount of olefin plus the amount of cyclopropane derivative was about equal to the amount of *t*-butylbenzene obtained. These results add further confirmation to the theory proposed by Morton and co-workers to explain condensations by sodium.⁵ With excess sodamide at 105–115° the chloride reacted slowly



No amine was obtained.

In liquid ammonia one mole of neophyl chloride required two gram atoms of sodium for complete reaction. The main reaction was that of reduction of the chloride to *t*-butylbenzene.

Neophyl chloride is reasonably stable to heat. When heated at 135° for forty-four hours only slight decomposition occurred. Decomposition occurred more rapidly at the boiling point, 222° (741 mm.), to give the following products



The stability of neophyl chloride to ordinary basic reagents is shown by the fact that it did not react to any appreciable extent with sodium ethylate, pyridine or fluorenylsodium. This corresponds to the inactivity of neopentyl chloride.

Neophyl chloride forms a Grignard reagent readily and in good yields. The corresponding alcohol and acid are obtained easily by oxidation or carbonation of the Grignard reagent.

Experimental

Preparation of Neophyl Chloride.—The benzene used in this preparation was washed twice with concentrated sul-

(1) For Paper III of this series see Whitmore and Zook, *THIS JOURNAL*, **64**, 1788–1785 (1942).

(2) Abbot Laboratories Fellow.

(3) Present address: Merck and Co., Rahway, New Jersey.

(4) Whitmore, Popkin, Bernstein and Wilkins, *THIS JOURNAL*, **63**, 124–127 (1941).

(5) Morton, *et al.*, *THIS JOURNAL*, **64**, 2239–2253 (1942).

furic acid and used without further treatment. The reaction was effected by dropping 603 g. (6.66 moles) of methallyl chloride (Shell Development Company), b. p. 71.5–72.5° (736 mm.), n_D^{20} 1.4274, into a vigorously stirred mixture of 1404 g. (18.5 moles) of benzene and 104 g. (1 mole) of concentrated sulfuric acid at 20°. The addition of the chloride required twelve hours. The mixture was allowed to stir an additional eleven hours at room temperature. The benzene solution was separated from the sulfuric acid and washed. The excess benzene was distilled without drying. Fractionation of the residue through an 8-plate column gave 765.5 g., 68% yield of neophyl chloride, b. p. 97° at 13 mm., 222° at 741 mm. (dec.), n_D^{20} 1.5250.

Reaction of Neophyl Chloride with Sodium.—The reaction was conducted under an atmosphere of nitrogen using 842.5 g. (5 moles) of neophyl chloride, n_D^{20} 1.5249–1.5250, and 24 g. (1 gram atom) of sodium. The sodium was added over a period of three hours and stirring and heating were continued for an additional nineteen hours. The liquid was separated from the residue and the residue dissolved in water. The aqueous solution was extracted with pentane and the extracts added to the original liquids. The pentane and the reaction products were fractionated from the excess chloride in an 8-plate column. At 13.5 to 9.5 mm. 92.4 g. of material, b. p. 42–91°, was obtained. This distillate was fractionated in a 65-plate column and the excess chloride was fractionated in the 8-plate column. The results taken from the fractionation curve⁶ obtained by plotting refractive index against weight of distillate in grams were as follows: *t*-butylbenzene, 46.4 g., 34.6% yield, b. p. 84.2° at 50 mm., $n_D^{20.4}$ 1.4924; 1-methyl-1-phenylcyclopropane, 15.7 g., 11.9% yield, b. p. 91° at 50 mm., $n_D^{20.4}$ 1.5150; β,β -dimethylstyrene, 18.1 g., 13.7% yield, b. p. 90° at 31 mm., $n_D^{20.4}$ 1.5400; neophyl chloride, 650.1 g., b. p. 93–95° at 10 mm., $n_D^{20.4}$ 1.5244–1.5248.

Reaction of Neophyl Chloride with Ethylsodium.—The procedure and apparatus used was essentially the same as that described by Whitmore and Zook.¹ The ethylsodium was prepared in 75% yield by the reaction of 148.3 g. (0.58 mole) of diethylmercury, b. p. 72° at 36 mm., with 23.5 g. (1.02 gram atoms) of sodium at 20–25° in 124.4 g. of olefin-free pentane. To the suspension of ethylsodium 168.5 g. (1 mole) of neophyl chloride, b. p. 97° at 13 mm., n_D^{20} 1.5250, was added over a period of two hours. The temperature of the reaction mixture was initially held at –10° but was allowed to rise slowly to 20° as the reaction proceeded. Gas was evolved at a rate of 2.38 liters per hour for five hours. The gas was collected over saturated sodium chloride solution and analysis in a modified Orsat apparatus showed it to be a mixture of ethane and ethylene in a ratio of 34 to 1. The pentane solution was separated from the residue and the residue was washed with pentane. The washings were combined with the original solution and charged to a 40-plate column. After the pentane was stripped off, fractionation of the residue gave: 1-methyl-1-phenylcyclopropane, 61.0 g., 61.6% yield (based on ethylsodium), b. p. 91° at 50 mm., n_D^{20} 1.5160; β,β -dimethylstyrene, 19.9 g., 19.2% yield, b. p. 100° at 50 mm.,

n_D^{20} 1.5380; neophyl chloride, 40.9 g., 24.2% recovery, b. p. 92–94° at 10 mm., n_D^{20} 1.5242–1.5248.

Reaction of Neophyl Chloride with Sodium in Liquid Ammonia.—The reaction was conducted in a 1-liter three-neck flask fitted with a mercury seal stirrer and a dry ice-acetone trap. The other neck of the flask was connected directly to an ammonia tank. To 169.3 g. (1.05 moles) of neophyl chloride, b. p. 97° at 13 mm., n_D^{20} 1.5250, was added about 500 ml. of liquid ammonia. The chloride did not dissolve completely in the ammonia. To the vigorously stirred suspension of chloride and liquid ammonia, sodium was added in small pieces over a period of two and a half hours after which time 52.6 g. (2.29 gram atoms) of sodium had been added and the blue color of excess sodium was apparent. From time to time more liquid ammonia was added to keep the liquid at its initial level. The reaction mixture was stirred forty-five minutes after the appearance of the blue color and a small amount of solid ammonium nitrate was added to destroy the excess sodium. The liquid ammonia was evaporated from the reaction flask into the trap and from the trap through a Gilman trap filled with water. The small amount of oil obtained was returned to the reaction flask. Addition of water to the flask caused the vigorous evolution of ammonia. The organic layer obtained by separation from and extraction of the aqueous layer with pentane was charged to a 65-plate column and the pentane stripped off. Fractionation of the residue through the same column gave the following results: *t*-butylbenzene, 100.0 g., 74.7% yield, b. p. 103° at 108 mm., n_D^{20} 1.4927–1.4920; 12.1 g., 9.05%, of impure material, n_D^{20} 1.4909–1.4890.

Reaction of Neophyl Chloride with Sodamide.—Neophyl chloride, 252.7 g. (1.5 moles), b. p. 97° at 13 mm., n_D^{20} 1.5250, was heated with stirring at 105–115° for sixty-four and a half hours with 86.3 g. (2.16 moles) of sodamide. The sodamide was prepared by the reaction of ammonia and sodium at 350°. The reaction product was decanted from the solid and the solid was washed with ether. The combined ether washings and the product were charged to a 65-plate column and the ether stripped off. The products were fractionated from the excess chloride and the chloride was then fractionated through an 8-plate column to give: 1-methyl-1-phenylcyclopropane, 21.3 g., 10.7% yield, b. p. 91° at 50 mm., n_D^{20} 1.5160; β,β -dimethylstyrene, 35.7 g., 18.0% yield, b. p. 101° at 50 mm., n_D^{20} 1.5400; neophyl chloride, 169.8 g., 70.7% recovery, b. p. 94° at 10 mm., n_D^{20} 1.5248–1.5249.

Pyrolysis of Neophyl Chloride.—Neophyl chloride, 168.5 g. (1 mole), b. p. 97° at 13 mm., n_D^{20} 1.5250, was charged to an 8-plate column and refluxed for seventeen hours during which time the lower boiling products were taken off. The temperature of the bath ranged from 235 to 255° and the distillation temperature ranged from 173° at 727.8 mm. to 222.5° at 741.3 mm. The product was washed and dried and fractionated in a 13-plate column. The results are as follows: 2-methyl-3-phenyl-1-propene, 31.0 g., 23.5% yield, b. p. 69–70° at 20 mm., n_D^{20} 1.5080; β,β -dimethylstyrene, 48.2 g., 36.5% yield, b. p. 79–80° at 20 mm., n_D^{20} 1.5400; benzylidimethylcarbinyl chloride, 15.1 g., 8.9% yield, b. p. 88° at 10 mm., n_D^{20} 1.5160; neophyl chloride, 43.8 g., 26% recovery, b. p. 94–95° at 10 mm., n_D^{20} 1.5250.

(6) All results of fractionations were taken from curves of this type.

Attempted Reaction of Neophyl Chloride with Fluorenylsodium.—This compound was prepared from 51.5 g. (0.25 mole) of fluorene, m. p. 113–114°, and 5.7 g. (0.25 gram atom) of sodium in 250 ml. of liquid ammonia. The liquid ammonia was added to 41.5 g. of the fluorene and the sodium was added in small pieces until 5.7 g. had been added. The blue color of excess sodium was discharged by the addition of 10 g. of fluorene. The ammonia was allowed to evaporate and 48.6 g. (0.29 mole) of neophyl chloride, b. p. 97° at 13 mm., n_D^{20} 1.5250, was added to the residue. The mixture was heated with stirring for fifteen hours. Fractionation of the reaction mixture gave 34.2 g., 70.4% recovery, of neophyl chloride, b. p. 94° at 10 mm., n_D^{20} 1.5245–1.5250.

Attempted Reactions of Neophyl Chloride with Sodium Ethylate and with Pyridine.—The chloride was recovered to the extent of 87.7 and 87.2%, respectively, after refluxing nine and one-half hours with pyridine and eleven and one-half hours with sodium ethylate in absolute alcohol. The constants of the recovered chloride were, respectively, as follows: b. p. 94° at 10 mm., n_D^{20} 1.5255; b. p. 95° at 10 mm., n_D^{20} 1.5245–1.5250.

Identification of Olefins Obtained in Reactions.—The olefins, β,β -dimethylstyrene and 2-methyl-3-phenyl-1-propene, were identified by ozonolysis. The following general procedure was used: 4.6 g. (0.0326 mole) of the olefin was ozonized in 100 ml. of olefin-free pentane. The ozonide was decomposed by stirring with 15 ml. of water. The pentane was distilled and the residue was steam distilled. The carbonyl compounds were identified by the melting points and mixed melting points of their 2,4-dinitrophenylhydrazones and semicarbazones. β,β -Dimethylstyrene gave benzaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 238–239°, acetone 2,4-dinitrophenylhydrazone, m. p. 123–124°, mixed m. p. 124–125°. 2-Methyl-3-phenyl-1-propene gave phenylacetone 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 153–154°; phenylacetone semicarbazone, m. p. 186–187°, mixed m. p. 184–186°. Formaldehyde was identified by color tests with Schiff reagent and with resorcinol.

Identification of *t*-Butylbenzene and 1-Methyl-1-phenylcyclopropane.—1-Methyl-1-phenylcyclopropane was hydrogenated in ether at 80–89° over Raney nickel at a pressure of 2000 lb./sq. in. to *s*-butylbenzene. Acetamino derivatives were prepared according to the method of Ipatieff and Schmerling.⁷ The *s*-butylbenzene yielded 4-acetamino-*s*-butylbenzene, m. p. 123–123.5°. Mixed

(7) Ipatieff and Schmerling, *THIS JOURNAL*, **59**, 1059 (1937).

m. p. with an authentic sample 123–124°. *t*-Butylbenzene yielded 4-acetamino-*t*-butylbenzene, m. p. 170–171° and 2,4-diacetamino-*t*-butylbenzene, m. p. 210–211°.

Identification of Benzyldimethylcarbinyl Chloride.⁸—The procedure used was that described by Underwood and Gale.⁹ The following amounts of reactants were used: 1.05 g. (0.006 mole) of the unknown chloride was dissolved in 50 ml. of anhydrous ether and 0.8 g. of activated magnesium turnings was added and the mixture was allowed to stand overnight. The addition of 1 ml. of phenyl isocyanate and treatment in the usual manner gave 0.434 g., 30.7% yield, of crude anilide. Two recrystallizations from petroleum ether, b. p. 60–90°, gave a white crystalline product, m. p. 107–108°; mixed m. p. with an authentic sample of benzyldimethylacetanilide (m. p. 107–108°) 107–108°.

Preparation of β -Phenylisovaleric Acid and 2-Methyl-2-phenyl-1-propanol.—Carbonation with solid carbon dioxide of the Grignard reagent prepared from 168.5 g. (1 mole) of neophyl chloride, n_D^{20} 1.5246, gave 145.2 g., 81.6% yield of crude β -phenylisovaleric acid, m. p. 56.5–58.5°. Two recrystallizations from petroleum ether, b. p. 60–90°, gave large white crystals, m. p. 58–59.5°.¹⁰

Oxidation of the Grignard reagent prepared from 337.0 g. (2 moles) of neophyl chloride, n_D^{20} 1.5250, gave 214.6 g., 71.6% yield, of 2-methyl-2-phenyl-1-propanol, b. p. 131° (30 mm.), n_D^{20} 1.5261; phenylurethan, m. p. 59.5–60.5°,¹¹ α -naphthylurethan, m. p. 91.5–92.5°.

Summary

1. Some reactions of neophyl chloride have been studied. These resemble the corresponding reactions of neopentyl chloride but the latter is more reactive with sodium and less reactive with ethylsodium. Both chlorides are inert to most basic reagents, with neophyl chloride showing slightly greater activity.

2. The relation of the Wurtz reaction to the action of a halide with an alkylsodium is further demonstrated.

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(8) Correction: This chloride appears as ethylmethylphenylcarbinyl chloride in the Abstract of papers given at the Detroit A. C. S. meeting, 1943.

(9) Underwood and Gale, *THIS JOURNAL*, **56**, 2117 (1934).

(10) Hoffman, *ibid.*, **51**, 2542–2547 (1929).

(11) Haller and Bauer, *Ann. chim.*, [9] **9**, 5–24 (1918).