

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

## The Preparation of Neopentyl Iodide and Neopentyl Bromide

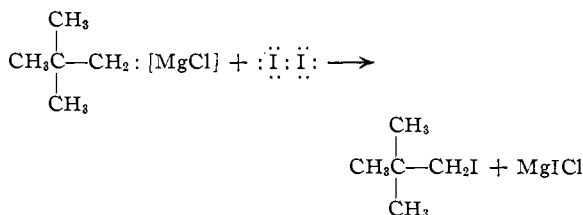
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Since neopentyl chloride is extremely inert<sup>1</sup> in practically all reactions of alkyl halides, it cannot be used for a study of the behavior of the neopentyl system in such reactions. It was therefore decided to prepare neopentyl iodide. Previous work<sup>2</sup> indicated that preparation of the neopentyl halides directly from the alcohol gives mainly rearranged products. Ingold and Patel<sup>3</sup> reported the formation of neopentyl iodide from the alcohol, phosphorus and iodine but gave no yield. In the present work, this reaction was shown to give only 4-9% of the iodide, the other products resulting from rearrangement.

Neopentyl iodide can be made without any rearrangement by treating neopentylmagnesium chloride with iodine. The product, however, is contaminated with hydrocarbon by-products difficult to eliminate completely. Pure neopentyl iodide is obtained by converting neopentylmagnesium chloride to the corresponding mercury compound, which is then treated with iodine.<sup>4</sup> Bromine with the mercury compound gives neopentyl bromide. The yields of the iodide and bromide, based on neopentyl chloride, are 83 and 74%, respectively.

	(Cottrell)		$n_D^{20}$	$d_4^{20}$	MR.	
	B. p. °C.	Mm.			Obsd.	Calcd.
Neopentyl chloride	83.3	740	1.4043	0.865	30.01	30.06
Neopentyl bromide	105.0	732	1.4370	1.109	32.98	33.01
Neopentyl iodide	132.6	734	1.4890	1.494	38.18	38.24

Formation of the pure neopentyl halides in such excellent yields and with the absence of rearranged isomers is in complete agreement with the current theory of rearrangements.<sup>5</sup> The neopentyl group in both the Grignard compound and the mercury compound retains its electron pair during the reactions



Contrary to the claims of Tissier,<sup>6</sup> neopentyl iodide possesses a high degree of stability. Fractionation at atmospheric pressure liberates a small trace of iodine but colorless fractions are obtained at reduced pressures. These showed no color or change in refractive index when stored in the dark for three years. In chemical reactions, the iodide is far less reactive than *n*-butyl iodide.<sup>7</sup>

### Experimental

The columns used in this work were of the total condensation adjustable take-off type packed with single turn glass helices.<sup>8</sup> Column A had a packed section  $30 \times 0.8$  cm.; column B,  $64 \times 1.1$  cm.

**Reaction of Neopentyl Alcohol with Phosphorus and Iodine.**—Neopentyl alcohol, 22 g., 0.25 mole, b. p. 110-111° (734 mm.), m. p. 52°, and 2 g. of red phosphorus were placed in a 500-cc. three-necked flask fitted with a stirrer and a reflux condenser. Iodine, 33 g., 0.26 mole, was added in small portions during one-half hour. The mixture, after standing for one week, was refluxed for six hours and the products then distilled. The iodides obtained were steam distilled to destroy the unstable tertiary isomer. Neopentyl iodide, which was not affected by this treatment, was then dried with anhydrous potassium carbonate and fractionated through column A to give eight fractions, b. p. 68-77° (100 mm.),  $n_D^{20}$  1.4730-1.4942. Fraction 2 gave a Grignard compound which, on treatment with oxygen, yielded neopentyl alcohol; phenylurethan, m. p. and mixed m. p. 108-110°. The Grignard compound from fractions 3 and 5 with phenyl isocyanate gave *t*-butylacetanilide, m. p. and mixed m. p. 129-130°. The *t*-butylacetanilide from fraction 6 was difficult to purify and had a m. p. 124-125° and a mixed m. p. 128-129°. A carbinol could not be prepared from fraction 8. Fractions 7 and 8 had a higher index of refraction and higher b. p. than neopentyl iodide. Fractions 2 to 6 were mainly neopentyl iodide, wt. 4.6 g., 9% yield. No attempt was made to identify the isomeric halide which was unstable and could not be purified.

**Neopentylmercuric Chloride.**—Neopentyl chloride, b. p. 82-83.5° (734 mm.),  $n_D^{20}$  1.4040-1.4044, was obtained in 30% yield by chlorination of neopentane.<sup>1</sup> The Grignard compound was prepared in 90% yield from 105 g., one mole, of the chloride, 24 g., one mole, of magnesium and 350 cc. of dry ether. The Grignard solution was added to 270 g. (32 g. excess) of powdered mercuric chloride suspended in a liter of dry ether at such a rate that gentle refluxing was maintained. Three portions of 100 cc. of ether were added as the reaction mixture became thick during the addition. When all of the Grignard solu-

(1) Whitmore and Fleming, *THIS JOURNAL*, **55**, 4161 (1933).

(2) Whitmore and Rothrock, *ibid.*, **54**, 3431 (1932).

(3) Ingold and Patel, *J. Chem. Soc.*, 6768 (1933).

(4) Cf. Whitmore and Sobatzki, *THIS JOURNAL*, **55**, 1171 (1933).

(5) Whitmore, *ibid.*, **54**, 3274 (1932).

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

(7) Whitmore, Wittle and Popkin, *THIS JOURNAL*, **61**, 1586 (1939).

(8) Whitmore and Lux, *ibid.*, **54**, 3451 (1932); Wilson, Laughlin and Parker, *ibid.*, **55**, 2795 (1933).

tion had been added, the mixture was stirred and refluxed for three hours. The ether was removed by distillation and the product stirred with and filtered from 1 liter of water. After crystallization from 2 liters of 95% ethyl alcohol, a yield of 239 g., 90% of neopentylmercuric chloride, m. p. 117–118°, was obtained.

**Preparation of Neopentyl Iodide.**—To 107.5 g., 0.54 mole, of neopentyl mercuric chloride in a liter of water was added a solution of 150 g., 0.59 mole, of iodine and 200 g. of potassium iodide in 400 cc. of water. The mixture was shaken for one hour, permitted to stand at room temperature for fourteen hours and then the excess iodine removed with sodium thiosulfate. The neopentyl iodide was extracted with ether, the ether solution washed with distilled water and dried with anhydrous potassium carbonate. The ether was removed and the iodide fractionated through column B to give 63.7 g., b. p. 70° (100 mm.),  $n_D^{20}$  1.4887–1.4890. This represents a 92% yield of neopentyl iodide from the mercury compound.

The Grignard compound prepared from neopentyl iodide, on treatment with phenyl isocyanate, gave the *t*-butylacetanilide, m. p. and mixed m. p. 130–131°.

**Reaction of Neopentylmagnesium Chloride with Iodine.**—To a cold solution of 55 g., 0.22 mole of iodine in 200 cc. of dry ether was added in four hours a solution of 0.2 mole of neopentylmagnesium chloride in 150 cc. of ether. The reaction mixture, present in two layers, was warmed to room temperature and stirred for two hours. This was then poured on 500 g. of ice and the excess iodine removed with sodium thiosulfate. The ether layer was dried with anhydrous potassium carbonate and fractionated through column B to give fraction 1, b. p. 40–67° (100 mm.),  $n_D^{20}$  1.4163, 1.6 g., and the remainder, b. p. 67–70° (100 mm.),  $n_D^{20}$  1.4630–1.4872, 32.5 g. Fraction 1 formed the phenylurethane of neopentyl alcohol, m. p. and mixed m. p. 110–111°, indicating a small amount of neopentyl alcohol. Fraction 2 was mainly neopentyl iodide since the Grignard reagent from it gave neopentyl alcohol with oxygen. Thus the product was neopentyl iodide, contaminated by neopentyl alcohol and probably by hydrocarbons formed

as by-products of the Grignard reaction. The yield of the impure iodide was 82% based on neopentylmagnesium chloride. Careful refractionation did not further purify the product.

**Preparation of Neopentyl Bromide.**—To 27.6 g., 0.09 mole, of neopentylmercuric chloride suspended in 50 cc. of water was added a solution of 19 g., 0.12 mole, of bromine and 25 g. of potassium bromide in 100 cc. of water. After shaking the mixture, an upper layer of neopentyl bromide had formed. Excess bromine was removed with sodium thiosulfate and the bromide steam distilled from the solution. The product was separated from the aqueous layer, washed with water and dried with anhydrous potassium carbonate. Fractionation through column A gave 11.3 g., b. p. 104.8° (732 mm.),  $n_D^{20}$  1.4370, of neopentyl bromide representing a yield of 82% based on neopentylmercuric chloride. Conversion of the bromide to the Grignard reagent and treatment with phenyl isocyanate gave *t*-butylacetanilide, m. p. and mixed m. p. 130–131°.

### Summary

1. The reaction of neopentyl alcohol with phosphorus and iodine gives neopentyl iodide in 4–9% yield.
2. The action of mercuric chloride on neopentylmagnesium chloride gives neopentylmercuric chloride in 90% yield. No rearranged products were found.
3. Neopentylmercuric chloride with iodine gives neopentyl iodide in 92% yield and with bromine neopentyl bromide in 82% yield. No rearranged products were found in either case.
4. Addition of neopentylmagnesium chloride to an ether solution of iodine gives impure neopentyl iodide in 82% yield.

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## The Common Basis of Intramolecular Rearrangements. VI.<sup>1</sup> Reactions of Neopentyl Iodide

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In the preceding paper<sup>2</sup> it was shown that neopentyl iodide can be prepared in good yield and without rearrangement from neopentyl chloride. The present paper presents studies on the chemical properties of this interesting halide. Neopentyl iodide, like neopentyl chloride,<sup>3</sup> is surprisingly stable and unreactive. It acts only slightly, if at all, with potassium cyanide under conditions

more vigorous than those which give complete reaction with *n*-butyl iodide. It is not suitable for use in the malonic ester synthesis since most of it can be recovered unchanged after long treatment with sodium ethyl malonate. It shows only slight reaction with sodium ethylate, potassium phenolate and dilute aqueous potassium hydroxide. With dilute alcoholic potassium hydroxide under conditions which completely converted *n*-butyl iodide, neopentyl iodide reacts only slightly.

(1) Paper V, THIS JOURNAL, **61**, 1324 (1939).

(2) Whitmore, Wittle and Harriman, *ibid.*, **61**, 1585 (1939).

(3) Whitmore and Fleming, *ibid.*, **55**, 4161 (1933).