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.), $n^{20}D$ 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.), $n^{20}D$ 1.4163, 1.6 g., and the remainder, b. p. 67–70° (100 mm.), $n^{20}D$ 1.4630–1.4872, 32.5 g. Fraction 1 formed the phenylurethan 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.), $n^{20}D$ 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.

The Common Basis of Intramolecular Rearrangements. VI.[1] Reactions of Neopentyl Iodide

BY FRANK C. WHITMORE, E. L. WITTLE AND A. H. POPKIN

In the preceding paper[2] 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,[3] 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).

With concentrated alcoholic potassium hydroxide, however, it reacts in a surprising way. In this reaction it was found necessary to use a concentrated solution containing a molecular ratio of potassium hydroxide to neopentyl iodide of ten to one, and to subject the mixture to long heating at 180° to convert the iodide completely. The products are most unusual. Neopentane is formed in 70–80% yields with equivalent quantities of hydrogen and acetate. The formation of these products may be represented by the following equation

$$C_5H_{11}I + KOH + C_2H_5OK \longrightarrow$$
$$C_5H_{12} + H_2 + KI + CH_3COOK$$
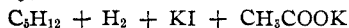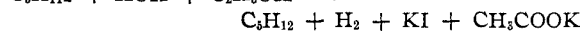
The other products are neopentyl ethyl ether, 12–13% yield and neopentyl alcohol, 3–5% yield. No olefins or other rearranged products could be found. In this connection it has been shown that t-amyl alcohol, one of the products to be expected from rearrangement, is stable under the conditions to which the reaction mixture was subjected and thus if formed would not have been lost through decomposition.

The neopentane was identified by its properties. It solidified to a white solid, liquefied and completely vaporized to a gas at room temperature, and on chlorination gave neopentyl chloride. The hydrogen was identified by a combustion analysis. The acetate was converted to acetic acid which was identified by titration and Duclaux numbers. Neopentyl ethyl ether, b. p. 90°, had the characteristic ether odor. It did not react with concentrated hydrochloric acid and had the same physical properties as a known specimen prepared from sodium neopentylate and ethyl iodide. Neopentyl alcohol was obtained as a white solid which gave the characteristic phenylurethan.

Neopentyl iodide readily reacts with aqueous silver nitrate and mercuric nitrate. The reaction mixture after being subjected to hydrolysis gives t-amyl alcohol in 97 and 80% yields, respectively. Thus practically complete rearrangement takes place with these acid reagents.

With potassium acetate, neopentyl iodide reacts completely only under strenuous conditions. The products are olefins and neopentyl acetate. Using ethyl alcohol as a solvent 10–20% of olefins, mainly trimethylethylene, and 40–70% of neopentyl acetate were obtained. With acetic acid as solvent a 45% yield of trimethylethylene and a 40% yield of neopentyl acetate were obtained. The neopentyl acetate was identified by hydrolysis to neopentyl alcohol.

Discussion

In the formation of a hydrocarbon on treatment with alcoholic potassium hydroxide, neopentyl iodide resembles the acetylenic halides. Nef[4] found that phenylbromoacetylene with alcoholic potassium hydroxide gave a small amount of phenylacetylene. With phenyliodoacetylene and alcoholic potassium hydroxide, sodium ethylate or potassium cyanide the main product was phenylacetylene. Grignard and Perichon[5] later confirmed this work and also treated undecyne bromide with alcoholic potassium hydroxide to form a 60% yield of undecyne. Both Nef and the later workers explain this reaction as being brought about by an addition of the ethyl alcohol to the halide atom, this atom then having an expanded valence shell. The complex which is thus formed would give rise to the acetylenic hydrocarbon and other products, one of which was thought to be aldehyde and its polymerization products. It is reasonable that hydrogen and acetate would be the final products. Nef further found that treatment of carbon tetraiodide with alcoholic potassium hydroxide gave rise to iodoform. Kharasch and co-workers[6] also found this to be the case but only when small amounts of aldehydes were present. These authors explain this reaction as due to aldehydes in the alcohol or alkali used. Very small amounts of carbon tetraiodide were used. This explanation does not apply to the present reaction since aldehydes were definitely proved to be absent, or present in the merest traces, and precautions were taken to exclude air from the reaction.

The formation of neopentyl ethyl ether and neopentyl alcohol with the absence of rearrangement may be explained on the basis of a mechanism[7] in which an ethylate ion or a hydroxyl ion collides with the carbon atom at the face of the tetrahedron which is opposite the iodine atom. In this reaction the carbon atom holding the iodine atom is at no time deficient in electrons, since the entering ion contributes electrons, and thus the neopentyl system cannot rearrange. This mechanism is probably the one by which neopentyl iodide reacts with dimethylamine to give t-butylcarbinyldimethylamine hydriodide,[8] appar-

(4) Nef, *Ann.*, **308**, 314 (1899).

(5) Grignard and Perichon, *Ann. chim.*, **5**, 5–36 (1926).

(6) Kharasch, Alsop and Mayo, *J. Org. Chem.*, **2**, 76 (1937).

(7) Bergmann, Polanyi and Szabo, *Trans. Faraday Soc.*, **32**, 843 (1936); Grant and Hinshelwood, *J. Chem. Soc.*, 258 (1933); Hughes, Juliusburger, Masterman, Topley and Weiss, *ibid.*, 1525 (1935); Young and Olsen, THIS JOURNAL, **58**, 1157 (1936); **58**, 393 (1936).

(8) Ingold and Patel, *J. Chem. Soc.*, 67–68 (1933).

ently without rearrangement. Such a mechanism gives rise to inversion of configuration when the halide is optically active and the carbon atom holding the halogen atom is the asymmetric atom.[9]

The facile reaction of neopentyl iodide with silver nitrate and mercuric nitrate with rearrangement is comparable to the reaction of neopentyl iodide with silver acetate[10] in which rearrangement also takes place. In this case the iodine atom is removed from the neopentyl iodide with its complete octet of electrons to form silver iodide. The "positive" neopentyl system which is thus formed undergoes rearrangement to give olefins and products having the t-amyl system. The reaction of neopentyl iodide with iodine monochloride in which it is quite probable that rearrangement takes place also probably proceeds by the above mechanism, a positive neopentyl system being formed. The reaction is similar to the reaction of isobutyl iodide with iodine monochloride in which t-butyl chloride is formed.[11] There may thus be two reaction mechanisms: one involving the reaction of neopentyl iodide with a negative ethylate or hydroxyl ion which gives rise to neopentyl ethyl ether and neopentyl alcohol without rearrangement, and the other, in the case of the silver salts, in which a positive silver ion removes the halogen atom, leaving a neopentyl system having only 30 electrons. In this case rearrangement is possible.

In the reaction of neopentyl iodide with potassium acetate in which both the "normal" and the "rearranged" products are formed, it is probable that both mechanisms operate. Should the mechanism described in the case for the silver salts take place exclusively, complete rearrangement would be expected. This is not the case. The mechanism giving rise to rearranged olefins takes place to approximately 20% in ethyl alcohol under the conditions used and to 45% with acetic acid as the solvent. The neopentyl acetate in 40–70% yield was formed without rearrangement by the reaction of an acetate ion with the neopentyl iodide.

These studies on the neopentyl halides are being continued.

Experimental

The columns used were of the usual type[2] (p. 1585). The neopentyl iodide was prepared from neopentylmercuric chloride[2] and had b. p. 70° at 100 mm., $n^{20}D$ 1.4887–1.4890.

(9) *Cf.* Whitmore and Bernstein, THIS JOURNAL, **61**, 1324 (1939).
(10) Whitmore and Fleming, *J. Chem. Soc.*, 1269 (1934).
(11) Linnemann, *Ann.*, **162**, 18 (1872).

Neopentyl Iodide with Potassium Cyanide.—A solution of 8.8 g. of neopentyl iodide, 0.044 mole, 3.4 g. of potassium cyanide (excess) and 8 cc. of 80% ethyl alcohol was placed in a 50-cc. flask fitted with a reflux condenser and heated to refluxing for twenty-seven hours. After cooling the flask, 0.5 g. of potassium cyanide was added and refluxing was continued for forty-eight hours. The solution was distilled from the flask and added to 100 cc. of water. The lower layer of iodide which formed was separated, dried over anhydrous potassium carbonate and distilled through column A to give 6.9 g. of slightly impure neopentyl iodide, b. p. 110–132° (735 mm.), $n^{20}D$ 1.4867–1.4880, yield 77% recovered. No other products were identified.

n-Butyl iodide in a parallel reaction but with refluxing for only twenty-four hours gave an 84% yield of n-butyl cyanide.

When the reaction mixture of neopentyl iodide and potassium cyanide was heated in a sealed tube at 150–200° for twenty-four hours, much decomposition took place. The odor of ammonia was apparent. A test for olefins was negative and no definite products were isolated. Neopentyl iodide was recovered to the extent of 20%.

With Malonic Ester.—Sodium, 0.46 g. or 0.02 mole, was dissolved in 10 cc. of absolute ethyl alcohol in a 50-cc. flask fitted with a reflux condenser protected by a calcium chloride tube. Ethyl malonate, 3.4 g., was added and the solution was allowed to stand for one hour, followed by the addition of 4 g., 0.02 mole, of neopentyl iodide. The solution was refluxed for twenty-six hours in an oil-bath at 105–110°. Only a small quantity of sodium iodide had separated. Water was added and the lower layer of neopentyl iodide was separated and dried, 2.5 g., 62% recovery.

n-Butyl iodide in a similar reaction but with three hours of refluxing gave approximately 80% ethyl n-butylmalonate.

With Sodium Ethylate.—Sodium, 0.5 g., was dissolved in 5 cc. of absolute ethyl alcohol by heating in an all-glass reflux apparatus. After cooling, 2 g., 0.01 mole of neopentyl iodide was added and the solution was refluxed in an oil-bath at 150–160° for eleven hours. At the end of this time the solution was clear. It was diluted with 50 cc. of water and titrated with standard acid. Only 8% of the iodide had reacted. Most of the iodide formed as a lower layer and 1.3 g. was recovered by separating and drying this layer, 65% recovery.

With Sodium Phenolate.—A solution of neopentyl iodide, 1 g., 0.005 mole, 0.01 mole of sodium phenolate and 5 cc. of absolute ethyl alcohol was refluxed for four hours at 160°. The solution was poured into 50 cc. of water and a lower layer of neopentyl iodide formed. On separation and drying it weighed 0.6 g., 80% recovery.

With Aqueous Alkali.—Neopentyl iodide, 2 g., 0.01 mole, was stirred with 115 cc. of 0.43 N potassium hydroxide solution, 0.05 mole, for ten hours at 100°. Titration of the cooled solution showed that about 9% of the iodide had reacted.

With Dilute Alcoholic Potassium Hydroxide.—n-Butyl iodide, 1.0 g., 0.005 mole, and neopentyl iodide, 1.08 g., 0.005 mole, were placed in 50-cc. flasks each containing 5 cc., 0.016 mole, of alcoholic potassium hydroxide and fitted with reflux condensers. The flasks were placed in the same

oil-bath and heated at 130–150° for five hours. After the first hour the flask containing *n*-butyl iodide showed a large quantity of sodium iodide and did not change appreciably on further heating. At the end of five hours the solution containing neopentyl iodide was still clear. Both solutions were rinsed into flasks and titrated with standard acid. The *n*-butyl iodide had reacted completely and the neopentyl iodide to the extent of about 8%.

The Reaction of Neopentyl Iodide with Alcoholic Potassium Hydroxide.—Small test reactions of neopentyl iodide with concentrated alcoholic potassium hydroxide showed that a ratio of 10 moles of potassium hydroxide to 1 mole of neopentyl iodide was necessary to convert the iodide completely. In a run using 0.1 mole of neopentyl iodide, 0.5 mole of potassium hydroxide (1:5) and 75 cc. of absolute ethyl alcohol, and refluxing the solution for ten hours at 150–160°, 45% of the neopentyl iodide was recovered unchanged.

Several large runs were carried out in which complete reaction was achieved. A typical run is given. The apparatus consisted of a 500-cc. flask fitted with a very efficient condenser, the outlet of which was connected to a mercury safety valve, a calcium chloride tube and a graduated gas carboy filled with saturated salt brine. In the flask, previously flushed with nitrogen, was placed 140 g., 2 moles, of crushed potassium hydroxide sticks (J. T. Baker U. S. P.), and a solution of 40 g., 0.2 mole, of neopentyl iodide in 60 cc. of absolute ethyl alcohol. The alcohol had been dried with sodium and distilled, and in comparative color tests using Schiff reagent with known acetaldehyde solutions it showed less than 0.05% aldehyde to be present. The condenser and gas collecting train were flushed with nitrogen to remove air and the flask was connected to the condenser and heated in an oil-bath. At 140° the mixture foamed noticeably and gas began to be evolved. The temperature was raised slowly to 180–190° and kept there for twenty hours. The flask was then allowed to cool. The volume of gas was 7400 cc. at 24° and 744 mm., indicating 0.3 mole. The gas and water solution on testing with Schiff reagent showed no aldehydes.

Analysis and Identification of the Gas.—Treatment of a sample of the gas in an Orsat apparatus with bromine water and sulfuric acid showed that no olefins were present. On passing the gas through a dry ice–acetone cooled trap it was found that a portion of it solidified to a white solid, neopentane, which on warming melted to a liquid and which vaporized completely at approximately 9°. This gas was identified definitely as neopentane by chlorination: 1.6 liters of the gas with 1 liter of chlorine was sealed in a Pyrex bomb tube and allowed to react by brief exposures to light over an interval of several days. Fractionation of the product so obtained, through Column A, gave neopentyl chloride 1 g., b. p. 80–81° (734 mm.). This gave a Grignard reagent which acted with phenyl isocyanate to give *t*-butylacetanilide, m. p. and mixed m. p. 129–130°. The remaining gas which passed the trap at −70° was found to be hydrogen by burning it with an excess of oxygen in a slow combustion pipet; 19.3 cc. of the gas containing 13% nitrogen gave 24 cc. contraction without any formation of carbon dioxide.

Attempts to analyze the original mixture of gas by burning it in a slow combustion pipet were not successful, vari-

able results being obtained, depending on the temperature of the platinum spiral used and on other factors.

It was found by slowly passing 6300 cc. of the original gas mixture through a dry ice–acetone trap that 2950 cc. of neopentane gas had solidified, leaving 3350 cc. of gas which contained 400 cc. of nitrogen and 2950 cc. of hydrogen. The solid neopentane on vaporizing gave 2950 cc. of gas. The 0.3 mole of gas which formed originally thus contained 0.15 mole of neopentane, 72% yield from the iodide and 0.15 mole of hydrogen. Other runs gave 70–80% yields of neopentane and equivalent quantities of hydrogen.

The Other Products.—The solution remaining in the reaction flask was distilled from this flask at 50 mm. into an ice-cooled receiver. A dry ice–acetone trap prevented loss. The distillate was redistilled through Column B to give fractions 1, b. p. 65–69°, two layers present; 2, 69–76°, n^{20}D 1.3752; 3, 76–78°, 1.3720; 4–7, 78°, 1.3702–1.3656, and a residue of 1.7 g. distilling above 78°. Fraction 1 showed no olefins when tested with bromine in carbon tetrachloride. Trimethylethylene could not be found in any of the reactions. Fractions 1–3 were a mixture of neopentyl ethyl ether and ethyl alcohol. Water was added to these in a quantity sufficient to cause a maximum separation of an insoluble upper layer. This was separated, dried and weighed, 2.9 g., 12.6%. The yields from three reactions were 12–13%. This ether was distilled using Column A, b. p. 88–90°, n^{20}D 1.3805–1.3840, the main portion, b. p. 90°, n^{20}D 1.3807. A sample of this ether was shaken for one hour with three times its volume of cold concd. hydrochloric acid. After washing with water, drying and distilling it was found to be unchanged. No *t*-amyl chloride could be found. The ether was further compared with a known sample below.

Fractions 4–7 were mainly ethyl alcohol with a small amount of neopentyl ethyl ether. The residue of 1.7 g. was distilled, using a small distilling flask, to give a small amount of ethyl alcohol and 0.5 g. of neopentyl alcohol, b. p. 100–112°. Several fractions solidified to the white solid neopentyl alcohol. The fraction b. p. 100–105° was treated with phenyl isocyanate to give the phenyl urethan, m. p. and mixed m. p. 110–112°. Yields of neopentyl alcohol in three reactions were 3–5%.

The residue in the reaction flask was dissolved in 1.5 liters of water, cooled in an ice-bath and carefully acidified with sulfuric acid. It was then distilled until the distillate was only faintly acid. No halogen acid was found. Titration of an aliquot part of the distillate showed 0.15 mole of acetic acid. This corresponds to the neopentane and hydrogen which were formed. Two 100-cc. samples of the acid gave the following Duclaux numbers (5.5, 6.3, 7.1) and (6.5, 7.0, 7.1), showing the acid to be acetic acid. It gave the odor of ethyl acetate when warmed with ethyl alcohol and sulfuric acid.

The Preparation of Neopentyl Ethyl Ether.—In a 200-cc. flask fitted with a reflux condenser and a calcium chloride tube was placed 88 g., 1 mole, of neopentyl alcohol and 5.8 g. of sodium, 0.25 mole. The sodium was added in small portions and dissolved by refluxing the alcohol. Ethyl iodide, 39 g., 0.25 mole, was added and the flask was warmed gently to 70° for ten hours followed by one hour at 120°. Sodium, 2.9 g., 0.12 mole, was again dissolved and then 20 g., 0.12 mole, of ethyl iodide was added and

the solution was refluxed for ten hours. The material was then distilled using Column B at 729 mm., b. p. 62–90.5°, n^{20}D 1.4325–1.3826. The main portion, b. p. 90.5°, n^{20}D 1.3830–1.3825, was neopentyl ethyl ether, 43.8 g., 37.8% yield. The residue consisted of 56% of the original neopentyl alcohol. The ether was refluxed with sodium and redistilled to give the main portion, b. p. 90.5° at 740 mm., n^{20}D 1.3807–1.3809, d^{20}_4 0.737. These physical constants correspond to those of the neopentyl ethyl ether obtained from neopentyl iodide. Both substances have the same odor. Long refluxing with sodium raised the index of refraction to n^{20}D 1.3812, apparently with the formation of sodium neopentylate.

Treatment of *t*-Amyl Alcohol with Potassium Hydroxide.—Crushed potassium hydroxide, 42 g., 20 cc. of ethyl alcohol and 4 g. of *t*-amyl alcohol were heated at 180° for nine hours. No olefins or gas were formed. The product was distilled to remove ethyl alcohol and the remaining *t*-amyl alcohol was treated with excess cold concd. hydrochloric acid to give the chloride, b. p. 82–84°, n^{20}D 1.3980–1.4042, 62% recovery, thus showing that *t*-amyl alcohol is stable to potassium hydroxide under these conditions.

Reaction of Neopentyl Iodide with Silver Nitrate and with Mercuric Nitrate.—Neopentyl iodide, 10 g., 0.05 mole, was placed in a three-necked flask fitted with a condenser and mercury seal stirrer and a solution of 10.2 g. of silver nitrate, 0.06 mole, in 75 cc. of distilled water was added. Reaction took place immediately, yellow silver iodide was formed and the flask became warm. The solution was allowed to stand overnight and then made slightly alkaline to litmus keeping the solution cold. After standing for one hour, the solution was distilled using column B to give 5.5 g. of a constant boiling *t*-amyl alcohol water solution, b. p. 87° at 740 mm., containing 45 mole per cent. of *t*-amyl alcohol, yield 4.3 g., 97%. This alcohol was identified by treatment with 20 cc. of cold concd. hydrochloric acid to give 4.6 g. of *t*-amyl chloride, b. p. 81–83°, n^{20}D 1.4050. This was identified further by preparing a Grignard reagent, treating it with phenyl isocyanate and isolating the dimethylethylacetanilide, m. p. 90–91°.

A similar reaction using mercuric nitrate gave an 80% yield of *t*-amyl alcohol.

The Reaction of Neopentyl Iodide with Potassium Acetate.—Preliminary tests showed that a temperature of 200° for twenty hours was necessary to completely convert neopentyl iodide with potassium acetate in ethyl alcohol. A solution of 10 g. of neopentyl iodide, 10 g. of potassium acetate and 10 cc. of commercial absolute ethyl alcohol was placed in a sealed tube and heated in a bomb furnace at 200° for twenty hours. The tube was then cooled in an ice–hydrochloric acid bath, opened, and 25 cc. of ether and 50 cc. of water were added. No gas formation could be noticed in any of the reactions. The ether was distilled from the solution using Column B. It contained the olefins formed. Titration with bromine and the weight of the dibromides so formed showed that 19% olefins had been

formed. The dibromide was hydrolyzed by refluxing with water. The product gave a 2,4-dinitrophenylhydrazone, m. p. 116–118°, indicating methyl isopropyl ketone and showing the olefin to be mainly trimethylethylene. The solution which had not been distilled was refluxed with potassium hydroxide to hydrolyze the ester. The alcohol so formed was extracted with ether and distilled from a small distilling flask to give 1.8 g. of neopentyl alcohol, b. p. 85–110°, which solidified to a white solid. Thus 41% of neopentyl acetate had been formed. The alcohol was identified as neopentyl alcohol by preparing the phenylurethan, m. p. and mixed m. p. 111–112°. Similar reactions gave 40–70% neopentyl acetate and 10–20% olefins.

Using acetic acid as a solvent instead of alcohol a 40% yield of neopentyl acetate and a 45% yield of olefins, mainly trimethylethylene, were obtained.

Reaction of Neopentyl Iodide with Iodine Monochloride.—Neopentyl iodide was found to react very vigorously with iodine monochloride even at very low temperatures. The product was a mixture which could not be separated or identified. It was found that *t*-amyl chloride reacts very vigorously with iodine monochloride, but that neopentyl chloride shows no reaction. The products of the reaction with *t*-amyl chloride were also quite complex and could not be identified. It is evident that rearrangement must take place to give rise to the complex products obtained.

Summary

1. Neopentyl iodide reacts only slightly with potassium cyanide, ethyl malonate, sodium ethylate, potassium phenolate and dilute alkali under conditions far more strenuous than those which completely convert *n*-butyl iodide.

2. Neopentyl iodide reacts completely with concentrated alcoholic potassium hydroxide under extreme conditions to give 70–80% yields of the hydrocarbon, neopentane, equivalent quantities of hydrogen and acetate, 12–13% yields of neopentyl ethyl ether, 3–5% yields of neopentyl alcohol but no olefins or other rearranged products.

3. Neopentyl iodide reacts with aqueous solutions of silver nitrate or mercuric nitrate to give complete rearrangement. It also gives rearrangement products with iodine monochloride.

4. Neopentyl iodide reacts with potassium acetate in ethyl alcohol or acetic acid to give neopentyl acetate, 40–70%, and olefins, 10–45%.

5. A discussion of reaction mechanisms for the normal and the rearrangement reactions is presented.