

were analyzed, using dry oxalic acid and pyridine. The reaction with aniline was investigated. The disproportionation induced by heat was found to be a convenient method for synthesizing symmetrical acid anhydrides.

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NEOPENTYL ALCOHOL AND ITS REARRANGEMENT PRODUCTS¹

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The literature on neopentyl alcohol (*tert.*-butylcarbinol) and the related halides³ is unsatisfactorily incomplete, especially in view of the fact that these substances represent the simplest case in which removal of the alcoholic hydroxyl results in complete or nearly complete rearrangement of the carbon skeleton.⁴

The present study fills some of the gaps in our knowledge of this interesting group of substances. Neopentyl alcohol is stable to heat. Seven weeks at 230–240° gives no change. Heating to similar temperatures with iodine, anhydrous potassium carbonate or traces of hydrogen chloride gives little or no change. It dissolves in cold concentrated sulfuric acid with the formation of an acid ester from which the original alcohol can be recovered.

The preparation of halides from neopentyl alcohol is extraordinarily difficult. Its reactivity is much less than that of *n*-butyl alcohol. Dry hydrogen bromide very slowly forms an oxonium salt with neopentyl alcohol. This is stable at 40° but is slowly converted at 65° to a mixture of amyl bromides containing approximately 72% tertiary amyl bromide, 8% of a secondary bromide, probably secondary isoamyl bromide and 20% of one or more primary bromides. The composition of this mixture is not changed by heating at 105°.

The problem of the neopentyl halides and their rearrangements is being intensively studied in this Laboratory.

Experimental

The neopentyl alcohol used in this research was prepared from *tert.*-butylmagnesium chloride and formaldehyde by R. W. Beattie, of the Intermediate Laboratory of the Public Health Institute of Chicago.

Stability of Neopentyl Alcohol on Heating.—The relatively high melting point of

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³ Tissier, *Ann. chim. phys.*, [6] 29, 357 (1893); Samec, *Ann.*, 351, 256 (1907); Richard, *Ann. chim. phys.*, [8] 21, 323 (1910); Ingold, *J. Chem. Soc.*, 123, 1706 (1923).

⁴ See p. 3279.

the alcohol (52°) was used in detecting any change due to the action of heat or reagents. This method was rendered more delicate by the large freezing point constant of the alcohol. This was found to be 11.0 ± 0.2 as compared with 5.1 for benzene and 1.86 for water. Thus 5% of water in the alcohol renders it liquid at room temperature.

A sample of neopentyl alcohol of m. p. 50° was sealed in a Pyrex tube filled with carbon dioxide, and heated at 230–240° for fifteen hours. The tube was then cooled and the melting point determined without opening the tube. The m. p. was 44–46°. The heating at 230–240° was then continued for forty-eight days, at the end of which time the m. p. was still 44–46°.

The Action of Reagents with Neopentyl Alcohol

(a) **Iodine.**—A sample of the alcohol (m. p. 50°) was sealed in a Pyrex tube with a crystal of iodine and heated at 230–240° for fifteen hours. A slight charring occurred and the m. p. dropped to 41–43°. After heating again for forty-eight days the m. p. was still 41–43°.

(b) **Anhydrous Potassium Carbonate.**—A sample of alcohol (m. p. 52°) was heated in a sealed tube with an equal weight of freshly dehydrated potassium carbonate at 225° for ten hours. The m. p. was 49°. After heating again for seven days at 225° the m. p. was 48–49°.

(c) **Traces of Hydrogen Chloride.**—Approximately 5 cc. of dry hydrogen chloride gas was passed into 4.5 g. of neopentyl alcohol (m. p. 51°) in a Pyrex tube. The tube was sealed and heated for thirty-four hours at 175°. The m. p. was 43–45°. The material was slightly pink. The tube was heated for two days more at 175°, three days at 200° and finally two weeks at 200° without any further change in the m. p. after each of these periods.

(d) **Cold Concentrated Sulfuric Acid.**—A mixture of 5 g. of neopentyl alcohol (m. p. 50°) and 5 cc. of c. p. sulfuric acid was prepared at 0°. About ten minutes' shaking was required to effect complete solution. The mixture was poured on 50 g. of finely ground ice. After the ice had melted, the solution was made barely alkaline with 25% sodium hydroxide solution and saturated with solid potassium carbonate. An upper layer (2 g.) separated which was neopentyl alcohol, m. p. 40–42°. The aqueous layer was extracted with ether, the ether solution dried with potassium carbonate and the ether removed by distillation. The residue reacted with phenyl isocyanate to give 3 g. of the phenyl urethan of neopentyl alcohol, m. p. 108–110°. This corresponded to 1.5 g. of the alcohol. Since the above experiment was carried out in such a way as to avoid mechanical loss of the alcohol and yet only 3.5 g. was recovered of the 5 g. used, it appeared that some other product was formed. This proved to be a stable acid ester of the alcohol, according to the following experiment.

A solution of neopentyl alcohol in c. p. sulfuric acid was allowed to stand at 20°. The solution first turned red and began to deposit crystals after twenty-four hours. After six days the entire mass was solid with crystals. The crystals were soluble in water, alcohol, benzene and ether. When the crystals were refluxed with water and steam distilled, neopentyl alcohol was recovered and identified as the phenyl urethan, m. p. 110–111°. Attempts to make a crystalline barium salt of the acid ester failed.⁵ Treatment of tertiary amyl alcohol with sulfuric acid under the same conditions gave only a red viscous liquid from which the alcohol was recovered on dilution.

Formation of Halides from Neopentyl Alcohol

1. **Action of Hydrogen Chloride.**—All attempts to repeat the work of Tissier and of Richard³ failed to give any chloride. Only one experiment will be described. Twenty-eight grams of neopentyl alcohol in a tube cooled to -10° was saturated with dry

⁵ Cf. Tissier, *Compt. rend.*, **112**, 1065 (1891).

hydrogen chloride gas and sealed. The tube was heated for 206 hours at 62–65°. The contents turned deep red-brown. Only one layer was present at any time. When the tube was cooled and opened, a violent evolution of hydrogen chloride occurred. The contents of the tube dissolved completely in 100 cc. of concentrated hydrochloric acid, indicating the absence of appreciable amounts of chlorides. Extraction with ether gave 10 g. of unchanged neopentyl alcohol. No trace of chloride was detected.

2. **Action of Thionyl Chloride.**—The method of Darzens,⁶ modified until it gave over 30% yields of *n*-butyl chloride from *n*-butyl alcohol, was applied to neopentyl alcohol. Twenty grams of neopentyl alcohol, 21 g. of dry pyridine and 22 cc. of dry ether were placed in a flask provided with a stirrer and a dropping funnel. The mixture was cooled to 0° and a solution of 29 g. of thionyl chloride in 27 cc. of dry ether was added slowly with vigorous stirring and cooling. After twenty-four hours the mixture was worked up in the usual way. This gave 16 g. of neopentyl alcohol, b. p. 108–112°, m. p. 41–43°, but no detectable chloride.

3. **Action of Phosphorus Tribromide.**—Twenty-nine grams of neopentyl alcohol, cooled to 0°, was treated slowly with 30 g. of phosphorus tribromide. After standing at room temperature for eight days, the mixture was poured into a large volume of ice water. A layer lighter than water separated. Most of this was unchanged alcohol, as shown by its solubility in concd. sulfuric acid. The total yield of bromide was 7 g. or 14%. A similar experiment with *n*-butyl alcohol gave a 50% yield.

4. **Action of 48% Hydrobromic Acid.**—Twenty grams of neopentyl alcohol was treated with 150 cc. of 48% hydrobromic acid in an all-glass reflux apparatus. On heating to 50°, the mixture turned black. The mixture was refluxed for twenty-five minutes and allowed to stand overnight. It was then distilled. A fraction passed over at 78–90°. This separated into two layers. The lower layer was water and the upper layer was completely soluble in concd. sulfuric acid, showing the absence of organic bromides. *n*-Butyl alcohol in a similar experiment gave an 80% yield of the bromide.

5. **Action of Dry Hydrogen Bromide.**⁷ (a) **At 40°.**—The work of Tissier³ could not be repeated. Eleven grams of neopentyl alcohol was saturated at –10° with dry hydrogen bromide prepared from bromine and boiling tetralin and purified by red phosphorus and phosphorus pentoxide. Even after this mixture was heated at 40° in a sealed tube for weeks, no separation into layers occurred.

(b) **At 65°.**—Only one of several experiments will be described. This used 188 g. (2.1 moles) of neopentyl alcohol, m. p. 48–50°. When dry hydrogen bromide was passed over the alcohol, the temperature rose rapidly to 50°. Hydrogen bromide was then passed through the liquid and cooling was applied. When it was saturated at 10°, 69 g. of the calculated quantity of 172 g. of hydrogen bromide had been absorbed. The reaction flask was capped with a stopper carrying two toy balloons coated inside with liquid paraffin. After standing for eight days the pressure of hydrogen bromide had dropped although no separate layers had appeared. The mixture was again saturated with hydrogen bromide, this time at 4° with a gain in weight of 37 g. After one day at room temperature, the mixture was again saturated with hydrogen bromide, now at –5°, with a gain in weight of 34 g. At further intervals of six and thirteen days 27 g. and 10 g. of hydrogen bromide were added at –10°. It thus required twenty-eight days to introduce slightly more than the calculated amount of hydrogen bromide. No layers separated.

In order to determine whether or not a stable bromide had been formed, two weighed samples were treated as follows. (1) Dry nitrogen was passed through until no more

⁶ Darzens, *Compt. rend.*, **152**, 1314, 1601 (1911).

⁷ This work was checked and extended by P. A. Krueger, while working in this Laboratory, under a Grant-in-aid from the National Research Council.

hydrogen bromide was driven out. The loss in weight was 49%. The residue smelled like neopentyl alcohol but did not solidify at -20° . It gave a qualitative test for an organic bromide. (2) Shaking for ten minutes with cold water removed 43% of the weight of the mixture as hydrogen bromide, which was determined as silver bromide.

Seventy-eight grams of the mixture containing 40 g. of neopentyl alcohol and 38 g. of hydrogen bromide was sealed in a 300-cc. Pyrex tube and heated at 65° . After twenty days no visible change had occurred. It was opened and saturated with hydrogen bromide at -20° . After five days more at 65° , a few drops separated on top. After two days more, the tube was opened, saturated again at -20° and heated at 65° . Four days later the two layers were about equal in volume. The upper layer increased in volume for nine days more. The upper layer then consisted of 61.5 g. of bromides and the lower layer of 20.1 g. of concd. hydrobromic acid. It thus took forty days at 65° to complete the conversion to bromides.

The bromide layer lost only 1.7 g. when washed with 21.3 g. of 40% hydrobromic acid. It was dried for nineteen hours at 0° over anhydrous calcium bromide. It was then distilled at 23–25 mm. at $22-32^{\circ}$. About 90% distilled at $22-24^{\circ}$ at this pressure. Only 1 cc. of residue was left. The distillate was water-white, of an organic bromide odor and free from hydrogen bromide, yield 53.0 g. A second tube treated in a similar way gave 47.5 g. of bromides distilling at $22-30^{\circ}$ at 25 mm.

Anal. Calcd. for $C_5H_{11}Br$: Br, 52.9. Found: Br, 53.2.

Nature of the Halides from Neopentyl Alcohol

1. **Freezing Point Studies.**⁸—The measurements were made by means of a Leeds and Northrup Type K potentiometer and a chromel-copel thermocouple standardized at the freezing points of pure *n*-heptane (-90.7°) and pure 2,2,4-trimethylpentane (-107.7°). The distilled samples of the bromides from neopentyl alcohol froze from -94 to -104° at which point complete solidification prevented stirring. Check determinations were made repeatedly with both preparations. Most of the material froze at -94 to -99° . Since the neopentyl halides reported in the literature are said to rearrange on heating, a sample was heated for nine hours at 105° . A slight darkening occurred. The bromide was subjected to a pressure of 20 mm. for a few seconds to allow any hydrogen bromide or olefin to boil out. The freezing point was then found to be unchanged, showing that the proportion of various bromides in the mixture had not been changed by heating.

Tertiary amyl alcohol, b. p. $101-101.5^{\circ}$ (735 mm.), was treated with constant boiling hydrobromic acid to form tertiary amyl bromide, b. p. $106.5-107^{\circ}$ (735 mm.). This froze at -82 to -85° . Addition of tertiary amyl bromide to the bromides from neopentyl alcohol raised the m. p. about 2 and 7° , respectively, for the addition of 2 cc. and 5 cc. of the tertiary amyl bromide to 5-cc. portions of the bromides from neopentyl alcohol. It was found that an equimolar solution of pure tertiary amyl bromide and pure ethyl bromide froze about 30° lower than the tertiary amyl bromide. Since the bromides from neopentyl alcohol froze about 10° lower than the tertiary bromide and had their freezing points raised by the addition of the latter, they must contain tertiary amyl bromide with about one-third of a mole of isomeric bromides for each mole of the tertiary bromide. The isomeric bromides were not converted to tertiary bromide by heating at 105° for nine hours.

2. **Analysis for Primary, Secondary and Tertiary Bromides.**—The method of Michael and Zeidler⁹ was used.

⁸ The mixture was studied by means of freezing point measurements because of the supposed instability of the mixture and its tendency to rearrange during chemical reactions.^{3,5}

⁹ Michael and Zeidler, *Ann.*, 385, 271 (1911).

(a) A weighed sample (about 0.2 g.) of the bromide was shaken vigorously for twenty-five minutes on a mechanical shaker with 10 cc. of distilled water. The solution was then analyzed by the Volhard method, carefully avoiding the presence of any appreciable excess of silver nitrate. In this way 38.2% of bromine was found. Thus 72% of the total bromine in the mixture was removed by hydrolysis with cold water in twenty-five minutes, indicating the presence of approximately that amount of tertiary halide. When an excess of the standard silver nitrate solution (about 0.1 *N*) was shaken with a sample of the bromide, an additional 4.2% of bromine was removed, thus indicating the presence of about 8% of secondary bromide in the mixture. The remaining 20% of bromide in the mixture is undoubtedly primary bromide and accounts for the nitrolic acid test for primary bromides obtained by Tissier.^{3,5} The small amount of the mixture of secondary and primary bromides obtained distilled at 100–115° (secondary isoamyl bromide, b. p. 114°, *sec.*-butylcarbinyl bromide, b. p. 116–118°). Attempts to prepare a Grignard compound from the primary bromide failed. Studies on the primary bromide obtained from neopentyl alcohol are being continued.

Summary

1. The inactivity of neopentyl alcohol to heat and reagents has been demonstrated.

2. The composition of the bromide mixture obtained from neopentyl alcohol has been further studied and found to consist mainly of rearrangement products.

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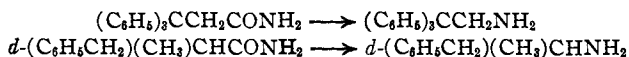
THE HOFMANN REARRANGEMENT OF THE AMIDE OF TERTIARY BUTYLACETIC ACID AND ITS SIGNIFICANCE IN THE THEORY OF REARRANGEMENTS^{1,2}

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In the Hofmann rearrangement of *N*-halogen amides, the migrating group has been regarded as positive by Jones³ and as negative by Stieglitz.⁴ The stability of the migrating group is shown by the more recent work of Hellerman⁵ and of Wallis.⁶ Although the stability of the opti-



¹ See THIS JOURNAL, p. 3274.

² Submitted by August H. Homeyer (Mallinckrodt Fellow) in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College.

³ Jones, *Am. Chem. J.*, **50**, 441 (1913); Jones and Hurd, THIS JOURNAL, **43**, 2422 (1921); Jones and Wallis, *ibid.*, **48**, 169 (1926).

⁴ Stieglitz and Leech, *ibid.*, **36**, 280 (1914); Stieglitz and Stagner, *ibid.*, **38**, 2047 (1916).

⁵ Hellerman, *ibid.*, **49**, 1735 (1927).

⁶ Wallis and Nagel, *ibid.*, **53**, 2787 (1931).