(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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[Contribution from the Chemical Laboratory of the School of Chemistry and Physics of the Pennsylvania State College]

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 Jones[3] and as negative by Stieglitz.[4] The stability of the migrating group is shown by the more recent work of Hellerman[5] and of Wallis.[6] Although the stability of the opti-

$$(C_6H_5)_3CCH_2CONH_2 \longrightarrow (C_6H_5)_3CCH_2NH_2$$

$$d\text{-}(C_6H_5CH_2)(CH_3)CHCONH_2 \longrightarrow d\text{-}(C_6H_5CH_2)(CH_3)CHNH_2$$

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[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).

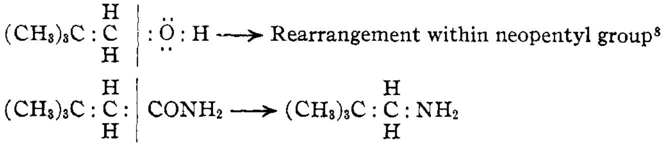
[4] Stieglitz and Leech, *ibid.*, **36**, 280 (1914); Stieglitz and Stagner, *ibid.*, **38**, 2047 (1916).

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

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

cally active migrating group in the latter case has been assumed to be due to a stable positive radical or carbonium ion, it can be explained equally well on the basis of a stable negative radical.[7]

In the present study it has been found that the amide of tertiary butylacetic acid reacts with sodium hypobromite to give a quantitative yield of neopentylamine and none of the tertiary amylamine which would be formed by a rearrangement of the migrating fragment. This marked difference in the behavior of the neopentyl group in different classes of compounds is best pictured on the basis that when the neopentyl group is deprived of an electron pair, it rearranges and when it is not so deprived it does not rearrange. The break in the molecules may be represented as follows



$$(CH_3)_3C:\overset{H}{\underset{H}{C}}\;\Big|\;:\overset{..}{\underset{..}{O}}:H \longrightarrow \text{Rearrangement within neopentyl group}^{8}$$

$$(CH_3)_3C:\overset{H}{\underset{H}{C}}:\;\Big|\;CONH_2 \longrightarrow (CH_3)_3C:\overset{H}{\underset{H}{C}}:NH_2$$

No rearrangement within the neopentyl group

Experimental Part

Rearrangement of Tertiary Butylacetamide to Neopentylamine.—Two and four-tenths cc. of bromine was added dropwise to a stirred solution of 7.2 g. of sodium hydroxide in 60 cc. of water cooled to 0°. To the clear yellow solution was added immediately 3.50 g. of *tert.*-butylacetamide, m. p. 131°, and stirring was continued at 0° for an hour after the amide had dissolved. Then the reaction mixture was allowed to warm slowly. At room temperature a yellow turbidity appeared; at about 50° the solution became colorless and an oily layer separated. After adding 100 cc. of water the reaction mixture was distilled until no more oil came over. The distillate was collected in dilute hydrochloric acid, giving a yellow solution which became colorless on heating and yielded neopentylamine hydrochloride as a white crystalline residue on evaporation. This was taken up in absolute alcohol, evaporated to dryness and washed with ether. After keeping *in vacuo* until constant weight was obtained, the product weighed 3.60 g. (theoretical yield, 3.76 g.) and melted with decomposition *ca.* 273°. Freund and Lenze[9] give the melting point of neopentylamine hydrochloride as *ca.* 275°.

Neopentylamine was identified by preparing the several derivatives described below. The melting points are uncorrected.

Sym.-Neopentylphenylthiourea.—The free amine liberated from 0.63 g. of its hydrochloride by adding excess dilute sodium hydroxide was extracted with ether, dried over anhydrous sodium sulfate and mixed with 0.60 g. of phenyl isothiocyanate. After concentrating, the thiourea was precipitated by adding petroleum ether. The product weighed 0.86 g. (theoretical yield 0.98 g.) and melted, without recrystallization, at 134.5°. Freund and Lenze[10] give the melting point of *sym.*-neopentylphenylthiourea as 136°.

Sym.-Neopentylphenylurea was prepared in an analogous manner. The melting point was 155°. Freund and Lenze give 155°.

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[7] Private communication from E. S. Wallis.

[8] See This Journal, p. 3431.

[9] Freund and Lenze, *Ber.*, **24**, 2156 (1891).

[10] Freund and Lenze, *ibid.*, **23**, 2868 (1890); **24**, 2158 (1891).

Benzoylneopentylamine was prepared from the amine hydrochloride by the Schotten–Baumann method. After recrystallization from petroleum ether it melted at 112–113°.

Rearrangement of Ethyldimethylacetamide.—It was desired to prepare *tert.*-amylamine and its derivatives for purposes of comparison with the neopentylamine. The Hofmann rearrangement of 3.50 g. of ethyldimethylacetamide, m. p. 103°, was carried out as described above. The distillate yielded 2.75 g. of *tert.*-amylamine hydrochloride, m. p. *ca.* 225°. Extraction of the residue in the distilling flask with ether and recrystallization of the product from alcohol gave 0.85 g. of *sym.*-(di-*tert.*-amyl)-urea which sublimed at about 220°.

The urea was identified by fusing with phthalic anhydride[11] to give *tert.*-amylphthalimide. After two recrystallizations from dilute alcohol it melted at 190°. *Tert.*-amylphthalimide was also prepared from the free amine. The melting point was 187–188° and a mixed melting point showed no depression.

Benzoyl-*tert.*-amylamine was prepared from the amine hydrochloride by the Schotten–Baumann method. After recrystallization from petroleum ether it melted at 92–93°. A mixture of this compound (2.2 mg.) with benzoylneopentylamine (2.7 mg.) melted at 77–100°.

Sym.-*tert.*-amylphenylthiourea prepared by the method described above melted at 117–118°. A mixture of this thiourea (2.5 mg.) with *sym.*-neopentylphenylthiourea (2.1 mg.) melted at 95–99°.

Sym.-*tert.*-amylphenylurea melted at 130–131°. A mixture of this urea (1.8 mg.) with *sym.*-neopentylphenylurea (2.1 mg.) melted at 100–112°.

Summary

1. *Tert.*-butylacetamide yields neopentylamine quantitatively by the Hofmann rearrangement.

2. The failure of the migrating neopentyl group to rearrange to a *tert.*-amyl group is discussed in its bearing on the mechanism of rearrangements.

3. Apparently a "negative" neopentyl group is stable whereas a "positive" neopentyl group undergoes rearrangement to a *tert.*-amyl group and related compounds.

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[11] Tingle and Brenton, THIS JOURNAL, **32**, 113 (1910).