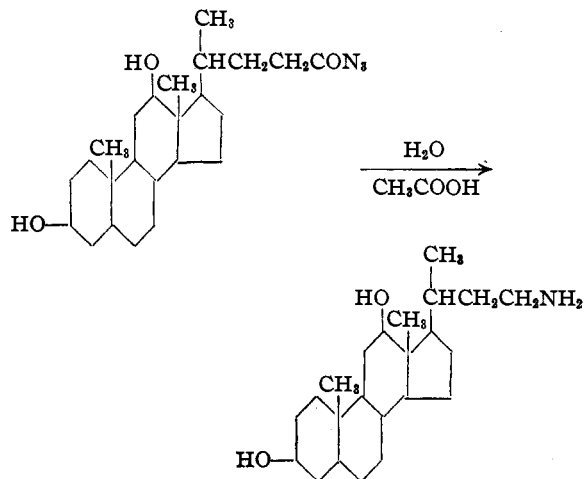


much stabler than cholamine. The crude base, m. p. about  $90^\circ$ , yielded a microcrystalline solid, m. p.  $118^\circ$ , after repeated purification; it was strongly alkaline to red litmus moistened with methyl or ethyl alcohol and formed a hydrochloride, m. p.  $247^\circ$ , whose aqueous solution was extremely bitter.

Since I had prepared a desoxycholamine which differed from that described by Dr. Vanghelovici in the melting points, both of the free base and its hydrochloride, as well as in the comparative ease with which it could be obtained in nicely crystalline form from methanol, I am submitting a description of its preparation and some of its characteristics. Although there are differences in melting points, the two amines are alike in being strongly alkaline to red litmus moistened with methyl or ethyl alcohol and in the striking bitterness of their hydrochlorides. It appears not illogical to assume that they are stereoisomers; possibly epimerization occurred during the alkaline hydrolysis used in the Curtius degradation, since this type of change is effected by other alkaline reagents such as sodium alcoholate or metallic sodium in xylene.



### Experimental Part

Twenty-two grams of desoxycholyhydrazide, m. p.  $203^\circ$ , was dissolved in 67 cc. of normal hydrochloric acid and 400 cc. of water. After adding 400 g. of ice, sodium nitrite (4.2 g.) in 50 cc. of water was added slowly with good stirring. The mixture was then stirred for an additional fifteen minutes and the azide filtered off with suction. The pressed, wet cake containing approximately 150 g. of water was transferred immediately to 210 g. of glacial acetic acid; it did not all dissolve but, upon gently warming on the steam-bath, the undissolved portion melted; evolution of gas began at about  $45^\circ$ , becoming more vigorous in the neighborhood of  $60^\circ$ ; at the same time the amount of oil

decreased but even after heating for four hours a small amount (about 1 g.) was visible. After cooling, the solution was filtered through a sintered glass funnel and cold aqueous potassium hydroxide added until the mixture became alkaline to phenolphthalein. The precipitate was then dissolved in alcoholic potassium hydroxide; after warming, this solution was diluted with a large amount of water and the precipitate washed by decantation with water until the aqueous washings gave no alkaline reaction with red litmus. The residual gum still contained a relatively large amount of non-basic material which was not investigated further; after its removal, the amine was purified by several recrystallizations from absolute methanol, from which it separated easily as fine, white crystals upon chilling and scratching the moderately concentrated solution.

Although these crystals were well formed and homogeneous, they did not melt sharply, their behavior depending upon the rate of heating; after beginning to soften at about  $70^\circ$ , they resolidified upon raising the temperature very slowly; finally, however, the substance melted sharply at  $157\text{--}158^\circ$ ; yield, 3 g. The amine is so insoluble in water that it gives no basic reaction to red litmus moistened with water, at least within a reasonable length of time; on the other hand, it imparts a bright blue color at once to red litmus moistened with methyl or ethyl alcohol.

Analysis of the crystals, dried at room temperature over soda-lime and calcium chloride, indicated that they contained one molecule of methanol of crystallization.

*Anal.* Calcd. for  $C_{23}H_{41}O_2N \cdot CH_3OH$ : C, 72.86; H, 11.46. Found: C, 72.63; H, 11.60.

The free base, m. p.  $158\text{--}159^\circ$ , after warming for three hours in a drying pistol over metallic sodium at 5 mm. and  $100^\circ$ , was analyzed.

*Anal.* Calcd. for  $C_{23}H_{41}O_2N$ : C, 75.97; H, 11.36; N, 3.85. Found: C, 75.31, 75.84; H, 11.39, 11.44; N, 3.87, 3.77. Vanghelovici found: C, 75.37; H, 12.00; N, 3.82.

The hydrochloride, made by passing gaseous hydrogen chloride into a methyl alcoholic solution of the base, melted at  $306^\circ$  after sintering slightly at  $300^\circ$ . Unlike the base it is easily soluble in water.

*Anal.* Calcd. for  $C_{23}H_{41}O_2N \cdot HCl$ : Cl, 8.88. Found: Cl, 8.48. Vanghelovici calcd.: N, 3.50. Found: N, 3.80.

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### The Preparation of Primary Amines

BY ALEXANDER GALAT AND GERTRUDE ELION

The transformation of alkyl halides into primary amines by the formation of a double compound with hexamethylenetetramine, followed by alcoholysis in the presence of hydrogen chloride, affords a very convenient means for the preparation of primary amines.<sup>1,2,3</sup> As this method has

- (1) Delépine, *Compt. rend.*, **120**, 501 (1895); **124**, 292 (1897); *Bull. soc. chim.*, [3] **17**, 290 (1897); [4] **31**, 108 (1922).
- (2) Mannich and Hahn, *Ber.*, **44**, 1542 (1911).
- (3) Foldi, *ibid.*, **53**, 1836 (1920).

been practiced in the past, the alkyl halide is added to a solution of hexamethylenetetramine in chloroform, and the addition compound, after it has precipitated, is filtered off. The alkyl iodides react with reasonable rapidity, but the chlorides and bromides react much more slowly, and if they are to be used as starting materials, they should be converted into the iodide by addition of sodium iodide in acetone solution.

This procedure has now been simplified by operating in a single solvent, alcohol, without isolation of the addition compound. The new procedure is as follows.

To a solution of 1 mole of hexamethylenetetramine in eight to ten times its weight of hot 95% alcohol slightly more than 1 mole of sodium iodide is added. One mole of the alkyl chloride or bromide is then added and the solution is allowed to stand until the precipitation is complete. The period of precipitation will vary from a few minutes to several weeks depending upon the substance. The longer the carbon chain the longer is the time required for the precipitation. The mixture containing the precipitate is saturated with hydrogen chloride gas, whereupon the precipitate dissolves and ammonium chloride precipitates. When the latter has been filtered off and the alcohol removed by distillation, the resultant impure hydrochloride is converted into the pure amine by distillation with an excess of sodium hydroxide.

The times of precipitation and the yields of several of the amines obtained were as follows: methylamine, one week, 72%; ethylamine, eight days, 82.5%; benzylamine, two hours, 82.5%; *p*-nitrobenzylamine, one day, 61%; phenylethylamine, three weeks, 54%. The products obtained were of high purity, having melting points closely in accord with the values given in the literature.

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### Synthesis of Organobismuth Compounds

BY HENRY GILMAN AND ALEXIS C. SVIGOON

Numerous methods are available for the preparation of organobismuth compounds. However, none among them starts with the diazonium complexes of bismuth salts, although such complexes have been described. Challenger and

Wilkinson<sup>1</sup> have reported the preparation of benzenediazonium chloride-bismuth chloride and *p*-toluenediazonium chloride-bismuth chloride complexes; and Supniewski and Adams<sup>2</sup> the benzenediazonium chloride-bismuth chloride complex. No organobismuth compound is formed by interaction of *metallic* bismuth with benzenediazonium chloride.<sup>3</sup>

We are now reporting the conversion of these and other related complexes to the corresponding organobismuth compounds.

In a typical preparation (tri-*p*-tolylbismuth), an ice-cold solution of 0.1 mole of bismuth chloride in 16 cc. of concd. hydrochloric acid was added with stirring to an iced solution of 0.1 mole of *p*-toluenediazonium chloride prepared in the customary manner by diazotization of 10.7 g. of *p*-toluidine. The mixture became quite pasty and of a solid-like consistency as the complex formed. On the addition of 300 cc. of an ice-cold mixture of methyl and ethyl alcohols, a flaky white complex was precipitated. This diazonium complex was filtered, washed with cold methyl alcohol, and dried. The yield was 32.5 g.

*Anal.* Calcd. for  $C_{21}H_{21}N_6BiCl_2$ : Bi, 26.9. Found: Bi, 27.2 and 27.0.

A suspension of the *p*-toluenediazonium-bismuth chloride complex (32.5 g.) in 100 cc. of cold acetone was treated with 52.8 g. of copper powder. An evolution of gas took place in several minutes, and the solution became dark brown in color. After one-half hour an equal volume of 25% ammonium hydroxide was added, and then the mixture was diluted to 450 cc. with water. After standing for one hour the solid which had precipitated was filtered, dried, and extracted with dry chloroform. The solid remaining after removal of the chloroform was crystallized from methyl alcohol. The yield of pure tri-*p*-tolylbismuth was 3.07 g. and identification was completed by a mixed melting point determination (m. p., 116-117°) with an authentic specimen which melted at 116-117°.

The diazonium complexes were precipitated by methyl alcohol, ethyl alcohol, and more effectively by mixtures of methyl and ethyl alcohols. Higher alcohols may be better precipitants, and these are being examined together with media other than acetone for decomposing the complexes. A later report will give details on organobismuth compounds not now available, particularly those with solubilizing groups and groups of interest in connection with the cleavage and relative reactivities of unsymmetrical organobismuth compounds.

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(1) Challenger and Wilkinson, *J. Chem. Soc.*, **121**, 91 (1922).

(2) Supniewski and Adams, *This Journal*, **48**, 507 (1926). See also, Kharrier, *Atti Accad. Lincei*, [6] **5**, 889 (1927); Nesmeyanov, Kocheshkov and Klimova, *Ber.*, **66B**, 1877 (1935); and Kocheshkov and Nesmeyanov, *J. Gen. Chem.*, (U. S. S. R.) **6**, 144 (1936).

(3) Waters, *J. Chem. Soc.*, 864 (1939).