

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

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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

Wilkinson¹ have reported the preparation of benzenediazonium chloride-bismuth chloride and *p*-toluenediazonium chloride-bismuth chloride complexes; and Supniewski and Adams² the benzenediazonium chloride-bismuth chloride complex. No organobismuth compound is formed by interaction of *metallic* bismuth with benzenediazonium chloride.³

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).