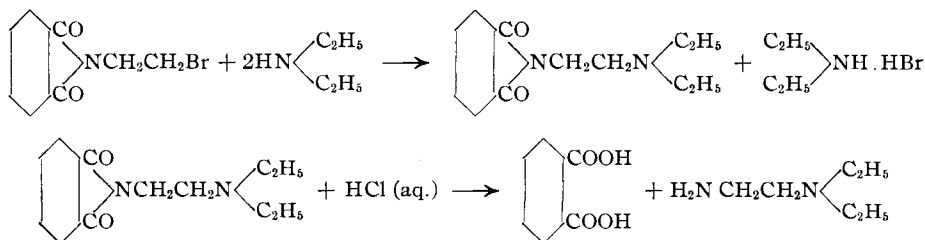


A CONVENIENT LABORATORY METHOD FOR THE PREPARATION OF UNSYMMETRICAL DIETHYL ETHYLENE DIAMINE.*

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The following is a detailed description of a modification of the method described by Ristenpart for the preparation of unsymmetrical diethyl ethylene diamine; it gives good results and is very convenient.



Procedure.—One hundred and twenty-three Gm. of bromethylphthalimide is boiled under a reflux condenser for 12 hours with 70 Gm. diethylamine dissolved in 300 cc. dry toluene. After the first 3 hours' boiling, the diethylamine hydrobromide is removed by filtration before continuing (*Note 1*). After removing the remainder of the diethylamine hydrobromide by filtration, the reflux condenser is replaced by a condenser arranged for downward delivery, and the toluene is removed by distillation. The reflux condenser is now returned into place and the residue is boiled for 3 hours with 420 cc. of 20% HCl. Upon cooling, the phthalic acid is filtered off and leached with warm (not hot) water to recover any product retained by it. The solution of the diamine hydrochloride is concentrated in an open dish on the steam-bath until it is a thick, viscous syrup and with good external cooling, the syrup is made strongly alkaline by means of 40% KOH. Now 25 cc. isopropyl alcohol is added, and then an excess of solid KOH, in small pellets, which causes the appearance of a copious precipitate of potassium chloride. The reaction mixture is allowed to settle out in a tall narrow cylinder or centrifuged. The isopropyl alcohol solution of the amine is dried carefully over solid KOH and subjected to distillation.

Thirty-two Gm. or 61% of material boiling at 143–147° C. is obtained (*Note 2*). The pure material boils at 145° C.

Note.—1. About 84% of the theoretical diethylamine hydrobromide is removable after 3 hours. About 14% additional is removable after 10 hours, and most of the remaining 2% is removable after 12 hours.

2. Practically all of the loss of yield is mechanical loss in separating the amine solution from the KCl and strong potash. Further extractions with isopropyl alcohol can be made, but the main product should not be dissolved in a larger volume of alcohol than that specified since much amine boils over with the alcohol, making rectification difficult.

Other Methods of Preparation.—Ristenpart (*Ber.*, 29 (1907), 2526) uses the same reactions, but condenses the diethylamine with the bromethylphthalimide

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in a sealed tube at 100° C. without a solvent. The method is inconvenient and usually incomplete due to caking of the phthalimide and the amine hydrobromide.

It has also been prepared by condensing diethylamino ethyl chloride with potassium phthalimide, followed by acid hydrolysis.

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STEROL GLUCOSIDES.

BY OLE GISVOLD.

Whereas a survey of the literature reveals the fact that phytosterols, for the most part, occur as such, it also shows that several sterol glucosides have been reported, the so-called phytosterolins (1). If the amounts of sterols present in plants are small, those of the phytosterolins reported are even smaller. Hence the sugars obtained upon hydrolysis have not been identified completely.

Under these circumstances it naturally seemed desirable to synthesize sterol glucosides with glucose and other sugars. Thus the glucose glucosides of sitosterol and cholesterol were prepared by Salway (2) in 1913, and that of ergosterol by Mac Corquodale (3) in 1930. Having worth-while amounts of several phytosterols on hand, the synthesis of as many of their glucosides as time and material permitted was undertaken.

The method of preparation employed was essentially that used by Power and Salway in 1913 in the preparation of the sitosterol and cholesterol glucosides and again by Mac Corquodale in 1930 in the preparation of ergosterol glucoside.

The procedure is essentially as follows, with some modification of deacetylation.

Two Gm. of dry sterol, 3 Gm. of pure, freshly crystallized tetracetyl bromoglucose were dissolved in 100 cc. of dry ether and 3 Gm. of dry freshly precipitated silver oxide were added. The mixture was shaken continuously for 8 hours, centrifuged, filtered and the ether distilled off. The residue thus obtained was recrystallized once from 95% alcohol. The partially purified product was dissolved in warm absolute alcohol and deacetylated with a solution of freshly prepared sodium ethoxide. The insoluble precipitate thus obtained was filtered off and washed twice with small quantities of hot alcohol. The crude product thus obtained was recrystallized from a hot saturated solution using a mixture of 95% alcohol and pyridine as a solvent. The glucoside crystallized very well and a pure product was thus obtained.

Preparation of Aceto-Brom Glucose (4).—The procedure employed was that described by Levene and Raymond, and excellent yields were obtained.

Dry HBr was passed into acetic anhydride until the latter contained 40 Gm. of the gas per 100 Gm. of the finished reagent. For each 50 Gm. of pure anhydrous powdered glucose, 250 cc. of the reagent were used. The glucose was divided into 10-Gm. portions, each kept in a stoppered test-tube. The reagent was cooled to 10° and the glucose added under constant shaking. The temperature was not allowed to exceed 30°. The first portion of glucose dissolved quite slowly but the later portions more rapidly. Before additional portions were added the solution was cooled to 10°. After all the glucose had been added, the solution was cooled to 0° and dry HBr was passed into it until the total content was 60 Gm. per 100 Gm. of acetic anhydride. The solution should be only a light straw color. It was permitted to stand for one hour and then concentrated to half its original volume. Thirty cc. of toluene were added and the distillation continued until the residue became a thick syrup. Three additional portions of toluene were added and removed by distillation. All reagents were removed as completely