

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

AN IMPROVED METHOD FOR THE PREPARATION OF PRIMARY ARSANILIC ACID.¹

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Introduction.

Until recently the literature on arsanilic acid, though extensive, has been rather meager as regards the exact details for preparing the acid. Lately Fichter and Elkind² have given brief directions, and Kober³ has described in detail a method for which he claims a 30% yield. We have obtained, however, only fair results using Fichter and Elkind's method and decidedly poorer results following Kober's directions.

The usual procedure in making arsanilic acid is to heat arsenic acid in an excess of aniline at 180° or higher for 2 or 3 hours. After conducting numerous experiments we have found that it is distinctly advantageous to use a large excess of aniline, thus keeping the reaction mixture fluid, and to work at lower temperatures and increase the time of the reaction, thus avoiding the formation of tarry impurities. The final procedure adopted is as follows:

Experimental.

Preparation of Reagents.—The arsenic acid was prepared by either of the following methods.

1. Pure arsenious oxide was oxidized with nitric acid. The resulting solution was evaporated over a free flame until the temperature of the liquid was 160°. It was then evaporated to dryness by heating in an electric oven at 120°.

2. Pure arsenic pentoxide (As_2O_5) was dissolved in water and the solution concentrated over a free flame and dried as in 1.

Crude arsenic acid (76%) evaporated as in 1 may be used. The aniline was dried over caustic and redistilled.

Procedure.—47 g. ($\frac{1}{3}$ mol.) of dry arsenic acid was placed in a 300-cc. Kjeldahl flask, 152 cc. ($\frac{8}{3}$ mol) of aniline added and the mixture heated in a paraffin bath for 12 hours. The temperature of the bath was kept at 150°–160°. At a temperature of about 110° the mixture solidified and then slowly melted and remained liquid throughout the subsequent heating. After heating, the mixture was poured into an 800 cc. beaker and the flask rinsed out with 200 cc. of hot water, the rinsings being added to the beaker. 60 cc. of 6 *N* sodium hydroxide solution was then poured

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² *Ber.*, 49, 239 (1916).

³ *THIS JOURNAL*, 41, 451 (1919).

into the flask, removing by this means any last traces of the product, and then added with vigorous stirring to the reaction product which had been cooled to room temperature. The whole was now poured into a separatory funnel. The upper layer consists mainly of aniline, from which 90% of the excess aniline used can be recovered by steam distillation. The lower layer containing the sodium arsanilate was drawn off into a beaker. 15-20 g. of infusorial earth was added and the solution filtered by suction, removing by this means any suspended aniline. To the filtrate, which was very light pink or colorless, 50 cc. of 6 *N* hydrochloric acid was added, and on standing a short time the arsanilic acid separated out as a colorless, finely crystalline precipitate. It was often necessary to stir the filtrate vigorously as there is a marked tendency for it to become supersaturated. Congo red paper may be used to indicate when sufficient acid has been added.

The filtered precipitate is pure enough for most purposes. However, it was usually recrystallized once from hot water with the addition of a small amount of animal charcoal. Prepared thus the product was usually perfectly colorless. The average yield of dry, recrystallized product was 26%.

The results of several analyses are given below, the samples having previously been dried under diminished pressure at 60°. The nitrogen was determined by the Kjeldahl-Gunning method, the arsenic by Ewins'¹ method, the latter slightly modified in that the iodine used for titration was standardized each time against a blank to which a known amount of arsenious oxide had been added.

	As. %.	N. %.		As. %.	N. %.
Product Sample A.....	33.61	6.30	Product Sample B.....	34.57	6.35
	34.37	6.32		34.11	6.39
	33.76		34.58	6.35
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Averages,	33.91	6.31	Averages,	34.42	6.36
	Calc.: As, 34.60%; N, 6.45%.				

Conclusions.

The process described seems simpler than any heretofore published and can be carried out fairly economically, since 90% of the excess aniline can easily be recovered. The yields are as good as if not better (since they are based on pure dried recrystallized product) than those obtained by other investigators. We advise against making the arsanilic acid in large amounts unless efficient stirring is provided for.

MADISON, WIS.

¹ *J. Chem. Soc.*, 109, 1356 (1916).