LXXXIV.—*Reduction of Emulsified Nitro-compounds. Part I. β-Phenylhydroxylamine from Nitrobenzene.*

By ARTHUR LAPWORTH and LEONORE KLETZ PEARSON.

A SURVEY of the methods available for the manufacture of phenacetin, of which drug there was a dearth in this country during the early stages of the war, led to inquiries being made as to available supplies of *p*-aminophenol, and during the course of these inquiries it was suggested by Dr. Herbert Levinstein that a simplified method for manufacturing β-phenylhydroxylamine from nitrobenzene, involving, for example, the use of cheap sulphides as reducing agents and aqueous solutions, was much to be desired.

It was well known that the desired reduction can be effected by the use of ammonium hydrosulphide, but in practice alcoholic solutions were used. Thus Willstätter and Kubli obtained β-phenylhydroxylamine from nitrobenzene in very fair yield in this manner (*Ber.*, 1908, **41**, 1936). It occurred to one of us that an aqueous solution might possibly be used if an emulsifying agent were added in order to facilitate the intimate admixture of the two non-miscible fluids.

Mixtures of nitrobenzene and ordinary ammonium sulphide solution with enough kieselguhr to form a permanent emulsion after agitation were therefore made, and in one instance the whole of the nitrobenzene disappeared during the night. On filtering, washing the residue with water, and saturating the united filtrates with common salt, crystalline β-phenylhydroxylamine was obtained in quantity approximating, after removal of sulphur, to 50 per cent. of that theoretically possible.

The effect of replacing ammonium sulphide with the cheaper sodium salt was then examined under a variety of conditions and by using solutions made from commercial sulphide with enough hydrochloric acid or hydrogen sulphide to convert the salt into hydrosulphide, satisfactory results were obtained, whilst trouble due to free sulphur was eliminated. During the course of these experiments it occurred to one of us (L. K. P.) to examine the effect of adding calcium chloride to the system at the beginning of the reaction, and a decided rise in the yield of product was observed. As it seemed probable that the principal effect of the added calcium chloride was an improved emulsification, the kieselguhr was ultimately omitted, and without ill effect on the yield of product. In these circumstances, the addition of calcium chloride causes the separation of a finely divided precipitate, doubtless calcium hydroxide or " basic " sulphides, and in presence of this emulsification takes place readily; there is, however, little doubt that the condition of the system as to its state of alkalinity is simultaneously and favourably affected, and it is not altogether a matter of indifference how much calcium chloride is added.

By regulating the conditions as to concentration, the bulk of the phenylhydroxylamine obtained in the modified process may be made to separate in solid form, but, if filtered off in presence of the precipitate of alkaline calcium compounds, it tends to oxidise in the air with considerable rise of temperature. In order to dissolve these compounds and to reduce alkalinity, we have found it most convenient to add ammonium chloride, which effects both purposes and does not tend to cause separation of sulphur. Possibly, on a large scale, a saving in expense would be effected by the cautious addition of hydrochloric acid, for example, and the use of an ammonium salt in minimal quantity, but we have not studied this matter in detail.

Preparation of β-Phenylhydroxylamine from Nitrobenzene.

The following procedure gives, with a little practice, yields of β-phenylhydroxylamine amounting to about 72—74 per cent. of that theoretically possible and without extraction of the aqueous mother-liquors. For much larger quantities of material it would perhaps be desirable to modify the procedure; for example, to operate in the first instance with a smaller proportion of water in the system and to regulate the temperatures at different stages by suitable additions of ice.

A solution of sodium sulphide is made by dissolving 27·6 grams of the moist crystals ($Na_2S,9H_2O$) in 21·8 c.c. of water, placing this in a narrow cylinder and cautiously adding, with constant stirring and by means of a funnel the lower end of which passes to the bottom of the cylinder, 10·5 c.c. of hydrochloric acid (D 1·16). The resulting solution of sodium hydrosulphide and chloride is placed at about 15° in a stoppered vessel * with 5 grams of nitrobenzene and 5 grams of calcium chloride dissolved in the minimal quantity of water. The whole, when vigorously agitated, emulsifies and subsequently needs shaking occasionally. The temperature rises, but should not exceed 30°, and the colour of the liquid becomes orange to deep orange-red. After an interval, usually about three-quarters of an hour, the oil becomes thicker and crystals appear. At the critical stage, the whole of the oil has disappeared and this point should be noted carefully, either by the use of a lens or by adding ammonium chloride to a test portion. At this stage, usually about one and a half hours from the beginning, 6 grams of ammonium chloride are added and the whole is shaken, when the inorganic deposits pass almost completely into solution. On filtering, about 3·3 grams of nearly pure, crystalline β-phenylhydroxylamine are retained on the filter.

Many variations on the foregoing procedure have been tried, but without any improvement; such have been, for example,

* As the reaction mixture absorbs oxygen somewhat rapidly, precautions to prevent this effect or to minimise its results may be necessary.

(1) the preparation of the hydrosulphide solution with gaseous hydrogen sulphide instead of by addition of hydrochloric acid; (2) the use of sodium sulphide instead of hydrosulphide, in which case the reduction process is slower and the end result less certain; (3) variation in the proportion of calcium chloride used.

The authors desire to express their indebtedness to the Department of Scientific and Industrial Research for a grant to one of us (L. K. P.), and also for permission to publish these results.

CHEMICAL LABORATORIES,
THE UNIVERSITY, MANCHESTER.

[*Received, May 3rd,* 1921.]