L.—*The Preparation of o-Chloroaniline.*

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THE preparation and purification of this aniline have hitherto offered considerable difficulties, as both the substances from which it has been obtained, namely, *o*-chloronitrobenzene and *o*-nitroaniline, are not easily prepared.

From the product of the nitration of chlorobenzene, the *o*-chloronitrobenzene cannot practically be obtained free from the *p*-derivative and the commercial material, which is by no means cheap, invariably contains large quantities of the latter. After reduction, the *o*- and *p*-chloroanilines have to be separated.

o-Nitroaniline also is not easily prepared, for although it is formed in considerable quantity in the nitration of acetanilide (or benzanilide), it is difficult to separate the *pure* ortho- from the para-compound. In addition, the subsequent conversion into *o*-chloroaniline is a wasteful process.

The authors have recently observed (Trans., 1900, 77, 797) that in the transformation of acetylchloroaminobenzene, *o*-chloroacetanilide is formed together with the *p*-chloro-derivative. Although the proportion of the ortho-compound is only small (5 to 8 per cent.), this method is found to be convenient for preparing *o*-chloroaniline.

One part of acetanilide is dissolved in 3 to 4 parts of glacial acetic acid, and the *calculated* quantity of a strong solution of bleaching powder (0.5 to 0.7 *N*) is gradually added.* Considerable heat is

* A solution of bleaching powder, about 0.7 *N*, can be obtained by allowing water to stand over excess of the solid for several hours.

developed, but no cooling is necessary. Crystals begin to separate as soon as the bleaching powder is added. After standing for some hours to allow of complete transformation of the chloroamino-derivative first formed, the crystalline mass, which consists of a mixture of *o*- and *p*-chloroacetanilide, is filtered off, and, together with any further quantity which separates from the mother liquor on dilution, dissolved in boiling alcohol. On cooling, *p*-chloroacetanilide separates in a nearly pure state. The alcoholic mother liquor is evaporated to half its volume, when a further quantity of the *p*-chloro-compound crystallises out. To the mother liquor is then added concentrated sulphuric acid (10 parts of acid for every 100 parts of acetanilide), and the mixture boiled under a reflux apparatus for $1\frac{1}{2}$ hours in order to hydrolyse the anilides. On distilling the *acid* product in steam, *o*-chloroaniline comes over, now mixed with only a small amount of the para-derivative. To the oil suspended in water is added an equal weight of sulphuric acid, the mixture afterwards being distilled in steam. In order to effect the final purification of the *o*-chloroaniline, the distillate is acetylated by warming for a short time with excess of acetic anhydride. After removing the excess of anhydride by evaporation, the anilide is recrystallised by boiling it with a considerable quantity of petroleum (b. p. 80—100°), and adding benzene in small quantities until it is all or nearly all dissolved. On cooling, pure *o*-chloroacetanilide crystallises out in needles, and the yield amounts to about 50 grams from a kilogram of acetanilide.

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