XCV.—*The Use of Aluminium Chloride and Ferric Chloride in the Preparation of Phenolphthalein.*

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THIS paper contains an account of some attempts made early in 1920 to improve Baeyer's method for the preparation of phenolphthalein (*Ber.*, 1876, **9**, 1230; *Annalen*, 1880, **202**, 68), in which sulphuric acid is used as a condensing agent. The substances which were used as condensing agents in this research were anhydrous aluminium chloride, anhydrous ferric chloride, and acetic anhydride.

Anhydrous aluminium chloride gives an improved yield of phenolphthalein when the phthalic anhydride and aluminium chloride are in molecular proportions and the phenol is in slight excess. Only poor yields are obtained by using an excess of either phenol or aluminium chloride. The reaction is smooth and easily controlled by adjusting the temperature of the reacting mixture. The product is clean and is easily purified.

Anhydrous ferric chloride is not so satisfactory as aluminium chloride. The yields are poor and the products more difficult to purify, being contaminated with other condensation products, chiefly 1- and 2-hydroxyanthraquinones and 2-*o*-hydroxybenzoyl-

benzoic acid. The formation of fluoran was not observed in any of these experiments (see Copisarow, T., 1920, **117**, 209).

Acetic anhydride has no action as a condensing agent in the preparation of phenolphthalein by this method.

EXPERIMENTAL.

Aluminium Chloride.

(1) Phthalic anhydride (10 grams), phenol (25 grams), and anhydrous aluminium chloride (15 grams) were mixed in a 250 c.c. flask and gently warmed in an oil-bath. At about 45° a vigorous reaction set in, hydrogen chloride being evolved, and the whole mass changed to a bright pink liquid. The temperature was gradually raised to 100° during one hour, when the reaction was apparently completed, as hydrogen chloride was no longer evolved and the product had set to a solid mass. The product was distilled in a current of steam and the residue extracted first with dilute hydrochloric acid to remove alumina and then with dilute sodium hydroxide solution. The crude phenolphthalein was precipitated by dilute acid and crystallised from 70 per cent. methyl alcohol. The first fraction consisted of almost pure, well-crystallised phenolphthalein. A further quantity was obtained from the mother-liquors, which finally deposited a glue-like mixture of hydroxy-anthraquinones and hydroxybenzoylbenzoic acid. The yield of phenolphthalein calculated on the phthalic anhydride taken was 35 per cent. of the theoretical.

(2) In this experiment, similar quantities were taken, but the heating was continued during five hours at 100°. The yield was again 35 per cent., so that the reaction is practically completed after one hour.

The results of several experiments are best summarised in the form of a table. Number 5 shows the quantities and conditions which gave the best result.

Phthalic anhydride, grams.	Phenol, grams.	Aluminium chloride, grams.	Period of heating, hours.	Yield, per cent.
10	25	15	1	35
"	"	"	5	"
"	50	"	5	20
"	20	20	0.25	trace
"	"	15	1	40

The temperature in all cases was gradually raised from 40° to 100°, except in experiment 4, when the mixture set to a solid mass at 60° after fifteen minutes.

Ferric Chloride.

Phthalic anhydride (10 grams), phenol (20 grams), and anhydrous ferric chloride (20 grams, freshly prepared) were mixed and gently heated. No reaction was apparent, but after heating at 130° during five hours and treating the product as before, a yield of 30 per cent. of the theoretical was obtained after a tedious process of purification from other condensation products.

Other experiments showed that an excess of phenol had no influence on the yield of phenolphthalein and the results are summarised in the following table :

Phthalic anhydride, grams.	Phenol, grams.	Ferric chloride, grams.	Period of heating, hours.	Yield, per cent.
10	20	20	5	30
„	25	25	„	35
„	50	20	„	„

The temperature in all cases was between 130° and 150°. The products were dark brown and could only be obtained pure after many crystallisations.

Acetic Anhydride.

In an experiment with acetic anhydride as the condensing agent, made in the hope of obtaining phenolphthalein diacetate, phenyl acetate was the only product of the reaction.

Addendum.

In March, 1920, while this work was in progress, Copisarow (*loc. cit.*) published a paper dealing with the condensation of phenols and phthalic anhydride in the presence of various condensing agents: boric acid and sulphuric acid, hydrogen chloride, zinc chloride (anhydrous), and hydrogen chloride. Phenolphthalein was obtained in 50 per cent. yield by the use of zinc chloride and anhydrous hydrogen chloride together as condensing agents and a method of purification similar to that employed in this research. As such a method is more economical, in addition to being more efficient, there was no object in continuing the present research.

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