were collected: up to 140°, 14 cc.; from 140–158°, 20 cc.; 158–168°, 11 cc.; 168–175°, 4 cc.; the liquid charred, 18 cc. By fractionating them again, the various pure chloroderivatives were obtained. Here we have *o*-chlorotoluene formed in predominating quantities and *p*-chlorotoluene is formed in tolerably good yield. Benzyl chloride is scarcely formed.

Mesitylene.—The chlorination of mesitylene has been effected by Fittig and Hoogewerff,[1] by passing chlorine through cold mesitylene when it acts vigorously with the formation of mono-, di-, and trichloromesitylenes. The chlorination of mesitylene by aqua regia has been found to be very satisfactory, and in about five minutes a mixture of the chloromesitylenes can be prepared.

Ten cc. of mesitylene were mixed with 50 cc. of conc. HCl and HNO_3 (2 : 1). The mixture was warmed on the water bath for five to ten minutes and was shaken nearly all the time. Oily drops were formed, which afterwards collected, on shaking more, into a thick viscous liquid. This was separated by decantation, and washed as described in the case of benzene, when it was obtained as a mass of soft, white crystals. This was next fractionally crystallized from alcohol to effect the separation of the different chloroderivatives formed, according to the procedure used by Fittig and Hoogewerff.

After a systematic fractionation, it was found that dichloromesitylene, $C_6HCl_2(CH_3)_3$, was formed in great quantity. Trichloromesitylene, $C_6Cl_3(CH_3)_3$, was produced in fairly large quantity while monochloromesitylene was scarcely formed in any significant quantity. It may be pointed out that besides the chloromesitylenes, no secondary products are formed.

We are at present engaged in systematically applying aqua regia as a chlorinating and oxidizing reagent and shall lay before the Society the results obtained from time to time.

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SIMULTANEOUS CHLORINATION AND OXIDATION BY MEANS OF AQUA REGIA. THE PREPARATION OF CHLOROANIL FROM *p*-PHENYLENEDIAMINE AND HYDROQUINONE.

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It was shown previously that aqua regia acts essentially as a chlorinating agent in cases where there is no possibility of oxidation, and as has been described before, the chlorination of hydrocarbons was effected with ease by means of this reagent. But in cases of chlorination where there is also the posibility of oxidation, both reactions occur rapidly. Now,

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[1] *Annalen*, 150, 323.

p-phenylenediamine is known to give chloroanil by simultaneous chlorination and oxidation, but only with great difficulty, repeated treatment with different reagents being necessary to attain the end desired. Since aqua regia acts both as a vigorous chlorinating and oxidizing agent, it is quite expected that this reagent would convert *p*-phenylenediamine into tetrachloroquinone with ease, and, in fact, this has been found to be the case. It has also been found that hydroquinone, which has hydroxy groups in the para position, is also readily chlorinated and oxidized, giving pure chloroanil.

Chloroanil is readily formed from organic compounds. Erdmann[1] obtained it by passing chlorine through an alcoholic solution of chloroisatin. It is also formed by the action of potassium chlorate and hydrochloric acid on a variety of substances. It has been obtained by this reagent from aniline, phenol,[2] salicylic acid, nitrosalicylic acid,[2] dinitrosalicylic acid,[3] tyrosin[4] and *m*-aminobenzoic acid.[5] Furthermore it is formed by the action of fuming nitric acid on perchlorophenol[6] and also on 1,2,4,5-tetrachlorobenzene.[7] It has been obtained from hexachlorobenzene by treatment with a mixture of nitric and sulfuric acids[8] and also from hexachlorophenol.[9]

Chloroanil is now prepared according to the method of Graebe,[10] by the action of potassium chlorate and hydrochloric acid on *p*-phenylenediamine. This method still prevails as the most satisfactory. A short summary of the process will indicate the trouble that has to be undergone and the reagents that have to be used to prepare a pure sample of the substance.

p-Phenylenediamine hydrochloride is suspended in water and to it coarse crystals of potassium chlorate are gradually added and then hydrochloric acid. The addition of chlorate takes a day and the temperature has to be maintained between 20–30°. The next day the mixture must be warmed on the water bath until all the chlorate is decomposed. The crude product which contains about 25% of trichloroquinone, is collected and washed. Then it must again be treated with hydrochloric acid on the water bath for 1–2 hours. After washing it is again oxidized with potassium dichromate and hydrochloric acid. Even then it is not obtained quite pure, but must be recrystallized from toluene in order to get a com-

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[1] *Ann.*, **48**, 309.

[2] Hofmann, *Ibid.*, **52**, 57.

[3] Stenhouse, *Ibid.*, **78**, 4.

[4] Staedeler, *Ibid.*, **116**, 99.

[5] Erlenmeyer, *Jahresb. Chem.*, **1861**, p. 404.

[6] Merz, Weith, *Ber.*, **5**, 460 (1872).

[7] Beilstein, Kurbatow, *Ann.*, **192**, 236.

[8] Israti, *Bull. soc. chim.*, [3] **3**, 184.

[9] Barral, *Ibid.*, [3] **11**, 705.

[10] *Ann.*, **263**, 6.

pletely pure product. It is, therefore, quite evident that a considerable amount of trouble has to be undergone to prepare pure chloroanil.

Preparation from p-Phenylenediamine.—The preparation of perfectly pure chloroanil from *p*-phenylenediamine can be effected very simply and in a very short time, by means of aqua regia, as follows: To 100 cc. of a mixture of nitric and hydrochloric acids (2 : 3), 15 g. of *p*-phenylenediamine hydrochloride are added and the substance is allowed to react, with occasional warming on the water bath. A very gradual change in the color of the substance is forthwith noticed, going through yellow-brown to bright yellow. Toward the end of the operation, the flask containing the acid mixture is left on the water bath continuously until all of the acid fumes are driven off and the transformation into chloroanil becomes complete. The product is next washed with water and dried. It consists of perfectly pure tetrachloroquinone, which sublimes completely without melting and leaves only a black stain in the subliming vessel. The sublimed product consists of fine yellow plates having a melting point of 290° in sealed capillary tubes. The yield obtained was 10 g. of chloroanil. It may sometimes happen, as a result of too rapid heating of the acid mixture, that *p*-phenylenediamine is not completely converted into chloroanil. In such cases, a fresh treatment of the resulting substance with a smaller quantity of acid mixture is necessary.

Preparation from Hydroquinone.—Hydroquinone, which is similar to *p*-phenylenediamine in structure, might be expected to yield chloroanil when similarly treated. Since hydroquinone has not as yet been treated with an oxidizing and chlorinating reagent, it was thought desirable to first test the possibility of formation of chloroanil from hydroquinone by the action of potassium chlorate and hydrochloric acid. For this purpose, hydroquinone is suspended in strong hydrochloric acid and to it potassium chlorate is gradually added, whereupon the substance turns yellow. The process is continued for sometime longer with fresh additions of potassium chlorate and warming on the water bath. After a considerable time, the product is found to consist of a mixture of the lower chloroquinones. Hence the mixture of potassium chlorate and hydrochloric acid is quite unable to transform hydroquinone completely into chloroanil.

Accordingly, hydroquinone was next treated with aqua regia similarly to *p*-phenylenediamine. By its action, the substance gradually turns more and more yellow until it is of a bright yellow color. The reaction is finished on the water bath, when it consists of a bright yellow substance which is pure chloroanil and can be sublimed quite completely without previous fusion. It gives a melting point of 290° in a sealed capillary tube as observed by Graebe.

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