few grams of phosphorus (which takes but a short time), large pieces weighing as much as 3–4 g. can be added in quick succession. The operation can, therefore, be very smoothly and quickly completed. Since some isopropyl iodide (b. p. 89°) is invariably produced in this reaction, the mixture boils at less than 100° and, hence, the major part of the distillation is finished on the water bath. The last traces can be distilled off by heating with a constantly moving luminous flame. The allyl iodide is dried and purified in the usual manner.

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CHLORINATION BY MEANS OF AQUA REGIA. THE CHLORINATION OF BENZENE, THIOPHENE, TOLUENE AND MESITYLENE.

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Received March 12, 1914.

Although several processes have been used for the chlorination of organic compounds, there has always been difficulty in finding a method which could be carried out economically, both as regards the time and the chemicals. The only method which has been applied rather extensively is the one in which chlorine is passed through a liquid, usually in the presence of a carrier. In this case, however, the chlorination of a single compound means the work of some hours, not to speak of the trouble necessitated by the conditions demanded, *viz.*, the influence of direct sunlight, etc.

Some of the difficulties, mentioned above, seem to be obviated by the use of a mixture of nitric and hydrochloric acids as a chlorinating agent. Some investigators have used it in some oxidizing experiments, but they have pronounced it as an unsatisfactory reagent, chiefly owing to its exceedingly active properties. While this is true for some compounds, it has been found that the reagent in many cases acts as a powerful chlorinating agent, and in others both as an oxidizing and chlorinating agent. It acts as a simple chlorinating agent towards compounds which are not easily susceptible of oxidation with nitric acid, while, if the substance in question is susceptible of oxidation by nitric acid, both the processes of oxidation and chlorination occur simultaneously. In fact, the changes that can occur under any circumstances may be described thus: We know that a mixture of nitric and hydrochloric acids yields chlorine and nitrosyl chloride, the latter decomposing in the presence of water into nitrous fumes and hydrochloric acid. Hence, either or both of the following reactions may take place: first, the strong nitric acid may oxidize or nitrate the body coming into contact with it; and secondly, the nascent chlorine may unite with great energy with such compounds. In the case of hydrocarbons, generally, the reagent acts simply as a chlorinating agent, with the production of the several chloroderivatives, according to the conditions under which the chlorination is carried out. It might be thought strange that it does not act as a nitrating agent too. That this is not probable may be seen by the fact that chlorine has a greater influence than nitro group; and wherever there is any chance of substitution, the chlorine is first to take the place, because it is not only active in nature but it is also in the nascent state. Again, the chlorination with aqua regia becomes more vigorous than with ordinary reagents owing to the mere presence of nitric acid. Evidence in favor of this will be adduced later on, where it will be shown that the reagent achieves some substitutions which cannot be achieved by nascent chlorine alone in other processes.

Thus the nascent chlorine, obtained from a mixture of hydrochloric and nitric acids, affords a rapid method of chlorinating hydrocarbons in general. In addition to the rapidity and consequent economy of time, the ease with which the chlorination is carried out is a further advantage. It is only necessary to warm the hydrocarbons with the acid mixture with occasional shaking. In a very short time the hydrocarbon is chlorinated with the production of a chlorocompound, or a mixture of chlorocompounds where there is a possibility of the formation of more than one derivative. Generally, it is found that the method may be used to prepare a particular chloroderivative, as required, by varying the conditions of the experiment. It can, however, be laid down as a general rule that the longer the liquid is kept in contact with the acid mixture, the greater is the percentage of higher chlorinated products.

The chlorination of the following hydrocarbons has been effected:

Benzene.—It is well known that chlorine gas acts both substitutively and additively on benzene to form the various chloroderivatives. Benzene hexachloride is prepared by the interaction of chlorine on benzene in sunlight[1] or by passing chlorine through boiling benzene.[2] Other additive chloroderivatives of benzene can be prepared by varying the process a little and sometimes by the intervention of a little alkali. The substitutive chlorocompounds, especially the monochloro- and dichlorobenzenes, can be prepared by the chlorination of benzene in the presence of a little iodine.[3] In this case only two dichlorobenzenes, the *o*- and *p*-derivatives, are produced, the latter in predominating quantity.[4] Monochlorobenzene can also be prepared by chlorinating benzene with sulfur chloride,[5] or with sulfuryl chloride.[6] The whole series of the chlorocompounds of benzene has been exhaustively studied by Beilstein and Kurbatoff.[7]

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[1] Faraday, *Ann. chim. phys.*, [2] 30, 274; Mitscherlich, *Pogg. Ann.*, 35, 370.

[2] Lesimple, *Ann.*, **137**, 123; Heys, *Z. Chem.*, **1871**, p. 293.

[3] Hasse, *Ber.*, **26**, 1053 (1893).

[4] Müller, *Jahresb.*, **1864**, p. 524.

[5] Schmidt, *Ber.*, **11**, 1173 (1878).

[6] Dubois, *Z. Chem.*, **1866**, p. 705.

[7] *Ann.*, **182**, 97 (1876); **192**, 229 (1878).

Later, the chlorination of benzene has been effected with ferric chloride with the production of monochlorobenzene.[1] Monochloro- or dichlorobenzene has been prepared by passing the calculated quantity of chlorine through a mixture of benzene and aluminium chloride heated to 50–55°.[2] By the method to be described here, both monochloro- and dichlorobenzenes could be prepared very easily and in a very short time.

100 cc. of benzene were mixed with 450 cc. of a mixture of concentrated hydrochloric and nitric acids (2 : 1) in a large flask. When the first action which generally takes place ceased, the flask was heated on the water bath with a reflux condenser for about an hour. The contents of the flask were well shaken from time to time during the progress of the reaction. The flask was then cooled, and the upper oily layer was separated from the acids below by means of a separating funnel. The oily liquid was washed several times with water, then with dilute alkali and finally again with water to remove all traces of free acids. After drying the oil with a few bits of calcium chloride, it was subjected to fractional distillation. For effecting the separation between the several chloro-compounds formed in the process, a two-bulb Würtz still-head was used. The distilling flask was heated on the wire gauze with a small flame. During the distillation the temperature rose very rapidly at first to 80°, at which temperature all the unchanged benzene passed over. Two fractions were collected: the first between 80–105°, and second between 150–172°. At 172° the temperature rise stopped abruptly and pure dichlorobenzene came over and solidified to thin, colorless leaflets, m. p. 53°. During the distillation of *p*-dichlorobenzene, the ordinary condenser was replaced by an air condenser. The remaining liquid in the flask charred after the distillation of *p*-dichlorobenzene was over. By refractionating the previous fractions, pure monochloro- and *o*-dichlorobenzenes were separated and the following products were obtained from 100 cc. of crude chlorinated product: Unchanged benzene, 50 cc.; monochlorobenzenes, 15 g.; *o*-dichlorobenzene, 4 g.; *p*-dichlorobenzene, 18 g.; charred liquid, 10 cc.

Hence, this method may serve as a convenient method of preparing both monochloro and *p*-dichlorobenzenes. The yield of *p*-dichlorobenzene could be increased by prolonging the chlorination process somewhat.

Thiophene.—Chloro derivatives of thiophene are prepared by passing chlorine through thiophene, whereby all the four chlorothiophenes are produced.[3] Monochlorothiophene can also be prepared by the interaction of thiophene and sulfuryl chloride in absolute alcohol.[4]

The chlorination of thiophene by aqua regia has been effected as follows:

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[1] Thomas, *Compt. rend.*, **126**, 1212.

[2] Mouneyart, Pouret, *Compt. rend.*, **127**, 1026.

[3] Weitz, *Ber.*, **17**, 794 (1884).

[4] Töhl, Eberhard, *Ber.*, **26**, 2947 (1893).

To a sufficient quantity of a mixture of nitric and hydrochloric acids in the proportion of 1 to 2, thiophene was added. A vigorous reaction ensued with the turning of the thiophene color into red passing transiently through a blue-black appearance. After several minutes the red liquid sank beneath the acid mixture, evidently on account of the increase of density of the liquid as a result of the formation of chlorothiophenes. The oil was separated from the acid mixture and treated with dilute alkali and water to free it from the acids. After drying it over calcium chloride, it was distilled and the following fractions were collected: (1) up to 100°; (2) 101–140°; (3) 141–180°; and (4) 181–205°. By repeating the fractionation twice over, the whole mixture was resolved into unchanged thiophene, monochloro-, dichloro- and trichlorothiophenes. The unchanged thiophene was about $^1/_3$ of the whole product, and the three chloroderivatives were obtained in almost equal quantities. It should be noted that the proportions of the different chloroderivatives vary with the duration of the reaction.

Toluene.—The chlorination of toluene has been effected with free chlorine sometimes in the presence of a carrier. The chlorine either enters the side-chain or the nucleus according to the conditions under which the reaction occurs. The chlorine enters the side-chain if toluene is chlorinated by boiling with phosphorus pentachloride as carrier. Some chlorotoluenes have also been prepared by heating toluene with ferric chloride, sulfuryl chloride, etc. The primary product of chlorination of toluene with aqua regia is benzyl chloride, the chlorine attacking the side-chain; besides that other chlorotoluenes are formed, the *o*-chlorotoluene being formed in predominant quantity. The other dichloro- and trichlorotoluenes which are invariably formed cannot be conveniently isolated.

The method followed in this case was exactly the same as the one used before, with the exception that the reflux condenser was dispensed with. The preliminary experiment was carried out with 30 cc. of toluene and 120 cc. of the mixture of acid (1 : 1). The liquid was heated on the water bath half an hour. The product was washed with alkali as usual, dried and fractionated with a still-head. The fractions were collected as follows: 20 cc. yielded (1) up to 132° —; (2) 132–155° 3–4 cc. (in reality all this came over at 155°); (3) 155–180° 15 cc. (in reality all this came over at 175°).

Thus we find that benzyl chloride was the principal product of the reaction, *o*-chlorotoluene being formed in fairly good quantities. The chloroderivatives may, however, be prepared as desired by varying the conditions as is shown by the following experiment:

100 cc. of toluene were mixed with 600 cc. of the mixture of conc. HCl and HNO_3 (2 : 1) and heated on the water bath for one hour, 70 cc. of the crude product being obtained. On distilling the following fractions

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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Received March 12, 1914.

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.