formed which on shaking exploded violently. Chlorine was passed through magnesium phenyl bromide prepared from 6 g. magnesium and 26 cc. phenyl bromide. The gas was generated by the action of hydrochloric acid on potassium permanganate and was carefully washed and dried by first passing through water and then through conc. sulfuric acid. The gas seemed to be absorbed with no special change, but after a long time a solid incrustation appeared. When the chlorine seemed to have no further action, the passage of the gas was stopped and the vessel taken out of the glass reaction chamber. Upon shaking the flask slightly to break the incrustation, it exploded with a loud report and a bright flash. The nature of the product could not, therefore, be ascertained on account of its great instability.

Action of Chlorine on Magnesium Phenyl Iodide.

By the action of chlorine on magnesium phenyl iodide a yield of 20 to 25% of phenyl chloride was obtained. Chlorine gas was passed through magnesium phenyl iodide prepared from 6 g. of magnesium and 20.4 cc. of phenyl iodide. The product was hydrolyzed with ice-water and, after the distillation of ether, was subjected to distillation, when phenyl chloride was obtained in 20 to 25% yield. The low yield was due to the fact that a considerable quantity of the reagent was decomposed by the chlorine.

Action of Chlorine on Magnesium *p*-Bromotoluene.

Chlorine gas was passed through magnesium *p*-bromotoluene, prepared from 6 g. of magnesium and 30 cc. of *p*-bromotoluene. After hydrolysis and fractional distillation of the product, magnesium *p*-chlorotoluene was obtained in 18 to 20% yield.

CALCUTTA, INDIA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY COLLEGE OF SCIENCE.]

HALOGENATION. XVIII. DIRECT IONIZATION BY MEANS OF IODINE AND NITRIC ACID.

BY RASIK LAL DATTA AND NIHAR RANJAN CHATTERJEE.

Received December 2, 1918.

In continuation of the researches on iodination by nitric acid[1] it has now been found that reaction takes place with considerable facility in the case of aromatic acids and aromatic haloid derivatives.

The following results have been obtained: *p*-Iodobenzene gives a good yield of *p*-diiodobenzene. It was noted in my previous communication on the subject[2] that a small quantity of trinitrophenol is formed as a result of the hydrolysis of iodobenzene and simultaneous nitration in the presence of nitric acid. In view of this reaction it was thought possible to develop a method for the catalytic preparation of trinitrophenol using

---

[1] Datta and Chatterjee, THIS JOURNAL, 39, 435 (1917).

[2] *Loc. cit.*

a small quantity of iodine with continued addition of benzene and nitric acid. But this expectation has not been realized, since iodobenzene is quite stable under the circumstances, and if there be any excess of iodine, *p*-diiodobenzene is formed, while, if there be any excess of nitric acid, *p*-iodonitrobenzene is formed. It has been found, however, that by the prolonged action of iodine and nitric acid on benzene, *p*-iodonitrobenzene is formed since *p*-diiodobenzene is decomposed by nitric acid to form *p*-iodonitrobenzene. By this method of exhaustive iodination of benzene with repeated additions of iodine and nitric acid, *p*-iodonitrobenzene can be prepared rapidly and in good yield. To allow the reaction to proceed satisfactorily the water collecting on account of the decomposition of nitric acid must be removed from time to time.

Iodobenzene on iodination with the required quantity of iodine and nitric acid gives *p*-diiodobenzene. Chlorobenzene has been found to give *p*-chloroiodobenzene; and bromobenzene gives *p*-bromoiodobenzene. *p*-Chlorotoluene and *p*-bromotoluene give *p*-chlorobenzoic acid and *p*-bromobenzoic, respectively. Here the methyl groups are oxidized to carboxyl groups and no entry of iodine atoms takes place. Benzoic acid yields *m*-iodobenzoic acid. From *o*-phthalic acid, 4-iodo-*o*-phthalic acid could be obtained. Phenyl acetic acid gives *p*-iodophenylacetic acid. From cinnamic acid, *p*-iodocinnamic acid could be prepared. Salicylic acid on treatment with iodine and nitric acid gives trinitrophenol in quantitative yield, the carboxyl group being detached. Complex hydroxy acids such as tannin give a small quantity of trinitrophenol. In fact, it has been found that small quantities of trinitrophenol frequently amounting to only a trace are formed in the iodination of the aromatic acids.

EXPERIMENTAL.

p-Diiodobenzene.

To 20 cc. of iodobenzene and 25 g. of iodine in a flask provided with a reflux condenser, was added 20 cc. of conc. nitric acid in about 5 cc. portions at intervals of an hour. The mixture was warmed on the sand-bath for 4 to 5 hours during which time a constant stream of nitrous fumes escaped. After the operation the product was allowed to cool, when the contents solidified to a dark solid which was taken out and washed with dilute alkali and subjected to steam distillation, thus removing the remaining iodine and the oily products. The residue after drying by suction was recrystallized from alcohol, in which it is slightly soluble. The recrystallized product, *p*-diiodobenzene, melts at 129.4°. The yield obtained was 16 g.

p-Chloroiodobenzene.

To 22 cc. of chlorobenzene and 25 g. of iodine in a flask provided with a reflux condenser and heated on a sand-bath, is added 10 cc. of nitric acid in portions of about 3 cc. each. Reaction soon began as indicated by the evolution of nitrous fumes. The mixture was warmed for 3 to 4 hours, giving a thick oil. This was taken out, washed with dilute alkali and then distilled. At first a little unchanged chlorobenzene came over at 132°, then the temperature rose to 220° and most of the liquid distilled over, leaving a little charred residue in the flask. The oil collected between 220 and 230° soon solidified to plates of crystals which were drained to free them from the mother liquor. The product recrystallized from alcohol was found to be *p*-chloroiodobenzene, melting at 56°. The yield obtained was 14 g.

p-Bromoiodobenzene.

Ten cc. of bromobenzene, 12 g. of iodine and 12 cc. of conc. nitric acid were heated under a reflux condenser on a sand-bath for 4 to 5 hours. The product was washed and dried in the usual way and then distilled. At first unchanged bromobenzene came over at 155°. The portion distilling at from 240 to 255° was collected separately on a crystallizing dish, whereupon it at once solidified. The substance was recrystallized from hot alcohol and was identified as *p*-bromoiodobenzine, melting at 92°. The yield obtained was 6 g.

Benzoic Acid. Preparation of 3-Iodobenzoic Acid.

Twenty g. of benzoic acid and 20 g. of iodine were dissolved in 100 cc. of glacial acetic acid, and placed in a flask fitted with a reflux condenser. To this about 25 cc. of conc. nitric acid was added in portions of about 2 cc. each at intervals of 15 minutes, until most of the iodine was taken up. The mixture was then heated on a sand-bath for 6 hours, during which time a gentle stream of nitrous fumes escaped. Afterwards the product was subjected to steam distillation, when most of the free iodine and the oily products are eliminated. The residue was boiled with water in a porcelain basin thereby volatilizing most of the unchanged benzoic acid. The product was filtered hot, when the iodo-derivative, being less soluble than the acid, separated. This was then washed with hot water, and finally recrystallized from glacial acetic acid. It melted at 185° and was identified as 3-iodobenzoic acid. The yield obtained was 6 g. It was noticed that a small quantity of trinitrophenol was formed as a by-product in the preparation of the substance which is probably due to the partial hydrolysis and detachment of the carboxyl group and simultaneous nitration of the product.

o-Phthalic Acid. Preparation of 4-Iodo-*o*-phthalic Acid.

o-Phthalic acid on treatment with iodine and nitric acid gives 4-iodo-*o*-phthalic acid. Eight g. of *o*-phthalic acid and 6 g. of iodine were dissolved in 25 cc. of glacial acetic acid, and the mixture was warmed on the sand-bath for 6 hours. To it about 12 cc. of nitric acid (sp. gr. 1.3) was then added. The product at the end of the operation was subjected to steam distillation, and then poured into a large volume of water, whereupon a white, crystalline precipitate was obtained. This was filtered and finally recrystallized from hot water. The crystals melted at 182°, and were identified as 4-iodo-*o*-phthalic acid. The yield was 6 g. The mother liquor obtained from the reaction was distinctly yellow and a little trinitrophenol was isolated from it.

Phenylacetic Acid. Preparation of *p*-Iodophenylacetic Acid.

Five g. of phenylacetic acid were dissolved in 50 cc. of glacial acetic acid, and to this 5 g. of iodine was added. The mixture was then warmed on a sand-bath under a reflux condenser. When the boiling temperature was reached conc. nitric acid was added by means of a pipet in portions of 2 cc. Reaction began soon afterwards, as was indicated by the evolution of nitrous fumes, and continued until about 12 cc. of nitric acid had been added, when the iodine was found to have been used up. The product was distilled in steam to get rid of a little free iodine, and was then poured into a basin of water, whereupon a white crystalline precipitate was formed which settled to the bottom. The mother liquor was drained off, and the residue washed with a little water. The substance was then boiled with water, when the iodo-derivative went into solution. This was at once filtered, and on evaporation beautiful shining crystals were obtained. These were recrystallized from hot water and were identified as *p*-iodo-phenylacetic acid, melting at 135°. The yield obtained was 2.5 g. A small quantity of trinitrophenol was formed as a side product in the reaction, for reasons previously indicated.

Cinnamic Acid. Preparation of *p*-Iodocinnamic Acid.

Ten g. of cinnamic acid was mixed with 12 g. of powdered iodine, and the mixture dissolved in 25 cc. of glacial acetic acid and warmed on the sand-bath for 5 hours. Conc. nitric acid, not more than 2 cc. at a time, was thereupon added. At first the reaction was somewhat violent, and torrents of nitrous fumes were liberated. After the operation the product was distilled in steam, and on cooling white crystals appeared which were drained from the mother liquor. The precipitate was boiled with water, when the unchanged cinnamic acid went into solution leaving the brown iodo-derivative undissolved, and this was at once filtered off. The iodo-compound recrystallized from glacial acetic acid melted at 225° and was identified as *p*-iodocinnamic acid. The yield obtained was about 2 g. A small quantity of *o*-iodo-derivative was also formed which was recovered by fractional crystallization. The formation of a little trinitrophenol was also observed.

CALCUTTA, INDIA.