

existence of the abnormality recorded. As a consequence, definite decision upon the suggested explanation of the varying values must be deferred until the results yielded by the weak acid in the conversion of hydroxyacid to lactone have been explained. A promising line of investigation is being followed with other lactones, and it is hoped, that in a succeeding communication, progress may be reported.

Summary.

The conversion of hydroxyacids to lactones, a reaction which is catalytically assisted by acids, has been re-examined with a view to ascertaining whether effects similar to those obtained with acid catalysis in ester hydrolysis are to be found.

It has been shown (a) that the catalytic influence of hydrochloric is not strictly proportional to the hydrogen-ion concentration as determined from conductivity measurements,

(b) that neutral salts having a common anion increase the catalytic activity of the hydrochloric acid,

(c) that the effect may be expressed in terms of a catalytic activity of hydrogen ion and undissociated molecule,

(d) that the catalytic ratio of these two effects is different, however, if calculated from a series of acid concentrations or from a series of constant acid and varying neutral salt concentrations,

(e) that the catalytic ratio in the case of hydrochloric acid is of the same magnitude as that observed in ester catalysis.

Certain abnormalities have been observed with monochloroacetic acid as catalyst which lack as yet any satisfactory explanation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]

HALOGENATION. XV. DIRECT IODINATION OF HYDROCARBONS BY MEANS OF IODINE AND NITRIC ACID.

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Iodine by itself cannot be directly introduced into aromatic hydrocarbons for reasons quite well known, but a separate oxidizing agent is needed to make clear the place for the occupation of iodine. Although some oxidizing agents, such as iodic acid, ferric chloride, potassium persulfate and sulfur iodide have been used for this purpose, the results obtained are of no practical utility, the yields of iodo compounds being quite insignificant. It has been found, as will be presently described, that iodine directly enters the ring in the presence of nitric acid with the production of iodo derivatives in very good yields. The nitric acid does not play the part of a catalyst but actually takes part in the reaction, being reduced to

lower oxides of nitrogen, the hydrogen of the hydrocarbon being oxidized and the iodine then taking the place thus rendered free. The assumption that the hydrocarbon is nitrated first and that the nitro group is subsequently replaced by iodine is not tenable as nitrobenzene cannot be converted into iodobenzene on heating with iodine. In the case of the lower hydrocarbons the chances of iodination are greater than the chances of nitration while the reverse is the case with the higher hydrocarbons. It is for that reason that the method of iodination is not applicable to the higher hydrocarbons as in those cases either a mixture of iodo and nitro derivatives or simply nitro derivatives are obtained. This is exactly in accordance with facts regarding chlorination and bromination in the presence of nitric acid, as has been pointed out in the previous communications.¹

That nitric acid, being such a strong hydrolyzing agent, instead of causing removal of halogens, should contribute towards their addition, may appear somewhat unusual. The reaction is not altogether free from such an influence; a small part, however, hydrolyzes into phenol and as there is nitric acid present, very small quantities of trinitrophenol are formed and have been found in the reaction product. The formation of iodo derivatives of aromatic hydrocarbons becomes possible by the fact that the aromatic halides, unlike the aliphatic ones, are quite stable and cannot be readily hydrolyzed, and as the nitric acid is added in small portions at a time, it never reaches a sufficiently high concentration to act destructively on the iodo derivatives. The iodo derivatives of the aliphatic hydrocarbons are hydrolyzed as soon as they are formed, but by careful working it has been found possible to prepare the iodo derivatives of some of the higher aliphatic hydrocarbons in very small yield. This is of importance since the direct introduction of iodine into aliphatic hydrocarbons has not been accomplished before.

The iodination of benzene has been carried out with the formation of monoiodobenzene. Toluene gives a mixture of *o*- and *p*-iodotoluenes which can be separated conveniently by freezing. *o*-Xylene yields 4-iodo-*o*-xylene on iodination; *m*-xylene and *p*-xylene give rise to 4-iodo-*m*-xylene and 2-iodo-*p*-xylene, respectively. Mesitylene gives monoiodomesitylene with great ease. Hexane, the type of aliphatic hydrocarbons, gives a small yield of iodo-hexane. Thiophene gives with dilute nitric acid and iodine in the cold, a good yield of iodothiophene, the use of strong nitric acid having a destructive effect upon it. Ethylbenzene gives its monoiodo derivative. Cymene yields monoiodocymene. Naphthalene gives rise to iodonaphthalene along with some nitronaphthalene. Anthracene is completely oxidized to anthraquinone upon treatment with iodine and nitric acid and no iodo derivative is formed at all.

¹ Datta and Fernandes, THIS JOURNAL, 36, 1007 (1914); 38, 1809 (1916).

Experimental.

Iodination of Benzene. Preparation of Iodobenzene.—30 cc. of benzene and 25 g. of iodine are taken in a flask fitted with reflux condenser and to it about 12 cc. strong nitric acid are added in portions of about 2 cc. at intervals of fifteen minutes. The addition of nitric acid is to be stopped when it is found that most or all of the iodine is taken up. During the progress of the reaction a gentle stream of nitrous fumes escapes from the reaction product and a heavy oil is deposited at the bottom of the flask. This is taken out, washed with dilute alkali, dried with a few bits of calcium chloride and distilled. At first some unchanged benzene distils over which is followed by iodobenzene. A very small quantity of *p*-diiodobenzene comes over at the end of the distillation. The iodobenzene obtained boiled at 186–188°. The yield of iodobenzene amounts to 75 to 80% of the theory. As has been pointed out before, a little trinitrophenol is formed as a result of the hydrolysis of iodobenzene and its simultaneous nitration in the presence of nitric acid. This was separated and identified from the reaction product as follows: The crude iodobenzene was washed with dilute caustic potash and the wash water, containing all of the trinitrophenol as its potassium salt, was evaporated to crystallization and the potassium salt purified by repeated crystallization and identified as usual.

Toluene. Preparation of *o*- and *p*-Iodotoluenes.—Toluene on treatment with iodine and nitric acid gives a mixture of *o*- and *p*-iodotoluenes. 21 cc. of toluene, 25.4 g. of iodine and 10 to 12 cc. of nitric acid (sp. gr. 1.35) are boiled under a reflux condenser on a sand bath for two hours. It is well to add the nitric acid in small portions at a time. The progress of the reaction is evident from the steady evolution of nitrous fumes, and at the end of the operation, a heavy oil is deposited. The oil was taken out, washed, dried and distilled. At first unchanged toluene distils over and then iodotoluene, a dark residue finally remaining. The yield of the mixture of *o*- and *p*-iodotoluenes amounts to 60% of the theory. The mixture is placed in a freezing mixture of ice and salt when the *p*-iodotoluene solidifies and is rapidly removed by filtration with suction, while the filtrate consists entirely of *o*-iodotoluene. The *p*-iodotoluene was purified by a second freezing and suction when it melted at 35°.

Calc.: I, 58.25. Found: I, 57.68.

The *o*-iodotoluene was purified by distillation and it boiled at 211–212°.

Calc.: I, 58.25. Found: I, 57.81.

***o*-Xylene. Preparation of 4-Iodo-*o*-xylene.**—*o*-Xylene, when treated with iodine and nitric acid, gives 4-iodo-*o*-xylene. 20 cc. of *o*-xylene and 20 g. of powdered iodine are taken in a flask provided with a reflux condenser and to this 8 to 10 cc. strong nitric acid are gradually added in small portions at a time and the mixture is heated on the sand bath. A reac-

tion soon begins as is evident from the steady evolution of nitrous gases. In the course of an hour and a half the reaction becomes complete and a heavy oil is seen at the bottom. When this is distilled with steam a violet liquid due to some free iodine distils over and a yellow viscous substance remains. The distillate is then treated with dilute alkali, washed, dried and distilled. No unchanged xylene comes over but the distillate consists of almost pure 4-iodo-*o*-xylene boiling at 225°. The yield obtained amounted to 65% of the theory.

Calc.: I, 54.74. Found: I, 54.58.

***m*-Xylene. Preparation of 4-Iodo-*m*-xylene.**—*m*-Xylene when treated with iodine and nitric acid gives 4-iodo-*m*-xylene. 16.8 cc. of *m*-xylene, 15 g. of iodine and 6.8 cc. of concentrated nitric acid are taken in a flask provided with a reflux condenser. The reaction begins at the ordinary temperature (30°), shortly after they are mixed, and upon warming on the water bath for twenty to thirty minutes and the operation is found to be complete, all of the iodine used having been taken up. The deep oil which is formed is then subjected to steam distillation and a yellow viscous substance remaining behind. The distillate is washed, dried and distilled. A little unchanged *m*-xylene distils over and then 4-iodo-*m*-xylene which on redistillation is found to boil at 220°.

Calc.: I, 54.74. Found: I, 54.50.

The yield amounted to 56% of the theory.

***p*-Xylene. Preparation of 2-Iodo-*p*-xylene.**—*p*-Xylene gives 2-iodo-*p*-xylene when treated with iodine and nitric acid. 20 cc. of *p*-xylene are mixed with 18 g. iodine in a flask fitted with a reflux condenser and to the mixture 8 to 10 cc. of concentrated nitric acid are gradually added. The reaction soon begins after warming on the sand bath, as is indicated by the steady evolution of nitrous fumes, and within an hour the reaction is complete. The heavy oil formed is distilled in steam when most of the liquid comes over along with the steam, leaving behind a small quantity of a thick, yellow oil. The distillate is then washed, dried and distilled as usual. At first a very small quantity of *p*-xylene distils and then 2-iodo-*p*-xylene comes over. It is redistilled and is found to boil at 217–218°.

Calc.: I, 54.74. Found: I, 54.45.

The yield amounts to 50% of the theory.

Mesitylene. Preparation of Monoiodomesitylene.—24 cc. of mesitylene and 20 g. of iodine are taken in a flask fitted with a reflux condenser and to this 8 to 10 cc. strong nitric acid are gradually added. Reaction starts even without warming and the mixture is warmed on the sand bath for 30 minutes. It is then distilled in steam, the iodo derivative with some unchanged mesitylene comes over, leaving behind a yellow viscous substance. The oil, after being washed and dried, is placed in a freezing

mixture, when it solidifies almost completely. This is placed upon a suction filter to free it from any unchanged mesitylene. By a repetition of the process, pure monoiodomesitylene is obtained melting at 30.5° . It is necessary to point out that the ordinary temperature of our laboratory being ($25-30^{\circ}$) the operation of filtering and handling of the salt was done in an ice-chamber. The yield obtained is 40% of the theory.

Calc.: I, 51.29. Found: I, 51.62.

Ethyl Benzene. Preparation of Monoiodoethylbenzene.—18 cc. of ethyl benzene are mixed with 14 cc. of powdered iodine and 6–8 cc. strong nitric acid. The mixture is warmed on the water bath with a reflux when the reaction ensues. After 3 to 4 hours the operation is found to be complete. The product is separated by steam distillation. It is then distilled. At first a small quantity of unchanged ethyl benzene distills over and then the iodo derivative. It is redistilled and is found to boil at $221-222^{\circ}$. This is monoiodoethylbenzene, the determination of the constitution of which is deferred for the present. The yield obtained amounts to 30% of the theory.

Calc.: I, 54.74. Found: I, 54.33.

Hexane. Preparation of Iodohexane.—Required proportions of hexane, iodine and nitric acid are taken in a sealed tube and heated in a bomb furnace between $100-130^{\circ}$ for three hours. It is found that the pressure inside the tube due to the reaction is so great that the tube broke each time, giving out large quantities of nitrous fumes. The operation was next carried out thus: 25 cc. of hexane, 20 g. of iodine and 8 to 10 cc. concentrated nitric acid were taken in a flask fitted with a spiral reflux condenser through which ice-cold water was allowed to circulate, as the ordinary temperature is very near the boiling point of the hydrocarbon. The mixture was allowed to boil under reflux on a water bath and the reaction was found to go on slowly, as was evident from the steady evolution of nitrous fumes. At the end of two hours the liquid refluxing became denser and did not distil so easily as before, and the operation is stopped. A deep violet-colored liquid remained out of which a good deal of iodine crystallized on cooling. The violet-colored liquid was then decanted from the lump of iodine, washed, dried and distilled. The greater part of unchanged hexane distilled over after which iodohexane comes over. This was redistilled and was found to boil at 170° . The yield obtained was quite small because a good deal of iodohexane is hydrolyzed by nitric acid as soon as it is formed.

Calc.: I, 59.90. Found: I, 59.57.

Thiophene. Preparation of Monoiodothiophene.—Required proportions of iodine and thiophene are taken in a flask and to this a few drops of concentrated nitric acid are added when a violent action takes place

and fumes are evolved, leaving behind a charred product. Treatment with dilute nitric acid is found to give satisfactory result, but the product is found to char on warming. The experiment was next carried out in the following way:

15 cc. of thiophene are taken in a flask, with 16 g. of iodine, and to this about 10 to 12 cc. of dilute nitric acid (50%) are slowly added in small quantities at a time. The mixture is then kept aside at the ordinary temperature (27°) and is shaken from time to time. After an hour a dark heavy oil is formed which collects under the aqueous layer, and the operation is found to be complete. The oil is then distilled in steam, and almost all of the violet-colored oil is carried away along with steam, leaving only a small amount of a black viscous product. The distillate is washed, dried and distilled. It boils between 180–182° and consists of monoiodothiophene. The yield amounts to 45% of the theory.

Calc.: I, 60.49. Found: I, 59.93.

Naphthalene. Preparation of Monoiodonaphthalene.—10 g. naphthalene are mixed with 10 g. of powdered iodine and the mixture is dissolved in a small quantity of benzene. It is next treated with 5 cc. of concentrated nitric acid and the mixture is warmed on the water bath under reflux for eight hours. After the operation a deep violet-colored oil is left behind with a little unacted-upon iodine and naphthalene. After evaporating off the dissolved benzene, the oil is distilled in steam. A violet-colored oil is carried away along with steam, while a crystalline substance is also found deposited within the condenser, which is found to be unchanged iodine. A yellow viscous heavy oil is left behind within the original flask. The distillate, obtained after steam distillation, consists of a mixture of nitronaphthalene and idonaphthalene which is separated by placing it in freezing mixture. The nitronaphthalene crystallizes out and the iodo derivative is drained off, which is then distilled under reduced pressure.

Calc.: I, 50.00. Found: I, 48.93.

Anthracene.—Anthracene does not yield any iodo derivative on treatment with iodine and nitric acid; on the other hand, it undergoes oxidation to anthraquinone.

1 g. of anthracene was taken in a flask and dissolved in sufficient quantity of chloroform. To this iodine and nitric acid was added and the mixture treated on the sand bath for two hours. At the end, a deep violet-colored oil was found deposited under colorless liquid. The oil was then subjected to steam distillation, after the evaporation of chloroform. Nothing passes over with the steam, showing that no iodo compound was formed. The residue which remained behind was found to consist of a yellow product. It was washed and dried and recrystallized from benzene. The recrystallized sample melted between 240–243°. The

product was found to sublime, when heated. The sublimed crystals melted at 260° and were identified as anthraquinone.

Investigations on similar lines are being continued.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]

HALOGENATION. XVI. IODINATION BY MEANS OF NITROGEN IODIDE OR BY MEANS OF IODINE IN THE PRESENCE OF AMMONIA.

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Iodination of Phenols and Nitrophenols.

The systematic iodination by means of nitrogen iodide, or by means of a potassium iodide solution of iodine in conjunction with liquor ammonia, which represents nitrogen iodide in the nascent state, was not attempted except in a few isolated cases. It has been found that not only the phenolic compound can be iodinated satisfactorily with the production of iodophenols but the nitrophenols can also be iodinated with the formation of idonitrophenols. In the case of the nitrophenols, the further introduction of iodine atoms increases the acidic nature of the phenols and as the formation of idonitrophenols takes place in the presence of ammonia, ammonium salts of varying degree of stability have been produced which have hitherto escaped isolation on account of the feebly acidic and inert nature of these idonitrophenols. It is in the nascent state that the formation of the ammonium salt becomes possible, the direct union of ammonia with the idonitrophenol being not successful.

The action of iodine and ammonia has been studied in the following cases: Phenol gives a quantitative yield of 2,4,6-triiodophenol. *o*-Cresol, *p*-cresol and *m*-cresol give in quantitative yield diiodo-*o*-cresol, diiodo-*p*-cresol and triiodo-*m*-cresol, respectively. From thymol, 6-iodo-thymol has been obtained. 1,4,5-Xylenol has been found to yield a monoiodo-derivative. Phenolphthalein yields tetraiodophenolphthalein. *o*-Nitrophenol gives on iodination 2,4-diiodo-6-nitrophenol which yields a stable ammonium salt. *m*-Nitrophenol yields 2-iodo-3-nitrophenol which, however, yields an unstable ammonium salt which decomposes on keeping. From *p*-nitrophenol 2,6-diiodo-4-nitrophenol has been obtained which does not give any ammonium salt. 3-Nitro-1,4-cresol has been found to yield 5-iodo-3-nitro-1,4-cresol and a stable ammonium salt. The special feature of this reagent is that in all cases quantitative yields of the products are obtained. In view of the fact that both ammonia and iodine in the mother liquor could be conveniently recovered, these methods would serve as the best modes of preparing these iodophenols and idonitrophenols on the large scale.