proper position to an hydroxyl in an adjacent substituent. For the aid granted by the trustees of the Wolcott Gibbs Fund in the prosecution of this research and for the assistance rendered on this account by Messrs. G. O. Gutekunst and Edgar C. Britton the writer wishes to express his appreciation and indebtedness.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]

HALOGENATION. XIV. BROMINATION OF HYDROCARBONS BY MEANS OF BROMINE AND NITRIC ACID.

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Received September 19, 1916.

In continuation of the researches of the action of *aqua regia* on organic bodies in general, the study of the action of a mixture of nitric and hydrobromic acids was taken in hand. In analogy with the action of *aqua regia*, it was thought that a mixture of nitric and hydrobromic acids, which is capable of giving bromine in the nascent state, would effect brominations more satisfactorily than bromine, and this has been found to be the case. The bromination of benzene has been effected by this reagent with the formation of monobromobenzene in good yield. As a considerable amount of nitric acid is used up, in the first instance, to liberate bromine from hydrobromic acid, it was found satisfactory to employ bromine and nitric acid only. In fact, the mixture of the acids is less active than bromine and nitric acid on account of the water added as the medium of hydrobromic acid.

As bromination could as well be carried out directly with or without the help of a carrier, the advantages of the method may be pointed out. In the case of ordinary bromination with or without carrier, the reaction is one of substitution, liberating an amount of hydrobromic acid equal to that of bromine which enters the molecule. But in the case of bromination in the presence of nitric acid, all the bromine enters the molecule, the nitric acid helping the oxidation of hydrobromic acid to bromine, as soon as it is formed. This bromine is available for further bromination. Hence it is evident that only half the usual amount of bromine will be required for brominations by this method. Here the nitric acid acts as the oxidizing agent facilitating the introduction of bromine, itself being reduced to nitrous gases. Furthermore, the reagent is very active, effecting brominations very rapidly and energetically, so much so that frequent rupture of substances subjected to its action is the result. Those brominations which require a considerable time for their course even with the help of a carrier, could be effected most speedily and satisfactorily. The method is specially suitable for tolerably light hydrocarbons but with the higher ones the process is not quite satisfactory as the chances of nitration are also great on account of the strong nitric acid, as has been pointed out before in the course of chlorination by means of *aqua regia.*[1] In fact, the chances of bromination are greater in the lower hydrocarbons whereas, in the cases of higher hydrocarbons the chances of nitration are greater. These also depend upon the specific nature of the compounds.

As has already been pointed out, a mixture of bromine and nitric acid has been found to be quite a satisfactory brominating agent, giving bromo-derivatives with the aromatic hydrocarbons, the proportion of any particular bromo-derivative depending upon the duration of the reaction. It will be shown later that the reagent is very active and has a simultaneous brominating and oxidizing action with the formation of tetrabromoquinone as end product of such actions. With other organic compounds, aliphatic or aromatic, which break up under the influence of this reagent, bromopicrin seems to have been generally produced.

The results obtained in the bromination of hydrocarbons by this reagent are interesting. Benzene gives a good yield of bromobenzene by carrying on the process for a short time. If, however, the process be prolonged for some time, *p*-dibromobenzene is the chief product. Toluene gives *o*-bromotoluene and 3,4-dibromotoluene on short action while pentabromotoluene is formed by the prolonged action of the reagent. *o*-Xylene yields monobromo-*o*-xylene readily, while tetrabrom-xylene is the main product of a prolonged action. In the latter case, the product is accompanied by small quantities of *p*-toluic and *o*-toluic acids due to the prolonged oxidizing influence of nitric acid. From *m*-xylene, monobromo-*m*-xylene as also dibromo-*m*-xylene have been obtained on acting with the reagent for a short time, while tetrabromo-*m*-xylene is the product of a somewhat prolonged action. *p*-Xylene gives monobromo-*p*-xylene and dibromo-*p*-xylene, while the prolonged action produces tetrabromo-*p*-xylene. Mesitylene forms monobromo-mesitylene in the cold, while tribromo-mesitylene is the chief product upon heating. With ethyl benzene, monobromo-ethyl benzene is the chief product, but on prolonged action a complicated product is formed which could not be separated and purified.

Mixture of Hydrobromic and Nitric Acid as a Brominating Reagent.

Bromination of Benzene.—Benzene could be brominated readily by a mixture of hydrobromic and nitric acids with the formation of bromobenzene.

Equal volumes of hydrobromic acid (47%) and nitric acid (sp. gr. 1.35) were gradually mixed in a flask fitted with a reflux condenser and to this benzene is added equal to a fourth part of the acid mixture. The heavy layer of nitrosyl tribromide[2] settles at the bottom while the benzene

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[1] THIS JOURNAL, 36, 1007 (1914).

[2] The detailed description of this substance will be communicated shortly.

floats at the top. The reaction is then started by placing the flask on the water bath, removing it from time to time when the vigor of the reaction becomes uncontrollable, which is evident from the escape of considerable amounts of bromine. All the time during the course of the reaction a steady evolution of nitrous fumes takes place. When the evolution of nitrous fumes has ceased the reaction becomes complete. A heavy brown oil is seen deposited at the bottom of the aqueous layer. This is washed with dilute alkali, dried and then distilled. Unchanged benzene comes over at 80°, then the temperature rises gradually and most of the product comes over between 153–154° which is the boiling point of bromobenzene. The fraction was again redistilled and the identity was established by a bromine estimation.

Calc., Br = 50.95. Found, Br = 50.35.

The yield obtained by this method is quite satisfactory amounting to 80% of the theory.

Bromination by Means of Bromine and Nitric Acid.

Benzene.—When the bromination is carried out with the calculated quantities of bromine and nitric acid for a comparatively short time, bromobenzene is the chief product, whereas, if the bromination be carried on with an excess of bromine and nitric acid for a good length of time, *p*-dibromobenzene is the chief product. Other higher bromo-derivatives of benzene could not be obtained, however long the action is carried out. For the preparation of monobromobenzene 36 cc. of benzene are taken in a flask fitted with a reflux condenser and to this 10 cc. of conc. nitric acid and 10.7 cc. (32 g.) of bromine are gradually added. The reaction does not seem to take place at the ordinary temperature. The flask is then placed on the water bath when the reaction begins to take place, as is evident from a steady evolution of brown fumes of oxides of nitrogen. The operation is continued for five hours with the further addition of a little more nitric acid. The mixture refluxes only slightly at the end due to the conservation of benzene into bromobenzene. The heavy oily layer underneath the aqueous layer is taken out, washed with dilute alkali and then dried by means of calcium chloride. It is next distilled over wire gauze in a flask provided with a two-bulbed still-head. Unchanged benzene comes over at about 80°, then the temperature rises to about 140° when the receiver is changed and bromobenzene is collected until the temperature rises to 170°. A dark, viscous residue is left behind within the flask weighing about 2–3 g., which is a mixture of the higher bromo-derivatives. The fraction 140–170° is redistilled and is found to boil at 153–154°. The yield obtained is 60% of the theory. To establish the complete identity of the substance, bromine in the sample was estimated.

Calc., Br = 50.95. Found, Br = 50.47.

It was thought that by using fuming nitric acid, the course of the reaction could be shortened a good deal, but in practice it was not possible. On the other hand, fuming nitric acid diminished the yield on account of its great hydrolyzing action.

For the preparation of *p*-dibromobenzene, 8 g. of benzene are taken in a flask with 12 g. of bromine and 3 cc. of nitric acid. The mixture is at the first instance warmed on the water bath for six hours, when it is found that the mixture refluxes no more, due to the formation of bromobenzene. Then 12 g. more of bromine are added with 3 cc. of nitric acid and the mixture is heated on a sand bath for six hours more when the operation is found to be complete. The semisolid product is separated from the layer of water and heated in a basin to drive off unchanged benzene and bromine, when, on cooling, it begins to solidify and the solidification is hastened by stirring with a glass rod. The crystals were next pressed between the folds of a blotting paper and then recrystallized from alcohol, when *p*-dibromobenzene is obtained in beautiful plates melting at 87°. The yield obtained is nearly quantitative.

Calc., Br = 67.80. Found, Br = 67.45.

Toluene.—Toluene gives a mixture of *o*-bromotoluene and 3,4-dibromotoluene by carrying the reaction for a very short time, while by carrying on the reaction for a rather long time with an excess of bromine and nitric acid, penta-bromotoluene is the chief product.

For the preparation of *o*-bromo- and dibromotoluene, 10 cc. of toluene are taken in a flask fitted with a reflux condenser and to this 4 cc. of nitric acid (sp. gr. 1.35) are added and to the mixture 6 cc. of bromine are gradually added in small portions at a time. The reaction takes place almost immediately the substances are mixed, and fumes of oxides of nitrogen are evolved. After a short time, the reaction subsides and nitrous fumes cease to evolve. The mixture is further warmed on the sand bath for half an hour more, when the reaction seems to proceed again with the evolution of nitrous fumes and at the end no more of it comes out, proving that the reaction is complete. The deep brown oil formed is next treated with dilute alkali, washed and dried by means of fused calcium chloride. The dried oil is next distilled. No unchanged toluene comes over; the first fraction was collected between 180–190° and the second fraction, between 200–250°. In the distilling flask there remained behind a charred liquid which consists of higher bromo-derivatives of toluene. On redistilling the first fraction 4 cc. (5.3 g.) of *o*-bromotoluene is obtained, boiling at 180°, while from the second fraction 1 cc. of 3,4-dibromotoluene, boiling at 240–241° has been isolated. Yield of *o*-bromotoluene is 40% of the theory.

For the production of pentabromotoluene the following details are carried out: 5 cc. of toluene are taken in a flask fitted with a condenser and to this 2 cc. of nitric acid are added from a pipet and then bromine is added gradually in the course of the reaction in 2 cc. at a time. The mixture is warmed on the sand bath, slowly at first, but gradually increasing the temperature of the bath, when it is found that the heavy liquid formed does not reflux so easily. Bromine and a little nitric acid are added from time to time as they are used up. The operation takes about three hours to complete. A dark brown, pasty product is obtained which is chiefly pentabromotoluene mixed with small quantities of the lower bromo-derivatives. For their separation, steam distillation has been found to be very effective. The lower bromo-derivatives come over with the steam, leaving behind a light yellow crystalline product, which is practically pure pentabromotoluene. The crystals were next washed with ether to free them from adhering impurities in which they are insoluble, giving pure pentabromotoluene. This is sublimed and the sublimed product is found to melt at 280°. The yield obtained is nearly quantitative.

Calc., Br = 82.13. Found, Br = 81.66.

In the case of toluene, a sweet smell is noticed during the progress of the reaction, which is especially noticeable when purifying the products. This sweet smelling vapor attacks the eyes most powerfully, causing an abundance of tears and considerable amount of pain. This is due to the formation of a small quantity of benzyl bromide.

_o_-Xylene.—This yields monobromo-*o*-xylene by the short action of bromine and nitric acid, while by the prolonged action, tetrabrom-*o*-xylene is obtained accompanied by *o*- and *p*-toluic acids. For the preparation of monobromo-*o*-xylene, 10 cc. of *o*-xylene are taken in a flask provided with a reflux condenser and to this about 5 cc. of strong nitric acid and 8 g. of bromine are added. The reaction at once starts in with the evolution of brown fumes. After the reaction has subsided the material is warmed on the sand bath for about half an hour, when the operation is found to be complete. The oil is washed, dried and distilled. At first a little unchanged *o*-xylene comes out, then the temperature rises rapidly to 210° and the liquid distilling between 210–220° is collected separately. After a second distillation it is found to consist of pure monobromo-*o*-xylene boiling at 214–215°, the yield obtained being 6 cc. (8.22 g.) or 60% of the theory.

Calc., Br = 43.24. Found, Br = 42.95.

The prolonged bromination of *o*-xylene is carried out as follows: 4 cc. of *o*-xylene are taken in a flask provided with a ground reflux condenser and to this about 2 cc. of strong nitric acid are added and bromine in considerable excess in small quantities from time to time. The whole mixture is heated on the sand bath for about ten hours, when a semisolid product is obtained. The semisolid mass is warmed on the water bath to free it from unchanged bromine. A brown oily substance is left behind, which is boiled with distilled water. The aqueous extract is decanted off and is allowed to evaporate on the water bath, when a white crystalline substance is obtained, which is found on examination to be *p*-toluic acid melting at 180°. The yellow oil obtained in the above operation is found to crystallize when kept aside for a day or two. It is next extracted by means of alcohol, when a part dissolves and gives crystals on evaporation which has been found to melt at 101° and on examination is found to be *o*-toluic acid.

The white crystalline substance remaining after alcoholic extraction is found to consist of impure tetrabromo-*o*-xylene, which could, however, be purified with difficulty. It melts between 250° and 256°.

Calc., Br = 75.82. Found, Br = 75.22.

m-**Xylene** forms a mixture of monobromoxylene and dibromoxylene by the action of bromine and nitric acid, but the product is tetrabromoxylene if the reaction be prolonged for a considerable time. For the preparation of monobromoxylene and dibromoxylene, 10 cc. of *m*-xylene are mixed with 5 cc. of strong nitric acid and 15 g. of bromine, when the reaction starts itself in the cold. After the first action has subsided the reaction mixture is warmed on the water bath for about two hours. The heavy oil that is found to have formed in the reaction is next washed, dried and distilled. Practically no unchanged xylene comes over. The distillate is collected in two fractions, one between 200–210° and the other between 245–260°. The first portion consists mainly of monobromo-*m*-xylene and the second portion contains dibromo-*m*-xylene. The first fraction is redistilled and found to boil at 205°. The yield of the monobromo-derivative obtained is 4 g.

Calc., Br = 43.24. Found, Br = 42.67.

The second fraction solidifies completely after allowing it to stand for some time. The crystals are pressed to free it from adhering liquor and then recrystallized and it is found to melt at 68°, the yield obtained being 4.5 g.

Calc., Br = 66.60. Found, Br = 60.27.

For the preparation of tetrabromoxylene 12 cc. of *m*-xylene are heated in the above manner with 4 cc. of nitric acid and an excess of bromine. The mixture is heated on the sand bath for ten hours, bromine being added in small quantities at a time. Occasional replenishing of nitric acid is also necessary. At the end of the operation a semisolid brown mass is obtained. It is first warmed on the water bath to drive off any free bromine present in it. The mass is boiled with water and on cooling the aqueous extract yields beautiful, white silky crystals. The crystals thus obtained are found to be pure tetrabromo-*m*-xylene, melting at 241°. The yield obtained is 6 g.

Calc., Br = 75.82. Found, Br = 75.34.

It is necessary to point out that the crystals obtained as the result of first solution in hot water consists of pure tetrabromo-xylene, while the product from subsequent washings contain impurities in the shape of lower bromo-derivatives. The yellow, viscous liquid consists of lower bromoxylenes amounting to 2.4 g. This can be separated, by the method given before, into monobromo- and dibromoxylenes.

***p*-Xylene.**—Eight cc. of *p*-xylene are taken in a flask with 2 cc. of conc. nitric acid and 2 cc. of bromine. Within a short time the reaction begins and nitrous fumes are seen to evolve. After warming on sand bath for fifteen or twenty minutes, the reaction is found to be complete. The oil is next washed, dried and distilled. At first only a small quantity of unchanged xylene comes over between 130–140°. Then the thermometer rises rapidly and monobromo-*p*-xylene distills over between 195–205°, the next fraction distilling between 255–265°, which consists of dibromo-derivative. The first fraction is redistilled and is found to boil at 199–200°. The yield obtained is 5 cc. (6.96 g.), *i. e.*, 55% of the theory.

Calc., Br = 43.24. Found, Br = 42.83.

The second fraction is purified by freezing, on placing it in a mixture of ice and salt. The crystals are pressed out from the adhering impurities. It melts at 75° and is found to be pure 2,5(s)dibromo-*p*-xylene. The yield obtained being 2 cc.

Calc., Br = 60.60. Found, Br = 60.12.

For the preparation of the higher bromo-derivatives of *p*-xylene, 4 cc. of *p*-xylene are heated on a sand bath for about twelve hours with nitric acid and bromine; the latter is added in small quantities from time to time. At the end a semisolid product is obtained which is freed from unchanged bromine by heating on water bath. The solid mass consists of a mixture of *p*-toluic acid and tetrabromo-*p*-xylene. A partial separation can be effected by treatment with alcohol but a complete separation to obtain pure products was not found successful.

Mesitylene.—Seven and five-tenths cc. of mesitylene are taken in a flask with a ground condenser and to it 2 cc. of nitric acid and 2 cc. of bromine are added. Reaction at once sets in and it is completed by warming for a few minutes on the sand bath. The heavy oil which is formed as a product of the reaction is washed, dried and distilled. It contains practically no unchanged mesitylene, the greater part is monobromo-mesitylene and comes over between 230–233°. The yield obtained is 4 g., or 46% of the theory.

Calc., Br = 40.21. Found, Br = 39.98.

A tarry residue is left behind in the flask which is a mixture of the higher bromo-derivatives.

By the prolonged action of bromine and nitric acid on mesitylene, tribromo-mesitylene is the chief product.

7.5 cc. of mesitylene are treated with 3 cc. of nitric acid and 6 cc. of bromine. The reaction starts at once and it is continued on a sand bath for three hours; bromine and nitric acid are added gradually in small portions at a time. A semisolid mass is obtained which is warmed on a basin with water to drive off the volatile matter. The product solidifies on cooling and consists of practically pure tribromo-mesitylene. The product on washing with benzene leaves behind white, silky crystals which are found to be pure tribromo-mesitylene, melting at 222–223°. The yield obtained is 5.5 g. of tribromo-mesitylene, or 33% of the theory.

Calc., Br = 67.22. Found, Br = 66.83.

Ethyl Benzene.—Ethyl benzene gives on short bromination with bromine and nitric acid, a mixture of *o*- and *p*-bromoethyl-benzene. For its preparation, 7 cc. of ethyl benzene are treated with 3 cc. of nitric acid and 4 cc. of bromine. The reaction begins at once with the evolution of nitrous fumes and generally the reaction becomes complete even without warming. The resulting product is washed, dried and distilled. After the passing out of unchanged ethyl benzene, the greater part boiled between 202–204°, which is a mixture of *o*-bromoethyl-benzene and *p*-bromoethyl-benzene. The yield obtained is 6 g., or 55% of theory.

Calc., Br = 43.24. Found, Br = 42.11.

After the distillation, a charred residue is left behind in the flask which is a mixture of higher bromo-derivatives of ethyl benzene.

Investigations on similar lines are being continued.

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[CONTRIBUTION FROM THE EXPLOSIVES LABORATORY OF THE BUREAU OF MINES, DEPARTMENT OF THE INTERIOR.]

APPLICATION OF THE NITROMETER FOR THE DETERMINATION OF CONSTITUTION AND ESTIMATION OF NITROGEN IN A CLASS OF NITROCOMPOUNDS. (NITROAMINES.)[1]

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Received September 21, 1916.

The nitrometer reaction was first noted by Crum[2] in 1847; but it was not until 1878 when Lunge[3] succeeded in developing a practical instrument which he called the "nitrometer" that this reaction came into general use. Undoubtedly the most common application of the nitrometer is for

[1] Published by permission of Director. Bureau of Mines.

[2] *Phil. Mag.*, [3] 30, 426 (1847).

[3] *Ber.*, **11**, 436; *Chem. News*, **38**, 18 (1878); *Dingler's Polytech. J.*, **228**, 448 (1878).