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HALOGENATION XX. THE REPLACEMENT OF SULFONIC ACID GROUPS BY HALOGENS.

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In a previous communication¹ investigations were described which showed that in few cases, chlorine could replace the sulfonic acid groups in aromatic compounds with the simultaneous production of aromatic chloro compounds. Further studies have proved that with chlorine and bromine this replacement takes place in aromatic compounds generally and may occur with iodine under special conditions. It frequently happens that a halogen atom not only takes the place of the existing sulfonic acid group, but more halogen atoms usually enter the ring with the formation of higher halogen derivatives. This has been found to be a perfectly general method for the preparation of aromatic halogen derivatives.

In ordinary halogenation, 2 difficulties arise; either the halogen atom enters the ring very slowly, or the vigor of the reaction causes considerable charring of the compound with a corresponding diminution in the yield. It has been found that the sulfonic acid group prevents the charring of the substances and in most cases, a satisfactory yield of pure halogen derivative can be obtained. This method also leads to the production of many halogen derivatives which previously could not be prepared. Another advantage of this method lies in the fact that it frequently leads to the determination of the constitutions of halogen compounds, provided the positions of the sulfonic groups in the sulfonic acid derivatives are known.

Groups already present in the nucleus exert a great influence upon the replacement. A general rule has been observed to govern the mode of reaction. Thus, the replacement of sulfonic acid groups by bromine takes place readily at ordinary temperatures in the case of compounds with one or more hydroxyl groups attached to the nucleus. The same replacement of sulfonic acid groups takes place readily by means of chlorine² and nitrous gases,³ in the latter case nitro compounds being formed. Furthermore, the replacement of sulfonic acid groups takes place also in the case of compounds with an amino group in the nucleus. This replacement of sulfonic acid group by nitro group by means of nitrous gases has also been found to take place with very great facility, though the original amino group is hydrolyzed at the same time into hydroxyl group by the action of nitrous gases.⁴ The presence of nitro groups, on the

¹ Datta and Mitter, *THIS JOURNAL*, 41, 2028 (1919).

² Datta and Mitter, *loc. cit.*

³ Datta and Varma, *THIS JOURNAL*, 41, 2039 (1919); U. S. Pat. 1,292,266, 1919.

⁴ Datta and Varma, Brit. Pat. 126,321, 1919.

other hand, retards the replacement of sulfonic acid groups, since nitrophenols and nitro-anilines have been found to be a little less reactive, although even in these cases the yields are good. In the case of hydroxycarboxylic acid, the replacement of sulfonic groups takes place by halogens although at the same time the carboxyl group is detached giving hydroxy haloid derivatives. An exactly similar reaction has been found to take place in the case of replacement of sulfonic acid group in hydroxycarboxylic acids by means of nitrous gases, carboxylic acid being split off and nitrophenols generated.¹

The reactivity is still less sluggish in the case of aromatic compounds already substituted by means of halogen atoms. Thus bromobenzene sulfonic acid gives with great difficulty the corresponding dibromo derivative and in the case of iodobenzene the replacement does not take place at all, though in the case of replacement by nitro group, nitrous gases can effect the substitution of sulfonic group in iodobenzene sulfonic acid with the production of iodo-nitrobenzene.

In the case of substitution by one or more alkyl groups, the replacement is difficult. In the case of toluene sulfonic acid, the replacement could not be effected by chlorine though it could be effected by bromine with very great difficulty. In the case of xylenes and mesitylene, the replacement of the sulfonic acid group is slightly easier, and chlorine and bromine could effect the replacement which is evidently due to the presence of more alkyl groups in the nucleus. When there are no groups in the benzene ring as in the case of benzene sulfonic acid, the replacement of sulfonic acid group does not take place at all.

Instead of free bromine, it has been found that a mixture of alkali bromide and bromate acts better in the replacement of sulfonic groups, since by this means the bromine is liberated very gradually with simultaneous substitution and the chances of charring and secondary reactions eliminated altogether. This reaction has the further advantage of being more active than that of free bromine alone. This process has been examined in some typical cases such as the sulfonic acids of phenol, phenetol, aniline, mesitylene, toluene, dimethyl-hydroquinone, guaiacol and naphthol, triphenylmethane, dibenzyl, retene, xanthone. Benzene sulfonic acid gives bromobenzene sulfonic acid on treatment with bromide and bromate. Toluene sulfonic acid on warming with bromide and bromate gives readily tribromo-*o*-toluene, whereas with free bromine the reaction takes place very slowly and only on long contact.

Similarly, a mixture of chlorate and chloride effects the replacement of sulfonic groups by chlorine but the results obtained were no better than those with chlorine itself. But a mixture of potassium iodide and iodate effected the replacement of the sulfonic group by iodine in mesitylene

¹ Datta and Varma, *loc. cit.*

sulfonic acid giving iodomesitylene, although the reaction fails altogether in the case of ordinary free iodine.

Moreover, it has been found that the detachment of the sulfonic acid group by halogens and nitro groups takes place more easily in the case of a monosulfonic acid than in the case of a di- or a trisulfonic acid. On this account, the monosulfonic acid is to be preferred in the preparation of its bromo derivatives.

The results are summarized below.

In the case of phenol sulfonic acid, bromine is immediately taken up and 2,4,6-tribromophenol is obtained. *o*-Cresol sulfonic acids give 3,5-dibromo-*o*-cresol; *m*-cresol sulfonic acids give 2,4,6-tribromo-*m*-cresol; and *p*-cresol sulfonic acids, 2,3,5-tribromo-*p*-cresol. With the sulfonic acid of 1,2,4-xylene, a new bromo product, 3,6-dibromo-1,2,4-xylene, m. p. 106°, is obtained; whereas the sulfonic acid of 1,3,4-xylene gives 2,5,6-tribromo-*m*-xylene. With carvacrol and thymol sulfonic acids, the detachment of the sulfonic acid groups occurs at the temperature of a water-bath; 3,5-dibromo-carvacrol and 2,6-dibromothymol, respectively, are formed. The action of bromine upon the sulfonic acids dihydrophenols is vigorous and the reaction should be carried out with pure sulfonic acids and very gradually. Resorcinol sulfonic acid gives 2,4,6-tribromo-resorcinol and hydroquinone sulfonic acid gives 2,3,5-tetrabromo-hydroquinone, whereas the sulfonic acid of orcinol is converted quantitatively into 2,2,4,4,5-pentabromo-resorcinol.

Catechol sulfonic acid in aqueous solution is oxidized by bromine. This is generally the case with those compounds which have 2 hydroxyl groups *ortho* to one another. By the action of bromine upon α - and β -naphthol sulfonic acids in aqueous solution, no bromo product is obtained. The result is a mixture of a various oxidation products. With very dilute bromine water a small amount of dibromo- α -naphthol (m. p. 110°) was obtained. Bromine acts upon phenetol sulfonic acid in aqueous solution to give a quantitative yield of 2,4,6-tribromo-phenetol, but no bromo product has been obtained by the action of bromine upon an aqueous solution of sulfonic acids of guaiacol or the dimethyl ether of hydroquinone. The sulfonic acids of *o*-, *m*- and *p*-nitrophenols yield 4,6-dibromo-*o*-nitrophenol, 2,4,6-tribromo-*m*-nitrophenol and 2,6-dibromo-*p*-nitrophenol, respectively, whereas the acid derived from 2,4-dinitrophenol gives 2,4-dinitro-6-bromophenol.

The replacement of the sulfonic acid group is an advantageous means for the preparation of tribromo compounds of aniline and *m*-toluidine, but with *o*- and *p*-toluidine sulfonic acid, the reaction is unsatisfactory. Care must be taken that the base has been completely sulfonated; if this precaution is not observed, a charred product will result.

In a similar way, sulfonic acids of *o*-, *m*- and *p*-nitro-anilines have given

4,6-dibromo-*o*-nitro-aniline, 2,4,6-tribromo-*m*-toluidine and 2,6-dibromo-*p*-nitro-aniline, respectively.

When sulfonic acids of the carboxylic acids are treated with bromine, the sulfonic acid groups as well as the carboxyl groups are eliminated simultaneously to form bromo compounds. Thus, the sulfonic acids of salicylic acid and of *p*-hydroxy-benzoic acid both give a quantitative yield of *s*-tribromophenol. This change occurs when the sulfonic acids with an excess of bromine are warmed on a water-bath, and is accompanied by a perceptible evolution of carbon dioxide. This is more evident in the case of the sulfonic acids of dihydroxy-carboxylic acids where the elimination of the carboxyl groups as carbon dioxide takes place when a solution of the acid is merely shaken with bromine. The reaction is completed at the temperature of a water-bath. Thus, *s*-tribromo-resorcinol has been obtained by the action of bromine upon the sulfonic acids of 2,4-dihydroxy-benzoic acid.

If toluene sulfonic acid is allowed to stand in contact with bromine for several days, about 40% of the calculated amount of 2,4,5-tribromotoluene is obtained. But, in the case of xylene sulfonic acids, the sulfonic acid group is eliminated when the sulfonic acids are warmed with bromine, though the yield is greater when the sulfonic acid solution is kept in contact with bromine for 2 or 3 days, and is subsequently warmed. Thus, *m*-xylene sulfonic acid gives 4,5-dibromo-*m*-xylene or 2,4,5,6-tetrabromo-*m*-xylene according to differences in the conditions, whereas *p*-xylene sulfonic acid gives 2,5-dibromo-*p*-xylene. Mesitylene sulfonic acid gives a quantitative yield of 2,4,6-tribromo-mesitylene when it is warmed with bromine. Ethylbenzene sulfonic acid forms an exception; it yields no product with bromine.

Sulfonic acids of diphenyl and of naphthalene behave as substituted benzene derivatives. This diphenyl sulfonic acid yields about 13% of *p,p'*-dibromo-diphenyl. Naphthalene sulfonic acids behave in a peculiar manner; the detachment of the sulfonic acid group does not take place with the β -sulfonic acid of naphthalene, but when bromine acts upon the α -sulfonic acid, 1,5-dibromo- and 1,7-dibromo-naphthalene, as well as naphthalene are formed, even at ordinary temperature; *i. e.*, in the latter case, the detachment of the sulfonic acid group takes place, but no bromine enters the nucleus.

No detachment of the sulfonic acid group and no formation of a bromo-derivative have been observed in the case of the sulfonic acids of benzene, of ethyl benzene, of iodobenzene, of dibenzyl, of triphenylmethane, or with those of complex hydrocarbons, such as retene or the complex ketone, xanthone.

In some instances the action of chlorine has been observed to produce an oxidizing effect more pronounced than that caused by bromine, es-

pecially if there are easily oxidizable 2 groups *para* or *ortho* to each other. In aniline sulfonic acid, where the sulfonic group is *para* to the amine group, chlorine eliminates both groups by oxidation with the simultaneous formation of chloroquinone and other secondary products. The action is so vigorous that no means could be found to moderate it. But, in the case of dihydroxy phenols whose sulfonic acids are easily oxidized by chlorine, it has been found that definite products can be obtained by regulating the process. Thus, catechol and quinol sulfonic acids when acted upon by chlorine in a medium of acetic acid yield tetrachloro-*o*-quinone and tetrachloro-*p*-quinone, respectively, as the principal products. Resorcinol sulfonic acid, however, gives no definite product, because of the great reactivity of its chloro compound. Sulfonic acids of dimethyl-hydroquinone and of guaiacol give no chloro-product with chlorine. Bromine showed a similar behavior.

Xylenol sulfonic acids yielded chloro products which were hitherto unknown. Thus, 1,4,5-xylenol sulfonic acid gives a dichloro-xylenol, m. p. 84°, and 1,2,4-xylenol sulfonic acid yields a dichloro-xylenol which boils at 232°.

Chlorine acts upon the sulfonic acids of *p*-xylene, mesitylene and bromobenzene to give 2,5-dichloro-*p*-xylene, 2,4,6-trichloro-mesitylene and *p*-chlorobromo-benzene respectively, though the yields of these products are poor compared with those produced by the similar action of bromine.

Experimental.

Replacement by Bromine.

Phenol.—By the action of liquid bromine upon an aqueous solution of phenol-monosulfonic acid, the sulfonic acid group is detached; a quantitative yield of 2,4,6-tribromophenol results. After recrystallization from glacial acetic the product melted at 96°.

Subs., 0.0732; AgBr, 0.1240.

Calc. for $C_6H_2Br_3(OH)$: Br, 72.51. Found: 72.07.

Its identity was also confirmed by a determination of the melting point of a mixture of it with a known sample of the bromophenol. No change in melting point was observed.

***o*-Cresol.**—By the action of bromine upon *m*-cresol sulfonic acid, obtained by the action of sulfuric acid upon *m*-cresol, the sulfonic acid group is detached with the formation of 2,4,6-tribromo-*m*-cresol quantitatively. After recrystallization from alcohol, the product melted at 81°.

Subs., 0.0994; AgBr, 0.1620.

Calc. for $C_6H(OH)(CH_3)Br_3$: Br, 69.56. Found: 69.34.

***p*-Cresol.**—When *p*-cresol sulfonic acid prepared by warming cresol with fuming sulfuric acid was treated with bromine, 2,3,5-tribromo-*p*-cresol was obtained. Yield, 90%. After recrystallization from alcohol it melted at 96°.

Subs., 0.0959; AgBr, 0.1560.

Calc. for $C_6H(OH)(CH_3)Br_3$: Br, 69.56. Found: 69.12.

1,2,4-Xylenol.—Liquid bromine acts upon a solution of 1,2,4-xylenol sulfonic acid to give a quantitative yield of 3,6-dibromo-1,2,4-xylenol, a new compound.

If an aqueous solution of xylenol sulfonic acid, obtained by warming xylenol with sulfuric acid is shaken with bromine, a white flocculent precipitate is formed. The reaction may be completed by application of heat. After recrystallization from glacial acetic acid the product melts sharply at 106°.

Subs., 0.0930: AgBr, 0.1260.

Calc. for $C_8HBr_2(CH_3)_2OH$: Br, 57.14. Found: 57.65.

Only one dibromo derivative, *viz.*, 3,5-dibromo-1,2,4-xylenol, is known. This compound melts at 39° to 40°. It is evident that the compound obtained by us must be a second dibromo compound, which shows that one bromine atom must be in Position 6 and the other one either in Position 3 or 5. Moreover, since the position of the sulfonic group in the monosulfonic acid is unknown, the fact of its displacement by bromine does not carry us further in our knowledge of orientation of the bromo compound. From the standpoint of the empirical law of the positions taken up by the groups entering the nucleus, the chances are equal that the bromine atom has entered the Position 3 or Position 5.

However, a consideration of other cases throws some light on this question. Thus, with 1,4,2-xylenol, it is found that there are 2 dibromides, *viz.*, 3,5-dibromo-1,4,2-xylenol and 3,6-dibromo-1,4,2-xylenol; the melting point of the former is 79°, and that of the latter is 90°, which shows that the melting point is higher when the 2 atoms of bromine are *para* to each other than when they are relatively in the *meta* position. This is the case generally. Moreover, the 5,6-dibromide of 1,4,2-xylenol and also of 1,3,4-xylenol, *i. e.*, compounds with the 2 bromine atoms side by side are unknown. Hence, it is most likely that the second bromine atom of the dibromide prepared by us is in Position 3, *i. e.*, *para* to the first bromine atom. The fact that a bromine atom in Position 5 would give a more unsymmetrical molecule increases the probability that bromine in the compound in question occupies Position 3.

From these facts and considerations it is evident that the product can only be 3,6-dibromo-1,2,4-xylenol.

It is a white crystalline substance insoluble in water, but partially decomposed by contact with it, giving a red tint. It is soluble in alcohol and in acetic acid. It is purified by recrystallization from glacial acetic acid. It gives up part of its bromine when it is heated with alcohol.

1,3,4-Xylenol.—By the action of bromine upon an aqueous solution of 1,3,4-xylenol monosulfonic acid obtained by warming xylenol with sulfuric acid, a quantitative yield of 2,5,6-tribromo-1,3,4-xylenol melting at 178° has been obtained.

Subs., 0.0533: AgBr, 0.0831.

Calc. for $C_8(CH_3)_2(OH)Br_3$: Br, 66.85. Found: 66.34.

Carvacrol and Thymol.—When an aqueous solution of carvacrol sulfonic acid obtained by warming carvacrol with fuming sulfuric acid is treated with a slight excess of bromine and finally warmed, an oil is produced which boils at 215–220° with decomposition. The product was dehydrated over fused calcium chloride and then distilled under reduced pressure. It has been identified as 3,5-dibromo-carvacrol.

Subs., 0.2660: AgBr, 0.3140.

Calc. for $C_8H(CH_3)(OH)(C_3H_7)Br_2$: Br, 51.95. Found: 50.23.

In a similar way 2,6-dibromo-thymol has been prepared from thymol sulfonic acid obtained by the action of sulfuric acid upon thymol. This substance distilled, with decomposition, between 180° and 186° .

Resorcinol.—When an aqueous solution of resorcinol sulfonic acid, obtained from resorcinol with sulfuric acid is shaken with a slight excess of bromine, a quantitative yield of 2,4,6-tribromo-resorcinol is obtained. After recrystallization it melts at 111° .

Subs., 0.1140: AgBr, 0.1842.

Calc. for $C_6H(OH)_2Br_3$: Br, 69.16. Found: 68.75.

Quinol.—A mixture of 2 g. of hydroquinone added slowly to sulfuric acid prepared from 4 cc. of conc. sulfuric and 2 cc. of fuming sulfuric acid, was heated to 50° for 3 hours. The sulfonic acid crystals thus formed dissolve when the product is diluted with water. When 3 cc. of bromine is added and the solution is shaken vigorously golden plates separate slowly. These crystals are soluble in hot water. They may be purified by recrystallization from glacial acetic acid. The product melts sharply at 137° and has been identified as 2,3,5-tribromoquinol. Special care must be taken in sulfonating hydroquinone since by strong heat or excess of acid, the reaction mixture will char; whereas, if less acid be added the reaction is only partial. The action of bromine gives good results only when bromine is added in slight excess.

Subs., 0.0900: AgBr, 0.1450.

Calc. for $C_6H(OH)_2Br_3$: Br, 69.15. Found: 68.57.

Orcinol.—When an aqueous solution of orcinol disulfonic acid, obtained by heating 4 g. of orcinol with 8 cc. of conc. sulfuric acid to 60 – 80° for an hour, is shaken with 8 cc. of bromine, a flocculent precipitate is obtained. This product is washed and recrystallized from glacial acetic acid, giving pure crystals which melt at 125° . The product has been identified as 2,2,4,4,6-pentabromo-orcinol. Yield, about 15 g.

Subs., 0.2880: AgBr, 0.5220.

Calc. for $C_7H_3O_2Br_5$: Br, 77.07. Found: 77.13.

If bromine is not added in slight excess, it has been found that tribromo-orcinol (m. p. 98°) is formed at the same time.

Phenetol.—When an aqueous solution of phenetol sulfonic acid obtained by heating phenetol with sulfuric acid for 2 hours at 90° , is shaken thoroughly with bromine, 2,4,6-tribromophenetol is formed. Yield, 50%. After recrystallization from acetic acid it melts at 74° .

Subs., 0.1038: AgBr, 0.1620.

Calc. for $C_2H_5O.C_6H_2Br_3$: Br, 66.84. Found: 66.42.

***o*-Nitrophenol.**—Three g. of *o*-nitrophenol was warmed with 2.5 cc. of fuming sulfuric acid on the water-bath. This gave *o*-nitrophenol-4-sulfonic acid. This product was cooled and diluted with water to secure a clear solution of the sulfonic acid. Then 3 cc. of bromine was added gradually and the mixture was heated on the water-bath. Yellow plates separated which melted at 117° after recrystallization from glacial acetic acid. This compound is 4,6-dibromo-*o*-nitrophenol. Yield, about 3 g., a little more than 50% of the calculated amount.

Subs., 0.1509: AgBr, 0.1899.

Calc. for $C_6H_2(OH)(NO_2)Br_2$: Br, 53.87. Found: 53.57.

When bromine is added in smaller quantity, only partial detachment of the sulfonic acid group occurs and bromo-sulfonic acid is produced at the same time; whereas,

on the addition of an excess of bromine, the whole product resinifies. The yield is good only when 2 mols of bromine are added.

m-Nitrophenol.—A mixture of 2 g. of *m*-nitrophenol and 3 cc. of fuming sulfuric acid was heated at 50° to 60° for about 3 hours. The product dissolved when water was added. The addition of an excess of bromine (4 cc.) to the warm solution caused an oil to separate. This oil solidified as the material cooled. It was recrystallized from absolute alcohol or from glacial acetic acid. The bromo derivative obtained had a sharp melting point of 86°, and has been identified as 2,4,6-tribromo-*m*-nitrophenol.

Subs., 0.1200: AgBr, 0.1782.

Calc. for $C_6H_3(OH)(NO_2)Br_3$: Br, 63.83. Found: 63.19.

The yield of the 2,4,6-tribromo-*m*-nitrophenol was 5 g.

p-Nitrophenol.—Four g. of *p*-nitrophenol was added gradually to 8 cc. of fuming sulfuric acid well cooled by ice, and after this mixture had been stirred for about 2 hours, ice-cold water was added, precipitating crystals of sulfonic acid which dissolved as the solution became more dilute. Six cc. of bromine was added slowly and the mixture was heated on a water-bath. This produced a substance which melted at 141° after recrystallization from glacial acetic acid, and was identified as 2,6-dibromo-*p*-nitrophenol. Yield, 8 g., or more than 90% of the calculated amount.

Subs., 0.1326: AgBr, 0.1675.

Calc. for $C_6H_2(OH)(NO_2)Br_2$: Br, 53.87. Found: 53.75.

2,4-Dinitrophenol.—When an aqueous solution of 2,4-dinitrophenol sulfonic acid obtained by dissolving one part of dinitrophenol in 5 parts of sulfuric acid was warmed with bromine, 2,4-dinitro-6-bromophenol was obtained in more than 50% yield. After recrystallization from glacial acetic acid the product melted at 118°.

Subs., 0.1602: AgBr, 0.1140.

Calc. for $C_6H_2(NO_2)_2(OH)Br$: Br, 30.28. Found: 30.42.

Aniline.—By the action of bromine vapor or of dilute bromine water upon sulfanilic acid suspended in water, or upon an aqueous solution of aniline sulfonic acid obtained by heating aniline with fuming sulfuric acid at 100°, 2,4,6-tribromo-aniline has been obtained in almost quantitative amount. After recrystallization from acetic acid the product melted at 118°. A mixture of these crystals with a sample of 2,4,6-tribromo-aniline had the same melting point.

m-Toluidine.—Two cc. of *m*-toluidine mixed with 3 cc. of fuming sulfuric acid was heated to 160–175° for about 3 hours, producing a solid mixture of *m*-toluidine-3-sulfonic acid and 2,4-disulfonic acid. Water was added and bromine vapor was passed into the mixture while it was stirred constantly. At first the bromosulfonic acid appeared, but when bromine was added in excess, as shown by the persistent color of bromine, a flocculent precipitate was obtained. This was then filtered and recrystallized from glacial acetic acid. The crystals melted sharply at 97°. It is 2,4,6-tribromo-*m*-toluidine. Yield, 60% of the calculated amount.

Subs., 0.0690: AgBr, 0.1120.

Calc. for $C_6H(NH_2)(CH_3)Br_3$: Br, 69.76. Found: 69.07.

o-Nitro-aniline.—One g. of *o*-nitro-aniline was dissolved in 5 cc. of fuming sulfuric acid. When this solution was heated on the water-bath for about 2 hours, *o*-nitro-aniline-4-sulfonic acid was formed. This was mixed with water and heated with animal charcoal to remove the color caused by slight charring of the product. After this solution had been filtered an aqueous solution of bromine was added to it and it was shaken until the color of bromine remained permanent. When the excess of bromine was driven off by application of heat, golden crystals were formed in more than 70% yield. After

recrystallization from glacial acetic acid the compound melted at 124–125°. It has been identified as 4,6-dibromo-*o*-nitro-aniline.

Subs., 0.0809; AgBr, 0.1033.

Calc. for $C_6H_2(NO_2)(NH_2)Br_2$: Br, 54.05. Found: 54.35.

m-Nitro-aniline.—One g. of *m*-nitro-aniline was added to 4 g. of solid fuming sulfuric acid well-cooled in a bath of ice. The temperature was raised slowly to 160° and the mixture was heated for about 3 hours when a sample of it dissolved in water left no residue. By this process, *m*-nitro-aniline-6-sulfonic acid was formed. This product was diluted with water and bromine water was added, while the solution was stirred until the color of the bromine remained permanent. When this mixture was heated on the water-bath, a yellow flocculent precipitate was formed which melted at 102° after it had been recrystallized from glacial acetic acid. This substance has been identified as 2,4,6-tribromo-*m*-nitro-aniline. Yield, about 2 g.

Subs., 0.0829; AgBr, 0.1229.

Calc. for $C_6H_2(NO_2)(NH_2)Br_3$: Br, 63.98. Found: 63.02.

p-Nitro-aniline.—Two g. of *p*-nitro-aniline was heated with 4 cc. of sulfuric acid about 140°, until a sample dissolved completely in water. Thus *p*-nitro-aniline sulfonic acid was formed. This product was diluted with water and bromine was added in slight excess. As this mixture was warmed, a flocculent precipitate was formed which melted at 203° after recrystallization. Ordinarily, a little bromosulfonic acid is produced but when the reaction is conducted at elevated temperatures and bromine is added in slight excess, the yield of 2,6-dibromo-*p*-nitro-aniline is almost quantitative.

Subs., 0.1042; AgBr, 0.1328.

Calc. for $C_6H_2(NO_2)(NH_2)Br_2$: Br, 54.05. Found: 54.20.

p-Oxybenzoic Acid and Salicylic Acid.—The *p*-hydroxybenzoic acid-3-sulfonic acid is prepared generally by passing sulfur trioxide into a chloroform solution of *p*-hydroxybenzoic acid; but it has been found that *p*-hydroxybenzoic acid is converted into its sulfonic acid when it is heated with about twice its own weight of ordinary fuming sulfuric acid (containing about 20% of sulfur trioxide) on an oil-bath and the temperature is gradually raised to about 180° and maintained at this temperature until a sample of the product is completely soluble in cold water.

An aqueous solution of this acid was treated with bromine and shaken, causing an evolution of gas. After the reaction had subsided, the solution was warmed. This procedure gave liquid 2,4,6-tribromophenol which solidified when it cooled, and, recrystallized, melted at 94–95°. Its identity was established by a mixed melting-point determination. When the reaction is conducted in a warm solution, the yield is approximately quantitative.

Similarly, by the action of bromine upon an aqueous solution of sulfosalicylic acid, formed by heating salicylic acid with fuming sulfuric acid at 160–170° for 2 hours, a quantitative yield of the same 2,4,6-tribromophenol has been obtained.

2,4-Dioxybenzoic Acid.—Two g. of *m*-dihydroxybenzoic acid was mixed with 5 cc. of conc. sulfuric acid. This mixture was heated on the water-bath for about 2 hours or until a sample taken from it dissolved in water without any residue, when the rest was dissolved in water, and bromine was added gradually while the solution was shaken. At first, a flocculent precipitate of bromosulfonic acid was formed which gave place to the final product when a slight excess of bromine was added. To complete the reaction the material was warmed on the water-bath. If a large excess of bromine is employed, the whole product is converted into a resin. The substance was dried and recrystallized from glacial acetic acid; the pure substance melted sharply at 112°. It is identical with 2,4,6-tribromo-resorcinol, which was obtained from re-

sorcicol sulfonic acid in the manner already described. The identity was confirmed by a mixed-melting point determination. Yield, about 40%.

Bromobenzene.—Bromobenzene-*p*-sulfonic acid (m. p. 88°) was obtained by heating a mixture of bromobenzene and fuming sulfuric acid on a water-bath. When this product was poured into water, the sulfonic acid was precipitated without the separation of any phenyl bromide.

Bromine in excess was added to one g. of the sulfonic acid suspended in water. The mixture was heated on a water-bath in order to expel the excess of bromine. When the product of the reaction was recrystallized from glacial acetic acid it gave beautiful glistening crystals which melted at 173–174°, and were identified as 1,2,4,5-tetrabromobenzene.

Subs., 0.0746: AgBr, 0.1420.

Calc. for $C_6H_2Br_4$: Br, 81.21. Found: 81.01.

The yield is quite good, *viz.*, 2 g. from 1 g. of the sulfonic acid.

Toluene.—*p*-Toluene-sulfonic acid, mixed with a little of the *ortho*-derivative was obtained by the action of fuming sulfuric acid upon an equivalent quantity of toluene. The sulfonic acid crystals were dissolved in a little water and bromine was added in excess. This material was then allowed to stand for 4 days and was shaken occasionally which caused crystals of bromotoluene to form. The mixture was then warmed to about 60° to complete the reaction and to expell the excess of bromine. The product obtained was dried and recrystallized from glacial acetic acid. When pure, it melted at 112°. It is 2,4,5-tribromo-toluene. Yield, about 40%.

Subs., 0.2271: AgBr, 0.3880.

Calc. for $CH_3C_6H_2Br_3$: Br, 72.95. Found: 72.70.

***m*-Xylene.**—Three cc. of *m*-xylene was placed in a long-necked flask and 3.5 cc. of about 30% fuming sulfuric acid was added slowly while the mixture was shaken and cooled by tap-water. This caused the product to solidify completely. The sulfonic acid was separated by the aid of a filter-pump which removed any unchanged xylene and free acid.

One g. of this material was dissolved in a little water and bromine in excess was added to the solution, while the mixture was shaken. As this mixture was heated on a water-bath, an oil separated, which solidified when cooled. Recrystallized from glacial acetic acid, the solid melted sharply at 72°. It is 4,6-dibromo-*m*-xylene. The yield is very small.

A concentrated solution of one g. of *m*-xylene sulfonic acid was mixed with an excess of bromine and allowed to stand for 3 days. It was shaken occasionally until crystals of the bromo derivative were formed, when excess of bromine was removed by application of heat or by exposure to the air. The crystals, recrystallized from glacial acetic acid, melted at 240–241°. This compound is 2,4,5,6-tetrabromo-*m*-xylene. The yield is more than 40%

Subs., 0.0861: AgBr, 0.1525.

Calc. for $C_8(CH_3)_2Br_4$: Br, 75.82. Found: 75.30.

***p*-Xylene.**—A mixture of 4 cc. of *p*-xylene and 4 cc. of weak fuming sulfuric acid was heated on a water-bath and then allowed to stand overnight. The addition of a little water caused the entire product to solidify. The sulfonic acid crystallizes with water of hydration. When these crystals are separated and dried by suction they melt at 95°.

One-half of this sulfonic acid was mixed with a little water and bromine in excess. This mixture was shaken occasionally and allowed to stand for some days, when a solid product was obtained. Recrystallization of this solid from glacial acetic acid gave

white glistening plates which melted at 75°. This is 2,5-dibromo-*p*-xylene. Yield, more than 50%.

Subs., 0.1927: AgBr, 0.2732.

Calc. for $C_6H_2(CH_3)_2Br_2$: Br, 60.61. Found: 60.32.

Mesitylene.—Four cc. of mesitylene was mixed with 4 cc. of fuming sulfuric acid. After this mixture had stood overnight the sulfonic acid was obtained as a solid. To this solid, dissolved in water, liquid bromine was added in slight excess, and the mixture shaken and warmed slightly giving a solid product which melted at 224° after recrystallization from glacial acetic acid. It is 2,4,6-tribromo-mesitylene. Yield, about 50%.

Subs., 0.1105: AgBr, 0.1740.

Calc. for $C_6(CH_3)_3Br_3$: Br, 67.22. Found: 67.01.

Diphenyl.—Three g. of diphenyl was mixed with 4.5 cc. of conc. sulfuric acid and heated on a water-bath to about 85°. From this solution crystals soon appeared accompanied by a liquid product which dissolved when water was added. By this method a mixture of ¹*p*-sulfonic and ^{1 2}*p,p*-disulfonic acids of diphenyl was obtained. When this solution was treated with an excess of bromine and heated on water-bath, a product was formed which melted at 167° after recrystallization from acetic acid. This compound is ^{1 2}*p,p*-dibromo-diphenyl. Yield, 13%.

Replacement by Chlorine.

Catechol.—It has been found that no definite product is formed by the action of chlorine upon catechol sulfonic acid in aqueous solution. In this case oxidation takes place. When chlorine acts upon catechol sulfonic acid in a medium of acetic acid, the sulfonic group is detached with the simultaneous formation of tetrachloro-*o*-quinone.

Catechol sulfonic acid was obtained from its barium salt. This salt was treated with the requisite amount of sulfuric acid; barium sulfate was removed and the filtrate evaporated. This solution was mixed with acetic acid and chlorine was passed into it for about half an hour. A little water was added and chlorine was passed into the solution again until saturation occurred, after about 2 hours. The product which separated when water was added was recrystallized from acetic acid. It gave orange-red crystals of tetrachloro-*o*-quinone which melted at 130°. The yield is good.

Hydroquinone.—By the action of chlorine upon hydroquinone sulfonic acid in acetic acid, tetrachloro-*p*-quinone has been obtained as a result of the simultaneous detachment of the sulfonic group and the oxidation of the 2 hydroxyl groups.

Four g. of quinol was dissolved slowly in 5 cc. of fuming and 5 cc. of conc. sulfuric acid, and the temperature of this solution was raised to 50° and held there for 3 hours. After this solution had been neutralized with barium carbonate and filtered, the barium sulfonate was obtained in crystalline form. After drying and washing this salt with ether, the free sulfonic acid crystals were produced by treatment with the required quantity of sulfuric acid, after which the solution was filtered and evaporated.

This sulfonic acid was mixed with glacial acetic acid and chlorine was passed into it for 4 hours when nearly all of the sulfonic acid dissolved. The solution was filtered and concentrated until crystals of tetrachloro-*p*-quinone were obtained which melted at 290° with decomposition in a sealed capillary tube. Beautiful golden crystals could be secured by sublimation. The portion insoluble in acetic acid consists of the chloro-sulfonic acid of quinone mixed with other materials.

Subs., 0.0550: AgCl, 0.1281.

Calc. for $C_6O_2Cl_4$: Cl, 57.72. Found: 57.61.

1,2,4-Xylenol.—A current of chlorine gas was passed into an aqueous solution of 1,2,4-xylenol sulfonic acid for about 3 hours when an immiscible liquid product appeared. This was extracted with ether and dehydrated over fused calcium chloride. It boiled at 232°.

This is a new compound. Qualitative tests proved it to be chloro-xylenol and a quantitative estimation of chlorine showed that it is dichloro-xylenol.

Subs., 0.0605: AgCl; 0.901.

Calc. for $C_8H(CH_3)_2(OH)Cl_2$: Cl, 37.18. Found: 36.84.

Since the positions of the sulfonic group in xylenol sulfonic acid are still unknown, the configuration of this new derivative could not be determined by the detachment of the sulfonic groups. The yield is low, and further investigation could not be carried on because of lack of materials, so the configuration of this dichloro-1,2,4-xylenol remains unsettled. The rule of substitution throws no light on the subject, for there are equal chances of the entrance of the halogen atom in the Positions 3, 5 and 6.

1,4,2-Xylenol.—By the action of chlorine upon xylenol sulfonic acid, the sulfonic acid group is removed and a new dichloro-xylenol has been obtained.

A current of chlorine gas was passed into an aqueous solution of xylenol sulfonic acid for 4 hours or until saturation occurred. A semi-solid product was obtained which solidified when it cooled. This substance, recrystallized from alcohol consisted chiefly of crystalline needles which melted at 84°. Qualitative tests proved that it was chloro-xylenol and that no rearrangement to form a keto-chloride, or a chloroquinone had occurred. A quantitative estimation of halogen gave values corresponding to dichloro-xylenol.

Subs., 0.0484: AgCl, 0.0722.

Calc. for $C_8H(CH_3)_2OHCl_2$: Cl, 37.18. Found: 36.91.

The yield of the chloro product is not quantitative. The positions of the 2 chlorine atoms which enter the nucleus remain unsettled. Since the position of the sulfonic acid group is unknown, no clue to the configuration of the chloro derivative is furnished by the replacement of the sulfonic group. The 3,5-dibromo-xylenol obtained by the action of bromine melts at 78°, but this dichloro compound melts at 84°, which leads to the conclusion that it is not 3,5-dichloro-xylenol, since in that case it would probably have melted at a lower temperature. A detailed study of this reaction could not be continued because of lack of materials.

Bromobenzene.—By the action of chlorine upon bromobenzene sulfonic acid *p*-chloro-bromobenzene has been obtained almost quantitatively.

Chlorine gas was allowed to act upon a suspension of *p*-bromo-benzene sulfonic acid in warm water for about 4 hours. A liquid product formed at first but solidified. When it became cold after recrystallization it melted at 68°. This compound is *p*-chloro-bromobenzene.

***p*-Xylene.**—A sample of *p*-xylene sulfonic acid which melted at 92° was dissolved in a little water, and a current of chlorine gas was passed into it until saturation oc-

curred. The mixture was then warmed to remove the excess of chlorine. This gave a white product of 2,5-dichloro-*p*-xylene which was recrystallized from acetic acid. It melted at 70–71°. The yield is not quantitative.

Mesitylene.—Mesitylene sulfonic acid was dissolved in water and a current of chlorine gas was passed into the solution. A white flocculent precipitate was obtained. After the solution was saturated with chlorine gas, it was warmed on a water-bath. The 2,4,6-trichloro-mesitylene formed was recrystallized from alcohol and then melted at 203–204°. The yield is not quite quantitative.

Subs., 0.1046; AgCl, 0.2010.

Calc. for $C_6(CH_3)_3Cl_3$; Cl, 47.75. Found: 47.54.

Replacement by Iodine.

Mesitylene.—When an aqueous solution of potassium iodide was added to an aqueous solution of pure mesitylene sulfonic acid, a crystalline product was obtained which has been found to be the potassium salt of mesitylene sulfonic acid. This occurs when the solution of potassium iodide is concentrated. On this account a potassium iodate solution was added first. When, then, potassium iodide solution was added slowly to this solution, a flocculent precipitate containing iodine was formed. This mixture was heated until all free iodine had escaped, giving a liquid which collected at the bottom of the vessel, and solidified, when it was poured into ice-cold water. After recrystallization, it melted at 31°. It is mono-iodo-mesitylene. The yield is good.

Subs., 0.1032; AgI, 0.0980.

Calc. for $C_6H_2(CH_3)_3I$; I, 51.63. Found: 51.33.

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CALCUTTA, INDIA.

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, HARVARD UNIVERSITY.]

THE STRUCTURES AND REACTIONS OF HYDROXYLAMINE AND ITS DERIVATIVES.

BY ARTHUR MICHAEL.

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Hydroxylamine is an endothermic compound, exploding violently at 70° to 80°, and acting as a reducing agent; on the other hand, it converts ferrous hydrate into ferric hydrate and zinc into zinc oxide, and in these instances apparently appears as an oxidizing agent. This, seemingly dual, chemical character, and other properties, of the base, have led some chemists to consider it a tautomeric substance, capable of reacting in the hydroxyl form, $H_2NOH(I)$, and the amine oxide form, $H_3NO(II)$.

Haber¹ called attention to the conversion of ferrous hydrate and of nitrites in the presence of alkali into higher oxidized compounds by hydroxylamine,² and to the reduction of ferric to ferrous sulfate in acid solution.³

¹ Haber, *Ber.*, **29**, 2444 (1896). Haber overlooked a paper by Dunstan and Dymond (*J. Chem. Soc.*, **51**, 655 (1888)), who found that ammonia and some nitrogen are formed in the reaction.

² Donath, *Ber.*, **10**, 766 (1877); Dunstan and Dymond, *loc. cit.*

³ Meyerhng, *Ber.*, **10**, 1042 (1877).