two standard thermometers in this neighborhood. Moreover in spite of the use of many different specimens of benzene, the doubt must always remain as to whether the samples employed were perfectly pure. That our material was purer than the specimen employed by J. Meyer is shown by the fact that our melting point is over 0.05° higher than his (5.44°). The preparation of any organic substance in a state of great purity is difficult, although benzene is more promising in this respect than the great majority, because of its convenient crystallization, its easy preparation, and its considerable stability. For a closer evaluation of the melting point of benzene, a prolonged and laborious investigation would be needful, for which we have not time at present. In the meantime it is safe to say that either the triple point, or the freezing point when saturated with air, is easily attained and very constant.

We are glad to express our obligation to the Carnegie Institution of Washington for pecuniary support in this research.

Summary.

1. Benzene saturated with air under atmospheric pressure melts 0.003° below the true triple point.
2. Benzene thus saturated has its freezing point but little altered by change of pressure.
3. Evidence of an important degree of supersaturation does not appear.
4. The effect of pressure in the absence of dissolved air is shown to alter the freezing point 0.029° per atmosphere.
5. Saturation with water lowers the freezing point of benzene 0.095°.
6. The true freezing point of benzene saturated with air is probably not far from 5.493°, and the true triple point not far from 5.496°.

CAMBRIDGE, MASS.

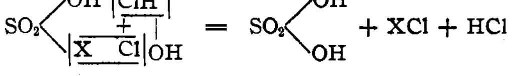
[CONTRIBUTION FROM THE UNIVERSITY COLLEGE OF SCIENCE OF CALCUTTA.]

HALOGENATION. XIX. THE REPLACEMENT OF SULFONIC GROUPS BY CHLORINE AND THE PREPARATION OF ORGANIC CHLORO-DERIVATIVES.

BY RASIK LAL DATTA AND HARAPARBUTTY KUMAR MITTER.

Received April 14, 1919.

It has been found that when a current of chlorine gas is introduced into an aqueous solution of sulfonic acid, the sulfonic group is detached with the simultaneous production of the corresponding chloro-derivative. The reaction that takes place may be represented as follows:



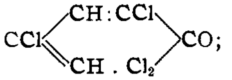
$$SO_2\Big\langle\begin{matrix}OH\ \boxed{ClH}\\ +\\ \boxed{X\quad Cl}\ OH\end{matrix} = SO_2\Big\langle\begin{matrix}OH\\ OH\end{matrix} + XCl + HCl$$

where X represents the organic radical to which the sulfonic group is attached.

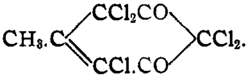
Besides throwing light on a fundamental and general reaction, this method has great practical value. The direct chlorination, in aqueous or glacial acetic acid solution by means of chlorine is generally unsatisfactory as a good deal of substance chars and oxidizes with a considerable diminution in the yield. But with the above reaction there is scarcely any secondary action, and no charring of the sulfonic acid takes place, the chloro-derivatives being almost invariably produced in high yield.

It has been found that aromatic bodies which already contain an hydroxy group, as in the case of phenols and oxyacids, exhibit a special facility in the displacement of the sulfonic group by chlorine. The same facility of replacement has also been found in the case of substances which already contain an amido group, as in the case of nitranilines.

The results that have been obtained are interesting. Anisol and phenetol sulfonic acids have given tetrachloro-ketodihydrobenzene,



phenol sulfonic acids yield 2,4,6-trichlorophenol; *o*-cresolo-5-sulfonic acid gives 5-chloro-*o*-cresol, *m*-cresol-6-sulfonic acid and *m*-cresol-2,6-disulfonic acid yield 2,6-dichloro-*m*-cresol; *p*-cresol-3-sulfonic acid gives a trichloro-*p*-cresol, whereas *p*-cresol-3,5-disulfonic acid yields 3,5-dichloro-*p*-cresol. From thymol mono- and di-sulfonic acids, 2,5,6-trichloro-thymol can be obtained, whereas carvacrol-5-sulfonic acid yields trichloro-carvacrol. Orcinol disulfonic acid yields 3,5-diketo-methyl-pentachloro-**R**-hexane,



From *o*-nitrophenol and *p*-nitrophenol sulfonic acids, 4,6-dichloro-*o*-nitrophenol and 2,6-dichloro-*p*-nitrophenol have been obtained, respectively. *o*-Nitroaniline sulfonic acid and *p*-nitroaniline sulfonic acid yield 4,6-dichloro-*o*-nitroaniline and 2,6-dichloro-*p*-nitroaniline, respectively, whereas *m*-nitroaniline does not give any definite product. *o*-Hydroxybenzoic acid on sulfonation and consequent treatment with chlorine gives 3,5-dichloro-*o*-hydroxybenzoic acid. 2,4,6-Trisulfonic acid obtained from *m*-oxybenzoic acid gives 2,4,6-trichloro-*m*-oxybenzoic acid, and 3-sulfonic-*p*-oxybenzoic acid yields on treatment with chlorine 3,5-dichloro-*p*-oxybenzoic acid.

The phenomena of the replacement of the sulfonic group by chlorine have not been systematically studied, although occasional instances can be found in literature. Kelbe[1] has shown that cymol sulfonic acid yields tetrachlorocymol by the action of chlorine. Meyer[2] has found that *p*-

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[1] *Ber.*, 16, 617 (1883).

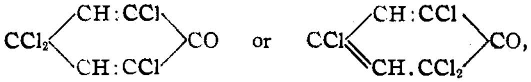
[2] *Monatsh.*, 36, 719 (1915).

dichlorobenzene is formed from *p*-chloro-benzosulfonic acid; and he also obtained α- and β-chloroanthraquinones from the corresponding α- and β-sulfonic acids when acted upon by chlorine. Chlorine replaces the sulfonic group of alizarin-β-sulfonic acid[1] to form chloroalizarin. Farbenfabriken vorm F. Baeyer & Co.[2] and Schillong[3] prepared chloro- and bromoanthraquinones from the corresponding sulfonic derivatives. Haller[4] studied the reaction in oxyanthraquinone. Sudborough and Lakhumalini[5] have studied it in amidobenzene-sulfonic acids.

Experimental.

Anisol.

By the action of chlorine upon an aqueous solution of anisol sulfonic acid, the sulfonic radical is detached with the formation of tetrachloro-keto-dihydrobenzene,



$$CCl_2\left\langle\begin{matrix}CH:CCl\\CH:CCl\end{matrix}\right\rangle CO \quad \text{or} \quad CCl\left\langle\begin{matrix}CH:CCl\\CH.CCl_2\end{matrix}\right\rangle CO,$$

and tetrachloroquinone as a secondary product. The ketochloride together with tetrachloroquinone has been previously prepared by the action of chlorine upon trichlorophenol.[6]

The sulfonic acid is prepared by heating anisol with conc. sulfuric acid on the water bath for about 3 hours when both the *para*- and *ortho*-compounds are formed at the same time.[7] Chlorine was passed through the diluted aqueous solution and after nearly an hour an oil collected. The current of the gas was continued until no more oil was formed. The oil was collected, washed and a part was treated with glacial acetic acid from which it was found to crystallize in colored prismatic needles melting at 122°. This has been identified to be tetrachloro-keto-dihydrobenzene. The glacial acetic acid solution of the substance acts upon the skin.

In order to study the mode of the reaction the experiment was repeated and the solution exhaustively treated with chlorine whereupon the oil formed as before, gradually solidified, and copious flakes of yellow shining crystals appeared in the aqueous solution. The floating crystals were collected separately, dried and recrystallized from glacial acetic acid. The crystals do not melt but sublime at high temperature and were identified as tetrachloroquinone. The semi-solid mass was found to crystallize well from a mixture of ether and ligroin and was then fractionally crystallized from glacial acetic acid, yielding tetrachloroquinone and a

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[1] *D. R. P.* 77179, 78642.

[2] *Brit. pat.* 1822 (1908).

[3] *Ber.*, **46**, 1066 (1913).

[4] *Ibid.*, **46**, 2703 (1913).

[5] *J. Chem. Soc.*, **111**, 41 (1917).

[6] Benedikt, *Monatsh.*, **4**, 233 (1883).

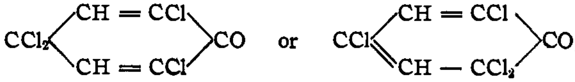
[7] Kekulé, *Z. Chem.*, 1867, p. 201; Cahours, *Ann.*, **52**, 33 (1844).

solid melting at 122° which was identified as tetrachloro-keto-dihydrobenzene.

The simultaneous formation of the above two substances may be explained by the assumption that anisol sulfonic acid is hydrolyzed to phenol which yields trichlorophenol, and the latter is further chlorinated to tetrachloroquinone and tetrachloro-keto-dihydrobenzene.

Phenetol.

By the action of chlorine upon an aqueous solution of phenetol sulfonic acid, the sulfonic group is detached with the formation of tetrachloroquinone, and tetrachloro-keto-dihydrobenzene,



as a secondary product. The keto-chloride and the tetrachloroquinone were previously prepared by the action of chlorine upon trichlorophenol.[1]

The sulfonic acid is prepared by the action of conc. sulfuric acid upon anisol and then heating on a water bath when both the *para-* and *ortho-*compounds are simultaneously formed.[2] Chlorine was passed through the warm dilute aqueous solution of the sulfonic acid when after nearly an hour an oil was found to collect. The passage of the gas was continued until no further increase in the volume of the oil occurred. The oil was collected, washed and treated with a mixture of ether and ligroin from which it crystallizes as a yellow solid, melting at 115–20°. On treatment with glacial acetic acid it yielded a small amount of white crystals melting at 122°. The substance has been identified as tetrachloro-keto-dihydrobenzene. The glacial acetic acid solution of the substance acts upon the skin.

In order to study the mode of reaction, the previous experiment was repeated and the solution treated exhaustively with chlorine as in the case of anisol, whereupon the oil as before gradually solidified and copious flakes of yellow shining crystals appeared in the aqueous solution. The floating crystals were collected separately, dried and crystallized from glacial acetic acid; they do not melt but sublime at high temperature. These crystals are very characteristic and have been identified as tetrachloroquinone. The semi-solid mass was found to crystallize from a mixture of ether and ligroin, and the resulting crystals were then fractionally crystallized from glacial acetic acid, yielding tetrachloroquinone and a solid melting at 122°, which was identified as tetrachloro-keto-dihydrobenzene.

The simultaneous formation of the above two substances can be explained by the assumption that phenetol sulfonic acid is hydrolyzed to phenol which yields trichlorophenol, and that this is further chlorinated

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[1] Benedikt, *Monatsh.*, 4, 233 (1883).

[2] Opl, Lippmann, *Z. Chem.*, 1869, p. 470.

to tetrachloroquinone, and tetrachloro-keto-dihydrobenzene. In the present case tetrachloroquinone forms the main product.

Phenol.

Phenol sulfonic acid on treatment with chlorine forms 2,4,6-trichlorophenol, the sulfonic groups being detached. This 2,4,6-trichlorophenol is also formed by passing chlorine into phenol.[1] It is prepared by the treatment of dil. phenol solution with sodium hypochlorite.[2] Vogel[3] has shown that it is formed by passing chlorine into an aqueous solution of potassium phenol sulfonate.

Into an aqueous solution of phenol monosulfonic acid, preferably freed from any unchanged phenol, chlorine was passed to saturation. The precipitate formed was collected and crystallized from glacial acetic acid, and white needle-shaped crystals obtained, melting at 67–8°, identified as 2,4,6-trichlorophenol. The yield is quantitative.

Into an aqueous solution of phenol disulfonic acid, prepared by sulfonating phenol with 4 parts of fuming sulfuric acid, chlorine was passed. The precipitate formed was separated by suction and crystallized from glacial acetic acid giving white, needle-shaped crystals of 2,4,6-trichlorophenol. The yield is nearly quantitative.

The crude trisulfonic acid obtained by sulfonating phenol with fuming sulfuric acid and phosphorus pentoxide was diluted with water and partially decolorized with animal charcoal. Into this solution, chlorine was passed for a comparatively long time, longer than in the case with phenol mono- and disulfonic acids. The precipitate was collected and crystallized from glacial acetic acid, forming white, needle-shaped crystals of trichlorophenol in small yield.

The yield is quantitative in the case of the monosulfonic acid but in the case of the disulfonic acid it is slightly less, while it is still less in the case of trisulfonic acid, this fact agreeing with the general experience that the greater the number of sulfonic groups to be replaced by chlorine, the greater the difficulty and the smaller the yield.

o-Cresol.

By the action of chlorine upon an aqueous solution of *o*-cresol-5-sulfonic acid, the sulfonic acid radical is detached with the formation of 5-chloro-*o*-cresol. It has previously been prepared by the action of chlorine upon an acetic acid solution of *o*-cresol in presence of iron.[4] It has also been prepared by the action of sulfuryl chloride on *o*-cresol.[5]

The sulfonic acid is prepared by the action of cold conc. sulfuric acid

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[1] Laurent, *Ann.*, **43**, 209 (1842).

[2] Chandelon, *Bull. soc. chem.*, **38**, 123 (1882).

[3] *Z. Chem.*, **1865**, p. 529.

[4] Claus, Jackson, *J. prakt. Chem.*, [2] **38**, 328 (1888).

[5] Penatoner, Condorelli, *Gazz. chim. ital.*, **28**, I, 211 (1898).

upon *o*-cresol. The 3-sulfonic acid is also produced at the same time, and being much less soluble in water, can thus be separated from the 5-sulfonic acid.[1] Four cc. of *o*-cresol was taken and 4 cc. of cold conc. sulfuric acid was gradually added to it, care being taken to keep it cold. The mixture was shaken from time to time and allowed to stand for some time. The whole of the syrupy liquid was then poured into water and the soluble portion was separated from the insoluble oily portion by means of a separating funnel. The soluble portion containing the 5-sulfonic acid was diluted with water and a current of chlorine was allowed to pass through it until the heavy oil which settles out is no longer formed. The whole was warmed on the water bath and the oil separated by means of a separating funnel, washed with water and dissolved in glacial acetic acid. On cooling and stirring it yielded 1.7 g. of white crystals melting at 47°, which were identified as 5-chloro-*o*-cresol.

m-Cresol.

By the action of chlorine upon an aqueous solution of *m*-cresol sulfonic acids, the sulfonic radicals are detached with the formation of 2,6-dichloro-*m*-cresol. This substance has been previously prepared by passing chlorine into boiling *m*-cresol.[2]

m-Cresol-6-sulfonic acid was obtained by warming *m*-cresol with an equivalent volume of conc. sulfuric acid.[3] A current of chlorine was passed through its aqueous solution for some time when a brown semi-solid mass was precipitated. The solid was collected, washed and crystallized from glacial acetic acid yielding white crystals melting at 45°. The yield from 5 cc. of *m*-cresol was 6.3 g. The substance was identified as the dichloro-*m*-cresol of Claus,[4] melting at 45°. As the substance was found to be identical with that obtained from *m*-cresol-2,6-disulfonic acid by the replacement of sulfonic groups by chlorine as noted below it is evidently 2,6-dichloro-*m*-cresol.

Into an aqueous solution of *m*-cresol-2,6-disulfonic acid prepared by heating one part of *m*-cresol with 6 parts of conc. sulfuric acid to 120–40°,[5] a current of chlorine was passed to saturation. The solid thus formed was collected, washed and crystallized from glacial acetic acid giving white crystals, melting at 45°. The substance was identified as the dichloro-*m*-cresol[6] of Claus; and as the chlorine atoms have replaced both the sulfonic groups in positions 2 and 6, the chloro derivative must be 2,6-dichloro-*m*-cresol. The yield obtained from 5 cc. of *m*-cresol was 8 g.

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[1] Claus, Jackson, *J. prakt. Chem.*, [2] **38**, 333 (1888).

[2] Claus, Schweitzer, *Ber.*, **19**, 930 (1886).

[3] Engelhardt, Latschinow, *Z. Chem.*, **1869**, 622; Claus, Krauss, *Ber.*, **20**, 3089 (1887).

[4] *Ibid.*, **19**, 930 (1886).

[5] Clauss and Krauss, *Ber.*, **20**, 3089 (1887).

[6] *Ibid.*, **19**, 930 (1886).

p-Cresol.

By the action of chlorine upon an aqueous solution of *p*-cresol-3-sulfonic acid, the sulfonic group is detached with the formation of a 2,3,6- or 3,5,6-trichloro-*p*-cresol, whereas 3,5-disulfonic acid yields 3,5-dichloro-*p*-cresol when similarly treated.

p-Cresol-3-sulfonic acid was prepared by the action of fuming sulfuric acid upon *p*-cresol[1] in requisite proportions in the cold. A current of chlorine was passed through the diluted solution for a long time when it yielded a small amount of a product which on recrystallization from glacial acetic acid was found to melt at 85–6°. This has been proved to be trichloro-*p*-cresol by an analysis for chlorine:

Subs., 0.0574: AgCl, 0.1274.

Calc. for $C_6H(CH_3)(OH)Cl_3$: Cl, 50.35. Found: 50.78.

The only trichloro-*p*-cresol known is 2,3,5-trichloro-*p*-cresol which melts at 66–7°, which cannot be identified with the substance obtained above. Hence this substance may be either 2,3,6- or 3,5,6-trichloro-*p*-cresol, the probability of the formation of these being equal.

3,5-Disulfonic acid was prepared by heating the potassium monosulfonate of *p*-cresol with fuming sulfuric acid[2] on the water bath. The diluted solution was then treated with a current of chlorine to saturation and warmed on the water bath. The oil which formed was collected, washed and crystallized from hot alcohol, yielding white crystals which melted at 39°. It has been identified as 3,5-dichloro-*p*-cresol. The yield obtained from 5 g. of *p*-cresol was 3 g.

Thymol.

By the action of chlorine upon an aqueous solution of a mixture of thymol mono- and disulfonic acids, the sulfonic radicals are detached with the formation of 2,5,6-trichloro-thymol. It has previously been obtained by passing chlorine into thymol.

Four g. of thymol was gradually digested with a mixture of equal volumes of conc. and fuming sulfuric acids and kept on the water bath[3] for about two hours when a clear solution was obtained by the addition of water. A current of chlorine was then passed through the diluted sulfonic acid solution for a long time and a white precipitate obtained. The solid when collected, washed and crystallized from boiling alcohol, yielded 5.7 g. of light brown crystals melting at 61°. It has been identified as 2,5,6-trichloro-thymol.

Carvacrol.

By the action of chlorine upon an aqueous solution of carvacrol-5-sulfonic acid, the sulfonic acid group is detached with the formation of trichloro-carvacrol.

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[1] Engelhardt and Latschinow, *Z. Chem.*, 1869, p. 619.

[2] Engelhardt and Latschinow, *Ibid.*, 1869, p. 620.

[3] Engelhardt and Latschinow, *Ibid.*, 1869, p. 46.

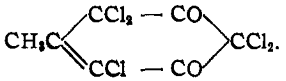
The sulfonic acid is prepared by the action of 5 cc. of conc. sulfuric acid upon 5 cc. of carvacrol[1] on the water bath for an hour. The resulting liquid was then diluted with water and treated with a current of chlorine gas to saturation, the solution gradually becoming turbid. An oil settles which was washed and dried over fused calcium chloride, yielding 3.8 cc. and was found to decompose on boiling at atmospheric pressure. It was shown to be trichloro-carvacrol.

Subs., 0.2980: AgCl, 0.5061.

Calc. for trichloro-carvacrol: Cl, 42.01. Found: 42.06.

Orcinol.

By the action of chlorine upon an aqueous solution of orcinol-disulfonic acid, the sulfonic groups are detached with the formation of pentachloro-orcinol or 3,5-diketo-methylpentachloro-R-hexane,



It has previously been prepared together with pentachloro-*m*-diketo-R-hexane[2] by the action of excess of chlorine hydrate or potassium chlorate and mineral acid on orcinol.[3]

The disulfonic acid of orcinol was prepared by warming 5 g. of orcinol with 12 cc. (an excess) of conc. sulfuric acid[4] to 60–80° on the water bath for an hour, when the mixture was found to be completely soluble in water. It was diluted with water and treated with chlorine. A precipitate of ash-colored solid substance was immediately obtained, and complete precipitation took place within an hour. The solid when collected, washed and crystallized from glacial acetic acid yielded 8 g. of white crystals, melting at 120.5°. It was identified as pentachloro-orcinol.

o-Nitrophenol.

By the action of chlorine upon an aqueous solution of *o*-nitrophenol-4-sulfonic acid, the sulfonic radical is detached with the production o 4 ,6-dichloro-*o*-nitrophenol. This substance has previously been prepared by the action of fuming nitric acid upon 2,4-dichlorophenol,[5] and also upon the sulfonic acid of 2,4-dichlorophenol.[6] It has also been produced by leading chlorine in 4-chloro-*o*-nitrophenol.[7]

The sulfonic acid is prepared by the action of 5 cc. of fuming sulfuric acid upon 4 g. of *o*-nitrophenol[8] in the cold to avoid charring. The mix-

[1] Claus and Fhrion, *J. prakt. Chem.*, [2] 39, 356 (1889).

[2] Zincke, *Ber.*, 26, 317 (1893).

[3] Stenhouse, *Ann.*, 163, 175 (1872).

[4] Hesse, *Ibid.*, 117, 324 (1861).

[5] Fischer, *Ann. Spl.*, 7, 185 (1870).

[6] Armstrong, *Z. Chem.*, 1871, p. 678.

[7] Faust and Saame, *Ann. Spl.*, 7, 195 (1870).

[8] Kekulé, *Z. Chem.*, 1867, p. 641.

ture was left to stand for an hour and then diluted with water and treated with chlorine. Solid accumulated gradually and care was taken to get the maximum yield. The solid was collected, washed and crystallized from glacial acetic acid, yielding 6 g. of yellow crystals, melting at 122–3°. It was identified as 4,6-dichloro-*o*-nitrophenol.

p-Nitrophenol.

By the action of chlorine on an aqueous solution of *p*-nitrophenol-2-sulfonic acid, the sulfonic acid radical is detached with the formation of 2,6-dichloro-*p*-nitrophenol. It has been prepared by leading chlorine through molten *p*-nitrophenol,[1] and by nitrating the dichlorinated *p*-phenol sulfonic acid.[2]

The sulfonic acid is prepared by the gradual addition of 3 cc. of fuming sulfuric acid to 4 g. of *p*-nitrophenol.[3] The mixture was allowed to stand for an hour, dissolved in water and treated with chlorine for some time, when there was a copious precipitation of a yellow substance. The solid was collected, washed, and crystallized from glacial acetic acid and yielding 5 g. of light brown crystals, melting at 125°. The substance was identified as 2,6-dichloro-*p*-nitrophenol.

o-Nitraniline.

By the action of chlorine upon an aqueous solution of *o*-nitraniline sulfonic acid the sulfonic radical is detached with the formation of 4,6-dichloro-*o*-nitraniline. This substance has previously been prepared by nitrating 2,4-dichloro-acetanilide[4] or by chlorinating 4-chloro-2-nitro-acetanilide,[5] also by leading chlorine into a solution of *o*-nitraniline dissolved in conc. hydrochloric acid.[6]

Two g. of *o*-nitroaniline and 8 cc. of conc. sulfuric acid were heated to 140–50°, in an oil bath for 8 hours. The solution was allowed to cool and then diluted with water. Chlorine passed through the diluted solution gave at once a copious brown precipitate, complete in about two hours. This precipitate was collected, washed with little water as it is fairly soluble in water. It is freely soluble in glacial acetic acid and can be crystallized from boiling dil. acetic acid, yielding brown crystals which melt at 100°. The nearly theoretical yield of 3.75 g. of pure substance was obtained. It was identified as 4,6-dichloro-*o*-nitroaniline.

p-Nitraniline.

By the action of chlorine gas upon an aqueous solution of *p*-nitroaniline sulfonic acid, the sulfonic acid radical is detached with the formation of

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[1] Schifert, *Ann. Spl.*, **7**, 189 (1870).

[2] Armstrong, *Z. Chem.*, **1871**, p. 518.

[3] Post, *Ann.*, **205**, 38 (1880); Korner, *Jahresb.*, **1872**, p. 604.

[4] Witt, *Ber.*, **7**, 1603 (1874).

[5] Witt, *Ibid.*, **8**, 820 (1875).

[6] Lauger, *Ann.*, **215**, 111 (1882).

2,6-dichloro-*p*-nitroaniline. It has previously been obtained by the action of chlorine upon *p*-nitroaniline.[1]

Two g. of *p*-nitroaniline and an excess of conc. sulfuric acid were heated in an oil bath to 140–50° for 8 hours. This digested solution was allowed to cool, diluted with water, and treated with chlorine. There was a copious precipitation, complete in about a half hour. The precipitate when collected, washed and crystallized from glacial acetic acid yielded 2.37 g. of yellow crystals melting at 189° which were identified as 2,6-dichloro-*p*-nitroaniline.

m-Nitraniline.

When *m*-nitraniline is sulfonated with excess of conc. sulfuric acid, heated in an oil bath to 140–50° and chlorine passed into the diluted solution a black solid gradually separates. Glacial acetic acid, benzene, ether and alcohol failed to give crystals from this solid. It smelled of chloroquinone and contained mostly tarry substances.

Salicylic Acid.

By the action of chlorine upon an aqueous solution of salicylic sulfonic acid, the sulfonic acid radicals are detached with the formation of 3,5-dichloro-salicylic acid. This has previously been prepared by cautiously heating one molecule of salicylic acid with 3 to 4 molecules of antimony pentachloride.[2] It has also been prepared by the action of chlorine upon an acetic acid solution of salicylic acid[3] and by the action of chlorine upon a cold solution of salicylic acid in potassium hydroxide.[4]

The sulfonic acid derivative was obtained by warming 6 g. of salicylic acid with 10 cc. of conc. sulfuric acid[5] slowly and carefully on the water bath until the mass becomes soluble in water. A current of chlorine was then passed through the solution for a long time. The solid thus obtained was collected, washed and crystallized from glacial acetic acid, giving 8.3 g. of white crystals melting at 215°, which were identified as 3,5-dichloro-salicylic acid.

m-Oxybenzoic Acid.

By the action of chlorine upon an aqueous solution of the trisulfonic-*m*-oxybenzoic acid, the sulfonic radicals are detached with the formation of 2,4,6-trichloro-*m*-oxybenzoic acid. It has previously been prepared by leading chlorine into an acetic acid solution of *m*-oxybenzoic acid.[6]

The sulfonic acid derivative is prepared by gradually treating 10 g. of *m*-oxybenzoic acid at 250° with a mixture of 10 cc. of conc. and 20 cc.

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[1] Korner, *Jahresb.*, **1875**, 323; Witt, *Ber.*, **8**, 143 (1875).

[2] Lossner, *J. prakt. Chem.*, [2] **13**, 429 (1876).

[3] Smith, *Ber.*, **11**, 1225 (1878).

[4] Tarugi, *Gazz. chim. ital.*, **30**, II, 487 (1900).

[5] Remsen, *Ann.*, **179**, 107 (1876).

[6] Zincke, *Ibid.*, **261**, 239 (1891).

of fuming sulfuric acid. Five g. of phosphorus pentoxide[1] was then added and the whole was gradually heated on the sand bath to 250° for 8 hours. The mass was then cooled and dissolved in a large volume of water. The solution was filtered from any undissolved substance and treated with chlorine for 12 hours when there was a copious precipitation; care was taken to get the maximum yield. The solid was collected, washed and crystallized from dil. acetic acid, and thus obtained in a yield of 12 g. of white crystals melting at 104–5°. It was identified as 2,4,6-trichloro-*m*-oxybenzoic acid. A small amount of tetrachloroquinone was also formed as a secondary product.

p-Oxybenzoic Acid.

By the action of chlorine upon an aqueous solution of 3-sulfonic-*p*-oxybenzoic acid, the sulfonic radical is replaced with the formation of 3,5-dichloro-*p*-oxybenzoic acid. It has previously been prepared by the action of antimony pentachloride on *p*-oxybenzoic acid.[2] It is also easily obtained by leading chlorine into a 10% acetic acid solution of *m*-oxybenzoic acid.[3]

The sulfonic acid was prepared by treating 7 g. of *p*-oxybenzoic acid with a mixture of 5 cc. of conc. and 5 cc. of fuming sulfuric acids and carefully heating on the sand bath. The mass solidified at first, whereupon another 10 cc. of fuming sulfuric acid was gradually added to it. The heating was continued for 8 hours, when the mass was found to dissolve completely in water. Chlorine was passed into this solution for 8 hours, precipitating a solid substance which was collected, washed and crystallized from glacial acetic acid, yielding 5 g. of a white solid which melted with decomposition at 255–6°. It was identified as 3,5-dichloro-*p*-oxybenzoic acid.

Investigations along similar lines are being continued.

Our thanks are due to Wolcott Gibbs Memorial Fund for a grant defraying part of the expenses of the investigation.

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[2] Loessner, *J. prakt. Chem.*, [2] 13, 434 (1876).

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