## Conclusions.

Oxides of the hydrocarbons can be dehydrated to the hydrocarbons of the butadiene series, at temperatures above 350° and in presence of catalysts.

The use of reduced pressures in these reactions is absolutely necessary; otherwise, the butadiene hydrocarbon suffers partial decomposition, giving rise, among other products, to hydrocarbons with one double bond. The hydrocarbons obtained with the use of high vacuum can be polymerized directly after distillation.

Methyl-1-butanal is capable of dehydration to isoprene.

In conclusion, I wish to thank my colleague, R. B. Earle, for helping me in carrying out the experiments described in this paper.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

# THE ACTION OF HALOGEN ON 4-NITRO-*m*-CRESOL.

BY L. CHAS. RAIFORD.

Received February 10, 1914.

In their proof of the position of the chlorine atom in the stereoisomeric oximes which they obtained from para chlorotoluquinone, Kehrmann and Tichvinsky[1] started out by chlorinating 4-nitro-*m*-cresol.[2] They obtained a product which they regarded as a monochloro compound, in which they assumed that chlorine had taken a position para to methyl. Without isolating their product, they reduced it to the corresponding aminocresol, which latter they reported as identical with the monochloroaminocresol obtained by the reduction of their oximes. In addition to the fact that, in the experiments cited, the intermediate products were not isolated, proof of the position of chlorine is further lacking to the extent that the oximes were not prepared from the base obtained by reduction of the chloronitrocresol; nor was it shown that this base could be oxidized into the quinone from which the oximes were prepared. The identity of the bases obtained from the two sources was claimed solely on the fact that they melted at the same temperature, and that their acetyl derivatives had identical m. p. It is not stated whether the corresponding products were melted together or not.[3]

The present writer, working with Stieglitz, in an attempt to prepare

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[1] *Ann.*, **303**, 20 (1898).

[2] *Ibid.*, **217**, 52 (1883).

[3] I have recently found that 6-chloro-4-amino-*m*-cresol (OH = 1), the base obtained by the reduction of Kehrmann's oximes, in the condition in which he obtained it, m. p. 206–207°, may be melted with 5-chloro-4-amino-*o*-cresol, m. p. 205–206°, without depression. This indicates that it would be unsafe to assume the identity of two products, in this class, at least, without evidence other than that obtained by melting them together.

stereoisomeric chloroimidoquinones[1] corresponding to the oximes referred to above, had occasion to repeat the work of Kehrmann and Tichvinsky on the chlorination of 4-nitro-*m*-cresol. In doing this their directions were followed as closely as the very brief descriptions would permit, except that all products were isolated, purified and analyzed. In this way it was proved conclusively[2] that chlorine must have persistently entered chiefly into the position ortho to methyl, that is, between methyl and hydroxyl, thus giving 2-chloro-4-nitro-*m*-cresol.

More recently, in preparing starting material for other work (now in progress) involving 2-chloro-4-nitro-*m*-cresol, it was decided to repeat the chlorination of 4-nitro-*m*-cresol in accordance with Kehrmann's method. The experiments were conducted by leading chlorine, diluted with an indifferent gas,[3] into an acetic acid solution of the nitrocresol, and also by using pure chlorine. Several portions were chlorinated in both ways, but in all instances the conclusions reached through the previous work were confirmed.

In order to secure the chlorinated product from these experiments, the reaction mixture (glacial acetic acid solution) was poured into water, which at once precipitated the product. The yield obtained in this way was fairly satisfactory (about 75% of the theory), and the material remaining in the filtrate was not, in the previous work, recovered. To decide, definitely, in the repetition of these experiments, whether any of the 6-chloro-4-nitro-*m*-cresol reported by Kehrmann was formed, the material in the filtrate was recovered and examined. In this way there was obtained a small quantity (about 5% of the amount theoretically possible)[4] of a monochloronitrocresol that melted at 143–144°,[5] and that turned out to be 6-chloro-4-nitro-*m*-cresol.

The position of chlorine in this compound was established by reducing it to the corresponding chloroaminocresol, and by showing that the latter is identical[6] with 6-chloro-4-amino-*m*-cresol, which was obtained by re-

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[1] *Am. Chem. J.*, **46**, 439 (1911).

[2] *Ibid.*, p. 439.

[3] Carbon dioxide was used.

[4] As this product is to be used in another investigation that has already been outlined, the conditions under which the yield can be increased will be made the subject of further study.

[5] It will be shown below that this compound is not identical with 2,6-dichloro-4-nitro-*m*-cresol, which melts at 143° with decomposition, and which was first prepared in the course of this work.

[6] Identity was not assumed on the basis of identical m. ps. for a single pair of substances alone, nor upon the failure of this pair, when melted together, to depress each other's m. p. The proof was regarded as certain only when, in addition to the behavior of the amines, two derivatives of each had been compared, and had failed to depress each other's melting point. In this case, also, the two products thought to be identical were separately melted with a third different, but closely re-

duction of Kehrmann's oximes, and whose structure has been conclusively proved.[1]

As only a very small quantity of 6-chloro-4-nitro-*m*-cresol was obtained by Kehrmann and Tichvinsky's method, it was decided to chlorinate 4-nitro-*m*-cresol in some other way. Accordingly, Kollrepp's[2] experiment was tried. This, as will be shown in the experimental part, gave nothing but 2,6-dichloro-4-nitro-*m*-cresol, although in the first experiments the amounts of the various materials used were those required by a monochloro compound. That the two chlorine atoms had taken positions 2 and 6 was shown by the fact that the dichloroaminocresol, obtained by reduction of the nitro compound under consideration, was easily oxidized to 2,6-dichlorotoluquinone, the structure of which is known.[3] The nitro compound was further identified by the preparation of several of its derivatives.

In connection with the work described in this paper, the behavior of chloroimidoquinones toward reducing agents is being studied. The experiments that have thus far been made indicate that, in at least some cases, those compounds having two chlorine atoms in the ring behave in a very different manner from the corresponding compounds having two bromine atoms similarly placed. It seemed a matter of interest, therefore, to test a chloroimide containing two different halogens attached to the ring. To secure such a compound, the start was made by preparing a bromine derivative of 2-chloro-4-nitro-*m*-cresol, by treatment of the latter with bromine in accordance with the method of Ling.[4] This gave 2-chloro-6-bromo-4-nitro-*m*-cresol, which was reduced to the amine, and the latter oxidized with hypochlorous acid in the usual way. This gave 2-chloro-6-bromo-3-methyl-4-chloroimidoquinone, while a portion of the material lost its nitrogen and was converted into the corresponding quinone (see experimental part), 2-chloro-6-bromo-3-methylquinone.

## Experimental.

The starting point in this work was *m*-cresol, which was obtained by fractionating Kahlbaum's purest product. The fraction boiling at 199–200° (uncorr.) was nitrated, in fifty-gram lots, in accordance with the method of Staedel and Kolb,[5] and the isomeric nitro products that resulted were separated by distillation with steam. The para compound, which is not volatile under these conditions, and which was obtained in

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lated, substance, and only when the two mixtures behaved exactly alike were the original products regarded as identical. This precaution was taken because of the behavior of the amines mentioned above.

[1] Raiford, *Am. Chem. J.*, **46**, 441 (1911).

[2] *Ann.*, **234**, 3 (1886).

[3] Raiford, *Am. Chem. J.*, **46**, 425 (1911).

[4] *J. Chem. Soc.*, **55**, 57 (1889).

[5] *Ann. Chem. (Liebig)*. **259**, 210 (1890).

crude form by allowing the distillation residue to cool, was further purified by repeated crystallization of its sodium salt from water. These crystals were then decomposed by treatment of their aqueous solution with dilute hydrochloric acid, and the free nitrocresol subsequently crystallized from hot water, from which it separated in nearly colorless crystals melting at 127–129°.

*The Action of Chlorine on 4-Nitro-m-cresol.*—A portion of the nitrocresol described above, weighing 10 g., was dissolved in eight times its weight of glacial acetic acid, and chlorinated in the way indicated by Kehrmann and Tichvinsky.[1] The solid that separated when the reaction mixture was poured into water was purified, and was found to have the same m. p., 133°, and other properties reported by Raiford[2] for this compound, which was shown to have the structure 2-chloro-4-nitro-*m*-cresol. The filtrate left after removing this product, as stated, was extracted with ether, and the ether removed by evaporation on a water bath. The residue was then heated in an open vessel until all acetic acid had been removed, after which the remaining solid was repeatedly crystallized from benzene until the m. p. was constant. In this way colorless, feathery crystals, radiating from a common center, were obtained. The substance is readily soluble in alcohol, chloroform and other organic solvents, but crystallizes best from benzene. It melts at 143–144° without decomposition.[3] It was at first thought that this material might be but a purer sample of 2-chloro-4-nitro-*m*-cresol, m. p. 133°, but this was shown not to be the case, by melting the two products together. The mixture melted at 108–118°. Analysis for chlorine indicated a monochloro compound.

0.1085 g. subs. gave 0.0824 g. AgCl. Calc. for $C_7H_6O_3NCl$: Cl, 18.90; found: 18.77.

In order to decide the position of chlorine in this new[4] substance, a portion of it was reduced to the corresponding aminohydrochloride, from which, by treatment with ammonium carbonate solution, the free base was obtained. This was repeatedly crystallized from alcohol, from which it separated in nearly colorless scales that melted with decomposition at 223–225°. A mixture of this substance with the chloroaminocresol[5]

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[1] *Am. Chem. (Liebig)*, 303, 23 (1898).

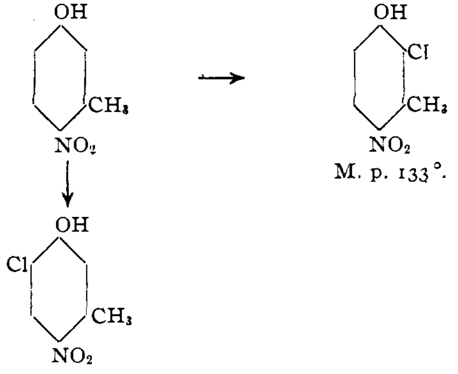
[2] *Am. Chem. J.*, 46, 448 (1911).

[3] It will be shown below that 2,6-dichloro-4-nitro-*m*-cresol melts at 143°, with decomposition.

[4] This compound was not isolated by Kehrmann, and though he reported derivatives of it, and assumed that chlorine occupied a position para to methyl in these derivatives, his proof of structure was not conclusive.

[5] Kehrmann and Tichvinsky, *loc. cit.*, reported the m. p. of this compound as 204–205°, but it does not appear that they recrystallized their material. In repeating their work I obtained the m. p. 206–207° for this base before recrystallizing it. After recrystallization it melted with decomposition at 223–225°.

obtained by the reduction of Kehrmann's stereoisomeric oximes, the structure of which I have shown[1] to be 6-chloro-4-amino-*m*-cresol, melts at the same temperature as either of them separately, which indicates that they are identical. To make the case certain,[2] a portion of the base was converted into the acetyl derivative by heating it with anhydrous sodium acetate and acetic anhydride. After three crystallizations from benzene, the product melted at 163°. When mixed with the acetyl derivative of the base secured by reducing Kehrmann's oximes, the mixture still melted at 163°. To show that the new product could not be an impure sample of the acetyl derivative obtained from 2-chloro-4-amino-*m*-cresol (which melts at 178°), the product in question was melted with the latter. The mixture melted at 140–149°, which is exactly the behavior[3] shown when the acetyl derivative obtained directly from Kehrmann's oximes is used in place of the product now being identified. Finally, a portion of the base under consideration was dissolved in very dilute hydrochloric acid, and a solution of ferric chloride added. After standing half an hour the mixture was distilled with steam. There was obtained a quinone that melted at 104–105°, and which did not depress the m. p., 105°, of para-chlorotoluquinone, from which Kehrmann prepared his oximes. These facts confirm the opinion tentatively expressed at the conclusion of the previous work,[4] to the effect that when 4-nitro-*m*-cresol is chlorinated in the manner indicated the isomers, 2-chloro-4-nitro-*m*-cresol and 6-chloro-4-nitro-*m*-cresol, are formed. The reaction may be expressed as follows:



M. p. 133°.

M. p. 143–144°.

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[1] *Am. Chem. J.*, 46, 441 (1911).

[2] This precaution was taken because the author has recently obtained evidence that, in this class of compounds at least, different substances may be melted together without depressing each other's m. p.

[3] *Am. Chem. J.*, 46, 449 (1911).

[4] *Ibid.*, 456 (1911).

*2,6-Dichloro-4-nitro-m-cresol.*—Five g. of 4-nitro-*m*-cresol were dissolved, as nearly as possible, by heating it under a reflux condenser with 250 cc. concentrated hydrochloric acid; then the liquid was shaken until it reached the room temperature. A mass of small crystals separated. To this mixture there was added, in the manner described by Kollrepp,[1] the quantity of potassium chlorate solution required by the theory to convert all the nitrocresol present into the monochloro derivative. When the reaction was complete the solid was collected on a filter, washed with cold water and dried on a clay plate. The crude product melted with decomposition at 138–140°, which indicated at once that the substance could not be 2-chloro-4-nitro-*m*-cresol, melting at 133° and which has been described elsewhere.[2] The compound was found to be readily soluble in alcohol, chloroform, and benzene. It was purified by crystallization from benzene, from which it formed colorless prisms, that melt at 143° with decomposition. That this compound was not identical with 6-chloro-4-nitro-*m*-cresol, m. p. 143–144°, described above, was shown both by melting the two together, and by analysis for chlorine. A mixture of the two substances melts at 115–120°, and analysis for halogen shows the present substance to be a dichloro compound.

0.2909 g. subs. gave 0.3724 g. AgCl. Calc. for $C_7H_5O_3NCl_2$: Cl, 31.95; found: 31.65.

In view of the analysis recorded above, and of the fact that in the preparation of the compound the amounts of the various materials used were those required to give a monochloro product, the question now arose as to whether any of the latter had been formed. In order to decide this, the combined mother liquors left during the crystallization of the dichloro compound were evaporated to dryness, and the residue mixed with an excess of ammonium hydroxide solution. The ammonium salt obtained was purified by fractional crystallization. Each fraction was composed of yellow needles. Analysis of a portion of one fraction for chlorine showed that the substance was a dichloro compound.

0.1765 g. subs. gave 0.2126 g. AgCl.
Calc. for $C_7H_8O_3N_2Cl_2$: Cl, 29.68; $C_7H_9O_3N_2Cl$: 17.34; found: 29.78.

When the various fractions of the above ammonium salt were separately decomposed by hydrochloric acid, the dichloronitrocresol described above, melting with decomposition at 143°, was obtained in each case.

*Hydrochloride of 2,6-Dichloro-4-amino-m-cresol.*—In order to further identify the dichloro product, 5 g. of the nitro compound were dissolved in 10 cc. hot alcohol, and to the boiling liquid there was added a hydrochloric acid solution of stannous chloride. From this mixture the aminohydrochloride separated, upon cooling, in nearly colorless crystals. Purification of the compound, by treatment of its hot water solution with

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[1] *Ann. Chem.* (*Liebig*), **234**, 3 (1886).

[2] *Am. Chem. J.*, 46, 447 (1911).

concentrated hydrochloric acid, gave colorless crystals that no longer responded to a test for tin salt. The hydrochloride is entirely soluble in water containing a little hydrochloric acid, but does not give a clear liquid in the absence of the acid. It dissolves readily in alcohol, and in sodium hydroxide solution, giving, with the latter, a solution that rapidly becomes dark colored on standing. It is not soluble in chloroform. When heated above 250° the substance blackens and appears to decompose without melting. A portion of it was dried *in vacuo* for several days over potassium hydroxide and then analyzed for chlorine.

0.3132 g. subs. gave 0.5894 g. AgCl. Calc. for $C_7H_8ONCl_3$: Cl, 46.57; found: 46.53.

*2,6-Dichloro-4-amino-m-cresol.*—The hydrochloride described above was dissolved in water, to which a little hydrochloric acid had been added, and the liquid filtered. To this solution there was added slightly more than the theoretically required amount of ammonium carbonate solution. The free amine, which was promptly precipitated, was at once collected on a filter, washed several times with cold water, and dried on clay plate. In this condition the compound melted with blackening and apparent decomposition at 174°. After crystallization from benzene it gave masses of interlaced needles, that melted with blackening at 175–176°.[1] The substance is readily soluble in alcohol and in chloroform, and but sparingly soluble in ligroin.

0.1702 g. subs. gave 0.2542 g. AgCl. Calc. for $C_7H_7ONCl_2$: Cl, 36.95; found: 36.92.

*2,6-Dichloro-4-acetylamino-m-cresol.*—A portion of the amine under consideration was converted into an acetyl derivative by mixing it with slightly more than the theoretically required amount of acetic anhydride to convert it into a diacetyl compound, along with some anhydrous sodium acetate. The reaction began at once, with the evolution of considerable heat. The mixture was boiled for a few minutes, and then allowed to cool, when it solidified. It is soluble in chloroform, benzene, and alcohol, but was best crystallized by treatment of its alcoholic solution with water. It gave colorless needles that melted at 204–207°.[2] It is readily soluble in solution of sodium hydroxide, which indicated a monoacetyl derivative. Analysis for chlorine confirmed this view.

0.1030 g. subs. gave 0.1232 g. AgCl. Calc. for $C_9H_9O_2NCl_2$: Cl, 30.31; found: 29.57.

*Oxidation of 2,6-Dichloro-4-amino-m-cresol.*—A portion of the amine, weighing 1.5 g. was rubbed into a thin paste with a mixture of 2 cc. concentrated sulfuric acid and 65 cc. water. This paste was cooled to about 0°, and to it was slowly added, with shaking, a cold solution of sodium

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[1] It should be noted that this compound melts at the same point as 2,6-dibromo-4-amino-*m*-cresol (*Am. Chem. J.*, **46**, 428 (1911)). A mixture of the two compounds melts to a black mass at 168–171°, which is but a very trifling depression.

[2] The quantity available was too small for further crystallization, therefore, the final product was not entirely pure. This was indicated both by m. p. and analysis.

dichromate and sulfuric acid, after which the whole was allowed to stand for half an hour. The quinone that formed was removed by filtration, washed repeatedly with cold water, and dried. It melted quite sharply at 103°. This product is probably identical with the dichlorotoluquinone prepared by Claus and Schweitzer[1] from what they reported as dichloro-*m*-cresol,[2] as well as with the product previously obtained by Southworth[3] by the treatment of *m*-cresol with hydrochloric acid and potassium chlorate. When the product under consideration here was melted with the dichlorotoluquinone in which Raiford[4] has shown that chlorine is in positions 2 and 6, the melting point was still 103°. The hydroquinone obtained from the present material was found to be identical with the hydroquinone prepared from 2,6-dichlorotoluquinone.[5]

*2,6-Dichloro-4-chloroimidotoluquinone*, $\overset{1}{O} : C_6HCl_2(\overset{3}{CH_3}) : \overset{4}{N}Cl$.—To prepare this compound, 4 g. of the hydrochloride of 2,6-dichloro-4-amino-*m*-cresol were dissolved in water to which a few drops of hydrochloric acid had been added, the solution cooled to about 0°, and then allowed to flow in drops into an acidified (HCl) solution of sodium hypochlorite,[6] in which pieces of ice were floating. A yellow solid separated at once. The reaction mixture was allowed to stand for half an hour, after which the solid was collected on a filter, washed with cold water until the odor of hypochlorous acid was no longer noted, and then dried in the air. In this condition the substance melted at 87°, and repeated crystallization did not change this. It was a matter of interest to note that this compound melts at the same temperature as 6-chloroimido-2-chlorotoluquinone,[7] obtained by starting with the same nitrocresol used in this work. That the products were not identical was shown by the fact that a mixture of the two melts lower than either of them separately, at 57–69°, and by analysis. The substance is soluble in alcohol, chloroform, and ligroin, and may be crystallized from either liquid, though alcohol seemed to give best results. It was obtained in the form of yellow prisms.

0.2123 g. subs. gave 0.4061 g. AgCl. Calc. for $C_7H_4ONCl_3$: Cl, 47.41; found: 47.29.

The chloroimidoquinones here described were prepared in order to secure material to be used in the study of the behavior of these compounds toward reducing agents. Preliminary experiments have shown that the reaction of the 2,6-dichloro-4-chloroimidotoluquinone described above is, in this respect, in marked contrast to that of the corresponding dibromo

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[1] *Ber.*, **19,** 931 (1886).

[2] See Crowther and McCombie, *J. Chem. Soc.*, **103,** 542 (1913).

[3] *Ann. Chem.* (*Liebig*), **168,** 270 (1873).

[4] *Am. Chem. J.*, **46,** 425 (1911).

[5] *Loc. cit.*

[6] Graebe, *Ber.*, **35,** 43, 2753 (1902).

[7] *Am. Chem. J.*, **46,** 451 (1911).

compound previously described by Raiford.[1] In order to study the action further, with the hope of learning, if possible, to what extent this behavior varies with the presence of various halogens, it was decided to prepare a chloroimidotoluquinone with two different halogen atoms attached to the ring. This was done through the compounds specified below.

*2-Chloro-6-bromo-4-nitro-m-cresol.*—A portion of 2-chloro-4-nitro-*m*-cresol, weighing 3.3 g., was dissolved in 30 cc. glacial acetic acid, and to this there was gradually added from a tap funnel a solution of 0.9 cc. (one mol) bromine dissolved in 7.5 cc. of acid. The mixture became warm, and was allowed to stand over night, during which time nearly colorless crystals, weighing 1.2 g., and melting at about 150°, with decomposition, separated out. These were removed by filtration, the filtrate was poured into six volumes of cold water, and the precipitate allowed to settle. After being collected on a filter and dried on a clay plate, this material weighed 3 g., and melted with decompositon at about 150°. It was found to be identical with the crystalline material mentioned above. The united product was twice crystallized from benzene, which gave nearly colorless prisms, still melting at 150° with decomposition. The compound dissolves readily in alcohol, but sparingly in ligroin.

0.4676 g. subs. gave 0.5796 g. AgHal. Calc. for $C_7H_5O_3NClBr$: Halogen, 43.33; found: 43.20.

*Hydrochloride of 2-Chloro-6-bromo-4-amino-m-cresol.*—A portion of the nitro compound, described above, was reduced to the corresponding aminohydrochloride by treatment of its hot alcoholic solution with hydrochloric acid solution of stannous chloride. The nearly colorless product was purified in the manner already stated, until it gave no reaction for tin compounds. It shows the same general properties stated for the corresponding dichloro compound. The purified substance was dried *in vacuo* over potassium hydroxide for several days, and then analyzed for halogen.

0.2132 g. subs. gave 0.3665 g. AgHal. Calc. for $C_7H_8ONCl_2Br$: Halogen, 55.28; found: 54.69.

*2-Chloro-6-bromo-4-amino-m-cresol.*—A portion of the aminohydrochloride was dissolved in acidulated (HCl) water, and to this there was added a slight excess of ammonium carbonate solution. The nearly colorless precipitate that formed was at once collected on a filter, washed with three or four small portions of cold water, and dried. In this form it melted, with blackening, at 186–187°, and was practically pure. After crystallization from benzene, in which it is but very sparingly soluble and from which it separated in colorless, transparent, rhombic crystals, it melted at 187°, with decomposition.

0.2312 g. subs. gave 3233 g. AgHal. Calc. for $C_7H_7ONClBr$: Halogen, 48.82; found: 48.70.

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[1] *Am. Chem. J.*, **46**, 426 (1911).

*2-Chloro-6-bromo-3-methylquinone,* $\overset{1}{O} : C_6H\overset{2}{Cl}\overset{6}{Br}(\overset{3}{CH_3}) : \overset{4}{O}$.—This compound was prepared by oxidation of the hydrochloride mentioned above. Three grams of the latter were rubbed into a thin paste with a mixture of 6 cc. concentrated sulfuric acid and 100 cc. water, and the whole cooled to about 0°. To this there was gradually added, with shaking, a cooled solution of sulfuric acid and sodium dichromate. The resulting mixture was allowed to stand for half an hour, then the yellow solid was removed by filtration, and washed several times with cold water. After being dried on clay plate this quinone weighed 2.5 g., which corresponds to about 97% of the theory—an unusually high yield for a quinone. The melting point of the material at this stage was 114–116°. It was found to be soluble in alcohol, chloroform, and ligroin, and was easily purified by distillation with steam or by crystallization from ligroin (b. p. 70–80°). Yellow scales of irregular shape, melting at 119°, were formed.

0.1904 g. subs. gave 0.2696 g. AgHal. Calc. for $C_7H_4O_2ClBr$: Halogen, 49.03; found: 49.35.

*2-Chloro-6-bromo-3-methylhydroquinone,* $H\overset{1}{O}.C_6H\overset{2}{Cl}\overset{6}{Br}(\overset{3}{CH_3}).\overset{4}{O}H$.—A portion of the quinone just described was rubbed to a thin paste with water, and the mixture saturated with sulfur dioxide. After standing for some hours the liquid was heated to the boiling point, and enough water gradually added, while the boiling was continued, to dissolve all solid. After filtration the liquid was again saturated with sulfur dioxide, and the flask set aside to cool. The hydroquinone settled out rapidly in colorless crystals. By recrystallization in the same manner, a substance that melted sharply at 163° was obtained. It may also be crystallized from ligroin. When brought in contact with sodium hydroxide solution, it gives first a green color, and goes into solution to form a brownish liquid.

0.1980 g. subs. gave 0.2768 g. AgHal. Calc. for $C_7H_6O_2ClBr$: Halogen, 48.62; found: 48.72.

*2-Chloro-6-bromo-3-methyl-4-chloroimidoquinone,* $\overset{1}{O}:C_6H\overset{2}{Cl}\overset{6}{Br}(\overset{3}{CH_3}):\overset{4}{N}Cl$.—To prepare this substance, 2.2 g. of the hydrochloride of 2-chloro-6-bromo-4-amino-*m*-cresol were dissolved in 100 cc. water with the help of a little hydrochloric acid. This solution was cooled to about 0°, and was then dropped into an acidified (HCl) solution of sodium hypochlorite which was surrounded by ice, and in which pieces of ice were floating. A yellow solid was at once formed, and this appeared to be distributed through the entire liquid in the form of an emulsion. The mixture was allowed to stand for half an hour, during which the solid settled, and the supernatant liquid became entirely clear. The chloroimide was collected on a filter, washed with cold water until the odor of hypochlorous acid had disappeared, and dried. The yield was nearly quantitative. In this state the material began to shrivel between 85 and 90°, and melted at 90–92°. It may be purified by crystallization from alcohol, from which the chloroimide separates in the form of square prisms that melt at 93–94°. From ligroin (b. p. 70–80°), it gives crystals of the same shape, melting at the same temperature. It decomposes suddenly, with charring, when heated above 176°.

0.3443 g. subs. gave 0.6079 g. AgHal. Calc. for $C_7H_4ONCl_2Br$: Halogen, 56.12; found: 56.14.

The mother liquor, left after crystallization of the above described chloroimidoquinone, was evaporated to a small volume and allowed to cool. The solid that separated melted at 111–113°, which showed that this material could not be the chloroimide. Further crystallization from alcohol raised the m. p. to 114–115°, but the small quantity of material available made it impossible to secure a product that was entirely pure. The substance crystallized in the form of the irregular scales characteristic of 2-chloro-6-bromo-3-methylquinone described above. A mixture of a pure sample of the latter, m. p. 119°, and the product here in question, melted at 115–119°, showing no depression. When the substance to be identified was mixed with a pure sample of 2-chloro-6-bromo-3-methyl-4-chloroimidoquinone, m. p. 93–94°, both of which were produced in the same experiment, the mixture melted at 75–86°. Analysis for halogen gave too high a value, which suggests a trace of a higher halogenated product.

0.0785 g. subs. gave 0.1130 g. AgHal. Calc. for $C_7H_4O_2ClBr$: Halogen, 49.03; found: 50.06.

## Summary.

1. When 4-nitro-*m*-cresol is chlorinated by passing pure or diluted chlorine into an acetic acid solution of the substance, a mixture of 2-chloro-4-nitro-*m*-cresol and 6-chloro-4-nitro-*m*-cresol, in which the first is present in largest amount, is formed.

2. When 4-nitro-*m*-cresol is chlorinated by means of a mixture giving so-called nascent chlorine, nothing but 2,6-dichloro-4-nitro-*m*-cresol is obtained.

CHICAGO, ILL.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

# TETRACHLOROFLUORESCEIN AND SOME OF ITS DERIVATIVES.

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## Historical.

Tetrachlorofluorescein was first prepared by Graebe[1] in the course of his investigation of tetrachlorophthalic acid. It was made by heating

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[1] *Ann. der Chemie*, **238**, 333 (1887).