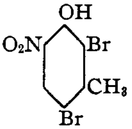
[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

4-BROMO-6-NITRO-*m*-CRESOL AND SOME OF ITS DERIVATIVES.

BY L. CHAS. RAIFORD AND GLADYS LEAVELL.

Received May 13, 1914.

In 1889 Claus and Hirsch[1] studied the behavior of *m*-cresol toward bromine and other reagents. Among the derivatives reported was a dibromo compound obtained by brominating 6-nitro-*m*-cresol,[2] which they named 2,4-dibromo-6-nitro-*m*-cresol, and to which they assigned the structure,



The analysis reported for bromine agreed with the formula given, but, beyond this, no details as to the method of preparation, properties, direct proof of structure of this compound or any of its derivatives are recorded. The melting point was given as 93°.[3]

In a study of chloroimidoquinones[4] one of the authors, working with Stieglitz, had occasion to nitrate 2,4,6-tribromo-*m*-cresol[5] by a modification of Zincke's[6] method, and found that the reaction gave a pair of mononitrodibromo-*m*-cresols that melted at 87° and 134°, respectively. These compounds were identified by the preparation and study of several of their derivatives, and their structures were decisively proved. The structure of the compound melting at 87° was established by preparing it from 2,4,6-tribromo-*m*-cresol, in which the positions of the bromine atoms are known, and by determining the relative positions of the hydroxyl and nitro groups in the substance itself. Through the preparation and reduction[7] of the nitrocarbonate, and the subsequent rearrangement of this reduction product to the corresponding urethane, these positions were found to be adjacent (ortho). Additional evidence tending to support the view that these groups are adjacent is found in the fact, recently observed, that the

---

[1] *J. prakt. Chem.*, [2] **39**, 62 (1889).

[2] *Ann. Chem.* (*Liebig*), **52**, 217 (1883), and 259, 210 (1890).

[3] It will be shown below that a dibromonitrocresol, probably identical with Claus and Hirsch's product, is formed under the same conditions and along with the monobromo compound mentioned in the title of this paper; though the most careful purification possible failed to raise the melting point above 87°. The dibromo compound here obtained was found to be identical with a substance (*Am. Chem. J.*, **46**, 427 (1911)) the structure of which was shown by one of us to be 2,4-dibromo-6-nitro-*m*-cresol.

[4] *Am. Chem. J.*, **46**, 417 (1911).

[5] *Bull. soc. chim.*, 46, 275 (1886).

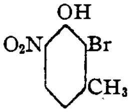
[6] *J. prakt. Chem.*, [2] **61**, 56 (1900).

[7] *Am. Chem. J.*, **23**, 14 (1900).

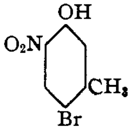
amine obtained by the reduction of the nitro compound may, under suitable precautions, react with nitrous acid to give a diazoxide.[1] Taken together, these facts show the compound to be 2,4-dibromo-6-nitro-*m*-cresol, with the structure suggested by Claus and Hirsch[2] for their product.

While the above-mentioned work on chloroimidoquinones was being done, an attempt was made to repeat Claus and Hirsch's experiment[3] with the hope of proving the identity of the compound melting at 87° with that reported to melt at 93°. It was noted that two products were formed but lack of time prevented further investigation then. It has now been found that, when 6-nitro-*m*-cresol is brominated in glacial acetic acid solution, starting the reaction at the room temperature, a monobromo product is formed to the extent of about 60% of that theoretically possible. After removal of this substance, which crystallizes rapidly from the reaction mixture after all bromine has been added, pouring the filtrate into water gives an additional product, the 2,4-dibromo-6-nitro-*m*-cresol, m. p. 87°, mentioned above. In this paper we have reported the results of our investigation of the monobromo compound, including some of its derivatives and the determination of its structure.

In order to determine the position of bromine in this compound, the purified product was subjected to the further action of bromine. A substance was obtained which, after crystallization from alcohol, melted at 87°. A mixture of this and 2,4-dibromo-6-nitro-*m*-cresol melted at the same temperature, which indicated that the products were identical, and that the monobromo compound must have formula (I) or (II) as given below:



(I)



(II)

The proof that in this compound bromine occupies position (II) or (IV) was further confirmed as follows: The monobromo compound, melting at 126°, was nitrated at a temperature (30–35°) slightly above that of the room, and gave a monobromodinitro compound, melting at 77°, which was characterized by the study of several of its derivatives (see experimental part). When the last named substance was nitrated at a higher

---

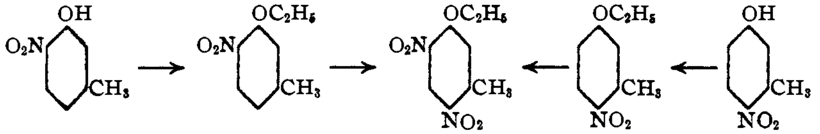
[1] Meldola, Woolcott and Wray (*J. Chem. Soc.*, **69**, 1332 (1896)) state that the formation of a diazo-oxide (or quinonediazide, Wolff, *Ann. Chem.* (*Liebig*), **312**, 126 (1900)) is proof of the ortho relationships of the nitro and hydroxyl groups. The literature, however, mentions cases where compounds having apparently the characteristics of diazo-oxides have been prepared from *p*-aminophenols.

[2] *Loc. cit.*

[3] They give no details as to methods.

temperature, bromine was replaced, and 2,4,6-trinitro-*m*-cresol[1] was obtained.

In order to gain further insight as to which of the two positions was occupied by bromine, it was proposed to study the ethyl ether of the compound in question. In their work on the derivatives of *o*- and *p*-nitro-*m*-cresol, Staedel and Kolb[2] found that 6-nitro-*m*-cresol was easily converted into its ethyl ether, and that when the latter was nitrated the second nitro group took a position para to the ethoxy group. The relative positions of these groups were determined by showing that the dinitro ether mentioned above is identical with that one obtained in a similar way from 4-nitro-*m*-cresol. These experiments were repeated by us, and Staedel and Kolb's conclusions confirmed, with a view to making use of them in determining the position of bromine in our compound. The reactions may be indicated as follows:



(I) (II) (III) (IV) (V)

The behavior of our monobromo-6-nitro-*m*-cresol, as has been indicated above, showed that bromine was in position II or IV. If in position 2, the ethyl ether of the monobromodinitro-*m*-cresol described on page 1506 should be identical with the product obtained by bromination of 4,6-dinitro-*m*-cresyl ether, formula (III) above. This ether was prepared and attempts were made to brominate it, but thus far all have failed. If the bromine in our product had been in position IV, then the ether described on page 1503, if it reacts with ammonia when heated in a sealed tube with the latter,[3] should give the nitro bromotoluidin ($NH_2:CH_3:Br:NO_2 = 1:3:4:6$) described by Nevile and Winther.[4] As will be shown below, the ether in question did not react with ammonia.

The proof that the bromine atom in our product occupies position IV was finally brought in another way. When the compound was chlorinated in the presence of iron as a carrier, one chlorine atom entered and this, as will be shown below, took position II. This monochloromonobromo-6-nitro-*m*-cresol was next reduced to the corresponding amine, and the latter treated with nitrous acid for the purpose of converting it into a diazonium salt which, it was hoped, could be decomposed by cuprous chloride, thus replacing the amino group by chlorine. As will be stated in detail in the experimental part, treatment of the amine with nitrous acid gave a

---

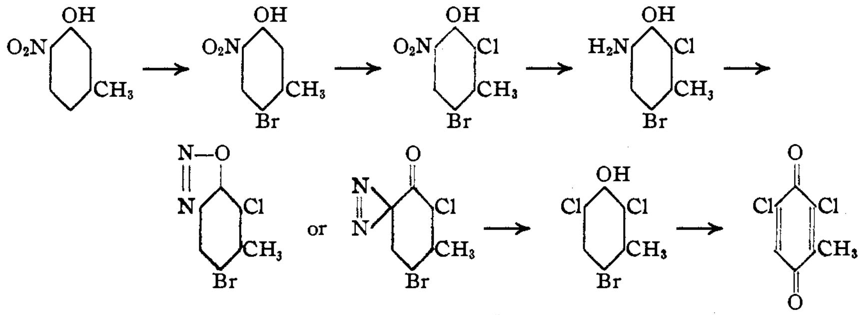
[1] Duclos, *Ann. Chem. (Liebig)*, **109**, 141 (1859).

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

[3] Staedel and Orth, *Ann. Chem. (Liebig)*, **259**, 210 (1890).

[4] *Ber. d. chem. Ges.*, **13**, 972 (1880).

diazo-oxide which was finally made to undergo, but with some difficulty, the Sandmeyer reaction. In this way there was obtained a monobromodichloro derivative, the structure of which turned out to be 2,6-dichloro-4-bromo-*m*-cresol. Oxidation of this product by means of the usual dichromate mixture gave a quinone that contained no bromine and which was found, both by analysis for halogen and by comparison of its melting point[1] with 2,6-dichlorotoluquinone, to be identical with the latter. Taken together these reactions show that in the monobromonitro-*m*-cresol under investigation the bromine is in position IV, that is, para to hydroxyl. The steps showing the proof of the structure may be briefly summarized as follows:



Experimental Part.

The starting point in this work was *m*-cresol, which was obtained by fractionating a pure commercial product. Fifty grams of the liquid, boiling at 199–200° (uncor.), were nitrated in accordance with the method of Staedel and Orth,[2] and the isomeric nitro compounds that resulted were separated by distillation with steam. The *o*- compound, 6-nitro-*m*-cresol, which is volatile under these conditions, was found to melt at 56°, as reported in the literature, and was used without further purification in the experiments described below.

---

[1] The fact that the product obtained here melted at the same temperature as 2,6-dichlorotoluquinone, and failed to depress the melting point of the latter, was not, alone, accepted as sufficient proof of the identity of the two products. The additional precaution of analyzing the compound in question was taken because we have found that in certain of the toluquinones chlorine may replace bromine without a change of melting point, and that the two products may be melted together without such a depression as would usually be regarded as showing that the products are different. Thus, a mixture of 2,6-dibromotoluquinone (*J. prakt. Chem.*, [2] **39**, 370 (1889); *Am. Chem. J.*, **46**, 430 (1911)), m. p. 117°, and 2-chloro-6-bromo-3-methylquinone (THIS JOURNAL, **36**, 679 (1914)), m. p. 119°, shows no sign of melting below 117°. Likewise, a mixture of *p*-chlorotoluquinone (*Ber.*, **20**, 2286 (1887)), m. p. 105°, and *p*-bromotoluquinone (*Ber.*, **27**, 1931 (1894)), m. p. 106°, melts at 103–104°; while a mixture of the corresponding hydroquinones, each of which melts separately at 176°, does not melt below 174°.

[2] *Ann. Chem. (Liebig)*, **217**, 51 (1883).

Action of Bromine on 6-nitro-m-cresol.—A portion of 6-nitro-*m*-cresol weighing 10.2 g. obtained as specified above, was dissolved in 75 cc. glacial acetic acid, and to this solution there was gradually added from a dropping funnel a solution of 6.7 cc. bromine (enough to convert all nitrocresol into dibromo derivative) in 30 cc. of glacial acetic acid. While the solution was slowly added the flask was frequently shaken. The operation was begun at the room temperature and lasted about one hour, during which time the temperature rose slightly. Crystals began to separate about the time all bromine had been added, and the mixture was allowed to stand for six hours in a cool place in order to secure as large a yield as possible. At the end of this time the crystals were collected on a filter, washed with a small quantity of glacial acetic acid, and dried on a clay plate. Chilling the filtrate increased the yield to 9.5 g., which is about 61% of the possible amount, if all had been converted into the monobromo product. In this condition the compound melted at 123°, and was very nearly pure. It was readily soluble in ether and alcohol, and was best purified by crystallization from the latter liquid, from which it separated in the form of yellow plates that melt at 126°. It may be purified by distillation with steam, though it does not pass over rapidly. It was analyzed for nitrogen by the Dumas combustion method, and for halogen by the Carius method. Both results agree with the formula for a monobromo product.

0.1803 g. subs. gave 0.1473 g. AgBr; 0.2643 g. subs. gave 14.9 cc. N at 749.3 mm. and 24° over 50% KOH solution.

Calc. for $C_7H_6O_3NBr$: Br = 34.48; N = 6.04; found: 34.76, 6.24.

The filtrate obtained when the monobromo product described above was removed was allowed to stand over night to see if it would deposit more solid. Nothing was deposited. The clear liquid was then poured with stirring into six volumes of ice water, and the precipitate allowed to settle during several hours. The yellow solid, after being collected on a filter and dried on a clay plate, weighed 7.2 g., less than 35% of that required by the theory on the basis of the formation of dibromo compound only. The substance was purified by repeated crystallization from alcohol, and was obtained in the form of yellow needles that melted sharply at 87°. A mixture of this product with 2,4-dibromo-6-nitro-*m*-cresol, m. p. 87°, obtained by the nitration[1] of 2,4,6-tribromo-*m*-cresol, melts at the same point as either of them separately, which shows that they are identical. This product, is, also, probably identical with that obtained by Claus and Hirsch[2] by brominating 6-nitro-*m*-cresol, though they report 93° as the melting point.

Salts of 4-bromo-6-nitro-m-cresol.—The monobromo compound described above reacts readily with bases to form salts. Several of these were stud-

---

[1] *Am. Chem. J.*, 46, 427 (1911).

[2] *Loc. cit.*

ied. The ammonium salt was obtained by allowing the pulverized nitro compound to stand over night with concentrated ammonia water. The solubility of the product in cold water is so slight that the yield of salt obtained by filtering the above mixture was nearly quantitative. The salt was purified by repeated crystallization from dilute ammonia water. It was found, in fact, that the nitro compound could be purified most easily in the form of ammonium salt, which latter could afterward be decomposed by hydrochloric acid. The salt crystallized in the form of orange colored needles.

0.2810 g. subs. gave 0.2138 g. AgBr; 0.2152 g. subs. gave 20.4 cc. N at 731.5 mm. and 21.5° over 50% KOH solution.

Calc. for $C_7H_9O_3N_2Br$: Br = 32.12; N = 11.26; found: 32.37, 10.59.

The potassium salt was prepared by dissolving the nitrocompound in a hot aqueous solution containing slightly more than the theoretical amount of potassium hydroxide, and then allowing the liquid to cool to the room temperature. Five grams of nitro compound gave 4.05 g. of potassium salt which was increased to 5.05 g. by working up the mother liquor. It was purified by two crystallizations from water, and formed deep red needle-shaped crystals.

Analysis for potassium was carried out by igniting the salt with dilute sulfuric acid.

0.2088 g. subs. gave 0.0669 g. K_2SO_4; calc. for $C_7H_5O_3NBrK$: K = 14.44; found: 14.38.

The sodium salt, prepared in the same way as the potassium compound, crystallized from water in red needles.

0.8654 g. subs. gave 0.2446 g. Na_2SO_4. Calc. for $C_7H_5O_3NBrNa$: Na = 9.07; found: 9.13.

The silver salt, which is but sparingly soluble in water, was prepared by adding a slight excess of silver nitrate solution to a solution of the sodium salt that had been purified by several crystallizations, and that was free from any considerable amount of alkali. The dark red precipitate that formed at once was filtered off, washed with water and dried on clay plate. It was used in the preparation of the ethyl ether that is described below.

Ethyl Ether of 4-Bromo-6-nitro-m-cresol.—Five grams of the above described silver salt were dried and pulverized. This powder was mixed with dry ether and considerably more than the theoretically required amount of ethyl iodide. To hasten and complete the reaction, which appeared to go very slowly at the room temperature, the mixture was heated for five hours under a reflux condenser on the water bath. The mixture was then filtered to remove silver iodide and any unchanged silver salt of the nitrocresol, and the residue extracted several times with dry ether. The ethereal solution was then shaken with sodium carbonate solution in order to remove any free nitro compound, and after separation from the alkaline liquid was evaporated to dryness by distilling off the ether. The residue weighed about 2 g. This was purified by crystallization from ligroin, 70–80°, from which it separated in the form of plates having a slight tan color. A second sample was repeatedly crystallized from alcohol, and gave nearly colorless crystals. The m. p. in both cases was 124°, which is very near that of the nitro compound (126°) from which we started. The two products, however, were shown to be different both by melting them together and by analysis. The mixture melted at 97–102°.

0.2472 g. subs. gave 0.1788 g. AgBr. Calc. for $C_9H_{10}O_3NBr$: Br = 30.76; found: 30.78.

The question of the behavior of this ether toward ammonia when the mixture was heated under pressure was next considered. Staedel and Kolb[1] found that the ethyl ether of 6-nitro-*m*-cresol reacted with ammonia under these conditions to replace the ethoxy by the amino group, and that the same reaction took place with the corresponding dinitro and trinitro ethers. Since their mononitro compound corresponded to our product, with the exception that theirs contained no bromine, it was expected that ours would react with ammonia, and, by replacement of the ethoxy group, give a nitrobromotoluidin (NH_2:CH_3:Br:NO_2 = 1:3:4:6) of known structure.[2] A portion of our product was mixed with concentrated aqueous ammonia, and heated in a sealed tube for eight hours at 150°. Nothing but the unchanged ether was recovered from the reaction mixture.

Hydrochloride of 4-Bromo-6-amino-m-cresol.—This compound was obtained by dissolving 5 g. of the corresponding nitro compound in boiling alcohol, and adding to the boiling liquid a solution of stannous chloride in concentrated hydrochloric acid. When reduction was complete, one volume of concentrated acid was added and the mixture allowed to come to the room temperature. The amino hydrochloride that separated was removed by filtration and purified as follows: The solid was dissolved in a small quantity of hot water, the solution filtered through paper, and the filtrate mixed with an equal volume of concentrated hydrochloric acid. Nearly colorlesss needle-shaped crystals, that were free from tin compounds were obtained.

0.2496 g. subs. gave 0.3476 g. AgHal; calc. for $C_7H_9ONClBr$: halogen = 48.41; found: 48.51.

4-Bromo-6-amino-m-cresol.—This free base was easily prepared by mixing with a faintly acid (hydrochloric) solution of the aminohydrochloride, described above, a slight excess of ammonium carbonate solution. The amine was promptly precipitated, and after a few minutes it was collected on a filter, washed several times with cold water, and dried on clay plate. It was found to be soluble in alcohol, benzene, and less so in ligroin. It

---

[1] *Ann. Chem.* (*Liebig*), **259**, 224 (1890).

[2] *Ber.*, **13**, 972 (1880).

was best purified by crystallization from benzene, from which it was obtained in nearly colorless crystals that melted sharply at 145°.

0.1532 g. subs. gave 0.0808 g. Ag (electrolyt. dep.); calc. for C_7H_8ONBr: Br = 39.55; found: 39.04.

Nitration of 4-bromo-6-nitro-m-cresol.—A portion of the monobromo product weighing 5 g. was finely powdered and then added to a mixture of 54 cc. nitric acid (sp. gr. 1.42) and 21 cc. sulfuric acid (sp. gr. 1.84), that had been cooled to the room temperature. After being shaken for about 15 min. the reaction mixture was filtered through glass wool to remove unchanged material, and the clear filtrate was poured into ten volumes of cold water. A light yellow precipitate was formed. The liquid was allowed to stand for half an hour, after which the solid was removed by filtration, washed with a little cold water, and dried on clay plate. In this condition the product melted at 72°–75°, due to the presence of trinitro-*m*-cresol, probably. To show that the latter had been formed during the nitration, some of the filtrate obtained as above was extracted with ether, the ether removed by evaporation, and the residue dissolved in water and converted into potassium salt. The latter was twice crystallized from water and then decomposed by hydrochloric acid. The free nitro compound was removed and crystallized from alcohol. It was melted with a sample of trinitro-*m*-cresol prepared in accordance with the method of Duclos,[1] without showing any depression of melting point. To show that the monobromomononitro compound could be easily and completely converted into trinitro-*m*-cresol in a single operation, a portion was nitrated by varying the above method slightly. In this case the reaction mixture was warmed sufficiently to bring all solid into solution, and when the latter was poured into water nothing was precipitated. Extraction with ether and purification as described for the filtrate above gave a compound that melted sharply at 106°, and that did not depress the melting point of a sample known to be trinitro-*m*-cresol.

In order to secure the dinitro compound in a pure form, the crude product melting at 72°–75° was converted into ammonium salt, and this was repeatedly crystallized from ammonium hydroxide solution. Orange colored crystals were obtained.

0.2798 g. subs. gave 0.1802 g. AgBr; calc. for $C_7H_8O_5N_3Br$: Br = 27.22; found: 27.40.

A portion of the pure ammonium salt was dissolved in water and then a slight excess of hydrochloric acid added. The free nitro compound that separated was collected on a filter, dried in the air, and crystallized twice from ligroin, 70°–80°. It gave fine yellow needles that melted sharply at 77°.

0.1287 g. subs. gave 0.0868 g. AgBr; calc. for $C_7H_5O_5N_2Br$: Br = 28.88; found: 28.70.

---

[1] *Ann. Chem.* (*Liebig*), **109**, 141 (1859).

Potassium Salt of 4-Bromo-2,6-dinitro-m-cresol.—The dinitro compound that has been described was further identified by the preparation of its potassium salt. The other reason for preparing this salt was to secure material for the preparation of the ether mentioned below. The salt was easily obtained by dissolving the nitro compound in a slight excess of hot potassium hydroxide solution, from which the product separated in scarlet plates which were further purified by a second crystallization from water.

0.2849 g. sub. gave 0.1711 g. AgBr; calc. for $C_7H_4O_5N_2BrK$: Br = 25.39; found: 25.55.

Silver Salt of 4-Bromo-2,6-dinitro-m-cresol.—The silver salt was prepared by mixing slightly more than the calculated amount of silver nitrate solution with a warm dilute solution of the potassium salt described above. Scarlet crystals of the silver salt formed rapidly. These were removed by filtration, washed with a small quantity of cold water, and then dried. It may be noted that this salt is much more soluble in water than the silver salt of the mononitro compound, mentioned on a previous page. It was used in the preparation of the ethyl ether.

Ethyl Ether of 4-Bromo-2,6-dinitro-m-cresol.—This ether was prepared for the purpose of securing a substance having the same composition and containing the same groups as the expected bromine derivative of the 4,6-dinitro-*m*-cresyl ether (p. 1500), which we were trying to obtain at that time, with the hope that a comparison of the properties of the two products would enable us to decide the position of the bromine atom. Though the failure of bromine to react with the dinitro ether prevented the comparison, it seemed worth while to report the preparation of the ether here described in order to call attention to the marked difference in the rates of reaction when the silver salts of 4-bromo-6-nitro-*m*-cresol, and 4-bromo-2,6-dinitro-*m*-cresol, respectively, were brought in contact with ethyl iodide. The first named, as has been pointed out above, reacted very slowly; the second, as indicated below, reacted rapidly. Three grams of the silver salt of monobromodinitro-*m*-cresol were mixed with 20 cc. of dry ether, and then slightly more than the calculated amount of ethyl iodide was added. Vigorous action began at once, with considerable rise of temperature, and the reaction was apparently complete in a short period (few minutes). Heating the mixture under a reflux condenser over a water bath caused no further change. The cooled mixture was filtered, the residue washed several times with small portions of dry ether, and the collected filtrate and washings shaken with a solution of sodium carbonate for the purpose of removing any free nitro compound. When the ethereal solution was placed in a distilling flask and the ether evaporated off, a brown, syrupy liquid was left. This was cooled with ice, but it failed to give any solid until allowed to stand for several hours in a vacuum desiccator. The brown solid finally obtained was crystallized from methyl alcohol, and gave nearly colorless crystals that melted at 64°–65°. The substance becomes yellow colored when kept. It was easily soluble in other organic solvents, but did not crystallize well from any but alcohol.

0.2223 g. subs. gave 0.0785 g. Ag (electrolyt. dep.); calc. for $C_9H_9O_5N_2Br$: Br = 26.25; found: 26.16.

The Action of Bromine on the Monobromo-6-nitro-m-cresol.—A portion of the monobromonitrocresol weighing 2 g. was dissolved in 15 cc. glacial acetic acid, and the solution warmed slightly. To this, a solution of bromine in acetic acid was added, and after being shaken for a few minutes, was cooled. No crystals of monobromo compound separated out. The liquid was poured, with stirring into six volumes of cold water, and gave a yellow precipitate. This was removed by filtration, dried, and crystallized from alcohol. Long yellow needles that melted at 87° were obtained. When a mixture of this product and the 2,4-dibromo-6-nitro-*m*-cresol obtained by the nitration of 2,4,6-tribromo-*m*-cresol was melted, the melting point was the same as that of either product separately, which indicates that they are identical. In the monobromo compound under investigation, then, bromine occupied position II or IV.

Chlorination of the Monobromo-6-nitro-m-cresol.—The first attempts to chlorinate this compound were made by passing chlorine into a glacial acetic acid solution of the substance. The yield was poor and the product was difficult to purify. A much better result was obtained by using carbon tetrachloride as a solvent and dry pulverized iron as a "chlorine carrier." Ten grams of the compound were dissolved in 290 cc. carbon tetrachloride, and about 2 g. of iron added. One molecule of chlorine, generated by dropping hydrochloric acid on potassium permanganate, was led into this liquid, while the flask was continually shaken. The temperature did not rise much above that of the room. At the end of the reaction the mixture was filtered through paper, and the clear filtrate reduced to a small volume by distilling off the carbon tetrachloride on the water bath. The dark colored residue was poured into a beaker and allowed to crystallize while the remainder of the solvent slowly evaporated. The solid weighed 11.2 g. and had a m. p. of 72°–75°. The compound dissolves readily in alcohol, and after four crystallizations from that solvent it had a constant m. p. of 80°. It can be purified quite easily in the form of its potassium salt, which separates from water in the form of crimson rhombic crystals. A second crystallization in this way gave a product that was shown by analysis to be pure.

0.3395 g. subs. gave 0.3691 g. AgHal; calc. for $C_7H_4O_3NClBrK$: Hal = 37.92; found: 37.87.

The free nitro compound, which turned out to be 2-chloro-4-bromo-6-nitro-*m*-cresol, was obtained from the potassium salt described above by treatment of an aqueous solution of the latter with hydrochloric acid.

The yellow precipitate was collected on a filter, washed with water, and at once crystallized from alcohol. It gave yellow needles that melted at 80°. It should be noted that a mixture of this compound and dichloro-6-nitro-*m*-cresol, m. p. 88°,[1] in which the halogen atoms are probably in positions II and VI, does not melt below 80°.

0.2089 g. subs. gave 0.2584 g. AgHal; calc. for $C_7H_5O_3NClBr$: Hal = 43.31; found: 43.11.

Hydrochloride of 2-Chloro-4-bromo-6-amino-m-cresol.—The nitro compound under consideration was further identified by the preparation of the corresponding aminohydrochloride. This was done in the manner already described, though it was found necessary to use much more alcohol than has been required in the cases of other nitro compounds.[2] This was due to the fact that both the nitro compound and the hydrochloride are almost insoluble in the hydrochloric acid used to dissolve the stannous chloride employed in the reduction. Consequently, unless enough alcohol is used to hold all nitro compound in solution, at the boiling point, even when it is diluted with an equal volume of an aqueous liquid, reduction will not be complete, and the solid that separates when the mixture cools will contain both nitro compound and aminohydrochloride. The very slight solubility of the hydrochloride in water made it necessary to modify the method described above for purifying these compounds. This one was best freed from tin salt by treatment of its solution in dilute alcohol with concentrated hydrochloric acid. The nearly colorless crystals that resulted were collected on a filter, pressed out on a porous plate and dried in air 24 hours, and then *in vacuo*, over potassium hydroxide, for 72 hrs. before analysis.

0.2561 g. subs. gave 0.4413 g. AgHal; calc. for $C_7H_8ONCl_2Br$: Hal = 55.28; found: 54.80.[3]

2-Chloro-4-bromo-6-amino-m-cresol.—The free base was obtained by decomposing the hydrochloride with ammonium carbonate. After washing with water and drying over night the base was crystallized from benzene. It gave nearly colorless scales that melted at 145°–146°. With acetic anhydride it reacts very vigorously to give a derivative that crystallized from alcohol in the form of long, colorless, silky needles that melted at 199°. This substance did not dissolve in solution of sodium hydroxide except on standing for several hours, and was regarded as a diacetyl com-

---

[1] Raiford and Baird, unpublished work.

[2] *Am. Chem. J.*, 46, 419 (1911).

[3] The low percentage of halogen was not regarded as indicating an impure substance, because in a closely related case (THIS JOURNAL, 36, 678 (1914)) the same facts were noted, while in that case, as in this, the free base (see below) obtained from the hydrochloride was found by analysis to be pure. The explanation of the low percentage of halogen in both hydrochlorides is the probable loss of hydrogen chloride by dissociation during the drying.

pound. A portion of the free base was dried *in vacuo* for 24 hrs., and analyzed.

0.2648 g. subs. gave 0.3722 g. AgHal; calc. for $C_7H_7ONClBr$: Hal = 48.82; found: 48.98.

Reaction of 2-Chloro-4-bromo-6-amino-m-cresol with Nitrous Acid.—In order to secure further proof of the position of the bromine atom in the compound under consideration, it was proposed to replace the amino group by chlorine, by means of the Sandmeyer reaction, and then try to oxidize the resulting cresol to the corresponding quinone. In such a case the halogen para to hydroxyl would be lost, and identification of the quinone would show whether chlorine or bromine occupied the *p*- position in the original substance. The preliminary attempts to diazotize the amine did not give satisfactory results. In the first place, the aminohydrochloride with which we started is nearly insoluble in water, and particularly so in the presence of the relatively large amount of hydrochloric acid necessary for the Sandmeyer reaction. Attempts to secure a paste by grinding the solid with water and acid did not give a homogeneous mixture. It was therefore found impossible to bring the sodium nitrite solution in contact with this material, and secure a uniform reaction, by agitating the containing flask in the usual way. This difficulty was further emphasized by the fact that the product of the reaction (which was not a diazonium salt) was quite as insoluble in water as the compound with which we started. To overcome these unfavorable conditions, in a measure, the mixture of aminohydrochloride, water and hydrochloric acid, after being rubbed into as smooth a paste as possible, was placed in a glass stoppered bottle; and after each addition of the sodium nitrite solution the bottle was removed from the cooling bath and shaken vigorously for several minutes. When, after such a mixing of the material, a test showed the presence of free nitrous acid, a portion of the brown solid was removed by filtration, washed with water and dried. It decomposed suddenly when heated above 155°. After two crystallizations from alcohol it was obtained in the form of brown needles that behaved as stated above. These properties indicated a diazo-oxide, and an analysis for halogen supported this view.

0.1995 g. subs. gave 0.2673 g. AgHal; calc. for $C_7H_4ON_2ClBr$: Hal = 46.65; found: 46.70.

Behavior of the Diazo-oxide toward Cuprous Chloride Solution.—Portions of the mixture containing the diazo-oxide were transferred in the usual way to the amount of cuprous chloride solution commonly employed in the Sandmeyer reaction. The yield was poor, and the product was a mixture that we did not succeed in separating. Only when 2.5 to 3.0 times the usual quantity of cuprous chloride solution was used, and when, after each addition of liquid containing the diazo-oxide, the mixture, contained in a stoppered bottle, was vigorously shaken for several minutes, was a satisfactory yield of fairly pure product obtained. Without these precautions the diazo-oxide tends to float on the surface of the liquid and escape action with the cuprous chloride. After mixing, the liquid was allowed to stand for half an hour, with frequent shaking, and was then distilled with steam. An oil that solidified partly in the condenser passed over. Cooling the receiving flask caused the entire product to solidify in the form of crystals that were slightly brownish in color. These were collected by filtration, and dried. The yield was about 65% and the substance melted at 63–64°. It was further purified by crystallization from ligroin (70°–80°), from which it separated in pale, fawn colored needles that melted at 65°. It is but sparingly soluble in water, and the solution develops no color when mixed with ferric chloride.[1] It is readily soluble in solution of sodium hydroxide, and from this it is completely precipitated by carbon dioxide. It cannot be distilled at atmospheric pressure without decomposition. Analysis for halogen showed that it is a monobromodichlorocresol.

0.2141 g. subs. gave 0.3986 g. AgHal; calc. for $C_7H_5OCl_2Br$: Hal = 58.90; found: 59.17.

Oxidation of 2,6-Dichloro-4-bromo-m-cresol.—One gram of the cresol was dissolved in 30 cc. glacial acetic acid, and the solution cooled as far as possible (to about 10°) without causing solid to separate. To this liquid there was gradually added, with shaking, a cold solution of sodium dichromate and sulfuric acid, and the mixture allowed to stand for half an hour. An equal volume of cold water was next added and the whole left for an hour. The quinone that subsided was removed by filtration, washed well with cold water, and dried. A yield of about 65% was obtained. In this condition the product melted at about 90°. After crystallization from ligroin (70–80°) it melted at 102°, and a mixture of it and 2,6-dichlorotoluquinone, obtained by oxidizing 2,4,6-trichloro-*m*-cresol in the manner described above, showed no depression. A small quantity of the substance was mixed with water and reduced by sulfur dioxide to the corresponding hydroquinone. This melted at 171°, and did not depress the melting point of 2,6-dichlorotoluquinone.[2] These facts, however, were not sufficient to establish, beyond question, the identity of the two products; for it has been found, as stated on a previous page, that in this group, at least, chlorine and bromine may replace each other without causing a change of melting point, and that the respective products may be melted together without appreciable depression. Our product, therefore, was analyzed.

0.1575 g. subs. gave 0.2378 g. AgCl; calc. for $C_7H_4O_2Cl_2$: Cl = 37.14; found: 37.33.

---

[1] See *Am. Chem. J.*, 46, 424 (1911).

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

Summary.

1. When 6-nitro-*m*-cresol is brominated in acetic acid solution, a mixture of 4-bromo-6-nitro-*m*-cresol and 2,4-dibromo-6-nitro-*m*-cresol is formed. The difference in solubility of these two products in acetic acid permits of almost complete separation by filtration of the reaction mixture. 4-Bromo-6-nitro-*m*-cresol, which had not previously been described, has been studied and its structure established.
2. The ortho positions of the hydroxyl and nitro groups in the mononitrodibromo-*m*-cresol (m. p. 87°) obtained by nitration of 2,4,6-tribromo-*m*-cresol[1] have been confirmed.
3. When 4-bromo-6-nitro-*m*-cresol is chlorinated in the presence of iron, chlorine enters position II, that is, between methyl and hydroxyl.
4. Treatment of 2-chloro-4-bromo-6-amino-*m*-cresol with nitrous acid gives a diazo-oxide that will react with cuprous chloride to give a trihalogenated cresol.

CHICAGO, ILL.

THE ACTION OF CHLORAL, CHLORAL HYDRATE AND BROMAL ON CERTAIN ORGANIC COMPOUNDS IN THE PRESENCE OF ALUMINIUM CHLORIDE.

BY G. B. FRANKFORTER AND W. KRITCHEVSKY.

Received May 13, 1914.

Part I.

The following pages are devoted to a new phase of the Friedel-Crafts reaction. This unique historical reaction[2] represents one of a series of chemical changes commonly classed under catalysis. Catalysis may be best defined as a chemical change, either analytic or synthetic, brought about by the influence of a substance but without that substance entering permanently into the reaction; or, as stated by Ostwald, an increase in the reaction velocity beyond the normal by some substance which does not enter the reaction.

As is well known, many of the true organic condensation processes are brought about by one of two common reactions, namely, the Friedel-Crafts and the Baeyer reaction, the one acknowledged as purely catalytic, eliminating hydrochloric acid—the other, perhaps dehydrolytic, eliminating water. It will be shown in this paper that although these two reactions have been regarded as separate and distinct in their behavior ever since they were discovered by the men whose names they bear, they do, in many cases, act alike; for aluminium chloride not only plays the part of a catalyst in breaking off hydrochloric acid, but it also acts as a substitute for sulfuric acid, removing water from the reacting components.

---

[1] *J. prakt. Chem.*, [2] 61, 561 (1900); *Am. Chem. J.*, 46, 426 (1911).

[2] *Compt. rend.*, 84, 1392 (1877); *Ann. chim. phys.*, [6] 449 (1884).