CLXXVIII.—*The Chlorination and Bromination of Substituted Toluenes.*

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A COMPARISON of the products obtained by chlorinating the isomeric chlorotoluenes, and by brominating the isomeric bromotoluenes, shows that the two halogens possess a different orienting effect. Cohen and Dakin (T., 1901, **79**, 1111) found that *o*-chlorotoluene, on chlorination in presence of the aluminium-mercury couple, gives mainly 2:4- together with some 2:3- and 2:6-dichlorotoluene; whilst Cohen and Dutt (T., 1914, **105**, 501) found that on bromination *o*-bromotoluene gives mainly 2:5-, with a smaller quantity of 2:4-dibromotoluene. In the case of the meta- and para-substituted toluenes the same products were obtained in both cases. It was thought that some further light might be thrown

on the orienting effect of these halogens by studying the products of chlorination of the isomeric bromotoluenes, and of bromination of the chlorotoluenes.

The only previous investigation on this subject which we have been able to find is one by Willgerodt and Salzmänn (J. pr. Chem., 1889, [ii], **39**, 465). They chlorinated ortho- and para-bromotoluene, using iron as catalyst, and also brominated ortho- and para-chlorotoluene. Their conclusions are based on the character of the chlorobromobenzoic acids obtained by oxidising these products derived from a comparison of their melting points with those of the pure substances. Since the melting points of the latter which they give are in every case wrong, the results are obviously worthless. The melting points obtained by them are tabulated alongside the correct ones obtained directly by Cohen and Raper (T., 1904, **85**, 1262).

Chlorobromobenzoic acid. Cl : Br.	M.P. (Cohen and Raper).	M. p. (Willgerodt and Salzmänn).
2 : 4	166—167°	156°
3 : 4	218	170
2 : 6	143	132
4 : 2	154—155	217

Following the method adopted by Cohen and Dutt, the isomeric chlorobromotoluenes, and such of their derivatives as afforded the best means of identification, were first prepared.

The Isomeric Chlorobromotoluenes.

These were all prepared by the methods adopted by Cohen and Raper (*loc. cit.*) with the exception of 2:3-chlorobromotoluene, which was obtained by Wynne's method (T., 1892, **61**, 1040). The substance melts at 18°. The 3:2-compound melts at 4—5°, and the 3:5-compound at 26—27°. The other isomerides are liquid at 0°. The derivatives were prepared in the same ways as those of the dichlorotoluenes (T., 1901, **79**, 1111), and tables of their melting points, together with those of the dichloro- and dibromo-compounds, are given below.

Melting Points of Mononitro-derivatives.

Substance.	Cl : Cl.	Cl : Br.	Br : Cl.	Br : Br.
2 : 3	50.5—51.5°	44—45°	58—59.5°	58—59°
2 : 4	54—55	65—66	64—65	79—80
2 : 5	50—51	68—69	66—67	87—88
2 : 6	53		50—52	49—50
3 : 4	63—64	72	67.5	86—87
3 : 5	61—62		69—71	66—67

In regard to the melting points of the chlorobromonitro-derivatives, the isomeride with the bromine atom nearest the methyl group has the lower melting point, with the exception of the 2:3-compound. It is a curious fact that the 2:3-dichloro-, 2:3-chlorobromo-, 3:2-chlorobromo-, and the 2:3-dibromo-mono-nitro-compounds crystallise in felted masses of fine needles, which on pressure form wax-like substances, whereas the others crystallise in hard needles which can be powdered.

Melting Points of the Dinitro-derivatives.

Substance.	Cl: Cl.	Cl: Br.	Br: Cl.	Br: Br.
2:3	71—72°	89—93°	81°	107—109
2:4	104	110—111	124·5	129—130
2:5	100—101	109—110	117·0	142—143
2:6	121—122		143—144	161—162
3:4	91·5—92·5	101—102	127·0	129—130
3:5	99—100		92	{ 156—157 } { 104·5—105 }

The isomeride with the bromine atom nearest the methyl group has the higher melting point, with the exception of the 2:3-compound. The order is exactly the reverse of that of the mononitro-derivatives.

Melting Points of the Sulphonyl Chlorides.

Substance.	Cl: Cl.	Cl: Br.	Br: Cl.	Br: Br.
2:3	liquid	81—84°	70—71°	93°
2:4	71	79	84	86—88
2:5	45—46	45—46	49—50	73—74
2:6	liquid		70	101
3:4	81	101	87—88	104—105
3:5	44—45		liquid	liquid

Melting Points of Sulphonamides.

Substance.	Cl: Cl.	Cl: Br.	Br: Cl.	Br: Br.
2:3	222°	200—201°	224°	214°
2:4	176	186	186	212—213
2:5	191—192	192	201	210—211
2:6	207		205	204
3:4	190—191	191—192	204·5	212
3:5	168—169		178	195

The isomeride with the bromine atom nearest the methyl group has the higher melting point.

Melting Points of the Substituted Benzoic Acids.

Substance.	Cl: Cl.	Cl: Br.	Br: Cl.	Br: Br.
2:3	163°	165°	143°	149—150°
2:4	159—160	166—167	154—155	168—169
2:5	153	155—156	153 ¹	153
2:6	139—140		143	146—147
3:4	200—201	218	214	229—230
3:5	182—183		189—190	213—214

¹ The melting point given by Cohen and Raper, namely, 149—150°, has been re-examined by us and was found too low.

The isomeride with the bromine atom nearest the carboxyl group has the lower melting point.

The crystalline form of the barium salts of the sulphonic acids was found to be of service in some cases in the process of identification. The 2:5-, 5:2-, 3:4-, 4:3-, and 2:3-chlorobromo-compounds form rhombohedral or hexagonal plates. The 4:2- and 2:6-compounds form rectangular plates. The 3:2-compound is very soluble, and forms hexagonal needles. The 3:5-compound forms highly refractive cubes, and the 2:4-compound appears as pyramids on a rectangular base.

*Bromination of the Chlorotoluenes.**Bromination of o-Chlorotoluene.*

Twenty-seven grams of *o*-chlorotoluene were mixed with 27 c.c. of carbon tetrachloride in a flask, and a small piece of aluminium-mercury couple dropped in. The calculated quantity of bromine (34 grams) dissolved in 27 c.c. of carbon tetrachloride was then slowly run in from a tap-funnel, the flask being cooled in ice. The brown product was shaken with sodium hydroxide solution, washed with water, and the colourless liquid dehydrated over sodium sulphate. The carbon tetrachloride was distilled off, and the remaining liquid fractionated under diminished pressure, 25 grams being collected at 110—120°/25 mm.

Sulphonation of the Mixed Chlorobromotoluenes.

Seven grams of the above product were mixed with 21 grams of fuming sulphuric acid, and warmed on the water-bath for fifteen minutes. The product was poured into water, boiled with barium carbonate, and filtered. The solution was then concentrated and allowed to crystallise, when there were obtained 9.6 grams of hexagonal plates, corresponding with the 2:5-compound. The mother liquor on further concentration deposited 1.5 grams of pyramidal crystals corresponding with the 2:4-barium salt.

Oxidation of the Mixed Chlorobromotoluenes.

The oxidation was carried out in sealed tubes at 160° with dilute nitric acid ($\text{HNO}_3 : 3\frac{1}{2}\text{H}_2\text{O}$). Twenty grams were oxidised, and the solid product was dissolved in sodium carbonate solution. After extracting with ether to remove impurities, the acid was precipitated with hydrochloric acid, filtered, and treated with barium carbonate. The solution was filtered, concentrated, and 10 grams of the barium salts were fractionally crystallised. The first fraction (8 grams) gave on precipitation an acid melting at about 150° , which after three crystallisations from alcohol melted at $155\text{--}156^{\circ}$ ($2:5=155\text{--}156^{\circ}$). The acid was precipitated from the mother liquor, giving 1 gram, melting, after two crystallisations from hot water, at $166\text{--}166.5^{\circ}$ ($2:4=166\text{--}167^{\circ}$).

Six grams of the mixed acids were esterified by Fischer and Speier's method, in the hope of separating the $2:6$ -compound. The esterification was, however, complete, and the absence of the $2:6$ -compound confirmed.

Since the melting points of the $2:5$ - and $2:4$ -dinitro-derivatives are almost identical, no attempt was made to effect separation by means of these compounds.

Bromination of *o*-chlorotoluene gives, therefore, the $2:5$ -compound as the main product, and a smaller quantity of the $2:4$ -compound.

Bromination of m-Chlorotoluene.

The bromination was carried out as described above, 33 grams of *m*-chlorotoluene yielding 34 grams, boiling at $100\text{--}103^{\circ}/15\text{ mm.}$, which was practically the whole product.

Sulphonation of the Mixed Chlorobromotoluenes

Eight grams of the above product were sulphonated, and yielded 11 grams of barium salts. These were fractionally crystallised, but all fractions consisted of mixtures of hexagonal and rhombohedral plates, corresponding with mixtures of the $2:5$ - and $3:4$ -compounds. The sulphonyl chlorides and amides were prepared from these, but no separation was effected by fractional crystallisation.

Oxidation of the Mixed Chlorobromotoluenes.

Nine grams of the mixed chlorobromotoluenes were oxidised, and the barium salts fractionated. The first fraction gave 2 grams of acid, which melted at $212\text{--}215^{\circ}$ after recrystallising from methyl alcohol. After another crystallisation the melting point was 216° ($3:4=218^{\circ}$). The remaining fractions, consisting of 6.2 grams,

melted at 152—153°. after crystallising from dilute methyl alcohol (2:5=153°). A small quantity of solid, melting at 135°, remained undissolved in the sodium carbonate, and was probably an aldehyde.

Nitration of the Mixed Chlorobromotoluenes.

Nitration was effected by heating the chlorobromotoluene on the water-bath with a mixture of equal parts of concentrated sulphuric and fuming nitric acids, until a test sample solidified on pouring into cold water. Five grams of the mixed toluenes gave 7.3 grams of crude product, which on recrystallisation from methyl alcohol gave 4 grams melting at 115—117° (2:5=117°). The mother liquor deposited an uncrystallisable oil, and a small quantity of crystals, which melted at 95—98° on recrystallising, and were probably the 3:4-compound (m. p. 101—102°).

The 2:5-compound appears to be the main product of bromination of *m*-chlorotoluene, accompanied by a smaller quantity of the 3:4-compound.

Bromination of p-Chlorotoluene.

Sixty grams of *p*-chlorotoluene were brominated, and gave 42 grams of product boiling at 100—110°/14 mm., and a small quantity of a solid trihalogen compound, which remained in the distilling flask. On analysis of the liquid distillate:

0.1773 gave 0.2844 AgBr + AgCl. Cl + Br = 55.61.

C₇H₆ClBr requires Cl + Br = 56.15 per cent.

Only two isomerides can be formed, namely, the 2:4- and 3:4-compounds; but as the melting points of the dinitro-compounds are very close together, and the barium sulphonates both form plates, only the chlorobromobenzoic acids could be used for separation and identification.

Oxidation of the Mixed Chlorobromotoluenes.

Eleven grams of the above product were oxidised, and the barium salts fractionated. The first fraction (5.5 grams) gave an acid melting at 214° after recrystallisation from alcohol (3:4=214°). The remainder (9.5 grams) gave an acid melting at 154—155° after recrystallisation, corresponding with the 2:4-compound.

Both possible isomerides are therefore formed when *p*-chlorotoluene is brominated, the 2:4-compound being the main product.

*Chlorination of the Bromotoluenes.**Chlorination of o-Bromotoluene.*

Chlorination was effected directly, using aluminium-mercury couple as carrier. 51.7 Grams of *o*-chlorotoluene were placed in a flask, and a small piece of the couple added. The whole was cooled in ice, and dry chlorine from a cylinder slowly bubbled through the liquid, until the weight of the apparatus increased by 10.4 grams, being the calculated increase for one atom of chlorine. Hydrochloric acid escaped from an exit tube fitted with a calcium chloride drying tube. The product was then washed and dried as before, and 35 grams boiling at 100—108°/10 mm. were collected:

0.1957 gave 0.3189 AgBr + AgCl. $\text{Cl} + \text{Br} = 56.5$.

$\text{C}_7\text{H}_6\text{ClBr}$ requires $\text{Cl} + \text{Br} = 56.15$ per cent.

As the melting points of the sulphonamides lie close together, the other methods of identification were employed.

Oxidation of the Mixed Chlorobromotoluenes.

Ten grams of the product were oxidised, the sodium salts formed, and the chlorobromobenzoic acids precipitated, giving 5 grams of dry acid. This was esterified by Fischer and Speier's method, and unchanged acid extracted with sodium carbonate. After removing the ester by extraction with ether, 1 gram of acid was precipitated which was not esterifiable, and therefore corresponds with the 2:6-compound. The ester was hydrolysed, and the barium salts of the acids formed and crystallised. The first fraction, containing most of the salt, gave an acid melting at 152—154° after crystallising from hot water. To distinguish between the 2:4- (m. p. 154—155°) and the 2:5-compound (m. p. 153°) the acid was mixed with an equal quantity of the pure 2:5- and also with the 2:4-acid, and the melting point redetermined. In the former case it was found to have fallen to 138—140°, and in the latter it remained unchanged. The acid must therefore correspond with the 2:4-compound, and is the main product. The acid precipitated from the mother liquor was very impure, and insufficient to purify by recrystallisation.

Nitration of the Mixed Chlorobromotoluenes.

Seven grams of the mixed chlorobromotoluenes gave 10 grams of crude product on nitration, which were fractionally crystallised from alcohol. The first fraction, 2.5 grams, melted at 144° after six recrystallisations (2:6 = 142—144°). A second fraction, 5 grams,

melted at 107—108° after repeated crystallisation, and might be either the 2:4- (m. p. 124·5°) or the 2:5-compound (m. p. 117°). Further evaporation produced an oily product, probably containing some mononitro-derivative:

0·1423 (m. p. 144°) gave 0·1616 AgBr + AgCl. Cl + Br = 39·55.

0·1171 (m. p. 107—108°) gave 0·1283 AgBr + AgCl. Cl + Br = 38·78.

$C_7H_4O_4N_2ClBr$ requires Cl + Br = 39·19 per cent.

A portion of the compound melting at 144° showed no fall in melting point when mixed with some of the pure 2:6-compound.

Chlorination of *o*-bromotoluene therefore gives the 2:4-compound as the main product, with a smaller quantity of the 2:6-compound.

Chlorination of m-Bromotoluene.

Twenty-two grams of *m*-bromotoluene were dissolved in 22 c.c. of carbon tetrachloride, a piece of aluminium-mercury couple added, and chlorine passed in until an increase in weight of 4 grams was obtained. On distillation 18 grams were obtained, boiling at 120—124°/35 mm., which contained approximately the correct amount of the halogen:

0·1970 gave 0·3059 AgBr + AgCl. Cl + Br = 54·10.

C_7H_6ClBr requires Cl + Br = 56·15 per cent.

Sulphonation of the Mixed Chlorobromotoluenes.

Two grams of the above product were sulphonated, and the barium salts fractionated. The first crystals to separate were mainly rhombohedral plates, 1·8 grams, corresponding with the 3:4-compound. The final fraction of 1 gram was hexagonal plates, almost free from rhombohedral plates, and was probably the 2:4-compound.

Oxidation of the Mixed Chlorobromotoluenes.

Eight grams of the product were oxidised, and the barium salts fractionally crystallised. The first fraction gave 1 gram of an acid melting at 213—214° after recrystallisation (3:4 = 214°). The remainder gave 4·5 grams of acid, which, after recrystallisation from alcohol, melted at 154—156°, corresponding with the 2:5-compound (m. p. 155—156°).

Nitration of the Mixed Chlorobromotoluenes.

Five grams of the product were nitrated, and gave 3 grams of a dinitro-compound melting at 121—124° (3:4 = 127°). No other

isomeride was separated, as the product obtained on concentrating the mother liquor was an oil.

Chlorination of *m*-bromotoluene therefore gives the 2:5-compound as the main product, with a considerable quantity of the 3:4-compound. The other isomerides were not detected.

Chlorination of p-Bromotoluene.

Dry chlorine was passed into 68 grams of *p*-bromotoluene containing the couple, until an increase in weight of 14 grams was obtained. On distillation, 52 grams of product boiling at 100—107°/15 mm. were obtained:

0.2028 gave 0.3270 AgBr + AgCl. $\text{Cl} + \text{Br} = 55.90$.

$\text{C}_7\text{H}_6\text{ClBr}$ requires $\text{Cl} + \text{Br} = 56.15$ per cent.

Sulphonation of the Mixed Chlorobromotoluenes.

Five grams of the above product were sulphonated, and the barium salts fractionated. All the fractions consisted of rhombohedral plates. The first fraction of 5.7 grams was converted into the sulphonyl chloride, melting at 68—72°. This was converted into the sulphonamide, which crystallised in colourless needles, melting at 191—192° (3:4 = 191—192°). The last fractions, weighing 2.5 grams, were converted into a liquid sulphonyl chloride, which gave a sulphonamide crystallising in needles and melting sharply at 186° (2:4 = 186°). An intermediate fraction of 1.2 grams was not treated, being probably a mixture of the two isomerides.

Oxidation of the Mixed Chlorobromotoluenes.

Ten grams of the product were oxidised to the corresponding chlorobromobenzoic acids, and the barium salts fractionated. The first fraction gave 1 gram of acid melting at 207—210° after recrystallisation (3:4 = 218°). The remaining fractions gave 7 grams of acid, which melted at 165—167° after crystallising from alcohol, corresponding with the 2:4-compound (m. p. 166—167°).

Nitration of the Mixed Chlorobromotoluenes.

Three grams of the product were nitrated, giving a viscid mass, melting completely at 96°. After nine recrystallisations from alcohol the melting point remained constant at 110—111° (2:4 = 110—111°).

The main product obtained by chlorinating *p*-bromotoluene is

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therefore the 2:4-compound, which is accompanied by a small quantity of the 3:4-compound.

These results are embodied in the table given below, which includes for comparison the results of brominating bromotoluene and chlorinating chlorotoluene. The main product is placed first, and a trace indicated by brackets.

Chlorination Products.

Bromo-toluene.	Products.	Chloro-toluene.	Products.
Ortho	2:4, 2:6	Ortho	2:4, 2:3, 2:6, (2:5)
Meta	2:5, 3:4	Meta	2:5, 3:4
Para	2:4, 3:4	Para	2:4, 3:4

Bromination Products.

Chloro-toluene.	Products.	Bromo-toluene.	Products.
Ortho	2:5, 2:4	Ortho	2:5, 2:4
Meta	2:5, 3:4	Meta	2:5, 3:4, (3:5)
Para	2:4, 3:4	Para	2:4, 3:4

In examining the above tables it will be seen that the only difference in the relative quantity and character of the products occurs in the case of the ortho-compounds.

The result of chlorinating the ortho-compounds is remarkably different from that produced by bromination, for whereas the former gives the 2:4-derivative as the principal product, the latter forms mainly the 2:5-compound, or, in other words, the entrant bromine atom is repelled more than the entrant chlorine atom by the ortho-halogen. In addition to this, however, there are noticeable differences in the proportions of the products of chlorination of *o*-bromo- and *o*-chloro-toluene; for in the first case the 2:6-compound occupies the second place, and no 2:3-derivative is formed; but in chlorination the 2:3-compound occupies the second place, and although the 2:6-compound is present, it is there in smaller quantity.

These somewhat remarkable irregularities only serve to emphasise our ignorance of the determining factors of orientation.

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