CXX.—*The Aluminium-Mercury Couple. Part III. Chlorination of Aromatic Hydrocarbons in presence of the Couple. The Constitution of the Dichlorotoluenes.*

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Introduction.

THE readiness with which the aromatic hydrocarbons undergo bromination in presence of the aluminium-mercury couple (Trans., 1899, **75**, 893) suggested a series of experiments on the chlorination of these hydrocarbons under similar conditions.

By passing dry chlorine into benzene in presence of a fragment of the couple, chlorination proceeds actively, the liquid becoming darker in colour whilst torrents of hydrochloric acid are evolved. The couple is only slightly attacked.

By interrupting the process when a certain increase in weight had been obtained, the different chlorination products from the monochlorobenzene to the hexachlorobenzene were, in turn, isolated. Where the products were solid, it was necessary to add carbon tetrachloride to keep the substance in solution during chlorination. Similar experiments were carried out with toluene.

The systematic study of the action of chlorine on toluene dates from the year 1866, when Beilstein and Geitner (*Annalen*, 1866, **139**, 331) discovered the action of chlorine on hot and cold toluene in producing substitution in the side-chain or nucleus, and showed at the same time that by the use of iodine—a halogen carrier first employed by Hugo Müller—substitution may be confined to the nucleus. Since then, the action of chlorine on toluene in presence of different "halogen-carriers" has been repeatedly investigated with the object of orienting the products formed.

The data which have thus been accumulated by different observers are very voluminous, but are so conflicting, that at the present time our knowledge of the products of this simple reaction is very indefinite.

It was in attempting to collect evidence of the constitution of the chlorine derivatives of toluene by reference to the work of previous observers that we first realised its unsatisfactory character and determined to make a complete study of the whole subject.

The conflicting nature of the evidence will be readily understood from the following brief summary.

Beilstein and Geitner (*loc. cit.*) and Beilstein and Kuhlberg (*Annalen,* 1869, **150**, 313; **152**, 224) in their first papers describe only one monochlorotoluene, whilst Hübner and Majert (*Ber.*, 1873, **6**, 790) announced the discovery of two, since identified as the ortho- and para-compounds. Beilstein and Kuhlberg (*Annalen*, 1869, **152**, 224) found one dichlorotoluene, which on oxidation gave a dichlorobenzoic acid, m. p. 201—202°. Curiously enough they appear to have overlooked the existence of a second isomer, although they obtained from the mixture a dichlorobenzylidene dichloride, $C_6H_3Cl_2{\cdot}CHCl_2$, which gave an aldehyde, and, on oxidation, an acid, m. p. 128°.

Aronheim and Dietrich (*Ber.*, 1875, **8**, 1401), however, using molybdenum pentachloride as carrier, gave proofs of the existence of two dichlorotoluenes by separating the two dichlorobenzoic acids, m. p. 201° and 122°, by fractional crystallisation of the barium salts. This agrees substantially with the results of Beilstein and Kuhlberg. R. Schultz (*Annalen*, 1877, **187**, 260) repeated the work of the previous investigators, and by fractional crystallisation of the barium salts of the benzoic acids obtained compounds of the m. p. 201°, 126°, and 156°, and thus brought evidence of the existence of a third dichlorotoluene. The orientation of these compounds could only be determined with certainty after the pure dichlorobenzoic acids had been prepared. This work was carried out by Lellmann and Klotz (*Annalen*, 1885, **231**, 308), who prepared four of the six isomers, the whole number being subsequently completed by Wynne and Greeves (Proc., 1895, **11**, 151). As certain discrepancies appear in the results of various observers, we have also prepared the same series of acids and the combined results are tabulated below.

Melting points of dichlorobenzoic acids.

$CH_3=1$.	Lellmann and Klotz.	Wynne.	C. and D.	Other observers.
2·3	—	164°	163°	156° (Claus) * 166° (Seelig)
2·4	158°	—	159—160	
2·5	153·5	152	153	
2·6	—	139	139—140	128° (Beilstein) 126·5° (Schultz) 132° (Claus)
3·4	201	202	200—201	
3·5	182	—	182·5—183	182° (Claus)

* Claus and Bucher (*Ber.*, 1887, **20**, 1621) obtained this acid by the action of bleaching powder or potassium chlorate and hydrochloric acid upon benzoic acid. It was then converted into a dichlorobenzene which was identified as the ortho-compound.

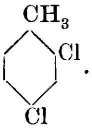
The melting points of Schultz's three acids are in fair agreement with those of the 3 : 4-, 2 : 4-, and 2 : 6-compounds, the only doubt existing between the 2 : 3- and 2 : 4-compounds. But a later investigation of Seelig (*Annalen*, 1887, **237**, 129) on the action of chlorine on toluene in presence of ferric chloride or molybdenum chloride has introduced new features into the problem. He gives evidence only of a 2 : 4- and a 2 : 3-compound, no mention being made either of a 3 : 4- or a 2 : 6-compound. As this is much the most elaborate investigation on the subject, the evidence which he adduces may now be briefly reviewed.

According to Seelig, the 2 : 3- and 2 : 4-dichlorotoluenes which are formed may be separated by fractional crystallisation of their calcium sulphonates.

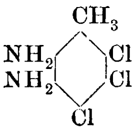
Each dichlorotoluene forms a crystalline dinitro-derivative, the 2 : 3-compound melting at 121° and the 2 : 4-compound melting at 101—102°.

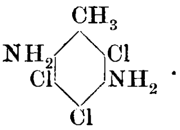
Evidence of their constitution is derived by Seelig from the following facts :

(1.) The first products of chlorination consist of a mixture of ortho- and para-monochlorotoluenes. If either of these compounds is chlorinated, a mixture of the same two trichlorotoluenes results. Two of the chlorine atoms in these compounds will therefore be in positions 2 : 4.



The position of the third chlorine atom is determined as follows. Each of the trichlorotoluenes was converted into a dinitro-derivative, which was reduced to a diamino-compound. One of the diamino-compounds when heated with acetic anhydride forms an anhydro-base, and therefore contains the two amino-groups in the ortho-position. The second diamino-compound, on oxidation, yields a quinone and consequently has the two amino-groups in the para-position. The two diaminotrichlorotoluenes will be represented thus :





that is to say, the trichlorotoluenes have the chlorine atoms in the 2 : 3 : 4- and 2 : 4 : 5-positions.

This leaves a choice between the 2 : 3- ; 2 : 4- ; 2 : 5-, and 3 : 4-formulæ for the dichlorotoluenes.

Now if ortho- and para-monochlorotoluene are chlorinated so as to form dichlorotoluenes, Seelig found that the ortho-compound yields two, an α- and β-dichlorotoluene, whereas the para-compound yields only one, namely, the β-compound. The β-compound, since it is derived from both ortho- and para-monochlorotoluene, must have the 2 : 4-formula, which Seelig confirmed by converting it into the 2 : 4-dichlorobenzoic acid, m. p. 158°, obtained by Lellmann and Klotz (*loc. cit.*). The constitution of the α-compound must lie between the 2 : 3- and 2 : 5-formula, since it is obtained from the *o*-monochlorotoluene. The α-compound yields on oxidation a dichlorobenzoic acid, m. p. 166°. This does not agree with the melting point of the 2 : 5-compound which Lellmann and Klotz had previously ascertained to be 153°. Seelig therefore concludes that the second or α-dichlorotoluene has the 2 : 3-formula.

Both Wynne and Armstrong throw doubt on this result. Wynne (Trans., 1892, **61**, 1051) regards the evidence in favour of the 2 : 3-formula as inconclusive, and from a comparison of the sodium and barium sulphonates considers the 2 : 5-formula as more probable.

Armstrong (Trans., 1892, **61**, 1035) bases his objection on the analogy offered by the bromination products of toluene studied by Miller, and he also points to the 2 : 5-formula as the more probable. Miller (Trans., 1892, **61**, 1023) states, but on no visible grounds, that by brominating ortho-bromotoluene, 2 : 5-dibromotoluene appeared as the chief and 2 : 4- as a subsidiary product, whilst from para-bromotoluene he obtained 3 : 4- as the chief and 2 : 4- as the subsidiary product.

On the other hand, contrary evidence is afforded by the work of Willgerodt and Salzmann (*J. pr. Chem.*, 1889, [ii], **39**, 465), who showed that by brominating *o*-chlorotoluene the bromine forms the 2 : 4- and 2 : 6-compounds, whilst by chlorinating *p*-bromotoluene, chlorine forms the 2 : 4- and 3 : 4-compounds, no 2 : 5-compound being observed. Since then Claus and Stavenhagen (*Annalen*, 1892, **269**, 224) have found that by chlorinating *o*-chlorotoluene—one of the products of the chlorination of toluene—two dichlorotoluenes are formed, which on oxidation give the 2 : 4- and 2 : 6-dichlorobenzoic acids, from which it appears almost certain that 2 : 6-dichlorotoluene is one of the direct products of chlorination, a fact which is in agreement with the previous observation of Schultz and confirms that of Willgerodt and Salzmann.

If we take the combined results of all these observers, we have more or less clear evidence of the existence of four dichlorotoluenes produced by chlorinating toluene in presence of molybdenum or ferric chloride: 2 : 3-, 2 : 4-, 3 : 4-, 2 : 6-, and a suggestion unsupported by any evidence of a fifth, 2 : 5-dichlorotoluene. No single observer has, however, succeeded in identifying more than three out of the five isomers referred to.

The reason for these conflicting views is readily explained. In chlorinating toluene, a liquid mixture of dichlorotoluenes is formed, from which it is impossible to isolate the different constituents by any process of fractional distillation, seeing that their boiling points lie within a few degrees of each other. The only method which is available is to convert the liquid into a solid derivative, of which the following are most readily prepared: nitro- or dinitro-compound, sulphonic acid, its salts, chloride, amide, or anilide, or the corresponding benzoic acid, and to separate the products by fractional crystallisation. The melting point may then be determined, and the identity of the substance established by comparison with that of a pure product of known constitution. This method may lead to a form of error into which earlier investigators fell. Unless the whole material is investigated from start to finish, some of the products may escape observation. Thus, Beilstein and Kuhlberg carefully fractionated their crude dichlorotoluene until a constant boiling fraction was obtained. No doubt a portion of the products was thus eliminated at the outset. This fraction was oxidised, and the acid which first separated was recrystallised until it had a constant melting point, no other product being sought for in the mother liquor. Thus the acids which were discovered later by Schultz escaped observation.

Seelig has committed errors of a much more serious kind, for he has, apparently, not only omitted to look for compounds obtained by previous observers, but has failed to compare some of his products with the pure substances of known constitution. To quote instances, no attempt was made to isolate the acid (m. p. 128°) obtained by Aronheim, and also by Schultz, and again, the dinitro-compound of m. p. 121° is assumed to be a derivative of the 2 : 3-dichlorotoluene, whereas if he had taken so elementary a precaution as to nitrate pure 2 : 3-dichlorotoluene, he would at once have convinced himself of his error, as this compound melts at 71—72°.

The process of fractional crystallisation is also attended with difficulties, which are emphasised in the case of compounds possessing, like the derivatives of the dichlorotoluenes, not only similar chemical properties, but often nearly identical solubilities in various media. Thus we obtained a nearly constant melting fraction on repeatedly recrystallising some of the dinitro-derivatives, which subsequently proved to be a mixture.

It is only by preparing a variety of derivatives from the liquid mixture that this difficulty may be overcome. A number of opportunities is thereby offered to each isomer of establishing its identity by a distinctive property of one at least of its derivatives.

In pursuing this idea, our research has necessitated the fractional crystallisation of certain of the nitro- and dinitro-derivatives, sulphonic acids, chlorides, amides, and benzoic acids of the mixed dichlorotoluenes, as well as the preparation of the pure substances for comparison. The latter are tabulated below, the table also including the results obtained by Wynne (Trans., 1892, 61, 1045).

Melting points of the derivatives of the dichlorotoluenes.

	Nitro.	Dinitro.	Sulphonic chlorides.		Sulphonamides.	
			Wynne.	C. and D.	Wynne.	C. and D.
2 : 3	50·5—51·5°	71—72°	i. 45° ii. 82	—	i. 221° ii. 183	222°
2 : 4	54—55	104	71	71°	177	176
2 : 5	50—51	100—101	43	45—46	191	191—192
2 : 6	53	121—122		—	204	204
3 : 4	63—64	91·5—92·5	82	81	189	190—191
3 : 5	61—62	99—100	45	44—45	168	168—169

We may sum up our results as follows:

Using the aluminium-mercury couple as 'carrier,' we have established the presence of the 2 : 3-, 2 : 4-, 2 : 6-, and 3 : 4-compounds, and the probable existence of small quantities of the 2 : 5-compound. This is in substantial agreement with the products formed with molybdenum or ferric chloride as 'carrier.' In other words, four, and probably five, out of the possible six isomers are produced, the only compound of which we could find no trace being the 3 : 5-isomer. Their presence has been determined from the following evidence.

We have taken as the starting point pure ortho- and para-monochlorotoluene, which were known to form the first products of the chlorination of toluene, which we have confirmed by oxidising the mixture to the benzoic acids and separating the ortho and para-compounds.

Chlorination of Para-chlorotoluene.

2 : 4-*Dichlorotoluene.*—Evidence of the presence of this compound was obtained by converting the mixture into the dinitro-derivative and fractional crystallisation. The dinitro-compound melting at 103° was isolated, which is identical with that obtained from the pure 2 : 4-dichlorotoluene. On oxidation of the mixed dichlorotoluenes to the corresponding benzoic acids, and by fractional crystallisation of the barium salts, the benzoic acid, m. p. 159°, was obtained, corresponding to the 2 : 4-benzoic acid. Also the sulphonic chloride, m. p. 70°, and the sulphonamide, m. p. 176°, were prepared by sulphonation of the mixed dichlorotoluenes and fractional crystallisation.

3 : 4-*Dichlorotoluene.*—The dinitro-derivative, m. p. 90—92°, was separated from the mother liquors in the fractionation of the above 2 : 4-dinitro-derivative. The corresponding benzoic acid was obtained from the crystallisation of the barium salts described above. It melted at 200—201° in agreement with that of the pure 3 : 4-compound.

Chlorination of Ortho-chlorotoluene.

2 : 3-*Dichlorotoluene.*—The product of chlorination was sulphonated, the barium salt fractionated, and the sulphonamide which was obtained melted at 221°, in agreement with the pure compound. The mixed barium salts were then desulphonated, and the dichlorotoluenes converted into their dinitro-derivatives. By fractional crystallisation, a portion was separated having the m. p. 72°.

2 : 6-*Dichlorotoluene.*—From another fraction of the same mixture of dinitro-compounds, the compound melting at 121—122° was isolated, corresponding to the pure 2 : 6-compound. The crude dichlorotoluene was also oxidised to the corresponding benzoic acid. On treating the mixed acids with methyl alcohol and hydrochloric acid in the cold, some free acid was isolated. According to Victor Meyer's "esterification law," this should be a diortho-substituted acid, and the melting point, 137—139°, corresponds to that of the 2 : 6-dichlorobenzoic acid.

2 : 4-*Dichlorotoluene.*—The portion unsulphonated with concentrated sulphuric acid was treated with fuming sulphuric acid, and the barium salts thus obtained were fractionated. One fraction was converted into the sulphonamide, m. p. 176°, which agrees with that of the pure compound. From the dinitro-derivatives, obtained by nitrating the mixture of chlorinated products, a compound melting at 103° was isolated.

2 : 5-*Dichlorotoluene.*—The only evidence obtained of the presence of this compound was from the crude dichlorotoluene sulphonated with fuming sulphuric acid, from which the previous (2 : 4-) derivative was prepared. This was converted into the sulphonamide and fractionated. The first crop of crystals melted at 189—191°, which corresponds to the 2 : 5-compound. The evidence is admittedly incomplete, and is due to the fact that none of the simple derivatives of the 2 : 5-compound show sufficiently marked characteristics to render them easy to identify.

Chlorination of Meta-chlorotoluene.

To make the series complete, we have included the chlorination of *m*-chlorotoluene within the scope of this research, a subject which has hitherto not been investigated.

2 : 5-*Dichlorotoluene.*—It was identified by the melting point,

100—101°, of the dinitro-compound, which was obtained by fractional crystallisation of the mixture of which it formed a large proportion.

3:4-*Dichlorotoluene.*—This formed the only other constituent, and was identified by oxidising it to the benzoic acid, m. p. 200—201°, and by isolating from the mixed dinitro-compounds a portion melting at 92°. No trace of either the 2 : 3- or the 3 : 5-compounds could be detected. The absence of the 3 : 5-compound would be anticipated from the well-known property of the chlorine atom to enter the ortho- or para- and not the meta-position to the methyl or halogen groups. But the reason for the absence of the 2 : 3-compound is not so apparent, and may be referred to space interference of the meta-groups, which might prevent the introduction of the halogen between them.

The unsatisfactory nature of the research on the bromination of toluene, to which reference has been made (p. 1114), has decided us to repeat this investigation on similar lines to the present one, and we have already made some progress in this direction. We are also completing the investigation of the trichlorotoluenes obtained by the chlorination of the dichlorotoluenes.

EXPERIMENTAL.

For purposes of reference, the experimental part has been divided into the following sections:

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I. Chlorination of benzene 1118
II. ,, toluene 1119
III. Preparation of the dichlorotoluenes and their derivatives from ortho-, para-, and meta-chlorotoluene 1121
IV. Preparation of the six pure dichlorotoluenes and their derivatives 1127

I. *Chlorination of Benzene.*

Monochlorobenzene.—Chlorine washed and dried by concentrated sulphuric acid was passed into benzene contained in a wash-bottle cooled in ice. Fifty grams of benzene, previously distilled over sodium, were introduced into the wash-bottle, together with about 0·5 gram of the aluminium-mercury couple. On passing in the chlorine, the benzene becomes first yellow, then rapidly turns dark violet, and torrents of hydrochloric acid gas are evolved, the couple remaining practically unattacked. When the benzene had increased 13 grams in weight, the process was stopped. The liquid was then washed with caustic soda solution, dehydrated over calcium chloride, and fractionated, with the following result:

Below 127°	4 grams.
127—137	50 ,,
137—160	5 ,,
Above 160	4 ,,

The amount of crude monochlorobenzene corresponds to about 70 per cent. of the theoretical yield.

Para-dichlorobenzene.—From the residue boiling above 160° a solid separated on cooling in ice and salt, which was drained and dried. It was recrystallised from dilute alcohol and melted at 54—56°, which is the melting point of *p*-dichlorobenzene.

Tri- and Tetra-chlorobenzene.—Ten grams of crude chlorobenzene and 10 grams of carbon tetrachloride were introduced into a U-tube with a small piece of the couple and chlorine passed in. The liquid first became yellow, and then a more vigorous action occurred, which was indicated by a rise of temperature and a rapid change of colour to dark brown. This sudden change may possibly correspond to the passage from the additive to the substitution compound, referred to by Seelig in the case of toluene (*Annalen*, 1887, **237**, 170). When the requisite amount of chlorine had been absorbed, the current of gas was stopped, and the mixture, to which a little more solvent was added to bring the solid into solution, was shaken with caustic soda, dehydrated, and distilled.

The portion boiling at 130—230°, and amounting to 14 grams, solidified on cooling. It was drained and recrystallised. The greater portion (7 grams) melted at 138°, which corresponds with the 1 : 2 : 4 : 5-compound. About half a gram melted at 127—130°. The oil which was drained off solidified in a freezing mixture, and is probably the 1 : 2 : 4-trichlorobenzene, which melts at 16°.

Hexachlorobenzene.—One gram of the pure tetrachlorobenzene was dissolved in 15 parts of carbon tetrachloride and introduced into a U-tube, with a fragment of the couple and chlorine passed in for some time. A vigorous reaction occurred, heat was evolved, and the liquid became dark violet. The product was washed, and the carbon tetrachloride removed by distillation. The solid residue was washed with ether to remove yellow colouring matter. A theoretical yield (1·4 grams) of hexachlorobenzene was obtained melting at 228—229°.

II. *Chlorination of Toluene.*

Monochlorotoluene.—Chlorine was passed into 62 grams of dry toluene in presence of the couple until an increase of 19·5 grams was obtained. The product was then washed, dried, and fractionated, as follows:

Below 140°	1·5 grams.
140—163	68·7 ,,
Above 163	2 ,,

The yield of crude chlorotoluene is about 80 per cent. of the theoretical. The larger portion was distilled with a Hempel column, and the following fractions were obtained :

Below 130°	3·2 grams.
130—150	7 ,,
150—155	41 ,,
155—163	17·5 ,,

With the exception of about a gram, the large fraction boiled constantly at 154—155°, and is therefore mainly *o*-chlorotoluene, b. p. 154°.

The para-compound, according to different observers, boils at 160° and 163°. In order to identify the ortho-compound, it was oxidised to chlorobenzoic acid. Five grams of the chlorotoluene, 16 grams of potassium permanganate, and 210 c.c. of water were boiled together for 7 hours with a reflux condenser. Sulphur dioxide was then passed into the liquid to dissolve the manganese dioxide and precipitate the acid. The chlorobenzoic acid was then boiled with water, which left 0·7 gram undissolved. This residue melted at 235°, and was therefore *p*-chlorobenzoic acid (m. p. 236°). The solution deposited 2·8 grams of crystals which, after recrystallisation, melted at 134—135°, corresponding to the melting point of the *o*-chlorobenzoic acid. The same process was repeated with a fraction boiling at 157—163°. This was much less readily oxidised, but eventually from 5 grams 2·65 grams of mixed acids were obtained, which were separated by hot water, and gave 0·9 gram of the ortho-compound melting at 132—134°, the remainder being the para-compound melting at 233—234°. The mixture of crude monochlorotoluenes consists therefore of, approximately, 65 per cent. of ortho- and 35 per cent. of para-compound. This agrees with Seelig's results (*loc. cit.*).

Dichlorotoluene.—Sixty grams of toluene were chlorinated as before until the increase in weight amounted to 36 grams. The liquid was purified and fractionated, as follows :

110—145°	18·5 grams.
145—180	7·5 ,,
180—210	65 ,,
Above 210	2 ,,

The portion boiling below 180° was again chlorinated and distilled. It gave :

Below 180°	12 grams.
180—210	12 ,,

Thus 77 grams of crude dichlorotoluene were obtained from 60 grams of toluene, corresponding to 74 per cent. of the theoretical yield. The 77 grams were refractionated.

160—194°	22 grams.
194—200	50 ,,
Above 200	5 ,,

The 22 grams, b. p. 160—194°, were subsequently re-chlorinated for the preparation of trichlorotoluene.

An attempt was made to identify the dichlorotoluenes by oxidation to the corresponding acids with potassium permanganate, but the process gave a very unsatisfactory result and was abandoned. From 30 grams of crude dichlorotoluene, after boiling with 80 grams of permanganate and 1200 c.c. of water for 7 days in a calcium chloride bath, only 3 grams of acid were obtained melting at 157—164°. A slight modification of this method, which was recommended by Claus and Stavenhagen (*Annalen*, 1892, **269**, 224), has not in any way helped to convince us of its efficacy (see p. 1132).

Trichlorotoluene.—The 22 grams of liquid boiling at 160—194°, obtained as above described in the preparation of dichlorotoluene, were further chlorinated until there was an increase of 4·5 grams in weight. After the usual purification, the liquid was fractionated as follows:

Below 220°	4 grams.
220—240	17 ,,
240—262	13 ,,

The last two fractions solidified on cooling. Both portions were separately recrystallised from alcohol, and the two principal fractions which were obtained melted at 82° and 40—42°. This agrees exactly with Seelig's melting points of the two trichlorotoluenes which he isolated. At least two trichlorotoluenes are therefore present.

III. *Dichlorotoluene and its Derivatives from Para-chlorotoluene.*

Sixty-one grams of *p*-chlorotoluene (b. p. 156—160°), prepared by Gattermann's method from *p*-toluidine, were treated with chlorine in presence of the couple, until an increase of 20 grams was obtained. The product was purified and distilled.

Below 190°	1·5 grams.
190—210	59·5 ,,
210—230	13·5 ,,
Above 230	2 ,,

The two intermediate fractions were redistilled.

190—197°	22 grams.
197—205	30 „

Nitration of the Mixed Dichlorotoluenes.

Each of the above two fractions was nitrated as follows.

Five grams of the dichlorotoluene were added in small quantities to a cooled mixture of 17 grams of concentrated sulphuric acid and 34 grams of fuming nitric acid (sp. gr. 1·5). The mixture was kept cool until all the dichlorotoluene had been added. It was then warmed on the water-bath for about 15 minutes and poured on to crushed ice. The solid was filtered, washed with water, and dried on a porous plate.

The substance was fractionally crystallised from alcohol and from glacial acetic acid. Five grams of dichlorotoluene, boiling at 190—197°, gave 5·4 grams of a dinitro-compound, of which 3·7 grams melted at 102—103°, corresponding to the 2 : 4-compound. The remainder melted indefinitely at about 80°, but by prolonged fractionation a small quantity of fine needles was obtained melting at 90—92°, which corresponds to the 3 : 4-derivative. Six grams of the fraction boiling at 197—205° gave 7·7 grams of dinitro-compound, of which 4·1 grams melted at 101—103°. The remainder melted at a lower temperature, and was probably a mixture of the 2 : 4- and 3 : 4-derivatives, as in the previous fraction.

Oxidation of the Mixed Dichlorotoluenes.

Five grams of the dichlorotoluene were heated for 6 hours at 140° in a sealed tube with a mixture of 13 c.c. of concentrated nitric acid (sp. gr. 1·4) and 15 c.c. of water. The product was made alkaline with caustic soda, and a trace of unoxidised substance removed by steam distillation. The mixed dichlorobenzoic acids were then precipitated by the addition of hydrochloric acid. After filtration and washing, the benzoic acids were converted into their barium salts by boiling the aqueous solution with a slight excess of baryta. The salts were repeatedly crystallised from hot water. The most insoluble barium salt, after three crystallisations, yielded a dichlorobenzoic acid melting at about 190°. The acid was then recrystallised four times from dilute spirit, when it melted sharply at 200°, corresponding to the 3 : 4-dichlorobenzoic acid.

The more soluble barium salt yielded an acid melting at about 150°. On repeatedly crystallising, a pure product was isolated melting at 159°, corresponding to the 2 : 4-dichlorobenzoic acid.

Sulphonation of the Mixed Dichlorotoluenes.

Five grams of the dichlorotoluene mixture were sulphonated with fuming sulphuric acid and the sodium salt separated by pouring into brine. This was converted into the sulphonic chloride with phosphorus pentachloride. On fractional crystallisation of the sulphonic chloride from petroleum, a product melting at 70° was obtained, corresponding to the 2 : 4-derivative. The sulphonamide was then prepared, which, on fractional crystallisation, indicated the presence of two compounds, only one of which, the 2 : 4-sulphonamide melting at 176°, could be prepared in the pure state.

Dichlorotoluene and its Derivatives from Ortho-chlorotoluene.

o-Chlorotoluene was obtained from *o*-toluidine by Wynne's modification of Sandmeyer's method (Trans., 1892, **61**, 1072). Fifty-four grams of the product boiling at 154—158° were chlorinated as previously described, and the following fractions obtained:

Below 190°	3·5 grams.
190—210	51 ,,
210—230	7 ,,
Above 230	3 ,,

The fraction boiling at 190—210° was then redistilled.

190—195°	7 grams.
195—208	42 ,,

Nitration of the Mixed Dichlorotoluenes.

Five grams of dichlorotoluene were nitrated as previously described and the product fractionated. 0·95 gram of a pure substance melting at 102° was isolated, which corresponds to the 2 : 4-derivative, and a large quantity of a mixture of the nitro-compounds, from which no pure product could be separated. This method of attacking the problem was therefore abandoned.

Sulphonation of the Mixed Dichlorotoluenes.

In order to obtain direct evidence of the existence of the different dichlorotoluenes in the mixture, the product was sulphonated, and the sulphonic acids separated and converted into the sulphonamides. Eighty grams of dichlorotoluene, boiling at 195—208°, were heated on the water-bath with four times the weight of concentrated sulphuric acid, and stirred continuously with a mechanical stirrer. The mixture was then diluted with water, and unchanged oil removed by distillation in steam. The sulphonic acid was converted into the soluble barium salt by the addition of barium carbonate, and the liquid filtered. The residue was boiled up repeatedly with fresh quantities of water and the united filtrates evaporated. In this way, 36 grams (fraction 1) of the barium salt crystallised out, and a further 7 grams (fraction 2) were obtained by evaporation of the mother liquor. The recovered portion, which had not been sulphonated, amounted to 58 grams, and was treated with 160 grams of 20 per cent. fuming sulphuric acid. The dichlorotoluene, on shaking, rapidly dissolved. It was diluted and distilled in steam, and 10·5 grams of unchanged dichlorotoluene were recovered. Fraction 1 gave a sulphonamide which softened at 204° and melted at 210—212°. After five recrystallisations from alcohol, a pure product melting at 221—221½° was obtained. The sulphonamide which was mixed with it was subsequently shown to be the 2 : 6-derivative melting at 204°.

The remainder of the barium salt from fraction 1 was then desulphonated by Armstrong and Miller's method (Trans., 1884, **45**, 148). Twenty-two grams of the barium salt, 8 c.c. of water, and 100 grams of concentrated sulphuric acid gave 8 grams of dichlorotoluene boiling at 195—196°. This dichlorotoluene was converted into the dinitro-compound in the ordinary way, and by careful fractional crystallisation from glacial acetic acid the following pure compounds were obtained. (i) A dinitro-compound melting at 120—121° corresponding to the 2 : 6-derivative; (ii) a compound melting at 71—72°, corresponding to the 2 : 3-derivative; (iii) a very small quantity of prisms melting at 103°, identified as the 2 : 4-compound.

The second small fraction of the barium salt gave a sulphonamide which melted indefinitely at about 180°. No pure product was separated from it. It was probably mainly the 2 : 4-derivative.

The third crop of barium salt was converted into the sulphonamide, which was then fractionally crystallised from alcohol. Two compounds were isolated, one melting at 176°, which was identified as the 2 : 4-derivative, the other melting at 189—191°, which was possibly the 2 : 5-derivative. The melting point was unchanged by recrystallisation.

Oxidation of the Mixed Dichlorotoluenes.

Five grams of the dichlorotoluene mixture were oxidised by heating for 6 hours to 130° in a sealed tube with 10 c.c. of nitric acid (sp. gr. 1·4) and 20 c.c. of water. The dichlorobenzoic acids were separated and purified as previously described, (p. 1122). Five grams of the acids were dissolved in 50 c.c. of methyl alcohol, and dry hydrochloric acid passed into the cold liquid to saturation. The liquid, after standing several hours, was poured into water, and the unchanged dichlorobenzoic acid and esters extracted with ether. The ethereal solution was then repeatedly extracted with small quantities of caustic soda solution, and the alkaline liquid, after boiling off any residual ether, was acidified with hydrochloric acid. The precipitated dichlorobenzoic acid contained some oily impurity, possibly nitro-compounds, which were removed as far as possible by careful draining and pressing on a porous plate. The residual acid was then crystallised from water, 0·65 gram of acid being obtained, which melted indefinitely at 120—134°. The acid was then treated with methyl alcohol and hydrochloric acid as before, and after recrystallisation from dilute spirit, melted at 137—139°. This corresponds to the melting point of the 2 : 6-dichlorobenzoic acid given by Wynne and Greeves (Proc., 1895, **11**, 151. See also p. 1131) and obtained by ourselves.

Dichlorotoluene and its Derivatives from Meta-chlorotoluene.

m-Chlorotoluene was prepared from *m*-toluidine by Sandmeyer's reaction, using cold cuprous chloride solution. The yield from 75 grams of the base amounted to 62 grams of the pure compound boiling at 158—161°. The chlorination was carried out in exactly the same way as previously described, the yield of the mixed dichlorotoluenes amounting to about 85 per cent. of the theoretical amount.

The details of one experiment are as follows. Thirty grams of *m*-chlorotoluene were chlorinated in presence of the couple until the theoretical amount of chlorine had been absorbed. Caustic soda was then added and the product distilled in steam. The distillate was then separated, dried, and fractionated.

Below 195°	1 gram.
195—201	33 ,,
Above 201	1·5 ,,

The constituents of the dichlorotoluene thus obtained were identified by means of their dinitro-derivatives and sulphonamides, and also by oxidation to the corresponding benzoic acids.

Nitration of the Mixed Dichlorotoluenes.

The dichlorotoluene mixture was nitrated in the ordinary way, and the dinitro-derivative separated and crystallised from acetic acid. The product melted indefinitely at 86—93°, indicating the presence of a mixture. It was then submitted to systematic fractional crystallisation, using acetic acid as solvent. The main product was found to consist of a dinitro-compound melting at 99—100°, identical with that obtained from 2 : 5-dichlorotoluene (m. p. 100—101°). From the mother liquors, a product was obtained melting indefinitely at 70—85°. On fractionating this further, a pure substance was separated melting at 92—93°, which is the same as that obtained from 3 : 4-dichlorotoluene melting at 91·5—92·5°. No other compounds having definite melting points were isolated.

Oxidation of the Mixed Dichlorotoluenes.

The oxidation was effected by heating the dichlorotoluene mixture with 7 parts by weight of dilute nitric acid in a sealed tube to 140° for 5 hours. The contents of the tube were dissolved in caustic soda, and the solution distilled in steam to remove a trace of unoxidised substance. The benzoic acids were then precipitated with hydrochloric acid. An unsuccessful attempt was made to separate the constituents of the mixture by fractional distillation in steam. The acids were therefore converted into the barium salts, which were fractionally crystallised. The most insoluble fraction yielded an acid melting at 180—195°, which, on recrystallisation from spirit, melted at 199—200°, and therefore corresponds to the 3 : 4-compound.

The more soluble barium salt yielded a large quantity of an acid which, after repeated crystallisation, melted at 146—148°. This acid probably consists mainly of the 2 : 5-compound (m. p. 153°), but the pure acid could not be obtained.

Sulphonation of the Mixed Dichlorotoluenes.

The sulphonation was undertaken with the special object of detecting the presence of any of the 2 : 3-derivative, as it yields a characteristic sulphonamide. An unsuccessful attempt was made to effect a partial separation of the mixture by using different strengths of sulphuric acid for the sulphonation. As ordinary sulphuric acid had little action, the sulphonation was effected by means of slightly fuming acid, and the product converted into the barium salt. The salt was fractionally crystallised from water, and then the fractions converted into the sulphonamides.

No indication was obtained of the 2 : 3-sulphonamide. The sulphonamides of the 3 : 4- and 2 : 5-compounds previously shown to be present melt too closely together to admit of separation, namely, 3 : 4- at 190—191° and 2 : 5- at 191—192°. No 3 : 5-dichlorotoluene could be detected in any of the reactions.

The conclusion is therefore drawn that of the four possible dichlorotoluenes theoretically obtainable from *m*-chlorotoluene, only the 2 : 5- and 3 : 4-compounds are formed, the former being present in the larger quantity.

IV. *Preparation of the Six Dichlorotoluenes and their Derivatives.*

Preparation of 2 : 3-*Dichlorotoluene.*

3-*Nitro*-2-*toluidine.*—2 : 3-Dichlorotoluene was prepared from the corresponding nitrotoluidine. Lellmann and Würthner (*Annalen*, 1885, **228**, 239) found that *o*-acetotoluidide gave on nitration two nitro-acetotoluidides, which were separated by means of fractional hydrolysis, followed by mechanical sieving of the mixed crystalline product. The two compounds were identified as the 2 : 3- and 2 : 5-nitro-derivatives. Reverdin and Crépieux (*Ber.*, 1900, **33**, 2498) have described a more convenient method of separating the two isomers. They find that if the mixed product of nitration be hydrolysed with concentrated hydrochloric acid and the acid liquid distilled in steam, the 2 : 3-compound is volatilised, whilst the 2 : 5-compound remains behind. From the results of a number of experiments, we find that the best results are obtained as follows.

Fifteen grams of powdered *o*-acetotoluidide are added in small portions to a mixture of 50 grams of fuming nitric acid and 18 grams of glacial acetic acid, the temperature being maintained at about 15°. If the liquid is cooled below this temperature, the reaction is suspended for a time until all the acetotoluidide has been added, when it sets in vigorously with rapid rise of temperature and ultimate decomposition. After standing some hours at the ordinary temperature, water is added to the solution, and the precipitated nitro-compounds filtered off and washed. The substance is then placed in a flask with the addition of 40 c.c. of concentrated hydrochloric acid and, without any preliminary heating, distilled in steam. After a short time, orange coloured crystals collect in the receiver, distillation being continued until no more solid matter is carried over, an operation which lasts about 6 hours. The yield amounts to 6—7 grams of 2 : 3-nitrotoluidine. The 2 : 5-compound may be separated from the acid liquid remaining in the distilling flask.

2-*Chloro*-3-*nitrotoluene.*—Three parts of finely powdered nitrotoluidine were suspended in 5 parts of concentrated hydrochloric acid and 4 parts of water, and the cooled liquid diazotised by the addition of solid sodium nitrite.

In this and in subsequent preparations we found the solid nitrite in coarse pieces to act more slowly and effectively and with a much smaller rise of temperature than the nitrite solution. When the base had gone into solution, the liquid was added to an ice-cold solution of

4 parts of cuprous chloride dissolved in concentrated hydrochloric acid as described by Wynne (Trans., 1892, 61, 1072).

When the evolution of nitrogen had ceased, the liquid was distilled in steam. An almost theoretical yield of chloronitrotoluene was obtained.

2-*Chloro*-3-*toluidine*.—The above nitro-compound was reduced by means of a slight excess of stannous chloride dissolved in an equal weight of concentrated hydrochloric acid. The reaction, which was at first very vigorous, was completed by heating for an hour on the water-bath. At the end of this time, a clear solution was obtained which was poured into a basin and left to crystallise. The crystalline mass was pressed on the filter, and washed with a little concentrated hydrochloric acid. A small quantity of tin was removed from the crystals by dissolving them in hot water and passing in sulphuretted hydrogen. The sulphide was removed by filtration, the filtrate concentrated, and the crystalline hydrochloride used in the subsequent process.

2 : 3-*Dichlorotoluene*.—The conversion of chlorotoluidine into di chlorotoluene is carried out in the same manner as in the preparation of chloronitrotoluene from nitrotoluidine. The yield was nearly theoretical. On fractional distillation, 90 per cent. boiled at 204—206° at 755 mm. pressure.

2 : 3-*Dichlorobenzoic acid*.—One part of dichlorotoluene was heated with 6 parts of dilute nitric acid (2·5 vols. of concentrated nitric acid sp. gr. 1·4, 3 vols. of water) for some hours in a sealed tube to 140°. The contents of the tube were made alkaline with caustic soda and distilled in steam to remove unchanged dichlorotoluene. The chlorobenzoic acid was precipitated in the residue on the addition of acid and recrystallised from hot water. It melted at 163°.

Nitro-2 : 3-*dichlorotoluene*.—This compound was prepared by adding to 1 part of dichlorotoluene a cold mixture of 2 parts of nitric acid (sp. gr. 1·4) and 3 parts of concentrated sulphuric acid. The mixture was then heated for some time on the water-bath, and the nitro-compound precipitated by pouring on to crushed ice. It was recrystallised from a mixture of alcohol and acetic acid, and was obtained in the form of felted masses of fine needles melting sharply at 50·5—51·5°.

0·1640 gave 0·2292 AgCl. Cl = 34·55.

$C_7H_5Cl_2 \cdot NO_2$ requires Cl = 34·41 per cent.

Dinitro-2 : 3-*dichlorotoluene*.—The dinitro-derivative was obtained by slowly adding to 1 part of dichlorotoluene 7 parts of fuming nitric acid (sp. gr. 1·5) and 3½ parts of concentrated sulphuric acid. The reaction was completed by heating for some time on the water-bath, and the product then poured into water. The precipitated dinitro-compound was filtered, washed and dried, and recrystallised from glacial acetic acid or alcohol. The product was fractionally crystallised and proved to be uniform. It melted at 71—72°.

0·1991 gave 0·2285 AgCl. Cl = 28·32.

$C_7H_4Cl_2(NO_2)_2$ requires Cl = 28·12 per cent.

2 : 3-*Dichlorotoluenesulphonamide.*—The dichlorotoluene was sulphonated by heating for a short time with three times the weight of fuming sulphuric acid, and the sulphonic acid converted into the barium salt in the usual way. The barium salt was then heated with an equal weight of phosphorus pentachloride, which yielded the sulphonic chloride, and this was converted into the amide in the usual way. The sulphonamide, after recrystallisation from alcohol, melted at 222°.

2 : 3-Dichlorotoluene has been stated by Wynne (Proc., 1895, **11**, 151) to yield two sulphonic acids on sulphonation, which may be separated by fractional crystallisation of their barium salts. Experiments made with the object of separating the two acids failed to indicate the presence of a second acid.

Preparation of 2 : 4-*Dichlorotoluene.*

Ordinary dinitrotoluene was used for the preparation according to the method of Lellmann and Klotz (*Annalen*, 1885, **231**, 308). The dinitrotoluene was first reduced to nitrotoluidine with ammonium sulphide. The product (m. p. 76°) was then submitted to the same series of reactions as previously described under 2 : 3-dichlorotoluene. The yields throughout were satisfactory. Fifty grams of dinitrotoluene yielded 18 grams of 2 : 4-dichlorotoluene boiling at 198—200°.

2 : 4-*Dichlorobenzoic Acid.*—This acid was obtained by oxidising the dichlorotoluene with dilute nitric acid in a sealed tube at 130—140°. The product was purified in the usual way, and crystallised from hot water in fine needles melting at 159—160°.

Nitro-2 : 4-*dichlorotoluene.*—This compound was prepared in the same way as the 2 : 3-compound, and crystallised from spirit in long, hard needles melting at 54—55°. Seelig gives 53° as the melting point of this substance.

Dinitro-2 : 4-*dichlorotoluene* was prepared in the manner described under the 2 : 3-compound. It crystallised from a mixture of glacial acetic acid and alcohol in fine prisms melting at 104° (Seelig gives 102°).

2 : 4-*Dichlorotoluenesulphonamide.*—2 : 4-Dichlorotoluene is readily sulphonated with fuming sulphuric acid. The sodium salt was separated by pouring the product into brine, which was then converted

into the sulphonic chloride. The latter crystallised from petroleum ether in hard prisms melting at 71°. The sulphonamide was repeatedly crystallised from spirit and melted sharply at 176°.

Preparation of 2:5-*Dichlorotoluene.*

The 2:5-dichlorotoluene was obtained in two ways, (i) by direct chlorination of *o*-acetotoluidide (Lellmann and Klotz, *Annalen*, 1885, **231**, 319), and (ii) by the action of sodium hypochlorite on *o*-acetotoluidide (Chattaway and Orton, Trans., 1900, **77**, 790). The two products were identical.

(i) Following Lellmann and Klotz's directions, *o*-acetotoluidide was dissolved in sufficient glacial acetic acid to prevent crystallisation on cooling, and a current of dry chlorine passed into the cooled liquid. A vigorous reaction occurs with considerable rise in temperature. After a time, the solution suddenly becomes almost solid. Water was then added, and the crude chloroacetotoluidide filtered off and recrystallised from spirit. On hydrolysis with concentrated hydrochloric acid, the hydrochloride of chlorotoluidine separated in the form of crystals with a satin-like lustre. The amino-group was replaced by chlorine by Wynne's modification of Sandmeyer's method already referred to. From 45 grams of *o*-acetotoluidide, 22 grams of crude dichlorotoluene were obtained, of which 19 grams boiled constantly at 198—199° under a pressure of 760 mm. The product solidified completely in a freezing mixture, and melted sharply at 5°.

(ii) Twenty grams of *o*-acetotoluidide were shaken up with 400 c.c. *N*/2 sodium hypochlorite solution containing 20 grams of sodium bicarbonate and left to stand 24 hours. A little chloroform was added and the lower layer of liquid withdrawn. About an equal volume of glacial acetic acid and a drop of concentrated sulphuric acid were then added to the chloroform solution, which was warmed on the water-bath. The greater part of the chloroform evaporated, and the chloroacetotoluidide was precipitated by pouring into water. The yield was nearly theoretical. The crude product was recrystallised from dilute spirit and hydrolysed by boiling with excess of concentrated hydrochloric acid. The subsequent operations were identical with those described under the first method. Twenty-four grams of the chlorotoluidine hydrochloride yielded 15 grams of pure dichlorotoluene boiling at 198—200° at 760 mm. and melting at 5°.

2:5-*Dichlorobenzoic acid* was obtained by oxidation with dilute nitric acid at 140°. The product was recrystallised three times from dilute spirit, and melted sharply at 153°.

Nitro-2:5-*dichlorotoluene.*—Great care was required in this preparation to prevent the formation of the dinitro-derivative. The following proportions gave satisfactory results. A cold mixture of 1½ parts of concentrated nitric acid (sp. gr. 1·4) and 3 parts of concentrated sulphuric acid were slowly added to 1 part of the dichlorotoluene, any great rise of temperature being avoided. The mixture was subsequently warmed on the water-bath and the nitro-compound precipitated by water. On recrystallisation from a mixture of alcohol and ether, the nitro-compound was obtained in the form of fine needles melting at 50—51°.

0·1192 gave 0·1655 AgCl. Cl = 34·33.
$C_7H_5Cl_2{\cdot}NO_2$ requires Cl = 34·41 per cent.

Dinitro-2 : 5-*dichlorotoluene* was prepared by the method already described in the case of the other dinitro-compounds. It was recrystallised from glacial acetic acid and melted at 100—101°.

0·2630 gave 0·3015 AgCl. Cl = 28·33.
$C_7H_4Cl_2N_2O_4$ requires Cl = 28·12 per cent.

2 : 5-*Dichlorotoluenesulphonamide*.—The dichlorotoluene was sulphonated with fuming sulphuric acid, and the product separated as the sodium salt. The sulphonic chloride prepared by the action of phosphorus chloride on the sodium salt crystallised from ether in large, colourless plates melting at 45—46°. The sulphonamide was obtained in the form of colourless needles melting at 191—192°.

Preparation of 2 : 6-*Dichlorotoluene.*

The 2 : 6-nitrotoluidine, which served as the starting point for the preparation of the dichlorotoluene, we owe to the great kindness of Messrs. Green and Lawson, who obtained it in small quanties as a by-product by nitrating *o*-toluidine (Trans., 1891, **59**, 1013). An almost theoretical yield of chloronitrotoluene was obtained in the form of fine, yellow crystals by using Wynne's modification of Sandmeyer's reaction. The reduction of the nitro-compound was effected with stannous chloride, when the hydrochloride of chlorotoluidine was obtained in the form of white, glistening plates. From the latter, the 2 : 6-dichlorotoluene was finally prepared. Ten grams of the nitrotoluidine yielded 4·5 grams of pure dichlorotoluene, boiling constantly at 198° at a pressure of 760 mm.

2 : 6-*Dichlorobenzoic acid* was obtained by oxidation in a sealed tube with nitric acid. After frequent recrystallisation, the product melted at 132—133°, which agrees with the number given by Claus and Stavenhagen (*Annalen*, 1892, **269**, 224), but is much lower than that given by Wynne and Greeves (139°) or previously obtained by us from the mixture of dichlorotoluenes prepared by chlorinating *o*-chlorotoluene (see p. 1125). We concluded, therefore, that both Claus' and our pro-

ducts were impure. In our case, the fact was easily explained, for 2 : 6-dichlorotoluene is very difficult to oxidise. Heated with very dilute nitric acid in a sealed tube, it is only slightly attacked, whereas with stronger acid nitro-compounds are formed which lower the melting point of the product. On the other hand, Claus and Stavenhagen's method (*loc. cit.*) of preparing 2 : 6-dichlorobenzoic acid from the crude chlorination product of *o*-chlorotoluene by oxidising with powdered potassium permanganate absolutely failed in our hands. Although we followed in detail the directions given, we found, after 2 days' boiling, that only a trace of dichlorotoluene had been attacked. We conclude that some important omission must have been made in the description of the method. We ultimately used the following method, which gave a satisfactory result.

Five grams of the dichlorotoluene were oxidised with 10 c.c. of concentrated nitric acid (sp. gr. 1·4) and 20 c.c. of water for a day at 140° in a sealed tube. Caustic soda was added to the product, and the liquid distilled in steam. A small amount of solid distilled, which was identified as 2 : 6-dichlorobenzaldehyde. On acidifying the alkaline solution, an acid was obtained melting at 128—132°. The impure acid was treated with a solution of 5 grams of stannous chloride in 10 c.c. of concentrated hydrochloric acid, and heated for an hour on the water-bath. The acid liquid was then extracted with ether, from which the dichlorobenzoic acid was obtained by washing with caustic soda solution. The acid was precipitated by the addition of hydrochloric acid. It was further purified by dissolving in methyl alcohol, saturating with dry hydrochloric acid, and allowing it to stand for a time. On pouring into water and extracting with ether, the acid went into solution in the ether, from which it was extracted with caustic soda solution. On acidifying the alkaline solution, the acid was precipitated, and, after crystallisation from water, formed colourless needles melting at 139—140°.

Nitro-2 : 6-*dichlorotoluene* was obtained in the usual way and crystallised from a mixture of alcohol and acetic acid in needles melting sharply at 53°.

0·1222 gave 0·1720 AgCl. Cl = 34·79.
$C_7H_5Cl_2 \cdot NO_2$ requires Cl = 34·41 per cent.

Dinitro-2 : 6-*dichlorotoluene* was prepared by the method previously described. It crystallised from alcohol in flattened needles melting at 121—122°.

0·0695 gave 0·0792 AgCl. Cl = 28·17.
$C_7H_4Cl_2(NO_2)_2$ requires Cl = 28·12 per cent.

2 : 6-*Dichlorotoluenesulphonamide*.—The dichlorotoluene was readily

sulphonated with fuming sulphuric acid, the product being separated as the sodium salt. The latter was converted into the sulphonic chloride and sulphonamide. The sulphonamide was crystallised from alcohol and melted at 204°.

Preparation of 3 : 4-*Dichlorotoluene.*

The starting point for this preparation was the 3 : 4-nitrotoluidine supplied by Kahlbaum in beautiful, large, red crystals. The various steps in the process are the same as described in the case of the other nitrotoluidines and call for no special remark. Fifty grams of the nitrotoluidine yielded 17 grams of pure dichlorotoluene boiling at 200—207°.

3 : 4-*Dichlorobenzoic acid* was obtained by oxidising with dilute nitric acid at 130—140°. The acid, which is slightly volatile in steam, melted at 200—201°.

Nitro-3 : 4-*dichlorotoluene.*—Care is required to prevent the formation of the dinitro-derivative. The best results were obtained by using 2 parts of concentrated nitric acid (sp. gr. 1·4) and 4 parts of concentrated sulphuric acid to 1 part of dichlorotoluene. The product crystallises from alcohol and acetic acid in fine, long needles melting at 63—64°.

0·1000 gave 0·1395 AgCl. Cl = 34·48.
$C_7H_5Cl_2\cdot NO_2$ requires Cl = 34·41 per cent.

Dinitro 3 : 4-*dichlorotoluene* was easily obtained, and crystallises from glacial acetic acid in long, nearly colourless needles melting at 91·5—92·5°.

0·2557 gave 0·2920 AgCl. Cl = 28·23.
$C_7H_4Cl_2N_2O_4$ requires Cl = 28·12 per cent.

3 : 4-*Dichlorotoluenesulphonamide* —The dichlorotoluene was readily sulphonated and converted into the sodium salt. The sulphonic chloride solidifies readily and crystallises from ether in long needles melting at 81°. The sulphonamide melts at 190—191°.

Preparation of 3 : 5-*Dichlorotoluene.*

The method employed for the preparation of the 3 : 5-dichlorotoluene is that described by Chattaway and Orton (Trans., 1900, **77**, 791).

Thirty grams of *o*-acetotoluidide were dissolved in 120 c.c. of glacial acetic acid, and a solution of 100 grams of bleaching powder in 2 litres of water were added. After standing 12 hours, the supernatant liquid was decanted from the yellow oil. To the latter, about an equal volume of glacial acetic acid and a few drops of concentrated sulphuric acid were added, and the solution was then warmed on the water-bath. After standing for a time, the solution was poured into water, when the dichloroacetotoluidide separated out. It was filtered, washed, and crystallised from spirit. The yield is nearly theoretical. The hydrolysis was effected by heating 1 part of the dichloro-compound with 3 parts of concentrated hydrochloric acid to 150° in a sealed tube for 8 hours. In this way, 21 grams of the dichlorotoluidine were obtained from 30 grams of the dichloroacetotoluidide. By using Claus' method, on the other hand, alcoholic potash only hydrolysed one-half of the compound after two days' boiling. This slow hydrolysing action of potash may be accounted for by space interference, as the amino-group is protected by two ortho-positions. The amino-group in dichlorotoluidine was eliminated by the method of Chattaway and Evans (Trans., 1896, **69**, 850).

Eleven grams of dichlorotoluene were obtained from 21 grams of the base. It possessed the melting point 26° which is that given by Lellmann and Klotz (*Annalen*, 1885, **231**, 320).

3 : 5-*Dichlorobenzoic acid* was obtained by oxidation with dilute nitric acid at 150°. After repeated crystallisation, the compound was obtained in the form of fine, long needles melting at 182—183°.

Nitro-3 : 5-*dichlorotoluene* crystallises from a mixture of alcohol and acetic acid in needles melting at 61—62°.

0·1306 gave 0·1820 AgCl. Cl = 34·45.

$C_7H_5Cl_2\cdot NO_2$ requires Cl = 34·41 per cent.

Dinitro-3 : 5-*dichlorotoluene*.—The first preparations of this compound contained the trinitro-derivative, which is readily formed and crystallises in lustrous leaflets melting at about 190°. The pure dinitro-compound was obtained by using the following quantities of materials. Four parts of nitric acid (sp. gr. 1·5) and 4 parts of concentrated sulphuric acid were added to 1 part of the dichlorotoluene. The product crystallises from alcohol in long, white needles melting at 99—100°.

0·1212 gave 0·1390 AgCl. Cl = 28·35.

$C_7H_4Cl_2N_2O_4$ requires Cl = 28·12 per cent.

3 : 5-*Dichlorotoluenesulphonamide*.—Sulphonation was readily effected in the ordinary way and the sulphonate converted into the sulphonic chloride, which crystallised from petroleum in large, thick prisms melting at 44—45°. The sulphonamide crystallised from spirit in needles melting at 168—169°.