CXXXIV.—*The Chlorination of the Dichlorotoluenes in Presence of the Aluminium-Mercury Couple. The Constitution of the Trichlorotoluenes.*

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THE present research is an extension of a previous investigation on the chlorination products of toluene (Trans., 1901, 79, 1111). It was shown that five out of six possible dichlorotoluenes were produced by the direct action of chlorine on toluene in the presence of a carrier ; and we have now investigated the further action of chlorine on these substances. A historical summary of investigations on this subject has already been given (*loc. cit.*), so that it is unnecessary to do more than briefly to state the results of previous observers. Limpricht (*Annalen*, 1866, 139, 303) obtained a trichlorotoluene melting at 73°, whilst Aronheim and Dietrich (*Ber.*, 1875, 8, 1401) obtained the same substance, together with a liquid which they considered to be an isomeric trichlorotoluene. Since all the trichlorotoluenes are solid at the ordinary temperature, the latter substance must have been impure. The solid trichlorotoluene, which was probably mainly composed of 2 : 4 : 5-trichlorotoluene, was also obtained by Schultz (*Annalen*, 1877, 187, 274). Seelig (*Annalen*, 1887, 237, 133) succeeded in isolating two trichlorotoluenes, and these are the only two compounds which have any claim to be regarded as pure substances. Both trichlorotoluenes were produced by the chlorination of either *o*- or *p*-chlorotoluene, and were separated by fractional sulphonation. Their constitution was determined as follows. The trichlorotoluene, m. p. 41°, gave a dinitro-com-

pound which was reduced to the corresponding diamine. This substance yielded an anhydro-base on boiling with acetic anhydride, indicating that it was an ortho-diamine, whence it follows that the parent substance is 2:3:4-trichlorotoluene:

In a similar way, the trichlorotoluene, m. p. 82° , gave a base which on oxidation yielded a quinone, indicating that it was a para-diamine, from which it follows that the parent substance is 2:4:5-trichlorotoluene:

It has previously been shown that 2:6-dichlorotoluene is one of the products of chlorination of toluene, and it is difficult to imagine that this substance would give either of the above trichlorotoluenes upon chlorination; it appeared probable that some trichlorotoluenes may have been overlooked by previous observers.

Since, as previously stated, five out of a possible six dichlorotoluenes are produced during the chlorination of toluene, we have used these pure dichlorotoluenes as a starting point for further chlorination. By this means, the number of isomerides which can be formed in each case is greatly reduced, and the possibility of detecting the different trichlorotoluenes is correspondingly increased. The products of chlorination, which are all solid at the ordinary temperature, were separated and identified by means of their melting points and by the melting points of their dinitro-derivatives and of the trichlorobenzoic acids which they give on oxidation. In order to compare the products thus obtained with pure substances of known constitution, we have synthesised the six trichlorotoluenes and have obtained from them the nitro- and dinitro-derivatives and the trichlorobenzoic acids.

Our results may be summarised as follows. The five dichlorotoluenes known to be produced by the chlorination of toluene give when further chlorinated three, and probably four, trichlorotoluenes. Thus out of fifteen mono-, di-, and tri-chlorotoluenes theoretically possible, no less than eleven have been isolated from the products of the chlorination of toluene. 3:5-Dichlorotoluene, which is not formed by the direct chlorination of toluene, gives rise to a fifth trichlorotoluene when further chlorinated.

The progressive chlorination of toluene is represented in the accompanying diagram, the arrows indicating the compound produced by the further action of chlorine.

Chlorination of toluene.

We are already engaged upon the investigation of the tetrachlorotoluenes, and so defer drawing any theoretical deductions until that part of the work is completed.

EXPERIMENTAL.

For purposes of reference the experimental part is divided into the following sections :

- (I) Preparation of the six trichlorotoluenes and their derivatives.
- (II) Chlorination of the six dichlorotoluenes.

I.—*Preparation of the Six Trichlorotoluenes and their Derivatives.*

2 : 3 : 4-Trichlorotoluene.

2 : 3 : 4-Trichlorotoluene was prepared from 4-nitro-2 : 3-dichlorotoluene. It was found that the dinitro-compound obtained by nitrating 2 : 3-dichlorotoluene (Trans., 1901, 79, 1128) gave a base, on reduction with tin and hydrochloric acid, which had the properties of a meta-diamine, indicating that the constitution of the dinitro-compound must be represented thus :

The regulated nitration of 2 : 3-dichlorotoluene gives rise to a mononitro-derivative, which must therefore be represented by one of the following formulæ :

On reducing this nitro-compound and substituting chlorine for the amino-group, a trichlorotoluene was obtained which was *not* identical with 2 : 3 : 6-trichlorotoluene prepared by other methods, and must therefore be the 2 : 3 : 4-compound. The trichlorotoluene agreed in all respects with the trichlorotoluene obtained by Seelig by the chlorination of both *o*- and *p*-chlorotoluenes, to which, for reasons already given, he also ascribed the 2 : 3 : 4-constitution.

A better method than that previously described for the preparation of 2 : 3-dichloro-4-nitrotoluene is to dissolve 2 : 3-dichlorotoluene in slightly more than its own volume of fuming nitric acid, keeping the mixture cool. After some time, water is added, and the precipitated nitro-compound filtered off and crystallised from alcohol. The nitro-group was reduced by means of tin and hydrochloric acid, the reaction,

which is very vigorous, being completed by warming on the water-bath. Excess of caustic soda was then added, and the base separated by steam distillation. The base readily solidifies and melts at 40—42°. It is very soluble in alcohol, and forms a finely crystalline hydrochloride.

The *acetyl* derivative, $C_7H_5Cl_2 \cdot NH \cdot CO \cdot CH_3$, was prepared by heating the substance with acetic anhydride, and crystallised well from alcohol in needles melting at 128—129°. On analysis :

0.1085 gave 0.1421 AgCl. $Cl = 32.4$.

$C_9H_9ONCl_2$ requires $Cl = 32.5$ per cent.

The hydrochloride of the base was diazotised, and the amino-group replaced by chlorine in the usual way, using cold cuprous chloride solution. On distillation in a current of steam, a good yield of trichlorotoluene was obtained. It crystallised from alcohol in needles melting at 40—41°.

2 : 3 : 4-Trichloronitrotoluene.—This substance was prepared by dissolving the finely divided trichlorotoluene in cold fuming nitric acid. After some time, the nitro-compound was precipitated with water and crystallised from alcohol. Long, white needles melting at 60—61° were obtained, agreeing in properties with the compound previously described by Seelig.

2 : 3 : 4-Trichloro-5 : 6-dinitrotoluene.—This substance was obtained by nitrating the trichlorotoluene as described by Seelig, and was crystallised from alcohol. White needles were obtained melting at 140—141°.

2 : 3 : 4-Trichlorobenzoic Acid.—The trichlorotoluene was oxidised with dilute nitric acid in a sealed tube at a temperature of 150°. After the usual purification, the substance crystallised from hot water in needles melting at 186—187°. On analysis :

0.0659 gave 0.1265 AgCl. $Cl = 47.4$.

$C_7H_5O_2Cl_3$ requires $Cl = 47.2$ per cent.

2 : 3 : 4-Trichlorobenzoic acid has been described by Seelig as melting at 129°. He obtained it from trichlorobenzylidene chloride, which was converted into the aldehyde and then oxidised to the acid by means of potassium permanganate. The description given leads us to infer that his acid was impure, for, amongst other properties, the substance melted under water at 80°, whereas the acid obtained from trichlorotoluene by means of nitric acid is solid at the temperature of boiling water.

2 : 3 : 5-Trichlorotoluene.

2 : 3 : 5-Trichlorotoluene was prepared by two different methods.

(a) Preparation from 3 : 5-dichloro-2-aminotoluene :—3 : 5-Dichloro-*o*-acetotoluidide is easily obtained by adding an excess of bleaching powder solution to *o*-acetotoluidide dissolved in five parts of glacial acetic acid. The oily "nitrogen chloride" of 5-chloro-2-acetotoluidide is precipitated, and after separation and warming with acetic acid and a trace of sulphuric acid, is almost quantitatively converted into 3 : 5-dichloro-2-acetotoluidide (Chattaway and Orton, *Trans.*, 1900, **77**, 791). The acetyl group was removed by hydrolysing the compound with hydrochloric acid in a sealed tube at a temperature of 130°. The base was separated by addition of caustic soda followed by steam distillation. The amino-group was replaced by chlorine by means of Sandmeyer's reaction, using cold cuprous chloride solution. The trichlorotoluene was readily volatile in steam and was collected and fractionated under the ordinary pressure. Twenty-five grams of dichloro-acetotoluidide gave 20 grams of pure trichlorotoluene, boiling at 229—231° under 757 mm. pressure. The substance solidified to a mass of hard crystals melting at 45—46° and crystallised readily from alcohol in the form of long, white needles.

(b) Preparation from 3-nitro-5-chloro-2-aminotoluene :—*m*-Chloro-*o*-acetotoluidide is readily prepared either by the direct action of chlorine on *o*-acetotoluidide (Lellman and Klotz, *Annalen*, 1885, **231**, 319) or by the action of sodium hypochlorite solution on *o*-acetotoluidide in presence of sodium bicarbonate (Chattaway and Orton, *Trans.*, 1900, **77**, 790).

Claus and Stapelberg (*Annalen*, 1893, **274**, 296) state that the nitration of 5-chloro-*o*-acetotoluidide is invariably accompanied by the production of tarry matter. They succeeded in isolating a nitro-derivative by working in sulphuric acid solution and separated the tarry matter by crystallisation from petroleum. Our experiments do not confirm these results. 5-Chloro-*o*-acetotoluidide may be readily nitrated by adding it in small portions at a time to a mixture of four parts of fuming nitric acid and one part of glacial acetic acid. The temperature should be kept between 15° and 20°. After standing for a short time, the solution is poured on to ice and the precipitated chloronitro-acetotoluidide crystallised from alcohol. There is not the smallest appearance of tarry matter and the yield is excellent. 5-Chloro-3-nitro-2-acetotoluidide crystallises in white, prismatic needles melting at 197—198°.

Claus and Stapelberg recommend that the hydrolysis of the acetyl derivative should be effected by heating for 12—14 hours with alco-

holic hydrochloric acid. It was found, however, that boiling the substance for a few minutes with sulphuric acid diluted with its own volume of water gave an equally satisfactory result. On diluting the acid solution, the base is precipitated and may be recrystallised from alcohol. The substance crystallises in fine, long, orange-yellow needles melting at 129—130°. It is noteworthy that the melting point of this base is very near to that of a substance obtained by Claus and Stapelberg by treating the nitrate of 5-chloro-2-aminotoluene with strong sulphuric acid, and regarded by them as containing the nitro-group in the para-position.

The chloronitroaminotoluene was converted into dichloronitrotoluene by means of Sandmeyer's reaction. The product is readily volatile in steam and crystallises from alcohol in long, slender needles melting at 54—55°. On analysis :

0.1125 gave 0.1575 AgCl. Cl = 34.6.

$C_7H_5O_2NCl_2$ requires Cl = 34.4 per cent.

The nitro-group was reduced by means of tin and hydrochloric acid. The solution was warmed for a short time to start the reaction, which subsequently proceeded vigorously. At first, a thick, solid mass separated out, which nearly all went into solution on further addition of hydrochloric acid. Sodium carbonate was subsequently added until a small permanent precipitate was obtained, and the dichlorotoluidine then separated by distillation in steam. The base crystallised very readily from alcohol in tufts of white needles melting sharply at 69—70°. On analysis :

0.0360 gave 0.0582 AgCl. Cl = 40.0.

$C_7H_7NCl_2$ requires Cl = 40.3 per cent.

The amino-group was replaced by chlorine, using the ordinary method, and the trichlorotoluene separated by steam distillation. The product melted sharply at 45—46°, and the melting point was unchanged by recrystallisation from alcohol. The yields throughout this rather long series of reactions were excellent, and the product was identical with that obtained by the more direct method.

2 : 3 : 5-Trichloronitrotoluene, $C_7H_4Cl_3 \cdot NO_2$.—This substance was prepared either by nitrating 2 : 3 : 5-trichlorotoluene with a mixture of three parts of concentrated nitric acid (sp. gr. 1.4) and four parts of concentrated sulphuric acid and heating the mixture ; or, preferably, by dissolving the finely divided trichlorotoluene in cold fuming nitric acid. The nitro-compound was precipitated by the addition of water, and after repeated crystallisation from alcohol or slightly diluted acetic acid, was obtained in felted masses of fine needles melting at 58—59°. On analysis :

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0.1151 gave 0.2080 AgCl. Cl = 44.6

$C_7H_4O_2NCl_3$ requires Cl = 44.2 per cent.

2 : 3 : 5-*Trichloro-4 : 6-dinitrotoluene*, $C_7H_3Cl_3(NO_2)_2$.—The addition of six parts of fuming nitric acid and four parts of sulphuric acid to one part of trichlorotoluene resulted in the formation of the dinitro-compound. The substance crystallises well from a mixture of alcohol and glacial acetic acid in shining, flattened needles melting at 149—150°. On analysis :

0.2028 gave 0.3006 AgCl. Cl = 36.7.

$C_7H_3O_4N_2Cl_3$ requires Cl = 37.2 per cent.

2 : 3 : 5-*Trichlorobenzoic Acid*.—Oxidation was effected by means of 20 per cent. nitric acid in a sealed tube at a temperature of 140°. The acid crystallises best from large quantities of hot water and melts at 162°. This trichlorobenzoic acid has also been obtained by Matthews (Trans., 1901, 79, 47) by the action of alkalis on the hexachloride of benzonitrile. The description of the properties of the substance there given accords with those of our preparation, and the synthesis of this acid from trichlorotoluene confirms the constitution arrived at by Matthews from indirect evidence.

2 : 3 : 6-*Trichlorotoluene*.

The starting point for the preparation of 2 : 3 : 6-trichlorotoluene was *o*-acetotoluidide, which was converted into 2 : 3-nitrotoluidine by the method of Reverdin and Crépieux (*Ber.*, 1900, 33, 2498). The 2 : 3-nitrotoluidine was diazotised and converted into chloronitrotoluene by means of Sandmeyer's reaction, and was then reduced with tin and hydrochloric acid to 2 : 3-chlorotoluidine. The latter was heated on the water-bath for an hour with an equal weight of acetic anhydride and converted into the acetyl derivative melting at 126—128°. A second chlorine atom was introduced by passing chlorine through the substance dissolved in ten times its weight of acetic acid. After a short time, crystals separated, and in spite of the large amount of solvent, the mass became pasty. When saturation was complete, water was added, when the crystals dissolved and a clear solution was obtained which soon became turbid through the deposition of a mass of needle-shaped crystals of the 2 : 6-dichloro-3-acetotoluidide. The substance was recrystallised from alcohol and forms long needles which melted at 120—122°. It was analysed with the following result :

0.1038 gave 0.1381 AgCl. Cl = 32.8.

$C_9H_9ONCl_2$ requires Cl = 32.5 per cent.

The acetyl compound was hydrolysed with strong hydrochloric acid at 130°, and the hydrochloride of the base, which was filtered off, was

converted into the trichlorotoluene by Sandmeyer's reaction. The base is precipitated from the hydrochloride with alkali, and crystallises from dilute alcohol in colourless needles which melt at 59—60°. 2:3:6-Trichlorotoluene crystallises from alcohol in colourless needles which melt at 45—46°. The position of the second chlorine atom was determined by replacing the amino-group in the dichlorotoluidine by hydrogen, using the method of Chattaway and Evans (Trans., 1896, 69, 850). The liquid obtained in this way formed a dinitro-derivative which melted at 121—122°, this being the melting point of 2:6-dichlorodinitrotoluene. The various reactions offer no difficulties and the yields are good throughout.

2:3:6-Trichloronitrotoluene, $C_7H_4Cl_3 \cdot NO_2$.—Finely divided 2:3:6-trichlorotoluene was dissolved in cold fuming nitric acid. The nitro-compound was precipitated with water and crystallised several times from alcohol. The substance forms brilliant, long needles melting at 57—58°. On analysis:

0.1148 gave 0.2050 AgCl. Cl = 44.1.

$C_7H_4O_2NCl_3$ requires Cl = 44.2 per cent.

2:3:6-Trichloro-4:5-dinitrotoluene, $C_7H_3Cl_3(NO_2)_2$.—This substance was obtained by nitration in the ordinary way, and crystallises from acetic acid in fine prisms melting at 140—142°. On analysis:

0.3491 gave 0.5210 AgCl. Cl = 36.9.

$C_7H_3O_4N_2Cl_3$ requires Cl = 37.2 per cent.

2:3:6-Trichlorobenzoic Acid.—On oxidation in the usual way, the trichlorotoluene gave 2:3:6-trichlorobenzoic acid, which crystallises from hot water in white, flaky crystals with a satin-like lustre and melts at 163—164°. On analysis:

0.0578 gave 0.1110 AgCl. Cl = 47.4.

$C_7H_3O_2Cl_3$ requires Cl = 47.2 per cent.

2:4:5 Trichlorotoluene.

(a) Preparation from *m*-acetotoluidide:—*m*-Acetotoluidide was chlorinated with bleaching powder solution in presence of acetic acid. The reaction is similar to the chlorination of *o*-acetotoluidide, studied by Chattaway and Orton (Trans., 1900, 77, 791).

A solution of 20 grams of *m*-acetotoluidide dissolved in 80 c.c. of glacial acetic acid was added to a filtered solution of 35 grams of bleaching powder in 600 c.c. of water. A heavy oil separated out and a considerable rise in temperature was noted. The oil was presumably the "nitrogen chloride" of 6-chloro-3-acetotoluidide. On standing, the oil was converted into a hard, white, crystalline mass

which was filtered off and repeatedly crystallised from 80 per cent. alcohol. The substance crystallised in fine, long, white needles melting at 156—157°, and was evidently the same substance as that obtained by Reverdin and Crépieux (*Ber.*, 1900, 33, 2503) by treating *m*-acetotoluidide with sodium chlorate in hydrochloric and acetic acid solution. The acetyl compound was readily hydrolysed with 50 per cent. sulphuric acid. On heating, the substance at first dissolved, and on subsequent warming on the water-bath, white crystals of the sulphate of the base separated out from solution. The base was separated by addition of caustic soda followed by distillation in steam. The yield amounted to 8 grams of dichlorotoluidine.

The amino-group was replaced by chlorine in the usual way and the trichlorotoluene purified by distillation in steam. The substance crystallised from alcohol in long, white needles melting at 81—82°.

(*b*) Preparation from *m*-chloro-*p*-toluidine:—3-Chloro-4-aminotoluene was prepared from *p*-acetotoluidide as described on p. 1336. Excess of dilute nitric acid was added to the base and the crystalline nitrate filtered off and thoroughly dried. The nitration was carried out as described by Claus and Davidsen (*Annalen*, 1891, 265, 343) by adding the nitrate in small portions at a time to cold concentrated sulphuric acid. After some time, the chloronitrotoluidine was separated by pouring the solution on to ice. The amino-group was replaced by chlorine by the ordinary method, and on steam distillation a good yield of 6-nitro-3:4-dichlorotoluene was obtained. This substance crystallised from alcohol in needles melting at 63—64° and was apparently identical with the product obtained by the nitration of 3:4-dichlorotoluene (*Trans.*, 1901, 79, 1113).

The nitro-group was reduced by means of stannous chloride and the base separated by addition of caustic soda followed by distillation in steam. The base crystallised from alcohol in plates possessing a silky lustre and melted at 100—101°. On analysis:

0.1213 gave 0.1965 AgCl. Cl = 40.0.

$C_7H_7NCl_2$ requires 40.2 per cent.

The amino-group was replaced by chlorine and the trichlorotoluene purified by distillation in steam. The substance crystallised from alcohol in long, white needles melting at 81—82°.

(*c*) Preparation from *p*-nitro-*o*-toluidine:—*p*-Nitro-*o*-toluidine is most easily prepared by the following method, which is a modification of that described by Green and Lawson (*Trans.*, 1891, 59, 1013).

The *o*-toluidine is poured into ten times its weight of concentrated sulphuric acid and cooled to 5° in a freezing mixture. The same weight as the toluidine taken of finely powdered potassium nitrate is gradually added, so that the temperature rises to 10° and remains

about that point. The process can be conducted pretty rapidly. Finally, a few c.c. of fuming nitric acid are added to complete the reaction, the end point being easily observed by watching the temperature of the mixture, which suddenly begins to fall. The viscid solution is at once poured on to a small block of ice, when a crystalline mass of the sulphate of the base separates and is drained from excess of acid. The sulphate is then dissolved in water, decomposed with sodium carbonate, and the base filtered off and crystallised from alcohol. The yield is rather more than the weight of the toluidine taken. The small quantity of 2:6-nitrotoluidine which is formed remains in the mother liquors.

The nitrotoluidine was converted into 2-chloro-4-nitrotoluene in the ordinary way, the product being about equal in weight to that of the base employed. The nitro-compound was reduced with stannous chloride and hydrochloric acid, the solution made alkaline with caustic soda, and extracted with chloroform, as distillation in steam reduces the yield; 38 grams of chloronitrotoluene gave 24 grams of chlorotoluidine.

The nitrate of the base was prepared by adding 10 grams of the base to about 6 c.c. of strong nitric acid diluted with twice its volume of water until methyl-violet paper was turned green. The nitrate was filtered, washed with a little water, and thoroughly dried. Fourteen grams of nitrate were dropped into 37 c.c. of concentrated sulphuric acid cooled in a freezing mixture; the product was poured into water and the nitro-compound crystallised from alcohol. It melted at 157—160°. It may be noted here that the original object of the last operation was to obtain 2:4:6-trichlorotoluene, on the assumption that, by the nitration in strong sulphuric acid, the nitro-group would enter the meta-position relatively to the amino-group. The present reaction offers, therefore, an interesting exception to the general rule, for the nitro-group enters the *o*-position to the amino-group and the *p*-position to the chlorine atom.

The replacement of the amino-group by chlorine requires double the calculated quantity of sodium nitrite, as the substance does not diazotise readily, but the yield is satisfactory. The 2:4-dichloro-5-nitrotoluene was reduced and then diazotised in the usual way. The crude trichlorotoluene melted at 75°, and after one crystallisation from alcohol at 80—82°. ▼

That the third chlorine atom had entered position 5 was confirmed by removing the amino-group in 2-chloro-5-nitro-4-amino-toluene, when chloronitrotoluene was formed, which melted at 45°, in agreement with the melting point of 2-chloro-5-nitrotoluene prepared by Goldschmidt and Hönig (*Ber.*, 1886, 19, 2438) from 5-nitro-2-aminotoluene.

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2:4:5-*Trichloronitrotoluene*.—This substance crystallises well from alcohol in needles melting at 91—92°. Seelig gives 92° as the melting point.

2:4:5-*Trichloro-3:6-dinitrotoluene*.—This substance was prepared in the usual way and melts at 226—227°, as described by Seelig. It is sparingly soluble in acetic acid and only very slightly so in alcohol.

2:4:5-*Trichlorobenzoic Acid*.—On oxidation with nitric acid, the trichlorotoluene gave 2:4:5-trichlorobenzoic acid, which crystallises from dilute alcohol in masses of white, silky needles melting at 162—164°.

2:4:6-*Trichlorotoluene*.

Symmetrical trichlorotoluene was obtained by the elimination of the amino-group from trichloro-*m*-acetotoluidide.

m-Acetotoluidide is readily chlorinated by means of sodium chlorate and hydrochloric acid (Reverdin and Crépieux, *loc. cit.*). Twenty grams of *m*-acetotoluidide were dissolved in 80 c.c. of glacial acetic acid; a slight excess of concentrated hydrochloric acid was then added and the solution maintained at 15—25° while 26 grams of sodium chlorate dissolved in the minimum amount of water were introduced. After standing for some time, the trichloroacetotoluidide was precipitated by the addition of water and crystallised three times from alcohol. The substance crystallises well in white, glistening needles. It was found that boiling hydrochloric acid hydrolysed the compound very slowly at the ordinary pressure, whilst 50 per cent. sulphuric acid was far more effective. On diluting the solution and distilling the acid liquid in steam, the base was carried over and at once solidified in the receiver.

2:4:6-Trichlorotoluidine crystallises from alcohol in fine, white glistening needles melting at 77—78°. On analysis:

0.1057 gave 0.2153 AgCl. Cl = 50.4.

$C_7H_6NCl_3$ requires Cl = 50.5 per cent.

The amino-group was removed by the method of Chattaway and Evans (Trans., 1896, 69, 850). The resulting trichlorotoluene is readily volatile in steam and crystallises from alcohol in long, white, shining needles melting at 33—34°.

2:4:6-*Trichloro-3-nitrotoluene*.—This substance was prepared by nitrating the trichlorotoluene in the usual way and was crystallised from a mixture of acetic acid and alcohol. It forms white, waxy needles melting, not very sharply, at 54°. On analysis:

0.0976 gave 0.1752 AgCl. Cl = 44.4.

$C_7H_4O_2NCl_3$ requires Cl = 44.2 per cent.

2 : 4 : 6-*Trichloro-3 : 5-dinitrotoluene*.—This substance readily crystallises from glacial acetic acid and melts at 178—180°. On analysis :

0.1093 gave 0.1652 AgCl. Cl = 37.3.

$C_7H_3O_4N_2Cl_3$ requires Cl = 37.2 per cent.

2 : 4 : 6-*Trichlorobenzoic Acid*.—On oxidation with dilute nitric acid, the trichlorotoluene was readily converted into the trichlorobenzoic acid, which after purification melted at 160—161°. This acid has also been prepared by Meyer and Sudborough (*Ber.*, 1894, 27, 3152) from *s*-trichloroaniline.

3 : 4 : 5-*Trichlorotoluene*.

This trichlorotoluene was prepared by two methods :

(a) Preparation from dichloro-*p*-acetotoluidide :—The chlorination of *p*-acetotoluidide does not take place with the same ease and regularity which characterise that of the *o*- and *m*-compounds. Of the various methods proposed, the more important are : (i) the direct action of chlorine on an acetic acid solution of *p*-acetotoluidide (Lellmann and Klotz, *Annalen*, 1885, 231, 311); (ii) the action of bleaching powder solution on *p*-acetotoluidide dissolved in acetic acid, followed by conversion of the resulting nitrogen chloride into the chloro-base by means of acid (Chattaway and Orton, *Trans.*, 1900, 77, 789); (iii) the action of sulphuryl chloride on *p*-acetotoluidide (Wynne, *Trans.*, 1892, 62, 1042). None of these methods is wholly satisfactory, and poor yields are the rule. In the course of some experiments on this subject, it was found that a yield of 80—83 per cent. of *m*-chlorotoluidine could be obtained by chlorinating *p*-acetotoluidide dissolved in glacial acetic acid with sodium chlorate and hydrochloric acid. At first, finely powdered potassium chlorate was employed, but subsequently it was found preferable to use a saturated solution of the very soluble sodium salt. If at the conclusion of the reaction the mixture be poured into water, a somewhat sticky mass separates, which solidifies after a short time, and from which considerable quantities of chloroacetotoluidide may be separated by careful crystallisation from alcohol. A much better plan, and one which gives a better yield and purer product, is to hydrolyse the crude acetyl derivative and separate the base by steam distillation. The following is a description of a typical experiment.

Fifty grams of *p*-acetotoluidide were dissolved in 100 c.c. of glacial acetic acid and 150 c.c. of concentrated hydrochloric acid. The solution was carefully cooled in ice and a cold solution of 15 grams of sodium chlorate dissolved in the minimum amount of water added in small portions at a time. After a further addition of 100 c.c. of hydrochloric acid, the clear reddish solution was boiled for two hours

under a reflux condenser. The acid liquid was then distilled in steam, by which means a trace of oily impurity and some of the acetic acid were removed. On cooling and rendering the solution alkaline with sodium carbonate and subsequently resuming the distillation, 43 grams of crude chlorotoluidine were obtained. The oil was collected, dried over potassium carbonate, and fractionated. It distilled as follows :

Below 220°.....	1 gram
220—225°	40·0 grams
Above 225°	2·0 „

Pure *m*-chloro-*p*-toluidine boils at 223—224°, and may be easily obtained by redistilling the large fraction boiling at 220—225° obtained above.

A portion of the base was converted into the acetyl derivative which melted at 113°. The benzyl derivative was also prepared and melts at 137—139°. The latter substance is much more readily crystallised than the acetyl derivative.

Although 3:5-dichloro-*p*-acetotoluidide may be obtained by the direct chlorination of *p*-acetotoluidide, it is preferable to start with pure 3-chloro-4-acetotoluidide prepared as just described. The further chlorination was carried out by means of sodium chlorate, in the same way as in the preparation of monochlorotoluidine. The dichloro-acetotoluidide was purified by crystallisation from alcohol and melted at 199°. The yield amounted to 47 per cent. of the theoretical amount. Lellmann and Klotz obtained small quantities of the same compound by the direct chlorination of *p*-acetotoluidide.

It may be here mentioned that, by the further action of sodium chlorate and hydrochloric acid, 2:3:5-trichloro-4-acetotoluidide, $C_7H_4Cl_3NH \cdot CO \cdot CH_3$, melting at 179°, may be prepared. It crystallises from alcohol in colourless needles. On analysis :

0·1000 gave 0·1693 AgCl. Cl = 41·9.

$C_9H_8ONCl_3$ requires 42·1 per cent.

The hydrolysis of the dichloro-*p*-acetotoluidide was effected by heating with concentrated hydrochloric acid in a sealed tube at a temperature of 130°. The amino-group was replaced by chlorine, and the trichlorotoluene separated by steam distillation. The substance melts at 44·5—45·5°. The conversion of dichloroacetotoluidide into trichlorotoluene is almost quantitative.

(b) Preparation from *m*-chloro-*m*-nitro-*p*-acetotoluidide. 3-Chloro-4-acetotoluidide is readily converted into a nitro-derivative when dissolved in a mixture of fuming nitric acid and glacial acetic acid (Claus and Davidsen, *Annalen*, 1891, 265, 344). Fifteen grams of 3-chloro-4-acetotoluidide, prepared as previously described, were added in small

portions at a time to a mixture of 15 grams of glacial acetic acid and 60 grams of fuming nitric acid. The temperature was maintained at about 20°. On pouring the solution into water and crystallising the product from alcohol, the nitro-compound was obtained in the form of fine needles as described by Claus and Davidsen. Hydrolysis was easily effected with boiling hydrochloric acid. 3-Chloro-5-nitro-4-amino-toluene is slightly soluble in water, and distils slowly in steam from both acid and alkaline solutions. It crystallises well from alcohol in orange needles melting at 72—73°. The amino-group was replaced by chlorine, and the dichloronitrotoluene distilled in steam. This substance crystallises from alcohol in slightly yellow needles melting at 49—50°. On analysis :

0.1019 gave 0.1420 AgCl. Cl = 34.4.

$C_7H_5O_2NCl_2$ requires Cl = 34.4 per cent.

The dichloronitrotoluene obtained was equal in weight to the chloronitrotoluidine taken.

The nitro-group was reduced with stannous chloride and hydrochloric acid. On cooling the solution, after reduction was complete, crystals of the hydrochloride of the base were deposited. These were filtered off, washed with a little hydrochloric acid, and then distilled in steam with the addition of sodium carbonate.

The base gave an *acetyl* derivative, $C_7H_5Cl_2NH \cdot CO \cdot CH_3$, crystallising from alcohol in needles melting at 158—159°. On analysis :

0.1742 gave 0.2285 AgCl. Cl = 32.3.

$C_9H_5ONCl_2$ requires Cl = 32.5 per cent.

The amino-group was replaced by chlorine, and after distillation in steam a good yield of trichlorotoluene resulted. The product thus obtained was identical with the trichlorotoluene prepared by the first method. The same substance has been obtained by Wynne (*Trans.*, 1892, 62, 1042) as a derivative of the products of the action of sulphuryl chloride on *p*-acetotoluidide.

3 : 4 : 5-*Trichloro-2-nitrotoluene*.—This substance crystallises from alcohol in sparingly soluble prisms melting at 81—82°. On analysis :

0.1000 gave 0.1770 AgCl. Cl = 43.8.

$C_7H_4O_2NCl_3$ requires Cl = 44.2 per cent.

3 : 4 : 5-*Trichloro-2 : 6-dinitrotoluene*.—The dinitro-derivative was prepared in the usual way. It crystallises from acetic acid in prismatic needles melting at 163—164°, and is very sparingly soluble in alcohol. On analysis :

0.2045 gave 0.3048 AgCl. Cl = 36.9.

$C_7H_3O_4N_2Cl$ requires Cl = 37.2 per cent.

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3:4:5-Trichlorobenzoic Acid.—The trichlorotoluene is readily oxidised with dilute nitric acid at 130°. 3:4:5-Trichlorobenzoic acid crystallises from dilute alcohol in white needles melting at 203°, as described by Claus and Böcher (*Ber.*, 1887, 20, 1626).

The melting points of the derivatives of the trichlorotoluenes are collected in the following table :

Methyl=1. Cl:Cl:Cl.	Trichloro- toluene.	Trichloronitro- toluene.	Trichlorodi- nitrotoluene.	Trichloro- benzoic acid.
2:3:4	40—41°	60—61°	140—141°	186—187°
2:3:5	45—46	58—59	149—150	162
2:3:6	45—46	57—58	140—142	163—164
2:4:5	81—82	91—92	226—227	162—164
2:4:6	33—34	54	178—180	160—161
3:4:5	44·5—45·5	81—82	163—164	203

II. Chlorination of the Six Dichlorotoluenes.

The dichlorotoluenes were prepared by the methods previously described (*Trans.*, 1901, 79, 1127), with the exception of 3:4-dichlorotoluene, which was obtained from 3-chloro-4-aminotoluene. Chlorination was effected by passing chlorine, dried by being led through concentrated sulphuric acid, into the substance to be chlorinated. A minute quantity of the aluminium-mercury couple was used as "carrier" in all cases. The reaction was prevented from becoming too violent by careful cooling and by regulating the current of chlorine. In most cases, it was unnecessary to add any solvent to keep the substance fluid; moreover, when crystallisation did occur, it was usually an indication that chlorination had proceeded sufficiently far. In no case was any difficulty experienced in effecting substitution, and the yields throughout were very satisfactory. The only point requiring particular care was to ensure that, on the one hand, the dichloro-compound was all chlorinated, and, on the other, to guard against the formation of higher chlorinated toluenes.

Chlorination of 2:3-Dichlorotoluene.

2:3-Dichlorotoluene, chlorinated in the way described, gave tri-chlorotoluene equal to 70 per cent. of the theoretical amount. The substance boiled at 230—240° under the ordinary pressure and melted at 38—40°. On repeated crystallisation from alcohol, a small quantity of a substance of higher melting point was eliminated, probably a tetrachlorotoluene.

Oxidation of the Trichlorotoluene.—The oxidation of the trichlorotoluene was especially undertaken with the object of detecting any 2:3:6-trichlorotoluene, since the trichlorobenzoic acid obtained from this substance could be separated from accompanying benzoic acids by reason of its property of not forming an ester when treated with an alcohol and hydrochloric acid. The crude trichlorotoluene was oxidised with dilute nitric acid in a sealed tube and the acids separated as usual. A portion of the trichlorobenzoic acid was dissolved in ten times its weight of either ethyl or methyl alcohol containing hydrochloric acid, according to Fischer and Speier's method (*Ber.*, 1895, 28, 1150). After the reaction was completed, the solution was poured into water and shaken up with ether or chloroform. "Unesterified" trichlorobenzoic acid was removed by washing with dilute caustic soda solution and subsequently precipitated from the alkaline solution by means of hydrochloric acid. It was found, however, that practically the whole (96 per cent.) of the acid had been converted into the ester, and on repeating the treatment with alcohol and hydrochloric acid no more than the merest traces of acid remained. It would therefore appear that no appreciable amount of 2:3:6-trichlorotoluene was present in the original chlorination product.

Another portion of the oxidation product of the trichlorotoluene was crystallised from hot water. The substance separated in white needles melting at 185—187° and was evidently 2:3:4-trichlorobenzoic acid.

Nitration of the Trichlorotoluene.—The dinitro-derivative was prepared in the usual way and crystallised from alcohol. The substance thus obtained melted at 134—137°. It was then fractionally crystallised from glacial acetic acid. No 2:3:5-dichloro-4:6-dinitrotoluene, m. p. 149—150°, was isolated, but a large quantity of a pure dinitro-compound was separated melting at 139—140°, and identical with 2:3:4-trichloro-5:6-dinitrotoluene.

It is therefore concluded that 2:3-dichlorotoluene on chlorination gives almost exclusively 2:3:4-trichlorotoluene, and this affords a simple method of obtaining the latter substance.

Chlorination of 2:4-Dichlorotoluene.

The chlorination of impure 2:4-dichlorotoluene, which is the main constituent of the mixture of dichlorotoluenes obtained by chlorinating toluene, has been undertaken by several observers. Seelig (*loc. cit.*) succeeded in proving the presence of two out of the three possible isomerides—the 2:3:4- and 2:4:5-compounds. Our results are in agreement with this, and also indicate the probability of a very small amount of the 2:4:6-compound being present.

Pure 2 : 4-dichlorotoluene from 2 : 4-nitrotoluidine was chlorinated and gave its own weight of a mixture of trichlorotoluenes boiling at 230—240°. A preliminary separation of its constituents was effected in the following way. The solid product was warmed to 52° in the water-bath and then quickly drained at the pump, the more infusible residue being washed with a little alcohol. By this means, 6·2 grams of almost pure 2 : 4 : 5-trichlorotoluene was separated from 12 grams of the original mixture. After a single crystallisation from spirit, the substance was obtained in the form of fine needles melting sharply at 81—82°.

The more fusible portion of the mixture was dissolved in hot spirit, and an attempt was made to separate further quantities of the 2 : 4 : 5-compound by crystallisation. This, however, was unsuccessful, so the alcohol was removed by evaporation and the trichlorotoluene converted directly into its derivatives.

Nitration of the Mixed Trichlorotoluenes.—A portion was nitrated in the usual way and the product crystallised from a mixture of alcohol and acetic acid. Crystals were obtained of two kinds, which were separated mechanically. The main constituent consisted of needles melting at 137—140°, and these were separated from a smaller quantity of indistinct, granular crystals of much higher melting point, which were mainly composed of 2 : 4 : 5-trichloro-3 : 6-dinitrotoluene. The needles, on recrystallisation, melted at 138·5—140·5°, and were thus identified as 2 : 3 : 4-trichloro-5 : 6-dinitrotoluene.

Oxidation of the Mixed Trichlorotoluenes.—The only other trichlorotoluene which could be present, besides the two already identified, is the 2 : 4 : 6-compound. Since the trichlorobenzoic acid derived from this substance is a di-*o*-substituted acid and does not readily form an ester when treated with an alcohol in the ordinary way, its separation was attempted by a similar method to that adopted in the case of the chlorination products of 2 : 3-dichlorotoluene. It was found that a small amount of trichlorobenzoic acid was present, which did not form an ester even after four successive treatments with alcohol and hydrochloric acid. The amount of acid thus separated was approximately 4 per cent. of the total weight of mixed acids taken and melted at about 136°. It was not found possible to purify the small quantity of acid at our disposal.

The chlorination of 2 : 4-dichlorotoluene, therefore, results in the formation of large quantities of 2 : 4 : 5-trichlorotoluene, a rather smaller amount of 2 : 3 : 4-trichlorotoluene, and probably a very small quantity of the 2 : 4 : 6-compound.

Chlorination of 2 : 5-Dichlorotoluene.

2 : 5-Dichlorotoluene is readily chlorinated, the yield of crude trichlorotoluenes boiling between 228° and 240° amounting to 86 per cent. of the theoretical amount. The melting point of the preparation was about 30°, but on repeated crystallisation from alcohol it rose to about 78°. It was therefore evident that more than one trichlorotoluene was present. After careful fractionation of the dinitro-compounds and separation of the trichlorobenzoic acids, the presence of the 2 : 4 : 5- and 2 : 3 : 6-compounds was determined. No evidence was obtained of the presence of the third possible trichlorotoluene—the 2 : 3 : 5-compound.

Nitration of the Mixed Trichlorotoluenes.—The dinitro-compounds were prepared in the usual way and crystallised repeatedly from alcohol or from acetic acid or from a mixture of both solvents. The main product was a substance, melting at 140—142°, identical with 2 : 3 : 6-trichloro-4 : 5-dinitrotoluene. After a very large number of crystallisations, a more sparingly soluble portion was obtained which melted at 225—227° and agreed in properties with 2 : 4 : 5-trichloro-3 : 6-dinitrotoluene.

Oxidation of the Mixed Trichlorotoluenes.—The trichlorotoluenes were next oxidised with nitric acid in the usual way. When treated with ethyl alcohol and hydrochloric acid, a portion of the trichlorobenzoic acids readily formed an ester. The ester was separated by pouring the alcoholic solution into water and extracting with chloroform. The non-esterified acid was removed by washing with caustic soda and the solution reserved for subsequent examination. On evaporation of the chloroform solution, the ester readily solidified and was purified by recrystallisation from alcohol. Well-defined, prismatic needles melting at 63—65° were obtained. The melting point of this substance agrees with that of ethyl 2 : 4 : 5-trichlorobenzoate, described by Beilstein and Kuhlberg (*Annalen*, 1869, 152, 234). The ester was hydrolysed with alcoholic potash and the acid crystallised from boiling water. The substance melted at 160—162° and agreed in properties with 2 : 4 : 5-trichlorobenzoic acid.

The caustic soda solution of the non-esterified trichlorobenzoic acid was acidified with hydrochloric acid and the precipitated acid recrystallised from hot water. Well-defined needles were obtained which melted at 163—164°, and were identical in appearance with 2 : 3 : 6-trichlorobenzoic acid.

Chlorination of 2:6-Dichlorotoluene.

2:6-Dichlorotoluene can only give two trichlorotoluenes on chlorination, and of these we have only been able to identify the 2:3:6-derivative. The only simple known derivatives of 2:3:6- and 2:4:6-trichlorotoluenes which show sufficient difference in melting point to render them of service in separating the two substances are the dinitro-compounds which melt at 142° and 180° respectively. The trichlorotoluene obtained boiled at 218—225°, and melted at 40—43°. After recrystallisation from alcohol, it melted at 42.5—45°, which is very near the melting point of pure 2:3:6-trichlorotoluene.

Nitration of the Trichlorotoluene.—The dinitro-compound was prepared in the usual way and exhaustively fractionated, using acetic acid, alcohol, and ethyl acetate successively as solvents. The main product melted at 140—142°, and was easily obtained in a state of purity. This substance is evidently 2:3:6-trichloro-4:5-dinitrotoluene.

The remaining portions melted indefinitely at temperatures varying from 110° to 126°; no pure substance could be isolated from them, and no indication of the presence of 2:4:6-trichloro-3:5-dinitrotoluene, m. p. 180°, was obtained. It is therefore concluded that 2:6-dichlorotoluene on chlorination yields the 2:3:6-derivative almost exclusively, and affords a simple method for its preparation.

Chlorination of 3:4-Dichlorotoluene.

Twenty grams of 3:4-dichlorotoluene, prepared from *m*-chloro-*p*-toluidine, gave 16 grams of trichlorotoluene boiling at 225—235°. The main portion distilled steadily at 230—231°. The product readily solidified, and melted sharply at 79—80°. A single crystallisation from alcohol gave perfectly pure 2:4:5-trichlorotoluene, crystallising in long, brilliant needles melting at 81—82°.

Nitration of the Trichlorotoluene.—The dinitro-compound was prepared and crystallised from glacial acetic acid. It melted at 226—227°, in agreement with pure 2:4:5-trichloro-3:6-dinitrotoluene. No other dinitro-compound was separated, so that it is concluded that the chlorination of 3:4-dichlorotoluene results solely in the formation of the 2:4:5-derivative, and that the reaction affords a good method for the preparation of that substance.

Chlorination of 3:5-Dichlorotoluene.

Since 3:5-dichlorotoluene is a solid substance (m. p. 26°), a small quantity (20 per cent.) of carbon tetrachloride was added to prevent solidification. The trichlorotoluene boiled at 235—243°, and melted at 43—45°.

The chlorination of 3:5-dichlorotoluene can only result in the formation of two trichlorotoluenes—the 2:3:5- and 3:4:5-derivatives—and of these only one, the 2:3:5-compound, appears to be formed.

Nitration of the Trichlorotoluene.—The trichlorotoluene was converted into the dinitro-compound in the usual way. The product at first melted at 149—150°, and after recrystallisation at 149—150°, thus corresponding to 2:3:5-trichloro-4:6-dinitrotoluene. No evidence was obtained of the presence of 3:4:5-trichloro-2:6-dinitrotoluene, which melts at 164°.

Oxidation of the Trichlorotoluene.—The trichlorobenzoic acid was obtained by oxidation in the usual way, and no trichlorobenzoic acid melting at a higher temperature than 162° was obtained, whereas 3:4:5-trichlorobenzoic acid melts at 203°, so that it is concluded that 2:3:5-trichlorotoluene is almost exclusively formed in the chlorination of 3:5-dichlorotoluene.

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