

CXXX.—*The Chlorination of the Trichlorotoluenes in Presence of the Aluminium-mercury Couple. The Constitution of the Tetrachlorotoluenes. Part V.*

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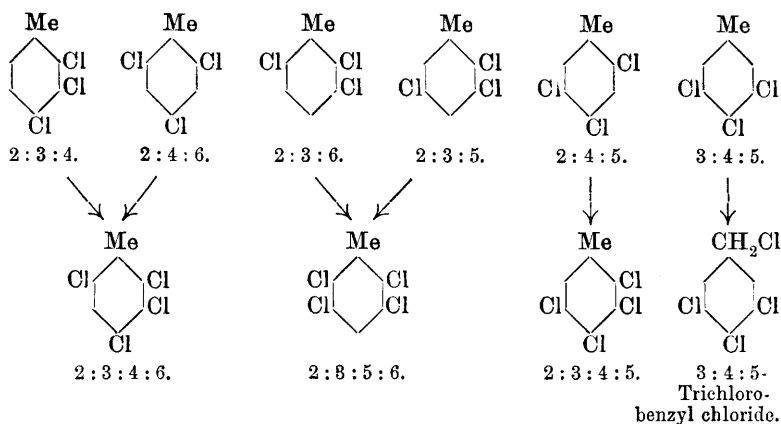
IN our previous papers (Part III, Trans., 1901, 79, 1111 ; Part IV, Trans., 1902, 81, 1325), the progressive chlorination of toluene has been traced as far as the formation of the trichlorotoluenes. We have now carried the investigation a step further, and determined the character of the products formed by introducing a fourth chlorine atom into each of the six trichlorotoluenes.

This stage of the investigation has been simplified, inasmuch as there are only three tetrachlorotoluenes into which the six trichloro-

toluenes could be converted, and of the latter the two symmetrical compounds, namely, the 2:4:6- and 3:4:5-isomerides, can theoretically only yield one product each, provided the chlorine atom enters the nucleus.

But, as the nucleus becomes loaded with chlorine, it is conceivable that steric hindrance might determine the entrance of the halogen into the side-chain, and we have strong evidence that this occurs with 3:4:5-trichlorotoluene. On chlorinating this compound at 0° in presence of the couple, a tetrachloro-compound is formed, which is quite distinct from 2:3:4:5-tetrachlorotoluene and gives a different nitro-derivative. The only explanation of this fact is that the fourth chlorine atom enters the methyl group and not the nucleus. The phenomenon, as far as we know, is quite unique, and leads us to anticipate the possibility of a similar behaviour on the part of the tetrachlorotoluenes when the fifth chlorine atom is introduced in the final stage of chlorination, an investigation upon which we are now engaged.

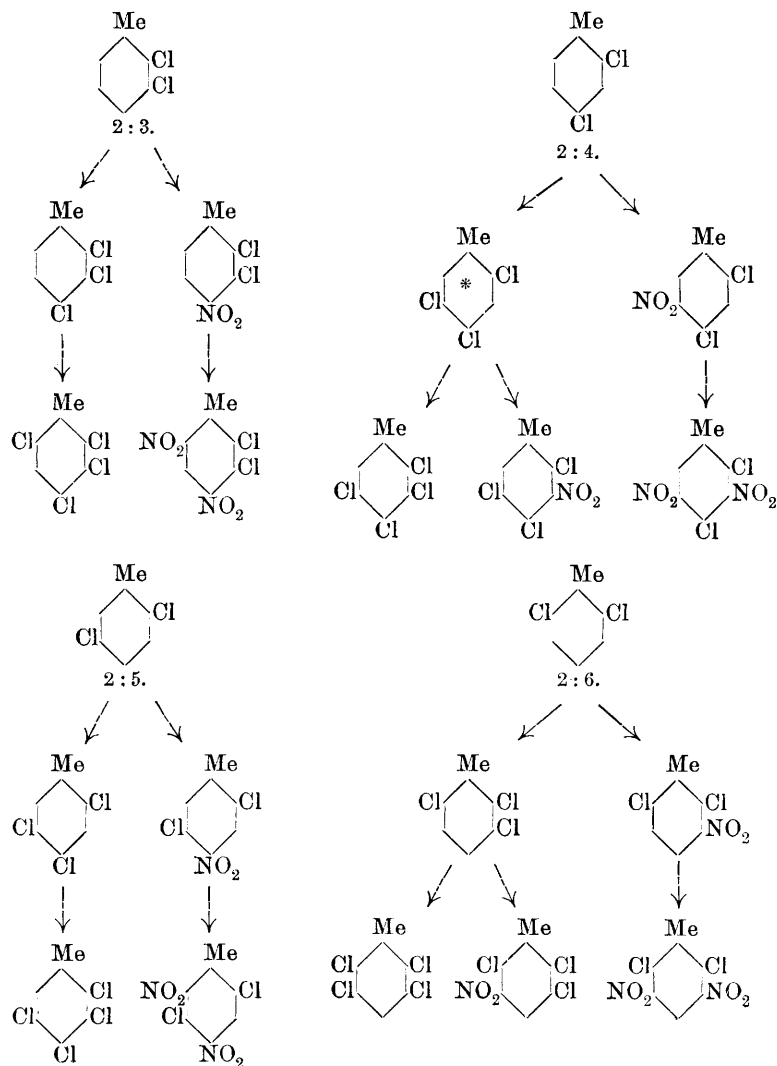
The result of the chlorination of the trichlorotoluenes is indicated by the following graphic scheme :



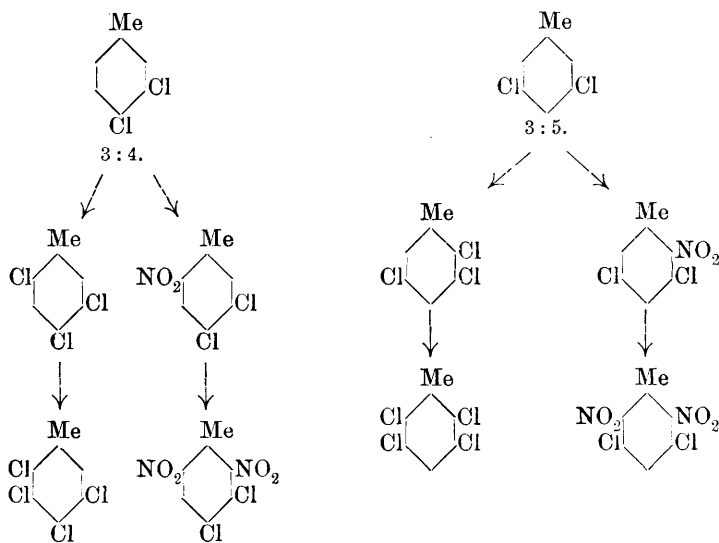
At first sight there appears to be no general law which determines the position assumed by the fourth entrant chlorine atom. It occupies both the ortho- and meta- (not, however, the para-) positions with respect to the methyl group; it enters between two contiguous chlorine atoms, between a chlorine atom and a methyl group, and again between methyl and chlorine or two chlorine atoms which are not contiguous. There is, moreover, no obvious reason why the fourth chlorine atom on entering the 3:4:5-trichloro-compound should seek a position in the side-chain. The chlorination seems to proceed in a purely arbitrary fashion.

On the other hand, there is a somewhat remarkable agreement

between the positions assumed by the third and fourth chlorine atoms on chlorination of the six dichlorotoluenes and those occupied by the first and second nitro-groups on nitration (Trans., 1902, 81, 1345); also by the fourth chlorine atom and first nitro-group effected by the chlorination and nitration of two of those trichlorotoluenes, the structure of which is known. This agreement will be apparent from the following scheme :



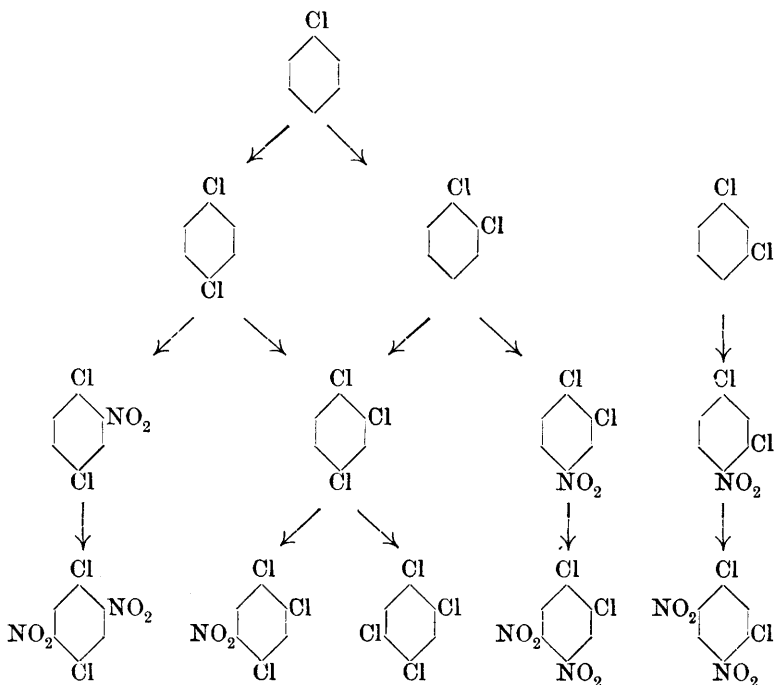
\* The main product of chlorination is taken.



There are only two exceptions to the general agreement which subsists between the products of the action of chlorine and nitric acid. In the case of the 2:5-dichlorotoluene, the 2:4:5-trichloro-compound is, according to our original observation (*Trans.*, 1902, 81, 1342), not the main product of chlorination, although it is formed at the same time; and, moreover, the fourth chlorine atom in the tetrachloro-compound should, according to the rule, occupy the ortho-position with respect to the methyl group. The other exception is the 3:4-dichlorotoluene, which gives ultimately the 2:3:4:5-tetrachloro-compound, whereas the corresponding dinitro-compound is the 3:4-dichloro-2:6-dinitrotoluene.

On closer inspection, however, it will be seen that these exceptions are correlated, for whilst the 2:4-, 2:5-, and 3:4-dichlorotoluenes give the same 2:4:5-trichlorotoluene, they each yield a different nitro-derivative. It follows, therefore, that if the second nitro-group follows the meta-law, three different dinitro-compounds must be formed, whereas the trichlorotoluene yields only one product. Agreement could only occur by the simultaneous production either of a second tetrachloro-derivative or of isomeric dinitro-compounds. Possibly a more careful examination may reveal the presence of small quantities of these products, and it will be interesting to see whether the nitro-groups in the remaining trichlorotoluenes follow the rule. Equally striking in their agreement with the above rule are the facts presented by the derivatives of dichlorobenzene, which we have taken partly from Beilstein and Kurbatoff's paper (*Annalen*, 1878, 192, 228),

and partly from our own observations. Benzene gives on chlorination *o*- and *p*-dichlorobenzenes, then, according to Jungfleisch (*Ann. Chim. Phys.*, 1869, [iv], 15, 186), Beilstein and Kurbatoff, and others, 1:2:4-trichlorobenzene and 1:2:4:5-tetrachlorobenzene, and no other isomerides. The following scheme represents the products of chlorination and nitration of the dichlorobenzenes:



The dinitro-derivatives of *ortho*- and *para*-dichlorobenzenes offer points of special interest. Hartley and Cohen (*Trans.*, 1904, 85, 869) have shown that the second nitro-group follows the meta-law completely in the case of *m*-dichlorobenzene, to the extent of about 80 per cent. in that of the *para*-compound (about 14 per cent. being *p*-dinitro *p*-dichlorobenzene), and not at all in that of the *ortho*-compound. The formation of the *p*- and *o*-dinitro-compounds is, however, in perfect harmony with the above scheme. May not the explanation of these apparent departures from the meta-law be associated in some way with the above rule?

Whatever the ultimate explanation may be, it is clear that after the first two chlorine atoms have been introduced into benzene and toluene the special rules which are usually applied to substitution are wholly or in part set aside in favour of a more general law which

includes both the chlorine atom and the nitro-group. The rule seems capable of wide and varied extension. We have already begun the repetition of Beilstein and Kurbatoff's work, which we shall extend so as to include the chlorination of *m*-dichlorobenzene. In the meantime we are tempted to predict, from the position which the nitro-group in the nitro-derivative is known to occupy, the formation of 1:2:4-trichlorobenzene and 1:2:4:5-tetrachlorobenzene from *m*-dichlorobenzene. It will, moreover, be interesting to see whether by chlorinating the isomeric chloronitrotoluenes the entrant chlorine atom occupies the same position as the first nitro-group in the nitrodichlorotoluenes, and, again, to discover whether the sulphonic groups follow the same law as the chlorine atom and nitro-groups.

### EXPERIMENTAL.

#### I. *Preparation of the Isomeric Tetrachlorotoluenes and their Derivatives.*

Before proceeding to study the action of chlorine on each of the six trichlorotoluenes, we have adopted our former plan of investigating first the properties of the pure tetrachlorotoluenes and such of their derivatives as might conveniently serve for identifying the products of chlorination.

The literature of the tetrachlorotoluenes is very scanty. By chlorinating toluene, Limpricht (*Annalen*, 1866, 139, 327) obtained a substance boiling at 276.5° and melting at 96°. Later, Beilstein and Kuhlberg (*Annalen*, 1869, 150, 286) repeated the work of Limpricht on the chlorination of toluene, which they carried out in the first stage with iodine and subsequently with antimony pentachloride as carriers. The product was fractionated, and a tetrachlorotoluene was obtained which crystallised in fine needles melting at 91–92° and boiling at 271°. Further, Pieper (*Annalen*, 1867, 142, 305) prepared a liquid tetrachlorotoluene (b. p. 280–290°) by heating the additive compound,  $C_7H_6Cl_8$ , with alcoholic potash at 110°. As none of the tetrachlorotoluenes is liquid at the ordinary temperature, the substance must have been either an impure product or more probably some totally different compound.

Beilstein and Kuhlberg's compound would be either the 2:3:4:6- or 2:3:5:6-tetrachlorotoluene, which melt at 91–92° and 93–94° respectively, or a mixture of the two, as both substances are formed on chlorination.

The following table gives the melting points of the tetrachlorotoluenes and their nitro-compounds. We were unsuccessful in preparing other derivatives. On oxidation with nitric acid under pressure, the substances are either very slightly attacked at lower temperatures

or entirely decomposed at higher temperatures, and the corresponding tetrachlorobenzoic acids were not obtained.

Methyl = 1. Cl : Cl : Cl : Cl	Tetrachloro- toluene.	Tetrachloronitro- toluene.
2 : 3 : 4 : 5	86—88°	86—88°
2 : 3 : 4 : 6	91·5—92	131—134
2 : 3 : 5 : 6	93—94	150—152

*2 : 3 : 4 : 5-Tetrachlorotoluene.*

The tetrachlorotoluene was prepared from 2 : 4 : 5-trichlorotoluene. Eight grams of the trichlorotoluene were nitrated with 25 grams of nitric acid (sp. gr. 1·4) and 30 grams of strong sulphuric acid. The nitro-compound was separated and reduced with tin and hydrochloric acid, the base being extracted from the acid solution with chloroform. This substance diazotised very slowly. The product was poured into cuprous chloride solution and distilled in steam. The solid distillate, when crystallised from alcohol, separated in fine needles which melted at 85—87°. The melting point, after two recrystallisations, remained stationary at 86—88°.

*2 : 3 : 4 : 5-Tetrachloro-6-nitrotoluene.*—The tetrachlorotoluene was warmed with 10 parts of fuming nitric acid; the product was then poured into water and the nitro-compound crystallised from alcohol or acetic acid; it separates in flattened needles and plates which melt at 86—88°.

0·1029 gave 0·2166 AgCl. Cl = 52·1.

$C_7H_3O_2NCl_4$  requires Cl = 51·6 per cent.

*2 : 3 : 4 : 6-Tetrachlorotoluene.*

The tetrachlorotoluene was prepared from trichloroaceto-*m*-toluidide (Trans., 1902, 81, 1335) which was hydrolysed and converted into the base. Eleven grams of the base, when diazotised in the usual way and distilled in steam, yielded 11 grams of crude tetrachlorotoluene melting at 89—90°. After two crystallisations from alcohol, from which it separates in shining needles, the product melted at 91·5—92°.

0·1492 gave 0·3727 AgCl. Cl = 61·7.

$C_7H_4Cl_4$  requires Cl = 61·7 per cent.

*2 : 3 : 4 : 6-Tetrachloro-5-nitrotoluene.*—Two grams of the tetrachlorotoluene were nitrated with a mixture of 10 c.c. of nitric acid (sp. gr. 1·4) and 10 c.c. of strong sulphuric acid. The product, which crystallised from the acid solution on cooling, is sparingly soluble in alcohol, and moderately soluble in acetic acid, from which it separates in

needles melting not very sharply at  $128^{\circ}$ . After several crystallisations from alcohol, the melting point rose to  $131$ — $134^{\circ}$ . The product is still not quite pure, as may be seen from the analysis; it probably contains a little unaltered tetrachlorotoluene.

0.1107 gave 0.2355 AgCl.  $\text{Cl} = 52.6$ .

$\text{C}_7\text{H}_3\text{O}_2\text{NCl}_4$  requires  $\text{Cl} = 51.6$  per cent.

If the action of the nitric acid is prolonged so as to nitrate the product completely, a second substance is formed which appears under the microscope in the form of highly refractive rectangular plates or broad, acicular prisms according to the position of the crystal; it melts gradually at  $153^{\circ}$ . We have not investigated the compound further, but its appearance dispersed among the needles of the nitro-compound is sufficiently characteristic to have enabled us to utilise the reaction in identifying the 2 : 3 : 4 : 6-compound (p. 1284).

#### 2 : 3 : 5 : 6-Tetrachlorotoluene.

The tetrachlorotoluene was prepared by nitrating 2 : 3 : 6-trichlorotoluene and replacing the nitro-group by chlorine. The trichlorotoluene was dissolved in twice its volume of fuming nitric acid (sp. gr. 1.5), which was kept cold in ice, and the product poured into water. The nitro-compound was reduced with tin and hydrochloric acid without further purification. In order to separate the base, which distils very slowly in steam, the acid solution was diluted with water and boiled, when the hydrochloride is hydrolysed and the free base, which is liquid at the boiling point of water, solidifies on cooling. The base was separated and crystallised from dilute methyl alcohol; it melts at  $66$ — $67^{\circ}$ . Six grams of trichloronitrotoluene gave 4 grams of the base. The diazotisation proceeds very slowly under ordinary conditions, and it was found necessary to use a large excess of strong hydrochloric acid and solid sodium nitrite. The quantities employed for 4 grams of the base were 15 c.c. of strong hydrochloric acid and 3 grams of finely powdered sodium nitrite. The liquid, which remains turbid from the separation of sodium chloride, was poured into the cuprous chloride solution prepared from 5 grams of copper carbonate. After the evolution of nitrogen had ceased, the tetrachlorotoluene was separated by simple filtration and well washed with water, when 3.5 grams of crude tetrachlorotoluene were obtained from 4 grams of the base. After crystallisation from methyl alcohol, it melted at  $92$ — $93^{\circ}$ , a second crystallisation raising the melting point to  $93$ — $94^{\circ}$ . The substance crystallises in opaque, white, felted needles resembling the mycelium of a fungus by the peculiar way in which the filaments cling together.



## 1282 COHEN AND DAKIN: THE CONSTITUTION OF THE

0.1524 gave 0.3801 AgCl.  $\text{Cl} = 61.6$ .

$\text{C}_7\text{H}_4\text{Cl}_4$  requires  $\text{Cl} = 61.7$  per cent.

2:3:5:6-*Tetrachloro-4-nitrotoluene*.—One part of the tetrachlorotoluene was dissolved in 10 parts of fuming nitric acid and heated for  $1\frac{1}{2}$  hours on the water-bath; the product was poured into water and crystallised from methyl alcohol; it forms small, hexagonal plates which melt at  $150-152^\circ$ .

0.1095 gave 0.2306 AgCl.  $\text{Cl} = 52.0$ .

$\text{C}_7\text{H}_3\text{O}_2\text{NCl}_4$  requires  $\text{Cl} = 51.6$  per cent.

## II. Chlorination of the Six Trichlorotoluenes.

The manipulative part of this section of the research offered unexpected difficulties. The preparation of the requisite quantity of each of the trichlorotoluenes has been in many cases a long and tedious operation. Moreover, the trichlorotoluenes are solids, and the use of an inert solvent in chlorinating was therefore necessary. Whilst carbon tetrachloride served this purpose excellently, provided the right proportion was used, its volatility added greatly to the difficulty of determining by the increase of weight how far the chlorination had proceeded. This is a matter of the utmost importance, as a slow reaction may yield too little of the tetrachloro-compound to identify with certainty, whereas too rapid chlorination may convert the whole of the material into higher chlorinated products. We eventually adopted the following method. A small quantity, varying from 1 to 5 grams, of the trichlorotoluene under examination was dissolved in an equal weight of carbon tetrachloride. The solution was placed in a stout test-tube provided near the top with a narrow side-piece, and connected to a second similar tube by a piece of glass-tubing which was attached to the side-tube of the first vessel and passed through the cork to the bottom of the second. Chlorine was passed for a time through the solution and the two tubes and connections then carefully counterpoised. The first tube, containing the solution, was placed in ice and the second empty tube in a good freezing mixture of ice and salt. The object of the second tube was to retain any carbon tetrachloride carried over from the first by the current of chlorine. A known weight (about 0.1 gram) of aluminium-mercury couple was then introduced into the solution, when a vigorous reaction very soon set in, which was allowed to moderate before fresh chlorine was introduced. A slow current of the dry gas was then passed through the solution until the theoretical increase in weight was obtained. The solution was left until effervescence nearly ceased and then poured off from the couple, rinsed out with fresh carbon tetrachloride into a basin, and left on the water-bath

until most of the solvent had evaporated. The residue, which solidified on cooling, was placed in a vacuum desiccator for a sufficient length of time to remove the remainder of the carbon tetrachloride. The product, which might, and usually did, contain in addition to the tetrachlorotoluene both unaltered substance and higher chlorinated compounds, was now submitted to careful fractional crystallisation from methyl alcohol, or, in some cases, to fractional sublimation on the water-bath. Less frequently it was converted directly into the nitro-derivative by heating it on the water-bath with fuming nitric acid. As a rule, a fraction melting at about 80—90° was eventually separated and in every case nitrated. The characters of the nitro-derivatives are sufficiently distinct to furnish unmistakable evidence of the constitution of the tetrachlorotoluene. It will be seen from the table on p. 1280 that there is a wide difference in the melting points of the three tetrachloronitrotoluenes, and if any doubt were likely to arise between the 2 : 3 : 4 : 6- and 2 : 3 : 5 : 6-compounds the appearance under the microscope of the two kinds of crystals in the case of the 2 : 3 : 4 : 6-compound already described would at once set the matter at rest.

*Chlorination of 2 : 3 : 4-Trichlorotoluene.*

The chlorination of 2 : 3 : 4-trichlorotoluene was conducted as already described. After fractional crystallisation from methyl alcohol, a portion melting at 89—91° was separated, which consisted of a felted mass of shining needles; a less soluble portion, consisting of hard needles and quite homogeneous in appearance, melted indefinitely at 128—165° and was not further investigated. The first fraction (m. p. 89—91°) was nitrated with fuming nitric acid on the water-bath. After crystallising the product from alcohol, it melted slowly at 153° and showed the mixture of crystals characteristic of the 2 : 3 : 4 : 6-compound. The process was repeated with a fresh quantity of trichlorotoluene, and a portion melting at 88—92° was isolated. The following experiment was then made. An equal quantity (about 0.5 gram) of the following four substances was placed in separate test-tubes, namely, the first fraction (m. p. 89—91°), the second fraction (m. p. 88—92°), 2 : 3 : 4 : 5-tetrachlorotoluene, and 2 : 3 : 4 : 6-tetrachlorotoluene. The same quantity (1 c.c.) of fuming nitric acid was added to each and the test-tubes placed in boiling-water, which was at once allowed to cool. On cooling, crystals were deposited in the tubes containing the two fractions and the 2 : 3 : 4 : 6-tetrachlorotoluene, but none in that of the 2 : 3 : 4 : 5-compound, the nitro-derivative of which is very soluble in the acid. The first three specimens were precipitated with water, crystallised once from alcohol, and the melting points determined simultaneously with the following result:—The product

## 1284 COHEN AND DAKIN: THE CONSTITUTION OF THE

from the pure 2:3:4:6-compound melted at 150°, that from the fraction (m. p. 89—91°) at 149°, and that from the fraction (m. p. 88—92°) at 145°. In all three cases, the presence of the two kinds of crystals could be detected under the microscope. In no experiment, and it was repeated four times with altogether 20 grams of material, was there any indication of a more fusible nitro-compound corresponding with the 2:3:4:5-tetrachlorotoluene.

*Chlorination of 2:3:5-Trichlorotoluene.*

The product obtained by chlorinating 2:3:5-trichlorotoluene was recrystallised and nitrated in the usual way. The following three fractions were obtained on recrystallising the nitro-compound; they melted at 148—150°, 145—147°, and 139—144°, and crystallised in hexagonal plates, characteristic of the 2:3:5:6-tetrachloronitrotoluene (m. p. 150—152°), with which the chlorination product must therefore be identified. There was no fraction melting at 86—88°, and 2:3:4:5-tetrachlorotoluene is absent.

*Chlorination of 2:3:6-Trichlorotoluene.*

After chlorination, the product was fractionally sublimed on the water-bath by heating the substance in a basin covered by a second basin containing ice-cold water; the sublimate consisted of long needles having the fungus-like appearance of the 2:3:5:6-compound. Three fractions were collected.

Fraction 1, m. p. 73—82°, gave a nitro-compound, m. p. 144—148°.

„ 2 „ 70—87° „ „ „ 148—149°.

„ 3 „ 89° „ „ „ 148—149°.

All the nitro-compounds crystallised in hexagonal plates, characteristic of 2:3:5:6-tetrachloronitrotoluene.

*Chlorination of 2:4:5-Trichlorotoluene.*

The chlorination was conducted in the usual way and the product crystallised and nitrated. The crude nitro-compound melted at 82—85°, the melting point after two crystallisations rising to 85—86°.

The melting point (86—88°) and crystalline appearance correspond with those of 2:3:4:5-tetrachlorotoluene. There was no less fusible nitro-compound, and no other tetrachlorotoluene was therefore formed.

*Chlorination of 2:4:6-Trichlorotoluene.*

If the chlorine enters the nucleus, only one derivative, namely, 2:3:4:6-tetrachlorotoluene, is possible. After chlorination, the

product was crystallised, and a fraction melting at  $89^{\circ}$  was obtained and nitrated. The nitro-compound crystallised in needles (m. p.  $125-130^{\circ}$ ) which were practically free from rectangular prisms, but, on further heating with nitric acid, the needles were almost wholly converted into rectangular prisms melting slowly at  $154^{\circ}$ , a transformation which is characteristic of the 2:3:4:6-tetrachloronitrotoluene.

*Chlorination of 3:4:5-Trichlorotoluene.*

After chlorination, the product was fractionally crystallised from methyl alcohol. Two principal fractions were obtained, a less soluble portion, which crystallised in fine silky needles and melted indefinitely from  $132^{\circ}$  to above  $150^{\circ}$ , and a second more soluble fraction, which also crystallised in needles and melted sharply at  $97-98^{\circ}$ , the melting point remaining unchanged on recrystallisation.

Fraction (m. p.  $132-150^{\circ}$ ). 0.1017 gave 0.2624 AgCl. Cl = 63.9.  
 $C_7H_3Cl_5$  requires Cl = 67.1 per cent.

Fraction (m. p.  $97-98^{\circ}$ ). 0.1364 gave 0.3353 AgCl. Cl = 60.9.  
 $C_7H_4Cl_4$  requires Cl = 61.6 per cent.

The first fraction is therefore a mixture of tetra- and penta-chlorotoluenes; the second is clearly a tetrachlorotoluene. On nitration, the latter gave a nitro-compound melting sharply at  $159^{\circ}$ . The experiment was repeated with a fresh quantity of 3:4:5-trichlorotoluene with the same result.

Now if chlorine enters the nucleus, only 2:3:4:5-tetrachlorotoluene (m. p.  $86-88^{\circ}$ ) can result, and this gives a nitro-derivative melting at the same temperature. In the present case, we have a tetrachloro-compound melting at  $97-98^{\circ}$ , which gives a nitro-compound melting at  $159^{\circ}$ . There is only one explanation possible; the fourth chlorine atom enters the side-chain. This explanation would account for the high melting point of the compound, since when chlorine enters the side-chain in toluene to form benzyl chloride, the substance is less volatile than the isomeric chlorotoluenes containing chlorine in the nucleus.

In conclusion, we wish to acknowledge our indebtedness to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this research.

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