

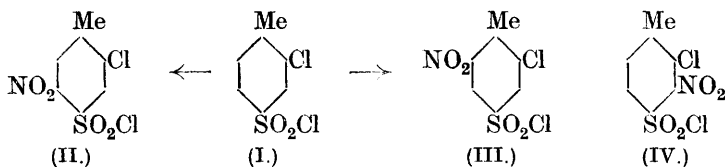
XCVI.—*The Cumulative Effect of the Chlorine Atom and the Methyl and Sulphonyl Chloride Groups on Substitution in the Benzene Nucleus. Part I.*

By WILLIAM DAVIES.

THE position taken up by a new, entering group under the directive influence of two groups already present in the benzene nucleus has been generalised in laws that have almost completely been established. When three groups are present, however, the problem where substitution will take place becomes more complicated, and no systematic attempt at its solution has been made. It was thought that the nitration of certain chlorotoluenesulphonyl chlorides would throw light on this problem.

The first part of the research is concerned with the constitution of the different mononitro-derivatives of 2-chloro-*p*-toluenesulphonyl chloride (I). The only literature on the subject is the mere statement in the German patent (D.R.-P. 145908; Friedländer, VII, 467) that 2-chloro-5-nitro-*p*-toluenesulphonyl chloride (II) is formed on nitration. No evidence of this is adduced.

Now it would at first sight be expected that the ortho-directing influence of the methyl group, together with the meta-directing influence of the sulphonyl chloride group, would be greater than the tendency, due to the chlorine atom, for substitution to take place in the para-position with respect to the chlorine atom. Therefore more of III would be expected than of II. The method of nitration and the analysis of the products are described in the experimental part of this paper.

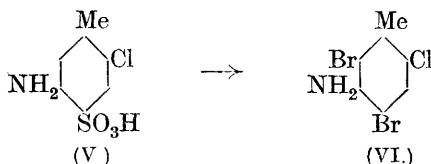


The orientation of 2-chloro-5-nitro-*p*-toluenesulphonyl chloride presented considerable difficulties. Heating in a sealed tube with fuming hydrochloric acid for periods of from twelve to thirty-six hours between 140° and 180° resulted in the sulphonyl chloride group being converted into the sulpho-group, but led to no further hydrolysis. Similarly, when the sodium salt in 80 per cent. sulphuric

acid was distilled in superheated steam at 250°, no oil passed over into the distillate. The conversion into a dichloronitrotoluene was then attempted by the elimination of sulphur dioxide. However, careful heating at the ordinary and under diminished pressure led to extensive decomposition, and only a trace of sulphur dioxide was formed. Efforts to replace the sulphonyl chloride group by chlorine were made by heating with phosphorus pentachloride, after the method described by Olivier (*Rec. trav. chim.*, 1920, **39**, 502). Negative results were obtained.

Finally, the powdered sodium chloronitrotoluenesulphonate was gently heated separately with potassium ferrocyanide, sodium formate, and sodamide, in order to replace the sulpho-group by a cyano-, carboxyl, and amino-group respectively. However, the sodium chloronitrotoluenesulphonate, which decomposes at about 220°, deflagrated in all these cases before the reagents could enter into reaction.

Since II could not directly be converted into known derivatives, its constitution was determined by a circuitous method. Sodium chloronitrotoluenesulphonate was reduced and converted into 6-chloro-*m*-toluidine-4-sulphonic acid (V), which was converted into a chlorodibromotoluidine and sulphuric acid by the action of bromine water. This compound is undoubtedly 6-chloro-2:4-dibromo-*m*-toluidine (VI).



The replacement by bromine of the sulpho-group in aminobenzenesulphonic acids, through the action of bromine water, has been found to occur only when the amino- and sulpho-groups are in the ortho- or para-position with respect to each other (Bahlmann, *Annalen*, 1877, **186**, 309; Evans, P., 1896, **12**, 235). When these two groups are in the meta-position to each other, the action of bromine water leads to the formation of bromoaminobenzenesulphonic acids.

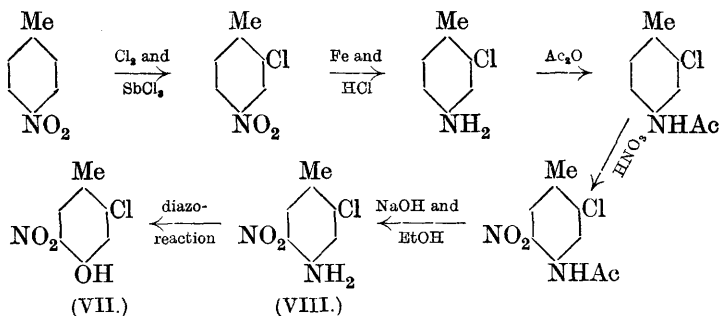
Therefore the conversion of the chlorotoluidinesulphonic acid in question into a chlorodibromotoluidine shows that the original chloronitrotoluenesulphonyl chloride is either II or IV.

This conclusion was borne out by the behaviour of the sodium chloronitrotoluenesulphonate when boiled with dilute sodium hydroxide solution. A red salt, almost insoluble in the boiling

solution, was gradually formed, and it was converted by acidification into a chloronitrocresol readily volatile in steam and possessing a faint smell recalling that of *o*-nitrophenol. Moreover, the alkali salts were intensely coloured. These properties show that the nitro-group in the chloronitrocresol is in the ortho-position with respect to the hydroxy-group, and therefore that the parent substance is either II or IV.

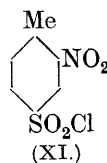
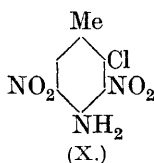
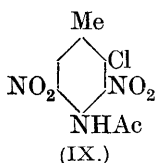
2-Chloro-5-nitro-*p*-cresol (VII), m. p. 71° , is of unusual interest because the sodium salt is sparingly soluble, whilst the potassium salt is moderately soluble in water. The sodium salt is readily formed as an amorphous red precipitate by double decomposition from the potassium salt. This reaction may be useful in estimating the amount of the sodium salt in a mixture of sodium and potassium salts.

Since the chloronitrocresol melting at 71° might possibly have been derived from the third possible chloronitrotoluenesulphonyl chloride (IV), the substance having the formula VII was prepared by a method that left no doubt as to its constitution, and the two chloronitrocresols were compared. The diagram below summarises the reactions involved in the synthesis.



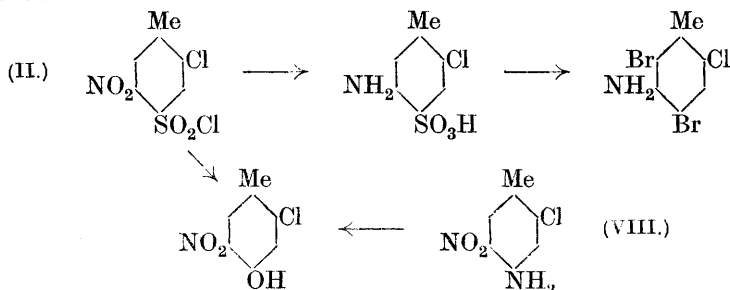
The chloronitrotoluidine (VIII), from which the chloronitrocresol (VII) was prepared, has already been described, and its constitution clearly established by its conversion into 2:4-dichloro-5-nitrotoluene (Blanksma, *Rec. trav. chim.*, 1910, **29**, 414). In the preparation of VIII, 2-chloroaceto-*p*-toluidide was nitrated at first with the quantity of nitric acid used by Claus and Bocher (*Annalen*, 1891, **265**, 354). The large excess of nitric acid, together with inadequate cooling, led to the formation of a dinitro-derivative, namely, 2-chloro-3:5-dinitroaceto-*p*-toluidide (IX), which can readily be hydrolysed to the corresponding amine (X). The nitration of 2-chloroaceto-*p*-toluidide was then carried out after the method of Blanksma (*loc. cit.*), and the chloronitroacetotoluidide and the

corresponding amine obtained possessed the melting points recorded by Blanksma.



The attempted transformation of the amine VIII into the corresponding phenol by means of the diazo-reaction at first gave negative results. Like many other diazo-compounds derived from halogen- or nitro-substituted amines (compare Cain, "The Diazo-compounds," 1920, 38), the diazo-compound produced in this case was very stable. It was found that the addition of the diazonium solution to boiling dilute sulphuric acid containing various amounts of sodium sulphate gave mere traces of a phenolic substance, but that when copper sulphate was present in the boiling acid mixture, the decomposition took the desired direction, and a 20 per cent. yield of the hydroxy-compound was obtained. It was shown by a mixed melting-point determination to be identical with the chloronitrocresol already obtained from the sodium chloronitro-toluenesulphonate.

It is therefore evident that the chloronitrotoluenesulphonyl chloride melting at 99.2° has the constitution indicated by II. The proof of the constitution of this substance is summarised as follows :



It was found later that a 5 per cent. yield of VIII was obtained by heating II under pressure with an alcoholic solution of ammonia.

The orientation of 2-chloro-6-nitro-p-toluenesulphonyl chloride (III), m. p. 70° , was also unexpectedly difficult. Attempts to replace the sulphonyl chloride group by hydrogen were made under conditions similar to those already referred to (p. 853), but without success. It was similarly found impossible to replace the sulphonyl chloride group by chlorine, through the elimination of sulphur dioxide.

A consideration of the formula of 2-nitro-*p*-toluenesulphonyl chloride (XI) shows that all three groups will cause substitution to take place at the vacant ortho-position with respect to the methyl group. Chlorination of this substance would therefore be expected to lead to the formation of III. By a comparison of the chlorination product with the chloronitrotoluenesulphonyl chloride melting at 70°, it was hoped that the constitution of the latter substance would be established. 2-Chloro-*p*-toluenesulphonyl chloride was accordingly prepared (compare Reverdin and Crepieux, *Ber.*, 1901, **34**, 2992), and exposed to the action of chlorine at various temperatures (70–130°) in the presence of catalysts. Chlorination could not be effected.

In repeating a preparation of 2 : 6-dinitro-*p*-toluenesulphonic acid after Reverdin and Crepieux (*loc. cit.*), a by-product of about 2 per cent. of 2 : 4-dinitrotoluene was obtained, indicating that a sulpho-group may, when meta to a nitro-group, be replaced by another nitro-group. In order to convert the chloronitrotoluenesulphonyl chloride under investigation into a known chlorodinitrotoluene, it was heated with a nitrating mixture, but the sulpho-group was not eliminated, even under drastic conditions.

The constitution of the chloronitrotoluenesulphonyl chloride was finally elucidated by the action of sodium hydroxide solution. After prolonged boiling with the alkaline solution, acidification led to the production of no chloronitrocresol, which would probably have been formed had the chloronitrotoluenesulphonyl chloride had the constitution expressed by IV. On the other hand, when the cold acid solution was treated with sodium nitrite and poured into an alkaline solution of β -naphthol, a red dye was produced, indicating that an amino-derivative had been formed by the action of alkali on the chloronitrotoluenesulphonyl chloride. It is therefore very probable that auto-oxidation and reduction had taken place, with the production of a derivative of anthranilic acid, just as the action of alkali on 2-nitro-*p*-toluenesulphonic acid leads to the formation of *p*-sulphoanthranilic acid (D.R.-P. 138188). This reaction is only known to occur when the nitro- and methyl groups in nitrotoluene derivatives are in the ortho-position with respect to each other. There can therefore be little doubt that the chloronitrotoluenesulphonyl chloride melting at 70° has the formula III.

The chlorination of 2-chloro-*p*-toluenesulphonyl chloride was undertaken to ascertain whether the entering chlorine atom, like the nitro-group, would be directed chiefly into the 5-position. *p*-Toluenesulphonyl chloride has indeed been dichlorinated (D.R.-P. 210856), and the chlorinated product yielded, on the removal of the sulpho-group, a large proportion of 2 : 6-dichlorotoluene, with

some 2 : 3 : 6-trichlorotoluene. As the only evidence mentioned in favour of the dichlorotoluene being the 2 : 6-isomeride was the boiling point (190—200°), it was felt, in the light of the research already described, to be improbable that XII was the sole dichloro-*p*-toluenesulphonyl chloride produced.

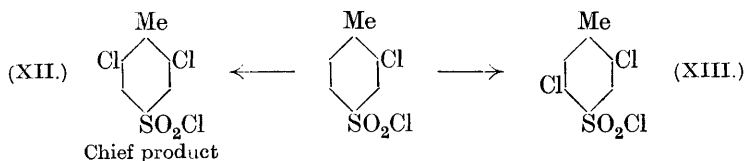
With antimony trichloride as catalyst, the chlorination of 2-chloro-*p*-toluenesulphonyl chloride took place smoothly at 65—70°. The patent seems to be practically justified, for the chief product was 2 : 6-dichloro-*p*-toluenesulphonyl chloride (XII). However, the presence of the expected isomeride (XIII) was shown.

The proportion of solid 2 : 6-dichloro-*p*-toluenesulphonyl chloride isolated was 66 per cent. of theory, and the amount actually formed must have been considerably greater, for it was not completely separated from the mixture of dichlorotoluenesulphonyl chlorides produced.

Sodium 2 : 6-dichloro-*p*-toluenesulphonate was hydrolysed very smoothly with the production of a dichlorotoluene which was converted into a dinitro-derivative melting at 121°. The dinitro-derivative of 2 : 6-dichlorotoluene melts at 121—122° (Cohen and Dakin, T., 1901, 79, 1130). The dichlorotoluene was partly oxidised by nitric acid in a sealed tube and the acid produced shown to be identical with 2 : 6-dichlorobenzoic acid.

Advantage was taken of the steric hindrance to oxidation with permanganate solution, shown by 2 : 6-dichlorotoluene, in order to prove that 2 : 5-dichloro-*p*-toluenesulphonyl chloride (XIII) had been produced. The oil from which the solid 2 : 6-dichloro-*p*-toluenesulphonyl chloride had been separated was converted into the corresponding mixture of dichlorotoluenes, which was then oxidised by potassium permanganate solution. 2 : 5-Dichlorobenzoic acid was obtained. The proportion of 2 : 5-dichloro-*p*-toluenesulphonyl chloride was not determined, but it was small.

The results of the chlorination of 2-chloro-*p*-toluenesulphonyl chloride are represented in the diagram below.

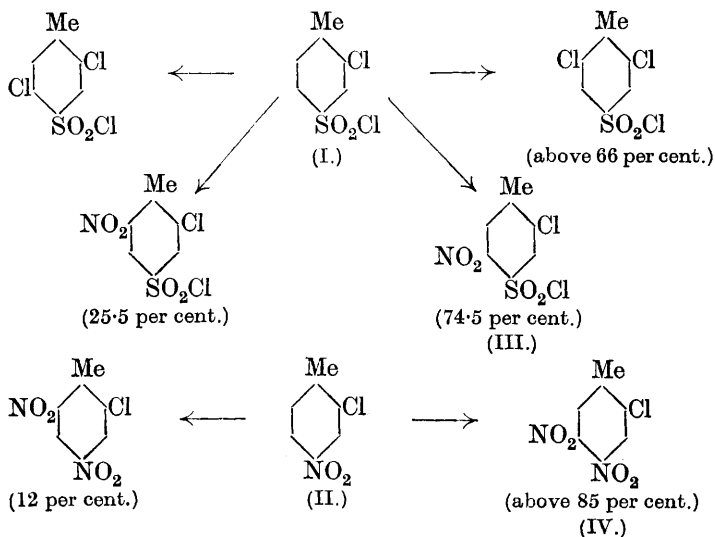


Discussion of Results.

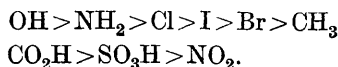
The nitration of I* shows that the para-directing influence of the chlorine atom is about three times as great as the combined ortho-

* The numbers used in the discussion refer to the formulæ on p. 859.

and meta-directing influences of the methyl and sulphonyl chloride groups respectively. An explanation of the apparently extraordinarily great influence of the chlorine atom can be deduced from a



consideration of the relative speeds of substitution caused by ortho-, para-, and meta-directing groups respectively. The order * in the two series is as follows :



Hence it is very probable that the directing influence of the chlorine atom in I, weakened as it is by the presence of the methyl group in the ortho-position, is nevertheless of the same order as, and possibly greater than, the influence of the sulphonyl chloride group. This deduction can be tested by the results obtained in the nitration of II (compare Morgan and Drew, T., 1920, **117**, 786). The speed of substitution in the meta-position caused by the nitro group is less than that caused by the sulpho-group (see above) and therefore presumably less than that caused by the sulphonyl chloride group. It would therefore be expected that the amount of substitution in the para-position with respect to the chlorine atom in I would be less than the amount of substitution in the same position in II. This expectation is borne out by the relative amounts of the nitro-derivatives actually formed.

* The order given in the two series is taken from Holleman's "Die direkte Einführung von Substituenten in den Benzolkern," 1910, 466, 469.

The results obtained show that in predicting the position chiefly taken up by a new fourth substituent, it is necessary to bear in mind the relative directing powers of the two positive * substituents. Even the difference in power of these two groups may be great enough to overwhelm the effect of the third, negative, group.

The foregoing remarks do not apply when the particular case of substitution is the entry of chlorine. It is, however, conceivable that when the directing influences of the substituents in the benzene nucleus more or less balance each other, the effect (usually quite secondary) of the nature of the entering group will then be much enhanced. This may be the reason why in I chlorination and nitration cause substitution to take place in different ways. This point is being studied with reference to other substances than I.

It is noteworthy that the sulphonyl chloride group in III and the nitro-group in the para-position to the chlorine atom (Morgan and Drew, *loc. cit.*) in IV are reactive towards ammonia and sodium hydroxide. This interesting and unexpected result may receive some explanation from the theory of Kenner (T., 1914, **105**, 2717; Kenner and Parkin, T., 1920, **117**, 852). This theory shows that the displacement of mobile substituents is presumably preceded by the formation of a molecular additive compound through the agency of the nitro-group in the ortho- or para-position with respect to the group which is actually displaced. The non-reactivity of the nitro-group in III indicates that the sulpho-group is incapable of forming such an additive compound.

EXPERIMENTAL.

2-Chloro-p-toluenesulphonyl Chloride.

The preparation, based on D.R.-P. 145908, was conducted as follows :

p-Toluenesulphonyl chloride (311 grams ; 1 mol.) was melted with antimony trichloride (6 grams), and chlorine introduced until the increase in weight was 57 grams (1 atom of chlorine). The chlorination took place very smoothly, and the temperature was maintained at 70—80° without external heating by adjusting the rate of flow of chlorine. The product, which solidified on cooling, was well stirred with water at 40°, extracted with warm benzene, the benzene solution filtered from antimony oxychloride, washed with dilute sodium hydroxide solution, then with water, and dried over

* The words "positive" and "negative" are used with the meaning generally accepted in discussions on orientation, namely, ortho-para-, and meta-directing, respectively. It is often convenient (although really incorrect) to call the halogens "positive" when describing their directive effect.

calcium chloride. The benzene was removed, and the sulphonyl chloride distilled under diminished pressure. A small amount of *p*-toluenesulphonyl chloride was obtained, b. p. 169°/38 mm., but the main fraction consisted of 276 grams of a colourless oil, b. p. 177—180°/38 mm. Finally, the dark residual liquid in the flask began to decompose, and was not examined.

The main fraction solidified on cooling, and melted at 32—36°. After redistillation it melted at 35—37°, and a portion crystallised from light petroleum in plates melting at 37—38°. The amide prepared from it melted at 137° after crystallisation from alcohol. Wynne and Bruce (T., 1898, **73**, 764) found the melting points of 2-chloro-*p*-toluenesulphonyl chloride and of the amide to be 37° and 134° respectively.

2-Chloro-*p*-toluenesulphonyl chloride boils at 166°/24 mm. and 178°/36 mm., and its smell closely resembles that of *p*-toluenesulphonyl chloride.

Nitration of 2-Chloro-p-toluenesulphonyl Chloride.

2-Chloro-*p*-toluenesulphonyl chloride (100 grams) was gradually added with stirring to a cold mixture of nitric acid (50 c.c.; D 1·50) and sulphuric acid (125 c.c.), and the mixture stirred for two hours. The sulphonyl chloride at first liquefied, but when the nitration was complete it was converted into a solid of a butter-like consistence. The temperature was kept throughout at 20—30°. The product was poured into a large volume of cold water, and the heavy nitrated portion repeatedly stirred and pressed with cold water until free from acid. The pale yellow mass was allowed to remain overnight, when it became quite hard and brittle. It was then powdered and dried on a porous plate in a vacuum over calcium chloride. The yield was 109 grams and the melting point about 50—80°.

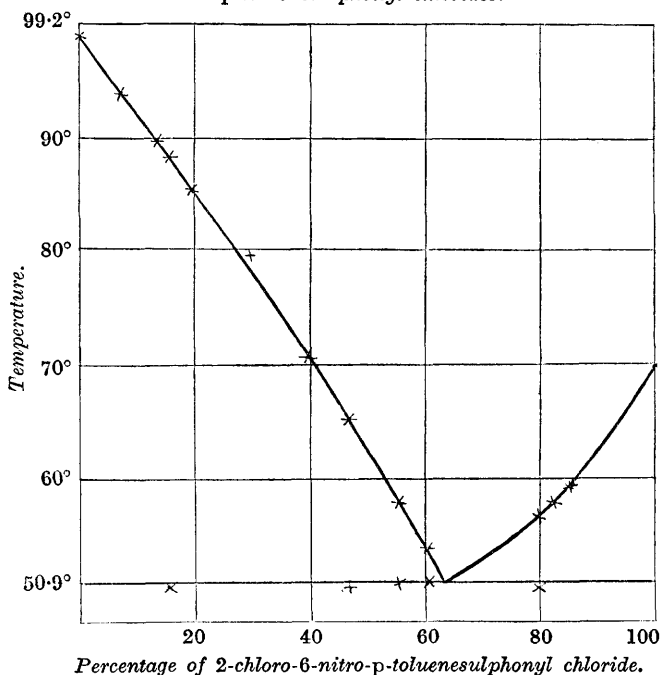
Slight hydrolysis of the sulphonyl chloride to the sulphonic acid occurred during nitration, but dinitro-derivatives were not produced even when ten times the amount of nitric acid theoretically required for mono-nitration were used.

Separation of the Isomerides.

A very convenient solvent for separating the isomerides formed was found to be light petroleum (b. p. 60—80°). After crystallising four times, most of the less soluble isomeride was obtained in prisms (60 grams), melting at 96—98°. The mother-liquor (500 c.c.) was concentrated to one-sixth of its volume, crystals and oil separated, and a further quantity of oil was formed on complete evaporation of the mother-liquor. The oil and crystals were mixed and

extracted with small portions of light petroleum (b. p. 40—60°) until half the mixture had gone into solution. The residue consisted almost entirely of the less fusible isomeride. The light petroleum solution slowly deposited long needles melting at 64—66°, together with some of the less fusible isomeride. By proceeding in this manner 12 grams of needles (m. p. 70°) and 80 grams of prisms (m. p. 99·2°) were obtained. The proportion of isomerides formed is, however, more accurately determined by the melting-point curve than by fractional crystallisation.

Melting-point curve of 2-chloro-5-nitro- and 2-chloro-6-nitro-p-toluenesulphonyl chlorides.



Proportion of the Isomerides formed in Nitration.

The melting-point curve of the two isomerides was obtained in the usual way. When the less fusible isomeride was present in a proportion greater than that required for the eutectic mixture, crystallisation took place very readily with only a small amount of supercooling, and the first-solidification points were obtained with a considerable degree of accuracy. But when the more fusible isomeride was in excess of the eutectic mixture, crystallisation became extraordinarily sluggish. With slight supercooling crystallisa-

tion took place so slowly that the thermometer in the mixture was scarcely affected, and even with considerable supercooling the solidification was extremely slow, although care was taken to have crystals of the more fusible isomeride on the sides of the tube. It is therefore probable that the first-solidification points obtained for the smaller branch of the curve are somewhat lower than they would have been had the crystallisation taken place with normal rapidity. This perhaps accounts for the fact that the shorter branch of the melting-point curve is slightly concave, as shown, whilst the longer branch is slightly convex. Slowness of crystallisation is not unknown in the case of mixtures of sulphonyl chlorides, especially when a large amount of the more fusible isomeride is present. For example, Holleman and Caland (*Ber.*, 1911, **44**, 2506), in finding the solidification points of mixtures of *o*- and *p*-toluenesulphonyl chlorides, give only one first-solidification point (but four second points), to determine the important portion of the curve corresponding with mixtures containing 60·4 to 100 per cent. of the more fusible isomeride.

It was fortunate that the portion of the curve required to determine the proportion of isomerides in the nitration product corresponds with mixtures, of which the first-solidification points were obtained without difficulty. It was therefore not thought necessary, for the purpose of this investigation, to determine the melting-point curve of the sulphonamides derived from the isomeric sulphonyl chlorides.

The solidification points obtained are as follows :

Percentage of the more fusible isomeride.	First-solidifi- cation point.	Second-solidifi- cation point.
0	99·2°	—
7·26	93·8	—
13·54	89·7	—
16·10	88·2	50·4°
19·54	85·2	—
28·94	79·6	—
39·50	70·6	—
46·98	65·2	50·5
55·40	58·0	50·8
60·72	54·0	50·9
79·68	56·6	50·5
82·10	58·0	50·8
85·41	59·2	—
100·00	70·0	—

The melting-point curve is constructed from these data. The eutectic mixture melts at 50·9° and contains 63·3 per cent. of the more fusible chloronitrotoluenesulphonyl chloride.

The nitration product (nitrated at 20—30° as described on p. 861) from pure 2-chlorotoluenesulphonyl chloride was washed free from

acid, powdered, and dried on a porous plate, and then allowed to remain under diminished pressure over phosphoric oxide.

The first- and second-solidification points were 81.5° and 49.8° respectively. Hence the nitration product was composed almost entirely of the two chloronitrotoluenesulphonyl chlorides isolated. Assuming the mixture to be a purely binary one, the proportion of the more fusible isomeride (2-chloro-6-nitro-*p*-toluenesulphonyl chloride) is therefore 25.5 per cent.

In order to ascertain whether a comparatively high temperature of nitration would considerably alter the proportion of isomerides formed, the nitration in the presence of sulphuric acid was carried out at $65-70^{\circ}$, with a slight excess of nitric acid; the weight of the product was 83.6 per cent. of theory. The two solidification points were 74.8° and $47-48^{\circ}$ respectively. The second point was not at all sharp, but the solid nitration product softened at $47-48^{\circ}$. Fractional crystallisation of the mixture by means of light petroleum resulted in the separation of only the two chloronitrotoluenesulphonyl chlorides melting at 70° and 99.2° , the less fusible one predominating.

Owing to the fact that a considerable amount of hydrolysis of the sulphonyl chloride group had taken place during nitration, and since the second-solidification point showed that the mixture was not altogether a binary one, the relative amounts of the two isomerides can be determined only very approximately by means of the melting-point curve. The first point (74.8°) corresponds with 35 per cent. of the more fusible isomeride. The experiment is of interest when compared with the chlorination of 2-chloro-*p*-toluenesulphonyl chloride at $65-70^{\circ}$ (see p. 871), because it shows that a comparatively high temperature is not the sole cause of substitution taking place in the ortho-position with respect to the methyl group.

2-Chloro-5-nitro-p-toluenesulphonyl Chloride (II, p. 853).

The above sulphonyl chloride crystallises from light petroleum in large, colourless prisms melting at 99.2° .* It is readily soluble in hot light petroleum (b. p. $60-120^{\circ}$), warm chloroform, cold ether, and benzene. It is only slightly soluble in cold light petroleum and in cold chloroform, and is much less soluble in these two solvents than the isomeride formed along with it (Found: $N=5.2$. $C_7H_5O_4NCl_2S$ requires $N=5.2$ per cent.).

* The melting points of all the new compounds described and of most of the other substances prepared in this series of investigations were taken with standardised, short, Anschütz thermometers.

The *amide* is prepared by the action of ammonia upon the sulphonyl chloride, and crystallises from water and from alcohol in small needles melting at 181° (Found: N=11.15. $C_7H_7O_4N_2ClS$ requires N=11.2 per cent.).

The *sulphonic acid* is formed by hydrolysing the sulphonyl chloride with concentrated hydrochloric acid in a sealed tube at 140 — 150° . It is moderately soluble in water, from which it crystallises in thick clusters of very small, non-deliquescent needles, and after drying at 120° melts at 123 — 128° .

The *sodium* salt, prepared by boiling the sulphonyl chloride with a slight excess of sodium hydroxide solution until the oil has disappeared (see p. 866), is very soluble in boiling water, moderately soluble in boiling alcohol (99 per cent.), and sparingly soluble in cold water and in cold alcohol. It crystallises from both solvents in very pale yellow needles, those from water containing two molecules of water of crystallisation. It can be obtained in colourless needles by neutralising the sulphonic acid. Both the sodium and barium salts are apt to decompose when heated above 220° , with the production of a black mass and of a vapour with a strong phenolic smell (Found: $H_2O=11.7$; Na=7.1. $C_7H_5O_5NCISNa, 2H_2O$ requires $H_2O=11.6$; Na=7.4 per cent.).

The *barium* salt is formed by boiling the sulphonyl chloride with aqueous barium hydroxide. It is too soluble in water to be conveniently prepared from the sodium salt by double decomposition. The barium salt is almost insoluble in boiling alcohol (95 per cent.), and is very soluble in hot and moderately soluble in cold water, from which it separates in colourless scales containing two molecules of water of crystallisation (Found: $H_2O=6.1$; Ba=19.9. $(C_7H_5O_5NCIS)_2Ba, 2H_2O$ requires $H_2O=5.35$; Ba=20.4 per cent.).

6-Chloro-m-toluidine-4-sulphonic Acid (V, p. 854).

Anhydrous sodium 2-chloro-5-nitro-*p*-toluenesulphonate (5 grams), dissolved in a mixture of hot water (50 c.c.) and glacial acetic acid (25 c.c.), was treated gradually with iron filings (7 grams) and the flask heated, with frequent shaking, on the water-bath. After one hour the amino-acid began to separate from the hot solution. The reaction liquid was made alkaline with dilute sodium hydroxide solution, filtered while hot, and the cold filtrate acidified with hydrochloric acid. The amino-acid was rapidly precipitated, and a further quantity was isolated by concentrating the mother-liquor. The total yield was 3.1 grams.

This *chlorotoluidinesulphonic acid* was only moderately soluble in boiling water, from which it was deposited on cooling in thin, small,

colourless, anhydrous plates, which readily turned red on exposure to light and air. The aqueous solution instantly decolorised bromine water, even in the cold (Found: in air-dried material, loss at $160^{\circ}=0.4$ per cent.; in dried acid, $N=6.4$. $C_7H_8O_3NClS$ requires $N=6.3$ per cent.).

6-Chloro-2:4-dibromo-m-toluidine (VI, p. 854).

The preceding chlorotoluidinesulphonic acid (1 gram) was dissolved in boiling water (50 c.c.), bromine water was added until it was no longer decolorised, and the flocculent precipitate produced was collected after remaining overnight. The filtrate contained sulphuric acid. The precipitate (1 gram) was crystallised from boiling alcohol.

6-Chloro-2:4-dibromo-m-toluidine is readily soluble in boiling alcohol and slightly soluble in cold alcohol, from which it crystallises in long, colourless needles melting at 99.5° , which, on keeping, become light red. It does not dissolve in dilute hydrochloric acid, and is slightly soluble in hot fuming hydrochloric acid [0.1214 gave 0.2079 ($AgCl+AgBr$); theo. for $C_7H_6NClBr_2$, 0.2106].

2-Chloro-5-nitro-p-cresol (VII, p. 855).

In the preparation of sodium 2-chloro-5-nitro-*p*-toluenesulphonate it was noticed that the alkaline solution became red and that the red colour disappeared on acidification. When the strongly alkaline solution was boiled for several hours a red, insoluble substance was formed, and very violent "bumping" ensued. This inconvenience was largely obviated when the hydrolysis was effected with dilute sodium hydroxide solution in the following way.

A mixture of the sulphonyl chloride (27 grams; 1 mol.) and *N*-sodium hydroxide (600 c.c.; 50 per cent. in excess of the 4 mols. theoretically required) was boiled under reflux for seventy-two hours, a glistening, red precipitate being gradually deposited. The red liquid was acidified by hydrochloric acid and the brown solution distilled in a current of steam. The pale yellow substance that solidified in the condenser melted without further purification at 70° . The yield was 4.1 grams or 22 per cent. of theory. The hydrolysis may be advantageously effected by potassium hydroxide solution, the potassium salt of the chloronitrocresol being so soluble that risk of "bumping" is eliminated.

When pure sodium chloronitrotoluenesulphonate was heated with sodium hydroxide solution, only a small amount of sodium chloride was produced. There was no appreciable quantity of

sodium nitrite formed even after boiling for seventy-two hours, for nitrous fumes were not produced on acidification.

2-Chloro-5-nitro-p-cresol sublimes in long, thin, lemon-coloured needles melting at 71° . It is very volatile with steam, and has a faint odour, much more pronounced in the hot, which recalls the tarry smell of *o*-nitrophenol. It is very soluble in cold ether, alcohol, acetone, or benzene, moderately soluble in cold chloroform, ethyl acetate, glacial acetic acid, or light petroleum (b. p. $60-80^{\circ}$), slightly soluble in hot water and sparingly soluble in cold water. It crystallises from all these solvents in long, yellow needles. The alkali salts are very intensely coloured. A colourless aqueous solution of the chloronitrocresol (1 : 100,000) becomes yellow on the addition of sodium hydroxide solution, and colourless again on acidification (Found : $N=7.41$; $Cl=19.0$. $C_7H_5O_3NCl$ requires $N=7.46$; $Cl=18.9$ per cent.).

The *benzoyl* derivative, prepared in the usual way, is easily hydrolysed by sodium hydroxide, and crystallises from alcohol in colourless needles melting at 129° (Found : $C=57.4$; $H=3.55$. $C_{14}H_{10}O_4NCl$ requires $C=57.6$; $H=3.4$ per cent.).

The alkali salts of the chloronitrocresol are of interest on account of their great difference in solubility.

The *sodium* salt, prepared by adding the finely powdered chloronitrocresol to a boiling, dilute solution of sodium hydroxide, and filtering when cold, is a red powder, amorphous when viewed under the microscope (Found : $Na=10.8$. $C_7H_5O_3NClNa$ requires $Na=11.0$ per cent.). It is very sparingly soluble in cold water, and slightly soluble in boiling water. The latter reagent slowly effects hydrolysis, chloronitrocresol volatilising in the steam. The sodium salt rapidly separates when a 5 per cent. solution of sodium sulphate is mixed with a cold, moderately concentrated solution of the potassium salt of the chloronitrocresol.

The *lithium* salt is also very slightly soluble in water, and is obtained from the potassium salt as an orange-red, amorphous powder.

The *potassium* salt, prepared by the action of potassium hydroxide solution on the chloronitrocresol, is very soluble in boiling water and moderately soluble in cold water, from which it separates in magnificent, long, anhydrous, crimson needles. When heated at 170° , the crystals become almost black, but regain their original colour on cooling (Found : in air-dried material, loss at $170^{\circ}=0.9$ per cent. In anhydrous material, $K=17.1$. $C_7H_5O_3NClK$ requires $K=17.3$ per cent.).

The *ammonium* salt is very soluble in hot dilute ammonia, from which it slowly separates on cooling in long, orange-red needles

H H*

It is very easily hydrolysed, ammonia being lost by mere exposure to the air.

The rubidium and caesium salts of the chloronitrocresol are not precipitated when aqueous solutions of any rubidium and caesium salts are separately added to a solution of the potassium salt.

Synthesis of 2-Chloro-5-nitro-p-cresol (VII, p. 855).

2-Chloro-*p*-nitrotoluene (b. p. $260^{\circ}/760$ mm.; m. p. $63-65^{\circ}$), prepared by the chlorination of *p*-nitrotoluene at $60-70^{\circ}$ in the presence of a small amount of antimony trichloride, was reduced almost quantitatively with iron filings and hydrochloric acid to 2-chloro-*p*-toluidine (m. p. 26° ; b. p. $242-244^{\circ}/760$ mm. Tellmann, *Ber.*, 1884, **17**, 535, gives 26° and $237-238.5^{\circ}$ respectively). This toluidine was acetylated, and the properties of the chloroacetotoluidide agreed with those described by Knuckell and Lillig (*J. pr. Chem.*, 1912, [ii], **86**, 715). They, however, incorrectly state that this chloroacetotoluidide is insoluble in water; it is slightly soluble in boiling water, from which it crystallises on cooling in needles about 3 cm. long.

The preparation of 2-chloro-5-nitro-*p*-toluidine (VIII, p. 855) by Claus and Bocher's method (*loc. cit.*) was attempted by gradually adding 2-chloroaceto-*p*-toluidide (10 grams) to well-cooled nitric acid ($D=1.5$; 40 c.c.) and after an interval of six hours pouring the dark red solution into water. The orange powder obtained was crystallised from alcohol, when 2-chloro-3:5-dinitroaceto-*p*-toluidide (IX, p. 855) separated in colourless leaflets, m. p. 238° (Found: $N=15.3$. $C_9H_8O_5N_3Cl$ requires $N=15.4$ per cent.). It was hydrolysed by stirring with cold sulphuric acid until a clear solution was formed, and after five minutes pouring the mixture into cold water, when a yellow precipitate was immediately produced, from which by crystallisation from alcohol 2-chloro-3:5-dinitro-*p*-toluidine (X, p. 855) was obtained in thin, golden-yellow needles melting at 137° (Found: $N=18.3$. $C_7H_6O_4N_3Cl$ requires $N=18.1$ per cent.). The alcoholic solution has an extremely pleasant, fruity smell. Both the amine and its acetyl derivative are only very slightly soluble in cold water. The amine dissolves with difficulty in cold concentrated hydrochloric acid, and is immediately precipitated on dilution.

Since 2-chloro-5-nitroaceto-*p*-toluidide had not been produced by the preceding method, the nitration of *o*-chloroaceto-*p*-toluidide was carried out after the method of Blanksma (*loc. cit.*). A comparatively small excess of nitric acid was used, the time of reaction was not prolonged, the temperature was kept below 15° during the nitration, and the liquid was finally poured on crushed ice. In

this way the chloronitroacetotoluidide required was obtained in good yield in pale yellow needles melting at 112°. Hydrolysis and simultaneous crystallisation of the amine were conveniently carried out by mixing the chloronitroacetotoluidide, dissolved in as little boiling alcohol as possible, with a slight excess of boiling 40 per cent. sodium hydroxide solution, when hydrolysis instantly took place and the amine rapidly separated in leaflets, m. p. 165°.

Conversion of 2-Chloro-5-nitro-p-toluidine into 2-Chloro-5-nitro-p-cresol.—A solution of the foregoing chloronitrotoluidine (5 grams) in a mixture of concentrated sulphuric acid (15 c.c.) and water (5 c.c.) cooled to 10°, was diazotised with sodium nitrite (3 grams) in water (10 c.c.), the temperature throughout being kept below 20°. The filtered diazonium solution was slowly added to a boiling mixture (b. p. about 116°) of 20 grams of crystallised copper sulphate, 45 grams of anhydrous sodium sulphate, 30 c.c. of concentrated sulphuric acid, and 100 c.c. of water. The phenol, being very volatile with steam, was driven over almost as fast as it was formed; the last traces were removed with the aid of steam. The oil in the distillate, which refused to solidify, was made alkaline with sodium hydroxide, the red sodium salt produced (1.2 grams), having been washed with water, alcohol, and ether, was acidified, and the phenol distilled with steam. It melted at 50–60°, and crystallised from alcohol, ether, benzene, or light petroleum in long, yellow needles, which did not, however, melt sharply, and even after sublimation the melting point was 57–63°. The substance was finally purified by conversion into the benzoyl derivative, which crystallised from alcohol in colourless needles, m. p. 129°. The benzoyl compound was hydrolysed by boiling for five minutes with a methyl-alcoholic solution of sodium hydroxide, the red salt filtered, washed with water and alcohol, acidified, and the phenol extracted with ether. It crystallised in long, yellow needles, which melted at 70°, and after sublimation at 71°. The 2-chloro-5-nitro-*p*-cresol obtained in this way was identified by the method of mixed melting-point with the chloronitrocresol obtained from the less fusible chloronitrotoluenesulphonyl chloride, the constitutions VII (p. 855) and II (p. 853) respectively of these two compounds being thereby established.

It was afterwards found that the sodium salt of the chloronitrotoluenesulphonic acid could be made to yield a small quantity of 2-chloro-5-nitro-*p*-toluidine as follows:

The anhydrous, finely powdered sodium salt (2 grams) was covered with 10 c.c. of 10 per cent. aqueous ammonia (about four times the theoretical amount) and heated in a sealed tube for thirty-six hours at 135–145°. A yellow solution was formed, which

deposited some unchanged sodium salt in needles. The ammonia was driven off and a current of steam passed through the residue, when a small quantity of a yellow solid distilled. The yellow distillate was extracted with ether, the ethereal solution dried over solid sodium hydroxide, the ether removed, and the yellow residue dissolved in alcohol, from which 2-chloro-5-nitro-*p*-toluidine separated in orange leaflets melting at 165° (yield 0.03 gram). It was identified by a mixed melting-point determination with the chloronitro-*p*-toluidine (m. p. 165°) prepared above.

A 5 per cent. yield was obtained by using, under the same conditions, alcoholic instead of aqueous ammonia. In neither case was ammonium (or sodium) chloride formed, and nitrite was shown to be absent by acidifying in the cold and pouring the solution into an alkaline solution of β -naphthol, when no red coloration was produced.

2-Chloro-6-nitro-p-toluenesulphonyl Chloride (III, p. 853).

This compound is far more soluble in chloroform or light petroleum than the isomeride already described, and it is extremely soluble in ether or benzene. The best crystallising medium is light petroleum (b. p. 40–60°), from which it separates in long, colourless needles melting at 70° (Found: N=5.1. $C_7H_5O_4NCl_2S$ requires N=5.2 per cent.).

The *amide* crystallises from water in shining scales, and slowly from alcohol in needles. Both forms melt at 182° (Found: N=11.1. $C_7H_7O_4N_2ClS$ requires N=11.2 per cent.).

The *sulphonic acid*, prepared by hydrolysis of the sulphonyl chloride with concentrated hydrochloric acid in a sealed tube at 165–185°, was obtained free from hydrochloric acid by adding water and evaporating almost to dryness on the water-bath, this process being repeated several times. In this way the acid was isolated in deliquescent plates very soluble in water.

The *sodium* salt was obtained by heating the chloronitrosulphonyl chloride (5 grams) with 5 per cent. sodium hydroxide solution (40 c.c.) on the water-bath until the oily sulphonyl chloride had disappeared. The solution was then neutralised by hydrochloric acid and concentrated, and the *sodium* salt which separated on cooling crystallised from water until free from sodium chloride.

The *sodium* salt forms colourless, anhydrous, microscopic plates, which are not altered by heating at 180°. It is far more soluble in cold water than the sodium salt of the isomeride (p. 865), and is almost insoluble in boiling 99 per cent. alcohol (Found: Na=8.8. $C_7H_5O_5NClSNa$ requires Na=8.4 per cent.).

The *potassium* salt rapidly separates in colourless laminæ when dilute solutions of the sodium salt and potassium sulphate are mixed.

The *barium* salt is formed by adding barium chloride solution to a concentrated aqueous solution of the sodium salt. It separates from cold water in colourless leaflets containing three molecules of water of crystallisation. It is readily soluble in boiling alcohol, from which it separates on cooling in glistening laminæ (Found: $\text{H}_2\text{O}=8.1$. $(\text{C}_7\text{H}_5\text{O}_5\text{NCIS})_2\text{Ba}\cdot 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=7.8$ per cent. Found: in anhydrous salt, $\text{Ba}=21.25$. $(\text{C}_7\text{H}_5\text{O}_5\text{NCIS})_2\text{Ba}$ requires $\text{Ba}=21.5$ per cent.).

The constitution of the chloronitrotoluenesulphonyl chloride was determined by the action of sodium hydroxide solution on the sodium salt of the acid.

The sodium salt (2 grams) was boiled for eight hours with 10 per cent. sodium hydroxide solution (20 c.c.). The solution rapidly became brown and very slightly turbid. Excess of hydrochloric acid was added and a portion of the solution, still brown, distilled in a current of steam. There was no evolution of sulphur dioxide and no organic substance distilled. The other portion of the solution did not yield any organic substance to ether.

Some of the acid solution was diluted until it was almost colourless, cooled, and after the addition of sodium nitrite poured into an alkaline solution of β -naphthol, when a deep red coloration was at once formed and a small quantity of red powder slowly separated.

Owing to the small amount of sodium chloronitrotoluenesulphonate available it was not possible to obtain the chloroaminosulphobenzoic acid in a pure state. It was found, however, that an amino-derivative was formed when the sodium chloronitrotoluenesulphonate was boiled for five minutes with 20 per cent. sodium hydroxide solution.

This experiment shows that the formula (III) assigned to the more fusible chloronitrotoluenesulphonyl chloride is correct.

The Action of Chlorine on 2-Chloro-p-toluenesulphonyl Chloride.

2 : 6-Dichloro-p-toluenesulphonyl Chloride (XII, p. 858).—A fused mixture of 2-chloro-p-toluenesulphonyl chloride (125 grams) and antimony chloride (5 grams) was chlorinated at $65-70^\circ$ for two hours until the necessary increase in weight (19.2 grams) was attained. The chlorinated product partly crystallised after remaining overnight in a desiccator. The crystals were collected and after drying on a porous plate weighed 68 grams and melted at $58-62^\circ$. The oily filtrate was purified from antimony chloride by pouring into water, extracting with benzene, and washing the

benzene solution with alkali and with water. After the extract had been dried with calcium chloride, the benzene was completely removed and the residual oil (71 grams) distilled in a vacuum. The first fraction, b. p. 168—178°/28 mm. (10 grams), consisted largely of unchanged chlorotoluenesulphonyl chloride. The second fraction (30 grams), b. p. 178—185°/28 mm., and the third fraction (23 grams), b. p. 185—195°/28 mm., were chiefly composed of dichloro-*p*-toluenesulphonyl chlorides. The three fractions were kept at 0° for several hours, and the crystals produced from each fraction in order of ascending boiling point weighed, after drying on porous plate at the ordinary temperature, 3, 10, and 18 grams respectively. The crystals melted at about 57—61° and were purified by crystallisation from light petroleum. The total yield of 2 : 6-dichloro-*p*-toluenesulphonyl chloride melting at 66—68° was 95 grams or 66 per cent. of the theoretical yield.

2 : 6-Dichloro-*p*-toluenesulphonyl chloride separates very slowly from cold light petroleum (b. p. 80—100°) in plates melting at 66—68°. Several recrystallisations are required to produce the pure substance in large, flat plates melting at 69°. The chief impurity, m. p. 218°, crystallises in fine, hair-like, colourless needles, is only slightly soluble in cold organic solvents, and appears to be pentachlorotoluene. The sulphonyl chloride is extremely soluble in cold benzene or ether, and moderately soluble in cold light petroleum (Found : Cl=40·2. $C_7H_5O_2Cl_3S$ requires Cl=41·0 per cent.).

It is very slowly oxidised by fuming nitric acid in a sealed tube at 230°.

The *sulphonic acid*, prepared from the barium salt in the usual way, crystallises in colourless, deliquescent plates and is very soluble in water.

The *amide* is slightly soluble in hot water, from which it separates in shining scales melting at 191° (Found : N=5·8. $C_7H_7O_2NCl_2S$ requires N=5·8 per cent.).

The *sodium* salt crystallises from water in clusters of fan-like, divergent, colourless needles, slightly soluble in cold, readily soluble in hot water. The crystals contain one molecule of water (Found : $H_2O=6·8$; Na=8·2. $C_7H_5O_3Cl_2SNa \cdot H_2O$ requires $H_2O=6·4$; Na=8·2 per cent.).

The *barium* salt is formed from a solution of the sodium salt by precipitation with barium chloride. It dissolves sparingly in cold water and is moderately soluble in hot water, from which it crystallises in thin, minute, silky needles containing three molecules of water of crystallisation (Found : loss at 180°=8·2. $C_{14}H_{10}O_6Cl_4S_2Ba \cdot 3H_2O$ requires $H_2O=8·05$ per cent. Found : in anhydrous material, Ba=22·7. $C_{14}H_{10}O_6Cl_4S_2Ba$ requires Ba=22·3 per cent.).

Conversion of the Dichlorotoluenesulphonic Acid into 2 : 6-Dichlorotoluene.

Hydrolysis occurred very readily when a solution of the hydrated sodium salt (9 grams) in water (15 c.c.) and sulphuric acid (50 c.c.) was distilled in superheated steam at 250°. The oil was extracted from the distillate with chloroform, the solution dried with solid sodium hydroxide, the chloroform removed, and the oil distilled, when it passed over almost completely at 197—199°/757 mm., and weighed 3.5 grams.

The dinitro-derivative of the dichlorotoluene was prepared in the usual way and melted at 121° (Cohen and Dakin, T., 1901, 79, 1132, give m. p. 121—122°) (Found: N=11.0. Calc., N=11.15 per cent.).

The dichlorotoluene obtained by the hydrolysis of the dichloro-*p*-toluenesulphonic acid was finally converted into 2 : 6-dichlorobenzoic acid, a process which presented some difficulty.

The dichlorotoluene was boiled for twelve hours with a slight excess of dilute aqueous potassium permanganate solution, whereby only a trace of the dichlorotoluene was attacked. It was impossible to detect any dichlorobenzoic acid, even when the aqueous solution was concentrated to a very small volume before decolorising by sulphur dioxide. It was similarly found impossible to prepare a dichlorobenzoic acid by oxidising the dichlorotoluene with potassium permanganate in acetone solution.

Cohen and Dakin (*loc. cit.*) partly oxidised 2 : 6-dichlorotoluene by heating with nitric acid in a sealed tube. The dichlorotoluene (2 grams) under investigation was accordingly heated with nitric acid (15 c.c.; D=1.2) in a sealed tube for a week. The oil produced partly solidified when cooled. The solid (0.5 gram) was collected, and treated with sodium carbonate solution, in which it only partly dissolved. The acid which was precipitated from the acidified filtrate crystallised from light petroleum (b. p. 80—100°) in needles melting at 136—138°. Repeated recrystallisation from different solvents failed to raise the melting point above 137—139°. Mixtures of these crystals with 2 : 6-dichlorobenzoic acid (m. p. 144°)* and with 2 : 5-dichlorobenzoic acid (m. p. 154°) melted at 137—140° and below 120° respectively.

* Holleman and Bornwater (*Rec. trav. chim.*, 1912, 31, 221) show how the melting points assigned to 2 : 6-dichlorobenzoic acid vary from 126.5° to 143.7°. A pure product is formed by the oxidation of 2 : 6-dichlorobenzaldehyde by potassium permanganate in acetone solution. I am greatly indebted to Mr. G. R. Clemo for pure specimens of 2 : 6- and 2 : 5-dichlorobenzoic acids.

The solid oxidation product that was insoluble in sodium carbonate solution crystallised from alcohol in colourless needles melting at 68°. It was shown not to be 2 : 6-dichlorobenzaldehyde (mixed melting point), and cannot be 2 : 6-dichloro-3-nitrobenzaldehyde, which consists of colourless plates melting at 76—77° (D.R.P. 199943). There was not enough of the substance for further examination.

These experiments clearly show that the dichlorotoluene in question is 2 : 6-dichlorotoluene, and that the dichlorotoluenesulphonyl chloride described has the formula XII.

The Formation of 2 : 5-Dichloro-p-toluenesulphonyl Chloride in the Chlorination of 2-Chloro-p-toluenesulphonyl Chloride.

The liquid portion of the fraction, b. p. 178—185°/28 mm. (p. 872), from which 2 : 6-dichloro-*p*-toluenesulphonyl chloride was separated, was boiled with excess of sodium hydroxide solution, and after cooling the precipitated sodium salts were collected. Hydrolysis was effected by dissolving the mixed sodium salts (10 grams) in a mixture of sulphuric acid (35 c.c.) and water (10 c.c.), and passing superheated steam at 250°. An oil (4 grams) was produced, which after being extracted with chloroform and dried with sodium hydroxide boiled at 160—200°, mostly at 180—200°. One gram of the fraction boiling at 180—200° (which must be free from any *o*-chlorotoluene, b. p. 160°) was boiled for ten hours with 2 grams of potassium permanganate dissolved in 200 c.c. of water. The oil was not completely oxidised, although the solution was still red. The solution was concentrated to 30 c.c. and treated with sulphur dioxide, whereby 0.3 gram of an acid was precipitated, which on crystallising from light petroleum (b. p. 60—80°) formed colourless needles melting at 136—142°. Recrystallisation failed to raise the melting point. A mixture with 2 : 5-dichlorobenzoic acid (m. p. 154°) melted at 136—142°, mostly 142°. Hence the acid melting at 136—142° was somewhat impure 2 : 5-dichlorobenzoic acid. It follows that a mixture of 2 : 6- and 2 : 5-dichloro-*p*-toluenesulphonyl chlorides is produced when 2-chloro-*p*-toluenesulphonyl chloride is chlorinated.

Summary.

(I) The nitration of 2-chloro-*p*-toluenesulphonyl chloride in mixed nitric and sulphuric acids at 20—30° leads to the formation of a mixture of isomeric mononitro-derivatives (more than 90 per cent. of the theoretical amount). The nitration product consists of

2-chloro-5-nitro-*p*-toluenesulphonyl chloride and 2-chloro-6-nitro-*p*-toluenesulphonyl chloride almost exactly in the proportion of three to one.

(II) The proportion of the two isomerides shows that the orientation due to the chlorine atom is much greater under these conditions than the united directive effects of the methyl and sulphonyl chloride groups. The proportion of isomerides is not greatly altered by nitration at 65–70°.

(III) The sulphonyl chloride group and not the nitro-group in 2-chloro-5-nitro-*p*-toluenesulphonyl chloride is somewhat reactive, and can be replaced by a hydroxy-group by boiling with dilute alkali hydroxide solution.

(IV) Monochlorination of 2-chloro-*p*-toluenesulphonyl chloride at 65–70° results in a mixture of isomerides, 2 : 6-dichloro-*p*-toluenesulphonyl chloride being the chief product (upwards of 66 per cent.). 2 : 5-Dichloro-*p*-toluenesulphonyl chloride is also formed.

(V) Hence the nature of the group entering the benzene nucleus in 2-chloro-*p*-toluenesulphonyl chloride may be an important factor in deciding the position of the substituent.

The author desires to express his thanks to Professor W. H. Perkin and to Dr. E. Hope for suggesting this research and for their advice. His thanks are also due to Mr. Fred Hall for assistance in the nitrogen, carbon, and hydrogen estimations, and to the Advisory Council for Scientific and Industrial Research for a grant which has partly defrayed the expenses of the first portion of this investigation. The author also wishes to make acknowledgment to the Ramsay Memorial Fellowship Trust for a Fellowship which has enabled this portion of the research to be completed.

THE DYSON PERRINS LABORATORY,
THE UNIVERSITY, OXFORD.

[Received, March 30th, 1921.]