158. *Studies in the Toluene Series. Part VI. Nitration of the 4-Chlorotoluene-2- and -3-sulphonic Acids, 3-Chlorotoluene-6-sulphonic Acid and their Sulphonyl Chlorides.*

By W. Palmer Wynne.

The investigation of the products obtained by the nitration of the *o*-, *m*- and *p*-chlorotoluenesulphonic acids owed its origin to an attempt to use sulphonation as a means of purifying dichlorotoluenes prior to the study of their physical properties. When it was found that hydrolysis of the purified sulphonates failed to give the desired result, as impurity was introduced owing to some decomposition at the temperature employed, attention was directed to a more detailed study of the dichlorotoluenesulphonic acids themselves. These acids it was found could have their constitution determined either through the chloronitrotoluenesulphonic acids by exchange of the nitro-group for chlorine or through the dichlorotoluidines by replacement of the amino-group by the sulphonic radical, but not through the chlorotoluenesulphonyl chlorides, as the attempt to substitute chlorine for the SO_2Cl complex, through the agency of phosphorus pentachloride, led to profound decomposition.

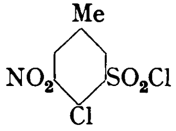
Nitration of the five readily accessible chlorotoluenesulphonic acids was undertaken in conjunction with Mr. A. Greeves (P., 1895, **11**, 152) and a large amount of material accumulated, but soon after its detailed examination had been begun the work was unavoidably interrupted and, although resumed at intervals with the aid of collaborators, has only now been brought to a stage suitable for publication.

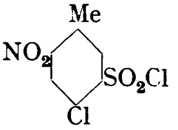
Attempts to separate the nitration products from each of the five chlorotoluenesulphonic acids by fractional crystallisation of the barium, potassium or sodium salts from water or from alcohol were not successful, but from the derived sulphonyl chlorides isolation of the constituents of the mixture was, except in one case, achieved without undue difficulty. By interaction with alkali hydroxide, each chloride was converted into the alkali salt, the constitution of which was ascertained by reduction of the nitro- to the amino-group, exchange of the latter for chlorine, hydrolysis of the ensuing dichlorotoluenesulphonic acid and oxidation of the emergent dichlorotoluene to the corresponding dichlorobenzoic acid.

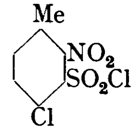
4-Chlorotoluene-3-sulphonic acid, the exception, with which this communication mainly deals differed from the other four in furnishing not merely all three rather than only two of the possible nitro-derivatives but also a mixture of sulphonyl chlorides resolvable apparently into four fractions, of which three were grouped round the m. p.'s 48—51°, 58—61° (main constituent 62·5°) and 120—122° (main constituent 122°) and the fourth over a wider range, 70—83° (main constituent 92°). For a long time the relationship of the first two was a source of perplexity: they seemed to be the slightly impure forms of two isomerides melting at about 49° and 61°, yet m. p. determinations made with mixtures of equal weights of the two gave intermediate values such as 52—54° and a similar experience was encountered with the respective sulphonamides, which had the m. p.'s 184° and 196°, differed in solubility in dilute alcohol and in appearance as each separated from solution, but gave the mixed m. p. 191°.

Three years ago, the earlier conclusions—irreconcilable as they seemed to be among themselves and devoid of any quantitative significance—were discarded and the investigation begun anew. Eventually, by the use of petrol * in place of ligroin the separation m. p. 48—51°, which from other solvents had resisted fractionation, was shown conclusively to be a mixture of the isomerides of m. p. 62·5° and 122° in which the latter was present in remarkably small proportion, escaping recognition despite its sparing solubility until the final crystalline separations from the much concentrated mother-liquors were examined.

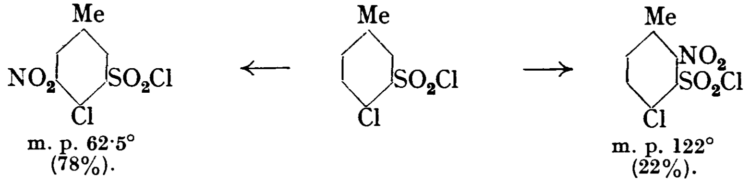
Reference to the table on p. 700 will show that the yield of crystalline sulphonyl chloride amounted at most to 64% of that calculated, the deficit being made up of non-crystalline chloride (7·3%)—presumably a mixture of isomerides—and of material not accounted for. Inasmuch as neither of the chlorides, m. p. 62·5° and 122°, was appreciably affected by being boiled for ½ hour with phosphorus pentachloride and oxychloride under reflux (as in the conversion of salt into chloride), the loss of material cannot be referred to decomposition involving the nitro-group. The composition of the crystalline product, in so far as it can furnish a clue to that of the nitrated chlorotoluenesulphonate, indicates the preponderance of the fraction m. p. 120—122°, its yield being almost twice that of the fraction 47—60°, the next in order of abundance. Assigning to each fraction the constitution and m. p. of its chief constituent, the isomeric chlorides obtained from the products of nitration were:


m. p. 62·5°
(31%).


m. p. 92°
(15%).


m. p. 122°
(54%).

In view of the element of uncertainty introduced by this loss in the conversion of salt into chloride, the nitration of 4-chlorotoluene-3-sulphonyl chloride was carried out under the conditions employed by Davies for *o*-chloro-derivatives (J., 1921, **119**, 853). The results as set out in the table on p. 704 showed that, whilst the yield was much more nearly quantitative, yet (i) the chloride, m. p. 92°, was not one of the products and (ii) the chloride, m. p. 122°, was now the minor product, being formed to a less extent than one-third of its isomeride:



When it is remembered that the medium in which nitration took place was concentrated sulphuric acid in both cases, the agent fuming nitric acid, and the temperature range in

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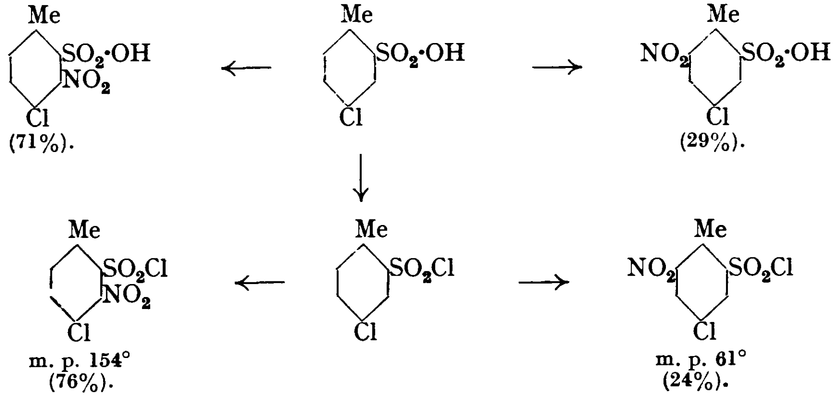
* The trivial names "petrol" and "ligroin" are used for the fractions of light petroleum, b. p. 40—60° and b. p. 60—80°, respectively.

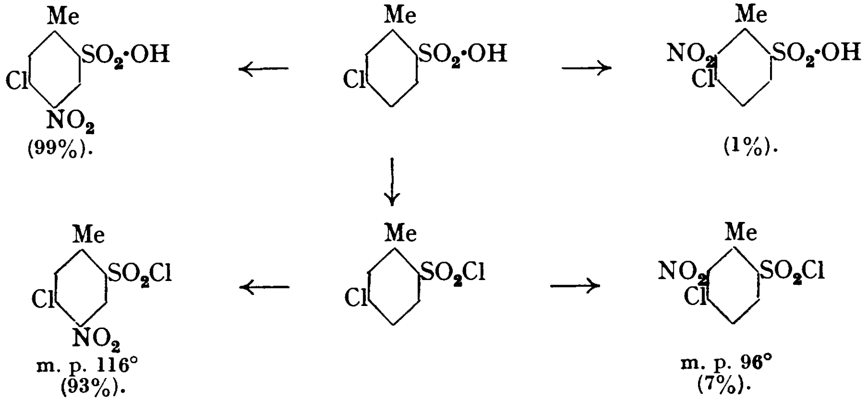
and duration of each operation practically the same, this difference in behaviour is sufficiently remarkable—search of the literature concerning the nitration of benzenesulphonic acid and its substitution products has failed to reveal a parallel case. The exchange of chlorine for hydroxyl within the sulphonic acid group does not at first sight appear to be a sufficient explanation of this difference of orientation unless, perhaps, the possibility of ionisation present in the one substance but absent in the other may be responsible. This question is discussed in detail in an addendum which follows these papers.

In addition to this 1 : 2 : 3 : 4-derivative, two others with the nitro-group intruded into the vacant 2- or 3-position were identified in the course of this investigation, being formed—each as the minor product of nitration whether acid or chloride be used—when :

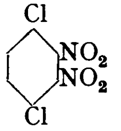
(i) either sodium 4-chlorotoluene-2-sulphonate or the 2-sulphonyl chloride is nitrated (pp. 704, 706)



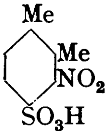
(ii) either 3-chlorotoluene-6-sulphonic acid or the 6-sulphonyl chloride is nitrated (pp. 706, 707)



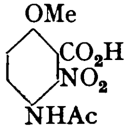
As the formation of nitro-derivatives of this type seems to occur only seldom, it may be of interest to record the following cases, in each of which all three isomerides were isolated,



(I.)

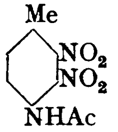


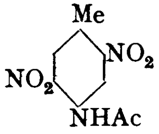
(II.)



(III.)

the yield being intermediate between that of the other two in the case of (I) and (II) (for I, cf. Holleman, der Hollander, and van Haefter, *Rec. trav. chim.*, 1921, **40**, 323; Macleod, Pfund, and Kilpatrick, *J. Amer. Chem. Soc.*, 1922, **44**, 2268; Page and Heasman, J., 1923, **123**, 3247; for II, cf. Simonsen, J., 1913, **103**, 1144) but the smallest of the three in the case of (III) (Simonsen and Rau, J., 1917, **111**, 220). On the other hand, 2-nitro-4-acetamido-


m. p. 74°.


m. p. 122°.

toluene gives only two dinitro-derivatives and of these the 1 : 2 : 3 : 4-isomeride is the major product (Scott and Robinson, J., 1922, **121**, 844; Page and Heasman, *loc. cit.*, p. 3235).

EXPERIMENTAL.

(I) *Nitration of Sodium 4-Chlorotoluene-3-sulphonate.*—The 4-aminotoluene-3-sulphonic acid used for the preparation of the 4-chloro-acid was prepared by stirring vigorously a mixture of *p*-toluidine (107 g.) and concentrated sulphuric acid (100 g.) heated in a dish on a sand-bath until the appearance of boiling died down, the material became almost dry and incipient charring occurred. After being rendered alkaline, the product was freed from *p*-toluidine (7—12 g.) by blowing steam through the solution. Tested for the presence of the 2-isomeride (cf. Buff, *Ber.*, 1870, **3**, 796; Schneider, *Amer. Chem. J.*, 1886, **8**, 274) without result, the amino-acid was further shown to be uniform by the systematic examination of the derived chlorotoluenesulphonic acid and of the derivatives obtained by nitration of this chloro-acid.

To the sodium salt (115 g.) of the chloro-acid dissolved in four times its weight of sulphuric acid, a mixture of fuming nitric acid (*d* 1·52; 38 g.) with an equal weight of sulphuric acid was added gradually, with continuous stirring during 1·5 hours, the temperature, kept at 5—10° during the addition, being then allowed to rise to that of the laboratory. Baryta was used to remove the excess of sulphuric acid as being more convenient than lime; the filtrate, after removal of excess of baryta by means of carbon dioxide, contained both barium and sodium salts of the nitro-acid; the proportion of barium salt, calculated from the weight of carbonate precipitated by the addition of sodium carbonate solution, amounted to 30% on the average. After this exchange of barium for sodium the yield of anhydrous sodium salt (130 g.) was 94% of that calculated.

Fractional crystallisation of this product from water proved to be fruitless owing to the great solubility. From alcohol, in which the solubility at the boiling point was about 1 in 30, mixed separations were obtained, consisting of small hemispherical granules, attached limpet-like to the wall of the beaker, with small spherical clusters of microscopic prisms, often looking like drops of oil in suspension, or with soft, fine, flexible needles which became opaque when dry. The less soluble fractions were pale yellow; those more soluble were, like the final mother-liquors, dark reddish-brown. These crystalline forms, even when isolated, were not characteristic, recrystallisation invariably giving rise to mixed separations during the cooling of the solution: moreover, determinations of water of crystallisation in forms apparently similar were frequently not concordant. That failure to achieve a separation was not due to choice of salt became evident when the nitration product from the potassium salt proved equally troublesome. In the end, the isomeric chloronitrosulphonates were obtained by conversion of the nitrated salt into sulphonyl chloride, isolation of the isomeric chlorides by fractional crystallisation and hydrolysis of these by the appropriate alkali.

Conversion of the nitration product into sulphonyl chloride. After a preliminary separation into four fractions, the finely powdered, dry sodium salt (1 pt.) suspended in 30 g. quantities or less in phosphorus oxychloride (2·5 pts.) was boiled gently with phosphorus pentachloride (1 pt.) under reflux during ½ hour, the greater part of the oxychloride being then removed by distillation and the product stirred into water. Under these conditions the conversion was almost complete; the unchanged salt recovered in the final preparation amounted only to 8·6 g. from the 130 g. employed. This in its turn was submitted to the same treatment, and the resulting chloride worked up with the main bulk.

The chloride from the less soluble fractions of the sodium salt solidified under water; that from the later fractions was vaselin-like. These dissolved easily and completely in benzene. To the hot benzene solution of each preparation several times its volume of ligroin was added to free it from any soluble mineral salt retained by the moist chloride, the clear solution left to crystallise, the mother-liquor distilled to remove the whole of the solvent, and the residual chloride fractionally crystallised from ligroin or, in the last stages, petrol. But only part of the dissolved chloride could be obtained crystalline: the remainder after removal of the solvent formed a viscid non-crystallisable residue: this in alcoholic solution was hydrolysed by sodium ethoxide with the separation of sodium chloride. By successive concentration of the alcoholic solution fractions wholly soluble in water were obtained, each of which after conversion into chloride furnished a crystalline separation and a non-crystallisable viscid residue. The table—from which it will be seen that four operations were necessary before the whole of the crystalline chloride obtainable from 130 g. of sodium chloronitrotoluenesulphonate (SO_2Cl calc., 128·2 g.) could be isolated—gives the initial fractionation, expressed in grams, of the product from the last of the series of nitrations.

Salt converted.	M. p. 47—60°.	M. p. 62—83°.	M. p. 112—120°.	Viscid chloride.
130·0	11·1	7·6	39·5	50·8 (49·4) *
49·4	5·5	5·0	3·8	29·6 (27·6)
27·6	5·8	0·1	0·4	17·2 (14·6)
14·6	2·9	—	0·4	9·4 (7·3) †
	25·3	12·7	44·1	7·3

* The weight of dry sodium salt obtained by hydrolysis with sodium ethoxide is given in parentheses.

† After hydrolysis, separation of the salt into a less and a more soluble fraction, followed by conversion of each into chloride, served only to regenerate the viscid product.

This yield of 82·1 g. or 64% of that calculated was the highest obtained. The isolation of the three isomerides, m. p. 62·5°, 92° and 122°, from these fractions led in the case of the first to the loss of much material and was rendered difficult owing to their ready solubility in the ordinary organic solvents other than light petroleum—eventually good results followed the use of petrol for the first (solubility about 2 g. in 100 c.c. at b. p.), ligroin with or without previous solution in a minimum amount of benzene for the second and benzene for the third.

Fraction, m. p. 48—60°. Repeated crystallisation of this material with petrol as solvent led to the accumulation of two fractions, one with m. p. 58—61°, the other and at first the larger with m. p. 48—52°—those of intermediate m. p. being resolvable gradually into these. From the former, the chloride, m. p. 62·5°, was isolated without much difficulty, but, with the latter, only after the most tedious fractionation was proof forthcoming that it was not the third isomeride (identification of this as the chloride, m. p. 92°, came later) but a mixture of the substance, m. p. 62·5°, with 4—5% of that melting at 122°.

With all fractions of low m. p., the solution in warm petrol became opalescent on cooling and a layer of " oil "—superfused mixture of the two chlorides—collected at the bottom of the beaker. Poured off, when it had become clear, and left over-night, the solution gave in addition to the crop of crystals a ring of " oil " above but in contact with its surface. This phenomenon became less marked with elimination of impurity, fractions of m. p. 59—62° being free from it.

Undisturbed, the layer of " oil " not infrequently remained for a day or two without crystallising: then, if in a thin layer, it would solidify in " diamond "-shaped forms, m. p. 47—49°. Despite the uniform appearance, these, dissolved in petrol, gave by slow spontaneous evaporation, crystals of mixed type, m. p. 49—53° or thereabouts, the final separations containing small rod-like prisms of the isomeride, m. p. 122°, which could be separated by hand. Thus 7·5 g. of this " oil," extracted by five successive 80 c.c. of petrol, gave the following fractions: m. p. 47—50°, 2·5 g.; m. p. 50—55°, 1·1 g.; m. p. 55—57°, 2·1 g.; m. p. 109—116°, 0·3 g. with a loss of 1·5 g. or 20%.

The slowness with which the separation of the constituents of the fraction, m. p. 48—60°, was achieved contrasts unfavourably with the more rapid parting of the isomerides from a mixture made by fusing together 4 g., m. p. 62·5°, and 1 g., m. p. 122°, at 140° for a short time. This solidified completely over-night, had m. p. 50—52°, and in one fractionation, involving nine successive crops of crystals, gave 3·3 g., m. p. 52—55°; 0·9 g., m. p. 58—61°; and 0·5 g., m. p. 109—119°—a total of 4·7 g.

The loss of material—the failure to obtain approximately as much crystalline substance from solution as taken up by it—seemed to be due for the most part to the final residues from crystallisation being oils, the constituents of which could not be separated by any method tried—freezing, fractional solution or hydrolysis. Accompanying the dissolution of fractions in the earlier stages of purification was a small amount of a viscid brown residue, less than 1% of the whole, which dissolved in water and was acid to test-paper, thus showing that slight hydrolysis had occurred between one crystallisation and the next. Such hydrolysis is not infrequent among chlorides when kept over long periods (cf. Turner and Wynne, following paper); that it should be so soon detected with the chlorides of relatively low m. p. under investigation seemed remarkable—the more so, because the pure isomeride, m. p. 62·5°, does not show it even after the lapse of some months.

4-*Chloro*-5-*nitrotoluene*-3-*sulphonic acid*. The ***barium*** salt, obtained by hydrolysis of the sulphonyl chloride, m. p. 62·5°, crystallised in very pale yellow scales, becoming anhydrous when kept during 2 days in a desiccator over sulphuric acid [Found : Ba, 19·8; H_2O, 4·8. $(C_7H_5O_5NClS)_2Ba,2H_2O$ requires Ba, 20·4; H_2O, 5·3%]. The easily soluble potassium salt (+ H_2O), large, colourless, thin plates, and sodium salt (+ H_2O), small scales or felted needles, sometimes as dihydrate in felted needles, were also prepared. At 15°, the weight of anhydrous salt contained in 100 g. of aqueous solution was Ba 0·79 g., K 2·52 g., and Na 14·25 g.

The *chloride* had m. p. 62·5° (Found : Cl, 26·6. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). Professor G. M. Bennett has been good enough to measure the crystals of this chloride and reports as follows :

" The substance crystallises well from benzene or a mixture of this solvent with light petroleum, the crystals being anorthic with axial ratios $a : b : c = 1{\cdot}385 : 1 : 1{\cdot}159$; $\alpha = 99°\,15'$, $\beta = 103°\,51'$, $\gamma = 100°\,15'$ and Federov angular elements : $d = 36°\,47'$, $e = 80°\,45'$, $ab = 76°\,57'$, $f = 42°\,3'$, $g = 76°\,9'$. The following is a list of the forms observed and the mean values of the angles from three crystals measured on a two-circle goniometer :

	a(100).	*b*(010).	*c*(001).	*q*(011).	*p*($\bar{1}$11).	*R*($\bar{1}$01).	*Q*(0$\bar{1}$1).
ϕ	0° 0′	*76° 57′	29° 14′	*67° 8′	102° 45′	*164° 43′	270° 26′
ρ	90° 0′	90° 0′	18° 26′	*55° 26′	55° 7′	*31° 37′	45° 38′

" Barker classification angles: *cr* 33° 14′, *ra* 40° 45′, *am* 45° 25′, *mb* 31° 32′, *bq* 35° 46′, *qc* 42° 35′.

FIG. 1.

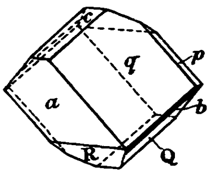


FIG. 2.

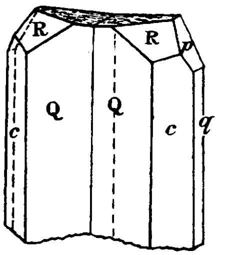


FIG. 3.

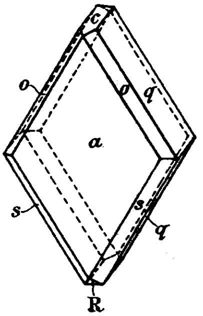
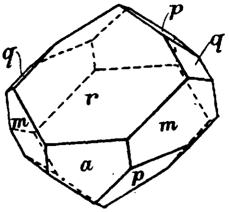


FIG. 4.



"The habit is shown in Fig. 1, but single crystals are rare, most crops consisting entirely of twinned crystals of the habit represented in Fig. 2. The twin plane is *q*(011). The mean angular values observed with seven of the twins were :

						on the second crystal.		
	q(011).	*c*(001).	*Q*(0$\bar{1}$1).	*R*($\bar{1}$01).	*p*($\bar{1}$11).	*Q*(0$\bar{1}$1).	*c*(001).	*q*(011).
ϕ	0° 0′	42° 35′	98° 32′	0° 0′	53° 45′	81° 28′	137° 25′	180° 0′
ρ	90° 0′	90° 0′	90° 0′	60° 43′	44° 33′	90° 0′	90° 0′	90° 0′

" Two faces often appear forming a re-entrant angle at the upper end of the twin, but these were so imperfect that they could not be exactly located or identified.

" The substance is biaxial, but the position of the optic axes was not found. The extinction on *Q* is at 35° to the edge *Qq*."

The *amide*, m. p. 196°, separated from dilute alcohol in long slender needles (Found : N, 11·5. $C_7H_7O_4N_2ClS$ requires N, 11·2%). It carbonised when its hydrolysis was attempted with either orthophosphoric or sulphuric acid and superheated steam.

4-*Chloro*-5-*aminotoluene*-3-*sulphonic acid*. Reduction of the nitro- to the amino-group was effected by adding " reduced " iron (12·5 g.) gradually to a boiling solution of the sodium nitro-salt (15 g.) in water (150 c.c.) acidified with concentrated sulphuric acid (12·5 c.c.). Usually much of the amino-acid separated before the addition was complete, the remainder being recovered from the filtrate. The *acid* (yield, 76% of that calculated) crystallised in clusters of very slender, colourless, silky needles, readily soluble in water but almost insoluble in alcohol (Found :

H_2O, 7·3. $C_7H_8O_3NClS,H_2O$ requires H_2O, 7·5%). The aqueous solution became violet on exposure to the air. The *barium* salt was highly soluble in water, but on the addition of alcohol crystallised in clusters of small, thin, almost colourless scales [Found: Ba, 22·4; H_2O, 4·2. $(C_7H_7O_3NClS)_2Ba,1\frac{1}{2}H_2O$ requires Ba, 22·7; H_2O, 4·5%]. The potassium salt (+ H_2O), scales from aqueous solution concentrated to a syrup but large, thin, colourless plates from dilute alcohol, and sodium salt (+ H_2O), thin, pale brown scales from dilute alcohol, were also prepared.

4 : 5-*Dichlorotoluene*-3-*sulphonic acid.* The *barium* salt, moderately soluble in water, crystallised in small, white, opaque, anhydrous granules, strung together in short rods [Found: Ba, 21·6. $(C_7H_5O_3Cl_2S)_2Ba$ requires Ba, 22·3%]. The potassium salt (+ H_2O), clear short needles which on exposure to the air became opaque, and sodium salt (+ H_2O), characteristic, thin, nacreous scales, both easily soluble in water, were also prepared. The *chloride*, m. p. 64°, readily soluble in petrol, crystallised from ligroin in rhomb-shaped monoclinic tables with an acute angle of 72° and an extinction angle of 18° (Found: Cl, 41·2. $C_7H_5O_2Cl_3S$ requires Cl, 41·0%). The *amide*, m. p. 158°, crystallised from alcohol in elongated, narrow, flat prisms (Found: N, 6·2. $C_7H_7O_2NCl_2S$ requires N, 6·1%).

Suspended in concentrated sulphuric acid (30 c.c.), the sodium salt (4·9 g.), hydrolysed by steam at 190—210°, gave 3 : 4-dichlorotoluene (1·4 g.), b. p. 198—200°/756 mm., identified by oxidation with dilute nitric acid (*d* 1·16) at 150° to 3 : 4-dichlorobenzoic acid, m. p. 206·5°.

Fraction, m. p. 62—83°. Isolation of the isomeride, m. p. 92°, from the fraction, m. p. 62—83°, although tedious, did not present any special difficulty. After experience gained with earlier preparations, 24 g. of the chloride collected from two nitrations were crystallised from ligroin and resolved eventually into the following fractions:

m. p. 48—57°	3·0 g.	m. p. 80—83°	14·9 g.
57—60°	0·6	116—122°	1·3
64—75°	1·0	not accounted for	2·2

By watching the crystallisation, the main constituent of this fraction, consisting of characteristic small, pale yellow, opaque clusters of minute prisms of m. p. above 77°, could often be removed in part before the remainder came out of solution mixed with aggregates of small transparent scales of lower m. p.: mixtures which in the last resort had to be separated by hand.

For the final purification, dissolution in the minimum volume of benzene, followed by the addition of 2—3 volumes of ligroin, gave the best result. With fractions of m. p. 90° and above, the crystalline form became that of clusters of small, pale yellow prisms no longer opaque but clear. The solubility of the chloride, m. p. 92°, in each of the three solvents—petrol, ligroin and benzene—was intermediate between that of the other isomerides.

4-*Chloro*-6-*nitrotoluene*-3-*sulphonic acid.* The *barium* salt, obtained by hydrolysis of the sulphonyl chloride, m. p. 92°, crystallised in moderately soluble, narrow, elongated scales, light yellow when dry but changing to a dirty grey on exposure to sunlight [Found: Ba, 19·6; H_2O, 5·7. $(C_7H_5O_5NClS)_2Ba,2H_2O$ requires Ba, 20·4; H_2O, 5·3%]. The potassium salt, long, slender, pale yellow, anhydrous needles, and sodium salt (+ H_2O), small, opaque, pale yellow aggregates, were also prepared. At 15°, the weight of anhydrous salt contained in 100 g. of aqueous solution was Ba 1·72 g., K 2·85 g., and Na 7·30 g. The *chloride*, m. p. 92°, highly soluble in benzene, separated from ligroin in radiating aggregates of prismatic crystals or minute rhomb-shaped crystals of acute angle 76° and with straight extinction, or, in the last stages of purification, in characteristic, small, semi-opaque aggregates of minute prisms, m. p. 86—89° (Found: Cl, 26·7. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). The *amide*, m. p. 188°, crystallised from dilute alcohol in short slender needles (Found: N, 11·4. $C_7H_7O_4N_2ClS$ requires N, 11·2%).

4-*Chloro*-6-*aminotoluene*-3-*sulphonic acid.* This acid (yield, 58% of that calculated), crystallised in lustrous, flat, anhydrous needles, moderately soluble in water. The *barium* salt formed thin laminated prisms, easily soluble in water [Found: Ba, 18·6; H_2O, 21·7. $(C_7H_7O_3NClS)_2Ba,9H_2O$ requires Ba, 18·5; H_2O, 21·9%]. The potassium salt (+ H_2O), long, flat, moderately soluble needles, clustered together, and sodium salt (+ $5H_2O$), thin, easily soluble, glistening scales, were also prepared.

4 : 6-*Dichlorotoluene*-3-*sulphonic acid.* The *barium* salt crystallised in readily soluble, long, slender, flat needles [Found: Ba, 21·0; H_2O, 5·1. $(C_7H_5O_3Cl_2S)_2Ba,2H_2O$ requires Ba, 21·0; H_2O, 5·5%]. The potassium salt, slender, flat, anhydrous needles or long, acicular, monohydrated needles, and sodium salt (+ $1\frac{1}{2}H_2O$), long slender needles, both easily soluble, were also prepared. The *chloride*, m. p. 72°, easily soluble in ligroin, crystallised in radiating needles with high double refraction and a straight extinction, and had the habit of climbing up the side of the beaker above the solvent, whether petrol or ligroin (Found: Cl, 40·7. $C_7H_5O_2Cl_3S$

requires Cl, 41·0%). The *amide*, m. p. 178°, crystallised from dilute alcohol in long slender needles (Found : N, 6·1. $C_7H_7O_2NCl_2S$ requires N, 6·1%).

On hydrolysis with orthophosphoric acid (*d* 1·75) and steam at 230—240°, the potassium salt (2·6 g.) yielded a dichlorotoluene (0·9 g.), b. p. 192—194°/756 mm., which on oxidation with nitric acid (*d* 1·16) at 150° gave 2 : 4-dichlorobenzoic acid, m. p. 161°.

Fraction, m. p. 112—120°. Isolation of the pure isomeride, m. p. 122°, from this fraction was easily achieved by first adding ligroin cautiously to the warm solution in benzene to precipitate impurity and then either concentrating the clarified liquid to crystallising point or throwing out the chloride by addition of ligroin in large amount.

4-*Chloro*-2-*nitrotoluene*-3-*sulphonic acid.* The *barium* salt, obtained from the sulphonyl chloride, m. p. 122°, by hydrolysis, was easily soluble in hot water, forming, on cooling, supersaturated solutions from which later it crystallised in thin, nacreous, colourless scales [Found : Ba, 17·3; H_2O, 18·3. $(C_7H_5O_5NClS)_2Ba,8H_2O$ requires Ba, 17·6; H_2O, 18·4%]. From alcohol, in which it was much less soluble than in water, it separated in scales (Found : loss, 14·4. Calc. for $6H_2O$, 14·5%). The potassium salt, thin, lustrous, anhydrous scales, and sodium salt (+ $3H_2O$), long, prismatic, pale yellow needles or, more usually, short slender needles which when washed with water on the pump formed a white felted mass, were also prepared. At 15°, the weight of anhydrous salt contained in 100 g. of aqueous solution was Ba 11·91 g., K 18·50 g., and Na 13·44 g. The *chloride*, m. p. 122°, crystallised from ligroin in flat, prismatic, faintly yellow needles or from light petroleum (b. p. 90—100°) in stout prisms or prismatic needles terminated by an oblique end at an angle of 52° and having an extinction angle of 23°. It was the least soluble of the three isomerides (Found: Cl, 26·1. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). The *amide*, m. p. 177°, crystallised from aqueous alcohol in small flat prisms or in slender needles changing over-night in the solvent to the prismatic form (Found : N, 11·0. $C_7H_7O_4N_2ClS$ requires N, 11·2%). It did not furnish ammonia by prolonged boiling with alcoholic sodium hydroxide.

4-Chloro-2-nitrotoluene was obtained when the sodium salt (10 g.), mixed with concentrated sulphuric acid, was heated at 220° in a current of steam. The yield was slightly less when the amide was used instead of the salt. It was identified by its crystalline form, m. p. 38·5°, and by conversion into 4-chloro-*o*-toluidine, m. p. 22° (acetyl derivative, needles, m. p. 138°).

4-*Chloro*-2-*aminotoluene*-3-*sulphonic acid.* This acid (yield, 60% of that calculated) crystallised from water, in which it was only sparingly soluble, in slender, silky, colourless, anhydrous needles. The *barium* salt formed faintly brown, small, flat needles or lustrous scales which decomposed at 140° [Found : Ba, 22·9; H_2O, 1·3. $(C_7H_7O_3NClS)_2Ba,\frac{1}{2}H_2O$ requires Ba, 23·4; H_2O, 1·5%]. The potassium salt, easily soluble, soft, anhydrous scales, and sodium salt (+ $1\frac{1}{2}H_2O$), thin elongated scales or prisms which became anhydrous when kept for a week in a desiccator over sulphuric acid, were also prepared.

2 : 4-*Dichlorotoluene*-3-*sulphonic acid.* The *barium* salt, obtained from the sulphonyl chloride by hydrolysis, crystallised in easily soluble, radiate groups of short stumpy needles [Found : Ba, 21·6; H_2O, 2·5. $(C_7H_5O_3Cl_2S)_2Ba,H_2O$ requires Ba, 21·6; H_2O, 2·8%]. The potassium salt, easily soluble, anhydrous, thin scales, and sodium salt (+ H_2O), minute scales highly soluble both in water and in alcohol, were also prepared. The *chloride*, very soluble in ligroin, was obtained as an oil which solidified in an ice-bath and had m. p. 19·5° (Found : Cl, 40·7. $C_7H_5O_2Cl_3S$ requires Cl, 41·0%). The *amide* crystallised from dilute alcohol in slender flat needles, m. p. 188° (Found : N, 6·4. $C_7H_7O_2NCl_2S$ requires N, 6·1%).

Suspended in orthophosphoric acid (*d* 1·75), both the sodium salt (20·5 g.) and the amide (16 g.), when hydrolysed by steam at 240°, gave a dichlorotoluene, b. p. 195—197°/756 mm. (the yields being 7·6 and 4·5 g. respectively), which on oxidation with dilute nitric acid (*d* 1·16) at 150° furnished 2 : 4-dichlorobenzoic acid, m. p. 161°.

(II) *Nitration of* 4-*Chlorotoluene*-3-*sulphonyl Chloride.*—Nitration of the sulphonyl chloride, m. p. 54°, was carried out under the conditions described by Davies (J., 1921, **119**, 853), the chloride (90 g.) in fine powder being dusted into a mixture of fuming nitric acid (*d* 1·52, 45 c.c.) and concentrated sulphuric acid (112·5 c.c.) continuously stirred and kept at 20—30°. At the end of an hour, the suspended solid had become a mass of liquid globules which eventually coalesced, stirring being maintained during a further 3 hours. Poured on to ice, the product solidified : it was ground, and washed repeatedly with water, cold at first and afterwards warm, until free from acid. The yield amounted to 98 g., but of this 4·7 g. were lost by accident—the remainder, 93·3 g., dissolved completely in benzene. For the separation of the isomeric chlorides, the methods already described were employed, the constituent of lower m. p. in the initial fractionation being collected in the fraction, m. p. 51—61°, with the exception of one crop of crystals (8·1 g.) of m. p. 47—49°. Separations having m. p.'s in the neighbourhood of 50° gave solutions in petrol which on cooling became opalescent and during spontaneous evaporation formed rings of " oil " above the surface, but fractionation was much less troublesome and purification easier than with the product obtained from the nitrated salt.

Despite repeated and careful search, no trace of the isomeride, m. p. 92°, was discovered—none existed in the fraction, m. p. 53—58°, which a test showed to be largely composed of the isomeride, m. p. 62·5°. From the table, which gives the results obtained in the examination of the nitration product, it will be seen that the proportion of the two isomerides, m. p. 62·5° and 122°, differs remarkably from that found when the salt was nitrated and afterwards converted into chloride (p. 700).

M. p.	53—62°	122°	"oil"	not accounted for	Total.
Grams	62·9	18·0	2·5	9·9	93·3

(III) *Nitration of Sodium 4-Chlorotoluene-2-sulphonate.*—In the original experiments, the 4-nitrotoluene-2-sulphonic acid required as the source of the chloro-acid was prepared by sulphonating *p*-nitrotoluene (1 pt.) with 23% oleum (2·5 pts.) at 50°, the yield amounting to 94% of that calculated. For a repetition of the earlier work sodium *p*-nitrotoluene-2-sulphonate (chloride, m. p. 46°) obtained by purchase was used.

Nitration of sodium 4-chlorotoluene-2-sulphonate (58 g.) in concentrated sulphuric acid solution was carried out exactly as described for the 3-sulphonate (p. 699), and the product isolated as sodium salt (64·8 g.), the yield being 93% of that calculated. Fractional crystallisation of the product from water, in which it was easily soluble, or from alcohol, in which the solubility was markedly less, led to no satisfactory result, but a separation of the two constituents was achieved without difficulty by conversion of the salt into the sulphonyl chloride. On crystallisation of this product from benzene or from benzene–ligroin the less soluble chloride, m. p. 154°, could be removed completely before the isomeride made its appearance. The table shows the yield of the various products.

M. p.	54—59°	154°	" oil " not examined further	not accounted for	Total
Grams	39·6	10·7	6·3	8·2	64·8

No trace of a third isomeride was encountered.

4-Chloro-6-nitrotoluene-2-sulphonic acid. The *barium* salt, obtained from the sulphonyl chloride, m. p. 61°, by hydrolysis, crystallised in sparingly soluble, slender needles [Found : Ba, 18·7; H_2O, 10·0. $(C_7H_5O_5NClS)_2Ba,4H_2O$ requires Ba, 19·3; H_2O, 10·0%]. The potassium salt (+ $\frac{1}{2}H_2O$), very small, opaque, spherical aggregates of minute needles, and sodium salt (+ $1\frac{1}{2}H_2O$), small opaque granules, both readily soluble in water but only sparingly in alcohol, were also prepared. The *chloride*, m. p. 60°, was easily soluble in benzene. From petrol it separated in well-formed small prisms (Found : Cl, 26·2. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%).

Professor G. M. Bennett has been good enough to measure the crystals of this chloride and reports as follows :

" The substance crystallises in the monoclinic system with axial ratios $a : b : c = 2{\cdot}073 : 1 : 1{\cdot}536$ and $\beta = 104°52'$. The following is a list of forms observed and of the means of angular measurements obtained from three selected crystals with the two-circle goniometer :

	a(100).	*c*(001).	$R(\bar{1}01)$.	*o*(111).	*q*(011).	$s(\bar{2}11)$.
ϕ	0° 0′	*75° 8′	116° 48′	*44° 6′	74° 42′	142° 1′
ρ	90° 0′	90° 0′	90° 0′	*43° 6′	33° 57′	46° 27′

" Barker classification angles : *cr* 31° 2′, *ra* 44° 6′, *am* 26° 31′, *bq* 33° 58′.

" The crystals are developed with *a* large (Fig. 3).

" The optic axial plane lies in *b*. One optic axis is seen to emerge almost perpendicular to the face *a*. The double refraction is strong and positive."

The *amide*, m. p. 167°, crystallised from dilute alcohol in radiate, long, slender needles (Found : N, 11·3. $C_7H_7O_4N_2ClS$ requires N, 11·2%).

4-Chloro-6-aminotoluene-2-sulphonic acid. This *acid* (yield, 67% of that calculated) crystallised in sparingly soluble, very slender needles (Found : H_2O, 5·1. $C_7H_8O_3NClS,H_2O$ requires

H_2O, 5·2%). The *barium* salt formed small, sparingly soluble, anhydrous scales [Found : Ba, 23·3. $(C_7H_7O_3NClS)_2Ba$ requires Ba, 23·7%]. The potassium salt (+ H_2O), clusters of scales, and sodium salt (+ H_2O), scales, both readily soluble, were also prepared.

4 : *6-Dichlorotoluene-2-sulphonic acid.* The *barium* salt crystallised in very sparingly soluble, anhydrous, silvery scales [Found : Ba, 21·7. $(C_7H_5O_3Cl_2S)_2Ba$ requires Ba, 22·3%]. The potassium salt (+ H_2O), somewhat sparingly soluble, small, glistening prisms, and sodium salt (+ H_2O), moderately soluble, long, flat needles, were also prepared. The *chloride*, m. p. 54°, was highly soluble in benzene, ligroin or petrol and after removal of the solvent frequently remained liquid until nucleated. It crystallised in small monoclinic tablets with an oblique extinction (extinction angle about 40°) (Found : Cl, 40·8. $C_7H_5O_2Cl_3S$ requires Cl, 41·0%). The *amide*, m. p. 186°, crystallised from dilute alcohol in thin flat needles (Found : N, 6·0. $C_7H_7O_2NCl_2S$ requires N, 6·1%).

On hydrolysis at 230—240° with steam, the sodium salt (8 g.), suspended in concentrated sulphuric acid, gave a dichlorotoluene (1·9 g.), b. p. 195—196°/765 mm., which on oxidation with dilute nitric acid (*d* 1·16) at 150° furnished 2 : 4-dichlorobenzoic acid, m. p. 161—162°.

4-*Chloro*-3-*nitrotoluene*-2-*sulphonic acid.* The *barium* salt, obtained from the sulphonyl chloride, m. p. 154°, by hydrolysis, crystallised in radiating groups of moderately soluble, colourless, long, brittle needles which became opaque on exposure to the air [Found : Ba, 18·7; H_2O, 13·1. $(C_7H_5O_5NClS)_2Ba,5H_2O$ requires Ba, 18·9; H_2O, 12·4%]. The potassium salt, readily soluble, radiate groups of small, slender, anhydrous needles, and sodium salt (+ $4H_2O$), radiate groups of short slender needles from highly concentrated solution, were also prepared. The *chloride*, m. p. 154°, crystallised from benzene in lustrous monoclinic needles with an extinction angle of 20° and was less soluble than its isomeride either in this solvent or in ligroin or petrol (Found : Cl, 26·1. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). The *amide*, m. p. 183°, crystallised from alcohol in sparingly soluble, short, slender, soft needles (Found : N, 11·2. $C_7H_7O_4N_2ClS$ requires N, 11·2%).

4-*Chloro*-3-*aminotoluene*-2-*sulphonic acid.* This acid crystallised in anhydrous slender needles and was more soluble in water than its isomeride. The *barium* salt, sparingly soluble in water, crystallised in very small aggregates of minute, glistening, anhydrous prisms, looking like a fine white sand when dry [Found : Ba, 23·2. $(C_7H_7O_3NClS)_2Ba$ requires Ba, 23·7%]. The potassium salt (+ H_2O), moderately soluble, four-sided tablets, and sodium salt (+ H_2O), lustrous, thin, square scales more soluble than the potassium salt, were also prepared.

3 : 4-*Dichlorotoluene*-2-*sulphonic acid.* The *barium* salt came out from solution in moderately soluble, anhydrous, coralline forms [Found : Ba, 21·8. $(C_7H_5O_3Cl_2S)_2Ba$ requires Ba, 22·3%]. The potassium salt, lustrous, elongated, anhydrous scales, and sodium salt (+ H_2O), lancet-shaped small needles, both readily soluble, were also prepared. The *chloride*, m. p. 49°, highly soluble in benzene, crystallised in stout monoclinic prisms or from petrol in monoclinic needles with straight extinction (Found : Cl, 41·0. $C_7H_5O_2Cl_3S$ requires Cl, 41·0%). The *amide*, m. p. 186°, separated from dilute alcohol in long, soft, silky needles (Found : N, 6·4. $C_7H_7O_2NCl_2S$ requires N, 6·1%). Mixed with 4 : 6-dichlorotoluene-2-sulphonamide (m. p. 186°), it melted at 160°.

On hydrolysis, the sodium salt (6·8 g.), suspended in concentrated sulphuric acid at 230°, gave a dichlorotoluene (2·3 g.) consisting mainly of a fraction, b. p. 198—201°/765 mm. (1·5 g.), which on oxidation with dilute nitric acid (*d* 1·16) at 150° gave 3 : 4-dichlorobenzoic acid, m. p. 206°.

(IV) *Nitration of* 4-*Chlorotoluene*-2-*sulphonyl Chloride.*—Fused 4-chlorotoluene-2-sulphonyl chloride, m. p. 24° (80·5 g.), nitrated under the same conditions as the 3-isomeride (p. 703), furnished a product (92 g.) which was completely soluble in benzene. Concentrated to 155 c.c., the solution gave a separation in elongated prisms, m. p. 153—154° (13·2 g.), and by further concentration to 100 c.c. deposited smaller but similar prisms, m. p. 154° (2 g.). From the mother-liquor, diluted with three times its volume of petrol, a third crop of small prisms was obtained, m. p. 154° (2·5 g.), but after removal of these the solution, left over-night, furnished an entirely different crystallisation in large, yellow, prismatic forms, m. p. 61° (26·2 g.). Subsequent concentration of the 400 c.c. of solution to 45 c.c. (now mainly benzene), followed by addition of three times the volume of petrol, led to the separation of an oil (13 g.), which after removal deposited large prisms, m. p. 60° (6·2 g.), while the mother-liquor by spontaneous evaporation gave successive crops (12·5 and 7·2 g.) of similar crystals, m. p. 60°, and eventually from the accumulation of oil (14·8 g.) by drying on porous earthenware a final separation in prisms, m. p. 58—59° (3·9 g.). As was the case with the nitration product from the sulphonic acid, the nitrated chloride was resolved sharply and speedily into its constituents. No trace of a third isomeride was detected. Summarised, the results obtained in the nitration were:

M. p.	61°	154°	" oil " not further examined	not accounted for	Total
Grams	56·0	17·7	10·9	7·4	92·0

these do not differ materially from those recorded for the nitration of the salt (p. 704).

(V) *Nitration of* 3-*Chlorotoluene*-6-*sulphonic Acid.*—As the 6-sulphonic acid is the only product formed when *m*-chlorotoluene is heated with three times its weight of pure (100%) sulphuric acid at 70° (Wynne, J., 1892, **61**, 1075; cf. Schraube and Romig, *Ber.*, 1893, **26**, 578), its nitration was effected by adding the requisite quantity (1·5 mols.) of nitric acid (*d* 1·48) gradually to the sulphonation melt at 0—5° and afterwards allowing the temperature gradually to become normal in the course of 2 hours. Converted into potassium salt and fractionally crystallised, the product from 200 g. of *m*-chlorotoluene amounted to 450 g. or 98% of that calculated. Of this, 446 g. were obtained in long, slender, anhydrous needles, but the last two separations, amounting only to 4 g. after recrystallisation, were in small anhydrous scales. Until nitration of 3-chlorotoluene-6-sulphonyl chloride under Davies's conditions had been shown to yield two isomerides in widely different proportion, this relatively minute fraction did not receive attention. But, on examination, it proved to be the potassium salt corresponding to the chloride, m. p. 96°, which forms the minor product from the alternative source (p. 707).

3-*Chloro*-4-*nitrotoluene*-6-*sulphonic acid.* The barium salt, obtained from the sulphonyl chloride, m. p. 116°, by hydrolysis, crystallised in sparingly soluble, long, pale orange needles [Found: Ba, 19·6; H_2O, 8·0. Calc. for $(C_7H_5O_5NClS)_2Ba,3H_2O$: Ba, 19·8; H_2O, 7·8%. Schraube and Romig found $2H_2O$]. The potassium salt, long, pale yellow, somewhat sparingly soluble, anhydrous needles, and sodium salt (+ H_2O), radiate groups of moderately soluble, pale yellow needles, were also prepared. The *chloride*, m. p. 116°, crystallised in pale yellow, lustrous prisms with a high double refraction and straight extinction and dissolved readily in benzene but only sparingly in ligroin (Found: Cl, 26·6. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). On digestion with boiling alcoholic potash both chlorine atoms were rapidly removed. The *amide*, m. p. 170°, crystallised from aqueous alcohol in thin long needles (Found: N, 11·1. $C_7H_7O_4N_2ClS$ requires N, 11·2%).

3-*Chloro*-4-*aminotoluene*-6-*sulphonic acid.* The acid (yield, 76% of that calculated) crystallised in somewhat sparingly soluble, anhydrous, slender needles. The *barium* salt formed pale yellow, moderately soluble aggregates of minute needles [Found: Ba, 22·4; H_2O, 5·6. $(C_7H_7O_3NClS)_2Ba,2H_2O$ requires Ba, 22·4; H_2O, 5·9%]. The potassium salt, highly soluble aggregates of small anhydrous scales, and sodium salt (+ H_2O), very small scales from 92% alcohol, were also prepared.

The constitution assigned to the nitro-derivative by Schraube and Romig was confirmed by conversion of the amino-compound into dichlorotoluenesulphonyl chloride (m. p. 84°) and sulphonamide (m. p. 190°), respectively identical with the corresponding derivatives of the acid obtained from 3 : 4-dichlorotoluene by sulphonation (Wynne, J., 1892, **61**, 1062).

Professor G. M. Bennett has been good enough to measure the crystals of this chloride and reports as follows:

" This substance crystallises in the monoclinic system with axial angle $\beta = 98° 15'$ and axial ratios $a : b : c = 1{\cdot}429 : 1 : 0{\cdot}747$. Barker classification angles: $a(100) : m(110) = 54° 44'$, $c(001) : r(101) = 25° 37'$, $r(101) : a(100) = 56° 8'$, $b(010) : q(011) = 53° 31'$. The following table gives a list of the forms observed and the mean angular measurements obtained with the two-circle goniometer from three selected crystals:

	$a(100)$.	$r(101)$.	$m(110)$.	$q(011)$.	$p(\bar{1}11)$.
ρ	90° 0′	90° 0′	*35° 16′	*53° 31′	55° 10′
ϕ	0° 0′	56° 8′	0° 0′	*81° 45′	110° 57′

The habit of the crystals is compact with $r(101)$ prominent (Fig. 4).

" The substance is doubly refracting and it was confirmed that the extinction divides the face $r(101)$ symmetrically and perpendicular to the edge *ra*. The position of the optic axes could not be observed."

3-*Chloro*-2-*nitrotoluene*-6-*sulphonic acid.* The *barium* salt, obtained by hydrolysis of the sulphonyl chloride, m. p. 96°, crystallised in sparingly soluble, glistening, pale yellow, anhydrous scales [Found: Ba, 22·3. $(C_7H_5O_5NClS)_2Ba$ requires Ba, 22·5%]. The potassium salt, pale yellow, anhydrous scales, and sodium salt, radiate groups of pale yellow, slender, anhydrous needles, both easily soluble, were also prepared. The *chloride*, m. p. 96°, crystallised from petrol in aggregates of small radiating plates with oblique extinction, opaque in the mass and more soluble than the 4-nitro-derivative (Found : Cl, 26·1. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). The *amide*, m. p. 176°, separated from 25% alcohol in lustrous nacreous scales (Found : N, 11·0. $C_7H_7O_4N_2ClS$ requires N, 11·2%).

3-*Chloro*-2-*aminotoluene*-6-*sulphonic acid*. The *acid* (yield, 52% of that calculated) crystallised in slender, sparingly soluble needles (Found : H_2O, 7·0. $C_7H_8O_3NClS,H_2O$ requires H_2O, 7·5%).

2 : 3-*Dichlorotoluene*-6-*sulphonic acid*. The *sodium* salt formed sparingly soluble, thin scales (Found : Na, 8·0; H_2O, 6·0. $C_7H_5O_3Cl_2SNa,H_2O$ requires Na, 8·2; H_2O, 6·4%). The chloride, m. p. 54°, did not depress the m. p. of 2 : 3-dichlorotoluene-6-sulphonyl chloride (Silvester and Wynne, this vol., p. 694) and its amide had m. p. 228°.

(VI) *Nitration of* 3-*Chlorotoluene*-5-*sulphonyl Chloride*.—For the preparation of the sulphonyl chloride, *m*-chlorotoluene (50 g.) was sulphonated in carbon disulphide solution with an equal weight (4 g. excess) of chlorosulphonic acid. After removal of the solvent and conversion of the product into sodium salt, a small amount (1·8 g.) of insoluble material was removed by filtration and proved to be 4 : 4′-*dichloro*-3 : 3′-*dimethyldiphenylsulphone*; this crystallised from benzene–petrol in small lustrous prisms, m. p. 130° (Found : Cl, 22·6. $C_{14}H_{12}O_2Cl_2S$ requires Cl, 22·5%).

For nitration, 3-chlorotoluene-6-sulphonyl chloride (56 g.) in fine powder was added gradually with continuous stirring to a mixture of nitric acid (*d* 1·5, 28 c.c.) and concentrated sulphuric acid (70 c.c.) at 25—30°, above which the temperature was not allowed to rise. At the end of 45 minutes, small solid globules began to separate and an hour later, when the operation was stopped, the mixture had become almost semi-solid. Washed free from acid and dried, the product (65·4 g.) dissolved completely in benzene, but the addition of several times the volume of ligroin precipitated the greater part (49 g.) of the main constituent, m. p. 116°. After removal of the solvent and extraction of the residue (16·4 g.) with successive quantities of petrol, followed by fractional separation from these solutions, an additional amount of this isomeride (4 g.) was isolated together with more soluble fractions (6·5 g.), m. p. 87—94°, from which by recrystallisation from this solvent uniform needles (4·1 g.), m. p. 96°, were eventually obtained. The later separations consisted of more soluble, ill-defined forms of much lower m. p. (3·7 g.) together with non-crystallisable oil (2 g.) and were not further examined.

The author desires to record his grateful acknowledgment of Professor Sir William Pope's kindness in placing a laboratory at his service which has made it possible for this investigation to be carried through. His thanks are due also to Miss E. Gertrude Turner for numerous analyses in the earlier stages of the work and to Mr. G. R. Purdy for the determinations of Cl and N, all of which were made by microchemical methods.

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