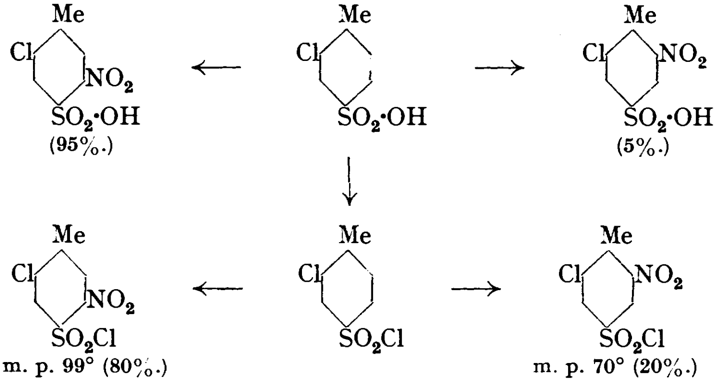
159. *Studies in the Toluene Series. Part VII. Nitration of 2-Chlorotoluene-4- and -5-sulphonic Acids and their Sulphonyl Chlorides.*

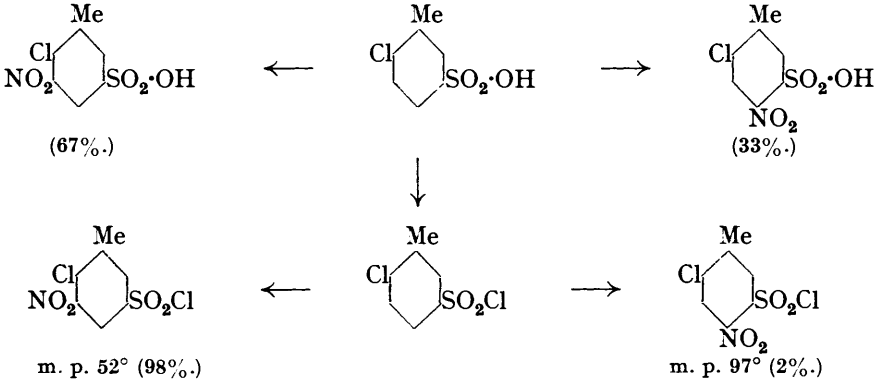
By (MISS) E. GERTRUDE TURNER and W. PALMER WYNNE.

NITRATION of the three *o*-chlorotoluenesulphonyl chlorides was investigated by Davies with the object of tracing the influence of the radicals present in the respective molecules on the orientation assumed by the NO_2-group, the constitution of the products being ascertained by means of the derived cresols (J., 1921, **119**, 853, 876; 1922, **121**, 785). Earlier, Wynne and Greeves had nitrated the potassium 2-chlorotoluene-4- and -5-sulphonates and arrived at the constitution of three of the products by the method already described (P., 1895, **11**, 152), but no attempt was then made to determine the relative proportion of the isomerides. The present communication removes that defect and moreover enables a comparison to be made between the yields obtained when in addition to the salt the derived sulphonyl chloride is nitrated under the closely similar conditions outlined in the preceding paper (p. 697). Expressed graphically, the following are the products isolated

(i) from the 4-derivatives :

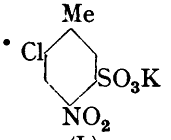


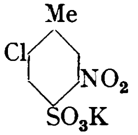
and (ii) from the 5-derivatives :

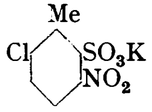


Unfortunately, a like comparison could not be made with the third isomeride, as potassium 2-chloro-5-nitrotoluene-6-sulphonate does not furnish a sulphonyl chloride but another type of product by interaction with phosphorus pentachloride in presence of oxychloride.

One remarkable feature of the interaction of pentachloride with the two sulphonates in which (a) the NO_2 and the SO_3K group are contiguous and (b) the NO_2 and the Cl group occupy relatively *para*-positions is the production of much reddish-brown non-crystallisable " oil " which does not furnish a definite salt when hydrolysed by aqueous caustic alkali or baryta. The isomeride (I), in which only one, the former, of these prerequisites is fulfilled, behaves normally, giving sulphonyl chloride with, it is true, an unusually large proportion of oil, but this is orange in colour and regenerates in part the sulphonate on hydrolysis. But (II), whilst giving sulphonyl chloride, gives also what seems to be a new type of reaction, the product of which at the moment of melting suddenly froths up the melting point tube : (III) also yields a similar compound as the sole crystalline product.


(I.)


(II.)


(III.)

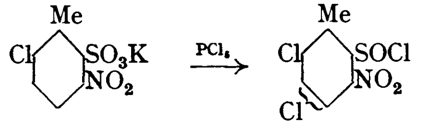
Analysed by Schoeller of Berlin, these compounds gave the following numbers :

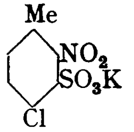
From (II) C, 29·3; H, 1·5; N, 4·7; Cl, 36·9; S, 11·1; O (diff.), 16·4%.

From (III) C, 29·4; H, 1·5; N, 4·7; Cl, 36·5; S, 11·0; O (diff.), 16·9%.

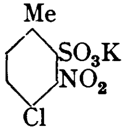
$C_7H_4O_3NCl_3S$ requires C, 29·1; H, 1·4; N, 4·85; Cl, 36·9; S, 11·1; O, 16·65%.

We are indebted to Professor G. M. Bennett for the suggestion that these are sulphinyl chlorides in the production of which an additional chlorine atom has entered the ring. On





(IV.)



(V.)

this view, not only has reduction of the SO_2Cl to the SOCl complex taken place, but simultaneously, to furnish the necessary chlorine, oxidation of one of the halogenated participants in the reaction must also have occurred.

It may be added that (I), in respect of its behaviour towards pentachloride, resembles the two *p*-chloro-derivatives (IV and V), from both of which, although the radicals NO_2 and SO_3K occupy contiguous positions, the products are sulphonyl chloride in good yield and pale brown oil from which sulphonate can be recovered by hydrolysis.

EXPERIMENTAL.

(I) *Nitration of Potassium 2-Chlorotoluene-4-sulphonate.*—In the original nitration experiments, *o*-toluidine-4-sulphonic acid, obtained as sole product by sulphonating *o*-toluidine hydrogen sulphate with twice its weight of 30% oleum at 20°, was the source of the potassium 2-chlorotoluene-4-sulphonate (Wynne and Greeves, P., 1895, **11**, 152). More conveniently the salt is prepared from the 2-chloro-derivative formed when toluene-4-sulphonyl chloride is chlorinated (cf. Davies, J., 1921, **119**, 860).

Nitrated in sulphuric acid solution under the conditions already described (this vol., p. 699), the dehydrated potassium salt (98 g.) gave a product which, after removal of the acid by baryta and of barium salt by potassium carbonate, separated from solution in the following fractions: from 1500 c.c., golden-yellow flat needles (72 g.); from the filtrate concentrated to 380 c.c., small golden-yellow prisms (21 g.); further to 50 c.c., similar prisms (11·3 g.); and to dryness, a residue (3·1 g.) largely inorganic. On recrystallisation the first separation seemed uniform and the second, so far as four-fifths, identical with it, but the third gave small crystalline granules. All were anhydrous.

Conversion of these fractions, suspended in phosphorus oxychloride, into sulphonyl chloride was incomplete unless the weight of phosphorus pentachloride used was twice that calculated. The product in each case was semi-solid and deep reddish-brown. Fractionally crystallised from ligroin, it was resolved into two isomerides together with much reddish-brown non-crystallisable oil from which nothing definite could be isolated either by prolonged standing or by hydrolysis with caustic alkali. The table shows the yields obtained:

	Wt. used.	Chloride, m. p. 91—95°.	Chloride, m. p. 69—70°.	Reddish-brown oil.
First separation ...	30 g.	14·8 g.	0·9 g.	9·1 g.
Second ,, ...	21	8·8	0·6	6·8
	51	23·6	1·5	15·9

From the third separation (11·3 g.) the product was mainly oil (5·7 g.), only a few needles (m. p. 65—66°) together with prisms (1·1 g., m. p. 90°) crystallising therefrom.

Although the amount of the isomeride of lower m. p. in each crystalline product is only about 6%, this proportion is probably too high. As will be seen later, the formation of the reddish-brown oil is associated exclusively with the conversion of (II) into sulphonyl chloride. If then, as seems not unreasonable, its weight be added to that of the chloride, m. p. 91—95°, the yield of the minor constituent will be reduced to 4% or thereabouts.

This fraction, m. p. 91—95°, proved to be a mixture. When first isolated, it did not as a rule fuse completely at this temperature—minute crystals remained, the pale yellow colour of the liquid then changed to reddish-brown and in the neighbourhood of 127° sudden decomposition occurred accompanied by much frothing. By repeated fractionation from light petroleum (b. p. 80—100°), 16·7 g. of this mixture gave 12·3 g. of sulphonyl chloride, m. p. 98—99°, which did not change colour below 150°, and 2·3 g. of a compound which became brown at 95—100°, and had m. p. 128°, decomposing suddenly and almost simultaneously with much frothing.

That the production of this mixture is characteristic of the interaction of pentachloride with the 2-chloro-5-nitrotoluene-4-sulphonate, and does not depend on the presence of some unrecognised third substance in the sulphonation melt, was shown by the use of sulphonate obtained by hydrolysis of (*a*) the sulphonyl chloride, m. p. 98—99°, isolated from the mixture, (*b*) the sulphonyl chloride, m. p. 98—99°, formed from 2-chlorotoluene-4-sulphonyl chloride by nitration (p. 711). In each case, the mixed product was reproduced—for example, in that of (*b*), the potassium salt (10 g.) with an equal weight of pentachloride gave prisms, m. p. 96—97° (3·2 g.), flat needles, decomp. at 124—125° (0·25 g.), and reddish-brown oil (2·2 g.), some unchanged salt (3·2 g.) being recovered.

Dichloro-5-*nitrotoluene*-4-*sulphinyl chloride*, $C_7H_4O_3NCl_3S$ (p. 708), separates from ligroin or light petroleum (b. p. 80—100°) in small, pale brown, monoclinic crystals which darken at 95—100° and decompose suddenly at 128°—if in quantity (0·05—0·1 g.) with an audible puff and the emission of much red nitrous gas. When boiled (*a*) with phosphorus oxychloride, a deep reddish-brown colour is developed; (*b*) with dilute nitric acid and silver nitrate, nitrous gas is evolved and silver chloride precipitated corresponding with 1 at. of chlorine (Cl found, 12·5; 1 at. Cl requires 12·3%); (*c*) with dilute (1%) caustic soda, rapid hydrolysis occurs giving a dark brown solution. Further it reduces nitric acid and ferric hydroxide—properties which, with its general instability and the evidence pointing to the continued presence of the NO_2 group, are in keeping with its suggested constitution. Warmed with dilute nitric acid, it is oxidised to a sulphonic acid, the crystalline *potassium* salt of which, dried at 120°, has the composition $C_7H_4O_5NCl_2SK$ (Found: K, 12·0. Required: K, 12·0% *).

2-*Chloro*-5-*nitrotoluene*-4-*sulphonic acid*. The *potassium* salt, sparingly soluble in water, crystallised in prismatic, pale yellow, anhydrous needles (Found: K, 13·1. $C_7H_5O_5NClSK$ requires K, 13·5%). The barium and sodium salts, chloride (m. p. 99°) and amide (m. p. 182°) had the properties described by Davies (*loc. cit.*, p. 865).

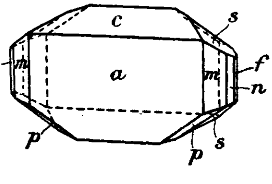
For measuring the crystals of the chloride we are indebted to Professor G. M. Bennett, who reports as follows :—

" This substance crystallises in the monoclinic system with axial angle $\beta = 112° 48'$ and axial ratios $a : b : c = 0{\cdot}749 : 1 : 0{\cdot}670$. Barker classification angles: $a(100) : m(110) = 34° 38'$, $c(001) : r(101) = 31° 34'$, $r(101) : a(100) = 35° 38'$, $b(010) : q(011) = 58° 17'$. The following is a list of the forms observed and the mean angular measurements obtained with the two-circle goniometer from three selected crystals :

	a(100).	*c*(001).	*m*(110).	*n*(120).	*b*(010).	*s*($\bar{1}$21).	*p*($\bar{1}$11).
ρ	90° 0′	90° 0′	*55° 22′	35° 54′	0° 0′	56° 15′	*59° 37′
ϕ	0° 0′	*67° 12′	0° 0′	0° 0′	all values	94° 1′	*119° 1′

" The common habit of the crystals is, as shown in the figure, elongated along the *b* axis with *a* and *c* large.

" The substance has strong positive double refraction. The optic axial plane is parallel to *b*(010) and the acute bisectrix is perpendicular to *a*(100). There is strong inclined dispersion of the median lines."



2-*Chloro*-5-*aminotoluene*-4-*sulphonic acid*. The amino-acid, obtained in 77% yield, crystallised from water in very sparingly soluble clusters of short, stumpy, anhydrous needles. Coupled with β-naphthol, it furnished red lakes (cf. Meister, Lucius, and Brüning, D.R.-P. 145908). The *barium* salt formed very sparingly soluble, four-sided scales which became " electrical " when moved by a spatula [Found: Ba, 23·0; H_2O, 2·8. $(C_7H_7O_3NClS)_2Ba,H_2O$ requires Ba, 23·0; H_2O, 3·0%]. The potassium salt ($2H_2O$) crystallised from supersaturated solutions on nucleation in very slender needles.

2 : 5-*Dichlorotoluene*-4-*sulphonic acid*. The constitution assigned by Wynne and Greeves (*loc. cit.*) to the nitro-compound depended on conversion of the amino-acid into the dichloro-acid, identified by comparison of the derived chloride (m. p. 43°) and amide (m. p. 196°) with the corresponding compounds obtained from authentic 2 : 5-dichlorotoluenesulphonic acid (Wynne, J., 1892, **61**, 1052).

2-*Chloro*-6-*nitrotoluene*-4-*sulphonic acid*. 2-Chloro-6-nitrotoluene-4-sulphonyl chloride, m. p. 70° (cf. Davies, *loc. cit.*), crystallised from ligroin in flat elongated prisms with an oblique termination and an extinction angle of 42°. The barium and sodium salts and the amide (m. p. 182°) had the properties described by Davies (*loc. cit.*). The *potassium* salt formed moderately soluble, pale yellow, anhydrous, prismatic needles (Found: K, 13·2. $C_7H_5O_5NClSK$ requires K, 13·5%).

* Microanalysis made by Weiler of Oxford.

2-*Chloro*-6-*aminotoluene*-4-*sulphonic acid.* The amino-acid, obtained in 70% yield, was moderately soluble in boiling water, from which it separated in anhydrous glistening scales or small prisms. The *potassium* salt formed thin, small, anhydrous scales (Found: K, 14·8. $C_7H_7O_3NClSK$ requires K, 15·1%).

2 : 6-*Dichlorotoluene*-4-*sulphonic acid.* Obtained from the amino-acid in the usual way, the *potassium* salt crystallised from water in anhydrous, moderately soluble, " electrical " scales (Found: K, 14·0. $C_7H_5O_3Cl_2SK$ requires K, 14·0%). The chloride, m. p. 69°, crystallising from ligroin in massive anorthic crystals with extinction angles of 8° and 17° on adjacent faces, and the amide, m. p. 192°, were identified as derivatives of 2 : 6-dichlorotoluene-4-sulphonic acid (cf. Davies, *loc. cit.*, p. 872).

(II) *Nitration of* 2-*Chlorotoluene*-4-*sulphonyl Chloride.*—To obtain an additional supply of the 2-chloro-6-nitro-derivative, 2-chlorotoluene-4-sulphonyl chloride (75 g.) was nitrated under Davies' conditions and the dry product (87·5 g.), which dissolved completely in benzene, was fractionated first from ligroin and, after removal of most of the less soluble constituent (51·2 g. in prisms, m. p. 98—99°), later from petrol, whereby prisms (5·4 g.), needles, m. p. 69—70° (9·6 g.), and non-crystallisable oil (15·7 g.) were separated, leaving 5·6 g. not accounted for. The percentage of needles isolated, therefore, was substantially the same as that recorded by Davies, being 14·5 as against 13.

Of the 15·7 g. of oil, 6·2 g. had been absorbed by porous earthenware or filter-paper. The remainder, 9·5 g., after hydrolysis gave dry potassium salt (9·8 g.) from which by extraction with boiling 70% alcohol a separation (3·6 g.) in minute prisms was obtained, identified as the 2-chloro-6-nitro-salt by conversion into the 2 : 6-dichlorotoluenesulphonyl chloride (0·6 g.), m. p. 66—67°, and amide, m. p. 190°. On the assumption that this fraction was uniform, the oil will have contained an additional 3·5 g. of the isomeride, m. p. 69—70°, bringing up the yield to 13·1 g. or 19%. The residue (6·2 g.) insoluble in 70% alcohol yielded, by similar conversion presumably into dichlorotoluenesulphonyl chloride (0·9 g.), a non-crystallisable oil.

In Davies' experiments, the yield of nitro-derivative, m. p. 50—80°, was 109 g. from 100 g. of chlorotoluenesulphonyl chloride and from it prisms (80 g.), m. p. 99·2°, and needles (12 g.), m. p. 70°, were isolated, leaving 17 g. not accounted for. Relying on the melting-point curve of the isomerides to give the proportion more accurately than fractional crystallisation, he estimated the percentage of the constituent, m. p. 70°, to be 25·5 (27·4 g.). Evidently the point had been overlooked that for this to be the case, the residue (17 g.) left after removal of the crystalline material would need to consist almost wholly (15·4 g.) of the needle form. Probably, the proportion differs little from 20%.

(III) *Interaction of Potassium* 2-*Chloro*-5-*nitrotoluene*-6-*sulphonate with Phosphorus Pentachloride.*—The fact that 2-chloro-5-nitrotoluene-6-sulphonyl chloride so closely resembles the 4-sulphonyl chloride in constitution made a study of the interaction of the derived potassium sulphonate with phosphorus pentachloride imperative. 2-Chlorotoluene-6-sulphonyl chloride (80 g.), m. p. 72°, was therefore nitrated under Davies' conditions (J., 1921, **119**, 882), and the viscous product, after being washed free from acid, converted into barium salt, which by extraction with absolute alcohol gave the more soluble 6-sulphonate (43·6 g.) in approximately 50% yield. Interaction of the corresponding potassium salt, suspended in phosphorus oxychloride, with pentachloride led to the complete suppression of sulphonyl chloride, the only crystalline product isolated being the presumed *dichloro*-5-*nitrotoluene*-6-*sulphinyl chloride*, $C_7H_4O_3NCl_3S$, which crystallised from ligroin or light petroleum in small, pale brown prisms probably monoclinic, fused at 119°, decomposed almost simultaneously, at 119—120°, and in all other respects closely resembled the 4-sulphinyl derivative in properties (p. 710).

2-*Chloro*-5-*nitrotoluene*-6-*sulphonic acid.* The *barium* salt, obtained as above, crystallised from absolute alcohol in minute anhydrous scales but from water in very soluble, small spheres [Found: Ba, 21·0; H_2O, 3·0. $(C_7H_5O_5NClS)_2Ba,H_2O$ requires Ba, 20·9; H_2O, 2·7%. Davies found $7H_2O$]. The sodium salt, equally soluble, separated from absolute alcohol in minute anhydrous scales.

Whether heated with phosphorus pentachloride (1·5 pts.) and oxychloride (3·5 pts.) under reflux for 10 minutes in one experiment or in an open dish in a second, the colourless suspension of the sodium salt quickly became reddish-brown. After removal of most of the oxychloride, the product was in each case an oil which showed no sign of crystallisation in the course of a week and was completely soluble in benzene. The solution, freed from tarry matter by the addition of ligroin, gave on concentration separations in thin plates and finally reddish-brown non-crystallisable oil. In the two operations, the yields were :

Salt used.	Plates.	Oil.	Tar.	Total.
5 g.	1·2	2·7	1·0	4·9
7 g.	1·3	3·5	1·5	6·3

The separation in plates (2·5 g.), twice crystallised from light petroleum (b. p. 80—100°), formed practically colourless, prismatic needles (1·9 g.) which fused at 119° and decomposed suddenly at 119—120°, frothing up the melting point tube.

As the expected sulphonyl chloride (m. p. 61°; Davies, *loc. cit.*) had not been isolated, the oil (6·3 g.) was hydrolysed in alcoholic solution by caustic soda, and the solution, after neutralisation, evaporated to dryness. From the dry residue, absolute alcohol extracted a fraction (1·7 g.) which did not crystallise from this solvent but separated from aqueous solution (2—3 c.c.) in microcrystalline form (0·25 g.). This dried on porous earthenware may have contained sodium chloronitrotoluenesulphonate (Found : Na, 10·1. Calc. for $C_7H_5O_5NClSNa$: Na, 8·4%) arising from the presence of sulphonyl chloride in small amount in the oil, but no way was found of verifying this conjecture.

2-*Chloro*-5-*aminotoluene*-6-*sulphonic acid*. The *acid*, obtained in 77% yield, crystallised in sparingly soluble, long, flat, pointed needles [Found : H_2O, 2·8. $C_7H_8O_3NClS,1/3H_2O$ requires H_2O, 2·6%]. The *sodium* salt formed easily soluble, thin, elongated, anhydrous scales (Found : Na, 9·3. $C_7H_7O_3NClSNa$ requires Na, 9·4%).

2 : 5-*Dichlorotoluene*-6-*sulphonic acid*. The *barium* salt crystallised in sparingly soluble, anhydrous, irregular prisms [Found : Ba, 21·9. $(C_7H_5O_3Cl_2S)_2Ba$ requires Ba, 22·3%]. The easily soluble potassium salt formed small anhydrous scales, and the sodium salt (H_2O), elongated scales. The *chloride*, m. p. 38°, showed marked superfusion on removal of solvent (petrol), but when nucleated or cooled in a mixture of ice and salt became a solid mass of thin scales (Found : Cl, 40·9. $C_7H_5O_2Cl_3S$ requires Cl, 41·0%). The *amide*, m. p. 180°, crystallised from 90% alcohol in clusters of slender needles (Found : N, 6·0. $C_7H_7O_2NCl_2S$ requires N, 5·8%).

Hydrolysed at 230° in concentrated sulphuric acid suspension by superheated steam, the sodium salt (4·8 g.) gave a dichlorotoluene (2·3 g.), b. p. 196—198°/756 mm., which on oxidation at 150° with dilute nitric acid (*d* 1·16) furnished 2 : 5-dichlorobenzoic acid, m. p. 153°, thus confirming the constitution assigned by Davies.

(IV) *Nitration of Potassium* 2-*Chlorotoluene*-5-*sulphonate*.—Potassium 2-chlorotoluene-5-sulphonate (123 g.), prepared from Nevile and Winther's *o*-toluidinesulphonic acid and nitrated under the conditions already described (Wynne, this vol., p. 699), gave a mixture of two potassium chloronitrosulphonates (130·2 g.), one of which was unusually sparingly soluble in water. Dissolved in 2100 c.c. of boiling water, this product furnished a separation (75·7 g.) in small granules : these, redissolved in the same volume, crystallised uniformly in anhydrous, pale yellow scales (58·0 g.). Later separations from the two mother-liquors, each concentrated initially to 350 c.c. and eventually to dryness, gave a series of easily soluble fractions (78 g.) crystallised in either small brown prisms or pale yellow scales, both anhydrous, which on recrystallisation did not separate invariably in the one form or the other and for closer investigation were converted into sulphonyl chloride.

Much unchanged salt remained when any of these fractions, suspended in phosphorus oxychloride, was heated under the usual conditions with an equal weight of phosphorus pentachloride : for complete conversion double this amount had to be used. But while the product from the less soluble salt, being almost free from oil, was easily dealt with, that from the more soluble proved troublesome owing to the slow—and doubtless incomplete—separation of crystalline material from the orange-coloured " oil " that accompanied it. Even so, the difference in the proportion of the isomeric sulphonyl chlorides isolated from the products of nitration of the sulphonate and of the sulphonyl chloride was not less marked than with the corresponding 4-derivatives.

2-*Chloro*-3-*nitrotoluene*-5-*sulphonic acid*. The salts of this acid were obtained by hydrolysis of the sulphonyl chloride, m. p. 52°, with the appropriate alkali hydroxide. The *barium* salt crystallised in moderately soluble, long, slender, silky needles [Found : Ba, 19·6; H_2O, 8·9. $(C_7H_5O_5NClS)_2Ba,3\frac{1}{2}H_2O$ requires Ba, 19·6; H_2O, 9·1%]. The potassium and sodium salts were anhydrous, but differed widely in solubility, the former separating in sparingly soluble, lustrous scales, difficult to wet when once dry. The *chloride*, m. p. 52°, obtained in 90% yield by the use of twice the calculated amount of phosphorus pentachloride, crystallised from ligroin in characteristic clusters of monoclinic, pale yellow prisms, some with straight extinction and others with an extinction angle of 40° (Found : Cl, 26·2. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). The *amide*,

m. p. 201°, crystallised from 92% alcohol in short slender needles (Found: N, 11·0. $C_7H_7O_4N_2ClS$ requires N, 11·2%).

2-*Chloro*-3-*aminotoluene*-5-*sulphonic acid*. The acid, obtained in 77% yield by reduction of the nitro-salt, crystallised from water in long, thin, easily soluble, anhydrous needles. It diazotised only very slowly at the ordinary temperature but more readily at 35—40°. The *potassium* salt, highly soluble in water, separated from 25% alcohol in long, thin, anhydrous scales (Found: K, 14·7. $C_7H_7O_3NClSK$ requires K, 15·1%). The sodium salt also formed anhydrous scales from 25% alcohol.

The constitution of these products was ascertained by conversion of the chloroamino- into the dichlorotoluene-5-sulphonic acid, the chloride (m. p. 90°) and amide (m. p. 184°) of which, by mixed m. p.'s, proved to be identical with the corresponding derivatives of 2 : 3-dichlorotoluene-5-sulphonic acid (Silvester and Wynne, this vol., p. 694).

2-*Chloro*-4-*nitrotoluene*-5-*sulphonic acid*. As repeated fractionation of the more soluble nitro-salt failed to bring about uniformity in crystalline appearance or marked variation in solubility, the whole in 10—12 g. quantities was converted into sulphonyl chloride under reflux with phosphorus pentachloride (2 pts.) and oxychloride (2·5 pts.). From 67·7 g., the yield of crude, semi-solid brown product was 61·3 g., which by fractionation gave prisms, m. p. 97°, irregular in form (12·4 g.) and an oil (42·3 g.) from which nothing crystalline had separated after the lapse of two months.

The *barium* salt, obtained by hydrolysis of the sulphonyl chloride, crystallised in moderately soluble, pale brown needles [Found: Ba, 20·2; H_2O, 5·9. $(C_7H_5O_5NClS)_2Ba,2H_2O$ requires Ba, 20·4; H_2O, 5·4%]. The potassium salt, anhydrous, and sodium salt ($\frac{1}{2}H_2O$) formed easily soluble, pale yellow needles. The *chloride*, m. p. 97°, sparingly soluble in ligroin, crystallised in elongated prisms with an oblique termination, of high double refraction, and with an extinction angle of 40° (Found: Cl, 26·2. $C_7H_5O_4NCl_2S$ requires Cl, 26·3%). The *amide*, m. p. 172°, separated from 92% alcohol in easily soluble, thin, flat needles (Found: N, 11·0. $C_7H_7O_4N_2ClS$ requires N, 11·2%).

2-*Chloro*-4-*aminotoluene*-5-*sulphonic acid*. The amino-acid, obtained in 62·5% yield, crystallised in sparingly soluble, short, anhydrous needles, and when dry, was wetted by water with difficulty. It has also been prepared by sulphonating 2-chloro-*p*-toluidine and, coupled with β-naphthol, furnishes scarlet lakes (cf. Badische Anilin- und Soda-Fabrik, D.R.-P. 175378, 217370). The *sodium* salt formed sparingly soluble, long but thin, anhydrous scales (Found: Na, 9·2. $C_7H_7O_3NClSNa$ requires Na, 9·5%).

Hydrolysis of the uncrystallisable oil (42·3 g.) by alkali left a resin (8 g.) which was not further examined. From the filtrate by reduction, a 62% yield of amino-acid (15·9 g.) was obtained, the sodium salt from which was unlike that just described and about twice as soluble, but on the addition of one-half the calculated quantity of hydrochloric acid gave a precipitate (7·5 g.) identified as the 4-amino-acid. That left in solution (8·1 g.), converted into dichloro-derivative, furnished an oily sulphonyl chloride (7·7 g.) which in the course of 10 days deposited radiate groups of needles (2·4 g.), but neither from these nor from the remaining oil (4·7 g.) was any definite substance isolated.

2 : 4-*Dichlorotoluene*-5-*sulphonic acid*. The *sodium* salt crystallised in moderately soluble, long needles (Found: Na, 8·7; H_2O, 6·1. $C_7H_5O_3Cl_2SNa,H_2O$ requires Na, 8·8; H_2O, 6·4%). The chloride, m. p. 72°, and amide, m. p. 176°, were identical with those formed from 2 : 4-dichlorotoluenesulphonic acid (Wynne and Greeves, P., 1895, **11**, 151).

The composition of the product obtained from potassium 2-chlorotoluene-5-sulphonate (123 g.) by nitration was: less soluble K salt (3-nitro-), 58 g.; more soluble K salt (4-nitro-), 26·5 (12·4 + 14·1, calc. from 7·5 g. of amino-acid on the basis of 62·5% yield); oil (sulphonyl chloride) from more soluble salt, calc. as K salt, 22·2; total, 106·7.

(V) *Nitration of* 2-*Chlorotoluene*-5-*sulphonyl Chloride*.—According to Davies (J., 1922, **121**, 788), nitration of 2-chlorotoluene-5-sulphonyl chloride furnishes a 90% yield of the 3-nitro-derivative, together with " several small rhombohedral crystals, m. p. 85—88° " occurring in final mother-liquors but in amount insufficient for analysis or identification. In view of the presence of much 4-nitro-compound in the product from the potassium salt (*supra*), repetition of the nitration of the chloride under Davies' conditions was thought desirable.

From 88 g. of the sulphonyl chloride, 99·7 g. of the dry nitro-compound, wholly soluble in ligroin, were obtained. Fractionally crystallised, this product gave 71·7 g. of the 3-nitro-derivative, m. p. 52°, together with 28 g. of an oil which slowly deposited needle-like crystals (16·1 g.) becoming almost semi-solid. These crystals on fractionation from petrol gave 6·6 g. of the 3-nitro-derivative, m. p. 52°, and an oil (9·1 g.) from which three separations in four-sided scales (1·05 g.), m. p. 97°, were subsequently removed and identified as the 4-nitro-compound. Later, this oil became semi-solid : dried on a porous tile, it lost 2·5 g., leaving a solid which, fractionally crystallised from petrol, gave 2·7 g. of the 3-nitro-derivative, m. p. 52°, followed by separation of the 4-isomeride in small tablets (1·15 g.), m. p. 84—89°—these recrystallised had m. p. 97°.

Left during some weeks, the oil (11·3 g.) separated from the 16·1 g. of crystals had deposited needles (2·5 g.), m. p. 48—50°. These removed, the residue on hydrolysis with caustic potash gave 6·2 g. (chloride equiv., 5·8 g.) of the characteristic non-wetting scales of the potassium 3-nitro-sulphonate, but nothing definite could be isolated from the mother-liquors.

Summarised, the yield of isomeric nitro-derivatives from 2-chlorotoluene-5-sulphonyl chloride was 89·3 g. of 3-nitrosulphonyl chloride (m. p. 52°) and 2·2 g. of 4-nitrosulphonyl chloride (m. p. 97°).

It may be of interest to record that crystallised 2-chlorotoluene-5-sulphonyl chloride (85 g.) prepared in 1895 and kept in a stoppered bottle in the dark had in the course of 40 years become largely hydrolysed. No pressure was observed and only a faint odour of hydrogen chloride noticed on opening the bottle, but on extraction by warm water from the unchanged chloride (19·2 g.) the highly acid solution obtained, neutralised by caustic potash, gave a dry residue (74 g.) of potassium salt containing some chloride. This agrees well with the amount (71·5 g.) calculated on the assumption that atmospheric moisture had diffused inwards and hydrogen chloride outwards owing to imperfect stoppering.

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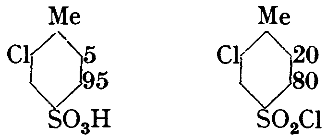
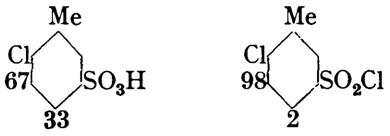
Addendum.

By G. MACDONALD BENNETT.

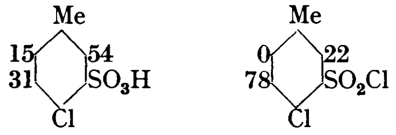
THE experimental results recorded in the foregoing papers are collected in summarised form in the following formulæ, the figure attached to any position being the observed percentage of mononitration product in which the nitro-group has entered that position :



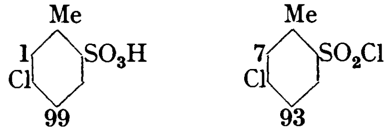
(A)



(B)



(C)



(D)

(E)

The most noticeable feature of these results is the difference in the proportions of the products when a sulphonyl-chloride is subjected to nitration in place of the corresponding free sulphonic acid. Five isomeric acids have been studied (A—E), and each compared with the acid chloride on nitration. In three of these considerable nitration of the free acid takes place in the position *ortho* to the sulphonic group (A 95%, B 33%, C 54%), but nitration of the corresponding chloride yields markedly lower proportions of *ortho*-substitution product (A 80%, B 2%, C 22%). In the remaining two instances there is no significant difference in behaviour between free acid and acid chloride, no *ortho*-nitration having been detected in one (D) and the variation in proportion of *ortho*-product in the other (E) being in the usual direction but almost negligible.

Substitution in the *ortho*-position is a common occurrence as a secondary feature of orientation by *meta*-directive groups such as NO_2,CHO,CO·R, CO_2H, etc., and this, occurring in spite of an inherent deactivating inductive effect, has been explained by Lapworth and Robinson as due to the association of a reagent such as nitric acid with the group in question, *ortho*-substitution being thereby favoured (*Mem. Manchester Phil. Soc.*, 1928, **72**, 43). The entry of the substituent into the position *ortho* to SO_3H is well known in nitrations (compare Obermiller, *J. pr. Chem.*, 1914, **89**, 70; 1930, **126**, 257) and, apart from contributory directive influences of other substituents already present (as in the cases now considered), this may in part be due to a similar cause as with the other *m*-directive groups above mentioned. The nitration of benzenesulphonic acid may, however, also be compared with the substitution of benzoic acid in alkaline solution recently re-examined by J. C. Smith (J., 1934, 213), who found the proportions : *o*- 47%, *m*- 33%, *p*- 20%. As regards benzenesulphonic acid the work of Limpricht (*Annalen*, 1875, **177**, 60) was corrected by Obermiller (*loc. cit.*), who found : *o*- 27%, *m*- 63%, *p*- 10%. The production of a considerable proportion of *para*-isomeride is the significant common feature of these two results which differentiates them in behaviour from such a substance as free benzoic acid. In both there appears to be a blend of *m*- with *op*-direction and an exaggeration of *o*-substitution. Bearing in mind that the benzoate in alkaline solution should be completely ionised and that the sulphonic acid, being a strong acid, should be completely ionised but, in solution in concentrated sulphuric acid, not completely dissociated, these two results are similar in type.

The important point here is that, whatever may be the mechanism responsible for these results, we must expect a suppression of both *o*- and *p*-products when the SO_3H group is converted into SO_2Cl, and this for several reasons. First, the SO_2Cl group will according to accepted views have a stronger electron-attracting inductive effect than SO_3H and so must tend to suppress *op*-substitution; secondly, the sulphonyl chloride is incapable of ionisation, so the group $SO_3^{\ominus}$ is eliminated; and lastly, if the *o*-nitration is in part due to an attraction of the nitric acid to the SO_2 group, the presence of the chlorine atom will counteract this by reducing any slight basic property of this group.

The operation of the change from acid to acid chloride upon orientation in nitration has already been noted in some analogous cases. Some figures for benzoic and benzylsulphonic acids are :

	Products, %.		
Substance nitrated.	*m*-.	*o*-.	Reference.
$C_6H_5·CO_2H$ (at 0°)	80	18·5	Hollemann, *Rec. trav. chim.*, 1899, **18**, 267.
$C_6H_5·COCl$ (at − 12·5°)	90	8—10	Cooper and Ingold, J., 1927, 836.
$C_6H_5·CH_2·SO_3H$ (at − 5—10°)	14	33·5	Ingold, Ingold, and Shaw, J., 1927, 813.
$C_6H_5·CH_2·SO_2Cl$	51	17	,, ,, ,, ,,

However, the nitration of benzenesulphonyl chloride itself, which is the most directly relevant case, appears not to have been studied hitherto. A study of this is now being made in Sheffield and it has been found that nitration with mixed acid yields approximately 90% of the *m*-product. A full account of this work will be published in due course. This result in conjunction with that of Obermiller quoted above (*o*-direction by SO_3H, 27%) confirms the tendency under discussion.

Other features of the results require little comment. The familiar principles that *op*-directive influences tend to take precedence of so-called *m*-directive effects, and that the *o*/*p* ratio for the methyl group is high and that of the chlorine atom is low suffice to account in a general way for the observations in cases A, C, D and E. Thus chlorine dominates the substitution of A, its low *o*/*p* ratio leading to attack in position 5 rather than 3 ,and the high *o*-directing power of methyl causes position 6 to be the next favoured. The same high *o*-directive power of methyl is again evident with C. The SO_3H group here acts chiefly to suppress substitution *para* to itself, and SO_2Cl inhibits more efficiently in both *p*- and *o*-positions. In D, chlorine and methyl jointly direct into position 4 with 2 as secondary position. Methyl and chlorine again show competitive *o*-direction in E, the SO_3H and the SO_2Cl group serving as restraints to prevent attack of position 3.

The substitution of B, although the effect of exchange of acid and acid chloride groups is clear, is nevertheless remarkable in that no reason is apparent why substitution does not occur to a considerable extent in position 6 between methyl and sulphonic acid groups.

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