157. *Studies in the Toluene Series. Part V.* Sulphinic and Sulphonic Acids of the Mono- and Di-chlorotoluenes.*

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In the course of their investigations of the isomeric mono- and di-chlorotoluenes, Wynne (J., 1892, **61**, 1042) and Wynne and Greeves (P., 1895, **11**, 151) converted these substances into their sulphonic acids for the purpose of characterising them. For the most part, the relative positions assumed by the SO_3H groups were not at that time ascertained, but since

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* Earlier papers—Wynne, J., 1892, **61**, 1036, 1042; Wynne and Greeves, P., 1895, **11**, 151; Wynne and Bruce, J., 1898, **73**, 730.

such information might be expected to throw light on the comparative directing effect of the Cl and CH_3 radicals, it seemed desirable to continue the work, particularly as a parallel study had been made of the corresponding nitro-derivatives (Cohen and Dakin, J., 1902, **81**, 1334).

The methods employed were two in number : (i) Introduction of a second Cl atom into the molecule of a monochlorotoluenesulphonic acid of known constitution by nitration, reduction and the Sandmeyer reaction, and comparison of the dichlorotoluenesulphonic acid thus obtained with acids formed from dichlorotoluenes by direct sulphonation; (ii) replacement of the NH_2 radical in dichlorotoluidines of known constitution by the SO_2H group, which in Gattermann's process depends on the interaction of diazonium acid sulphites with copper powder, and oxidation of the sulphinic to sulphonic acids (*Ber.*, 1899, **32**, 1136).

By the first of these methods the constitution of the 2 : 5- and 3 : 4-dichlorotoluenesulphonic acids was ascertained by Wynne and Greeves and by the second that of the remaining members in the course of the present investigation. In the table, in which the relative position of the SO_3H group in each acid is given, the constitution of the nitro-derivatives obtained by nitrating the dichlorotoluenes (Cohen and Dakin, *loc. cit.*) is also included for purposes of comparison.

Dichlorotoluene (Me in position 1).	Position of SO_3H.	M. p. of SO_2Cl.	M. p. of $SO_2{\cdot}NH_2$.	Position of NO_2 in nitro-derivative.
2 : 3	6 (89%) 5 (11%)	51—52° 87	228° 185	6 (10%) 4 (90%)
2 : 4	5	72	176	5
2 : 5	4	43	191	4
2 : 6	3	60	204	3
3 : 4	6	82	189	6
3 : 5	2	45	168	2

These results are in general agreement with the course of substitution in benzene derivatives except in two noteworthy cases, the remarkable feature of which is the difference in position taken up by the entrant radical according as it is the SO_3H or the NO_2 group. Of these departures from uniformity the first is that recorded for 2 : 3-dichlorotoluene in the table; the second is exhibited by *p*-chlorotoluene, which when sulphonated gives as product a mixture of the 2-sulphonic acid (86%) with the 3-sulphonic acid (14%), but when nitrated, a mixture of the 2-nitro- (42%) with the 3-nitro-derivative (58%) (Wynne and Bruce, J., 1898, **73**, 733; Van der Arend, cf. Holleman, " Die direkte Einfuhrung von Substituenten in den Benzolkern," ed. 1910, p. 235).

In connexion with the synthesis of 2 : 6-dichlorotoluene-3-sulphonic acid from 2 : 6-dichloro-*m*-toluidine, opportunity was taken to investigate the chlorination of aceto-*m*-toluidide, which seemed to have received a less complete study than that of its *o*- and *p*-isomerides. Reverdin and Crépieux, using sodium chlorate and hydrochloric acid as the agent, isolated 6-chloro- and 4 : 6-dichloro-aceto-*m*-toluidide from the product (*Ber.*, 1900, **33**, 2503), but both their description and that of later workers under other conditions suggest the presence of one or more isomerides. In our experiments, after it had been found that the passage of chlorine (1 mol.) into a solution of aceto-*m*-toluidide in glacial acetic acid gave in addition to mono-substituted products both 4 : 6- and 2 : 6-dichloro-derivatives mixed with a noteworthy amount of unchanged toluidide, rendering the isolation of any one constituent difficult, it proved possible by the use of sulphuryl chloride to effect either mono- or di-substitution at will. Of the three monochloro-, the 6-, and of the two dichloro-, the 4 : 6- is the chief product.

EXPERIMENTAL.

*Monochlorination of Aceto-*m*-toluidide.*—For the production of 6-chloro-*m*-toluidine in the absence of more highly chlorinated compounds the best methods were found to be :

(i) Chlorination of aceto-*m*-toluidide in dilute aqueous solution (1 g. in 250 c.c.) with the calculated volume of chlorine water. After the lapse of a day the solution was extracted with chloroform, and the oily extract hydrolysed. From 34 g. of aceto-*m*-toluidide, 7 g. of 6-chloro-

m-toluidine, m. p. 85—86°, were obtained, the remainder of the product being mostly unchanged *m*-toluidine.

(ii) Chlorination with sulphuryl chloride (cf. Wynne, *loc. cit.*). In this preparation, sulphuryl chloride (1 pt.) was added to a solution of aceto-*m*-toluidide (1 pt.) in dry carbon disulphide (5 pts.) and, after removal of the solvent by distillation, the viscid residue which did not solidify was hydrolysed by hot hydrochloric acid. From the crystalline hydrochloride, which separated on cooling, almost pure 6-chloro-*m*-toluidine was obtained, but addition of alkali to the mother-liquor precipitated an oily mixture, the yield of chlorinated base being 98% of that calculated.

Cumulative fractional distillation separated from this oily mixture further quantities of 6-chloro-*m*-toluidine and a small amount of unchanged *m*-toluidine. The intervening fractions, b. p. 210—220°, 220—225° and 225—230°, when dissolved separately in 2*N*-sulphuric acid gave, on cooling, the remainder of the 6-chloro-compound as the comparatively insoluble sulphate. Re-acetylated, the oily bases separately regenerated from the soluble sulphates were fractionally extracted by cold alcohol, leaving a residue of 2-chloroaceto-*m*-toluidide, m. p. 132°, which on oxidation gave 2-chloro-3-acetamidobenzoic acid, m. p. 205°, whilst the more soluble constituent, m. p. 88—90°, proved to be 4-chloroaceto-*m*-toluidide, since in common with mixed acetyl derivatives remaining as a gummy mass after removal of the solvent, it was converted almost quantitatively into 4-chloro-3-acetamidobenzoic acid, m. p. 263°, on oxidation.

Three monochloro-derivatives therefore were produced under these conditions, the yields being approximately 80% of 6-chloro-, 12% of 4-chloro- and 8% of 2-chloro-aceto-*m*-toluidide.

Further chlorination of 6-chloroaceto-*m*-toluidide (5 pts.), dissolved in carbon disulphide, by sulphuryl chloride (4 pts.) gave a product from which after removal of the solvent the isomeric dichloroaceto-*m*-toluidides could not be separated by crystallisation and were therefore hydrolysed. Eventually a still imperfect separation of the bases was achieved by converting them into the sulphates and fractionally decomposing the mixture, suspended in water, by aqueous caustic soda. The fractions extracted by ether and recrystallised from light petroleum (b. p. 90—110°) gave 4 : 6-dichloro-*m*-toluidine, which separated in small hard prisms, m. p. 85°, from the more soluble 2 : 6-isomeride, m. p. 60°, in flat needles.

(I) 3-*Chlorotoluene-sulphinic and -sulphonic Acid.*—(*a*) 3-Chlorotoluene-4-sulphinic acid was prepared by diazotising 3-chloro-*p*-toluidine (13 g.), b. p. 226—230°/759 mm., dissolved in sulphuric acid (30 g. in 100 c.c. of water) at 5—10°, adding more sulphuric acid (40 g. with 30 c.c. of water), and saturating the solution with sulphur dioxide (25 g.) at about 0°. A slow current of the gas being maintained, copper paste—obtained by decomposing copper sulphate solution with zinc dust—was stirred into the product until nitrogen was no longer evolved. The mixture, rendered alkaline with caustic soda, was filtered and excess of sulphuric acid added to the filtrate, whereupon the sulphinic acid partly separated as a flocculent mass, the remainder being extracted by ether. Recrystallised from this solvent, it formed silky needles, m. p. 110°, but decomposed somewhat readily. The *barium* salt, obtained by extracting the crude acid with hot baryta solution, crystallised in moderately soluble, radiating masses of thin scales [Found : Ba, 23·2; H_2O, 12·0. $(C_7H_6O_2ClS)_2Ba,4H_2O$ requires Ba, 23·3; H_2O, 12·2%].

Potassium 3-*chlorotoluene-4-sulphonate*, formed by oxidising the sulphinate with potassium permanganate, tended to give supersaturated solutions from which it separated in anhydrous irregular prisms (Found : K, 16·0. $C_7H_6O_3ClSK$ requires K, 16·0%). The *chloride* crystallised from ligroin in splendid rhombs, m. p. 46° (Found : Cl, 31·8. $C_7H_6O_2Cl_2S$ requires Cl, 31·6%), and the *amide* from aqueous alcohol in scales, m. p. 186° (Found : N, 6·8. $C_7H_8O_2NClS$ requires N, 6·8%).

(*b*) 3-Chlorotoluene-6-sulphinic acid, prepared from 5-chloro-*o*-toluidine (b. p. 245—247°/745 mm.) by the method already described, was isolated as a mass of radiating needles, m. p. 102—103°. The *barium* salt crystallised from dilute solution in long flat needles [Found : Ba, 23·1; H_2O, 11·9. $(C_7H_6O_2ClS)_2Ba,4H_2O$ requires Ba, 23·3; H_2O, 12·2%] or as dihydrate (Found : H_2O, 6·8%) in a hard mass of scales from concentrated solutions quickly cooled. By oxidation it furnished the 6-sulphonate which, as its chloride, m. p. 54°, and amide, m. p. 185°, showed, was identical with the product obtained from *m*-chlorotoluene by sulphonation (Wynne, *loc. cit.*), thus confirming the constitution of that acid regarded as probable by Schraube and Romig (*Ber.*, 1893, **26**, 578).

(II) *Dichlorotoluene-sulphinic and -sulphonic Acids.*—As Cohen and Dakin were unable to confirm the statement that 2 : 3-dichlorotoluene, differing from its isomerides, gives two sulphonic acids on sulphonation, an independent scrutiny of the reaction was made by Dr. (now Prof.) Kenner some years later, to whom our thanks are due for his report which is summarised as follows :

2 : 3-Dichlorotoluene (50 g.), prepared by each of the first two of the three methods employed by Wynne and Greeves (*loc. cit.*), was sulphonated by shaking with 10% oleum (100 g.) at 50°, more of the acid (50 g.) being added at the end of 1½ hours. On completion of the reaction in the course of 3 hours, the product was poured on to ice, a trifling amount of unchanged dichlorotoluene removed by distillation with steam, and the solution neutralised by baryta. Following exhaustive extraction of the barium sulphate sludge, the contents of the solution were fractionally crystallised, which brought about the separation of two salts differing sharply in solubility and appearance—the less soluble, granules and the more soluble, needles. The less soluble barium salt gave an anhydrous *potassium* salt crystallising in scales or needles according to conditions (Found : K, 14·0. $C_7H_5O_3Cl_2SK$ requires K, 14·0%), a chloride in radiate needles, m. p. 50°, and an amide, m. p. 228° ; whereas the more soluble barium salt furnished an anhydrous potassium salt crystallising in long prisms (Found : K, 14·0%), a chloride in large prisms, m. p. 88°, and an amide in scales, m. p. 183°.

In the first sulphonation, 2·8 g. of unchanged dichlorotoluene were recovered and 51·6 g. of potassium salt obtained (calc., 73·6 g.) exclusive of residues and last fractions, the yield from the less soluble barium salt being 44·7 g. as against 6·9 g. from the other. With the second sulphonation, these figures were 47·4 and 4·6 respectively. Later, it was shown (*v. infra*) that the sulphonic group occupies the 6-position in the less but the 5-position in the more soluble barium salt, whence it follows that, on the average, the production of the former is eightfold that of the latter.

On hydrolysis in orthophosphoric acid suspension with superheated steam, 2 : 3-dichlorotoluene was recovered from each salt, and that collected from the 6-isomeride, when resulphonated, gave the two series of derivatives as at first.

(i) 2 : 3-*Dichlorotoluene*-6-*sulphinic acid*. For a supply of the 5 : 6-dichloroaceto-*o*-toluidide (D.R.-P. 217,896) we were indebted to the Badische Anilin- und Soda-Fabrik. It was a white crystalline powder, crystallising from aqueous alcohol in needles, m. p. 143°, and on hydrolysis with its own weight of 50% sulphuric acid at 90° gave the sulphate—sparingly soluble in water—from which the base, m. p. 33°, b. p. 288—290°/739 mm., was obtained.

Suspended in dilute sulphuric acid, the sulphate submitted to the Gattermann reaction gave a product in which the whole of the sulphinic acid was retained in the filter cake. This, extracted by cold 2*N*-caustic soda, precipitated from the concentrated solution by acidification, and crystallised from ether, had m. p. 133°, dissolved readily in alcohol or ligroin but only sparingly in water, benzene or chloroform and was unstable. The *barium* salt formed rosettes of flattened needles [Found : Ba, 20·8 ; H_2O, 11·1. $(C_7H_5O_2Cl_2S)_2Ba,4H_2O$ requires Ba, 20·9 ; H_2O, 11·0%]. On oxidation, it furnished the 6-sulphonate which, as its chloride, m. p. 51—52°, and amide, m. p. 228°, showed, was identical with the salt obtained from the major sulphonation product of 2 : 3-dichlorotoluene.

(ii) 2 : 3-*Dichlorotoluene*-5-*sulphonic acid*. Although 5 : 6-dichloro-*m*-toluidine (m. p. 88° ; Wynne and Greeves, *loc. cit.*) would have served the purpose, the source of this acid was 3-chloro-*o*-toluidine-5-sulphonic acid (D.R.-P. 218370, 229525) for a supply of which we were again indebted to the Badische Anilin- und Soda-Fabrik. This *o*-toluidine derivative crystallised from water in colourless needles, and its *barium* salt in blunt needles [Found : Ba, 21·4 ; H_2O, 8·3. $(C_7H_7O_3NClS)_2Ba,3H_2O$ requires Ba, 21·7 ; H_2O, 8·5%]. When heated with 75% sulphuric acid at 160°, it gave 3-chloro-*o*-toluidine as an oil, the acetyl derivative of which had m. p. 163° (cf. D.R.-P. 218370).

By Sandmeyer's method it was converted into the 2 : 3-dichlorotoluene-5-sulphonic acid, a 97% yield being obtained, which by its chloride, m. p. 88°, and amide, m. p. 184—185°, was shown to be identical with the minor sulphonation product of 2 : 3-dichlorotoluene. The *barium* salt crystallised in silky needles [Found : Ba, 20·1 ; H_2O, 8·5. $(C_7H_5O_3Cl_2S)_2Ba,3H_2O$ requires Ba, 20·5 ; H_2O, 8·1%], and the *sodium* salt in needles (Found : Na, 8·3 ; H_2O, 3·5. $C_7H_5O_3Cl_2SNa,\frac{1}{2}H_2O$ requires Na, 8·6 ; H_2O, 3·3%).

2 : 3-*Dichloro*-p-*toluidine*. The 2 : 3-dichloro-*p*-toluidine required for the preparation of 2 : 3-dichlorotoluene-4-sulphonic acid was obtained by reducing the 4-nitro-derivative formed when 2 : 3-dichlorotoluene is nitrated. Preliminary experiments showed that Cohen and Dakin's method of shaking the dichloro-derivative with 80% nitric acid (*loc. cit.*) was ill adapted for preparation in bulk. Nitration in glacial acetic acid solution was also unsatisfactory, but the following procedure gave good results and, without modification, was adopted also in later nitrations.

To 2 : 3-dichlorotoluene (64 g.), partly dissolved by stirring in concentrated sulphuric acid (50 c.c.), was added gradually a cold mixture of nitric acid (*d* 1·42, 1 mol.) with sulphuric acid

(50 c.c.) at a temperature not exceeding 50°. When all had been added, stirring was continued at 50° for $\frac{1}{2}$ hour and while the mixture cooled. The nitro-compound, obtained in pellets, was easily collected on asbestos, the filtrate on dilution giving less than 0·5 g. of a pasty oil which on reduction and acetylation gave an impure acetyl derivative, m. p. 150—160°, indicating the probable presence of the 6-nitro-isomeride in minute amount.

The crude product formed a hard butter-like mass, m. p. 47°, and clarifying at 50°. Crystallised from petrol or from alcohol–acetic acid, it had m. p. 50—51° and was highly soluble in the usual organic solvents, but, although a mixture, could not be purified by fractional distillation under reduced pressure (*ca.* 270°/40 mm.) or by crystallisation. On reduction with tin and hydrochloric acid it gave a dichlorotoluidine which was not completely crystalline: the solid constituent had m. p. 40° and its acetyl derivative, m. p. 131°, but the acetyl derivative from the liquid melted at a higher temperature. Thereupon the acid solution obtained by reducing 40 g. of dichloronitrotoluene was fractionally neutralised, the liberated base being removed by distillation with steam, giving

(a) when $\frac{2}{3}$ of the necessary soda added	11 g. solid base
(b) when $\frac{1}{6}$ more of the necessary soda added	15 g. pasty ,,
(c) when excess of soda added	2 g. oily ,,

The oil, removed from the pasty separation by spreading on porous earthenware, left an additional 11 g. of the solid base, m. p. 40°, b. p. 271—276°/40 mm., giving an acetyl derivative, m. p. 131°, and being therefore pure 2 : 3-dichloro-*p*-toluidine (Cohen and Dakin gave m. p. 40—42° and 128—129° respectively). Extracted from the porous earthenware by chloroform, the oil (4 g.) united with (c) and acetylated proved to be a mixture of the foregoing, m. p. 131°, with a smaller amount of a substance, m. p. 140°, which by a mixed m. p. test was identified as 2 : 3-dichloroaceto-*o*-toluidide. The proportion of the 6-amino-derivative in the reduction product was estimated to be about 10%.

(iii) 2 : 3-Dichlorotoluene-4-sulphinic acid, prepared from 2 : 3-dichloro-*p*-toluidine, had m. p. 142° and its *barium* salt crystallised from hot solution in scales changing to needles after some time in the cold [Found : Ba, 23·1; H_2O, 3·7. $(C_7H_5O_2Cl_2S)_2Ba,H_2O$ requires Ba, 22·8; H_2O, 3·0%].

Potassium 2 : 3-*dichlorotoluene*-4-*sulphonate*, obtained from the sulphinate by oxidation, crystallised in anhydrous nacreous scales (Found : K, 13·9. $C_7H_5O_3Cl_2SK$ requires K, 14·0%); the chloride separated from ligroin in prisms, m. p. 40—41°; and the *amide* from alcohol in scales, m. p. 237° (Found : N, 6·2. $C_7H_7O_2NCl_2S$ requires N, 5·8%).

(iv) 2 : 4-*Dichlorotoluene*-5-*sulphinic acid*. The source of the acid was 4 : 6-dichloro-*m*-toluidine, part of which was isolated from the dichlorination product of aceto-*m*-toluidide (p. 693), and the remainder more easily as sole product from 2 : 4-dichlorotoluene by nitration and reduction as described for the 2 : 3-derivative (above). Conversion into sulphinic acid followed the usual procedure : the product separated from ether in irregular groups, m. p. 132°. The *potassium* salt, less soluble than the barium salt, crystallised in scales (Found : K, 13·8; H_2O, 6·7. $C_7H_5O_2Cl_2SK,H_2O$ requires K, 13·9; H_2O, 6·4%). By oxidation it gave potassium 2 : 4-dichlorotoluene-5-sulphonate, containing apparently $2H_2O$ of which only one mol. was lost at 190° (Found : K, 12·2; H_2O, 6·3. $C_7H_5O_3Cl_2SK,2H_2O$ requires K, 12·4; H_2O, 5·7%), but otherwise—as its chloride, m. p. 72°, and amide, m. p. 176°, showed—identical with the sulphonation product from 2 : 4-dichlorotoluene (Wynne and Greeves, *loc. cit.*).

(v) 2 : 6-*Dichlorotoluene*-3-*sulphinic acid*. The 2 : 6-dichloro-*m*-toluidine required for the preparation of this acid was obtained by nitrating 2 : 6-dichlorotoluene, b. p. 199—200°/760 mm., under the conditions described for the 2 : 3-isomeride (above). The nitro-derivative crystallised from alcohol–ether had m. p. 50° (cf. Cohen and Dakin, *loc. cit.*) and on reduction gave solely the amine, m. p. 57°, b. p. 266—268°/760 mm., identical with the 2 : 6-dichloro-*m*-toluidine isolated from the dichlorination product of aceto-*m*-toluidide (p. 693).

Owing to the marked instability of the diazonium sulphite solution, leading to the formation of much red tarry material during the passage of sulphur dioxide, conversion of the base into sulphinic acid, even at − 10°, gave only a poor yield. The acid had m. p. *ca.* 105° and its *barium* salt crystallised in clusters of needles [Found : Ba, 20·8; H_2O, 10·4. $(C_7H_5O_2Cl_2S)_2Ba,4H_2O$ requires Ba, 20·9; H_2O, 11·0%]. By oxidation this gave the 3-sulphonate which, as its chloride, m. p. 59°, and amide, m. p. 203°, showed, was identical with the salt obtained from 2 : 6-dichlorotoluene by sulphonation.

(vi) 3 : 5-*Dichlorotoluene*-2-*sulphinic acid*. This was prepared from 3 : 5-dichloro-*o*-toluidine obtained by passing the calculated quantity of chlorine slowly into a cold solution of 5-chloro-aceto-*o*-toluidide (100 g.) in glacial acetic acid (200 g.) and some hours later, after warming the whole to 75° and adding water at 75° (175 c.c.), allowing it to cool. From the separation consisting of almost pure 3 : 5-dichloroaceto-*o*-toluidide (60 g.), m. p. 180°, the base, m. p. 45°, was isolated after hydrolysis by boiling with hydrochloric acid (5 pts.) during 8 hours. The sulphinic acid derived from it was the most stable of the isomerides and, recrystallised from ether or petrol, formed clusters of scales, m. p. 115—116°. Its *barium* salt crystallised in scales [Found : Ba, 20·3; H_2O, 11·9. $(C_7H_5O_2Cl_2S)_2Ba,4H_2O$ requires Ba, 20·9; H_2O, 11·0%]. By oxidation the 2-sulphonate was obtained, the chloride, m. p. 43°, and amide, m. p. 168°, from which were identical respectively with the corresponding derivatives from the sulphonation product of 3 : 5-dichlorotoluene.

(vii) 3 : *5-Dichlorotoluene-4-sulphinic acid.* In the best method found for preparing 3 : 5-dichloro-*p*-toluidine, chlorine (24 g.) was passed during 2 hours into 3-chloroaceto-*p*-toluidide (46 g.) dissolved in glacial acetic acid (184 c.c.), the solution after the lapse of a few hours being warmed to 70°, diluted with warm water (200 c.c.) and then allowed to cool. Hydrolysis of the crystalline separation of 2 : 3-dichloroaceto-*p*-toluidide (25 g.), m. p. 198°, required several hours' boiling with hydrochloric acid (20 pts.) for its completion. The base, b. p. 249°/772 mm., gave by Gattermann's method the sulphinic acid, m. p. *ca.* 127°, the highly soluble potassium salt of which on oxidation furnished *potassium* 3 : *5-dichlorotoluene-4-sulphonate*, this forming moderately soluble, irregular crystals (Found : K, 13·2; H_2O, 6·7. $C_7H_5O_3Cl_2SK,H_2O$ requires K, 13·2; H_2O, 6·1%), convertible into the chloride, prisms, m. p. 56°, and the *amide*, scales, m. p. 154—155° (Found : N, 5·9. $C_7H_7O_2NCl_2S$ requires N, 5·8%).

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