

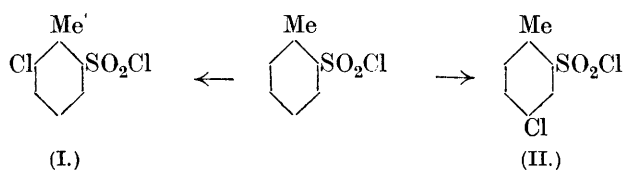
XCVII.—*The Cumulative Effect of the Chlorine Atom and the Methyl and Sulphonyl Chloride Groups on Substitution in the Benzene Nucleus. Part II.*

By WILLIAM DAVIES.

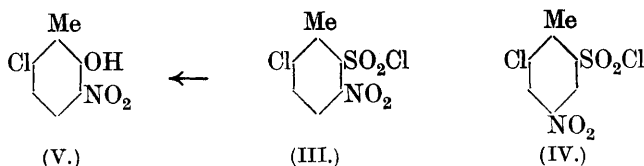
It has been shown in the previous communication, by the nitration of 6-chloro-*p*-toluenesulphonyl chloride, that the para-directing influence of the chlorine atom is greater than that of the sulphonyl chloride group, together with the ortho-directing influence of the methyl group. In order to determine whether the combined para- and meta-directing influences of the methyl and sulphonyl chloride groups would similarly be overpowered, the nitration of 6-chloro-*o*-toluenesulphonyl chloride was studied.

6-Chloro-*o*-toluenesulphonyl chloride (I) was isolated in nearly 40 per cent. yield from the product of chlorination of *o*-toluenesulphonyl chloride. Its constitution was shown by converting it into *o*-chlorobenzoic acid. The other isomeride formed—doubtless 4-chloro-*o*-toluenesulphonyl chloride (II)—boils at the same temperature, and a complete method of separation has not yet been devised.

6-Chloro-*o*-toluenesulphonyl chloride (m. p. 71–72°) was converted into the corresponding *sulphonic acid* and the characteristic *sodium* and *barium* salts. The *amide* (m. p. 180°) was transformed by gentle oxidation into “6-chlorosaccharin” (m. p. 210–212°), which is more than half as sweet as “saccharin,” but has a somewhat astringent taste.

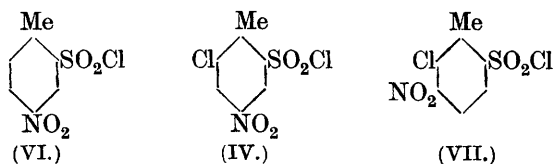


The nitration of 6-chloro-*o*-toluenesulphonyl chloride at 20–30° leads to the formation of a mixture of 6-chloro-3-nitro-*o*-toluenesulphonyl chloride (III) and 6-chloro-4-nitro-*o*-toluenesulphonyl chloride (IV) in the proportion of 40 and 60 per cent. respectively. The two substances can be partly separated by means of light petroleum, in which III is slightly less soluble than IV. A thorough separation is effected by means of the barium salts of the corresponding acids, that derived from III being extremely soluble in alcohol.



6-Chloro-3-nitro-*o*-toluenesulphonyl chloride (III) could not be converted into a chloronitrotoluene by hydrolysis of the sulphonyl chloride group. It was, however, transformed into the sodium salt of a chloronitrocresol by boiling with sodium hydroxide solution. The chloronitrocresol, which could not be benzoylated, had the properties of an *o*-nitrophenol and melted at  $64^{\circ}$ . It was shown to be identical with 6-chloro-3-nitro-*o*-cresol (V), a specimen of which was prepared from 6-chloro-*o*-nitrotoluene in the manner described by Noetting (*Ber.*, 1904, **37**, 1015). The 6-chloro-*o*-nitrotoluene required was obtained in 24·7 per cent. yield by the chlorination of *o*-nitrotoluene at  $55$ – $60^{\circ}$  in the presence of a small proportion of antimony trichloride (compare Jansen, D.R.-P. 107505).

The constitution of 6-chloro-4-nitro-*o*-toluenesulphonyl chloride (IV) was shown by its behaviour towards boiling sodium hydroxide solution. A dark red solution was rapidly formed and the coloration was not destroyed by acidification, but on the contrary the solution stained the skin dark yellow. For purposes of comparison, 4-nitro-*o*-toluenesulphonyl chloride (VI) was boiled with sodium hydroxide solution and similar colorations were produced. It is therefore very probable that the dyes formed by the action of alkali on the chloronitrotoluenesulphonyl chloride are of the same type as those formed by the same treatment of 4-nitro-*o*-toluenesulphonyl chloride. The latter dyes, however, are stilbene derivatives (compare Cain and Thorpe, "The Synthetic Dyestuffs," p. 48), which are never formed by the action of alkalis on derivatives of *m*-nitrotoluene. Hence the chloronitrotoluenesulphonyl chloride under investigation cannot have the formula VII, and must therefore have that indicated by IV.



This research shows that the chlorine atom in 6-chloro-*o*-toluenesulphonyl chloride has a slightly smaller orientating effect than the other two groups acting together, as far as substitution by the

nitro-group is concerned. It is interesting to note that the chlorine atom in 2-chloro-6-nitrotoluene has, under somewhat similar conditions (Morgan and Jones, this vol., p. 187), an almost overwhelming directive influence. It follows that the sulphonyl chloride group has a more powerful orientating effect than the nitro-group.

## EXPERIMENTAL.

### *Purification of o-Toluenesulphonyl Chloride.*

*o*-Toluenesulphonyl chloride, kindly supplied by Messrs. Boots, Ltd., was obtained almost completely pure by distillation in a vacuum after the method of Ullmann and Lehner (*Ber.*, 1905, **38**, 730). It was found advisable to distil under somewhat greater pressure than they used, the difference in boiling points of the ortho- and para-isomerides thus being increased, and the decomposition that ensued being quite negligible. In this way the first fraction finally obtained gave an amide melting at 155°. As *o*-toluenesulphonamide melts at 156.3° (McKie, T., 1918, **113**, 801), the *o*-toluenesulphonyl chloride had evidently been obtained in an almost pure state.

The ortho-isomeride boils at 151°/33 mm. and 154°/36 mm., and the para-isomeride at 164°/33 mm. and 167°/36 mm.

### *6-Chloro-o-toluenesulphonyl Chloride.*

6-Chloro-*o*-toluenesulphonyl chloride was first made by chlorinating *o*-toluenesulphonyl chloride in the presence of antimony trichloride and working up the product as described in the preparation of 2-chloro-*p*-toluenesulphonyl chloride (this vol., p. 860). The mixture of monochloro-*o*-toluenesulphonyl chlorides produced boiled at 165–169°/33 mm., and about 41 per cent. of this liquid solidified on cooling. The solid portion consisted of the desired isomeride in an almost pure state.

A considerable improvement in the method of preparation was effected by using only a small amount of the catalyst. Chlorination so rapid that the temperature (75–90°) was maintained without external heating could be brought about (with anhydrous materials) when the weight of the antimony trichloride was 1 per cent. of the weight of *o*-toluenesulphonyl chloride. With no catalyst present, however, a reaction did not take place at all readily. In this way, by allowing the pale yellow chlorinated product to remain in a freezing mixture, the 6-chlorotoluenesulphonyl chloride separated out, and by filtering at the ordinary temperature (in order to prevent the separation of a eutectic mixture of the isomerides),

it was obtained in greater yield than by the tedious process indicated above.

The chlorinated product (740 grams containing 40 grams of antimony trichloride) gave 270 grams of dry 6-chloro-*o*-toluenesulphonyl chloride, the yield being 38·6 per cent. of the theoretical. The product was almost pure, and after one crystallisation from light petroleum (b. p. 80—100°) melted at 69—70°. It is noteworthy that the yield is materially decreased by using *o*-toluenesulphonyl chloride not completely freed from *p*-toluenesulphonyl chloride.

*6-Chloro-o-toluenesulphonyl chloride* crystallises in large, thick, white prisms closely resembling potassium iodide in appearance, and the smell recalls that of *o*-toluenesulphonyl chloride, but is comparatively faint. The substance is very soluble in cold benzene, much less so in cold light petroleum, and is obtained by recrystallisation from light petroleum (b. p. 60—80°) in plates softening at 71° and melting at 72°. It is very slowly oxidised by fuming nitric acid in a sealed tube at 230° (Found: Cl=31·0.  $C_7H_6O_2Cl_2S$  requires Cl=31·55 per cent.).

The constitution of this chlorotoluenesulphonyl chloride was shown by converting it into *o*-chlorobenzoic acid. The sulphonyl chloride (15 grams) was gently boiled under reflux with a mixture of sulphuric acid (40 c.c.) and water (10 c.c.), and when the oil had disappeared, steam at 150° was passed through the dark red solution until the distillate was no longer cloudy. The oil (5 grams) was extracted with chloroform, dried with calcium chloride, the chloroform removed, and the oil distilled. It boiled almost entirely at 150—160°. The oil (2 grams) was boiled for five hours with potassium permanganate (5 grams) dissolved in water (300 c.c.), and the solution was concentrated and then treated with sulphur dioxide until it became colourless. Long, colourless needles slowly separated, which after drying on a porous plate melted at 140°. The melting point was unchanged by admixture of *o*-chlorobenzoic acid, m. p. 140°.

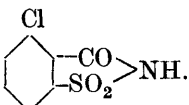
*6-Chloro-o-toluenesulphonic acid*, prepared from the barium salt in the usual way, forms thin, lustrous, non-deliquescent laminae. It is readily soluble in cold water, melts at 60—70°, and when anhydrous melts at about 72° (Found: in anhydrous material, C=40·5; H=3·5.  $C_7H_7O_3ClS$  requires C=40·7; H=3·4 per cent.).

The *amide* crystallises in glistening scales from hot water, in which it is moderately soluble. It melts at 180° and tastes slightly bitter (Found: N=6·7.  $C_7H_8O_2NClS$  requires N=6·8 per cent.).

The *sodium* salt is formed by hydrolysing the sulphonyl chloride with sodium hydroxide solution. It is slightly soluble in boiling

alcohol, readily soluble in hot, and slightly soluble in cold water, from which it separates in large, glistening laminae containing one molecule of water of crystallisation (Found:  $\text{H}_2\text{O}=7.6$ ;  $\text{Na}=9.0$ .  $\text{C}_7\text{H}_6\text{O}_3\text{ClSNa}\cdot\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=7.3$ ;  $\text{Na}=9.3$  per cent.).

The *barium* salt is conveniently made by adding dilute barium chloride solution to a hot solution of the sodium salt, when the barium salt is rapidly precipitated. It is almost insoluble in boiling alcohol, slightly soluble in boiling, and sparingly soluble in cold water, from which it crystallises in small, lustrous flakes containing one molecule of water of crystallisation (Found: loss at  $180^\circ=3.1$ ;  $\text{Ba}=24.1$ .  $[\text{C}_7\text{H}_6\text{O}_3\text{ClS}]_2\text{Ba}\cdot\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=3.2$ ;  $\text{Ba}=24.3$  per cent.).

6-Chloro-*o*-benzoicsulphinide ("6-Chlorosaccharin"), 

Difficulty was encountered in the preparation of this saccharin. When a dilute aqueous solution of 6-chloro-*o*-toluenesulphonamide was boiled with the theoretical amount of potassium permanganate solution, oxidation was extremely vigorous, the pink colour rapidly disappearing. Much of the amide was recovered unchanged, and only a trace of sweet substance was produced. It was found that passing a stream of carbon dioxide through the boiling oxidising solution resulted in a yield of the saccharin of about 1 per cent. After several experiments, the following procedure was found to be satisfactory.

The sulphonamide (10.2 grams) and sodium hydroxide (4 grams) were dissolved in boiling water (1000 c.c.) and a slow stream of carbon dioxide was passed through the solution, the temperature being maintained at  $96-97^\circ$  throughout the experiment. Potassium permanganate (17.4 grams; 10 per cent. excess) dissolved in hot water (250 c.c.) was added very gradually to the sulphonamide solution, the pink colour being allowed to disappear before each fresh addition. After seven hours, when the whole of the permanganate solution had been decolorised, the liquid was concentrated to 400 c.c. and treated with sulphur dioxide until the manganese dioxide had gone into solution. A white precipitate which had formed was filtered off after remaining overnight, and dissolved in dilute sodium hydroxide solution (150 c.c.), phenolphthalein was added, and the solution titrated with dilute hydrochloric acid until the pink colour had disappeared. The chlorosulphonamide, being a weak acid like *o*-toluenesulphonamide (D.R.-P. 64624), was precipitated, while the "chlorosaccharin" remained in solution as the sodium salt. After remaining several hours at the ordinary

temperature the sulphonamide was filtered off, and dilute hydrochloric acid added to the filtrate. The "chlorosaccharin" was rapidly precipitated as a crystalline mass and was collected after remaining overnight, when 3.1 grams melting at 201—207° were obtained.

The yield was increased by concentrating the mother-liquor, advantage being taken of the great solubility of the sulphonamide and the "chlorosaccharin" in cold acetone to separate them from inorganic matter. The amide was separated as before, and the "chlorosaccharin" finally purified by crystallisation from aqueous acetone. The weight of the latter was 4.0 grams and of unchanged amide (m. p. 172—179°) 4.2 grams. The yield of "chlorosaccharin" from the amide actually used was therefore 62 per cent. (Found N=6.65; C=38.8; H=2.07.  $C_7H_4O_3NClS$  requires N=6.4; C=38.6; H=1.84 per cent.).

6-Chloro-o-benzosulphinide is sparingly soluble in cold, slightly soluble in hot water, and extremely soluble in acetone, from which it crystallises in small, shining plates melting at 210—212°. It is apparently more than half as sweet as saccharin, but has a somewhat astringent taste, except in very great dilution. An aqueous solution of the "chlorosaccharin" (1 in 5000) was unanimously declared by six tasters to be sweeter than a solution of "saccharin" of half the concentration. Opinions differed as to the relative sweetness of solutions of the same concentration. The sodium salt of the "chlorosaccharin" is also very sweet.

#### *Nitration of 6-Chloro-o-toluenesulphonyl Chloride.*

To a cold mixture of sulphuric acid (150 c.c.) and nitric acid (45 c.c.; D=1.5), 6-chloro-o-toluenesulphonyl chloride (50 grams) was slowly added and the mixture stirred. After a few minutes the nitration began, for there was a rise in temperature, the sulphonyl chloride melted, and the formerly colourless nitration mixture became yellow. The temperature was kept between 20° and 30° by cooling in ice-water, and a further 50 grams of the sulphonyl chloride added at such a rate that these limits were not exceeded. The nitration was complete in two hours, the product of the reaction poured into a litre of cold water, and the heavy oil separated and stirred vigorously with water until free from acid. The oil, which soon became very viscous, was converted into a pale yellow solid by being left overnight in a cold place. It was found that the presence of a small amount of acid seriously hindered solidification. The solid nitration product was powdered and dried on a porous plate in a vacuum over phosphoric oxide. In this way 106 grams

of minute crystals melting at 23—33° were obtained (Found:  $N=5.29$ .  $C_7H_5O_4NCl_2S$  requires  $N=5.18$  per cent.).

### *Separation of the Isomerides.*

The separation of the isomerides proved to be a far more difficult matter than the separation of the isomerides formed by nitrating 2-chloro-*p*-toluenesulphonyl chloride (this vol., p. 860). Cooling the light petroleum solution resulted in the separation of an oil. However, it was found that a very dilute solution in light petroleum (b. p. 60—80°), when left for six weeks, deposited large, thick prisms and also some needles, the latter being slightly less soluble than the prisms. By taking advantage of this fact, a few grams of each isomeride were obtained in a pure state. The method is, however, extremely laborious and unsatisfactory, owing to the fact that either isomeride tends to separate as an oil when even a small amount of the other isomeride is present in the solution. However, the isolation of a few grams of each isomeride led to the development of the efficient method of separation described below.

### *The Relative Proportion of the Isomerides in the Mixture.*

The percentage of nitrogen in the nitration product shows that either it consists of chloromononitrotoluenesulphonyl chlorides, or unchanged chlorotoluenesulphonyl chloride is present together with chloropolynitrotoluenesulphonyl chlorides. The second alternative is very improbable. With the object of determining the proportion of substances in the nitration product, attempts were made to obtain in the usual way the melting-point curve of the two pure isomerides. Unfortunately, solidification took place so sluggishly that neither the first- nor second-solidification points could be determined with satisfactory accuracy.

However, the eutectic point was determined with some degree of accuracy by melting the two isomerides together, allowing the melt to become quite hard, and then noting the temperature at which the powdered mixture began to soften and adhere to the sides of the tube. It was found that artificial mixtures of the two isomerides softened between 24.5° and 25.5°, and that the nitration product softened at 23—24°. Hence the nitration product consisted almost entirely of the two isomerides which had been obtained in a pure state.

The relative amount of these two isomerides was found by converting them into the easily separable barium salts of the corresponding sulphonic acids. The method is based on the observation



(p. 884) that the barium salt derived from the isomeride that crystallises in needles is very soluble in water and in alcohol (hot and cold), whilst the barium salt from the other isomeride is almost insoluble in boiling alcohol, and only slightly soluble in hot water.

The dry nitrated product (31.50 grams) was gently boiled under reflux with a solution of barium hydroxide (30 grams) in water (450 c.c.) until the oil had disappeared. The solution was just acidified with hydrochloric acid, and then evaporated to dryness on the water-bath. The light brown mass was extracted three times with boiling 99 per cent. alcohol (100 c.c. each time). The first extract was light brown in colour and the third colourless; the last gave only a faint cloudiness with dilute aqueous potassium sulphate solution, and with silver nitrate solution. The alcoholic extract was concentrated to 100 c.c. and allowed to remain overnight, the small quantity of barium chloride and chloronitrotoluenesulphonate precipitated was added to the insoluble mass that had been extracted with alcohol, the alcoholic solution was completely evaporated, and the pale brown residue dried at 120° until the weight was constant (15.05 grams).

The residue insoluble in boiling alcohol was boiled with 200 c.c. of water for some time, and filtered hot. The undissolved barium chloronitrotoluenesulphonate was set aside on a porous plate, the filtrate containing barium chloride and barium chloronitrotoluenesulphonate treated with dilute sulphuric acid to remove the barium, and the filtered solution concentrated on the water-bath until the sulphonic acid began to separate. Water was then added, the solution again evaporated, and this process repeated until the smell of hydrogen chloride could no longer be detected. A small portion of the residue dissolved in dilute nitric acid failed to give a precipitate with silver nitrate solution. The residue, consisting of the sulphonic acid, was dissolved in water (150 c.c.), and the solution neutralised to phenolphthalein by barium hydroxide. The solution was then evaporated to dryness, the light brown residue mixed with the barium chloronitrotoluenesulphonate which had not dissolved with the barium chloride, and the mixture dried at 160° until the weight was constant (22.06 grams).

The 31.50 grams of chloronitrotoluenesulphonyl chloride taken should produce 37.23 grams of barium chloronitrotoluenesulphonates, and 37.11 grams were actually obtained. Hence the percentage of the barium salt soluble in alcohol is 40.42, and of the barium salt insoluble in alcohol 59.27. This result is deduced on the assumption that the third possible isomeride (the amount of which must be very minute—see p. 882) is entirely absent.



## 6-Chloro-3-nitro-o-toluenesulphonyl Chloride (III).

This sulphonyl chloride crystallises in long, colourless needles melting at  $60^{\circ}$ . It is readily soluble in cold benzene, ether, or chloroform, and moderately soluble in cold light petroleum, in which it is slightly less soluble than the isomeride formed with it (Found:  $N=5.3$ .  $C_7H_5O_4NCl_2S$  requires  $N=5.2$  per cent.).

The *sulphonic acid*, prepared by hydrolysing the sulphonyl chloride with hydrochloric acid in a sealed tube, crystallises in very deliquescent, microscopic prisms and is extremely soluble in cold water.

The *sulphonamide* is somewhat soluble in boiling water, but dissolves sparingly in cold water, from which it crystallises in minute needles melting at  $181^{\circ}$  (Found:  $N=11.3$ .  $C_7H_7O_4N_2ClS$  requires  $N=11.2$  per cent.).

The *sodium* salt, prepared by neutralising the sulphonic acid or by hydrolysing the sulphonyl chloride with sodium hydroxide solution, is very soluble in hot or cold alcohol, and in water, and from the latter it separates in colourless needles apparently containing four molecules of water of crystallisation (Found: loss at  $110-130^{\circ}=20.3$ ;  $Na=6.6$ .  $C_7H_5O_5NCISNa, 4H_2O$  requires  $H_2O=20.8$ ;  $Na=6.7$  per cent. The crystals may be combined with  $3\frac{1}{2}$  molecules of water, for  $C_7H_5O_5NCISNa, 3\frac{1}{2}H_2O$  requires  $H_2O=18.7$ ;  $Na=6.8$  per cent.). It decomposes at about  $140-150^{\circ}$ , long, colourless needles being formed in small quantity, which sublime from the black tar produced and melt and decompose at  $270-280^{\circ}$ .

The *barium* salt is formed either by neutralising the sulphonic acid with barium hydroxide or by hydrolysing the sulphonyl chloride with barium hydroxide, neutralising with sulphuric acid, filtering, evaporating the filtrate to dryness, extracting the barium salt with hot alcohol, and finally concentrating the alcoholic solution. It crystallises in compact clusters of microscopic needles, which are very soluble in hot or cold water, and in alcohol. The latter solvent retains in solution nearly its own weight of the barium salt at the ordinary temperature. The salt crystallises from its concentrated aqueous solution in small needles containing seven molecules of water of crystallisation. The needles decompose at about  $140^{\circ}$  with the evolution of a vapour having a strong phenolic smell (Found: loss at  $110-125^{\circ}=16.7$ ;  $Ba=17.5$ .  $[C_7H_5O_5NCIS]_2Ba, 7H_2O$  requires  $H_2O=16.5$ ;  $Ba=17.9$  per cent.).

*Determination of the Constitution.*—Replacement of the sulphonyl chloride group by hydrogen was attempted by heating the sulphonyl chloride (1 gram) with 7 c.c. of fuming hydrochloric acid at  $140-$

150° in a sealed tube for seventy-two hours, and it was found that a small quantity of oil was produced, which disappeared, however, with the formation of a clear solution after heating again for twenty-four hours. The oil was evidently unchanged sulphonyl chloride, and the solution contained only a very minute quantity of sulphuric acid.

The conversion into 6-chloro-3-nitro-*o*-cresol (V) was effected by boiling the chloronitrotoluenesulphonyl chloride (2 grams) with 10 per cent. sodium hydroxide solution (50 c.c.) for ten hours. The sulphonyl chloride was hydrolysed, forming a pale yellow solution which soon assumed a deep red colour. Only a small quantity of a precipitate was formed and no "bumping" took place. The solution was acidified with hydrochloric acid, whereby it became almost colourless, and was distilled in a current of steam, when the smell of sulphur dioxide was noticed. The yellow solid in the distillate was extracted with ether, the ethereal solution dried with sodium sulphate, and most of the ether removed. As the residual ether evaporated at the ordinary temperature yellow needles were produced melting at 64°. The yield was 0.47 gram (34 per cent.).

This chloronitrocresol gives a red salt with sodium hydroxide, is somewhat volatile with steam, and when heated has a smell recalling that of *o*-nitrophenol. It is noteworthy that it requires about three times as long to distil in a current of steam as the chloronitrocresol described previously (this vol., p. 868). It is very soluble in organic solvents, slightly soluble in cold water, and separates from all solvents in thin, yellow needles melting at 64°. Benzoylation by the Schotten-Baumann method could not be effected (Found : N=7.6. Calc., N=7.5 per cent.).

6-Chloro-3-nitro-*o*-cresol has already been prepared by Noelting (*loc. cit.*), and its properties agree closely with those of the substance described above. In order to place the constitution of the foregoing chloronitrocresol beyond dispute, a specimen of that discovered by Noelting was prepared, and the two substances (m. p. 64°) were found to be identical by a mixed melting-point determination. Hence the formula assigned to the parent chloronitrotoluenesulphonyl chloride is justified.

#### *6-Chloro-4-nitro-o-toluenesulphonyl Chloride (IV).*

This compound is very readily soluble in cold benzene, ether, or chloroform, and is moderately soluble in cold light petroleum. It usually crystallises in large, thick prisms, but sometimes separates (especially from light petroleum of low b. p.) in very thin, colour-

less laminæ. Both modifications melt at 63–64° (Found :  $N=5.2$ .  $C_7H_5O_4NCl_2S$  requires  $N=5.2$  per cent.).

The *sulphonic acid* is obtained by hydrolysing the sulphonyl chloride with water in a sealed tube. It crystallises from cold water, in which it is moderately soluble, as a mass of colourless, flattened needles. It is only slightly hygroscopic, a portion left on a porous plate not completely disappearing in the course of a week.

The *amide* crystallises in minute needles melting at 161°, and is slightly soluble in water and moderately soluble in alcohol. When boiled for a few minutes with ammonia the solution becomes red (Found :  $N=11.2$ .  $C_7H_7O_4N_2ClS$  requires  $N=11.2$  per cent.).

The *sodium* salt is formed by neutralising the sulphonic acid with sodium hydroxide solution, and when prepared in this way crystallises in colourless plates. When prepared by the hydrolysis of the sulphonyl chloride by sodium hydroxide solution, the salt is obtained quite colourless only with difficulty. It is slightly soluble in boiling alcohol, from which it separates on cooling in flattened needles, and is moderately soluble in water, separating therefrom in plates containing one molecule of water of crystallisation (Found :  $H_2O=6.55$ ;  $Na=8.1$ .  $C_7H_5O_5NClSNa \cdot H_2O$  requires  $H_2O=6.2$ ;  $Na=8.2$  per cent.).

The *barium* salt formed by neutralising the sulphonic acid with barium hydroxide, is almost insoluble in alcohol. It is somewhat soluble in boiling water, from which it separates on cooling in colourless needles containing one molecule of water of crystallisation (Found :  $H_2O=3.0$ ;  $Ba=20.7$ .  $[C_7H_5O_5NClS]_2Ba \cdot H_2O$  requires  $H_2O=2.75$ ;  $Ba=20.9$  per cent.).

*Determination of the Constitution.*—The chloronitrotoluene-sulphonyl chloride (2.7 grams) was boiled with 20 per cent. sodium hydroxide solution (25 c.c.) for three hours. The colour quickly became very dark red and a brown powder was precipitated. The solution was cooled and acidified with hydrochloric acid, when a gas was evolved, but the liquid still remained deeply coloured. Part of the solution was distilled in a current of steam, an operation which was accompanied by much frothing, but no organic substance distilled. The other portion of the solution was extracted with ether, which, however, was found to have dissolved no organic substance.

It was noticed that the solution after acidification stained skin a dark yellow, and that the colour was fairly fast to light and soap. For purposes of comparison, 4-nitro-*o*-toluenesulphonyl chloride was heated with sodium hydroxide solution under analogous conditions, and a coloration was produced similar to that described above.

There can therefore be little doubt that the nitro-group in the chloronitrotoluenesulphonyl chloride is in the para-position with respect to the methyl group.

*Summary.*

(I) The monochlorination of *o*-toluenesulphonyl chloride in the presence of antimony trichloride leads to the formation of a mixture of isomerides, from which 6-chloro-*o*-toluenesulphonyl chloride crystallises in a yield of 38·6 per cent.

(II) The nitration at 20—30° of 6-chloro-*o*-toluenesulphonyl chloride in mixed nitric and sulphuric acids results in the production of 6-chloro-4-nitro-*o*-toluenesulphonyl chloride (about 60 per cent.) and 6-chloro-3-nitro-*o*-toluenesulphonyl chloride (about 40 per cent.).

(III) The sulphonyl chloride group and not the nitro-group in 6-chloro-3-nitro-*o*-toluenesulphonyl chloride is replaceable by the hydroxyl group by boiling with sodium hydroxide solution. This fact may afford an interesting confirmation of the steric hindrance (due to the methyl group) postulated in the theory of Kenner (T., 1920, 117, 852).

The thanks of the author are due to Professor W. H. Perkin and to Dr. E. Hope for their advice. He also wishes to make acknowledgment to the Ramsay Memorial Fellowship Trust for a Fellowship which has enabled this portion of the research to be completed.

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[Received, March 30th, 1921.]