CCCLXXI.—*The Orienting Influence of Free and Bound Ionic Charges on Attached Simple or Conjugated Unsaturated Systems. Part IV. The Nitration of Toluene-ω-sulphonic Acid and of Toluene-ω-sulphonyl Chloride.*

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THE work of Vorländer (*Ber.*, 1919, **52**, 262) proved that an atom bearing a positive charge when directly attached to the aromatic nucleus has a powerful *m*-directive effect, and on the lines of electronic theories this may be interpreted as meaning that a group having a strong attraction for electrons has a *m*-directive effect. The discovery of the largely predominating *meta*-nitration of benzyltrimethylammonium nitrate (Part I, J., 1926, 1655) justified this view in the most convincing manner. It may be fairly claimed that the connexion between polarity and orientation thus firmly established is less hypothetical in character than any other in organic chemistry. The proof that *m*-substitution in benzene derivatives is *sometimes* due to a general electrical effect of the first substituent suggests that *m*-direction may *always* be initiated in this way.

Among *m*-directive groups the only one which seems to present difficulty from this point of view is the sulphonic acid group. At first sight it is hard to reconcile the net negative charge of the sulphonic ion with an assumed tendency to attract electrons. It must be remembered, however, that sulphuric acid is a powerful dibasic acid and therefore $H\overline{S}O_4$, which may be written $HO{\cdot}\overline{S}O_3$, is evidently able to donate a proton to acceptor molecules, and this means that the $-\overline{S}O_3$ group, in spite of its charge, retains a high electron affinity. The phenomenon is doubtless connected with incomplete neutralisation of the charge of the sulphur atom by the distorted oxygen ions surrounding it (see the preceding communication) and with the partial neutralisation of the field of the oxygen ions by neighbouring kations and kationoid complexes.

The possibility that the sulphonic acid group is *m*-directive for the same reason that the ammonium-salt group is *m*-directive would become a probability if it could be shown that the effect is produced when a saturated carbon atom separates the sulphur atom from the benzene nucleus; we accordingly studied the nitration of toluene-ω-sulphonic acid. This substance is nitrated to a predominating extent in the *op*-positions, but the proportion of the *m*-nitro-isomeride produced is much greater than that obtained in the nitration of toluene. This result confirms the view that the sulphonic ion group, $\overset{-}{S}O_3$, has a higher electron affinity than has a hydrogen atom, and we may confidently attribute the *m*-substitution of benzenesulphonic acid to the occurrence of the condition $Ph\longrightarrow\overset{-}{S}O_3$.

Toluene-ω-sulphonyl chloride, $Ph\longrightarrow CH_2\overset{(a)}{\longrightarrow}SO_2\overset{(b)}{\longrightarrow}Cl$, may be regarded as a sulphone in which the normal displacement (a) is reinforced by that (b) due to the chlorine atom. In harmony with our theory, the percentage of the *m*-isomeride formed in the nitration of this substance is much greater than that formed in the nitration of toluene-ω-sulphonic acid and considerably greater than that formed in the nitration of benzyl-*m*-nitrophenylsulphone.

The publication of Ingold, Ingold, and Shaw (this vol., p. 813), dealing with the nitration of substances of the form $CH_2Ph\cdot SO_2R$, appeared when our work was at a stage where the determinations of the proportion of *m*-isomeride formed in the nitrations had been completed. In view of it, the experimental section of this communication has been curtailed so that all repetition of description has been avoided. We carried out, for example, identifications of the products as nitrotoluene-ω-sulphonamides (compare Mohr, *Annalen*, 1883, **221**, 218; Purgotti and Monti, *Gazzetta*, 1900, **30**, ii, 254) and no further reference to this part of our work is deemed necessary.

EXPERIMENTAL.

Method of Estimation of the Proportion of m-*Isomeride formed in the Nitrations.*—Francis and Hill's method of bromination after reduction of the nitro-compounds with titanous chloride (*J. Amer. Chem. Soc.*, 1924, **46**, 2498) has been found to be applicable to the sodium nitrotoluene-ω-sulphonates. Small corrections were applied for the deviations from the stoicheiometric relations found for sodium *o*-, *m*-, and *p*-nitrotoluene-ω-sulphonates.

Sodium *o*-nitrotoluene-ω-sulphonate was crystallised from semi-saturated brine and dried at 100—120° (Found: NaCl, 20·3; sodium nitrotoluenesulphonate estimated by titanous chloride, 79·4%). On reduction and bromination, the deviation from the theoretical value (in the volume of potassium bromate solution required for bromination) was $-$ 0·4%. Sodium *m*-nitrotoluene-ω-sulphonate was crystallised from semi-saturated brine and dried at 130—140° (Found: NaCl, 7·1; sodium nitrotoluenesulphonate, 92·4%; deviation from theory on reduction and bromination, $+$ 0·9%). The *o*-isomeride loses $1H_2O$ at 100°, but the *m*- and *p*-isomerides retain their water of crystallisation below 125°. Sodium *p*-nitrotoluene-ω-sulphonate was crystallised from brine and dried at 140° (Found: NaCl, 1·9; sodium nitrotoluenesulphonate, 96·6%; deviation from theory on reduction and bromination, + 1·1%).

Some difficulty was experienced in obtaining satisfactory end-points in the final titrations with sodium thiosulphate, and this was overcome by using not too large an excess of bromine and by neutralising part of the acid after the liberation of iodine.

Nitration of Sodium Toluene-ω-sulphonate.—Sodium toluene-ω-sulphonate crystallised from 95% alcohol in lustrous leaflets, and the specimens employed were anhydrous and free from sodium chloride.

In a preliminary experiment, 20 g. of the salt were nitrated and 16·5 g. of washed sodium nitrotoluenesulphonates (dried at 100°) were obtained (Found: loss at 140° or H_2O, 6·0; NaCl, 8·6; sodium nitrotoluenesulphonates, 85·3%; *meta*, 20·2, 19·8, 18·5, 19·4%). The true yield was 57·6% and therefore the minimum value for the proportion of *m*-isomeride formed is 11—12%.

In attempts to improve the yield products were obtained containing sodium nitrate, which interfered seriously with the determinations. In subsequent experiments, the absence of nitrates was always confirmed.

Ultimately, the following nitration conditions were adopted: Sodium toluene-ω-sulphonate (10 g.) was added during 30 minutes to nitric acid (15 c.c.; *d* 1·5) at 0°, a further quantity of the acid (5 c.c.) being used to wash the sides of the container. Three hours from the commencement the ice-bath was removed and 1 hour later the solution was mixed with water (120 c.c.) and neutralised by means of sodium carbonate (20 g.), and after the addition of sodium chloride (30 g.) the liquid was heated until a clear solution resulted. The cooled liquid was kept at 0° for 3 hours and the separated solid was then washed twice with 15% brine (10 c.c.) and dried at 100° (Specimen A, 12·8 g.) (Found: H_2O, 4·9; NaCl, 10·0; sodium nitrotoluenesulphonate, 84·8%; *meta*, 11·7, 11·0, 10·6, 10·3, 9·6, 9·6%). The yield of sodium nitrotoluene-ω-sulphonates was therefore 88% and the minimum value for the proportion of *m*-isomeride formed is 9·2% (maximum, 21·2%). Another specimen (B) was prepared in the same manner (purity, 82%; true yield, 88%).

Nitration of Toluene-ω-sulphonic Acid.—The free acid (9 g.), prepared by Böhler's method (*Annalen*, 1870, **154**, 50), was treated exactly as described above for its sodium salt. The isolated, washed, and dried solids amounted to only 8·0 g. A further amount of sodium chloride (20 g.) was therefore added and 6·0 g. of the mixed salts were obtained. The products were free from nitrates and were mixed (Found : H_2O, 3·3; NaCl, 39·9; sodium nitrotoluenesulphonates, 56·8%; *meta*, 14·2, 13·7, 14·2%). Here the true yield was 63·6% and the minimum value for the proportion of *m*-isomeride is 8·9%. We are unable to account for the variations in yield which were observed, but since the actual amount of the *m*-isomeride obtained was as great in this experiment (yield, 64%) as in the one previously described (yield, 88%), we may conclude that the proportion formed is greater in the nitration of the acid than in that of the salt. The point is not raised in the introduction, because it is hoped to follow up this indication by fresh experiments before the interesting theoretical implications are discussed.

Nitration of Toluene-ω-sulphonyl Chloride.—Toluene-ω-sulphonyl chloride (10 g.) was added during 30 minutes to nitric acid (15 c.c.; *d* 1·5) at 0°, a further amount of nitric acid (5 c.c.) being employed to wash the sides of the container. After 3 hours, the ice-bath was removed and 1 hour later the product was precipitated by water, collected, and boiled with a solution of sodium carbonate (11 g.) in water (100 c.c.) until no oil remained (about 1 hour). The liquid was filtered hot, sodium chloride (20 g.) introduced, and the mixture kept at 0° for 3 hours; the separated solid was then collected, washed twice with 15% brine (10 c.c.) at 0°, and dried at 100° (yield, 10·2 g.) (Found : H_2O, 5·7; NaCl, 12·3; sodium nitrotoluenesulphonates, 77·6%; *meta*, 44%). The yield was 63% and the minimum value for the proportion of *m*-isomeride formed is 28%. The specimen contained carbonate, and this probably accounts for the fact that the water, sodium chloride, and nitro-compounds determined totalled only 95·6%. Another nitration was carried out in exactly the same manner, but the alkaline solution was neutralised with hydrochloric acid and the sodium nitrotoluenesulphonates were salted out in two crops (mixed, 15·7 g.) (Specimen C) by means of sodium chloride (total, 50 g.) (Found : H_2O, 3·8; NaCl, 40·2; sodium nitrotoluenesulphonates, 55·8%; *meta*, 56, 54, 56, 56%). The true yield was 70·5% and the minimum value for the proportion of *m*-isomeride formed is 39% (maximum, 67·5%).

Comparison of these experiments shows that more efficient salting out increases the percentage of the *m*-isomeride in the product, and hence the true value for the *m*-isomeride content should be considerably greater than the minimum; it must also, of course, be much less than the maximum.

Estimation of the Proportions of the p-*Isomeride in Specimens A, B, and C.*—On heating at 100° with concentrated aqueous potassium hydroxide, the *o*- and *m*-nitrotoluene-ω-sulphonates develop no coloration, whereas the *p*-isomeride gives a yellowish-orange solution. Attempts to apply this reaction in a colorimetric method gave unintelligible results until it was found that the colour produced by the *p*-isomeride is more intense in the presence of the *o*-isomeride and still more intense in the presence of the *m*-isomeride. The *o*- and *m*-isomerides give no coloration when mixed and heated with aqueous potassium hydroxide.

Solutions were made up to contain 1·0% of the pure *o*-, *m*-, and *p*-isomerides and of the nitro-compounds in specimens A, B, and C. 10 C.c. of one of these solutions or of a mixture of them were mixed with 25 c.c of a solution of potassium hydroxide (100 g.) in water (100 c.c.) and heated in a bath of boiling water for about 2 hours. All the comparisons were direct under identical conditions, and in addition to the determination of the intensity of the colour the rapidity of its appearance afforded valuable guidance. In making up the standards, the ascertained percentage of the *m*-isomeride in the specimen to be tested was introduced and kept constant, the proportions of the *p*- and *o*-isomerides being varied.

In the case of specimen C, the colour was practically identical with that of a standard made from 5·5 c.c. of the *m*-isomeride solution and 4·5 c.c. of the *p*-isomeride solution and was distinctly stronger than that obtained from the standard—*m*-, 5·5; *p*-, 4·0; *o*-, 0·5 c.c. The colours were estimated after dilution of the solutions to 40 c.c. by means of the Zeiss "Stufenphotometer." The specimen C, obtained in 70·5% yield from the nitration of toluene-ω-sulphonyl chloride, does not, therefore, contain an appreciable amount (<5%) of the *o*-isomeride.

No difference could be detected in the behaviour of the specimens A and B when a direct comparison was made; most of the experiments were therefore made with B, because a larger quantity of this specimen was available. A series of comparisons with standards showed that the colour derived from B was more intense than that from the standard—*m*-, 1·0; *p*-, 4·5; *o*-, 4·5 c.c., and less intense than that from the standard—*m*-, 1·0; *p*-, 5·0; *o*-4·0 c.c.

The actual intensity measurements of these and four other standards compared with the solution from B were used to construct a graph, by means of which the solution exactly equivalent to the B solution was found to be—*m*-, 1·0; *p*-, 4·8; *o*-, 4·2 c.c. This was experimentally confirmed with solutions made up from quantities weighed on a micro-balance.

A specimen was made by admixture of the *o*-, *m*-, and *p*-isomerides and sodium chloride that contained 82% of the pure sodium nitrotoluene-ω-sulphonates (*m*-, 10; *o*-, 40; *p*- 50%) and was found in numerous quantitative trials under different conditions to resemble B closely in behaviour. The colours were developed a very little the more rapidly with the artificial mixture. Finally, the specimen A was reproduced on the same basis and with the same results.

The colour reactions observed with alkaline solutions also guarantee the absence of sodium dinitrotoluene-ω-sulphonates. A specimen of the latter (probably the 2 : 4-dinitro-derivative) was prepared by nitration of sodium *o*-nitrotoluene-ω-sulphonate with a hot mixture of sulphuric and nitric acids. The sodium salt crystallised in colourless leaflets and developed a green colour with cold, dilute aqueous sodium hydroxide; on heating, an intense bluish-green solution was obtained.

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