CCCLXX.—*The Orienting Influence of Free and Bound Ionic Charges on Attached Simple or Conjugated Unsaturated Systems. Part III. The Nitration of* m-*Nitrophenylbenzylsulphone.*

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THE hypothesis (Allan, Oxford, Robinson, and Smith, J., 1926, 401) that the positive charge of the dipole in the nitro-group of phenylnitromethane is the cause of the *m*-substitution observed by Holleman, and the related wider theory, can be tested experimentally in many directions, the most obvious of which is the study of the orienting influence in aromatic substitution of polar and dipolar groups situated at various distances from the nucleus. This field of systematic work is too large to be covered by any one group of investigators, but the exploitation of it by Ingold and his co-workers has involved some duplication of research, particularly in connexion with the nitration of phenylethylamine derivatives and of substances of the forms Ph·CO·R and Ph·CH_2·SO_2R. Some preliminary experiments in the latter group are described in this and the following communication.

The interest of the toluene-ω-sulphonyl compounds resides in their theoretical analogy with the phenylnitromethanes, the double dipole $-\overset{++--}{\mathrm{SO}_2}$ being compared with the single dipole $-\overset{+-}{\mathrm{NO}_2}$, and in the fact that the effect of varying the group R can be observed. We selected the case of *m*-nitrophenylbenzylsulphone because we thought that the group $-C_6H_4 \cdot NO_2$(*m*-) should be almost neutral and the results could therefore be ascribed to the influence of the sulphone group. The proportions of the *o*-, *m*-, and *p*-isomerides formed on nitration, estimated by colorimetric methods which are fully described in the experimental section, were approximately 25, 28, and 47%, respectively. The double semi-polar double bond of the sulphone group has thus a smaller *m*-orienting effect than the single semi-polar double bond of the nitro-group. This constitutes a definite argument against the view that the charges in the semi-polar double bonds are integral and effective as such.

As Born (compare *Ann. Reports*, 1926, 261) has shown, kations and anions are distorted and polarised in the neighbourhood of each other, and if this is true of the components of a molecule of sodium chloride, how much more must it be true of the bound ions in a semi-polar double bond. In fact, the intensity of the external fields may be chiefly governed by this atomic polarisation. On this basis, we may conclude that the kationic charge of the sulphur atom in the sulphone group is less effective than that of the nitrogen in the nitro-group and that this is due to the relatively greater degree of polarisation of the oxygen atoms in the sulphone; this again is clearly connected with the larger nuclear charge of the sulphur atom and the smaller electron density of its outer shell.

Ingold, Ingold, and Shaw (this vol., p. 813) found that the nitration of benzylmethylsulphone gave about 30% of the *m*-nitro-isomeride, but these authors attributed the result (comparison with phenylnitromethane) to absorption of the effect of the ionic charge of sulphur in passing through the outer shells of the atom. This suggestion appears to be fallacious owing to the circumstance that in the calculation of the kationic charges, for example, + 1, + 2, or + 6, in various theories respecting sulphur compounds, the electrons of the outer shells are taken into account or assumed to be donated to other atoms. Probably the distance separating the centres of sulphur and carbon atoms in C—S is greater than that separating the centres of carbon and nitrogen atoms in C—N and this must reduce the effectiveness of equivalent charges in accordance with Coulomb's Law; if the charges are not equivalent, the validity of this explanation is greatly impaired.

Our view that the bound oxygen ions are polarised, thus reducing the net charge of the sulphur atom, is closely connected with the theory of electrostriction of sulphonium kations by free anions; it is, in fact, intramolecular electrostriction. It should be noted that this hypothesis emphasises the importance of the part played by the central atom and can be correlated experimentally with work on the distribution of electrons in crystals. The hypothesis is also connected with the strength of the sulphonic acids, for it is surely the polarisation of the oxygen atoms in the $R{\cdot}SO_3$ ion that loosens the grip of their electrons on the proton (alternatively, increases the repulsion of the proton by the oxygen nucleus).

EXPERIMENTAL.

m-*Nitrophenylbenzylsulphone*, $NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}CH_2Ph$.—A mixture of sodium *m*-nitrobenzenesulphinate (20 g.), benzyl chloride (15 g.), and 95% alcohol (60 c.c.) was refluxed for 4 hours, and the product (18 g.) precipitated by the addition of water. The *sulphone* crystallised from alcohol in very pale yellow needles, m. p. 151—152° (Found: C, 56·8; H, 4·5; N, 5·2. $C_{13}H_{11}O_4NS$ requires C, 56·3; H, 4·0; N, 5·1%).

m-*Nitrophenyl*-o-*nitrobenzylsulphone* was similarly prepared from *o*-nitrobenzyl chloride (8 g.), the yield being 14·7 g. It crystallised from acetone in pale yellow plates, m. p. 192—193° (Found: C, 48·6; H, 3·5; N, 9·0. $C_{13}H_{10}O_6N_2S$ requires C, 48·5; H, 3·1; N, 8·7%).

m-*Nitrophenyl*-m-*nitrobenzylsulphone* crystallised from alcohol in almost colourless, microscopic cubes, m. p. 194—195° (Found: C, 48·5; H, 3·0; N, 8·5%).

m-*Nitrophenyl*-p-*nitrobenzylsulphone* crystallised from acetone in very pale yellow needles, m. p. 180—181° (Found: C, 48·8; H, 3·6; N, 9·0%). The three isomerides are very sparingly soluble in most organic solvents and although the *o*-isomeride is the most sparingly soluble in alcohol, neither this nor any other solubility property could be employed for their separation.

Nitration of m-*Nitrophenylbenzylsulphone*.—The finely powdered substance (5·00 g.) was gradually added during 15 minutes to nitric acid (40 c.c.; *d* 1·5) kept at − 5° to 0°. Each addition produced a brownish-red, evanescent coloration. After 1 hour, the mixture was allowed to reach the room temperature and the product was precipitated by water after 3 hours. It was ground under water, washed, and dried (5·63 g. or 97%). In a second similar experiment the yield was 98·5% (Found: C, 48·6; H, 3·4%).

Various attempts to fractionally crystallise this material were made, but no suitable solvent could be found, and after experimenting with oxidation methods, which also we were compelled to abandon on account of the sparing solubility of the isomerides, we adopted the following colorimetric method. The *p*-isomeride gives a carmine coloration in alcoholic solution on the addition of 10% aqueous sodium hydroxide, whereas the *o*- and *m*-isomerides give no coloration under these conditions. In dilute solutions, the intensity of this colour was roughly proportional to the concentration of the *p*-isomeride and it was not affected by the presence of the *o*- or *m*-isomeride. A Zeiss " Stufenphotometer " was employed for the measurements and all the comparisons were direct, and not through a standard. The liquids were mixed in the adjustable vessels so that the colours could be compared as quickly as possible, and stirring was necessary before the caps were screwed on. Remarkably consistent results were obtained. Solutions of the nitration product (0·1987 g.), the *o*-isomeride (0·2018 g.), the *m*-isomeride (0·2098 g.), and the *p*-isomeride (0·2023 g.) in absolute alcohol (1000 c.c. each) were prepared. Taking 10 c.c. of the standard solution and adding 2 c.c. of 10% aqueous sodium hydroxide, it was found that the solution of the *p*-isomeride was roughly twice as concentrated (in *p*-isomeride) as the solution of the nitration product, columns of 5·35, 6·0, and 6·9 mm. balancing columns of 10·7, 11·9, and 13·8 mm., respectively. A closer comparison was then made by diluting the solution of the *p*-isomeride with an equal volume of alcohol and producing the colour as before; the solution of the *p*-isomeride was distinctly the stronger, the measurement indicating that the nitration product contained 47% of the *p*-isomeride. A mixture of the solution of the *p*-isomeride (45 c.c.) and alcohol (55 c.c.) gave a perceptibly weaker colour than the solution of the nitration product, the measurement again indicating that the nitration product contained 47% of the *p*-isomeride. The experiment was twice repeated with exactly the same results, so that the determination of the proportion of the *p*-isomeride in the mixture was considered to be sufficiently accurate to be employed in further work.

The estimation of the proportions of the *o*- and *m*-isomerides was much more difficult and the method was not capable of very great accuracy; the experiments were, however, frequently repeated and it is hoped that the results are not seriously in error. The *o*-isomeride gives an intense violet coloration with strong alkalis in alcoholic acetone (or pure acetone) solution, whereas the *m*-isomeride gives no immediate coloration. The following solutions were employed: (1) *o*-isomeride (5 c.c.), *p*-isomeride (20 c.c.), alcohol (17·5 c.c.); (2) *o*-isomeride (10 c.c.), *p*-isomeride (20 c.c.), alcohol (12·5 c.c.); (3) *o*-isomeride (15 c.c.), *p*-isomeride (20 c.c.), alcohol

(7·5 c.c.); (4) *o*-isomeride (20 c.c.), *p*-isomeride (20 c.c.), alcohol (2·5 c.c.); (5) nitration product (42·5 c.c.). Sodium ethoxide solution (10 c.c.) (from 10 g. of sodium in 250 c.c. of alcohol) and then pure acetone (50 c.c.) were added to each mixture. The colour developed by the nitration product was found to lie between those produced by solutions (2) and (3) and was much closer to that of (2). Experiments with solutions of compositions between those of (2) and (3) confirmed this and indicated that the nitration product contained 25—30% of the *o*-isomeride. The colour-tone match was not perfect, however, and it was then noticed that the *m*-isomeride slowly developed a brownish-red coloration in acetone solution in the presence of sodium ethoxide. A fresh series of solutions was therefore made up in which the pure alcohol was replaced by the appropriate volume of the *m*-isomeride solution; a colour-tone match was then obtained and the intensity showed that the proportion of the *o*-isomeride in the nitration product was 23—27%. This was confirmed by a direct estimation of the content of *m*-isomeride.

The three isomerides develop colorations when solid potassium hydroxide is added to their cold solutions in acetone, but if, after a short time, water is added, the colorations due to the *o*- and *p*-isomerides are discharged and the *m*-isomeride gives a brownish-yellow solution. A series of mixtures was prepared as before from the standard alcoholic solutions and, after the alcohol had been removed, acetone (30 c.c.) and potassium hydroxide (2 cm. stick) were added. The mixture was stirred for 5 minutes, water (50 c.c.) was then added, and the colour compared with that obtained from the nitration product under identical conditions. The proportion of the *m*-isomeride in the nitration product was thus found to lie between 25 and 32%. A mixture of the *o*-isomeride (0·250 g.), the *m*-isomeride (0·280 g.), and the *p*-isomeride (0·470 g.) was then made and its colour reactions were compared with those of the nitration product, the substances being weighed on a micro-balance, with the result that no difference could be detected. The mixture after fusion, resolidification, and grinding had m. p. 152—156° and the nitration product had m. p. 153—157°; a mixture of the two had m. p. 152—156°.

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