CXIX.—*The Nature of the Alternating Effect in Carbon Chains. Part XIV. The Directive Action of Groups of the Form* -$CH_2{\cdot}SO_2{\cdot}R$ *in Aromatic Substitution.*

By Christopher Kelk Ingold, Edith Hilda Ingold, and Florence Ruth Shaw.

The characteristic actions of a pole and of a dipole in controlling the position of substitution of a benzene derivative having been established in broad outlines by recent investigations (see below), a number of subsidiary influences required elucidation. The following will be considered.

(i) *Influence of neutral * atoms in modifying the orienting effect of a charged atom.* The nitro-group contains a neutral as well as a negative oxygen atom, and when comparing the electron-

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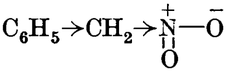
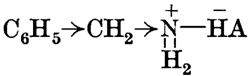
* Here, as previously, the term "neutral" is used relatively and is not intended to exclude atoms carrying the feeble charges represented by $\delta+$ and $\delta-$.

affinities of the nitro- and ammonium salt groups, as measured by their meta-directive effects in the nitration of phenylnitromethanes and benzylamine salts; Baker and Ingold (J., 1926, 2462; this vol., p. 261) assumed that the influence of the neutral



$C_6H_5 \rightarrow CH_2 \rightarrow \overset{+}{\underset{\underset{O}{\|}}{N}} - \overset{-}{O}$

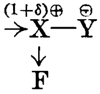
(meta, 50%)



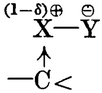
$C_6H_5 \rightarrow CH_2 \rightarrow \overset{+}{\underset{\underset{H_2}{\|}}{N}} - \overset{-}{H}A$

(meta, 49%)

atoms attached to the positive ends of the dipoles would be small in comparison with the effect of the dipoles themselves. This is doubtless correct in the cases considered, but it is nevertheless conceivable that atoms of greatly differing electron-affinities (*e.g.*, carbon and fluorine) might allow their electrons to be attracted by a charged atom in such different degrees as to modify the effective charge on that atom, if not largely, at least to an appreciable extent :



$\rightarrow \overset{(1+\delta)\oplus}{\underset{\underset{F}{\downarrow}}{X}} - \overset{\ominus}{Y}$



$\overset{(1-\delta)\oplus}{\underset{\underset{-C<}{\uparrow}}{X}} - \overset{\ominus}{Y}$

This effect has been searched for and has now been detected.

(ii) *Influence of a second charged atom : Compensation by the more distant end of a dipole.* The smaller *m*-directive action observed in phenylnitromethanes and benzylamine salts of the above types, as compared with the benzyltrialkylammonium ion (meta, 85—88%) (Goss, Ingold, and Wilson, J., 1926, 2440; Goss, Hanhart, and Ingold, this vol., p. 250), has been attributed (J., 1926, 2445) to partial compensation by electron-repulsion from the more distant negative end of the dipole. In the above examples, however, the negative charges are carried by different kinds of atoms, and for a strict demonstration of this principle it is desirable (see below) that atoms of the same kind should be used, and only the total charges varied. This method is employed in the present work, and the effect of varying the compensating charge in the ratio 3/2 is recorded.

(iii) *Damping action of external electron-shells in positively charged atoms.* The diminution in the *m*-directive influence of a positively charged atom separated from the nucleus by an increasing number of neutral atoms (Part X, *loc. cit.*) shows that each group of electrons through which the electron-strain is transmitted exerts an appreciable damping action :

$Ph{\cdot}\overset{+}{N}Me_3$ 100% $Ph{\cdot}CH_2{\cdot}\overset{+}{N}Me_3$ 88% $Ph{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}Me_3$ 19%

$Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}Me_3$

5±2% of *m*-nitro-derivative.

Since the positive electricity with which the strain originates resides at the *nucleus* of the charged atom, a similar damping action may be expected to arise during the passage of the effect through the successive shells of electrons belonging to the charged atom itself, and this consideration enables us to forecast the relative orienting influences of equivalent ionic charges carried by different atoms. Phosphorus and sulphur atoms in the combined state possess a group of eight electrons external to the ten which correspond with the ten in the combined nitrogen atom; arsenic, selenium, and iodine atoms contain groups additional to those present in phosphorus and sulphur. It follows that phenyl- and benzyl-phosphonium and -thionium ions should exhibit weaker *m*-directive action than the analogous phenyl- and benzylammonium ions; that phenyl and benzyl sulphoxides (dipole) should show weaker *m*-orientation than the corresponding aromatic nitro-compounds; that aromatic arsonium and selenonium salts should show weaker *m*-reactivity than the comparable phosphonium and thionium salts, and so forth.* Of course, apart from this screening action of the outer electrons, the magnitude of the effect escaping from a charged atom will depend on the ionic charge; whence it follows, also, that aromatic sulphones (double dipole) should show stronger *m*-orienting action than the corresponding sulphoxides (unit dipole). The testing of such predictions as these is necessarily a lengthy task, but we are already able to advance evidence showing that the nitrogen and sulphur atoms stand in the anticipated order.

Results.

In the experimental section a comparative study is recorded of the nitration of a series of benzylsulphonyl compounds of the general formula $C_6H_5{\cdot}CH_2{\cdot}SO_2{\cdot}R$. The results, so far as they bear upon the three topics raised, may be summarised as follows:

Nitration of Benzylsulphonyl Compounds, $C_6H_5{\cdot}CH_2{\cdot}SO_2{\cdot}R$ *in Nitric Acid* (d^{18° 1·494) *at* − 10° *to* − 5°.

Group R	CH_3	NH_2				OH	Cl
Meta (%)	30	31				14	51
Group R		NHMe	NHEt	NMe_2	NEt_2	OMe	
Meta (%)		29	28	28	25	32	

Although based for the most part on tolerably consistent triplicate determinations (for details, see Table, p. 832), these figures can

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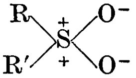
* The same principles, applied to the fractional dipoles discussed in the following paper, show that $C_6H_5{\cdot}SiCl_3$ and $C_6H_5{\cdot}CH_2{\cdot}SiCl_3$ should exhibit weaker *m*-orientation than $C_6H_5{\cdot}CCl_3$ and $C_6H_5{\cdot}CH_2{\cdot}CCl_3$ respectively, and we propose to study these and the other comparisons mentioned.

only be regarded as approximate; nevertheless, it appears probable that they place the various groups in the correct order, excepting possibly in the cases of some of those which gave closely similar values.

Discussion of Results.

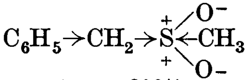
The above group of compounds was selected for study because it appeared likely to yield evidence regarding the three anticipated subsidiary influences already alluded to.

According to Sugden, Reed, and Wilkins (J., 1925, **127**, 1525) the sulphone group contains two semi-polar double linkings, so that the structure of sulphones must be represented thus :



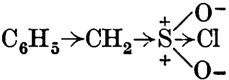
and there is ample chemical evidence that these semi-polar double linkings are not easily depolarised. The static neutral character of methanesulphones ($\cdot CH_2\cdot SO_2$), contrasted with the acid nature of nitromethanes ($\cdot CH_2\cdot NO_2$; one true double bond), shows—if we accept the theory (E. H. Ingold, J., 1923, **123**, 1717, *et seq.*) that triad tautomerism represents internal addition to an unsaturated centre—that there is no real or potential unsaturated linking in the sulphone group. Similarly, the non-formation of sulphonamides from sulphonic esters and aqueous ammonia, in contrast to the ready production of carboxylamides from carboxylic esters, accords with the assumed structural difference ($^-SO_2\cdot OMe$, no double bond; $^-CO\cdot OMe$, one double bond) if, as Gane and Ingold suggested (J., 1926, 11), aldehyde-ammonia addition is the first stage in the formation of carboxylamides from esters. For these and other reasons, we may regard the valency-octet of sulphur in sulphones as fixed for most reactions, and the charge on the core of the atom (nucleus + 10 electrons) as fixed also.

(i) *Influence of neutral atoms.* Of the simpler available groups, R (R′ = benzyl), the greatest disparity was to be expected (p. 814) between $^-CH_3$ and ^-F, but we have not troubled to prepare benzylsulphonyl fluoride because the readily obtained chloride gave a perceptibly higher meta-value than the methyl sulphone :



$$C_6H_5\rightarrow CH_2\rightarrow \overset{+\diagup O^-}{\underset{+\diagdown O^-}{S}}\leftarrow CH_3$$

(meta, 30%)



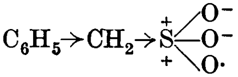
$$C_6H_5\rightarrow CH_2\rightarrow \overset{+\diagup O^-}{\underset{+\diagdown O^-}{S}}\rightarrow Cl$$

(meta, 51%)

On the other hand, all the other instances investigated (excepting R = OH—see below) yielded values differing only slightly from that given by the methyl sulphone, and from this we may conclude that the fractional charges set up by the varying electron affinities of neutral atoms are insignificant in comparison with such integral ionic charges as the charge inherent in the sulphur atom of a sulphone, excepting in the case of strongly electro-polar atoms such as those of the halogen family.

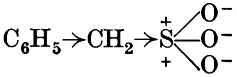
(ii) *Influence of charged atoms.* Since the meta-value for R = F should be at least as great as that for R = Cl, it will be evident from the above table that $^-$OH falls out of its place in the possible sequence $NH_2 < OH < F$. A rough estimate of the meta-value expected for R = OH [made by noting the value obtained for the methyl ester (R = OMe) and the relationship between the figure for the amide ($R = NH_2$) and those for the substituted amides (R = NHMe, NMe_2, etc.)] would be about 35%, which does lie between the limits set by $R = NH_2$ and Cl; but the observed value (14%) falls far short of this.

The difference, however, is readily interpreted on the grounds that sulphonic acids are strong acids and may be assumed to be almost completely ionised in solution; in other words, the case of benzylsulphonic acid corresponds, not with R = OH, but with R = O′, the depression of the meta-value representing the effect of introducing a third negatively charged oxygen atom in addition to the two already present in the sulphone group. We can call to mind no clearer proof than this of the compensating action of the more remote end of a dipolar group : *



$C_6H_5\rightarrow CH_2\rightarrow \overset{+}{\underset{+}{S}}\begin{matrix}\diagup O^- \\ - O^- \\ \diagdown O\cdot\end{matrix}$

(meta, *ca.* 35%)



$C_6H_5\rightarrow CH_2\rightarrow \overset{+}{\underset{+}{S}}\begin{matrix}\diagup O^- \\ - O^- \\ \diagdown O^-\end{matrix}$

(meta, 14%)

(iii) *Influence of the sulphur electrons.* If the meta-value 35% approximately represents the effect of the two-fold dipole in the sulphone group, the unit dipole contained in a similarly situated sulphoxide group must correspond with a much smaller meta-value, and although we have as yet made no experiments with benzylalkylsulphoxides, we feel sure that under comparable conditions they would not yield more than small proportions (*e.g.*,

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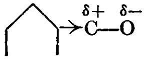
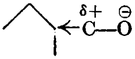
* The *op*-substitution of benzoic acid in alkaline solution (Lossen, D.R.-P. 146174), in contrast to its *m*-substitution in acid media, is regarded (see following paper) as an illustration of the reversal of the effect of a *fractional* charge by an *integral* charge of opposite sign situated at a greater distance :

(*meta-*) 

 (*ortho-para-*).

It follows that benzenesulphonic acid should not show the same marked difference of behaviour under the two conditions, since (unlike benzoic acid) the free acid would be nearly as strong an electrolyte as its salts.

5—10%) of *m*-isomeride. Comparison with the value (50%) established for the unit dipole in the analogously situated nitro-group (p. 814) shows that the effect of a positive ionic charge on sulphur must suffer relatively greater loss within the atom itself than is the case with nitrogen.

EXPERIMENTAL.

(A) *Preparation of Benzylsulphonyl Compounds.*

Benzylmethylsulphone, $C_7H_7{\cdot}SO_2{\cdot}CH_3$.—Benzylsulphonyl chloride (50 g.) was reduced with zinc dust (24 g.) and boiling alcohol (1000 c.c.) as described by Fromm and Palme (*Ber.*, 1906, **39**, 3312), and the neutralised liquid (70 g. of anhydrous sodium carbonate were used) evaporated to dryness under reduced pressure. The residue was extracted with hot alcohol (1000 c.c.), and the filtered solution evaporated to dryness, also under diminished pressure. The residue from this evaporation was dissolved in 200 c.c. of water, and the filtered solution shaken with 25 c.c. of methyl sulphate at 40° until crystals began to appear. Sodium hydroxide (40 c.c. of 8*N*-solution) was gradually added and the shaking continued until the temperature began to fall; the mixture was then heated to 75°, shaken for a further 15 minutes, and allowed to cool. Yield, 21 g.; m. p. 123—125°. The specimen used for nitration was crystallised first from aqueous alcohol and then from chloroform–ligroin.

Benzylsulphonamide and the Sulphonalkylamides.—The unsubstituted amide was prepared as recommended by Johnson and Ambler (*J. Amer. Chem. Soc.*, 1914, **36**, 380) and purified by crystallisation from water. Benzylsulphonmethylamide, $C_7H_7{\cdot}SO_2{\cdot}NHMe$, prepared by dissolving the sulphonyl chloride in 33% aqueous methylamine and boiling off most of the excess of the base, separated from aqueous alcohol or from ethyl acetate–ligroin in laminæ, m. p. 108—109° (Found: S, 17·7. Calc.: S, 17·3%). Johnson and Ambler (*loc. cit.*) obtained the same substance along with the dimethylamide (below) by methylation of the simple amide.

Benzylsulphonethylamide, $C_7H_7{\cdot}SO_2{\cdot}NHEt$, was similarly prepared, excepting that the excess of ethylamine was neutralised with hydrochloric acid, and crystallised first from aqueous methyl alcohol below the ordinary temperature and finally from ether–ligroin, from which it was obtained as leaflets, m. p. 65—66° (Found: S, 16·0. $C_9H_{13}O_2NS$ requires S, 16·1%).

Benzylsulphondimethylamide, $C_7H_7{\cdot}SO_2{\cdot}NMe_2$, was obtained by means of aqueous dimethylamine, and crystallised first from dilute methyl alcohol and then from chloroform–ligroin; it formed large, thin plates, m. p. 101° (Found: S, 15·9. Calc.: S, 16·1%).

Benzylsulphondiethylamide, $C_7H_7{\cdot}SO_2{\cdot}NEt_2$, prepared by dissolving the chloride in excess of pure diethylamine and pouring the solution into dilute sulphuric acid, crystallised from ether–ligroin below 0° in leaflets, m. p. 29° (Found: S, 14·2. $C_{11}H_{17}O_2NS$ requires S, 14·1%).

Benzylsulphonic Acid and its Methyl Ester.—The sodium salt of the acid prepared by Johnson and Ambler's method (*loc. cit.*) was crystallised three times from water. The *methyl* ester was prepared by boiling the chloride with a slight deficit of methyl-alcoholic sodium methoxide for 15 minutes, after which the suspension was cooled and mixed with water, and the crystalline precipitate, which contained a little unaltered chloride, was collected and ground for 1·5 minutes with aqueous ammonia (*d* 0·880). The mixture was diluted with water, and the solid was collected, washed with an abundance of cold water, dried, and crystallised from ether; large, lustrous prisms then separated, m. p. 61—62° (Found: C, 52·0; H, 5·2; S, 17·3. $C_{10}H_8O_3S$ requires C, 51·6; H, 5·4; S, 17·2%). On boiling with water for 5 minutes, complete hydrolysis takes place.

Benzylsulphonyl Chloride.—This was prepared as recommended by von Pechmann (*Ber.*, 1873, 6, 534). The specimen used for nitration was crystallised twice from chloroform–ligroin.

(B) *Nitration of Benzylsulphonyl Compounds and Estimation of the* m-*Isomeride: General Method.*

It was found possible to effect the smooth mononitration of all the substances investigated except one (the diethylamide) under the same set of conditions. The proportion of nitric acid ($d^{18°}$ 1·494) was 1 kg. per g.-mol. of substance, the latter being added in small portions at the uniform rate of 0·2 g. per minute to the rapidly stirred acid at − 10° to − 5°. The mixture was warmed to 0° during 1 hour and then mixed with ice. The method of isolating and separating the nitration product varied with the different examples, but in all cases excepting the methylsulphone, the sulphonic acid, and the diethylamide the pure *m*-isomeride was isolated; in the case of the methylsulphone, it was obtained in an impure condition and in the case of the sulphonic acid it was isolated as a derivative.

For the estimation of the *m*-isomeride, the method of oxidation by permanganate and separation of the nitrobenzoic acids (Baker and Ingold, *loc. cit.*; Goss, Hanhart, and Ingold, *loc. cit.*) was employed, and although the yields of mixed nitrobenzoic acids were not quantitative (they were mostly in the neighbourhood of 80—85%) it was possible to correct for any small disparities in the percentage conversions of the different isomerides by noting the yields obtained on oxidation of the separated isomerides and of mixtures of them of different composition,* precautions being taken to keep the conditions of oxidation comparable in each group of experiments. In most experiments, partial separation of the original nitration product was effected before oxidation was resorted to.

(C) *Details relating to Individual Cases.*

(*a*) *Benzylmethylsulphone.* — (i) *Qualitative separation.* The nitration product was obtained in a total yield of 97·6%, of which 70·3% was precipitated on the addition of ice and 27·3% was extracted by chloroform from the neutralised filtrate. The precipitated part (Found : C, 45·1; H, 4·0. Calc. : C, 44·7; H, 4·2%) had m. p. 90—140°, and 1·00 g., crystallised from 40 c.c. of benzene, yielded 0·57 g. of a product, m. p. 160—165°, which, crystallised from alcohol, yielded (in two fractions) 0·48 g., m. p. 167—168°. Further crystallisation did not change this m. p., and since oxidation yielded *p*-nitrobenzoic acid, m. p. 234—236° unpurified (mixed m. p. 235—236°), this compound must be p-*nitrobenzylmethylsulphone* (Found : C, 44·4; H, 4·5; N, 6·7. $C_8H_9O_4NS$ requires C, 44·7; H, 4·2; N, 6·5%). The product contained in the mother-liquors, on crystallisation from alcohol and from ethyl acetate–alcohol, gave needles (0·25 g.), m. p. 105—106°, which, although consisting mainly of m-*nitrobenzylmethylsulphone* (Found : C, 44·3; H, 4·5; N, 6·6%), still contained a small proportion of the *p*-isomeride. This was shown by oxidation and separation of the nitrobenzoic acids. The extracted part of the nitration product (Found : C, 44·6; H, 4·2%) had m. p. 75—105°; after three crystallisations from ethyl acetate–alcohol, it gave needles, m. p. 85—87°, consisting (as was shown by oxidation to the nitrobenzoic acids) mainly of o-*nitrobenzylmethylsulphone* (Found : C, 44·5; H, 4·6; N, 6·6%) but contaminated with an appreciable quantity of the *m*-isomeride.

(ii) *Estimation of* m-*isomeride* (Expt. 14). The yield of nitration product was 99·9%, of which 85·7% was precipitated (Found : C, 44·9; H, 4·0. Calc. : C, 44·7; H, 4·2%) and 14·2% extracted

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* If $100x$, $100y$, and $100z$ represent the percentage conversions of *o*-, *m*-, and *p*-nitro-isomerides, respectively, and if three mixtures give yields of mixed nitrobenzoic acids amounting to $100Y_1$, $100Y_2$, and $100Y_3$, these products having compositions represented respectively by $100o_1$, $100m_1$, $100p_1$%; $100o_2$, $100m_2$, $100p_2$%; and $100o_3$, $100m_3$, $100p_3$% of *o*-, *m*-, and *p*-nitro-acids, then x, y, and z are given by :

$$x \begin{vmatrix} M_1P_1 1 \\ M_2P_2 1 \\ M_3P_3 1 \end{vmatrix} = y \begin{vmatrix} P_1O_1 1 \\ P_2O_2 1 \\ P_3O_3 1 \end{vmatrix} = z \begin{vmatrix} O_1M_1 1 \\ O_2M_2 1 \\ O_3M_3 1 \end{vmatrix} = \begin{vmatrix} O_1M_1P_1 \\ O_2M_2P_2 \\ O_3M_3P_3 \end{vmatrix}$$

where $O_1 = o_1Y_1$, $O_2 = o_2Y_2$ . . . $M_1 = m_1Y_1$ . . . $P_3 = p_3Y_3$.

with chloroform (Found: C, 44·6; H, 4·2%). The precipitated part on oxidation gave nitrobenzoic acids in 80% yield (*M*, by titration, 167; benzoic acid, by sublimation, nil), which on separation gave 48·9% * of *p*-nitrobenzoic acid, m. p. 234—235°, mixed m. p. 235—236°, and 28·5% * of *m*-nitrobenzoic acid, m. p. 134—138°, mixed m. p. 139—140°. The crude recovered *o*-nitrobenzoic acid (containing *m*-acid) had m. p. 133—143°, mixed m. p. 143—145°, and the total recovery of separated acids was 98·8%. The extracted portion gave nitrobenzoic acids (*M*, 166; benzoic acid, nil) in >74% yield, the exact figure being unknown, as a little of the solution was accidentally lost. Separation gave 9·2% of *p*-acid having m. p. 225—230° (mixed m. p. 230—233°) and 35·7% of *m*-acid, m. p. 133—136° (mixed m. p. 138—141°). The recovered *o*-acid (containing a little *m*-acid) had m. p. 133—137°, mixed m. p. 135—140°.

(Expt. 15.) *p*-Nitrobenzylmethylsulphone was isolated in 34·5% yield, and the residue divided by crystallisation into two fractions amounting to 51·4% and 14·1% of the whole, the total yield in this experiment being quantitative. The first fraction, on oxidation, gave nitrobenzoic acids in 82% yield (*M*, 168; benzoic acid, nil), and these, on separation, gave 9·5% of *p*-acid, m. p. 232—234°, mixed m. p. 234—235°, and 49·4% of *m*-acid, m. p. 130—136°, mixed m. p. 138—140°. The second fraction gave an 81% yield of nitrobenzoic acids (benzoic acid, nil) which on separation yielded 9·4% of *p*-acid, m. p. 224—228°, mixed m. p. 230—234°, and 35·9% of *m*-acid, m. p. 131—134°, mixed m. p. 137—139°.

(Expt. 16.) The yield of nitration product was 98·4%, and from this 38·4% of the theoretical (39·0% of the actual) yield of the pure *p*-isomeride was isolated. The residues, on oxidation, gave nitrobenzoic acids in 84·6% yield (*M*, 167; benzoic acid, nil) which on separation yielded 5·8% of *p*-acid, m. p. 225—230°, and 50·5% of *m*-acid, the precipitated part of which (42·6%) had m. p. 136—137° and mixed m. p. 140°, whilst the part extracted with ether (7·9%) had m. p. 120—130°, mixed m. p. 135—138°.

(Calculations.) From these three experiments we find: para $= 0·858 \times 48·9 + 0·142 \times 9·2 = 43·3\%$, $34·5 + 0·514 \times 9·5 + 0·141 \times 9·4 = 40·7\%$, $39·0 + 0·610 \times 5·8 = 42·6\%$; meta $= 0·858 \times 28·4 + 0·142 \times 35·7 = 29·5\%$, $0·514 \times 49·4 + 0·142 \times 35·9 = 30·6$, $0·610 \times 50·5 = 30·8\%$, the disparities in the oxidation conversions being negligible in this case. The mean values are, therefore, para, 42·2%; meta, 30·3%; ortho (by difference), 27·5%.

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* These, and all other yields of *p*- and *m*-nitrobenzoic acids recorded in this section are corrected for the solubility of the *p*-acid and the *m*-barium salt (Baker and Ingold, *loc. cit.*).

(*b*) *Benzylsulphonamide*.—(i) *Qualitative separation*. Part of the nitration product (28·1%) was precipitated on the addition of ice, and this consisted mainly of *p*-nitrobenzylsulphonamide (Mohr, *Annalen*, 1883, **221**, 218) which was purified by crystallisation from hot water and obtained as clusters of small needles, m. p. 203—204° (Found : C, 39·3 ; H, 3·8. Calc. : C, 38·9 ; H, 3·7%). The same substance was obtained by the action of aqueous ammonia on *p*-nitrobenzylsulphonyl chloride. On oxidation, it yielded only *p*-nitrobenzoic acid, m. p. 234—235° (unpurified). The nitric acid solution, on complete evaporation with water, deposited first further quantities of the same isomeride and later the crude *m*-compound as plates, m. p. 150—160°. On recrystallisation, these yielded long, felted needles, m. p. 161°, consisting of pure *m*-nitrobenzylsulphonamide (Purgotti and Monti, *Gazzetta*, 1900, **30**, [ii], 254), as was proved by oxidising them to pure *m*-nitrobenzoic acid, m. p. 139—140° (unpurified), mixed m. p. 139—140°. The same compound was obtained from *m*-nitrobenzylsulphonyl chloride by treatment with aqueous ammonia. It is much more soluble in water than the *p*-amide.

(ii) *Estimation of the* m-*isomeride* (Expt. 21). The precipitated portion of the nitration product corresponded with 27·8% of the theoretical yield and had m. p. 160—190° (Found : C, 38·5 ; H, 3·9. Calc. : C, 38·9 ; H, 3·7%). On oxidation, nitrobenzoic acids (*M*, 166 ; benzoic acid, nil) were obtained in 83·2% yield, and these on separation gave 82·6% of *p*-acid, m. p. 230—232°, mixed m. p. 231—234°, and *m*-acid which was obtained in two portions, the first (6·7%, precipitated) having m. p. 137—139°, mixed m. p. 140°, and the second (2·2%, extracted with ether) m. p. 125—135°, mixed m. p. 135—140°. The dilute nitric acid solution was evaporated, with several additions of water, to dryness in a vacuum ; the residue was not weighed, but, as there was no opportunity for loss, was taken to correspond with 72·2% (Found : C, 38·3 ; H, 3·7%). Nitrobenzoic acids were obtained in 74·4% yield (*M*, 167 ; benzoic acid, 0·2%), and their separation gave *p*-acid, m. p. 228—232°, mixed m. p. 230—234° (28·7%), precipitated *m*-acid, m. p. 137—139°, mixed m. p. 140° (30·0%), and extracted *m*-acid, m. p. 125—132°, mixed m. p. 138° (7·5%).

(Expt. 22.) The precipitated portion of the nitration product (28·1%) on crystallisation from water yielded 21·4% of *p*-nitrobenzylsulphonamide (m. p. 203—204°). The residue obtained by evaporating the nitric acid solution was crystallised in successive fractions from water, yielding 9·7% of *p*-amide (m. p. 203—204°), 0·6% of *p*-amide (m. p. 202—204°), and 6·2% of impure *m*-amide (m. p. 150—160°) which, after a further crystallisation, yielded

5·2% of pure *m*-amide (m. p. 161°). All mother-liquors were now combined and evaporated, and the residues (60·7% instead of 63·1%) oxidised as usual. The nitrobenzoic acids (yield, 81·3%; *M*, 166; benzoic acid, nil) on separation gave *p*-acid, m. p. 228—230°, mixed m. p. 232—234° (13·1%); *m*-acid (precipitated), m. p. 136—137°, mixed m. p. 140° (28·5%); and *m*-acid (extracted), m. p. 125—131°, mixed m. p. 136—140° (10·1%).

(Expt. 25.) The precipitated part of the nitration product was crystallised from water, and the filtrate was combined with the dilute nitric acid solution and evaporated, with additions of water, in a vacuum. The *o*- and *m*-amides were extracted with hot water from the sparingly soluble *p*-amide, and were allowed to crystallise after evaporation of the solution to a small bulk; the final filtrate was evaporated to dryness. The yield of *p*-amide (m. p. 203—204°) was 35·6%, of " crystallised mixture " (Found : C, 38·6; H, 3·7. Calc.: C, 38·9; H, 3·7%) 58·7%, and of " evaporated mixture " 5·6% (loss 0·1%). Two independent oxidations of the crystallised mixture gave nitrobenzoic acids in 83·2 and 82·5% yields, respectively, and an average sample of the combined products (*M*, 167; benzoic acid, nil) on separation gave *p*-acid (7·1%), m. p. 220—230°, mixed m. p. 229—232°; *m*-acid (precipitated, 39·6%), m. p. 137°, mixed m. p. 140°; *m*-acid (extracted, 8·6%), m. p. 125—130°, mixed m. p. 135—138°. The nitrobenzoic acids (*M*, 165; benzoic acid, 0·3%) obtained from the evaporated mixture yielded no *p*-acid, and 32·6% of *m*-acid, m. p. 125—135°, mixed m. p. 137—140°, and the *o*-acid recovered had m. p. 130—135° (unpurified), 143—145° (after one crystallisation from chloroform), mixed m. p. 145°.

(Expt. 26.) By a method similar to that used in Expt. 22 the *p*-amide (23·9%, m. p. 203—204°, plus 12·2%, m. p. 202—204°, plus 2·0%, m. p. 200—204°) and *m*-amide (11·6%, m. p. 158—161°) were partly separated, the crop of *m*-amide being obtained by crystallisation from 50% alcohol, and the residues oxidised (yield 83·3%) to nitrobenzoic acids. Separated, these gave 6·2% of *p*-acid, m. p. 225—230°, mixed m. p. 230—232°, and 40·9% of *m*-acid, of which the bulk (precipitated) had m. p. 137—138° (mixed m. p. 140°) and the remainder (extracted), m. p. 124—135° (mixed m. p. 136—139°).

(Calculations.) The isolated *p*-amide on oxidation gave *p*-nitrobenzoic acid in (*a*) 86·0, (*b*) 86·6% yields, and the *m*-amide yielded the *m*-acid in (*a*) 78·1, (*b*) 79·0% yields. A mixture of 0·500 g. of each amide gave mixed acids in 83·2% yield, and these on separation yielded 52·8% of *p*-acid, m. p. 230—233°, and 47·2% of *m*-acid, of which 37·6% had m. p. 136—138° and the remainder

(9·6%) m. p. 124—130°. From these experiments, and the data obtained in Expts. 25 (crystallised mixture) and 26, it is calculated that the percentage conversions of the *o*-, *m*-, and *p*-amides are 87·2, 78·5, and 86·3%, respectively. These figures being used, Expt. 21 gives para, 0·278 × 81·8 + 0·722 × 27·7 = 42·7%; meta, 0·278 × 10·8 + 0·722 × 39·7 = 31·7%; ortho, 25·6%: Expt. 22 gives para, 31·7 + 0·631 × 12·7 = 39·7%; meta, 5·2 + 0·631 × 40·8 = 31·0%; ortho, 29·3%: Expt. 25 gives para, 35·6 + 0·587 × 6·8 = 39·6%; meta, 0·587 × 50·6 + 0·057 ×35 = 31·6%; ortho, 28·8%: Expt. 26 gives para, 38·1 + 0·503 × 6·0 = 41·1%; meta, 11·6 + 0·503 × 43·2 = 33·3%; ortho, 25·6%. Since Expt. 26 does not agree well with the other three, it is excluded from the following mean values: Para, 40·7%; meta, 31·4%; ortho (by difference), 27·9%.

(*c*) *Benzylsulphonmethylamide.*—(i) *Qualitative separation.* The precipitated portion of the nitration product, after crystallisation successively from methyl alcohol, ethyl acetate, and chloroform, gave needles, m. p. 143—145° (Found: C, 41·4; H, 4·4. $C_8H_{10}O_4N_2S$ requires C, 41·7; H, 4·4%), which consisted of p-*nitrobenzylsulphonmethylamide*, since oxidation with permanganate yielded only *p*-nitrobenzoic acid, m. p. 232—234° (unpurified), mixed m. p. 234°. The same methylamide was prepared from the *p*-nitro-chloride and aqueous methylamine. In another experiment, the whole nitration product was extracted with ethyl acetate after neutralisation, and the bulk of the *p*-isomeride allowed to crystallise from this solvent. The mother-liquors on evaporation gave a residue which, on slow crystallisation from methyl alcohol, yielded stellate clusters of needles, m. p. 106—107° (Found: C, 41·4; H, 4·5%). This compound was identified as m-*nitrobenzylsulphonmethylamide*, since, on oxidation with permanganate, it yielded only *m*-nitrobenzoic acid, m. p. 137—140° (unpurified), mixed m. p. 139—140°. It was also prepared from *m*-nitrobenzylsulphonyl chloride and aqueous methylamine.

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 32). The diluted nitric acid solution was evaporated in a vacuum, without collection of the precipitated nitro-compounds, and the product oxidised as usual. The nitrobenzoic acids (yield, 76·8%; *M*, 166·5; benzoic acid, nil) gave 42·2% of *p*-acid, m. p. 228—231°, mixed m. p. 230—234°; 21·1% of precipitated *m*-acid, m. p. 134—137°, mixed m. p. 140°; and 7·3% of extracted *m*-acid, m. p. 120—133°, mixed m. p. 134—138°.

(Expt. 36.) The precipitated nitration product (yield 98·4%) was extracted with ethyl acetate after neutralisation (Found: C, 41·6; H, 4·6. Calc.: C, 41·7; H, 4·4%), and after separation of 32·6% (calculated on the actual yield) of the *p*-isomeride, the remaining amide was oxidised in 82·2% yield to nitrobenzoic acids which on separation gave 10·4% of *p*-acid, m. p. 234—235°, 33·7% of precipitated *m*-acid, m. p. 134—137°, mixed m. p. 139—140°, and 73% of extracted *m*-acid, m. p. 123—136°, mixed m. p. 137—140°.

(Expt. 37.) The product isolated by complete evaporation was separated by crystallisation, giving 29·5% of *p*-methylamide of m. p. 138—141°, 6·2% of m. p. 138—140° and 1·7% of m. p. 137—139°, and 6·8% of *m*-methylamide, m. p. 99—101°. A mixture of the second and third specimens of *p*-compound gave only *p*-nitrobenzoic acid, m. p. 230—234°, and the separated *m*-compound yielded only *m*-nitrobenzoic acid, m. p. 137—139°, on oxidation. Oxidation of the residues was effected in 83·5% yield, and the nitrobenzoic acids (*M*, 166; benzoic acid, 0·9%) on separation gave 11·0% of *p*-acid, m. p. 220—230°, mixed m. p. 227—232°; 29·5% of precipitated *m*-acid, m. p. 134—135°, mixed m. p. 141°; and 9·0% of extracted *m*-acid, m. p. 122—130°, mixed m. p. 135—140°.

(Calculations.) The isolated *p*- and *m*-methylamides gave corresponding nitrobenzoic acids in 85·2 and 80·5% yields, respectively, and it is calculated from Expts. 36 and 37 that the *o*-compound would give about 84·0% under the same conditions. Hence, para = 41·5%, $32{\cdot}6 + 0{\cdot}674 \times 10{\cdot}2 = 39{\cdot}5\%$, $37{\cdot}4 + 0{\cdot}558 \times 11{\cdot}3 = 43{\cdot}7\%$; meta = 29·5%, $0{\cdot}674 \times 42{\cdot}3 = 28{\cdot}5\%$, $6{\cdot}8 + 0{\cdot}558 \times 39{\cdot}8 = 29{\cdot}0\%$. The mean values are: Para, 41·5%; meta, 29·0%; ortho (by difference), 29·5%.

(*d*) *Benzylsulphonethylamide.*—(i) *Qualitative separation.* The precipitated portion of the nitration product was rubbed with a little cold methyl alcohol, and the sparingly soluble portion crystallised from this solvent in needles, m. p. 110—111°. These consisted of p-*nitrobenzylsulphonethylamide* (Found: C, 44·2; H, 5·1. $C_9H_{12}O_4N_2S$ requires C, 44·3; H, 4·9%), since on oxidation they yielded only *p*-nitrobenzoic acid, m. p. 230—234° (unpurified). The same substance was also prepared from *p*-nitrobenzylsulphonyl chloride and aqueous ethylamine. m-*Nitrobenzylsulphonethylamide* was isolated in small amount by fractional crystallisation of the residues from dilute methyl alcohol. It formed stellate bunches of needles, m. p. 90—91° (Found: C, 44·0; H, 5·2%), and on oxidation gave only *m*-nitrobenzoic acid, m. p. 137—139° (unpurified), mixed m. p. 139—140°. The same isomeride was prepared from *m*-nitrobenzylsulphonyl chloride and aqueous ethylamine.

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 42). The residue from the diluted and evaporated solution (Found: C, 44·2;

H, 5·1%) was oxidised in 78·4% yield to nitrobenzoic acids (*M*, 167; benzoic acid, 0·9%) which on separation (after removal of the benzoic acid) gave 42·8% of *p*-acid, m. p. 225—230°, mixed m. p. 228—232°; 20·6% of precipitated *m*-acid, m. p. 135—137°, mixed m. p. 140°; and 7·1% of *m*-acid, m. p. 125—132°, mixed m. p. 135—140°, which was extracted with ether.

(Expt. 45.) The *p*-ethylamide (36·6%), m. p. 108—110°, was separated by means of methyl alcohol, and the residues were oxidised to the mixed acids (yield, 79·0%; *M*, 165·5; benzoic acid, nil) which on separation gave 10·9% of *p*-acid, m. p. 224—228°, mixed m. p. 227—231°, 33·7% of precipitated *m*-acid, m. p. 134—139°, mixed m. p. 140°, and 10·4% of *m*-acid, m. p. 124—130°, mixed m. p. 136—140°, extracted with ether.

(Expt. 47.) Preliminary separation gave 32·4% of *p*-amide, m. p. 108—111°, 5·7% of m. p. 107—109°; and 8·1% of *m*-amide, m. p. 86—89°, and 0·6%, m. p. 85—87°. The residues yielded nitrobenzoic acids (yield, 81·0%; *M*, 167; benzoic acid, nil), which on separation gave 6·8% of *p*-acid, m. p. 228—230°, mixed m. p. 230—234°, and 36·7% of *m*-acid, of which 28·5% (precipitated) had m. p. 135—138° and 8·2% had m. p. 125—130° (mixed m. p.'s 140° and 138—139°, respectively).

(Calculations.) The isolated *p*- and *m*-ethylamides gave the corresponding nitrobenzoic acids in 80·4 and 79·1% yields, respectively, and the yields obtained from mixtures were all of this order. Hence the experiments cited give para: 42·8%, $36·6 + 0·634 \times 10·9 = 43·6\%$, $38·1 + 0·532 \times 6·8 = 41·9\%$; meta: 27·5%, $0·634 \times 44·1 = 28·0\%$, $8·7 + 0·532 \times 26·7 = 28·2\%$, the means being: para, 42·8%; meta, 27·9%; ortho (by difference), 29·3%.

(*e*) *Benzylsulphondimethylamide.*—(i) *Qualitative separation of isomerides.* The precipitated part of the nitration product, crystallised first from methyl alcohol and then from ethyl alcohol, gave leaflets, m. p. 167°, consisting of p-*nitrobenzylsulphondimethylamide* (Found: C, 44·6; H, 4·7. $C_9H_{12}O_4N_2S$ requires C, 44·3; H, 4·7%). On oxidation by permanganate, it yielded only *p*-nitrobenzoic acid, m. p. 233—234° (unpurified), and it was identical with the substance obtained by dissolving *p*-nitrobenzylsulphonyl chloride in aqueous dimethylamine. m-*Nitrobenzylsulphondimethylamide* was obtained from the mother-liquors as leaflets, m. p. 116—119°, which was not depressed by admixture with a specimen, m. p. 118—119°, obtained from the pure *m*-nitro-chloride (Found: C, 44·3; H, 5·1%). The substance was oxidised by permanganate to *m*-nitrobenzoic acid, m. p. 137—140° (unpurified), mixed m. p. 139—140°.

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 52). The whole nitration product obtained by dilution and evaporation in a vacuum (Found : C, 44·0; H, 4·4%) was oxidised in 76·7% yield to mixed acids (*M*, 166; benzoic acid, 0·2%) which on separation gave 44·5% of *p*-acid, m. p. 225—233°, mixed m. p. 230—235°, and 27·5% of *m*-acid, of which the bulk (precipitated) had m. p. 138°, mixed m. p. 141°, and the remainder, extracted with ether, m. p. 120—130°, mixed m. p. 136—139°.

(Expt. 55.) The *p*-derivative was isolated in 31·1% yield, m. p. 164—166°, and the residues oxidised in 70·1% yield to mixed acids, which on separation gave 16·7% of *p*-acid, m. p. 230—232°, mixed m. p. 234—235°, and 39·6% of *m*-acid, of which 30·0% had m. p. 133—137°, mixed m. p. 139—140°, and 9·6% had m. p. 125—130°, mixed m. p. 135—138°.

(Expt. 57.) A series of crystallisations yielded 33·7% of the *p*-compound, of which 26·7% had m. p. 164—166° and 7·0% m. p. 163—165°, and 10·6% of *m*-compound, of which 10·3% had m. p. 114—117° and the remainder m. p. 112—116°. The residues (55·0% instead of 55·7%) on oxidation gave nitrobenzoic acids (yield 74·7%) which on separation gave 17·9% of *p*-nitrobenzoic acid, m. p. 220—230°, mixed m. p. 230—234°, and 34·2% of *m*-acid, of which the bulk (precipitated) had m. p. 132—137°, mixed m. p. 139—140°, and the remainder m. p. 120—130°, mixed m. p. 136—139°.

(Calculations.) Independent oxidations of the *p*-compound gave 78·9 and 79·4% yields, and of the *m*-compound 73·8 and 75·6% yields, whence from Expt. 57 the *o*-isomeride should give a 73·3% yield under the same conditions. Hence the data given lead to para : 43·8%, $31{\cdot}1 + 0{\cdot}689 \times 15{\cdot}6 = 41{\cdot}8\%$, $33{\cdot}7 + 0{\cdot}557 \times 16{\cdot}8 = 43{\cdot}0$; meta : 28·1%, $0{\cdot}689 \times 39{\cdot}8 = 27{\cdot}5\%$, $10{\cdot}6 + 0{\cdot}557 \times 34{\cdot}3 = 29{\cdot}7\%$. The mean values are therefore : para, 42·9%; meta, 28·4%; ortho (by difference), 28·7%.

(*f*) *Benzylsulphondiethylamide*.—Difficulty was experienced with the nitration of this substance owing to its tendency to oxidise, but in one experiment (63) it was shown that nitration occurs in the *m*-position to a substantial extent. The substance (1·500 g., this small amount being used owing to the difficulty of keeping the temperature down when oxidation sets in if larger quantities are employed) was nitrated at − 10° to − 5° as usual, and the solution, after being kept for 10 minutes, was mixed with ice and sodium carbonate solution and extracted with ether. The extract was concentrated without drying, and when the bulk was small, water was added and the solution was boiled to expel the remainder of the ether and treated with permanganate. The mixed acids (yield, 53·7% calculated as nitrobenzoic acids on the basis of the diethylamide used for nitration) lost 8·6% of their weight at 100°, and the residual mixed nitro-acids (*M*, 166) consisted, as was found by separation, of 47·2% of *p*-nitro-acid, m. p. 220—225°, mixed m. p. 228—233°; 25·1% of *m*-acid, of which the bulk (precipitated) had m. p. 133—135°, mixed m. p. 138—141°, and the remainder (extracted) had m. p. 115—125°, mixed m. p. 132—139°; and (by difference) 27·7% of *o*-acid. The recovered *o*-acid, crystallised once from chloroform, had m. p. 140—146°, mixed m. p. 144—145°. These figures, namely, para, 47·2%; meta, 25·1%; ortho, 27·7%, are regarded as an approximation to the proportions of the nitro-diethylamides originally formed.

(*g*) *Benzylsulphonic Acid.*—This substance has been nitrated by Böhler (*Annalen*, 1870, **154**, 55), who, however, obtained no individual substance, and by Mohr (*loc. cit.*), who showed that the *p*-nitro-derivative was the principal product and that the *o*-isomeride was also formed; the *m*-isomeride was not detected.

(i) *Qualitative examination.* The solution obtained by adding sodium benzylsulphonate to nitric acid under the usual conditions was evaporated in a vacuum after the addition of water, and the residue was crystallised from aqueous alcohol; sodium *p*-nitrobenzylsulphonate (Purgotti and Monti, *loc. cit.*) was then obtained. On oxidation it yielded only *p*-nitrobenzoic acid, m. p. 232—234° (unpurified). The mother-liquors were evaporated, and the residues were washed with a little aqueous alcohol, which removed part of the very soluble sodium *o*-nitrobenzylsulphonate, and treated with phosphorus oxy- and penta-chlorides at 90° for 0·5 hour. The sulphonyl chlorides, collected after decomposition with water of the excess of phosphorus chlorides, when crystallised from chloroform–ligroin, gave *m*-nitrobenzylsulphonyl chloride as plates, m. p. 101°, which in some fractions were mixed with prisms from which they could be mechanically separated. On hydrolysis, they yielded Purgotti and Monti's *m*-nitrobenzylsulphonic acid (*loc. cit.*).

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 72). The well-dried nitration product was converted into the mixed chlorides with phosphorus penta- and oxy-chlorides at 90°, and the chlorides transformed by ammonia in dry ether into the amides, which were oxidised. The nitrobenzoic acids (yield, 74·6% calculated on the original sodium benzylsulphonate; *M*, 166; benzoic acid, nil) on separation gave *p*-acid (53·9%), m. p. 227—233°, mixed m. p. 230—235°, and *m*-acid (12·5%), the greater portion of which had m. p. 135—137° (mixed m. p. 139—140°) and the remainder m. p. 125—131° (mixed m. p. 136—140°). The recovered *o*-acid (33·6%; loss nil) after one crystallisation from chloroform had m. p. 140—143°, mixed m. p. 143—146°.

(Expt. 73.) The same method being followed initially, the nitro-chlorides (93·7% yield) were prepared, and crystallised from chloroform–ligroin; 29·3% of the *p*-nitro-chloride (prisms, m. p. 89—90°) were then separated. The mother-liquors yielded a small crop (2·2%) of the *m*-derivative (plates, m. p. 99—100·5°). The remaining material was converted into amides and oxidised in 76·0% yield (calculated on the nitro-chlorides) to mixed acids (*M*, 167; benzoic acid, nil), which on separation gave 33·7% of *p*-acid, m. p. 225—231°, mixed m. p. 230—235°, and 16·0% of *m*-acid, of which 11·0% (the precipitated part) had m. p. 135—137°, mixed m. p. 139—140°, the remainder having m. p. 125—131°, mixed m. p. 135—138°.

(Expt. 74.) The method was the same as in Expt. 72, and the separation yielded 54·6% of *p*-acid, m. p. 230—231°, mixed m. p. 231—234°, and 12·8% of *m*-acid (isolated altogether), m. p. 130—132°, mixed m. p. 137—140°.

(Expt. 75.) The method of Expt. 73 being adopted initially, the chlorides were separated, yielding 23·7% of *p*-chloride (m. p. 89—90°) and 3·1% of *m*-chloride (m. p. 98—100°), and the residues converted into amides, which on partial separation yielded 9·8% of *p*-amide (m. p. 200—203°). The final residues on oxidation gave nitrobenzoic acids (yield, 70·7%; *M*, 166; benzoic acid, 0·5%), which on separation yielded 29·7% of *p*-acid, m. p. 225—230°, mixed m. p. 230—234°, and 14·6% of *m*-acid, of which the bulk (precipitated) had m. p. 130—136°, mixed m. p. 139—140°, and the remainder (extracted) m. p. 120—130°, mixed m. p. 136—139°. The recovered *o*-acid, after one crystallisation from chloroform, had m. p. 141—143°, mixed m. p. 143—145°.

(Calculations.) From the previously determined oxidation-conversions of the amides, the following values are calculated: para $= 53{\cdot}2\%$, $29{\cdot}3 + 0{\cdot}685 \times 33{\cdot}1 = 52{\cdot}0\%$, $54{\cdot}0\%$, $33{\cdot}5 + 0{\cdot}634 \times 29{\cdot}2 = 52{\cdot}0\%$; meta $= 13{\cdot}6\%$, $2{\cdot}2 + 0{\cdot}685 \times 17{\cdot}4 = 14{\cdot}1\%$, $13{\cdot}9\%$, $3{\cdot}1 + 0{\cdot}634 \times 15{\cdot}8 = 13{\cdot}1\%$. Thus, the mean values are: para, 52·8%; meta, 13·7%; ortho (by difference), 33·5%.

(*h*) *Methyl Benzylsulphonate.*—(i) *Qualitative separation of isomerides.* Almost the whole of the nitration product was precipitated, on the addition of ice, as an oil which soon solidified. *Methyl* p-*nitrobenzylsulphonate* was readily separated by grinding the mixture with ether and crystallising the undissolved portion from ethyl acetate–ligroin, from which it separated in small, hard cubes, m. p. 113° (Found: C, 41·7; H, 3·8. $C_8H_9O_5NS$ requires C, 41·6; H, 3·9%). On oxidation by permanganate, it was converted almost quantitatively into *p*-nitrobenzoic acid, m. p. 234—235°

(unpurified). Probably hydrolysis precedes oxidation, since boiling with water for a short time converts the ester into the free sulphonic acid and methyl alcohol. By crystallising the part which dissolved in ether from ethyl acetate–ligroin, methyl *m*-nitrobenzylsulphonate was obtained as thin, rhomboidal leaflets, m. p. 99—100° (Purgotti and Monti, *loc. cit.*, record m. p. 77°), and a further quantity of the same isomeride was obtained from the mother-liquors of the *p*-compound by mechanical separation of the crystals (Found: C, 41·2; H, 3·9%). The orientation was proved by boiling with water, evaporating the neutralised solution of the sulphonic acid to dryness, and digesting the residue with phosphorus pentachloride and oxychloride at 90° for a few minutes; *m*-nitrobenzylsulphonyl chloride (m. p. 100—101°) was then obtained.

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 83). The precipitated nitration product (yield 94%) was hydrolysed by boiling with water and the nitrosulphonic acids were converted into their amides as in the preceding series of experiments, and oxidised in that form. The mixed acids gave 47·0% of *p*-acid, m. p. 210—220°, mixed m. p. 220—230°, and 28·0% of *m*-acid, m. p. 127—130°, mixed m. p. 135—140°.

(Expt. 84.) The nitration product was extracted with ethyl acetate (yield 95%) and treated as in the preceding experiment. The nitrobenzoic acids gave 42·3% of *p*-acid, m. p. 225—231°, mixed m. p. 228—234°, and 31·2% of *m*-acid, of which 25·9% (precipitated) had m. p. 137—139°, mixed m. p. 139—140°, and the remainder (extracted) m. p. 122—129°, mixed m. p. 136—138°.

(Expt. 87.) The *p*-nitro-derivative was partly separated from the nitration product by means of ether and ethyl acetate (29·0% having m. p. 113°, and 4·3% having m. p. 110—113°), and the residues were converted into amides and oxidised. The acids gave 13·2% of *p*-acid, m. p. 230—232°, mixed m. p. 234—235°, and 48·1% of *m*-acid, of which 37·9% had m. p. 138—139°, mixed m. p. 140°, and the remainder had m. p. 125—130°, mixed m. p. 136—137°.

(Calculations.) Using the oxidation data for the amides, we have para $= 45{\cdot}7\%$, $41{\cdot}0\%$, $33{\cdot}3 + 0{\cdot}667 \times 12{\cdot}7 = 41{\cdot}8\%$; meta $= 29{\cdot}9\%$, $33{\cdot}5\%$, $0{\cdot}667 \times 50{\cdot}5 = 33{\cdot}7\%$, and the means are: para, 42·9%; meta, 32·4%; ortho (by difference), 24·7%.

(*i*) *Benzylsulphonyl Chloride.*—(i) *Qualitative separation.* The nitration product was completely precipitated on addition of ice, and the bulk of the *m*-nitro-derivative was readily separated as leaflets, m. p. 100—101° (compare Purgotti and Monti, *loc. cit.*), by crystallisation from chloroform–ligroin (4 : 1 by vol.) (Found: C, 36·1; H, 2·8%). Its identity was shown by conversion into the *m*-amide and by oxidation to *m*-nitrobenzoic acid. p-*Nitrobenzylsulphonyl chloride* was obtained from the mother-liquors as large, inclined prisms, m. p. 90° (Found : C, 36·1 ; H, 2·7. $C_7H_6O_4NClS$ requires C, 35·7 ; H, 2·6%). On oxidation with permanganate it yielded only *p*-nitrobenzoic acid, m. p. 230—234° (unpurified), and on treatment with ammonia gave the *p*-nitro-amide.

(ii) *Estimation of the proportion of* m-*isomeride* (Expt. 92). The precipitated nitration product (yield 96·9%) (Found : C, 35·7 ; H, 2·8. Calc. : C, 35·7 ; H, 2·6%) was crystallised from 1·5 parts by weight of chloroform mixed with one-quarter of its volume of ligroin; 38·4% (calculated on the yield *isolated*) of pure *m*-compound, m. p. 100—101°, then separated. The residues, on conversion into the amides and on oxidation gave nitrobenzoic acids (*M*, 166; benzoic acid, nil) which, when separated, were found to consist of 53·2% of *p*-acid, m. p. 222—230°, mixed m. p. 230—234°; 20·5% of *m*-acid, m. p. 133—135°, mixed m. p. 138°; and 26·3% of *o*-acid (by difference).

(Expt. 93.) The whole product was converted into amides and oxidised to mixed acids (*M*, 167; benzoic acid, nil) which on separation gave 36·7% of *p*-acid, m. p. 220—230°, mixed m. p. 230—232°, and 45·9% of *m*-acid, of which 30·0% had m. p. 136—137°, mixed m. p. 140°, and 15·9% had m. p. 120—130°, mixed m. p. 135—139°.

(Expt. 96.) Fractional crystallisation from chloroform–ligroin containing gradually increasing proportions of ligroin gave 39·8% of *m*-chloride, m. p. 99·5—101°, 3·0% having m. p. 99—100°, and 0·3% having m. p. 97—99°, together with 9·1% of *p*-chloride, m. p. 88—90°, and 0·2% having m. p. 87—89°. The residues, on oxidation after conversion into amides, gave nitrobenzoic acids (yield, 80·0%; *M*, 166; benzoic acid, nil) which, when separated, yielded 49·5% of *p*-acid, m. p. 224—232°, mixed m. p. 230—234°, and 17·0% of *m*-acid, of which 10% had m. p. 134—138°, mixed m. p. 140°, and 7% had m. p. 125—130°, mixed m. p. 136—139°.

(Calculations.) By the method already illustrated, the above data gave para : $0{\cdot}616 \times 52{\cdot}2 = 32{\cdot}1\%$, 34·8%, $9{\cdot}3 + 0{\cdot}476 \times 48{\cdot}7 = 32{\cdot}5\%$; meta : $0{\cdot}616 \times 22{\cdot}1 = 52{\cdot}0\%$, 48·6%, $43{\cdot}1 + 0{\cdot}476 \times 18{\cdot}4 = 51{\cdot}9\%$. The means, neglecting Expt. 93, are : para, 32·3%; meta, 52·0%; ortho (by difference), 15·7%. The means, including Expt. 93, are : para, 33·1%; meta, 50·8%; ortho (by difference), 16·9%.

(D) *Summary of Results.*

The following tabular summary is appended for convenience in reference :—

Nitration of Benzylsulphonyl Compounds by Nitric Acid (d^{18° 1·494) *at* − 10° *to* − 5°.

R in directing group, $CH_2 \cdot SO_2 \cdot R$.	Isomerides formed (%).				
	Para.	Mean.	Ortho.	Meta.	Mean.
CH_3	43·3 40·7 42·6	42·2	27·5	29·5 30·6 30·8	30·3
NH_2	42·7 39·7 39·6	40·7	27·9	31·7 31·0 31·6	31·4
NHMe	41·5 39·5 43·7	41·5	29·5	29·5 28·5 29·0	29·0
NHEt	42·8 43·6 41·9	42·8	29·3	27·5 28·0 28·2	27·9
NMe_2	43·8 41·8 43·0	42·9	28·7	28·1 27·5 29·7	28·4
NEt_2	47·2	47·2	27·7	25·1	25·1
OH (doubtless ionised)	53·2 52·0 52·0	52·8	33·5	13·6 14·1 13·1	13·7
OMe	45·7 41·0 41·8	42·9	24·7	29·9 33·5 33·7	32·4
Cl	32·1 34·8 32·5	33·1	16·9	52·0 48·6 51·9	50·8

The figures recorded in the last column are rounded in the abridged table given in the introduction.

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