

172. *The Nitration of Benzenesulphonyl Chloride and Fluoride.*

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A modification of the Holleman extraction method for proximate analysis has been elaborated, use being made of the refractive index as a measure of concentration. This has been used to examine the products of the nitration of benzenesulphonyl chloride. The mixed nitrobenzenesulphonyl chlorides were converted into sulphonanilides for analysis by the thermal method and by the modified extraction method. The mixture obtained by nitrating benzenesulphonyl fluoride was examined directly by the thermal method. In the nitration of benzenesulphonyl chloride a trinitrohydroxy-by-product has been detected and shown to amount to 2% of the products.

In a comparison of the SO_2Cl and the SO_2F group with related *m*-directing radicals the results are shown to be in agreement with current views, but one discrepancy which emerges may require further investigation.

THE directive powers of groups SO_2X , where X is OH, Cl, $\text{O}\cdot\text{CH}_3$, and NR_2 , have been compared in the benzyl series, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{SO}_2\text{X}$ (Ingold, Ingold, and Shaw, J., 1927, 813).

In the simple phenyl series, $C_6H_5 \cdot SO_2X$, the sulphonic acid is the only substance which has been studied (Obermiller, *J. pr. Chem.*, 1914, **89**, 70). Arising from a comparison recently made between the nitration of substituted sulphonic acids and their chlorides (Turner and Wynne, *J.*, 1936, 707), the nitration of unsubstituted benzenesulphonyl chloride was studied in detail. In order to facilitate the proximate analysis, the easily-hydrolysed nitrated sulphonyl chlorides were converted into the more stable mixed nitrobenzenesulphonanilides. There was obtained a 96% yield of anilides which gave correct ultimate analysis figures. A check experiment showed that the 4% loss was evenly distributed over all three possible products. The mixture was analysed by a thermal method, using the thaw-point device, and by an extraction method (Holleman, "Die Direkte Einführung von Substituenten in den Benzolkern," p. 17) in which the refractive index of the solution was used as a measure of concentration. A suitable extracting liquid of low volatility, low refractive index, and sufficient solvent power was found in amyl valerate.

The first figures obtained by the extraction method were evidently erroneous: their sum was 109.4%, and the proportion of *m*-isomeride (97.9%) greatly exceeded the proportion detected by the thermal method (91.7%). At the same time, artificial mixtures of the three nitrobenzenesulphonanilides could be analysed with the accuracy expected. Although special experiments showed that neither under- nor over-nitration had occurred, direct refractive index tests clearly indicated the presence of a fourth substance, formed by some unexplained reaction. Any such substance would be extracted independently and would therefore raise the percentage found in the determination of each isomeride. Moreover, even if the satisfactory ultimate analyses given by the nitration mixture appeared to rule out the presence of an impurity, they would admit a small proportion of a substance not very different in ultimate composition from the anilides.

Direct experiments on the nitration mixture at last successfully separated a specimen of this fourth substance, which was identified as 2:4:6-trinitro-3-hydroxydiphenylamine (Blanksma, *Rec. Trav. chim.*, 1902, **21**, 261; Ullmann and Bruck, *Ber.*, 1908, **41**, 3939). A direct extraction test proved the absence of any fifth substance.

The presence of this diphenylamine implied that during the nitration some trinitro-*m*-hydroxybenzenesulphonyl chloride had been formed as a by-product. When this subsequently reacted with aniline, the entire sulphonyl chloride group was eliminated. The occurrence of hydroxy-by-products in the nitration of benzene, toluene, and xylene was noted many years ago (Nölting, *Ber.*, 1885, **18**, 2670; 1888, **21**, 3158) and emphasised by Armstrong and Rossiter (*P.*, 1891, **7**, 89). It appears to have been investigated no further except for nitrations in the presence of mercuric salts. The formation of such by-products in other simple nitrations will be discussed in a future paper.

Theoretically the Holleman extraction method may be applied to a mixture containing any number of components, although hitherto its use appears to have been confined to mixtures of not more than three. To analyse a four-component mixture, four concentration-refractive index curves are required: these were therefore constructed. The proportions determined were: *o*-, 5.8; *m*-, 91.6; *p*-, 2.4; trinitrodiphenylamine, 2.0% (total 101.8%). These figures were reduced to a 100% basis, and corrected for differences in molecular weight: the products of nitration are then given as: *m*-, 91.3 ± 0.5 ; *o*-, 5.2 ± 1 ; *p*-, 1.8 ± 1 ; by-product, $1.7 \pm 1\%$.

It was impossible to convert the nitrobenzenesulphonyl fluorides quantitatively into anilides; the proximate analysis here was therefore carried out directly by the thermal method. The proportion of *m*-product was $95.6 \pm 0.5\%$.

These figures (sulphonic chloride, 91.3% *m*-; fluoride, 95.6% *m*-) are to be compared with those obtained by Obermiller in the nitration of the sulphonic acid (63% *m*-, 27% *o*-, 10% *p*-). The contrast between the nitration of an acid and its chloride is well known and easily explained (compare Bennett, *J.*, 1936, 715). The observed difference between sulphonyl fluoride and chloride would also have been anticipated.

Comparison of the inductive effects of methyl and chlorine would seem to indicate the sulphonic chloride group as more powerfully *m*-directing than the methanesulphonyl group. This conclusion was justified in the benzyl series (Ingold, Ingold, and Shaw, *loc. cit.*), where benzylmethylsulphone yields 30% of *m*-nitration product and benzylsulphonyl chloride

51%. Yet the figure of 91.3% for benzenesulphonyl chloride must be contrasted with one of 97—98% for phenylmethylsulphone (Twist and Smiles, J., 1925, 127, 1278; Baldwin and Robinson, J., 1932, 1445). It is possible that the higher *m*-directing power of the sulphone may be explained by its superior tendency to unite with the sulphuric acid present, a tendency which increases the proportion of *m*-isomeride in nitration and has already been demonstrated for benzaldehyde (Baker and Moffitt, J., 1931, 314); but the figure quoted by Twist and Smiles was admittedly not a precise estimate, and those quoted by Baldwin and Robinson represent more a comparison of related substances than an absolute value for any one. The question might be settled by a more detailed investigation of the nitration of phenylmethylsulphone.

EXPERIMENTAL.

I. Nitration of Benzenesulphonyl Chloride.

Preparation of the Three Nitrobenzenesulphonanilides.—For accurate analyses, the anilides described below were recrystallised three times from alcohol and once from benzene. (a) *m*-Nitrobenzenesulphonanilide, m. p. 125°. (b) *o*-Nitrobenzenesulphonanilide, m. p. 115°, was made by oxidising *oo'*-dinitrodiphenyl disulphide to *o*-nitrobenzenesulphonic acid (Blanksma, *Rec. Trav. chim.*, 1901, 20, 115), converting the powdered anhydrous acid into its chloride (Ullmann, *Ber.*, 1910, 43, 2700), and treating the chloride with aniline. Low yields of sulphonyl chloride may possibly be explained by the formation and breakdown of a sulphanyl chloride (compare Turner and Wynne, J., 1936, 701).

(c) *p*-Nitrobenzenesulphonanilide. *pp'*-Dinitrodiphenyl disulphide, prepared from sodium disulphide and *p*-chloronitrobenzene (Blanksma, *loc. cit.*), melted at 181° after repeated crystallisation from benzene, acetic acid, and ethyl acetate. This substance has been described as melting at 171° (Blanksma, *loc. cit.*; Elgersma, *Rec. Trav. chim.*, 1929, 48, 752; Zincke, *Annalen*, 1913, 400, 1), and the existence of two forms has been asserted (Hodgson and Wilson, J., 1925, 127, 440). All these observations are explained by the presence in the crude disulphide of quantities of the monosulphide. Our crude material melted from 145° to 180°, and in the tedious purification we isolated a specimen of the monosulphide, m. p. 153—157°, identical with a specimen prepared by condensing potassium *p*-nitrothiophenoxide with *p*-bromonitrobenzene in alcohol. Oxidised with fuming nitric acid, both specimens yielded the sulphoxide, m. p. 177—179° (Found: C, 49.7; H, 2.5; N, 9.5; S, 10.9. Calc.: C, 49.4; H, 2.7; N, 9.6; S, 10.9%), and, with chromic acid mixture, the sulphone, m. p. 251—254° (Found: S, 10.5. Calc.: S, 10.4%). Fromm and Wittmann (*Ber.*, 1908, 41, 2269) gave this m. p. as 282°.

The disulphide was oxidised to the sulphonic acid by means of fuming nitric acid. When the crude disulphide was used, *pp'*-dinitrodiphenyl sulphoxide (m. p. 179°, mentioned above) was formed as a by-product insoluble in water (cf. Witte, *Rec. Trav. chim.*, 1932, 51, 290). The acid chloride from the potassium salt yielded *p*-nitrobenzenesulphonanilide, m. p. 171° (Found: C, 51.7; H, 3.3. C₁₂H₁₀O₄N₂S requires C, 51.8; H, 3.6%).

Crystal Forms of the Above Anilides.—(i) *m*-Nitrobenzenesulphonanilide. This substance crystallises in the sphenoidal class of the monoclinic system, the development being clearly enantiomorphous; both left- and right-handed crystals were observed. The elements are $a : b : c = 1.938 : 1 : 1.651$; $\beta = 118^\circ 0'$.

The forms observed were $a(100)$, $r(101)$, $c(001)$, $R(\bar{1}01)$, $m(110)$, $m'(1\bar{1}0)$, and either $q(011)$ or $q'(0\bar{1}1)$. The typical habit of a right-handed crystal from alcohol is shown in Fig. 2. The following angular values were obtained from six crystals, from measurements on the two-circle goniometer:—

	$a(100)$.	$m(110)$.	$r(101)$.	$c(001)$.	$R(\bar{1}01)$.	$q(011)$.
ϕ	0° 0'	*59° 42'	0° 0'	0° 0'	180° 0'	*72° 10'
ρ	90° 0'	90° 0'	56° 47'	*28° 0'	23° 4'	*60° 2'

The following are the Barker classification angles: $cr(001 : 101) = 28^\circ 47'$; $ra(101 : 100) = 33^\circ 13'$; $am(100 : 110) = 59^\circ 42'$; $bq(010 : 011) = 34^\circ 37'$.

A straight extinction was observed on a . The substance has a high double refraction and dispersion. In convergent light, an optic axis is visible emerging perpendicular to the face c , and from the appearance of the brushes it is clear that the optic axial angle is near 90°.

(ii) *o*-Nitrobenzenesulphonanilide. The substance crystallises in the monoclinic system with axial ratios $a : b : c = 1.650 : 1 : 0.938$, and axial angle $\beta = 118^\circ 59'$. The following is a list of the forms observed and the mean angular measurements obtained from two selected crystals:

	$a(100).$	$l(210).$	$m(110).$	$r(101).$	$R(\bar{1}01).$	$o(111).$	$q(011).$	$p(\bar{1}11).$
ϕ	0° 0'	35° 54'	*55° 17'	0° 0'	180° 0'	37° 55'	*59° 27'	95° 31'
ρ	90° 0'	90° 0'	90° 0'	50° 15'	5° 10'	56° 44'	*47° 27'	43° 15'

The usual habit is shown in Fig. 1, with R large. The Barker classification angles (observed or calculated) are : $cr(001 : 101) = 21^\circ 16'$; $ra(101 : 100) = 39^\circ 45'$; $am(100 : 110) = 55^\circ 17'$; $bq(010 : 011) = 50^\circ 38'$.

FIG. 1.

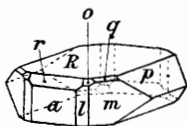


FIG. 2.

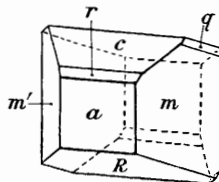
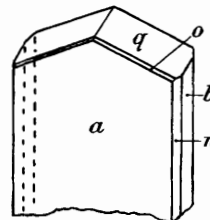


FIG. 3.



A straight extinction, observed on the face R , confirmed the position of the plane of symmetry. The optic axes were not observed.

(iii) *p*-Nitrobenzenesulphonanilide. The crystals from various solvents were imperfect and formed curved faces : the measurements are less accurate than those for the other two isomerides. Examination of five crystals gave the following angles :

	$a(100).$	$n(120).$	$b(010).$	$o(111).$	$q(011).$
ϕ	0° 0'	70° 50'	90° 0'	*32° 43'	*49° 6'
ρ	90° 0'	90° 0'	90° 0'	*36° 57'	*28° 10'

The habit of these crystals is illustrated in Fig. 3. The substance is monoclinic, with axial angle $\beta = 109^\circ 19'$ and axial ratios $a : b : c = 1.443 : 1 : 0.405$. The Barker classification angles are : $cr(001 : 101) = 13^\circ 1'$; $ra(101 : 100) = 57^\circ 40'$; $am(100 : 110) = 53^\circ 43'$; $bq(010 : 011) = 69^\circ 6'$.

The straight extinction on the face a confirms the position of the plane of symmetry.

Sodium Salts of the Nitrobenzenesulphonanilides.—From concentrated sodium hydroxide solutions the sodium salts of the anilides crystallised out; their considerable solubility in water prevented adequate washing of the crystals. The sodium content of the salts was found by direct titration against 0.1N-hydrochloric acid, results being consistently 0.6% high because of adsorbed alkali. The sodium salt of *m*-nitrobenzenesulphonanilide (Found : Na, 7.4. $C_{12}H_9O_4N_2SNa \cdot 2H_2O$ requires Na, 6.9%) when heated afforded the red anhydrous salt (Found : loss, 11.2. $2H_2O$ requires loss, 10.8%. Found, in anhydrous salt : Na, 8.5. $C_{12}H_9O_4N_2SNa$ requires Na, 7.7%). The yellow dihydrated salt of *o*-nitrobenzenesulphonanilide (Found : Na, 7.45%) when heated lost $2H_2O$ (Found : loss, 12.6%), partly liquefied, and cooled to give a red anhydrous solid (Found : Na, 8.5%). *p*-Nitrobenzenesulphonanilide gave only an anhydrous vermilion salt (Found : Na, 8.3%).

Thermal Examination of the System : o-, m-, p-Nitrobenzenesulphonanilides.—Observations were made by the thaw-point method (Rheinboldt and Kircheisen, *J. pr. Chem.*, 1926, 113, 348; cf. Bennett and Wain, *J.*, 1936, 1118) : the temperatures are corrected, T_1 being the point at which liquid was first detected and T_2 that at which the last solid disappeared. The mixed molten anilides set to a glass unless incubated 10° below their eutectic temperature.

(i) System *m*- and *o*-nitrobenzenesulphonanilide.

<i>o</i> -Anilide, mols. %	0.0	3.7	9.1	9.2	11.4	14.2	17.1
T_2	124.8°	121.6°	119.0°	119.6°	117.6°	116.1°	115.3°
<i>o</i> -Anilide, mols. %	19.3	21.2	44.2	70.9	100.0		
T_2	112.7°	112.2°	101.1°	101.7°	115.4°		
<i>o</i> -Anilide, mols. %	29.8	50.9	51.8	61.7	76.9	80.0	89.7
T_2	109.7°	96.3°	92.2°	96.5°	104.9°	110.6°	112.4°
T_1	88.7	87.9	87.4	87.5	88.2	87.8	89.0

The curve shows a simple eutectic at 87.7° , 55 mols. % of *o*-nitrobenzenesulphonanilide.

(ii) System *m*- and *p*-nitrobenzenesulphonanilide.

<i>p</i> -Anilide, mols. %	0.0	2.8	3.2	6.8	9.5	13.8	16.4
T_1	—	109.1°	108.3°	108.3°	108.3°	108.1°	108.8°
T_2	124.2	122.5	122.2	120.8	118.8	117.1	115.2
<i>p</i> -Anilide, mols. %	18.7	21.8	22.5	24.8	28.8	31.2	38.2
T_1	107.9°	107.9°	108.2°	107.8°	108.6°	108.3°	108.3°
T_2	113.8	112.2	111.9	112.0	114.8	118.5	125.5
<i>p</i> -Anilide, mols. %	41.6	51.3	61.2	66.1	78.0	85.0	100.0
T_1	108.0°	109.2°	108°	107°	108°	110°	—
T_2	129.9	139.2	150	152	160	165	171°

The curve shows a simple eutectic at 108.3°, 24 mols. % of *p*-nitrobenzenesulphonanilide.

(iii) System *o*- and *p*-nitrobenzenesulphonanilide.

<i>p</i> -Anilide, mols. %	10.4	19.1	30.2	40.8	59.4	59.8	70.6	77.8	89.1
T_1	103.4°	103.8°	103.8°	—	104.0°	—	—	—	—
T_2	110.9	105.7	120.1	131.9°	—	147.1°	156°	160½°	166½°

The curve shows a simple eutectic at 103.8°, 18 mols % of *p*-nitrobenzenesulphonanilide.

(iv) *The ternary eutectic.* The mean value of the ternary eutectic temperature was 82.2°, determined by the thaw-point method; no eutectic temperatures could be detected on cooling curves.

Nitration of Benzenesulphonyl Chloride.—During 1 hour, a weighed amount (about 6 g.) of benzenesulphonyl chloride (m. p. 15.5°) was dropped slowly into a stirred mixture of nitric acid (5 c.c., 100%) and sulphuric acid (20 c.c., 100%) held at 30°. The product was not affected by severer precautions against overheating, by altering the time of nitration from 15 to 140 minutes, by twice redistilling the benzenesulphonyl chloride, or by using more nitric (25 c.c.) and less sulphuric acid (5 c.c.) at 60°. The nitration mixture was poured on ice, and the precipitated chlorides extracted with benzene. Their solution was dried by the addition of thionyl chloride (3 c.c.), driven off by an hour's boiling. A further hour's heating with aniline (20 c.c., redistilled) gave the sulphonanilides, which were extracted by warm 2*N*-sodium hydroxide, and precipitated by an excess of dilute nitric acid (1 : 1). Yields averaged 96%. Pure *m*-nitrobenzenesulphonanilide was obtained in 99% yield from *m*-nitrobenzenesulphonyl chloride by this method. Each of the three anilides could be recovered pure and without appreciable loss from the benzene solution by this extraction method.

The mixed anilides without further purification gave no reactions for sodium ion, chloride, or aniline, and analysed correctly (Found, for one individual nitration product: C, 51.7; H, 3.5; S, 11.3; N, 9.9; for the mixed products of six nitrations: * C, 51.6; H, 3.7; S, 11.3; N, 10.1. Calc.: C, 51.8; H, 3.6; N, 10.1; S, 11.5%).

Analysis of the Nitration Product (Series A).—(i) *By direct fractional crystallisation.* From benzene, 80% was obtained as *m*-nitrobenzenesulphonanilide.

(ii) *Thermal analysis.* Both *o*- and *p*-nitrobenzenesulphonanilide depressed the m. p. of the *m*-isomer to approximately equivalent extents (cf. Nichols, *J. Amer. Chem. Soc.*, 1918, **40**, 400). The extent of this depression was determined by the thaw-point method:

<i>o</i> -Anilide, mols. %	3.7	9.1	9.2	11.4	14.2	17.1	19.3	21.2	29.8
T_2	121.6°	119.0°	119.6°	117.5°	116.1°	115.3°	112.7°	112.2°	109.7°
<i>p</i> -Anilide, mols. %	2.8	3.2	6.8	9.5	13.8	16.4	18.7	21.8	22.9
T_2	122.5°	122.2°	120.8°	118.8°	117.1°	115.2°	113.8°	112.2°	111.9°
								111.9°	112.0°
									114.8°

An artificial mixture was analysed from the value of T_2 determined by the thaw-point method (Found: *m*-, 89.3. Mixture contained: *m*-, 90.0; *o*-, 6.0; *p*-, 4.0%). To check the thaw-point figures, cooling curves were plotted, by cooling about 10 g. of the mixture in a bath whose temperature was held 4° below that of the mixture. The curves obtained showed a bowl-shaped portion due to supercooling, followed by a peak and a final straight line; T_2 was obtained by extrapolating back from the straight portion to the original downward slope. No eutectic could be detected by careful cooling (Found, by cooling curves, *m*-, 90.4%).

For clearer vision with the dark-coloured nitration mixture, thaw-point tubes with an oval cross-section were used; T_2 was determined as 119.43°, and from cooling curves as 119.45°. The nitration mixture therefore contains 91.7% of *m*-nitrobenzenesulphonanilide.

(iii) *Extraction method.* The refractive index, determined on an Abbé refractometer, was

* Analyses by Weiler: unmarked analyses by Schoeller.

chosen as a measure of solubility. Amyl valerate (b. p., 190°; n_D^{20} , 1.4130) was chosen as solvent because its high b. p. minimised evaporation, because it dissolved about 5% each of the anilides, and because, its refractive index being low, a small amount of dissolved highly-refractive anilide would be easily detected. Suitable amounts of amyl valerate and the anilides were stirred in tubes in a thermostat ($20^\circ \pm 0.1^\circ$) for 3 hours, and were allowed to recover for an hour from the heat generated by stirring.

The solubility of the third anilide in a solution saturated with the other two was measured by the increasing refractive index. Curves were drawn and checked against a made-up mixture. The nitration mixture was analysed from these curves to contain nitrobenzenesulphonanilides : *o*-, 6.9; *m*-, 97.9; *p*-, 4.6% (total 109.4%). Repetitions of the nitration and the analysis under various conditions made it clear that this figure was in excess of 100% not as a result of any impurity in the materials or of under- or over-nitration. After many experiments it was concluded that the 9.4% excess must be due to the presence in the nitration mixture of a fourth substance. A direct test was possible : the refractive index of a solution saturated with the three anilides was 1.4310, and after this solution had been stirred with an amount of nitration product corresponding to 23 g. per 100 g. of amyl valerate the value was 1.4324, the increase of 0.0014 indicating a fourth substance.

A Hydroxy-by-product.—When the nitration mixture was stirred with water, part dissolved to a slightly acid, yellow solution, from which mineral acids precipitated a yellow solid (X). To isolate this substance in quantity, 1250 g. of benzenesulphonyl chloride were nitrated and converted into mixed sulphonanilides, which were extracted with hot 2% sodium acetate solution. The cold filtered extracts were acidified, and the yellow solid collected and purified. It formed yellow needles, m. p. 161—162°, from acetic acid. The substance was identified as 2 : 4 : 6-trinitro-3-hydroxydiphenylamine (Found : C, 45.2; H, 2.7; N, 16.9. Calc. : C, 45.0; H, 2.5; N, 17.5%), identical with that synthesised from *m*-nitrophenol (Blanksma, *Rec. Trav. chim.*, 1902, 21, 261) and from styphnic acid (Ullmann and Bruck, *Ber.*, 1908, 41, 3939). Both X and the synthetic material with *p*-toluenesulphonyl chloride and diethylaniline gave small orange prisms of 3-chloro-2 : 4 : 6-trinitrodiphenylamine, m. p. 147—148° (Found : C, 43.0; H, 2.2; N, 16.8; Cl, 10.7. $C_{12}H_7O_6N_4Cl$ requires C, 42.5; H, 2.7; N, 16.5; Cl, 10.5%), which condensed with aniline to give 2 : 4 : 6-trinitro-1 : 3-dianilinobenzene, m. p. 215—216° (compare 207°; Van Duin, *Rec. Trav. chim.*, 1919, 38, 93) (Found : N, 17.95. Calc. : N, 17.7%), and with piperidine to afford the piperidino-compound, yellow plates with a straight extinction, m. p. 161—162° (Found : C, 52.7; H, 4.4; N, 18.1. $C_{11}H_{17}O_6N_5$ requires C, 52.6; H, 4.4; N, 18.0%).

Analysis of the Nitration Product (Series B).—(i) *The extraction method.* Four refractive-index curves were obtained : the symbols W_o , W_m , W_p , W_x denote respectively the weights of *o*-, *m*-, *p*-nitrobenzenesulphonanilides and 2 : 4 : 6-trinitro-3-hydroxydiphenylamine per 100 g. of amyl valerate. About 1 c.c. of solution was sufficient for one determination. The figures for the curves were :

(a) Amyl valerate saturated with <i>o</i> -, <i>p</i> -, and X; increasing amounts of <i>m</i> - added.						
W_m	0.00	2.03	3.29	5.53	7.75	
n	1.42325	1.4260	1.4280	1.4310	1.4346	
(b) Saturated with <i>m</i> -, <i>p</i> -, and X; increasing amounts of <i>o</i> -.						
W_o	0.00	0.48	0.59	1.185	1.82	3.76
n	1.4291	1.4299	1.4300	1.4310	1.4315	1.4344
(c) Saturated with <i>o</i> -, <i>m</i> -, and X; increasing amounts of <i>p</i> -.						
W_p	0.00	0.445	0.70	0.78	0.96	1.56
n	1.4326	1.4333	1.43345	1.4338	1.4340	1.43505
(d) Saturated with <i>o</i> -, <i>m</i> -, and <i>p</i> -; increasing amounts of X.						
W_x	0.00	0.475	1.12	1.57		
n	1.4310	1.4318	1.4332	1.4343		

A new nitration mixture was prepared, the final precipitation of the anilides being carried out slowly at 0°, with vigorous stirring to minimise ultimate sampling errors (Found : *C, 51.8; H, 3.2; S, 11.1; N, 10.2%). The refractive index of a solution saturated with all four components was approached by long stirring, and by cooling a solution saturated at 50° : $n = 1.4360$. When this solution was stirred with an amount of the new nitration mixture corresponding to 23 g. per

100 g. of solvent, the refractive index was unchanged. Therefore no fifth substance was present. From the curves, the nitration mixture was analysed to : *o*-, 5.8; *m*-, 91.6; *p*-, 2.4; X, 2.0%.

Component.	<i>o</i> -.	<i>o</i> -.	<i>m</i> -.	<i>m</i> -.	<i>p</i> -.	<i>p</i> -.	X.	X.
Wt. of mixture	0.1029	0.1007	0.0518	0.0513	0.1000	0.0977	0.0995	0.1011
Wt. of solvent	1.0192	1.1416	1.1697	1.0519	1.0254	1.0874	1.0399	1.0774
<i>n</i>	1.4300	1.42985	1.42905	1.4297	1.42205	1.4329	1.4314	1.43135
<i>W</i>	0.61	0.52	4.04	4.50	0.28	0.18	0.20	0.18
%	6.04	5.49	91.0	92.2	2.87	2.00	2.09	1.91

The probable error of the *m*-determination is of the order $\pm 0.5\%$; of the others, $\pm 1.0\%$.

As a further check on the trustworthiness of the whole process, 6 g. of a mixture of *o*- (6.0%), *m*- (90.0%), and *p*- (4.0%) nitrobenzenesulphonyl chlorides were stirred with nitric acid (5 c.c., 100%) and sulphuric acid (20 c.c., 100%). The product was isolated as a 96% yield of mixed nitrobenzenesulphonanilides, of unchanged composition : *m*-, 91.8 (thermal analysis); *m*-, 90.3; *o*-, 6.8; *p*-, 5.9% (extraction method). The *p*-determination is the least accurate owing to the low solubility of the *p*-anilide.

(ii) *Thermal analysis.* To the figure previously determined, a correction must be made for the difference in molecular weight of *m*-nitrobenzenesulphonanilide (278) and 2 : 4 : 6-trinitro-3-hydroxydiphenylamine (320); the final figure becomes 91.45%, which a consideration of probable errors shows as accurate to $\pm 0.5\%$.

Summary.—Reducing these figures to a 100% basis, and allowing for the formation of the diphenylamine by a chemical reaction different from anilide formation, we find that in the nitration of benzenesulphonyl chloride, there are formed 91.3 ± 0.5 , 5.2 ± 1 , and $1.8 \pm 1\%$, respectively, of *m*-, *o*-, and *p*-nitrobenzenesulphonanilide and $1.7 \pm 1\%$ of 2 : 4 : 6-trinitro-3-hydroxybenzenesulphonyl chloride.

II. Nitration of Benzenesulphonyl Fluoride.

Benzenesulphonyl fluoride, prepared by the method of Davies and Dick (J., 1931, 2104), was redistilled to constant b. p. ($93^\circ/14.5$ mm.) (Found : equiv. by hydrolysis, 79.8. Calc. : 80.0).

The isomeric nitrobenzenesulphonyl fluorides were obtained by similar methods : *m*-nitrobenzenesulphonyl fluoride, m. p. $45\text{--}46^\circ$ [Found : equiv. by hydrolysis after 4 hours' boiling with 0.5*N*-sodium hydroxide, 102.5. Calc. : 102.5. (A blank titration was necessary because of the solvent action of the alkali on the flask)]; *p*-nitrobenzenesulphonyl fluoride, m. p. 79° (Found : C, 35.4; H, 2.0; N, 7.1; equiv. by hydrolysis, 102.5. $C_6H_4O_4NSF$ requires C, 35.1; H, 2.0; N, 6.8%); *o*-nitrobenzenesulphonyl fluoride, m. p. 59° (Found : C, 35.6; H, 2.1; N, 7.0%; equiv., 102.5).

Nitration.—Benzenesulphonyl fluoride was nitrated with a mixture of nitric acid (15 c.c., 100%) and sulphuric acid (25 c.c., 100%). As it was found impossible to convert *m*-nitrobenzenesulphonyl fluoride quantitatively into its anilide, the product here was extracted with chloroform, subsequently removed by prolonged evaporation. Yield, 97% (equiv., 102.5); the nitration mixture hydrolysed to an orange solution.

The depression of the m. p. of *m*-nitrobenzenesulphonyl fluoride by the *p*-isomeride was determined :

<i>p</i> -Fluoride, mols. %	0.0	0.99	2.10	4.04	7.35
T_2	45.6°	45.5°	44.65°	43.8°	42.45°

Determinations of T_2 on the nitration mixture gave 43.63° by the thaw-point method, and 43.65° by a cooling curve, corresponding to 95.6% of *m*-fluoride.

When, by the addition of *p*-fluoride to the nitration mixture, the percentage of *m*- was reduced to 91.0%, T_2 determinations (41.5°) detected 91.2% *m*-fluoride.

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