

737. *The Reactions of Organic Derivatives of Elements Capable of Valency-shell Expansion. Part IX.* Relative Rates and Partial Rate Factors for the Nitrations of Ethyl Phenyl Sulphone and of Benzyl Ethyl Sulphone.*

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Ethyl phenyl and benzyl ethyl sulphones have been nitrated in acetic anhydride in competition with chlorobenzene or benzene, respectively, and also alone. The rates of nitration of the two compounds relative to that of benzene have been determined in each case, and also the proportions of *ortho*-, *meta*-, and *para*-, isomers formed. From these, the partial rate factors for each position on the nucleus have been calculated. Both sulphones are deactivated relative to benzene but the *ortho*- and *para*-positions of the phenyl sulphone are very much more deactivated than the *meta*-position and hence *meta*-substitution is predominant. Overall deactivation is less in the case of benzyl ethyl sulphone and mainly affects the *meta*-position leading to predominant *ortho-para*-orientation. The results are explained by considering polarisability effects enhanced by a postulated expansion of the valency-shell of the sulphur atom.

SUBSTITUENTS which are strongly *meta*-directing when directly attached to the nucleus can be arranged into two classes.¹ One of these is still predominately *meta*-directing when substituted into the side-chain of toluene and can be exemplified by benzyltrimethylammonium picrate and by phenylnitromethane. The other class includes benzyltrimethylphosphonium and -arsonium picrates which orient almost exclusively *ortho* and *para*. Alkyl benzyl sulphones occupy an intermediate position and here *meta*-nitration can be as high as 30% though it tends to be smaller with increasing size of alkyl group.² It was suggested by one of us¹ that the *ortho*- and *para*-transition states were stabilised by hyperconjugation involving the hydrogen atoms of the methylene group and enhanced by incipient *2p-3d* π -bond formation which utilises the *d*-orbitals of the polar atom. At that time it was known that, qualitatively, nitration in the phenyl series was slower than that of benzene but nothing was known about the relative reactivities of the nuclear positions in any of the derivatives under consideration. In this Paper we describe the nitrations of ethyl phenyl and benzyl ethyl sulphones and in the next, that of trimethylbenzyl-arsonium and -phosphonium picrates.

One of the reasons for including in our work the nitration of ethyl phenyl sulphone was that Baldwin and Robinson had reported that though the chief product was the *meta*-nitro-derivative, the yields of *ortho*- and *para*-isomers was quite appreciable. The quantities which we wished to determine were the total rate of nitration relative to that of benzene, the proportions of *ortho*, *meta*, and *para* nitration, and to derive from them the "partial rate factors"³ defined by Ingold and Smith⁴ as the factor by which the replacement of a hydrogen atom in benzene by an orienting substituent alters the probability of substitution at a nuclear carbon atom. The competitive method for determining the total relative rate of nitration initiated by Ingold and Shaw⁵ and further developed in later Papers^{3,6,7} was adopted, making the necessary experimental modifications and using the mathematical framework described in the earlier Papers.^{3,4} In the present work conditions

* Part VIII, *J.*, 1963, 2463.

¹ Rothstein, *J.*, 1953, 309.

² Baldwin and Robinson, *J.*, 1932, 1445.

³ Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959.

⁴ Ingold and Smith, *J.*, 1938, 905.

⁵ Ingold and Shaw, *J.*, 1927, 2918.

⁶ Bird and Ingold, *J.*, 1938, 918.

⁷ Ingold and Shaw, *J.*, 1949, 575.

were chosen such that the results could be compared directly with those of other workers. In carrying out a competitive nitration a limited quantity of the nitrating agent is used, so that at the end of the reaction, there is usually present, in addition to the mixture of nitrated products up to 70% of the unchanged starting materials. Nitration of ethyl phenyl sulphone is very slow, *i.e.*, the ratio of the rates, $K_{\text{sulphone}}/K_{\text{benzene}}$ is small, and its direct determination by nitrating its solution in benzene necessitates the estimation of a very small quantity of nitro-sulphone in the presence of a large proportion of nitrobenzene. However, the quantity $K_{\text{PhCl}}/K_{\text{benzene}}$ had been accurately determined⁶ and therefore slow nitrations were performed in chlorobenzene solution using standard conditions of solvent, nitrating agent and temperature. The procedures were adapted from those described,³⁻⁷ and were checked at each stage by the use of artificial mixtures. It was also ascertained that there was no reaction between the sulphone, chlorobenzene, and their nitro-derivatives. The total concentration of nitro-derivatives was determined by titanous chloride titration, and that of the chloronitrobenzenes by hydrolysis in methanolic alkali followed by electrometric titration of the liberated chloride ion. When benzene was used (in competitive nitration with benzyl ethyl sulphone), the nitrobenzene was separated by fractional distillation and was estimated separately from the ethyl nitrobenzyl sulphones. Finally, the proportions of isomeric nitro-derivatives formed in the non-competitive nitrations was determined by the use of near ultraviolet absorption spectra.

DISCUSSION

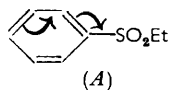
A summary of the results of nitrations of ethyl phenyl and benzyl ethyl sulphones is listed in Table I which also includes the corresponding figures for ethyl benzoate,⁴ ethyl phenylacetate,⁷ chlorobenzene,⁶ benzyl chloride,⁷ and nitrophenylmethane.⁸

TABLE I.

Orientation and partial rate factors for the nitration of phenyl derivatives, Ph·X and Ph·CH₂X, by nitric acid in acetic anhydride at 25°.

Phenyl derivative	Reactivity relative to benzene	Orientation (%)			Partial rate factors		
		<i>o</i>	<i>m</i>	<i>p</i>	<i>o</i>	<i>m</i>	<i>p</i>
-SO ₂ Et	0.00351	8.1	88.6	3.3	0.0009	0.0093	0.0007
-CH ₂ SO ₂ Et	0.229	35.6	21.9	42.5	0.245	0.150	0.584
-CO ₂ Et	0.00367	28.3	68.4	4.3	0.0026	0.0079	0.0009
-CH ₂ CO ₂ Et	3.66	42.0	10.6	47.4	4.62	1.16	10.41
-Cl	0.0353	31.0	—	69.0	0.0329	—	0.146
-CH ₂ Cl	0.302	32.0	15.5	52.5	0.290	0.140	0.951
-CH ₂ NO ₂	0.122	22.5	54.7	22.8	0.0822	0.200	0.167

The partial rate factor for the *ortho*-position of ethyl phenyl sulphone is 35% that of ethyl benzoate though their rates of nitration are almost identical. Deactivation at the *meta*-position is largely due to a $-I$ effect,⁴ and though the observed differences are small and not very significant, the rate factors of the *meta*-positions of the two compounds are if anything, in the reverse order from that which might have been anticipated by inspection of the overall rates of nitration. It can be inferred therefore that there is present an additional deactivating influence which operates by a conjugative ($-M$) effect indicated in the annexed diagram¹ (A), and mainly influences the *ortho*- and *para*-positions, the relay to the *meta*-position being negligible. The latter assumption may not be unreasonable since, in the opposite sense, the partial rate factor for the *meta*-position of chlorobenzene (0.0009)⁹ is also so low (in relation to the overall reactivity of 0.0353) that it does not appear that the ground-state mesomeric ($+M$) release of electrons reaches that position to any appreciable extent. A negative electromeric effect in the sulphone would not of course operate



⁸ Knowles and Norman, *J.*, 1961, 2938.

⁹ Roberts, Sanford, Sixma, Cerfontain, and Zagu, *J. Amer. Chem. Soc.*, 1954, **76**, 4525.

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because it would oppose the formation of the transition state. The sulphonyl group appears to be comparable to ethoxy carbonyl in deactivating the nucleus but is very much less effective than a nitro-group in spite of a comparable structure, $-\text{S}^+(\text{O}^-)_2\text{Et}$, $-\text{N}^+(\text{O})\text{O}^-$, which would be present if it had a purely dipolar structure. The relative reactivity of nitrobenzene as calculated from data given by de la Mare and Ridd,¹⁰ is approximately 10^{-5} and this seems a very great difference even allowing for the electron release of the alkyl of the sulphonyl group. Consequently, it can be concluded that the dipolar structure of the latter is not much in evidence so far as the phenyl derivative is concerned.

In the benzyl series, the ethylsulphonyl group exerts a deactivating effect closely resembling that of chlorine, although the position is reached in different ways. The overall deactivations of both benzyl ethyl sulphone and benzyl chloride are co-existent with partial rate factors which are smallest for the *meta*-positions. This is interpreted that deactivation of all three nuclear positions by inductive effects is accompanied by reactivation of the *ortho*- and *para*-positions only and furthermore, unlike inductive effects, mesomeric effects tend selectively to influence the *para*-position.¹¹ The disappearance in the benzyl compound of a $-M$ effect postulated for sulphonyl directly attached to the nucleus should therefore lead to greater *para*-reactivation and in fact the ratios of the partial rate factors, $F_{\text{PhOEt}\cdot\text{SO}_2\text{Et}}/F_{\text{PhSO}_2\text{Et}}$ are, *ortho*, 288; *meta*, 16; *para*, 840. One further point may be mentioned. If there were no reactivation process, the values of the partial rate factors in a deactivated molecule should be in the order, *ortho*, *para* < *meta*, leading to predominant *meta*-nitration; for example, the factors for nitrophenylmethane⁹ are *ortho*, 0.0822; *meta*, 0.200; and *para*, 0.167, and since the inductive effect, as measured by the rate factor for the *meta*-positions, of $\text{CH}_2\cdot\text{NO}_2$ is not very different from that of $\text{CH}_2\cdot\text{SO}_2\text{Et}$, it follows that in the absence of other considerations, the two sets of figures for the *ortho*- and *para*-positions should also have been similar.

EXPERIMENTAL

Preparation of Materials.—(a) Ethyl phenyl sulphone,¹² was recrystallised from ethanol and then twice from ethanol and petrol (b. p. 60–80°). Distillation (b. p. 98–102°/0.02 mm.) under nitrogen afforded a product, m. p. 42.5–43.0° (Found: C, 56.4; H, 5.8. Calc. for $\text{C}_8\text{H}_{10}\text{O}_2\text{S}$: C, 56.4; H, 5.9%).

(b) *Ethyl o-nitrophenyl sulphone.* *o*-Nitrobenzenethiol was obtained by boiling *o*-nitrophenyl disulphide¹³ with sodium hydroxide and acidifying the product. Boiling the latter with ethyl bromide in aqueous-alcoholic alkali yielded ethyl *o*-nitrophenyl sulphide¹⁴ which was oxidised by hydrogen peroxide in a mixture of acetic acid and acetic anhydride. The resulting sulphone was repeatedly recrystallised from ethanol–petrol (b. p. 40–60°) and had a final m. p. 43.5–44.0° (yield, 49%) (Found: C, 44.8; H, 4.4; N, 6.4. Calc. for $\text{C}_8\text{H}_9\text{NO}_4\text{S}$: C, 44.7; H, 4.2; N, 6.5%).

(c) *Ethyl m-nitrophenyl sulphone.* *m*-Nitrobenzenesulphonyl chloride, m. p. 62°, was obtained by sulphonating nitrobenzene with chlorosulphonic acid,¹⁵ and was recrystallised once from 70% acetic acid and twice from petrol (b. p. 60–80°). Reduction by aqueous sodium sulphide¹³ afforded the sulphinic acid, m. p. 94–95°, which was boiled with ethyl iodide in aqueous-ethanolic alkali yielding the required sulphone (52%), m. p. 100°. It was purified by passing an ethanolic solution through alumina (grade I) followed by repeated crystallisations from benzene–petrol (b. p. 60–80°) and finally from methanol; the m. p. was then 102.5–103.0° (Found: C, 44.5; H, 4.2; N, 6.5; S, 14.8. Calc. for $\text{C}_8\text{H}_9\text{NO}_4\text{S}$: C, 44.7; H, 4.2; N, 6.5; S, 14.9%).

¹⁰ P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, 1959, p. 83, Table 6, 2, footnote.

¹¹ C. K. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell, London, 1953, section 20e and p. 267.

¹² Ullman and Pasdermadjian, *Ber.*, 1901, **34**, 1151.

¹³ *Org. Synth.*, 1941, Vol. I, 220.

¹⁴ Foster and Reid, *J. Amer. Chem. Soc.*, 1924, **46**, 1937.

¹⁵ Hodgson and Whitehurst, *J.*, 1944, 482.

(d) *Ethyl p-nitrophenyl sulphone.* *p*-Chloronitrobenzene was converted into *p*-nitrophenyl disulphide by boiling it with sodium disulphide, and *p*-nitrothiophenol obtained by treating the disulphide with sodium hydroxide.¹⁶ The thiophenol, m. p. 75—78° (78%) was boiled with alkaline ethyl iodide and yielded ethyl *p*-nitrophenyl sulphide, m. p. 42—43° (82%), after three recrystallisations from ethanol. Oxidation by 30% hydrogen peroxide in glacial acetic acid yielded the sulphone which was recrystallised twice from ethanol and had m. p. 138.5—139.0° (Found: C, 44.9; H, 4.2; N, 6.3; S, 14.4. Calc. for C₈H₉NO₄S: C, 44.7; H, 4.2; N, 6.5; S, 14.9%).

(e) *Benzyl ethyl sulphone.* This sulphone, m. p. 84°, was prepared (88%) by oxidation of the sulphide.¹⁷ It was first recrystallised from ethanol, then left over activated charcoal at 0.1 mm. and finally repeatedly recrystallised again from ethanol (Found: C, 59.2; H, 6.6. Calc. for C₉H₁₂O₂S: C, 58.7; H, 6.5%).

(f) *Ethyl p-nitrobenzyl sulphone.* *p*-Nitrobenzyl chloride (m. p. 72°) was boiled with dilute ethanolic sodium thiosulphate and the product hydrolysed by 30% sulphuric acid¹⁸ yielding *p*-nitrotoluene- α -thiol, m. p. 164°/15 mm., and after crystallisation from ethanol, m. p. 53—54° (72%). Ethylation in ethanol yielded only di-*p*-nitrobenzyl disulphide. The thiol (17 g.) was therefore dissolved in 4% aqueous sodium hydroxide (100 c.c.) and boiled for 2 hr. under reflux with redistilled ethyl bromide (15 g.) in a current of nitrogen. The orange sulphide (84%) crystallised on cooling and after distillation, b. p. 182°/16 mm., it was oxidised by 30% hydrogen peroxide in (8:1) acetic acid-acetic anhydride. *Ethyl p-nitrobenzyl sulphone* was dissolved in benzene and passed through alumina and after removing the solvent, the residue was repeatedly recrystallised from benzene-petrol (b. p. 60—80°), then having m. p. 141—142° (56%) (Found: C, 47.3; H, 4.8; N, 6.2. C₉H₁₁NO₄S requires C, 47.2; H, 4.9; N, 6.1%).

(g) *Ethyl m-nitrobenzyl sulphone.* This was obtained from *m*-nitrobenzyl chloride (m. p. 45—45.5°) by the method used for the *para*-isomer. The following compounds were isolated: *m*-nitrotoluene- α -thiol, m. p. 10° (91%); ethyl *m*-nitrobenzyl sulphide, b. p. 181°/16 mm. (72%); *ethyl m-nitrobenzyl sulphone*, recrystallised three times from benzene-petrol (b. p. 60—80°), m. p. 102.5—103.0° (Found: C, 47.1; H, 4.9; N, 6.5. C₉H₁₁NO₄S requires C, 47.2; H, 4.9; N, 6.1%).

(h) *Ethyl o-nitrobenzyl sulphone.* The starting material for the preparation of this sulphone was *o*-nitrobenzyl chloride but the commercial qualities were unsatisfactory and it was synthesised as follows. *o*-Nitrobenzaldehyde was obtained either by the oxidation of toluene,¹⁹ or by reaction of *o*-nitrobenzenediazonium chloride with formaldoxime followed by hydrolysis,²⁰ and then reduced to the alcohol by aluminium isopropoxide in isopropyl alcohol. *o*-Nitrobenzyl chloride obtained from the above alcohol by reaction with phosphorus pentachloride was converted into the thiol by boiling it with 50% ethanolic sodium thiosulphate followed by hydrolysis of the product using 20% sulphuric acid at 100°. To prevent formation of the disulphide, ethyl *o*-nitrobenzyl sulphide was prepared by a modified procedure. A solution of *o*-nitrotoluene- α -thiol (4.8 g.) in ethyl bromide (15 c.c.) and an aqueous solution (115 c.c.) containing 1% w/v of sodium hydroxide were added drop by drop simultaneously to a boiling mixture of ethyl bromide (60 c.c.) and water (50 c.c.) under nitrogen. The addition required 2 hr. and was followed by boiling the liquid for a further hr. after which it was cooled and the organic layer extracted with chloroform. The sulphide (2 c.c.) was a non-distillable oil and was therefore oxidised without further purification. The wax-like product was boiled in chloroform-petrol (b. p. 60—80°) solution with activated charcoal and the crystalline solid, m. p. 65° (3.4 g.), which was deposited when the filtered liquid was cooled, was dissolved in benzene and passed down an alumina column. Distillation of the solvent afforded a residue which was recrystallised several times from ethanol-petrol (b. p. 60—80°) thus affording pure *ethyl o-nitrobenzyl sulphone*, m. p. 82.0—82.5° (Found: C, 47.0; H, 4.9; N, 6.2. C₉H₁₁NO₄S requires C, 47.2; H, 4.9; N, 6.1%).

Solvents and Reagents.—(a) *Acetic anhydride.* The analytical grade was fractionated three times (b. p. 139.6°/745 mm.) and redistilled immediately before use.

(b) *Nitromethane.* The commercial product could not be sufficiently purified. A specimen,

¹⁶ Price and Stay, *J. Amer. Chem. Soc.*, 1946, **68**, 498.

¹⁷ Böhme and Krause, *Ber.*, 1949, **82**, 430.

¹⁸ Price and Twiss, *J.*, 1909, **95**, 1725.

¹⁹ Bachman, Hass, and Platau, *J. Amer. Chem. Soc.*, 1954, **76**, 3973.

²⁰ Beech, *J.*, 1954, 1297.

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b. p. 98.7°/727 mm., which was obtained after three fractionations still contained materials which interfered with the procedures described. It was therefore prepared from chloroacetic acid²¹ and the faintly yellow liquid, b. p. 99.7°/750 mm., redistilled, b. p. 21°/15 mm., a completely colourless product resulting.

(c) *Chlorobenzene*. The laboratory grade was dried (CaCl₂) and fractionated through a packed column. It was then dried (P₂O₅) again and fractionated twice more. The final product had b. p. 131.8°/759 mm., $n_D^{20.5}$ 1.5243. Timmerman²² gives b. p. 132°/760 mm., n_D^{20} 1.52460 (\equiv 1.5243 at 20.5°). The solvent was again redistilled from P₂O₅ immediately before use.

(d) *Benzene*. The analytical grade was boiled under reflux for 1 hr. with aluminium chloride (10 g./l.),²³ distilled, washed (aq. KOH, H₂O), dried (P₂O₅), and fractionated twice.

(e) *Nitric acid* (d 1.529/20°) was obtained by two distillations of the AnalaR grade (70%) from concentrated sulphuric acid in the proportions 1 : 4.

(f) *Ethanol*. The solvent used for u.v. spectroscopic measurements was 95% ethanol which was first boiled with potassium hydroxide (50 g./l.) and then with aluminium foil (10 g./l.). The first 5% of the product of fractionation was discarded; the remainder had good transmission down to 205 μ .

(g) *Titanous chloride*. The reagent was prepared by boiling the 15% w/v solution (300—400 c.c.) for 10 min. with concentrated hydrochloric acid (250 c.c.), cooled under carbon dioxide, and diluted to 1000 c.c. with oxygen-free water. It was stored under carbon dioxide which had been passed through, first, 5% titanous chloride which had been buffered to pH 5.9 in order to increase its sensitivity,²⁴ and then through methanol.

Analytical Procedures.—(a) *Determination of total nitration product*. Acetic anhydride reacts with nitric acid affording a mixture of all four nitromethanes²⁵ three of which can be extracted by alkali but the fourth, tetranitromethane, is destroyed by reduction with sodium sulphite as recommended by Ingold and Smith.⁴ The efficiency with which nitro-products were removed was tested by mixing the anhydride with nitric acid, the conditions approximating to that of an actual nitration, and then estimating the residual product. A mixture of acetic anhydride (30 c.c., 0.3 mole) and nitric acid (d 1.53; 2.5 c.c., 0.06 mole) was prepared at -70° and quickly warmed to 25°. It was stirred at this temperature for 3—17 hr. and then decomposed by crushed ice, and the liquid neutralised with sodium hydrogen carbonate. An ethereal extract of the solution was washed (aq. NaOH, H₂O), dried (MgSO₄), and reduced to a small volume, and the residue shaken mechanically for a number of hr. with aqueous sodium sulphite. Titration with titanous chloride gave the results shown in Table 2. Experiments 14 and 15 differ from the remaining ones in that silicone grease replaced vaseline used on the stopcocks of the burettes.

TABLE 2.
Residual nitro-group after removal of the nitromethanes.

Expt. No.	11	12	13	14	15
Nitration time (hr.)	3	4	9	12	17
Na ₂ SO ₃ wash time (hr.)	1	2	5	6	5
Residual nitro-group (10 ⁻⁵ mole)	7.5	6.7	5.2	3.4	4.5

The last traces of reducible material could not be removed but as in an actual competitive nitration the amounts formed would of necessity be less than those indicated on Table 2, and *i.e.*, well within the experimental error, corrections to the final calculations were not applied.

Titration was carried out in methanol solutions in a stream of carbon dioxide, 50 c.c. of the reagent being used for each 0.001 mole of the nitro-derivative. Concentrated hydrochloric acid (10 c.c.) followed by standard titanous chloride solution (20—25 c.c.) were added, the liquid boiled for 10 min., and the excess of reagent estimated in the conventional manner by back titration with ferric ammonium sulphate, using 20% ammonium thiocyanate (10 c.c.) as an indicator. It was essential to use an excess of titanous chloride equivalent to 20—25 c.c. of the ferric solution, to add not less than 10 c.c. of the acid, and to avoid the presence of excessively

²¹ Ref. 12, p. 401.

²² J. Timmerman, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, London, 1950, p. 283.

²³ Haller and Michel, *Bull. Soc. chim. France*, 1896, **15**, 1067.

²⁴ Augood, Hey, and Williams, *J.*, 1952, 2097.

²⁵ Chattaway, *J.*, 1901, **97**, 2099.

large amounts of benzene (or chlorobenzene) which would tend to remove nitro-compounds from the aqueous methanol layer. Because of the organic solvent, the recommendation by Augood, Hey, and Williams²⁴ that the titanous chloride can be advantageously used at room temperature if buffered by trisodium citrate to pH 5.9, could not be followed. Standardisation of the reducing agent just before use was by AnalaR quality *p*-nitroaniline or *p*-chloronitroaniline. The latter could be estimated (average of 10 determinations) to an accuracy of $\pm 0.1\%$, whilst for pure ethyl nitrophenyl sulphone it was $\pm 0.3\%$ (average of four determinations).

(b) *Estimation of chloronitrobenzenes.*⁶ A portion of the reaction mixture containing 0.001–0.002 mole chloronitrobenzenes was boiled under reflux with 5% sodium methoxide in methanol (100 c.c.) for 24 hr. The cooled liquid was diluted with water, the methanol removed by distillation, and the residue neutralised by 10*N*-nitric acid. After organic material had been extracted with ether (5 × 20 c.c.), the aqueous layer was diluted to exactly 250 c.c. and aliquot portions titrated potentiometrically for labile chloride ion. A silver electrode was used in conjunction with a reference electrode consisting of a Ag^+/Ag half-cell stabilised by a cationic exchange resin containing silver and hydrogen ions. The cell was similar to that suggested by Goodall and Mellor²⁶ but contained "Dowex 50" 100–200 mesh resin (50 g.) instead of the "Zeo-Carb 225" resin originally specified.

Potentiometric titrations were consistently accurate to 0.4% and were unaffected by large quantities of nitrate ion. Separate tests showed that no trace of chloride ion was obtained from chlorobenzene by methanolysis. Free nitric acid (1–2%) led to somewhat low titrations and a slight excess of calcium carbonate was added to the solutions just before titration. One source of error was unexpected. The method as first used gave inconsistently low results (80–95% of the theoretical value). There was no physical loss of chloro-derivative during methanolysis nor was any unchanged chloronitrobenzenes detected. It appeared likely that reduction by methoxide ion had led to the formation of *pp'*-dichloroazoxybenzene²⁷ in which the halogen is rather inert. This had not been encountered by Bird and Ingold⁶ because the artificial mixtures they had used for testing the method had contained nitrobenzene. Although in actual competitive nitrations the error would be reduced by the nitro-sulphones, as an additional safeguard, a small quantity of nitrobenzene was added before methanolysis. Artificial mixtures of chlorobenzene with *o*- and *p*-chloronitrobenzenes afforded consistent results when so treated, but even so, the values were *ca.* 2% low and the appropriate corrections were made when nitration mixtures were analysed.

(c) *Estimation of proportions of ortho-, meta-, and para-isomers.* The u.v. spectra of the various nitro-derivatives were sufficiently well differentiated so as to afford a basis for estimating the relative amounts of *ortho*-, *meta*-, and *para*-isomers. The validity of Beer's law being assumed, then at any given wavelength, the optical density *R*, of a mixture of three isomers is given by the expression:

$$R = x_1 A_1 / c_1 + x_2 A_2 / c_2 + x_3 A_3 / c_3 \quad (1)$$

where x_1 , x_2 , and x_3 are the concentrations of the three isomers, respectively, and A_1 , A_2 , and A_3 are the optical densities of the pure substances at concentrations C_1 , C_2 , and C_3 . A refinement of the method was devised by Dewar and Urch,²⁸ who took into account the whole of the absorption spectrum, thus division of equation (1) by A_2 gives:

$$R/A_2 = x_1/c_1 \cdot A_1/A_2 + x_2/c_2 + x_3/c_3 \cdot A_3/A_2 \quad (2)$$

and this can be used to determine x_1 , x_2 , and x_3 .

Optical densities were measured on a Unicam S.P. 500 spectrophotometer using 10-mm. fused silica cells, the path lengths of which were identical when checked with a standard solution. They were not, however, matched in other respects and a correction term was obtained at each of the selected wavelengths by measuring the absorptions when the cells each contained the same solvent. The slit-widths chosen for any particular wavelength were the same both for the standard solutions of pure isomers and for the solutions of the experimental mixtures. Values of A_o , A_m , and A_p were measured by using solutions of the pure isomers at 20–25 points between

²⁶ Goodall and Mellor, *Analyt. Chim. Acta*, 1952, **6**, 373.

²⁷ Richardson, *J.*, 1926, 522.

²⁸ Dewar and Urch, *J.*, 1957, 345.

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220 and 320 $m\mu$ these being selected by preliminary inspection of the absorption spectra so as to give the most suitable ratios. The intensities were such that all the solutions were sufficiently dilute for a linear relationship to exist between concentration and optical density, this being tested by examining solutions of different concentrations at different wavelengths. Standard solutions of the sulphones were prepared in the usual way and had final concentrations of 0.00005—0.00006 mole/l. Where there was not a preponderating proportion of one of the isomers, the absorption of the experimental mixture was balanced by pure solvent in the reference cell; in other cases, the accuracy of the measurements was increased by balancing out all or part of one of the components of the mixture by placing a known weight of this component into the relative optical density by using increased concentrations. The extent to which this could be done was limited by the reduced response of the spectrophotometer and this could not entirely be overcome by the use of large slit widths and high sensitivities. In practice, the maximum concentration of a balancing solution of a compound having ϵ_{\max} 10,000 was approximately 0.00015 mole/l., giving an apparent increase in concentration of the two other isomers of about fourfold. The applicability of Beer's law to the six sulphones within the range of concentrations considered in this paper was tested by measuring absorptions of suitable artificial mixtures. Table 3 gives the optical densities and the ratios of optical densities used in the estimation of ethyl *o*-, *m*-, and *p*-nitrophenyl sulphones, and Table 4 gives the figures for the corresponding ethyl nitrobenzyl sulphones.

Artificial mixtures of the three ethyl nitrophenyl sulphones and of the three ethyl nitrobenzyl sulphones were analysed by using Tables 3 and 4. Compensating solutions of the *meta*-isomer

TABLE 3.

Optical densities and ratios of absorptions of pure ethyl nitrophenyl sulphones dissolved in 95% ethanol.

(a) Ethyl <i>o</i> -nitrophenyl sulphone. Conc'n. (10^5 mole/l.), 7.94.											
λ ($m\mu$)	<i>D</i>	A_o/A_m	λ ($m\mu$)	<i>D</i>	A_o/A_m	λ ($m\mu$)	<i>D</i>	A_o/A_m	λ ($m\mu$)	<i>D</i>	A_o/A_m
220	0.722	1.172	228	0.495	1.820	238	0.291	0.871	265	0.143	0.486
224	0.620	1.640	230	0.433	1.665	239	0.280	0.801	270	0.138	0.657
225	0.587	1.726	232	0.387	1.455	240	0.270	0.748	275	0.135	0.912
225.4	0.576	1.767	234	0.346	1.223	245	0.231	0.550	280	0.116	1.036
226	0.555	1.802	235	0.332	1.129	250	0.199	0.442	283	0.101	1.058
226.6	0.539	1.827	236	0.316	1.036	255	0.172	0.395	285	0.091	1.046
227.2	0.520	1.831	237	0.305	0.953	260	0.152	0.405			

(b) Ethyl <i>m</i> -nitrophenyl sulphone. Conc'n. (10^5 mole/l.), 5.93.							
λ ($m\mu$)	<i>D</i>	λ ($m\mu$)	<i>D</i>	λ ($m\mu$)	<i>D</i>	λ ($m\mu$)	<i>D</i>
220	0.616	228	0.272	238	0.334	265	0.294
224	0.378	230	0.260	239	0.347	270	0.210
225	0.340	232	0.266	240	0.361	275	0.148
225.4	0.326	234	0.283	245	0.420	280	0.112
226	0.308	235	0.294	250	0.450	283	0.095
226.6	0.295	236	0.305	255	0.435	285	0.087
227.2	0.284	237	0.320	260	0.375		

(c) Ethyl <i>p</i> -nitrophenyl sulphone. Conc'n. (10^5 mole/l.), 6.15.											
λ ($m\mu$)	<i>D</i>	A_p/A_m	λ ($m\mu$)	<i>D</i>	A_p/A_m	λ ($m\mu$)	<i>D</i>	A_p/A_m	λ ($m\mu$)	<i>D</i>	A_p/A_m
220	0.259	0.420	228	0.363	1.335	238	0.573	1.716	265	0.449	1.527
224	0.302	0.799	230	0.403	1.550	239	0.594	1.712	270	0.316	1.505
225	0.311	0.915	232	0.444	1.669	240	0.614	1.701	275	0.214	1.446
225.4	0.323	0.991	234	0.488	1.724	245	0.693	1.650	280	0.159	1.420
226	0.328	1.065	235	0.520	1.774	250	0.722	1.644	283	0.140	1.474
226.6	0.342	1.159	236	0.531	1.741	255	0.686	1.577	285	0.136	1.563
227.2	0.353	1.243	237	0.554	1.731	260	0.589	1.571			

were used in the reference cell for the phenyl sulphones but not in the benzyl series. The mean percentage deviations found for the phenyl sulphones were *o*, 0.50; *m*, 1.03; *p*, 0.53 and for the benzyl sulphones they were *o*, 0.40; *m*, 0.45; *p*, 0.40.

Nitration of Ethyl Phenyl Sulphone alone.—*Note.* In this and subsequent experiments, all extractions were carried out 6—8 times, using 20—50 c.c. of solvent. All wash liquids, whether aqueous or organic were re-extracted, and the extracts suitably washed and added to the original extracts.

TABLE 4.

Optical densities and ratios of pure ethyl nitrobenzyl sulphones dissolved in 95% ethanol.

Concentrations (10^5 mole/l.): *ortho*, 6.164; *meta*, 6.534; *para*, 4.244.

λ (m μ)	D			A_p/A_m	λ (m μ)	D			A_p/A_m		
	(<i>o</i>)	A_o/A_m	(<i>m</i>)			(<i>p</i>)	(<i>o</i>)	A_o/A_m		(<i>m</i>)	(<i>p</i>)
210	0.943	—	1.242	0.343	260	0.303	0.584	0.519	0.457	0.880	
215	0.817	—	1.110	0.316	265	0.283	0.571	0.496	0.493	0.994	
220	0.598	0.777	0.769	0.237	0.308	267.5	0.268	0.573	0.468	0.497	1.062
225	0.463	1.089	0.425	0.137	0.322	270	0.249	0.580	0.429	0.491	1.158
230	0.329	1.366	0.241	0.120	0.498	275	0.211	0.621	0.340	0.453	1.332
235	0.240	1.101	0.218	0.145	0.665	280	0.178	0.709	0.251	0.387	1.542
240	0.227	0.832	0.273	0.189	0.692	285	0.154	0.832	0.185	0.315	1.702
245	0.251	0.717	0.350	0.246	0.703	290	0.134	0.964	0.139	0.243	1.748
250	0.282	0.651	0.433	0.321	0.741	300	0.102	1.186	0.086	0.125	1.453
255	0.302	0.607	0.497	0.396	0.797						

TABLE 5.

Optical densities of mixed nitro-sulphones obtained by nitration of ethyl phenyl sulphone by acetyl nitrate and by nitric acid at 25°.

λ (m μ)	Nitration 1			Nitration 2		
	D	R/A_m	R/A_m'	D	R/A_m	R/A_m'
224	0.635	1.680	1.221	—	—	—
225	0.588	1.729	1.245	0.584	1.718	1.304
225.4	0.572	1.755	1.260	0.570(5)	1.750	1.326
226	0.549	1.782	1.272	0.554(5)	1.768	1.336
226.6	0.529	1.793	1.281	0.528(5)	1.791	1.353
227.2	0.512	1.803	1.291	0.511	1.799	1.359
228	0.495	1.820	1.310	0.494	1.816	1.378
230	0.467	1.796	1.330	0.469	1.804	1.404
232	0.467(5)	1.757	1.350	0.469	1.763	1.415
234	0.482	1.703	1.360	—	—	—
236	0.504	1.652	1.363	0.512	1.679	1.431
237	0.520	1.625	1.359	0.529	1.653	1.424
238	0.537	1.608	1.362	0.547	1.638	1.430
239	0.551	1.589	1.364	0.564	1.625	1.433
240	0.566(5)	1.569	1.360	0.580(5)	1.608	1.428
245	—	—	—	0.655	1.560	1.428
250	0.661	1.469	1.345	0.686(5)	1.525	1.419
255	—	—	—	0.656	1.508	1.414
260	0.545	1.453	1.340	0.567	1.512	1.414
265	0.531	1.468	1.332	0.446(5)	1.519	1.403
270	0.316	1.504	1.320	0.327	1.558	1.400
275	0.233	1.575	1.320	0.237	1.602	1.384
283	0.153(5)	1.617	1.322	—	—	—

λ (m μ)	Nitration 3			Nitration 4		
	D	R/A_m	R/R_m'	D	R/A_m	R/A_m'
224	0.618	1.635	1.258	0.361(5)	0.956	0.759
225	0.571	1.679	1.282	0.335	0.985	0.778
225.4	0.552(5)	1.695	1.289	0.325	0.997	0.785
226	0.530(5)	1.722	1.307	0.309	1.003	0.787
226.6	0.512(5)	1.737	1.317	0.299(5)	1.015	0.796
227.2	0.494	1.739	1.318	0.290	1.021	0.801
228	0.477	1.754	1.335	0.280(5)	1.031	0.813
230	0.454	1.746	1.363	0.266	1.023	0.823
232	0.453	1.703	1.369	0.267(5)	1.006	0.831
234	0.471	1.864	1.382	0.277	0.979	0.832
236	0.496	1.626	1.388	0.294(5)	0.965	0.841
237	0.510	1.594	1.385	0.303(5)	0.948	0.834
238	0.526	1.575	1.374	—	—	—
239	0.544	1.568	1.383	0.324	0.934	0.837
240	0.561(5)	1.555	1.383	0.335	0.928	0.838
245	0.629	1.498	1.372	0.381	0.907	0.841
250	0.661(5)	1.470	1.368	0.400	0.889	0.836
255	0.632	1.453	1.362	—	—	—
260	0.546	1.456	1.363	0.330	0.880	0.831
265	—	—	—	0.260	0.884	0.826
270	—	—	—	0.189(5)	0.902	0.823

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Nitric acid (d 1.529; 0.10 mole) was gradually added to a stirred solution at -70° of ethyl phenyl sulphone (0.025 mole) in acetic anhydride (0.02 mole). The temperature was then rapidly raised to 25° and the reaction allowed to proceed for 6—16 hr. After adding the mixture to crushed ice and water, the liquid was neutralised with sodium hydrogen carbonate and extracted with chloroform. The extract was washed successively by sodium sulphite (4%), sodium hydrogen carbonate (1%), sodium hydroxide (5%); and by water after which it was dried (CaCl_2), concentrated to 10 c.c. and passed down a column (5×1.4 cm.) containing grade III alumina to remove a trace of yellow acid material. Removal of the solvent gave a pale cream crystalline mixture of nitro-sulphones which was dissolved in ethanol (95%) and the solution diluted to give a concentration of approximately 0.00023 mole/l.

A blank "nitration" omitting the sulphone was also carried out, the procedure being identical with that described above. The final solution had no absorption between 215 μ and 300 μ showing that extraneous material had not been introduced as a result of the "working up" operations. Some compounds, notably phenols,²⁹ methoxy-derivatives,³⁰ and acylated amines,³¹ show an increased *ortho*:*para* ratio when nitrated by dinitrogen pentoxide or by acetyl nitrate. In these substances the substituent groups are strongly *ortho*:*para* directing but this effect is also to be attributed to the *meta*-directing sulphonyl group as was shown by nitrating ethyl phenyl sulphone for 16 hr. by an excess of pure nitric acid (nitration 4). In this case, the wash by the aqueous sodium sulphite was omitted.

The relative proportions of isomers were obtained from the u.v. absorption spectra (Table 5). Compensating solutions of the *meta*-isomer in the reference cell were used in all four nitrations (14.92×10^{-5} mole/l. in nitrations 1—3, and 16.01×10^{-5} mole/l. in nitration 4). Expression (3) was used for the calculations,

$$R/A_m = x_o/c_o \cdot A_o/A_m + x_m/c_m + x_p/c_p \cdot A_p/A_m \quad (3)$$

where x_o , x_m , x_p , A_o , A_m , and A_p had the values given in Table 5. The intercept of the final derived linear relationship was then x_m/c_m , the slope was x_p/c_p , and the "factor" was x_o/c_o . The quantity R/A_m refers to the value of R/A_m after correction for the absorption due to the third component x_o (obtained by trial and error).

Table 5 then afforded the results shown in Table 6 which also gives the explicit values of the intercepts, x_m/c_m , the slopes, x_p/c_p , and the "factors" x_o/c_o . The probable errors in the mean percentages of the three ethyl nitrophenyl sulphones were calculated in the usual way.

TABLE 6.

Percentages of isomers formed in the nitrations of ethyl phenyl sulphone. (All concentrations are expressed in 10^5 mole/l.)

No.	x_p/c_p	ρ	x_o/c_o	o	x_m/c_m	m	Total m	Total isomers	Isomers (%)		
									o	m	p
1	0.142	0.873	0.280	2.22	1.117	6.624	21.544	24.637	9.0	87.5	3.5
2	0.143	0.879	0.240	1.91	1.185	7.027	21.947	24.736	7.7	88.7	3.6
3	0.120	0.738	0.230	1.83	1.175	6.968	21.888	24.456	7.5	89.5	3.0
4	0.078	0.480	0.120	0.95	0.706	4.187	20.197	21.628	4.4	93.4	2.2

Mean percentages in acetic anhydride (nitrations 1, 2, and 3): *ortho*, 8.1 ± 0.4 ; *meta*, 88.6 ± 0.4 ; *para*, 3.3 ± 0.1 .

Percentage in nitric acid alone (nitration 4): *ortho*, 4.4; *meta*, 93.4; *para*, 2.2.

The Nitration of Ethyl Phenyl Sulphone in Competition with Chlorobenzene.—(a) *Preliminary experiments.* In view of the somewhat complex nature of the isolation processes, the following preliminary experiments were performed. (i) Fractional distillation of solutions of chloronitrobenzenes in methanol afforded distillates which showed no u.v. absorptions. (ii) None of the nitro-derivatives reacted when their ethereal solutions were shaken for twice the time actually used in the nitration experiments with either aqueous potassium hydroxide or sodium sulphite solutions of the stated concentrations. (iii) Minute quantities of stopcock greases

²⁹ Francis, *J.*, 1906, **89**, 1.

³⁰ Arnall, *J. Soc. Chem. Ind.*, 1929, **48**, 157T.

³¹ Griffiths, Walkey, and Watson, *J.*, 1934, 631.

such as "vaseline" or silicone grease tended to dissolve into the ether extracts and be reprecipitated by the addition of methanol. Tests with artificial mixtures showed that the titanous chloride titrations were not affected. (iv) It was first of all ascertained that chloro-2,4-dinitrobenzene could be recovered unchanged when subjected to the extraction and washing procedures used to isolate the nitration products. The absence of dinitration was then shown by "nitrating" *p*-chloronitrobenzene at 25° for 11 hr. by using the standard method and isolating the product by the usual procedure. A portion of the unchanged chloronitrobenzene (80%) was distilled and the residue dissolved in 95% ethanol. This solution was transparent in the regions where u.v. absorption could have been attributed to 1-chloro-2,4-dinitrobenzene though had it been present in the residue in a concentration of less than 1%, it could easily have been detected.

(b) *Nitration procedure.* Nitric acid (*d* 1.529; 0.062 mole) was slowly added to a cooled (−70°) mixture of ethyl phenyl sulphone (0.050 mole), chlorobenzene (0.050 mole), and acetic anhydride (0.30 mole). The temperature was raised to 25° (±0.02°) and the solution stirred for 5–12 hr., the time being such that only a minimum of polynitromethanes was likely to be formed. At the end of the allowed time, the product was decomposed by crushed ice (200 g.; prepared from distilled water), the liquid neutralised by sodium hydrogen carbonate and then extracted with ether. The extract was washed (5% KOH, H₂O), dried (MgSO₄), and slowly distilled through a Dufton column until the volume was reduced 100–150 c.c. The residual liquid was first shaken for 6 hr. with a mixture containing 50 c.c. each of 4% aq. sodium sulphite and 2% aq. sodium hydrogen carbonate and then washed first by 5% potassium hydroxide and then by water. The aqueous layers were extracted with ether, and the ether extract, after purification, added to the original ethereal solution. Finally, the combined liquids were concentrated to 10–15 c.c., the volume made up to 50 c.c. with methanol, and the total nitro-derivatives, and the chloronitrobenzenes estimated. In Table 7, the quantity K_s/K_c (*i.e.*, $k_{\text{sulphone}}/k_{\text{chlorobenzene}}$) was calculated from $K_s/K_c = \log(y/y_0)/\log(x/x_0)$ where y_0 and x_0 were the original concentrations of sulphone and chloronitrobenzenes, respectively, and y and x their concentrations at the time the nitration was stopped. Since there was not an appreciable change in total volume during the reaction, it was possible to substitute molar quantities for concentrations without introducing appreciable errors.

TABLE 7.

Nitration of ethyl phenyl sulphone in competition with chlorobenzene by nitric acid in acetic anhydride.

Temp. 25.00 ± 0.02°. Initial quantities: EtPhSO₂ = PhCl = 0.05 mole. All concentrations expressed in 10³ mole/l.

No.	Time (hr.)	Total NO ₂ group	Chloronitrobenzenes		Nitro-sulphones	K_s/K_c
			Found	Corrected		
7	5	7.342	6.285	6.468	0.874	0.128
8	5	7.481	6.665	6.852	0.629	0.086
9	13	8.636	7.798	7.986	0.650	0.076
10	12	8.502	7.528	7.714	0.788	0.095
11	12	8.576	7.463	7.650	0.926	0.112

The mean value for K_s/K_c was 0.0994 ± 0.0070.

Since under the same conditions, $K_{\text{PhCl}}/K_{\text{PhH}} = 0.0353 \pm 0.0007$.

Then $K_s/K_{\text{PhH}} = 0.00351 \pm 0.00025$

and the partial rate factors were:

$F_{\text{ortho}} 0.00085 \pm 0.00006$; $F_{\text{meta}} 0.00933 \pm 0.00066$; $F_{\text{para}} 0.00069(5) \pm 0.00005$.

Nitration of Benzyl Ethyl Sulphone Alone.—The conditions used were similar to those described for the corresponding competitive nitration (below) but benzene was omitted from the reaction mixture and more time was allowed for complete nitration. The normal extraction process was followed by passing the concentrated yellow solution of the nitro-derivatives in chloroform through a column of alumina which removed the colour. The residue obtained when the solvent was removed was dissolved in methanol and its composition determined by

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reference to its u.v. absorption spectrum (Table 8). The percentages of the isomeric ethyl nitrobenzyl sulphones is given in Table 9.

TABLE 8.

Optical densities of mixed nitro-sulphones obtained by nitration of benzyl ethyl sulphone by acetyl nitrate and by nitric acid at 25°.

λ (m μ)	Nitration 1			Nitration 2			Nitration 3		
	D	R/A_m	R/A_m'	D	R/A_m	R/A_m'	D	R/A_m	R/A_m'
220	0.357	0.464	0.322	0.316	0.411	0.294	0.374	0.486	0.347
225	0.233	0.548	0.411	0.208	0.489	0.366	0.243	0.572	0.427
230	0.167	0.693	0.480	0.148	0.614	0.424	0.173	0.718	0.494
235	0.153	0.702	0.418	0.137	0.628	0.375	0.158	0.725	0.426
240	0.177	0.648	0.353	0.158	0.579	0.315	0.184	0.674	0.363
245	0.218	0.622	0.322	0.195	0.557	0.289	0.229	0.650	0.334
250	0.269	0.621	0.305	0.240	0.554	0.272	0.282	0.651	0.318
255	0.314	0.632	0.292	0.281	0.565	0.261	0.331	0.666	0.307
260	0.343	0.661	0.285	0.307	0.595	0.256	0.363	0.699	0.303
265	0.350	0.706	0.282	0.314	0.633	0.254	0.370	0.746	0.399
267.5	0.344	0.735	0.282	0.307	0.656	0.281	0.365	0.780	0.302
275	0.294	0.865	0.296	0.262	0.770	0.263	0.310	0.912	0.313
280	0.246	0.980	0.322	0.219	0.872	0.285	0.259	1.031	0.337
285	0.199	1.076	0.349	0.177	0.957	0.309	0.209	1.129	0.363
290	—	—	—	0.139	1.000	0.334	0.164	1.180	0.393

λ (m μ)	Nitration 4			Nitration 5		
	D	R/A_m	R/A_m'	D	R/A_m	R/A_m'
220	0.403	0.524	0.377	0.614	0.798	0.579
225	0.262	0.616	0.462	0.391	0.920	0.691
230	0.187	0.776	0.538	0.271	1.124	0.770
235	0.172	0.789	0.471	0.254	1.165	0.693
240	0.198	0.725	0.394	0.301	1.103	0.612
245	0.245	0.699	0.362	0.377	1.077	0.578
250	0.303	0.700	0.345	0.468	1.081	0.555
255	0.355	0.713	0.391	0.550	1.107	0.541
260	0.389	0.749	0.328	0.602	1.160	0.535
265	0.396	0.798	0.322	0.613	1.236	0.530
267.5	0.390	0.833	0.324	0.597	1.276	0.522
275	0.332	0.976	0.338	0.507	1.491	0.545
280	0.277	1.104	0.365	0.419	1.669	0.574
285	0.224	1.211	0.396	0.336	1.816	0.608
290	0.176	1.266	0.429	—	—	—
300	—	—	—	0.151	1.756	0.724

TABLE 9.

Percentages of isomers formed in the nitrations of benzyl ethyl sulphones.

Equation: $R/A_m = x_o/c_o \cdot A_o/A_m + x_m/c_e + x_p/c_p \cdot A_p/A_m$. Intercept = x_m/c_m ; slope = x_o/c_o ; "factor" = x_p/c_p . All concentrations are expressed in 10^5 mole/l.

No.	x_o/c_o	o	x_p/c_p	p	x_m/c_m	m	Total isomers	Isomers (%)		
								o	m	p
1	0.252	1.553	0.427	1.812	0.139	0.908	4.273	36.3	21.2	42.5
2	0.224	1.381	0.381	1.617	0.124	0.810	3.808	36.3	21.3	42.4
3	0.247	1.522	0.450	1.910	0.154	1.006	4.438	34.3	22.7	43.0
4	0.276	1.701	0.479	2.033	0.164	1.072	4.806	35.4	22.3	42.3
5	0.311	1.917	0.710	3.013	0.352	2.300	7.230	26.5	31.8	41.7

Mean percentages in acetic anhydride (nitrations 1—4): *ortho*, 35.6 \pm 0.4; *meta*, 21.9 \pm 0.3; *para*, 42.5(5) \pm 0.1(1).

Percentage in nitric acid alone (nitration 5): *ortho*, 26.5; *meta*, 31.8; *para*, 41.7.

The Nitration of Benzyl Ethyl Sulphone in Competition with Benzene.—(a) *Analytical details.* Nitrobenzene formed during the nitration was separated from the mixed ethyl nitrobenzyl sulphones by distillation into a receiver cooled by solid carbon dioxide. Liquid nitrogen (used in preliminary experiments) was less suitable because small amounts of liquid air condensed in the receiver and interfered with the subsequent distillation of the contents. The flask containing the nitro-derivatives was filled with glass-wool to ensure even heating and was immersed to a level just above the side-arm in an oil bath which was heated to a carefully controlled temperature. At 0.01–0.02 mm., a temperature of 100° gave a practically quantitative yield of nitrobenzene in 30 min. At higher temperatures (*e.g.*, 120°) some unchanged benzyl ethyl sulphone distilled, entraining traces of nitrobenzene remaining in the atmosphere of the flask. At 130°, the nitrated sulphones began to come over. After separation the nitro-derivatives were dissolved in hot methanol, the solutions cooled, made up to 100 c.c., and aliquot parts titrated with titanous chloride. The process was tested by using artificial mixtures indicating that a 99.8 and 100% recovery of nitrobenzene and nitrosulphones, respectively, could be expected.

A check for non-volatile nitration products was made by nitrating benzene alone under standard conditions. The reaction was stopped by adding the mixture to ice-water, and then a sample of pure benzyl ethyl sulphone was added. The subsequent operations were those described above and led to the isolation of small amounts of tarry materials the nitro-content of which was well within experimental error and was ignored in subsequent calculations.

TABLE 10.

Nitration of benzyl ethyl sulphone in competition with benzene by nitric acid in acetic anhydride.

Temp. 25.00 ± 0.02°. Initial quantities: PhCH₂·SO₂Et = C₆H₆ = 0.020 mole. All concentrations are expressed in 10⁵ mole/l.

No.	Time (min.)	Nitrobenzyl sulphones	Nitrobenzene	K_a/K_b
1	45	653.7	1619	0.239
2	50	711.1	1660	0.248
3	60	300.4	994	0.236
4	30	493.9	1445	0.221
5	50	535	1516	0.219
6	30	475.6	1454	0.209

} 0.229 ± 0.005

The partial rate factors are: F_{ortho} 0.245 ± 0.005; F_{meta} 0.150 ± 0.003; F_{para} 0.584 ± 0.012.

(b) *Nitration procedure.* A solution of benzene (0.0200 mole) and benzyl ethyl sulphone (0.0200 mole) in acetic anhydride (0.03 mole) was cooled to -70° and nitric acid (*d* 1.529; 0.036 mole) added with stirring, the temperature then being raised to 25°. Stirring was continued for 30–60 min., after which the mixture was added to ice-water, and the liquid extracted with chloroform. The extract was treated in the same way as in the case of ethyl phenyl sulphone, dried (Na₂SO₄) and fractionated, and the nitrobenzene and ethyl nitrobenzyl sulphones estimated as described. The results are given in Table 10.