

CCXXV.—*The Nature of the Alternating Effect in Carbon Chains. Part XXXIII. The Nitration of some Aromatic Sulphonium and Selenonium Salts.\**

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IN the examination initiated by Ingold, Ingold, and Shaw (J., 1927, 813) on the effect of various subsidiary influences on the now well-established *m*-directive action of a positive pole attached to a phenyl nucleus, it was shown that the electronic strain originated by the kationic charge ( $-I$  effect) might be modified by the damping effect of the outer groups of electrons belonging to the charged atom itself. There is, however, a second modifying factor which must also be considered, namely, the possibility of *op*-directive tautomeric electron displacements ( $+T$ ) due to the presence of unshared electron pairs in the outer group, providing that this tendency is not too strongly resisted by the positive charge on the atom (since any sharing of these unshared electrons would cause the atom to become still more positive). The first of these conclusions has already been verified in the case of nitrogen and sulphur (*loc. cit.*) and for nitrogen, phosphorus, arsenic and antimony (Ingold, Shaw, and Wilson, J., 1928, 1280).

The present communication, which refers to the nitration of phenyl- and benzyl-dimethylsulphonium and phenyl- and benzyl-dimethylselenonium salts, extends the comparison to the elements sulphur and selenium and provides data relevant to the second possible modifying influence. The results are summarised in Table I.

In the phenyl series (Nos. 1—5), almost exclusive *m*-nitration occurs; the nitro-product, isolated in high yield, contained no detectable trace of *o*- and *p*-nitro-derivatives, and their absence was confirmed by examination of the residual solution coupled with solubility determinations of the synthetic isomerides. This

\* After the MS. of this paper had been submitted for publication, Professor Robinson called our attention to the fact that he had investigated the nitration of a derivative closely similar to one of the four types investigated in this paper, namely, a benzyldialkylsulphonium salt (see this vol., p. 1765).

We regret that we had unfortunately overlooked his statement to this effect (*Chem. and Ind.*, 1926, 836) and had based the continuance of our investigation on a later reservation covering a similar field (J., 1927, 815, footnote). It was therefore agreed that the two investigations should be published simultaneously. In any event, knowledge of Pollard and Robinson's data for the benzyldiethylsulphonium salt would not have suited the purposes of our comparisons, which, for the elements nitrogen, phosphorus, arsenic, antimony, sulphur, and selenium, have uniformly employed methyl-substituted salts, both in the phenyl and in the benzyl series.

result, together with the exclusive meta-substitution observed in the case of diphenyliodonium nitrate (Vorländer and Büchner, *Ber.*, 1925, **28**, 1898), indicates that the second modifying influence (+ *T* effect) is inoperative in orientation, the mobility of the unshared electron pairs being effectively restricted by the charge on the atom. This agrees with the accepted conclusion derived from the resolution of sulphonium salts, sulphinic esters, and sulphoxides, that the unshared electron pair of sulphonium sulphur tends strongly to maintain its place in the sulphur tetrahedron, and gives point to Phillips's suggestion that the optical stability of sulphonium compounds is connected with the presence of a positive charge.

In the corresponding benzyl series the (approximately constant) additional damping caused by the intercalated methylene group (Goss, Hanhart, and Ingold, *J.*, 1927, 250) makes it possible to detect the effect of the extra electron group present in selenium, nitration of benzyldimethylselenonium picrate yielding a much smaller percentage of the *m*-isomeride (Nos. 9—11) than is found in the case of the corresponding sulphonium compound (Nos. 6—8).

TABLE I.

No.	Kation.	Nitration Nos.	Yield of mono-nitration product,* %.	Percentage of <i>m</i> -isomeride.
1	Ph·S <sup>⊕</sup> Me <sub>2</sub>	1—3	94	100
2	Ph·CH <sub>2</sub> ·S <sup>⊕</sup> Me <sub>2</sub>	6—8	95	52
3	Ph·Se <sup>⊕</sup> Me <sub>2</sub>	4—5	99	100
4	Ph·CH <sub>2</sub> ·Se <sup>⊕</sup> Me <sub>2</sub>	9—11	99	16

\* Corrected for solubility in the case of phenyl compounds.

*Directive Action and the Periodic Classification of the Elements.*—The data recorded and references cited herein, together with the results obtained for ammonium nitrogen (Vorländer and Siebert, *Ber.*, 1919, **52**, 283), oxonium oxygen (Le Fèvre, *J.*, 1929, 2771), and the neutral benzyl halides (Ingold and Ingold, *J.*, 1928, 2249; Flürscheim and Holmes, *ibid.*, p. 160), make it possible to take a moderately comprehensive survey of the directive action of the elements in this section of the periodic table. The data are in Table II.

In agreement with the theoretical considerations summarised in this paper the proportion of *m*-substitution observed (1) *decreases* with increase in atomic number for elements in the same *group* of the table and (2) *increases* with increasing atomic number in any one *period*, and the data now available make it possible to predict

TABLE II.  
Increasing  $-I$   
Decreasing  $+T$

Increasing meta-nitration.	N 88	*100 0	O —	100 0	F —	— 17.5
	P 10.1	100 —	S 52	100 —	Cl —	(?) 15
	As 3.4	98.2 —	Se 16	100 —	Br —	— 8
	Sb —	86.3 —	Te† —	— —	I —	100 —

Increasing meta-nitration.

Key

A	x	A = symbol of the element.				
y	z	x = % <i>m</i> -compound in the nitration product of Ph—A <sup>⊕</sup>				
		y = " " " " " " Ph—CH <sub>2</sub> —A <sup>⊕</sup>				
		z = " " " " " " Ph—CH <sub>2</sub> —A <sup>⊕</sup>				
		(n = neutral form)				

\* 100% is tabulated where careful qualitative examination of the nitration product revealed no trace of isomerides.

† It is intended to investigate the analogous tellurium derivatives.

approximately the proportion of *m*-nitration which would occur in certain cases not yet investigated. For instance, the similar order of magnitude of the ratios  $R_{\text{Ph-CH}_2\text{-SMe}_2^{\oplus}}/R_{\text{Ph-CH}_2\text{-SeMe}_2^{\oplus}} = 1.08/0.19 = 5.7$  and  $R_{\text{Ph-CH}_2\text{-PMe}_2^{\oplus}}/R_{\text{Ph-CH}_2\text{-AsMe}_2^{\oplus}} = 0.11/0.035 = 3.2$  [ $R = m/(o + p)$ ] suggests that it would be admissible to make an approximately quantitative comparison between similarly constituted pairs of oxonium and sulphonium salts on the one hand, and of ammonium and phosphonium salts on the other. Such a comparison would probably be most justifiable in the case of the pairs (A) benzylbenzopyrylium–benzylsulphonium (B), and (C) 2-benzylpyridinium\*–benzylphosphonium (D). The values of R for B, D (this paper and cited references), and C (Bryans and Pyman, J., 1929, 549, who found 10.4% of the *m*-isomeride) are known and hence the value for benzylbenzopyrylium salts can be estimated from the relationship  $R_A(x)/R_B(1.08) = R_C(0.12)/R_D(0.11)$ , and it may be predicted that even in this case a considerable proportion of *m*-substitution (probably >50%) will occur, and Le Fèvre's determination of the experimental value will be awaited with considerable interest.

\* 2-Benzylquinolinium would provide a more just comparison; the data for this kation, however, are not available.

## EXPERIMENTAL.

## A. Preparation of Materials.

Phenyl methyl sulphide, b. p. 191—192°, was prepared in theoretical yield by reduction of diphenyl disulphide (1 mol.) with sodium sulphide (0.5 mol.) and sodium hydroxide (2 mols.) in boiling aqueous-alcoholic solution (compare Blanksma, *Rec. trav. chim.*, 1901, **20**, 128) and methylation, without isolation, of the thiophenol so formed with methyl sulphate (1 mol.) (Brand and Stallmann, *Ber.*, 1921, **54**, 1578). This method was found to be of fairly general application for the preparation of the corresponding nitro-derivatives in both the sulphur and the selenium series.

*Phenyldimethylsulphonium picrate.* Phenyl methyl sulphide (22 g.) was heated with a slight excess of methyl sulphate at 100° for 2.5 days. An aqueous solution of the resulting methosulphate was converted by interaction with a saturated aqueous solution of sodium picrate into the *picrate* (yield, 46 g.), m. p. 101—102° after crystallisation from methyl alcohol-ligroin (Found: C, 46.1; H, 3.8.  $C_{14}H_{13}O_7N_3S$  requires C, 45.8; H, 3.5%). The same picrate was also obtained in less satisfactory yield from the corresponding tri-iodide described by Steinkopf and Müller (*Ber.*, 1923, **56**, 1926).

*m-Nitrophenyldimethylsulphonium picrate.* *m*-Nitrophenyl xanthate (prepared from 13 g. of *m*-nitroaniline by Leuckart's method, *J. pr. Chem.*, 1890, **41**, 197) was hydrolysed by boiling alcoholic sodium hydroxide for  $\frac{1}{2}$  hour, 5 g. of methyl sulphate were added, and boiling was continued for 2—3 hours. After the product had been cooled and poured into water, 5 g. of crude *m*-nitrophenyl methyl sulphide were obtained as a red oil by extraction with ligroin (b. p. 40—60°). The sulphide was heated with 3.9 g. of methyl sulphate at 100° for 2 days, and the resulting methosulphate converted into the required *picrate* in the usual manner. After crystallisation from methyl alcohol this had m. p. 163° (Found: C, 40.7; H, 2.9.  $C_{14}H_{12}O_9N_4S$  requires C, 40.8; H, 2.9%). This derivative was also obtained by nitration of phenyldimethylsulphonium picrate.

*p-Nitrophenyldimethylsulphonium picrate.* *p*-Nitrophenyl methyl sulphide (34 g.; Brand and Stallman, *loc. cit.*) was similarly converted into the required *picrate*, m. p. 137° after crystallisation from methyl alcohol-ethyl acetate (yield, 12 g.) (Found: C, 40.6; H, 2.9%).

*Phenyldimethylselenonium picrate.* This was originally prepared in accordance with the scheme:  $Ph_2Se \longrightarrow Ph_2Se_2 \longrightarrow Ph \cdot SeMe \longrightarrow Ph \cdot \overset{\oplus}{Se}Me_2 \} \overset{\ominus}{O}SO_4 \longrightarrow Ph \cdot \overset{\oplus}{Se}Me_2 \} \overset{\ominus}{O} \cdot C_6H_2(NO_2)_3$ . Diphenyl selenide (50 g.), prepared by Schöller's method (*Ber.*, 1919, **52**,

1517), was converted into diphenyl diselenide (19 g.) by heating on a sand-bath with 20 g. of powdered selenium at 150—170° for 2 days (compare Krafft and Lyons, *Ber.*, 1894, **27**, 1761). The product was converted into phenyl methyl selenide by Pope and Neville's method (*J.*, 1902, **81**, 1553). Addition of methyl iodide to phenyl methyl selenide gives very unsatisfactory yields of the selenonium iodide even when the reactants are heated together in a sealed tube at 60°, but satisfactory results were obtained by using methyl sulphate. Phenyl methyl selenide (5 g.) and methyl sulphate (3 g.) were heated together at 100° for 4 hours, a theoretical yield of the methosulphate being obtained. This was converted in the usual manner into the required *picrate*, m. p. 87—89° after crystallisation from ethyl acetate (Found: C, 40.1; H, 3.0.  $C_{14}H_{13}O_7N_3Se$  requires C, 40.1; H, 3.1%).

If phenyldimethylselenonium methosulphate is treated with a large excess of saturated sodium picrate solution, the normal picrate is produced together with a substance, m. p. 136—144° (decomp.), which is obtained moderately pure when phenyldimethylselenonium picrate is crystallised from a saturated aqueous solution of sodium picrate, and the product again crystallised from ethyl acetate. Analysis suggests that this substance is the *double picrate*  $2\{Ph\cdot\overset{\oplus}{Se}Me_2, C_6H_2(NO_2)_3\cdot\overset{\ominus}{O}\}$ ,  $C_6H_2(NO_2)_3\cdot ONa$  [Found: C, 37.7; H, 3.0;  $C_6H_2(NO_2)_3\cdot O\cdot$ , 64.5, 65.1, 65.5.  $C_{34}H_{28}O_{21}N_9Se_2Na$  requires C, 37.8; H, 2.6;  $C_6H_2(NO_2)_3\cdot O\cdot$ , 63.4%]. The picrate radical was determined gravimetrically as nitron picrate by the method of Busch and Blume (*Z. angew. Chem.*, 1908, **31**, 354). Crystallisation from solvents other than ethyl acetate (*e.g.*, water or alcohol) lowers the m. p., and pure sodium picrate crystallises when a hot solution of the double salt in nitrobenzene is cooled.

It was subsequently found that phenyl methyl selenide is best obtained by Taboury's method (*Bull. Soc. chim.*, 1903, **29**, 761). The mixture of diphenyl diselenide and selenophenol obtained by this method was reduced to the sodium derivative of the latter with sodium and boiling alcohol. This was methylated, without isolation, with methyl sulphate, and the resulting phenyl methyl selenide, b. p. 201°, converted into the required picrate as described above.

*pp'-Dinitrodiphenyl selenide.* Application of the method used by Bogert and Andersen (*J. Amer. Chem. Soc.*, 1927, **49**, 2011) for the preparation of *oo'*-dinitrodiphenyl diselenide to *p*-chloronitrobenzene yielded the mono- and not the di-selenide. Phosphorus pentaselenide (24 g.) was boiled with 23 g. of powdered selenium in an aqueous-alcoholic solution of sodium hydroxide for 2—3 hours. To

the resulting solution a hot alcoholic solution containing 39 g. of *p*-chloronitrobenzene was slowly added and boiling was continued for a further 2 hours. The precipitated solid was washed with water and extracted with boiling ethyl acetate. After crystallisation from this medium the *selenide* had m. p. 170—171° (Found : C, 44.4; H, 2.5.  $C_{12}H_8O_4N_2Se$  requires C, 44.7; H, 2.5%).

*p*-Nitrophenyl methyl selenide was obtained from *p*-nitrophenyl selenocyanate in a similar manner to the corresponding *m*-derivative, or by reduction of the *pp'*-dinitrodiphenyl selenide with sodium sulphide in alkaline solution and methylation with methyl sulphate in the usual manner. After crystallisation from methyl alcohol the selenide had m. p. 54—56° (Found : C, 39.2; H, 3.3.  $C_7H_7O_2NSe$  requires C, 38.9; H, 3.2%).

*p*-Nitrophenyldimethylselenonium picrate. The above selenide (2.2 g.) was heated with 1.3 g. of methyl sulphate at 60° for 14 hours, the resulting crude methosulphate dissolved in water, and a saturated solution of sodium picrate added. The precipitated oily picrate was redissolved and impurities were removed by boiling the solution with "norit." The filtered solution deposited crystals of the *picrate* on cooling. After crystallisation from 90% alcohol this had m. p. 122—123° (Found : C, 36.5; H, 2.7.  $C_{14}H_{12}O_9N_4Se$  requires C, 36.6; H, 2.6%).

*m*-Nitrophenyl methyl selenide. *m*-Nitrophenyl selenocyanate (Challenger, J., 1928, 1364) (8 g.) was heated with an aqueous-alcoholic solution of 4 g. of sodium hydroxide at 80—90° for ½ hour, 4.5 g. of methyl sulphate were added, and the mixture was boiled for 3 hours. The resulting black sticky mass was extracted with ether. The residue from the dried ethereal solution was a red oil which was distilled under reduced pressure. The fraction, b. p. 165°/13 mm., solidified on cooling in ice and consisted of pure *m*-nitrophenyl methyl selenide, m. p. 30—31° (Found : C, 39.1; H, 3.4%).

*m*-Nitrophenyldimethylselenonium picrate. The above selenide was heated with methyl sulphate (1 mol.) at 90° for 12 hours, and the methosulphate converted into the *picrate* in the usual manner. After crystallisation from ethyl acetate this had m. p. 156° (Found : C, 36.9; H, 2.8%). It was also obtained by direct nitration of phenyldimethylselenonium picrate.

*Benzyl*dimethylsulphonium picrate is best prepared from the corresponding bromide obtained by the interaction of benzyl bromide and dimethyl sulphide. Benzyl bromide (42 g.) was added with efficient cooling to 15 g. of dimethyl sulphide. After 5 hours, the semi-solid mass crystallised completely when rubbed. The crystals were washed with dry ether, the hygroscopic bromide

was dissolved in the minimum quantity of water, and the *picrate* precipitated in the usual manner; after crystallisation from alcohol it had m. p. 134° (yield, 45 g.) (Found: C, 47.2; H, 3.95.  $C_{15}H_{15}O_7N_3S$  requires C, 47.2; H, 4.0%).

The mononitro-derivatives were prepared in a similar manner from the appropriate nitrobenzyl iodides. *o*-Nitrobenzyl dimethylsulphonium *picrate* has m. p. 150—153° after crystallisation from methyl alcohol-ethyl acetate (Found: C, 42.5; H, 3.4.  $C_{15}H_{14}O_9N_4S$  requires C, 42.3; H, 3.4%). *m*-Nitrobenzyl dimethylsulphonium *picrate* crystallises from water in clusters of needles, m. p. 167.5—168.5° (Found: C, 42.0; H, 3.2%). *p*-Nitrobenzyl dimethylsulphonium *picrate* has m. p. 148.5—149° after crystallisation from dilute alcohol (Found: C, 42.5; H, 3.4%).

*Benzyl dimethylselenonium picrate* was originally prepared from the corresponding tri-iodide described by Jackson (*Annalen*, 1875, **179**, 5), who, however, gives no details concerning the optimum conditions of methylation. The best yield of the tri-iodide was obtained when dibenzyl diselenide was digested on a steam-bath with 4—5 times the theoretical quantity of methyl iodide for 3 days. The tri-iodide was dissolved in an excess of sulphurous acid and converted into the corresponding hydroxide by addition of a 15% excess of freshly prepared silver oxide. After filtration of the silver iodide, the sulphate present was precipitated by addition of the theoretical amount of baryta solution, the solution again filtered, and the *picrate* precipitated by the addition of the theoretical quantity of aqueous picric acid. It was subsequently found more convenient to prepare this compound by the action of benzyl bromide on dimethyl selenide. Dimethyl selenide (28 g., prepared according to Jackson's method, *loc. cit.*) was added with cooling to 43 g. of benzyl bromide, the resulting brown mass dissolved in water, and the *picrate* (38 g.) precipitated with aqueous sodium *picrate*. It crystallised from alcohol in small needles, m. p. 118° (Found: C, 42.2; H, 3.6.  $C_{15}H_{15}O_7N_3Se$  requires C, 42.0; H, 3.5%).

The corresponding *o*-, *m*-, and *p*-nitro-derivatives were prepared similarly from the nitrobenzyl bromides or iodides.

*o*-Nitrobenzyl dimethylselenonium *picrate* was prepared by allowing equivalent quantities of *o*-nitrobenzyl iodide and dimethyl selenide to react for 15 minutes only, washing the crude iodide formed with ether to remove any excess of the reagents, and precipitating the *picrate* from an aqueous solution of the iodide with a saturated solution of sodium *picrate*. After several crystallisations from methyl alcohol the *picrate* had m. p. 145—148° (Found: C, 38.0; H, 3.1.  $C_{15}H_{14}O_9N_4Se$  requires C, 38.1; H, 3.0%).

*m*-Nitrobenzyl dimethylselenonium *picrate*. The bromide, m. p. 112°

(decomp.), was obtained in 66% yield by the interaction of *m*-nitrobenzyl bromide and dimethyl selenide in the cold for 2—3 days. It was converted in the usual manner into the *picrate*, m. p. 132—134° after crystallisation from dilute alcohol (Found : C, 38.3; H, 3.1%).

*p*-Nitrobenzyl dimethylselenonium *picrate*, m. p. 152° (Found : C, 38.3; H, 2.8%), was similarly prepared in theoretical yield from *p*-nitrobenzyl bromide. This derivative was also isolated in a pure state from the products of nitration of benzyldimethylselenonium *picrate* (compare No. 9, Table IIIb).

#### B. Conditions of Nitration and Isolation of the Products.

*Phenyldimethyl-sulphonium and -selenonium Picrates*.—After trial experiments under various conditions it was found that these derivatives could be mononitrated in mixed acids (95% sulphuric acid and nitric acid,  $d_4^{15}$  1.53) at 60°. The *picrate* was added in small portions, with mechanical stirring, to the nitrating mixture, and the whole maintained at 60° for 7—8 hours and then kept at the ordinary temperature for 14 hours. The solution was poured on ice and exactly neutralised at 0° with sodium hydroxide solution, and the whole diluted to 800 c.c. with water and warmed to 70° to effect solution; the bulk of the *m*-nitro-derivative was then allowed to crystallise at 13°. This was filtered off, washed with the minimum quantity of cold water, dried at the ordinary temperature, and weighed. In the case of the selenium derivative some inorganic material was also precipitated and the *picrate* was therefore redissolved in 900 c.c. and crystallisation repeated. The combined filtrates were evaporated at 30—40°/20 mm., the residue repeatedly extracted with dry acetone, and the extract evaporated to dryness under reduced pressure at the ordinary temperature. The residue was dissolved in 20% hydrochloric acid, the *picric acid* extracted with benzene, and the solution again evaporated to dryness at the ordinary temperature. Only a slight residue, consisting almost exclusively of inorganic material, remained after evaporation of the acetone extract of the final residue. No trace of the *o*- or *p*-nitro-isomeride could be detected, and the small amount of the *m*-nitro-derivative remaining in the original mother-liquor was calculated from its solubility (see Section C), since it seemed to decompose under the mild but necessarily prolonged series of evaporations of the mother-liquors.

*Benzyldimethyl-sulphonium and -selenonium Picrates*.—All nitrations in this series were carried out by addition of the powdered *picrate* to nitric acid ( $d_4^{15}$  1.53) at -15°. Two alternative methods were employed in the isolation of the product. (1) The nitration mixture was poured on ice, and the solution evaporated to dryness



at the ordinary temperature in a vacuum, small quantities of water being added towards the end to prevent excessive concentration of nitric acid. (2) The solution obtained by pouring the nitration mixture on ice was neutralised with gaseous ammonia and evaporated to dryness on a steam-bath; the residue was extracted with boiling ethyl acetate and boiling anhydrous acetone in the sulphur and the selenium series respectively. In the latter case the re-evaporation to dryness and re-extraction with hot acetone was necessary to remove all inorganic salts.

The numerical particulars of all nitrations except analyses are given in Table IIIa and b, the analytical details and results are in Tables I, IV, and V.

### C. Determination of the Isomerides.

In the phenyl series the pure *m*-nitro-derivative was isolated in 88% yield, the small amount remaining in solution being calculated on the basis of the following solubility data.\*

*Solubility of*  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{RMe}_2 \} \text{Pic. in water at } 13^\circ.$

Isomeride.	100 C.c. of saturated solution contain (g.).**	
	R = S.	R = Se.
<i>p</i> -	0.161	0.076
<i>m</i> -	0.050	0.050
<i>m</i> - + <i>p</i> -	0.165	0.105

\*\* All evaporations were carried out at 30°/20 mm.

In the benzyl series the proportion of the isomerides present in the mixed mononitro-compounds, isolated as described in Section B, was determined either by Goss, Ingold, and Wilson's modification of Francis and Hill's bromination method (J., 1926, 2447) under carefully standardised conditions, or by oxidation of the mixture with boiling 3% potassium permanganate solution and reduction and bromination of the mixed nitrobenzoic acids by the method of Flürscheim and Holmes (J., 1928, 448). In the former method correction curves were plotted by determination of the bromination number (*F*) for the pure isomerides and for various artificial mixtures of these. Consistent and reproducible results could be obtained only under the following (additional) standardised conditions. The initial boiling (10 minutes) in alcoholic hydrochloric acid (after removal of the picric acid by extraction with benzene) and the reduc-

\* Addition of amounts of inorganic salts (equivalent to those present in the nitration products after neutralisation) to an aqueous solution saturated with both *m*- and *p*-nitro-picrates caused only a negligible precipitation and hence all solubilities were subsequently determined in pure water.

tion with a known excess of titanous chloride in boiling solution (a further 5 minutes) were carried out in a current of carbon dioxide in a bath maintained at 140°. The solution was then rapidly cooled by addition of crushed ice, the volume made up to 500 c.c., and bromination with the standard bromide-bromate mixture allowed to proceed for 5 minutes at -4°. The following values were obtained with artificial mixtures, the values being the means of several concordant observations :

Mixture of

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SMe}_2 \} \text{Pic.}$	<i>p</i> -	<i>p, m</i>	<i>p, m</i>	<i>p, m</i>	<i>p, m</i>	<i>m</i>
% meta .....	0	25.8	40.5	50	65.5	100
<i>F</i> .....	2.544	2.648	2.741	2.766	2.834	3.010

Mixture of

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SeMe}_2 \} \text{Pic.}$	<i>p</i> -	<i>p, m</i>	<i>p, m</i>	<i>o, p, m</i>	<i>m</i>
% meta .....	0	14.0	20.15	23.8	100
<i>F</i> .....	2.685	2.750	2.763	2.787	3.035

In nitration No. 10, the determination was carried out under slightly different conditions, for which the following correction figures were obtained :

Mixture of

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SeMe}_2 \} \text{Pic.}$	<i>p</i> -	<i>p, m</i>	<i>p, m</i>	<i>p, m</i>	<i>m</i>
% meta .....	0	20.5	51.4	79.5	100
<i>F</i> .....	2.570	2.708	2.846	2.978	3.040

Oxidation of the mixed nitrobenzylidimethyl-sulphonium or -selenonium picrates was carried out under the following standardised conditions. The mixed nitro-picrates (2 g.), dissolved in 800 c.c. of water, were treated at the boiling point with small successive portions of 3% potassium permanganate solution as long as decolorisation occurred. A further 20 c.c. excess of the permanganate solution was added and boiling continued for 4 hours; the solution then still remained pink. Under these conditions the following (mean) yields were obtained.

Substance oxidised.	<i>o</i> -.	<i>m</i> -.	<i>p</i> -.
$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{SMe}_2 \} \text{Pic.}$	100	92.4	90.7 %
$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{SeMe}_2 \} \text{Pic.}$	100	60.5	93 %

The proportions of the isomerides in the mixed nitrobenzoic acids obtained by oxidation were determined by reduction and bromination in the usual manner. The detailed results are in Tables IIIb and IV. The values given in the summary on p. 1733 have been corrected for the oxidation yields on the basis of the above data.

TABLE IIIa.

Nitration No.	Kation nitrated.	Wt.	Nitric acid, $d_{4}^{15}$ , 1.53.	95% Sulphuric acid.	Pure <i>m</i> -isomeride isolated.	Solubility corr.	Total <i>m</i> -compd., corr. for solubility.
1	Ph· $\overset{\oplus}{S}$ Me <sub>2</sub>	1.466	15	18	1.337	0.12	1.457
2	„	3.941	38	46	3.225	0.30	3.525
3	„ $\oplus$	5.211	38	55	5.093	0.40	5.493
4	Ph·SeMe <sub>2</sub>	1.266	12	15	0.954	0.12	1.074
5	„	6.218	38	46	6.075	0.85	6.925

All the above nitrations were carried out at 60° for 8 hours and the nitration mixture was left at room temperature for a further 12 hours. All quantities are expressed in grams.

TABLE IIIb.

Nitration No.	Kation nitrated.	Wt.	Nitric acid, $d_{4}^{15}$ , 1.53.	Time Temp. (hrs.).	Pro-duct.	Oxid-ised.	Acids.
6	Ph·CH <sub>2</sub> · $\overset{\oplus}{S}$ Me <sub>2</sub>	4.467	30	{ -15°, 0.8 } { room, 1.5 }	4.778	2.222	0.495
7	„	5.817	38	{ -15°, 1.5 } { room, 1.0 }	5.52*	2.131	0.571
8	„	6.464	45	{ -15°, 1.0 } { room, 1.0 }	6.856	2.335	0.797
9	Ph·CH <sub>2</sub> · $\overset{\oplus}{Se}$ Me <sub>2</sub>	4.03	45	{ -15°, 1.5 } { room, 1.5 }	4.420	1.615†	0.445
10		2.39	30	{ -15°, 1.5 } { room, 1.5 }	2.20	—	—
11		5.044	30	{ -15°, 1.5 } { room, 1.5 }	5.178	2.093	0.477

\* Some mechanical loss.

† After 58.7% of pure *p*-isomeride had been separated.

TABLE IV.

Nitration No.	Acids ana-lysed.	Composition of acids *							Percentage of nitro-isomerides.*	
		Recovered :			(mols. %) :				<i>o</i> - & <i>p</i> -.	<i>m</i> -.
		Benzoic acid.	Tribromo-aniline.	Tribromo-amino benzoic acid.	Benzoic.	<i>o</i> - & <i>p</i> -Nitro-benzoic.	<i>m</i> -Nitrobenzoic.			
7	0.527	0.009	0.447	0.571	2.5	45.8	51.7	47.0	53.0	
8	0.699	0.026	0.514	0.733	5.7	41.8	52.5	44.3	55.7	
9	0.425†	0.042	0.549	0.258	12.7	61.9	25.4	70.8	29.1	

\* Uncorrected for oxidation yields.

† Acids obtained by oxidation of the residue after 58.7% of pure *p*-isomeride had been isolated from the nitration product.

TABLE V.

Nitration No.	Bromination Nos. ( <i>F</i> ).	Mean value of <i>F</i> .	Percentage of <i>m</i> -isomeride (see p. 1731).
6	2·780, 2·744, 2·776, 2·752 (2·704)	2·763	50·3
7	2·813, 2·745, 2·759, 2·729	2·761	50·0
10	2·693, 2·679, 2·639	2·670	17·0
11	2·760, (2·700), 2·727, 2·741, 2·739	2·742	14·5

*Summary of Results.*

The following tabular summary is appended for convenience in reference :

*Nitration of phenyl- and benzyl-sulphonium and -selenonium salts.*

Nitration No.	Kation nitrated.	Yield of mononitro-product (corrected for solubility) (g.).				Mean % <i>m</i> -cmpd.
		Proportion of <i>m</i> -isomeride (%).				
		By oxidation and bromination (corrected).	By direct separation.	By direct bromination.		
1	Ph·S <sup>⊕</sup> Me <sub>2</sub>	88·5	—	100	—	} 100
2	„	79·7	—	100	—	
3	„	94·0	—	100	—	
4	Ph·Se <sup>⊕</sup> Me <sub>2</sub>	76·6	—	100	—	} 100
5	„	99·0	—	100	—	
6	Ph·CH <sub>2</sub> ·S <sup>⊕</sup> Me <sub>2</sub>	95·8	—	—	50·3	} 52·1
7	„	85·1*	52·6	—	50·0	
8	„	94·9	55·5	—	—	
9	Ph·CH <sub>2</sub> ·Se <sup>⊕</sup> Me <sub>2</sub>	99·2	15·5	—	—	} 15·7
10	„	83·6	—	—	17·0	
11	„	93·1	—	—	14·5	

\* Some mechanical loss.

The figures given in the last column have been rounded off in the abridged table on p. 1723.

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