

CCCXXV.—*The Nature of the Alternating Effect in Carbon Chains. Part IX. The Directive Influence of Groups of the Form $-CRR'\cdot NO_2$ in Aromatic Substitution.*

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As the result of a quantitative study of the nitration of eleven benzylamine derivatives, Goss, Ingold, and Wilson recently concluded (see preceding paper)

(i) that benzylammonium ions substitute very largely in the meta-position (more than 85% for the benzyltriethylammonium ion);

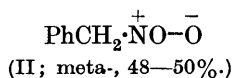
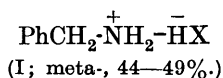
(ii) that undissociated salts also give large proportions of meta-derivatives (less than the ions, however); and

(iii) that the free amines do not yield appreciable amounts of meta-compounds, but on the contrary, give *op*-products.

These inferences were based on a hypothesis of electronic strain transmission (Ingold and Ingold, this vol., p. 1310) and conclusion (i) was regarded as definitely proved by experiment; conclusions (ii) and (iii), however, although affording a completely satisfactory

explanation of the experimental data, could not be considered to be established in the same final manner. Further evidence on these two points was therefore required, and in this paper independent evidence is brought to bear on conclusion (ii), which is of particular importance from the point of view of these memoirs, since it distinguishes the theoretical views advanced therein from those advocated by Robinson and Flürscheim, according to whom (*Chem. and Ind.*, 1926, **45**, 219, 220) undissociated benzylamine salts should substitute ortho- and para-.

The basis of conclusion (ii) was that the action of the dipole contained in the salt-grouping in setting up electronic strain in the relatively rigid systems imagined by Goss, Ingold, and Wilson, must be qualitatively similar to, and not very much smaller than, that of the free charge in the corresponding ion. The difficulty of establishing the point by direct experiment with benzylamine compounds lies, however, in the fact that the dipole arrangement in benzylamine salts is unstable, and that two modes of disruption (into ion and base) give rise to disturbances the extent of which cannot be exactly foretold. We therefore decided to investigate a series of substances analogous to benzylamine salts, but containing a *stable* dipole, and for this purpose selected phenylnitromethane derivatives, in which the salt-like dipole grouping is kept from dissociation by inclusion in a semipolar double-bonded arrangement (Sugden, Read, and Wilkins, J., 1925, **127**, 1525). Should our conclusions be correct, it is to be expected that phenylnitromethane derivatives would, in general, give considerable proportions of meta-derivatives, and that phenylnitromethane itself (II) would nitrate in the *m*-position to approximately the same extent (44—49%) as benzylamine, which Goss, Ingold, and Wilson assumed to substitute mainly through the undissociated salt (I) (*loc. cit.*). In verification of this prediction we have found that phenylnitromethane yields 48—50% of the *m*-nitro-derivative.



In spite of this very close agreement we deemed it essential to supplement the result by studying a series of derivatives of phenylnitromethane—for reasons which can be explained only by reference to the history of phenylnitromethane substitutions.

The nitration of phenylnitromethane itself was first carried out by Holleman (*Rec. trav. chim.*, 1895, **14**, 123) who obtained the *m*-nitro-derivative, which, he stated, constituted the bulk of the nitration product. When summarising the previous literature on directive action in aromatic substitution, Flürscheim, in 1902 (*J.*

pr. Chem., **66**, 328), referred to Holleman's observation as the only recorded instance of orientation in a direction which appeared to be contrary to the requirements of his theory. Since, according to that theory, the nitro-group is bound to carbon more feebly than is hydrogen (compare the explanation given for the meta-directive action of the nitro-group in nitrobenzene), the group $-\text{CH}_2\cdot\text{NO}_2$ should be more strongly bound to the benzene ring than the group $-\text{CH}_3$; that is to say, the nitromethyl group in phenylnitromethane should direct ortho-para- (III) even more strongly than does the methyl group in toluene. Toluene gives 3% of *m*-nitrotoluene, and consequently phenylnitromethane should give definitely less than 3% of the *m*-derivative. Therefore, to account for Holleman's result Flürscheim advanced the suggestion that phenylnitromethane substitutes through an *aci*-form (IV) containing unsaturated tervalent nitrogen :

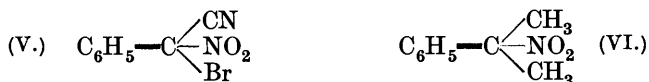


It is evident, however, that this could not occur in the case of a tertiary nitro-compound, $\text{C}_6\text{H}_5\cdot\text{CR}_2\cdot\text{NO}_2$, and, to establish his mechanism, Flürscheim investigated the nitration of phenylbromocyanonitromethane (V). In this case he observed (*loc. cit.*) the exclusive *op*-substitution demanded by his theory, a detailed search failing to reveal the presence of any trace of *m*-compound.

We were led to re-examine this case, first, because the suggested analogy with benzylamine salts, which distinguishes our view from Robinson's, remains valid only provided that phenylnitromethane substitutes through its ordinary form (III), and not through the *aci*-form (IV); secondly, because Flürscheim's theory of aromatic substitution, both in its original and present forms (Flürscheim and Holmes, this vol., p. 1562) is fundamentally dependent on the correctness of the explanation he has given for the substitution of phenylnitromethane; and, thirdly, because the exclusive *op*-substitution of phenylbromocyanonitromethane claimed by Flürscheim is unequivocally contrary to, and would, if true, overthrow, our own view as developed in the preceding parts of this series.

Regarding the first point, it seemed to us highly improbable, despite the apparently convincing character of Flürscheim's experimental demonstration, that phenylnitromethane should substitute in an *acid* medium through an *aci*-form such as (IV). Even if this form be present, the proportion must be excessively small, and therefore in order to account for the predominating *m*-substitution it has to be assumed that the velocity of *m*-nitration of (IV) is so

much greater than the velocity of *op*-nitration of (III) that the large disparity in the active masses is counterbalanced. This is entirely contrary to general experience, according to which *op*-directed substitutions have the greater velocity (compare Ingold and Ingold, this vol., p. 1313). To render the matter certain, however, we have repeated the nitration of phenylbromocyanonitromethane (V) with the same reagent and at the same temperature as used by Flürscheim, and have found that, contrary to his statement, relatively little of the *p*-isomeride is produced and that more than 50% of the product consists of the *m*-nitro-derivative. This shows conclusively that phenylnitromethanes nitrate through their ordinary forms, as the analogy with benzylamine salts requires; it also confirms our view that the undissociated benzylamine salts are largely *m*-substituting, against the contrary views of Robinson and Flürscheim.



Although significant and historically interesting, since, had the original experimental work been correctly performed, Flürscheim's theory, outlined in the same paper, could scarcely have been advanced, the case of phenylbromocyanonitromethane is not the most crucial one that can be devised in order to test that theory; for the bromine atom *might* be assumed, improbable as it may appear, to give rise to the condition $C_6H_5-C \begin{cases} \text{CN} \\ \text{NO}_2 \\ \text{Br} \end{cases}$, leading to *m*-substitution, despite the contrary action of the nitro- and cyano-groups.* We have therefore also investigated the nitration of β -phenyl- β -nitropropane (VI). According to Flürscheim's theory, the methyl group has an intrinsic affinity demand approximately equal to that of hydrogen, and, when joined to a saturated atom, cannot form a bond of greater affinity content (*J. pr. Chem.*, 1907, 76, 197; *Chem. and Ind.*, 1925, 44, 249, 563). Therefore it follows from this theory (but not from ours, see below) that the methyl groups in phenylnitropropane will offer no disturbance, and, since the nitro-group is tertiary, the side-chain must necessarily direct practically wholly *ortho-para*. In direct opposition to this hypothesis, we find that about 30% of the *m*-nitro-derivative is formed. This result seems absolutely contrary to Flürscheim's theory, both in its original form and in all the extended forms in which it has

* This appears to be the only possible alternative, since it is admitted that the polar and steric factors ("*p*" and "*s*") are negligible in this case (Flürscheim and Holmes, *ibid.*, p. 1563).

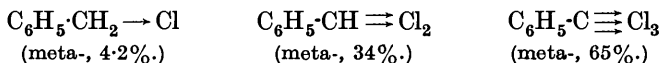
been advanced up to the present—excepting in so far as our own view is admittedly an extension, based partly on that theory.



It remains to be added that, although the electronic-strain hypothesis appears to afford a very satisfactory explanation of the proportions of the isomerides obtained in these cases, two other instances were studied in order to test its applicability more thoroughly. These were phenylbromonitroethane (VII) and phenyldibromonitromethane (VIII). The methyl group attached to saturated carbon is an electron-source (Holmes and Ingold, this vol., p. 1305), and, as such, must oppose *m*-substitution. An illustration of this type of action by methyl is provided by the nitration of methyl and ethyl benzoates (Holleman, *Rec. trav. chim.*, 1899, **18**, 267; *Z. physikal. Chem.*, 1899, **31**, 79; the nitration of other esters of benzoic acid is being investigated):

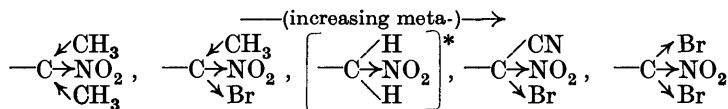


The bromine atom, analogously situated, attracts electrons, and therefore must promote *m*-substitution, the action being similar to, but less powerful than (*Chem. and Ind.*, 1926, **45**, 357), that of chlorine (Holleman, *Rec. trav. chim.*, 1914, **33**, 1):

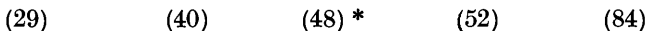


The influence of a single similarly placed cyano-group which contains within itself the elements of both these opposing effects would probably be small. Thus we have the following theoretical sequence of groups arranged in order of their *m*-directive power:

Theoretical Order:



Found (% meta-):



* Compare benzylamine salt.

The figures recorded in the lower line represent the approximate proportions of meta-isomeride observed for each case and serve to show how closely the theoretical requirements are fulfilled.

EXPERIMENTAL.

(A) Preparation of Phenylnitromethane Derivatives.

1. *Phenylnitromethane*, $\text{CH}_2\text{Ph}\cdot\text{NO}_2$.—This was prepared by Holleman's method (*Rec. trav. chim.*, 1894, **13**, 405) from benzyl chloride and silver nitrite. The product had b. p. $110^\circ/8$ mm. (Found: C, 61.3; H, 5.3. Calc.: C, 61.2; H, 5.1%).

2. *Phenylbromocyanonitromethane*, $\text{CPhBr}(\text{CN})\cdot\text{NO}_2$.—The sodium salt of *aci*-phenylcyanonitromethane was prepared by Wislicenus and Ender's method (*Ber.*, 1902, **35**, 1757) and carefully purified by crystallisation from absolute alcohol. The pure salt was converted into phenylbromocyanonitromethane by Flürscheim's method (*loc. cit.*) [Found: (Sample A) C, 40.2; H, 2.3; (Sample B) C, 40.4; H, 2.3. Calc.: C, 39.8; H, 2.1%].

3. β -*Phenyl- β -nitropropane*, $\text{CMe}_2\text{Ph}\cdot\text{NO}_2$.—This was prepared by side-chain nitration of *isopropylbenzene* (compare Konovalov, *Ber.*, 1895, **28**, 1856) under the following conditions. *iso*Propylbenzene (32 c.c.) was boiled under reflux for 10 hours with 250 c.c. of dilute nitric acid (d 1.075), and the cooled mixture made strongly alkaline with potassium hydroxide and extracted with ether. The residue from the ether was fractionally distilled, a large amount of unchanged hydrocarbon being recovered and used again, and a small fraction of the nitro-compound, b. p. 120 — $140^\circ/15$ mm., obtained. After many repetitions of this experiment the fractions of nitro-compound were combined and redistilled repeatedly until a fraction, b. p. 123 — $128^\circ/12$ mm., was obtained. Benzoic acid is also formed in this experiment, and the loss of material through this cause was greatly increased when it was attempted to secure a greater degree of nitration in one operation [Found: (Sample A) C, 65.5; H, 6.6; (Sample B) C, 65.2; H, 6.3. Calc.: C, 65.5; H, 6.7%].

4. α -*Phenyl- α -bromo- α -nitroethane*, $\text{CMePhBr}\cdot\text{NO}_2$.— α -Phenyl- α -nitroethane was first prepared by side-chain nitration of ethylbenzene. Konovalov states (*J. Russ. Chem. Soc.*, 1893, **25**, 527; compare *Chem. Zentr.*, 1894, I, 465) that this reaction takes place when 4 c.c. of ethylbenzene are heated with 25 c.c. of nitric acid (d 1.075) at 107° in a sealed tube for 5—6 hours, but under these conditions we found it difficult to avoid almost complete oxidation to benzoic acid. Better results were obtained by carrying out a series of partial nitrations as described for phenylnitropropane, except that the mixture, instead of being made strongly alkaline before extraction with ether, was in this case exactly neutralised with sodium carbonate. The nitro-hydrocarbon, which had b. p. $135^\circ/25$ mm., was treated in concentrated alcoholic solution with alcoholic sodium ethoxide, and the sodio-derivative collected,

washed with alcohol and ether, and dried on porous porcelain. It was then decomposed in aqueous solution with the theoretical amount of bromine, α -phenyl- α -bromo- α -nitroethane being then precipitated as a pale yellow oil. As this substance decomposed on distillation, it was extracted with pure ether and the last traces of ether were removed in a good vacuum (Found : C, 41.8; H, 3.7. Calc. : C, 41.7; H, 3.5%).

5. *Phenyldibromonitromethane*, $\text{CPhBr}_2 \cdot \text{NO}_2$.—This was prepared by Ponzio's method (*Gazzetta*, 1908, **38**, ii, 418) from phenylnitromethane [Found : (Sample A) C, 29.8; H, 1.9; (Sample B) C, 29.6; H, 2.1. Calc. : C, 28.5; H, 1.7%].

(B) *Nitration of Phenylnitromethanes and Determination of the Proportion of m-Isomeride : General Procedure.*

(Details peculiar to the procedure in individual cases are given in Section C.)

Nitration of Phenylnitromethanes.—The phenylnitromethane derivative was delivered slowly from a dropping-funnel the constricted end of which dipped under the surface of about 8 parts of fuming nitric acid (d 1.49) maintained at a known temperature. The addition usually occupied 2—4 hours and the mixture was then kept at the same temperature for a further period. The temperature, the period of addition, and the time for which the mixture was kept after the addition was finished were varied slightly from case to case according to the conditions required to effect complete nitration and to avoid an undue amount of oxidation. The reaction mixture was then poured on ice, basified with sodium hydroxide below 10° (except in the case of phenylnitromethane—see Section C), and the precipitated nitro-compound extracted with ether. The extract was dried with sodium sulphate, and the residue obtained after removal of the ether desiccated in a good vacuum. The aqueous mother-liquors were acidified with hydrochloric acid and the acid fraction recovered and weighed in order to determine the proportion of the phenylnitromethane which had become oxidised.

Oxidation of the Nitration Product to Nitrobenzoic Acids.—The oxidation of the nitration products to mixtures of *o*-, *m*-, and *p*-nitrobenzoic acids was usually effected by means of hot dilute nitric acid, which in all cases gave good yields (about 90%). (In the case of phenylbromocyanonitromethane, permanganate was also used.) The general method was to boil the nitration product with excess of nitric acid (d 1.10—1.15) for periods varying from 2—10 hours, according to the example under investigation. It was shown experimentally that benzoic acid is not nitrated under these conditions. On cooling the nitric acid solution, part of the

nitrobenzoic acids crystallised, and this portion was sometimes collected and treated separately. The remainder was extracted with pure ether and freed from nitric acid and colouring matter in the manner described by Holleman ("Die Direkt Einführung von Substitution in den Benzolkern," p. 121).

Estimation of the Proportion of m-Nitrobenzoic Acid in the Mixed Nitrobenzoic Acids obtained by Oxidation of the Nitration Products.—For this purpose, the mixed nitrobenzoic acids were reduced to aminobenzoic acids by means of titanous chloride and these were brominated with bromide-bromate solution under the conditions used by Goss, Ingold, and Wilson (*loc. cit.*) to estimate the proportion of meta-isomeride in nitrobenzylamine derivatives, except that in the present cases the bromination was effected at -10° . Experiments with artificial mixtures of *o*-, *m*-, and *p*-nitrobenzoic acids showed that calculation of the meta-contents from the quantities of bromine absorbed on a strictly theoretical basis led to results about 4% too high on the average, and an empirical connexion between the meta-content and the bromination number *F* (*loc. cit.*) was therefore established in order to give the correction appropriate to various compositions :

Mixture.	<i>p</i> .	<i>o</i> , <i>p</i> , <i>m</i> .	<i>p</i> , <i>m</i> .	<i>o</i> , <i>p</i> , <i>m</i> .	<i>p</i> , <i>m</i> .	<i>p</i> , <i>m</i> .	<i>m</i> .
% meta- ...	0.0	18.0	40.5	48.3	71.2	90.6	100.0
<i>F</i>	2.089	2.263	2.422	2.516	2.763	2.931	3.000

Since all these points lie on or about a straight line, it is evident that the necessity for correction arises solely on account of the production of small amounts of *s*-tribromoaniline. The corrections to be applied to the theoretically calculated *m*-content are :

Apparent <i>m</i> -content (%)	30	40	50	60	70	85
Correction (%)	-6	-5	-4	-3	-2	-1

The results obtained by this method were confirmed by the separation of *m*-nitrobenzoic acid from the mixtures.

Separation of m-Nitrobenzoic Acid from the Mixed Acids produced by Oxidation of the Nitration Products.—The *m*-acid was separated from its isomerides by making use of the large differences in the solubility of the three isomerides in cold chloroform and the large solubility of the barium salt of the *o*-acid in cold water. The solubilities in question were taken as having the following values in g. per 100 g. of solvent :

	Ortho.	Meta.	Para.
Acids in chloroform at 20°	1.09	4.07	0.101
Barium salts in water at 20° ...	Very sol.	0.377 (+4H ₂ O)	0.400 (+5H ₂ O)
" " " 100° ...	"	5.2	12.5

A known weight of the mixture was triturated at 20° with rather more than sufficient chloroform to dissolve all the *m*-acid present,

the amount having previously been determined by reduction and bromination (above). In general, this quantity of chloroform was sufficient to dissolve all the ortho-compound present also; a small amount of the *p*-acid also dissolved, and the approximate quantity could be calculated from the solubility data given above. The undissolved portion usually consisted of practically pure *p*-nitrobenzoic acid. The chloroform extract was evaporated in a vacuum and the residual acids neutralised with standard barium hydroxide using phenolphthalein as an external indicator. The solution was then concentrated to a volume calculated to be sufficient to retain the whole of the salt of the *p*-acid in solution at 20°, and the *m*-salt, which crystallised at this temperature, was collected and washed with alcohol and ether. In some cases, the salt was recrystallised from a known quantity of water and washed as before. It was then dissolved in hydrochloric acid and the *m*-acid extracted with pure ether, any precipitated *m*-acid being collected separately in some cases. The extract was dried with sodium sulphate and evaporated, and the residual *m*-nitrobenzoic acid weighed. Allowance can be made for the small amounts of the barium salt of this acid retained in solution during the crystallisations. If any benzoic acid (arising from incomplete nitration of the original phenylnitromethane) is present, this separation is somewhat interfered with, the solubility of benzoic acid being about 14 g. in 100 g. of cold chloroform, and that of its barium salt about 5 g. in 100 c.c. of water, and in this case the m. p. of the separated *m*-nitro-acid may be 10—15° too low. It is, however, readily purified to an acid of the correct m. p. by crystallisation from a small volume of ethyl acetate-ligroin.

A mixture of nitrobenzoic acids containing ortho-, 0.105 g.; meta-, 0.485 g.; para-, 0.410 g. (total weight 1.000 g.) was triturated with 13.0 g. of chloroform, which should dissolve all the *o*- and *m*-acids present and about 0.013 g. of the *p*-acid. The undissolved residue weighed 0.380 g. and had m. p. 234—235° (para-). The dissolved *p*-acid is equivalent to 0.022 g. of barium salt, which is soluble in 5.5 c.c. of cold water. The acids remaining after evaporation of the chloroform (0.62 g.) were converted into barium salts, which were allowed to crystallise from 7.0 c.c. of water. The *m*-acid regenerated from the crystallised salt weighed 0.460 g. and had m. p. 135—137°. The weight corresponding with the meta-barium salt retained in solution is 0.013 g., and this may be applied as a correction :

Proportion of <i>m</i> -acid present	= 48.5%	} Total 47.3%
Proportion of <i>m</i> -acid isolated	= 46.0%	
Solubility correction	= 1.3%	

The deficit is therefore 1.2%. In the case of mixtures obtained by the oxidation of nitration products, and analysed by the bromination method, the deficit was usually a little greater (mean, 2.5%).

(C) *Details relating to Individual Cases.*

1. *Phenylnitromethane*.—Holleman (see p. 2463), when nitrating this substance and isolating the *m*-nitro-derivative, did not establish the presence of any other isomeride, although the formation of the *o*-derivative was inferred from the taste of the nitrobenzoic acids obtained by oxidation of the residues. We find that the *p*-derivative is also formed, but we confirm Holleman's observation that the *m*-isomeride is the principal product.

Details peculiar to this case are as follows: (Expt. 2) Reagent: nitric acid (*d* 1.49). Temperature: 0°. Speed of addition: 1.0 g. per hour. The general method was followed except that the nitration product, which was precipitated in a crystalline form by pouring on ice, was collected by filtration, and the filtrate nearly neutralised with sodium hydroxide, then fully neutralised with precipitated calcium carbonate, and extracted with ether (yield 92% of theory) (Found: C, 45.3; H, 3.5. Calc.: C, 46.1; H, 3.3%). The remaining material was accounted for as acid products formed by oxidation.

Analysis: The nitrobenzoic acids (yield 91%), after reduction, absorbed bromine indicating an apparent meta-content of 52%; when corrected, this becomes 48%.

Separation: The separated *p*-nitrobenzoic acid had m. p. 233—234° (mixed m. p. 235°); yield 14%. The *m*-nitrobenzoic acid was collected in two portions. One (precipitated) had m. p. 140° (mixed m. p. 140°); yield 32%. The second (extracted from solution by ether) had m. p. 115—125° (mixed m. p. 135—140°), and when crystallised once from ligroin-ethyl acetate had m. p. 139° (mixed m. p. 140°); yield before crystallisation, 18%. Total yield of *m*-nitrobenzoic acid 50% (Found: C, 50.0; H, 3.3. Calc.: C, 50.3; H, 3.0%).

Since *m*-nitrophenylnitromethane crystallises well from glacial acetic acid an attempt was made to separate as much as possible from the nitration product. The mixture (0.635 g.) was crystallised from 1.0 c.c. of glacial acetic acid, and the mother-liquor decanted as completely as possible from the crystals, which were drained on porous porcelain. They weighed 0.261 g. and had m. p. 92° (the pure *m*-compound has m. p. 94°); yield 41%. By evaporation of the mother-liquors a further small quantity of impure *m*-compound, m. p. 70—75°, was obtained; yield 0.013 g. = 2%. Total amount separated, 42 ± 1%.

2. *Phenylbromocyanonitromethane*.—Flürscheim (see p. 2464) employed 8 parts of "fuming" nitric acid and conducted the nitration "in a freezing mixture." We have adhered to the same conditions (see below) in so far as they are specified by these statements. For the oxidation, Flürscheim used permanganate; we employed the same reagent, which gives a good yield, and also dilute nitric acid (Section B), with practically identical results. In order to ascertain whether the marked discrepancy between Flürscheim's results and our own (see pp. 2464—2465) in this important experiment was due to some accidental variation in the procedure, we repeated our experiments a number of times, using three different samples of initial material, and introducing several minor variations into the manipulation; the results, however, were sensibly the same.

(Expt. 24). Reagent: 8 parts of nitric acid (d 1.49). Temperature: -15° . Rate of addition: 2.0 g. per hour. Material used: 13.0 g. of Sample B (analysis, Section A). After the addition, the mixture was kept at -15° for 1.5 hours and at $+15^{\circ}$ for 0.5 hour and then poured on ice. The mixture was nearly neutralised with potassium hydroxide and extracted with ether, and the extract washed five times with dilute sodium carbonate, dried with sodium sulphate, and evaporated in a vacuum over phosphorus pentoxide. Flürscheim describes his nitration product as an oil; ours partly crystallised. Flürscheim's yield is not recorded; our yield, in this experiment, was 75% of the theoretical, the remaining material having apparently undergone oxidation; 10% was recovered as acid products formed by oxidation.

Analysis: The nitrobenzoic acids, which were obtained in 86% yield by oxidation with dilute nitric acid (Section B) (Found: C, 49.6; H, 3.2. Calc.: C, 50.3; H, 3.0%), when analysed by reduction and bromination, gave an apparent *m*-content of 57%. The corrected proportion of *m*-isomeride is therefore 54%.

Separation: The separated *p*-nitrobenzoic acid had m. p. 215—220° (mixed m. p. 228—231°); yield 12%. The *m*-nitrobenzoic acid was collected in two portions. One (precipitated) had m. p. 133—136° (mixed m. p. 141°) and, after one crystallisation from ethyl acetate-ligroin, 140°; the other (extracted from solution) had m. p. 128—133° (mixed m. p. 139—140°) and, after one crystallisation, 141°; total yield 47%.

(Expt. 21). Material used: 5.8 g. of Sample A (analysis, Section A). Yield of nitration product, 70% of the theoretical (Found: C, 35.0; H, 1.9. Calc.: C, 33.6; H, 1.4%). Yield of nitrobenzoic acids obtained by oxidation with dilute nitric acid 79%. Analysis by the bromination method gave an apparent meta-content of 53%, which, on correction, corresponds with 50% of *m*-isomeride.

(Expt. 22). Material used : 7.1 g. of Sample A (analysis, Section A). In this experiment, the nitration product (yield 74%; yield of acid by-product, 14%) was washed with alcohol and so divided into a crystalline portion sparingly soluble and an oil readily soluble in alcohol. The crystalline portion (42% of the whole), on oxidation by dilute nitric acid to nitrobenzoic acids (yield 82%) (Found : C, 49.0; H, 3.1%), gave no *p*-acid and 58% of the *m*-acid (m. p. 130—135°; mixed m. p. 135—140°). The oily portion (58% of the whole) on oxidation (yield 82%) gave 28% of the *p*-acid, m. p. 200—210°; mixed m. p. 225—228° (Found : C, 49.1; H, 3.3%) and 26% of the *m*-acid (m. p. 133°; mixed m. p. 140—141°). The yield of *p*-acid calculated on the whole product is 16% and the yield of *m*-acid is 44%. Analysis by the bromination method gave a meta-content of 51% (corrected).

(Expt. 25). Flürscheim oxidised his material by means of permanganate, and in order to ascertain whether this method leads to selective destruction of the *m*-isomeride, we employed it also. Oxidation by 1% permanganate, added gradually to a suspension of the material in sodium hydrogen carbonate solution on the steam-bath, gave nitrobenzoic acids in 89% yield, and, from these, 50% of *m*-nitrobenzoic acid (m. p. 125—132°; mixed m. p. 139—140°).

The specimens of mixed nitrobenzoic acids obtained in these nitration products of phenylbromocyanonitromethane usually had the odour of benzoic acid and small amounts of this acid were separated by sublimation. Since the presence of benzoic acid, which Flürscheim also observed, indicates incomplete nitration of the original nitromethane derivative, it follows that the real proportion of *m*-substitution is probably slightly higher than is indicated by the yields of *m*-nitrobenzoic acid recorded above.

3. *β*-Phenyl-*β*-nitropropane.—Reagent : nitric acid (*d* 1.49). Temperature : — 15°. Rate of addition : 1.3 g. per hour. The mixture was kept for 3 hours at — 15° after completing the addition and then poured on ice.

(Expt. 38). Material used : 4.0 g. of Sample B (analysis, Section A). The yield of nitration product was 85%, and the whole of the remaining material (15%) was accounted for as acid products formed by oxidation. The yield of nitrobenzoic acids was quantitative. The separated *p*-nitrobenzoic acid had m. p. 225—227° (mixed m. p. 230—232°); yield, 38%. The *m*-acid was collected in two portions. One (precipitated) had m. p. 138—141° (mixed m. p. 141°); yield 14%. The other (extracted from solution) had m. p. 130—132° (mixed m. p. 135—138°); yield 7%. Total yield 21%.

(Expt. 33). Material used : 5.0 g. of Sample A (analysis, Section A). The yield of nitration product was 94% of the theoretical (Found : C, 50.7; H, 4.5. Calc. : C, 51.5; H, 4.8%). The yield of mixed nitrobenzoic acids was 95% (Found : C, 49.9; H, 3.6%). The separated *p*-nitrobenzoic acid had m. p. 215—222° (mixed m. p. 234—236°) and, when crystallised, had m. p. 232—234°; yield 35%. The *m*-acid commenced to soften at 125° and melted at 140°; yield 35%.

(Expt. 37). Material used : 3.8 g. of Sample A. The percentage yields at each stage were identical with those of Expt. 38, except that the total yield of *m*-acid was 26%.

(Expt. 39). The nitration product (Found : C, 52.4; H, 4.5%) on oxidation gave nitrobenzoic acids (Found : C, 49.3; H, 3.0%) in 95% yield. The proportion of *m*-acid found by the bromination method was 29% (corrected).

4. *α-Phenyl-α-bromo-α-nitroethane*.—Considerable difficulty was experienced in obtaining a completely nitrated product, but ultimately the following process was adopted : (Expt. 44). 3 G. of the nitroethane were run during 2.25 hours into 4.5 g. of nitric acid (*d* 1.49) at 15°, and the product was kept for a further 2.25 hours at this temperature before pouring on ice. A considerable amount of oxidation took place, and the nitration product, which was isolated in only 40% yield (Found : C, 37.4; H, 3.0), gave nitrobenzoic acids in a yield of 80%. The separated *p*-acid had m. p. 220—225° (mixed m. p. 232°); yield, 25%. The *m*-acid was obtained in two portions. One (precipitated) had m. p. 134—135° (mixed m. p. 141°) and, after crystallisation from ligroin-ethyl acetate, 141°; yield 24%. The second (extracted from solution) had m. p. 125—130° (mixed m. p. 140°) and after crystallisation melted at 137° (yield 14%) (Found : C, 49.4; H, 3.1%). The total yield of *m*-acid was therefore 38%. The proportion of *m*-isomeride was not determined by bromination in this case, and in the table in Section D the above value is rounded to 40% since the average loss of *m*-acid during these separations is calculated to be 2.5%. These figures are regarded as approximate only.

5. *Phenyldibromonitromethane*.—Reagent : nitric acid (*d* 1.49). Temperature : — 15°. Rate of addition : 2 g. per hour. After the addition was complete, the mixture was kept at — 15° for a further 3 hours and then poured on ice and worked up as usual.

(Expt. 52). Material : 5.0 g. of sample A (analysis, Section A). Yield of nitration product, 88% of the theoretical (Found : C, 25.1; H, 1.7. Calc. : C, 24.7; H, 1.2%).

Analysis : A portion of the nitration product, on oxidation, gave an 87% yield of mixed nitrobenzoic acids (Found : C, 49.7;

H, 3.0%). Reduction and bromination gave an apparent *m*-content equal to 85%, which on correction becomes 84%.

Separation: A second portion of the same nitration product was oxidised, and the yield of mixed nitrobenzoic acids was in this case 100% (Found: C, 50.9; H, 3.5%). The separated *p*-acid had m. p. 221° (yield 6%). The *m*-acid had m. p. 120–125° (mixed m. p. 137–139°) (yield 80%).

(Expt. 53). Material: 5.3 g. of sample B (analysis, Section A). Yield of nitration product, 87% (Found: C, 25.5; H, 1.3%).

Analysis: Oxidation gave nitrobenzoic acids in 93% yield. Reduction and bromination of these gave 85% of *m*-isomeride (corrected).

Separation: Yield of separated *p*-acid, 6%. The separated *m*-acid was collected in two fractions: precipitated portion (m. p. 138–139°; mixed m. p. 141°), 60%; extracted portion (m. p. 125°; mixed m. p. 134–139°), 19%. The extracted portion after one crystallisation melted at 136–138° (mixed m. p. 141°). Total yield of *m*-acid 79%.

(D) Summary of Results.

The following tabular summary is appended for convenience in reference.

Nitration of Phenylnitromethanes by Nitric Acid (d 1.49).

RR' in directing group, CRR'·NO ₂ .	Temp.	Conversion to nitrobenzoic acids (%).	Separation of isomerides (%).				% <i>Meta</i> - (by estimation).	Mean % <i>meta</i> -.
			<i>Para</i> -.	Mean.	<i>Meta</i> -.	Mean.		
Me, Me	-15°	98	38	37	21	27	29	29
			35		35			
			38		26			
Me, Br	+15	80	25	25	38	38	—	40
H, H	± 0	91	14	14	50	50	48	48
CN, Br	-15	84	12	14	47	47	54	52
			16		44			
			—		50			
Br, Br	-15	93	6	6	80	79	84	84
			6		79			
			—		85			

The rough parallelism between the successive decreases in *para*- and increases in *meta*-, on passing through the series, is noteworthy.

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