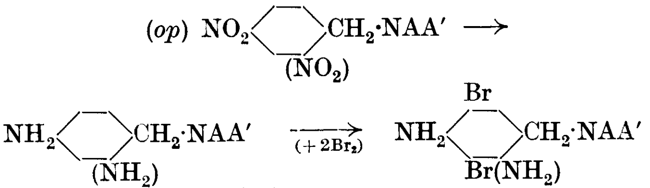
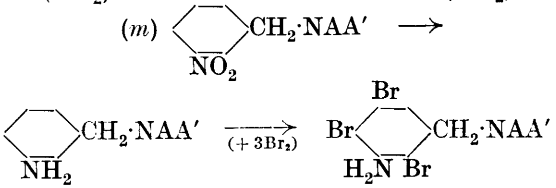
CCCXXIV.—*The Nature of the Alternating Effect in Carbon Chains. Part VIII. The Nitration of Some Benzylamine Derivatives with Special Reference to the Respective Rôles of the Ions, Salts, and Bases.*

By FRANK ROBERT GOSS, CHRISTOPHER KELK INGOLD, and IAN STUART WILSON.

IN Part III of this series (Holmes and Ingold, J., 1925, **127**, 1800) it was shown that whilst benzyl ethers and esters, $C_6H_5{\cdot}CH_2{\cdot}OA$, nitrate exclusively in the *op*-positions in the benzyl group, benzylamine derivatives, $C_6H_5{\cdot}CH_2{\cdot}NAA'$, frequently give large proportions of *m*-isomerides. The contrast between these two classes of compounds is very strongly marked, but experiments of a quantitative kind are required to enable conclusions to be drawn regarding the effect of structure on the tendency to *m*-substitution of the individual benzylamines amongst themselves, and it is in this direction that the present paper extends the previous work.

It has been found that benzylamine derivatives are not appreciably altered by cold dilute bromine solution under conditions in which aniline and its nuclear substitution products are rapidly and quantitatively brominated. We have therefore utilised Francis and Hill's method of quantitative bromination by means of acidified bromide–bromate solution (*J. Amer. Chem. Soc.*, 1924, **46**, 2498) to determine the proportion of *m*-derivative formed in the nitration of different benzylamine compounds: the mixture of isomeric nitro-compounds is first reduced to the amino-benzylamine derivatives, which are then brominated; in the simplest instance the proportion of *m*-isomeride can be directly calculated from the quantity of bromine entering the molecule since the *m*-aminocompound can take up three atoms of bromine, whilst its *o*- and *p*-isomerides can yield only dibromo-derivatives :





The table below summarises the results obtained by this method for eleven benzylamine derivatives. In seven of the cases, more than one experiment was carried out in order to show the degree of reproducibility of the results when every effort is made to keep the conditions of nitration identical. The figures in col. 4 show that exact reproducibility is extremely difficult to attain, but the mean values (col. 5) are regarded as approximately representative of the varying tendencies to *m*-substitution in the different cases. Individual results which, not being considered typical, have been excluded from the calculation of the mean values, are shown in square brackets. Since the experimental error is expected to be similar, no matter whether the proportion of *m*-isomeride is large or small, it will in the latter case bear a correspondingly greater ratio to the values given.

Nitration of Benzylamine Derivatives.

(Reagent : Nitric Acid, *d* 1·50.)

			Proportion of *m*-isomeride (%).	
Class.	Formula.	Temp.	Individual results.	Mean.
Quaternary salt.*	(1) $BzNEt_3^+$	−5°	85	85‡
Primary base.	(2) $BzNH_2$	0	[34], 40, 41, 43, 44, 48, 49†	44
Secondary base.	(3) Bz_2NH	0	[68], 75, 76, 76, [87]	76
Tertiary bases.	(4) Bz_3N	0	53, [60]	53
	(5) Bz_2NMe	0	52, 64	58
	(6) $BzNMe_2$	0	57, 58, 60	58
	(7) $BzNEt_2$	0	51	51
Monoacyl derivs.	(8) BzNHAc	0	6, 8	7
	(9) BzNMeAc	0	8	8
	(10) Bz_2NAc	0	23, 26	25
Diacyl deriv.	(11) BzNSuccinyl	−12	1	1

* Picrate used. † By separation.

‡ Compare *Chem. and Ind.*, 1926, **45**, 43.

The detailed descriptions of these experiments are to be found in the experimental portion, but the following notes regarding the extent to which the above data are confirmed by the actual separation of the isomerides may appropriately be given :

(1) The substitution of the quaternary salt is theoretically important, and the very large degree of *m*-substitution characteristic of benzyltriethylammonium picrate has been confirmed by the isolation of 79% of the *m*-nitro-derivative in the pure condition—*i.e.*, all but 6% of the quantity estimated to be present (p. 2450).

(2) Benzylamine is the fundamental compound of the series and its nitration has therefore been studied with particular care. Methods have been elaborated whereby the bulk of the *m*- and *p*-isomerides can be separated in the pure state, and the unseparated residue has been oxidised to the readily separable nitrobenzoic acids. In this way, the following independent estimation of the proportions of the isomerides has been made :

Ortho-, 8% ; *meta*-, 49% ; *para*-, 43%.

The figure for the *m*-content is included in the table given above. For the reasons given on p. 2453, Holmes and Ingold's estimate of the *m*-content is certainly too high.

(3), (8), (9), (10), and (11). Qualitative separations recorded either by Holmes and Ingold or by ourselves confirm these results, and also show that in the case of the acyl derivatives substitution occurs mainly in the *p*-position. In the case of the secondary base, as with the primary base, the chief by-product is a *p*-derivative, and an *o*-compound is also produced. The qualitative examination of another secondary base is described on p. 2461.

(4), (5), (6), and (7). The four tertiary bases yielded closely similar results. Benzyldiethylamine has been nitrated by Noelting and Kregczy (*Bull. Soc. chim.*, 1916, **19**, 335) and by Flürscheim and Holmes (this vol., p. 1567), who obtained values varying from 34 to 54% of *m*-isomeride according to the conditions. Most of these experiments, however, refer to nitration in sulphuric acid. Holmes and Ingold examined the nitration product of dibenzylmethylamine and isolated only the *pp'*-dinitro-isomeride in the crystalline condition, but the results now described show that considerable quantities of the *mp'*- or *mm'*-dinitro-compound (probably both) must have been present.

Directive Action of the Ions, the Undissociated Salts, and the Bases.

When an amine is dissolved in water, or in acid solvents, such as concentrated nitric and sulphuric acids, which are good ionising media but poor electrolytes, the following equilibria obtain,

$$\underset{(ion)}{R_3NH^+} + X^- \rightleftharpoons \underset{(salt)}{R_3NHX} \rightleftharpoons \underset{(base)}{R_3N} + HX,$$

and any effects which are observed (*e.g.*, nuclear substitution) will be the sum of the effects on the three forms implicated. To determine the behaviour of the three forms is the object of experiments such as those described herein, but for this purpose some assistance from theory is required.

The results recorded in Parts IV, V, VI, and VII of this series (this vol., pp. 1305, 1310, 1328, 1684) were interpreted in the light of a hypothesis of electronic strain, the main suppositions underlying which (so far as concerns the case under discussion) may be summarised as follows: (i) Electronic strain, originating in a substituting atom, may be transmitted from carbon atom to carbon atom by two *unidirectional* * processes (*A*) and (*B*),

$$\begin{array}{l} \ \overset{\rightarrow}{}\ \overset{\rightarrow}{}\ \overset{\rightarrow}{}\ \overset{\rightarrow}{}\ \ .\ .\ .\ .\ .\ .\ .\ (A) \\ \mathrm{C—C—C—C—C} \\ \ \ \ \rightarrow\ \ \ \ \ \ \rightarrow\ \ .\ \ \ .\ .\ .\ .\ .\ (B) \end{array}$$

(*A*) predominating in saturated chains and (*B*) in chains of unsaturated carbon atoms owing to the assumed looser binding of the valency electrons in the double linking. (ii) The *direction* of the effect is prescribed by the principle of resistance to disturbance of the octets, and its *magnitude* by the assumed octet-stability of the substituting atom as deduced from its position in the periodic classification (*e.g.*, proximity to the inert-gas group); naturally the disturbance will diminish with distance from the substituting atom.

In applying these views to the nuclear substitution of bases in acid media, it is necessary to form a picture of the molecular condition of the base. Moore and Winmill have shown (J., 1912, **101**, 1635) that the ammonium hydroxides corresponding with primary, secondary, and tertiary amines exist largely undissociated in aqueous solution, in equilibrium, on the one hand, with varying amounts of the amines and water (which is in large excess), and,

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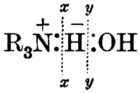
* Alternating strain, or displacement $\underset{+}{\mathrm{C}}\overset{\rightarrow}{—}\underset{-}{\mathrm{C}}\overset{\leftarrow}{—}\underset{+}{\mathrm{C}}\overset{\rightarrow}{—}\underset{-}{\mathrm{C}}\overset{\leftarrow}{—}\underset{+}{\mathrm{C}}$ such as is required by the theory of alternate polarities as usually applied, is regarded as disproved by the comparison of benzylamines and benzyl ethers referred to above, and by the sequences N>O>F and S>O established for *op*-directive power in Parts V, VI, and VII. Also, the nitroamine hypothesis by the aid of which Flürscheim's theory was applied to the nitration of benzylamine derivatives is definitely abandoned by the present authors for reasons shown in this and the following paper.

on the other, with somewhat small proportions of the ammonium and hydroxide ions :

$$NR_3 + H_2O \underset{x}{\rightleftharpoons} NR_3H{\cdot}OH\ ^* \underset{y}{\rightleftharpoons} NR_3H^+ + OH^-.$$

Partly in order to account for the presence of these large quantities of undissociated hydroxides, and partly to explain the enormous increase of strength which occurs in passing from primary, secondary, or tertiary bases (all of which are weak electrolytes) to quaternary bases, which resemble the hydroxides of the alkali metals, Moore advanced the suggestion (*ibid.*, p. 1673) that in the undissociated primary, secondary, and tertiary hydroxides the hydroxyl group is attached through hydrogen (*Y*). An electronic interpretation of this, based on the theory of co-ordinated hydrogen, would be represented by (*Z*), where the dotted lines *xx* and *yy* indicate the two possible ways in which dissociation can occur to enable the negative hydrogen atom—it has a half-share in four electrons—to recover its neutrality. These two modes of dissociation correspond with the reactions (*x*) and (*y*) in the above equation. Obviously structures (*Y*) and (*Z*) are not applicable to quaternary compounds, which, as strong electrolytes, would be expected to be fully ionised, free dissociation being limited only by the electrostatic attraction of the ions.

(*Y*) $R_3N{-}H{-}OH$



$$R_3\overset{+}{N}{:}\overset{-}{H}{:}OH$$

(*Z*)

Now there seems to be no structural reason why this hypothesis concerning ammonium hydroxides dissolved in water should not be applied to the salts dissolved in the corresponding non-aqueous media—the nitrates in nitric acid, the hydrogen sulphates in sulphuric acid, etc. Nitric and sulphuric acids are both feebly conducting, but highly dissociating solvents. The conductivity of quaternary ammonium salts is of a similar order to that of the hydroxides (Noyes, *J. Amer. Chem. Soc.*, 1925, **47**, 3025). In non-aqueous solvents, the dissociation of neutral salts is evidently considerably less than in corresponding aqueous solutions (Kraus, " Properties of Electrolytically Conducting Systems," 1922), and Walden and Centnerszwer's measurements (*Z. physikal. Chem.*, 1902, **39**, 528) indicate the same " jump " in conductivity in passing from salts of primary, secondary, and tertiary bases to salts of quaternary bases, as is observed in aqueous solution in the case of the bases

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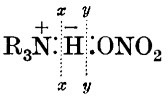
* If any non-ionising amine-hydrate (NR_3,H_2O) were present, this would be included in the proportions given by Moore and Winmill for NR_3, and would not be confused with the potentially ionising, but actually undissociated, ammonium hydroxide, $NR_3H{\cdot}OH$.

themselves. We therefore adopt the view that in nitric acid solutions of primary, secondary, and tertiary amines the entity (*C*) is present, largely undissociated, but also to some extent dissociated in the two ways represented.* In the case of the quaternary salts, however, we have condition (*D*), in which ionisation is complete, and the separation of the free ions is limited only by electrostriction.

(*C*) 

$$R_3\overset{+}{N}\underset{x}{\overset{x}{\vdots}}\overset{-}{H}\underset{y}{\overset{y}{\vdots}}ONO_2$$

$[R_4N]^+ONO_2^-$ (*D*)

It is now possible to determine the behaviour of the three entities present, or potentially present, under the conditions of the nitration of a benzylamine derivative.

(i) *The Ion.*—According to the hypothesis summarised at the commencement of this section the benzylammonium ion (*E*) should substitute largely in the *m*-position,† a conclusion identical with that already advanced by Robinson (*Chem. and Ind.*, 1925, **44**, 1563) and by Flürscheim and Holmes (*loc. cit.*) on rather different grounds. To precisely what *extent* *m*-substitution should occur it is impossible to foretell on a purely theoretical basis, but it does follow that the proportion of *m*-substitution in a perfectly free ion would be greater than is observed for a quaternary salt at finite dilution. Combining this theoretical inference with the results of experiment (p. 2441), we may say that the free benzylammonium ion should be *almost wholly* m-*substituting.*

(ii) *The Salt.*—For similar reasons the undissociated benzylammonium salts must be *largely* m-*substituting*, although less completely so than the ions; for the effect of the dipole ($\beta\gamma$) on the electrons of the carbon atom (α) in (*F*) must be qualitatively similar to, although somewhat smaller than, the corresponding effect of the free positive charge in (*E*).‡ This conclusion does not accord with that derived by Flürscheim (*Chem. and Ind.*, 1926, **45**, 220) and Robinson (*ibid.*, p. 219) from their respective views, but it appears to be consistent with the experimental data,§ and is strongly

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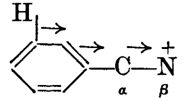
[*] It has to be remembered that the dissociated portions may never be entirely out of reach of one another's influence. An undissociated salt of type (*D*) should show diminished but still substantial *m*-substitution.

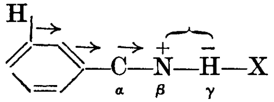
[†] In confirmation, it has been found that trimethyl-β-phenylethylammonium picrate gives only about 20% of *m*-derivative on nitration in nitric acid.

[‡] Thus, if the atomic distances were equal and the charges acted as though concentrated at the centres of the atoms, the attraction of the dipole on the electrons of Cα would be 75% of that of the free positive charge.

[§] Flürscheim and Holmes (*loc. cit.*) have provided evidence that *m*-nitration of benzylamine derivatives is diminished by depressing the ionic dissociation, but it does not seem to us to follow from their work that the true salt would substitute wholly *op*-.

supported by analogy with the type $C_6H_5·CR_2·NO_2$, the discussion of which is, however, deferred to the following paper.

(*E*)




(*F*)

(iii) *The Base.*—Since, according to the hypothesis summarised, any *m*-substitution in the types $C_6H_5·CH_2X$, $C_6H_5·CHX_2$, etc., where X is a *neutral* atom, must be caused by electronic restraint, originating in the firm binding of the electrons in X and transmitted as in (*E*), it follows that the effect must be greatest for fluorine (most stable octet) and least for nitrogen (least stable octet) in the series $F > Cl > O > N$ (compare *Chem. and Ind.*, 1926, **45**, 357). Combining Hove's work on the nitration of benzal fluoride (*Bull. Acad. roy. Belg.*, 1913, **3**, 1082), Swartz's on benzotrifluoride (*ibid.*, 1920, **6**, 389), Holleman's on benzyl-, benzal-, and benzotri-chlorides (*Rec. trav. chim.*, 1914, **33**, 1), Staedel's (*Annalen*, 1883, **217**, 177) and Holmes and Ingold's (*loc. cit.*) on benzyl ethers, and Dr. J. W. Baker's (private communication) on benzal acetals, we obtain the following data :

Nitration of	F	>	Cl	>	O	>	N	
$C_6H_5·CH_2X$	—		4		0*		—	% *meta*
$C_6H_5·CHX_2$	65*		35		0*		—	,,
$C_6H_5·CX_3$	99		64		—		—	,,

* Approximate values.

This verifies the theoretical sequence for F, Cl, and O, and also indicates that free benzylamines, and indeed all completely uncharged benzylamine derivatives, must be *almost wholly op-substituting.*

The interpretation of the experimental results on the basis of these generalisations requires little elaboration. The quaternary salt (1) illustrates most closely the directive action of the ion, and the primary, secondary, and tertiary compounds (2—7) that of the undissociated salts. Two views are possible as to the reason for the variation (44—76%) of the *m*-content in these latter cases; either, the lower figure is nearest that proper to the salt,* in which case increases must be ascribed to dissociation at *yy* (formula *C*); or, the upper figure represents most nearly the effect of the salt, diminutions being attributed to dissociation at *xx*. Actually we incline to the former view, since on this assumption the results agree

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* That is, the primary salt; the proportions of *m*-substitution appropriate to the secondary and tertiary undissociated salts should be less, owing to electron repulsion by the alkyl groups.

with anticipation based on Moore and Winmill's data for the "real" ionisation constants of primary, secondary, and tertiary aliphatic bases, steric and electrical effects being superposed. In the cases of the acyl derivatives (7—10), dissociation at *xx* also becomes important, however, and this leads to low values for the monoacyl and still lower ones for diacyl derivatives.*

In conclusion, it should be remarked that, in applying the above views to our experiments, we have not lost sight of the fact that Flürscheim's theory, as recently extended by Flürscheim and Holmes (*loc. cit.*), and Robinson's theory are also applicable, although on rather a different basis (ion : *m*- ; salt : *op*-). We propose, however, to defer the discussion of these views to a later paper in which further evidence will be brought to bear on the fundamental question as to whether the undissociated salt exclusively directs *op*-.

Should further investigation confirm the interpretation given, it would be applicable along obvious lines to bases of other types (*e.g.*, aniline and β-phenylethylamine derivatives) and would lead to new interpretations of the anomalies observed in the substitution of bases generally.

At the time of writing, Ing and Robinson's full results on the nitration of benzylamine derivatives are not available, but in a preliminary publication (*Chem. and Ind.*, 1926, **45**, 10) Holmes and Ingold's results were criticised on the grounds that the primary and secondary bases give appreciable quantities of *p*-nitro-derivatives on nitration at 100°, that *mm'*-dinitrodibenzylmethylamine is contained in the nitration product of dibenzylmethylamine, and *p*-nitrodiacetylbenzylamine in that of diacetylbenzylamine. Although the last-mentioned compound is probably not nitrated as such under the conditions employed (see p. 2461), it may at once be agreed that these criticisms are justified inasmuch as the present quantitative investigation accords more closely with the general conclusions of Ing and Robinson than with those of Holmes and Ingold in each of these three particulars (compare pp. 2442, 2456 and 2457).

EXPERIMENTAL.

General.—The ratio of *m*- to *op*-substitution obtaining in the mononitration of the eleven benzylamine derivatives mentioned below was determined by means of Francis and Hill's quantitative bromination process (*loc. cit.*) modified in details. In two of the cases, *viz.*, benzylamine and triethylbenzylammonium hydroxide, the results thus obtained are closely confirmed by the actual separ-

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* It is assumed that the nitrogen atom does not acquire a sufficiently strong or permanent charge by betaine isomerisation (Ingold and Ingold, this vol., p. 1311) for any considerable *m*-substitution to arise from this cause.

ation of the isomerides, and in the last-mentioned instance a combination of separation and analysis by the bromination method was employed in order to obtain the final value. The separations are described in the individual cases, but the following remarks regarding the bromination process apply generally.

The modifications introduced into Francis and Hill's method are based partly on those advocated by Kolthoff and Robinson (*Rec. trav. chim.*, 1926, **45**, 169), and partly on our own experience. Potassium bromide–bromate solution and sodium thiosulphate solution were made exactly $N/10$ by standardisation against freshly-distilled aniline. Titanous chloride, prepared in accordance with Francis and Hill's directions, was standardised daily against the other two solutions under the conditions employed in the estimation itself. For the estimation, a quantity (B grams) was dissolved in 25 c.c. of 96% alcohol in a flask fitted with a tube leading to the bottom for the introduction of carbon dioxide, and with a short tube into which the nozzle of the burettes could be inserted; 25 c.c. of 50% sulphuric acid were added, and the mixture heated to boiling whilst a rapid stream of air-free carbon dioxide was passed through. The passage of gas was continued whilst a known volume of standard titanous chloride, containing not less than 0·007 equiv., was run in through the short tube out of contact with air, after which the solution was boiled for 5 minutes and then cooled to 0°. Sufficient ice was then added to maintain the temperature at —4° throughout the remainder of the estimation, and standard bromate solution was run in until a blue colour was given immediately by starch–iodide solution used externally.* The current of carbon dioxide which had been continued up to this stage was then stopped, and a further 3 c.c. of bromate were added (total D c.c.). After a further 5 minutes, during which the reaction proceeded to completion, 0·5 c.c. of saturated potassium iodide solution and 1 c.c. of concentrated starch solution were introduced, and the mixture was made up to 500 c.c. with water and quickly titrated with thiosulphate (E c.c.). The end-point usually consists of a change from blue to yellow or brown, the exact shade depending on the particular derivative under examination. If A represents the number of equivs. of titanous chloride used, and C the molecular weight divided by the number of nitro-groups in the molecule, then F, the bromination number, is given by $F = 3 - C\{A - 0{\cdot}0001\ (D - E)\}/2B$. In the simplest case, the proportion of *m*-isomeride in the mixture examined can be directly calculated from this, but the procedure we employed was a more complex one for the following reasons: Francis and Hill

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* After sufficient experience this test can be dispensed with, the changing tint of the solution being an adequate guide.

discuss the various sources of error which may affect the results in certain cases, and mention particularly (*a*) oxidation with destruction of the molecule, (*b*) the precipitation of incompletely brominated products, and (*c*) the replacement by bromine of the directing group. Error (*b*) is overcome by the use of sufficient alcohol, and (*a*) and (*c*) by working at a low temperature, and for each compound there is a temperature below which these disturbances do not enter. In most of the cases which we have investigated, error (*b*) is unimportant under the conditions indicated in the above description, but (*c*) is concerned in varying degrees in the different cases, and in some of them (*a*) appears to enter also. These disturbances are certainly minimised, as Francis and Hill state, by the use of low temperatures, but as the temperatures below which they became inconsiderable were often inconvenient or inaccessible, we have adopted the expedient of working at a uniform temperature, *viz.*, $-4°$, which is as low as is consistent with rapid working, under strictly standard conditions, and then deducing the proportion of *m*-isomeride from the bromination number by means of an empirically found relationship between these two quantities, this relationship being determined for each of the cases thus dealt with, by carrying out similar estimations with the pure isomerides and with artificial mixtures of them. The following examples will illustrate the procedure : 0·1538 G. of *mm'*-dinitrodibenzylamine, for which $C = 143{\cdot}6$, was reduced with 0·00790 equiv. of titanous chloride; the excess of titanous chloride was removed and the bromination effected by the addition of 84·0 c.c. of $N/10$-bromate–bromide solution; the excess of bromine then required 4·8 c.c. of $N/10$-thiosulphate; hence, $F = 3{\cdot}0093$. From this, by calculation according to Francis and Hill's equations, the *m*-content is 100·9%. Duplicate determinations gave 100·0, 99·1, and 100·0%. In the various isomeric dinitrodibenzylamines, the disturbances (*a*) and (*b*) mentioned above are inappreciable under the conditions used, and this example also illustrates the fact that disturbance (*c*) cannot affect *m*-compounds. It does, however, affect the *p*-compounds in this series to the extent of about 8% on the value of F for the *pp'*-dinitro-compound. To illustrate the method of using the empirical relation in such cases, the following example may be given: A mixture containing 53·6% of *mm'*-dinitrodibenzylamine and 46·4% of the *pp'*-isomeride was reduced and brominated, the value $F = 2{\cdot}593$ being obtained. Direct calculation of the *m*-content from this would involve an error of 6%. However, by interpolation from the values of F for the two constituents it is found that $F = 2{\cdot}593$ corresponds with a *m*-content of 53%, an error of 0·6% only. It should be added that, since the empirical relation between F and the *m*-content has been determined mainly by means of the *m*- and *p*-isomerides, there is a tacit assumption, in applying this relation to products of nitration, that any *o*-compound present will behave like the *p*-compound. Such experiments as we have done on the estimation of *o*-nitrobenzylamine derivatives (see pp. 2456 and 2460) show that this is the case, and in any event all the more complete separations of nitration products of benzylamine derivatives which have hitherto been effected agree in showing that the amount of *o*-substitution is always small. For these reasons, we believe that no serious error is introduced in connexion with the above assumption regarding the behaviour of *o*-compounds.

The nitration products may be used for these estimations in the form of either the free nitro-bases, or their hydrochlorides or acetyl derivatives, but the use of nitrates or picrates leads to undesirable complications owing to the action of the titanous chloride on the anion. Nitrates were therefore first converted into acetyl derivatives by boiling with acetic anhydride and sodium acetate as described below; and picrates were weighed as such and dissolved in hydrochloric acid, the picric acid being quantitatively extracted by shaking with benzene and the hydrochloric acid solution being taken for the estimation.

(1) *Nitration of Benzyltriethylammonium Picrate.*

Benzyltriethylammonium Picrate.—Benzyltriethylammonium iodide was prepared by the action of ethyl iodide on diethylbenzylamine (Meyer, *Ber.*, 1877, **10**, 310), and converted into the *picrate*, which crystallised from water as yellow prisms, m. p. 124° (Found : C, 54·1; H, 5·8. $C_{19}H_{24}O_7N_4$ requires C, 54·3; H, 5·7%).

m-*Nitrobenzyltriethylammonium Picrate.*—*m*-Nitrobenzyldiethylamine was prepared by the action of diethylamine on *m*-nitrobenzyl chloride (compare Noelting and Kregczy, *Bull. Soc. chim.*, 1916, **19**, 335) and converted into the quaternary iodide, following the method used by Meyer (*loc. cit.*) in the case of the parent substance. The *picrate*, precipitated as in the previous instance, and crystallised from water, formed yellow prisms, m. p. 149° (Found : C, 48·9; H, 4·8. $C_{19}H_{23}O_9N_5$ requires C, 49·0; H, 5·0%).

p-*Nitrobenzyltriethylammonium Picrate.*—This was prepared from *p*-nitrobenzyl chloride *via* *p*-nitrobenzyldiethylamine and the quaternary iodide exactly as in the previous case. It forms yellow prisms, m. p. 155° (Found : C, 48·8; H, 4·9. $C_{19}H_{23}O_9N_5$ requires C, 49·0; H, 5·0%).

Proportion of m-*Substitution.* (a) *By Estimation.*—Benzyltriethylammonium picrate was added in small portions to 7·5 times its weight of nitric acid (*d* 1·5) kept at — 5°. After an hour, by which time atmospheric temperature had been attained, ice was added equivalent to 1·5 vols. of water. Gaseous ammonia was then passed in (the temperature meanwhile rising to 70—80°) until the solution was alkaline. The precipitate, which was collected from the cooled solution, consisted of the pure *m*-isomeride; it had m. p. 150° and did not depress the m. p. of the synthesised specimen. The yield was 64·0%. The filtrate from this was evaporated to dryness and extracted repeatedly with hot acetone in which ammonium nitrate is scarcely soluble. The residue from the acetone was then crystallised once from water to remove any trace of ammonium salts if present. The yield was 28·8%, thus leaving 7·2% to be accounted for either as material put out of action by oxidation or as nitro-compounds which could not be separated from the inorganic salts. The 28·8% was obviously a mixture of isomerides. It had m. p. 125—130°, which was raised by admixture with either the *m*- or *p*-compound, and gave correct figures on analysis (Found : C, 48·9; H, 5·2%). It was converted into chloride by means of benzene and hydrochloric acid, and the chloride reduced and brominated as previously described, the value $F = 2{\cdot}609$ being obtained. Pure *p*-nitrobenzyltriethylammonium picrate, similarly treated, gave $F = 2{\cdot}149$, and the pure *m*-nitro-compound $F = 3{\cdot}011$. The rectilinear character of the line connecting F with the *m*-content of mixtures was confirmed by the analysis of mixtures of the *m*- and *p*-isomerides. A mixture containing 32·1% of *m*-compound gave $F = 2{\cdot}402$, and one containing 73·3% gave $F = 2{\cdot}803$. From this it follows that $F = 2{\cdot}609$ corresponds with a *m*-content of 54·5%. This means that $64{\cdot}0 + 28{\cdot}8 \times 0{\cdot}545 = 79{\cdot}7\%$ of the whole or 86% of the mononitro-compounds isolated (92·8%) is the *m*-derivative. If it be assumed that the composition of the material unisolated is the same as that of the second fraction, the total *m*-content would be 84%; hence we may accept *85*% as an approximation to the true value.

(b) *By Separation.*—Benzyltriethylammonium picrate (10 g.) was added in small quantities to 25 c.c. of 95% nitric acid at 20°. The addition occupied 0·5 hour and the solution was kept for a further hour at the same temperature. Crushed ice (50 g.) was then added, and gaseous ammonia passed into the solution through a fine capillary tube. The temperature rose to 70°, and when the alkaline solution had cooled, the precipitate (10·0 g; 91%) was collected. This had m. p. 140—142°, which was raised by addition of the *m*-compound, and therefore consisted mainly, but not wholly, of this isomeride. One crystallisation from water raised the m. p. to 146°, and a second to 148°; further crystallisations effected no appreciable change. Admixture with the synthesised *m*-compound then caused no depression of m. p., and admixture with the *p*-isomeride caused a large depression. The specimen, m. p. 148°, may therefore be regarded as practically pure *m*-nitro-compound. The yield was 8·70 g. (79% of theory) which agrees closely with the value obtained in (a), *viz.*, 85%.

(2) *Nitration of Benzylamine.*

(a) *Estimation.*—Several experiments were carried out conforming as closely as possible to the following conditions : The base was run through a capillary tube into ten times its weight of nitric acid (*d* 1·5), contained in a vessel cooled by ice, at just such a rate that no brown fumes were evolved. After 2 hours, the mixture was allowed to warm to the room temperature during another 2 hours, and then mixed with ice. After a further 2 hours the precipitated salt was collected, and the filtrate evaporated to dryness at the ordinary temperature in a high vacuum. The nitrobenzylammonium nitrates thus obtained, m. p. 160—190°, were converted into acetyl derivatives by boiling them with acetic anhydride (40 parts) and sodium acetate (1 part) for 15 minutes; the products were warmed with water to destroy acetic anhydride, basified with potassium hydroxide, and extracted with chloroform. The yields were uniformly 94—95%, the remaining 5—6% probably representing material destroyed or converted into benzoic acid by oxidation. Desiccation for several days in a good vacuum was necessary to remove the last traces of chloroform. The product was quite solid, but always melted over a long range (about 60—100°) [Found : (nitrates) (i) C, 39·0; H, 4·3; (ii) C, 38·9; H, 4·6; (iii) C, 39·6; H, 4·2; (acetyl derivatives) (iv) C, 54·6; H, 5·3; (v) C, 55·5; H, 5·4; (vi) C, 55·1; H, 5·0. Calc. : C, 39·2; H, 4·3 and C, 55·6; H, 5·1%, respectively]. For the establishment of the relation between the bromination number and the *m*-content of mixtures of the isomeric nitro-acetyl derivatives, the three isomeric nitrobenzylamines were prepared and converted into the acetyl derivatives in the way described. The m. p.'s of the *o*-, *m*-, and *p*-hydrochlorides were 248°, *225*°, and *256*° (decomp.); those of the nitrates 174°, *187*°, and *214*° (decomp.); and those of the acetyl derivatives 99°, *107*°, and *133*°, respectively, the italicised numbers being in correction of the m. p.'s recorded by Amsel and Hofmann (*Ber.*, 1886, **19**, 1286), Gabriel and Henders (*Ber.*, 1887, **20**, 2869), Hafner (*Ber.*, 1890, **23**, 330), and Holmes and Ingold (*loc. cit.*). Aceto-*p*-nitrobenzylamide gave $F = 2{\cdot}674$, and mixtures with the *m*-nitro-isomeride containing 40·0, 47·6, and 53·2% of *m*-compound gave $F = 2{\cdot}930$, 2·973, and 3·032, respectively, the relationship between these being linear. The following values of F were obtained from the nitration products :

(i) 2·958; (ii) 2·951; (iii) 2·932; (iv) 2·936; (v) 2·982; and (vi) 2·889. These correspond with the following meta-contents: (i) 44%, (ii) 43%, (iii) 40%, (iv) 41%, (v) 48%, (vi) 34%, respectively. Omitting (vi), the mean is 43%, and the maximum individual variation is 5%. The investigation described below shows that about the same amount of *p*-compound is simultaneously formed, and that the *o*-isomeride is also present.

(b) *Separation.*—The nitrates of *m*- and *p*-nitrobenzylamine tend to crystallise together, and both pure substances and mixtures melt with decomposition. Satisfactory separation by means of this salt, such as was attempted by Holmes and Ingold, cannot be effected, and the fractions they obtained were certainly not pure isomerides. A moderately satisfactory separation can, however, be carried out by the combined use of the picrates and dichromates, the facts utilised being (*a*) that the *m*- and *p*-picrates, which are highly characteristic substances, show little tendency to crystallise together, (*b*) that the *p*-compound is less soluble in water than the *m*-compound, and (*c*) that the *p*-dichromate is more soluble in water than the *m*-dichromate. *Experiment* (*A*). Benzylamine was nitrated under conditions conforming as closely as possible to those specified above; 70·5% of the material isolated (total yield 93·6%) was obtained as precipitated salt (α), and 29·5% as residue (β). These were examined separately. Fraction (α) was crystallised from 25 parts of hot water and the crystallised portion dissolved in water and treated with aqueous sodium picrate, 30·3% of nearly pure *p*-nitrobenzylammonium picrate being obtained, m. p. 191°. This salt on admixture with genuine *p*-salt (m. p. 194°) melted at 192—193°, and on admixture with the *m*-isomeride (m. p. 197°) melted at about 175°. The filtrate from the first crystallisation was also mixed with sodium picrate, and gave 11·7% of quite pure *m*-nitrobenzylammonium picrate, m. p. 197°. Its identity was similarly confirmed by mixed m. p. determinations with genuine specimens of the corresponding *m*- and *p*-picrates. The mother-liquors from both these crystallisations of picrate were combined, strongly acidified with sulphuric acid and extracted with benzene to remove picric acid. After neutralisation with potassium hydroxide, the solution was evaporated and alcohol added to precipitate the bulk of the potassium sulphate. After filtering, the alcohol was removed by evaporation, and to the well-cooled aqueous solution a concentrated solution of potassium dichromate was added. The base isolated from the crystallised *m*-dichromate was dissolved in dilute nitric acid and the neutralised solution treated with aqueous sodium picrate, 9·2% of the pure picrate of the *m*-nitro-compound, m. p. 197°, being obtained. (The reason for thus converting the *m*-dichromate into picrate is that the dichromates decompose on heating, and it is therefore difficult to establish their identity.) Fraction (β) was dissolved in water and treated with sodium picrate; the precipitated picrate had m. p. 193—195°, and consisted of the nearly pure *m*-salt (5·1%). The material in the filtrate was converted into dichromate and the dichromate reconverted into picrate; 6·0% of *m*-picrate, m. p. 195—196°, was obtained. The total quantities thus isolated were: *meta*- 32·0%, *para*- 30·3%. The mother-liquors from these crystallisations almost certainly contained further quantities of each of these isomerides together with the ortho-compound, but the presence of the last rendered separation difficult.

Experiment (*B*). In this separation the picrates were employed whenever possible in order to obtain the most complete isolation of para-isomeride, since there is, at present, no other means of estimating accurately the proportion of this substance. Nitration under the conditions described above led to the isolation of 94·4% of the theoretical quantity of nitrobenzylamine nitrate, which was obtained as two fractions, (α) and (β), constituting respectively 70·6% and 29·4% of the total. Fraction (α) was then crystallised from water as before, and the solid and mother-liquors separately converted into picrate. This was crystallised in a series of fractions, which were regulated by changing the solvent according to the substance tending to separate; when the *m*-compound (stout prisms) was being deposited in greater quantity than the *p*-isomeride (long, slender needles), the deposition of the latter could be largely prevented by adding methyl alcohol, whilst when the *p*-compound tended to separate it could be obtained quite free from the *m*-isomeride by boiling off the methyl alcohol and crystallising from water, in which the *p*-salt is only slightly soluble. The following table indicates the progress of the separation:

Fraction α (70·6%).

Filtrate.	Crystallised material.
(1) *meta*-, m. p. 195—196°, 9·6%.	(4) *para*-, m. p. 192—193°, 21·2%.
(2) *meta*-, m. p. 197°, 3·1%.	(5) *para*-, m. p. 192°, 6·9%.
(3) *para*-, m. p. 192°, 5·1%.	(6) *para*-, m. p. 192°, 1·6%.

Mother-liquors now combined :

(7) *para*-, m. p. 190—191°, 3·0%. (8) *meta*-, m. p. 195°, 4·3%.
(9) *para*-, m. p. 191°, 1·8%.

At this stage the separation was rendered difficult by the presence of the ortho-picrate, and the residues were therefore converted into dichromates and back again into picrates as in experiment (*A*):

(10) *para*-, m. p. 190°, 2·5% (from dissolved dichromates).

Fraction (β) was dissolved in water and converted into picrates, the fractions of which were as follows :

(11) *meta*, m. p. 195°, 1·5%. (12) *meta-*, m. p. 193°, 2·1%.
(13) *meta-*, m. p. 193°, 1·5%.
(14) *meta-*, m. p. 196°, 4·8% (from precipitated dichromates).
(15) *meta-*, m. p. 195°, 1·2% (from precipitated dichromates).

The remaining dichromate fractions on reconversion to picrates gave mixtures which could not be satisfactorily separated. Combined yields : *meta-* 28%, *para-* 42% (total 70%). The following experiment shows that practically the whole of the *p*-isomeride had been separated by this treatment. For use in identifying the above fractions m-*nitrobenzylammonium picrate*, stout prisms, m. p. 197° (Found : C, 40·9, H, 2·9. $C_{13}H_{11}O_9N_5$ requires C, 40·9; H, 2·9%), and p-*nitrobenzylammonium picrate*, slender needles, m. p. 194° (Found : C, 41·1; H, 3·0%), were prepared from the corresponding nitrobenzyl chlorides.

(c) *Oxidation of Unseparated Portion.*—The unseparated portion in the above experiment was converted into free bases and oxidised by adding slightly more than the theoretical quantity of 5% potassium permanganate solution to its boiling suspension in 600 parts of water, the addition being timed to keep pace with decolorisation. After 20 hours' boiling the oxides of manganese were filtered off, and treated with steam in the usual way, and the combined filtrates evaporated, acidified and extracted three times with ether. By drying with sodium sulphate and evaporating, a mixture of nitrobenzoic acids (free from benzoic acid) was obtained as a dry, almost white powder, m. p. 105—110° (Found : C, 50·2; H, 2·9. Calc. : C, 50·3; H, 3·0%) (yield 67%). This was completely soluble in 60 parts of cold chloroform, thereby showing that it could not contain as much as 6% of *p*-nitrobenzoic acid. The barium salt was then prepared and crystallised twice from 35 times its weight of water, and the acid regenerated. In this way, *m*-nitrobenzoic acid, m. p. 136—139°, was obtained, the mixed m. p. with a genuine specimen being 139—140°. The yield was 54% of the original mixed acids; correcting for the solubility of the barium salt in the water used, the proportion of meta- in the mixture becomes 69%. The filtrate from the first crystallisation of the *m*-salt was worked up for acids by means of ether. The acids isolated amounted to 37% of the mixture and contained, by calculation, 8% meta-, 0—6% para-, and 29—23% ortho-. The m. p. was 119—128° and, on admixture with *o*-nitrobenzoic acid, 139—144°; after crystallisation from 20 parts of chloroform 19% of almost pure *o*-nitrobenzoic acid, m. p. 142—145° (mixed m. p. 145—147°), was isolated. Correcting for the solubility of *o*-nitrobenzoic acid in chloroform, 27% of the original mixture is accounted for as *o*-nitrobenzoic acid. An experiment with a mixture of the *m*- and *p*-compounds having indicated that the oxidation is not seriously selective, the following estimate of the proportions of the isomerides may be given :

	Ortho-.	Meta-.	Para-.
By separation	0%	28%	42%
Oxidation of residues	8	21	1
	—	—	—
Total	8	49	43

The nitration of benzylamine was also carried out at 100° as described by Holmes and Ingold (*loc. cit.*), and since the product contained some impurity which rendered the bromination process inapplicable and also interfered with the picrate separation, the whole product was oxidised to a mixture of acids, which did not, however, consist wholly of mononitrobenzoic acids, but which gave 16% of moderately pure *p*-nitrobenzoic acid on separation. Almost all the remaining material gave a sparingly soluble barium salt from which, however, impure *m*-nitrobenzoic acid, m. p. 115—120°, was recovered.

(3) *Nitration of Dibenzylamine.*

Several nitrations were carried out, adhering as closely as possible to the conditions specified in the nitration of benzylamine (p. 2452). The total yields of nitrates were always close to 97% and the product melted at 205—210° (decomp.). The nitrates were converted into the free bases by extraction with chloroform in the presence of potassium hydroxide, and the *m*-content of the bases was determined by the bromination method [Found : (bases) (i) C, 58·2; H, 4·4; (ii) C, 58·1; H, 4·4; (nitrates) (iii) C, 47·8; H 4·1; (iv) C, 48·6; H, 3·8; (v) C, 48·2; H, 3·7. Calc. : C, 58·7; H, 4·2% and C, 48·2; H, 3·7%, respectively].

To establish the relation between the bromination number and the *m*-content of mixtures, *mm'*-dinitrodibenzylamine (m. p. 83°), and *pp'*-dinitrodibenzylamine (m. p. 93°) and mixtures of these containing 53·6% and 66·3% of the former were submitted to analysis in the manner described above; the following results were obtained for the four cases in the order named : $F = 3{\cdot}000$, 2·153, 2·593, 2·727. This establishes a straight line relation. An approximate determination made with a rather small quantity of *oo'*-dinitrodibenzylamine gave $F = 2{\cdot}110$, in fair agreement with the value for the *pp'*-compound.

Analysis of the nitration products yielded the following values of F : (i) 2·797; (ii) 2·785; (iii) 2·884; (iv) 2·794; (v) 2·682; which correspond respectively with the following *mm'*-contents : (i) 76%; (ii) 75%; (iii) 87%; (iv) 76%; (v) 68%. The mean of all these is

76%, and the mean of the three closely-agreeing results (i), (ii), and (iv) is the same. The maximal variation (experiment iii) amounts to 11%.

The base was also nitrated at 100° and the product oxidised; 16% of nearly pure *p*-nitrobenzoic acid (m. p. 230—234°) and 41% of nearly pure *m*-acid (m. p. 125—131°) were isolated (18% unseparated).

(4) *Nitration of Tribenzylamine.*

Tribenzylamine hydrochloride was prepared by Matter's method (D.R.-P., 1917, 301450, compare Friedländer, 1916—1921, **13**, 247), and the free base liberated and crystallised from methyl alcohol (m. p. 92·5°).

pp′*p*″-Trinitrotribenzylamine was prepared by a modification of Strakosch's method (*Ber.*, 1873, **6**, 1056). *p*-Nitrobenzyl chloride (10 g.) and ammonia (30 c.c.; *d* 0·880) were heated in a closed tube for 4 hours at 100°, and the resulting brown paste boiled with 10% hydrochloric acid. The suspension thus obtained was extracted with benzene without filtering, and the crystals formed on concentrating the benzene solution were crystallised from ethyl acetate. The nitro-base had m. p. 168° (Found: C, 59·4; H, 4·3. Calc.: C, 59·7; H, 4·3%).

mm′m″-*Trinitrotribenzylamine* was prepared similarly from *m*-nitrobenzyl chloride, the contents of the tube being extracted with methyl alcohol, in which the required base is insoluble. It separated from ethyl acetate in colourless needles, m. p. 163° (Found: C, 59·9; H, 4·4. $C_{21}H_{18}O_6N_4$ requires C, 59·7; H, 4·3%).

Tribenzylamine has been nitrated by Marquardt (*Ber.*, 1886, **19**, 1030) but the products were not definitely identified. The base was nitrated as in the preceding cases, but instead of being worked up for nitrates the mixture was basified and extracted with chloroform. The product was thus obtained as a stiff gum, and the removal of the last traces of chloroform necessitated heating at 100° at a pressure below 1 mm. [Found: (i) C, 59·9; H, 4·0; (ii) C, 59·7; H, 4·4%].

Bromination of the synthetic *p*- and *m*-nitro-compounds gave $F = 2{\cdot}120$ and 2·638 respectively, and a mixture containing 58·2% of the *m*-isomeride gave $F = 2{\cdot}403$, indicating the linear relation.

Nitration product (i), yield 74%, gave $F = 2{\cdot}433$, which corresponds with 60% *m*-substitution. Product (ii), yield 100%, gave $F = 2{\cdot}394$, which is equivalent to *53*% *m*-substitution. The latter result is regarded as the more trustworthy.

(5) *Nitration of Dibenzylmethylamine.*

Benzyl chloride (20 g.), ethyl alcohol (200 c.c.) and 33% aqueous methylamine (40 c.c.) were mixed and kept for 1 hour at the ordinary temperature, and then heated to 60° in a closed vessel to complete the reaction. The alcohol was evaporated, sodium hydroxide added, and the mixed bases extracted with ether and distilled. A first fraction, b. p. about 60°/1 mm., consisting essentially of benzylmethylamine was obtained, the bulk of the dibenzylmethylamine distilling at 143°/1 mm.

The base was allowed to flow into 10 parts of nitric acid (*d* 1·5) at 0° as described in case (2), the basic nitration product, which was only partly solid, being isolated as in case (4). Prolonged exposure in a mercury-pump vacuum was necessary to eliminate the last traces of chloroform [Found : (i) C, 60·6; H, 4·9; (ii) C, 59·8; H, 5·4. Calc. : C, 60·0; H, 5·0%].

For the determination of the relation between *m*-content and the bromination number, *mm'*-dinitrodibenzylmethylamine, *pp'*-dinitrodibenzylmethylamine, and mixtures of these containing 40·3% and 72·1% of the *mm'*-isomeride were employed, the corresponding values of F being 2·334, 3·022, 2·566, and 2·832, respectively. The relationship is linear. The nitration products gave (i) $F = 2{\cdot}697$, (ii) $F = 2{\cdot}776$, which correspond with meta-contents (i) 52%, (ii) 64%. Mean: *58%*.

(6) *Nitration of Benzyldimethylamine.*

This base was prepared as described by Sommelet and Guioth (*Compt. rend.*, 1922, **174**, 687), and was nitrated exactly as in the preceding instance, the product, which was an oil, being isolated with the aid of chloroform as described above. The yield was 89—90% of the theoretical, and it is possible that the bases evaporate slightly during the removal of the chloroform [Found : (i) C, 60·7; H, 6·4; (ii) C, 60·7; H, 6·5; (iii) C, 60·2; H, 6·3. Calc.: C, 60·0; H, 6·7%].

m-*Nitrobenzyldimethylamine.*—Hexamethylenetetramine (15 g.) was dissolved in the smallest possible quantity of boiling alcohol, and a hot alcoholic solution of *m*-nitrobenzyl chloride added. The quaternary salt which separated on cooling was collected, dissolved in the minimal quantity of hot water and heated with 100 c.c. of absolute formic acid for 16 hours on the steam-bath. The evolution of carbon dioxide having ceased, the solution was made alkaline and extracted with ether, and the base remaining after removal of the ether purified by distillation. It was thus obtained as a clear, pale yellow oil, b. p. about 195°/18 mm. (Found: C, 59·8; H, 6·6. $C_9H_{12}O_2N_2$ requires C, 60·0; H, 6·7%).

p-Nitrobenzyldimethylamine has previously been prepared by Friedländer and Mosczyc (*Ber.*, 1895, **28**, 1141) who, however, record neither the b. p. nor any analytical data. We prepared it from *p*-nitrobenzyl chloride by the method used for the *m*-isomeride, and obtained a yellow oil, b. p. 146—148°/18 mm. (Found : C, 60·3 H, 6·7. Calc. : C, 60·0 ; H, 6·7%). The large difference of b. p. between these *m*- and *p*-nitro-compounds is very remarkable, and somewhat similar disparities were observed by Noelting and Kregczy (*loc. cit.*) in the b. p.'s of the homologous *o*-, *m*-, and *p*-nitrobenzyldiethylamines.

To determine the relationship between *m*-content and the bromination number, the above *p*- and *m*-nitro-bases, and artificial mixtures of them containing 55·9% and 57·6% of the *m*-derivative, were analysed under the usual conditions. The results obtained were $F = 2{\cdot}169$, 3·186, 2·717, and 2·750, respectively, which established the linear relation.

Bromination of the nitration products of benzyldimethylamine gave $F =$ (i) 2·752 ; (ii) 2·741 ; (iii) 2·776, which correspond with the following proportions of the *m*-isomeride : (i) 58% ; (ii) 57% ; (iii) 60%. Mean : *58*%.

(7) *Nitration of Benzyldiethylamine.*

This base has been nitrated by Noelting and Kregczy (*loc. cit.* and by Flürscheim and Holmes (*loc. cit.*) who obtained for the proportion of *m*-isomeride values ranging from 34—54% according to the conditions. Under the conditions employed for the other tertiary bases, we obtained a nitration product (Found : C, 63·1 ; H, 7·6. Calc. : C, 63·4 ; H, 7·7%) which gave $F = 2{\cdot}749$ on bromination. The synthesised *p*- and *m*-derivatives gave $F = 2{\cdot}110$ and 3·046, respectively, and mixtures containing 69·8, 51·4 and 32·7% of the *m*-isomeride gave $F = 2{\cdot}933$, 2·694, and 2·549, respectively, from which it follows that the nitration product contained *51*% of *m*-isomeride.

(8) *Nitration of Acetobenzylamide.*

Acetobenzylamide, prepared by Amsel and Hofmann's method (*loc. cit.*), had b. p. 150°/1 mm. and m. p. 133° (A. and H. give m. p. 125°). It was nitrated and the product isolated with the aid of chloroform as described in case (4). After removal of the chloroform in a vacuum, the residue solidified, but the solid softened and melted indefinitely between about 50° and 100°. Two experiments were performed [Found : (i) C, 55·4 ; H, 4·8 ; (ii) C, 55·2 ; H, 5·0. Calc. : C, 55·6 ; H, 5·1%]. On bromination these gave respectively $F = 2{\cdot}711$ and 2·729. From the known relation between F and the *m*-content (case 2), these values correspond with (i) 6%, (ii) 8% of meta-isomeride. The mean of these is *7*% *meta-*. The main constituent is para- (Holmes and Ingold, *loc. cit.*).

(9) *Nitration of Acetobenzylmethylamide.*

This amide was prepared as described by Holmes and Ingold (*loc. cit.*); it had b. p. 143°/1 mm. Nitration was effected as in the preceding case, and the product, m. p. 45—65°, isolated by means of chloroform in the same way (Found: C, 57·7; H, 5·8. Calc.: C, 57·7; H, 5·8%). Bromination by the usual method gave $F = 2{\cdot}707$.

Aceto-*m*- and *p*-nitrobenzylmethylamides were prepared as described by Holmes and Ingold (*loc. cit.*). The m. p. of the *p*-compound was raised to 83° (previously recorded, 81°). Bromination of the *p*-compound and of mixtures of this with the *m*-isomeride containing 49·1% and 54·1% of the latter gave $F = 2{\cdot}653$, 2·962, and 2·994, respectively; the value of F obtained for the nitration product therefore corresponds with *8% meta-*. The main constituent is para- (*loc. cit.*).

(10) *Nitration of Acetodibenzylamide.*

Dibenzylamine hydrochloride was boiled with acetic anhydride and sodium acetate, and after treatment with water and an excess of sodium hydroxide, the amide was isolated by extraction with ether and distilled, b. p. 194—195°/3 mm. Nitration was effected as in the preceding case and the product, m. p. 135—155°, isolated as usual [Found: (i) C, 58·6; H, 4·6; (ii) C, 58·3; H, 4·3. Calc.: C, 58·4; H, 4·5%].

Aceto-*oo'*-, *mm'*-, and *pp'*-dinitrodibenzylamides were prepared as described by Holmes and Ingold. The m. p. of the *p*-compound was raised to 185° (previously recorded, 183—184°). On bromination, the *oo'*-compound gave $F = 2{\cdot}227$, the *mm'*-compound $F = 2{\cdot}850$, and the *pp'*-compound $F = 2{\cdot}252$; a mixture of the *mm'*- and *pp'*-isomerides containing 61·5% of the former gave $F = 2{\cdot}614$.

The nitration products on bromination gave the following numbers: (i) $F = 2{\cdot}386$; (ii) $F = 2{\cdot}407$, which correspond respectively with 23% and 26% of *m*-compound. The mean may be taken as *25% meta-*. The main nitration product is para-, and ortho- is also formed.

(11) *Nitration of Succinbenzylimide.*

Succinbenzylimide was prepared as described by Werner (J., 1889, **55**, 629), who recorded m. p. 98—99°. Our product, after careful purification for the nitration experiment, had m. p. 103°. Succin-*p*-nitrobenzylimide was similarly prepared by the method of Hoogewerff and van Dorp (*Rec. trav. chim.*, 1899, **18**, 362), who gave m. p. 150—152°; our specimen melted at 153°.

The nitration of succinbenzylimide was carried out just as in the preceding case except that during the addition of the imide to the nitric acid, and afterwards until ice was added, the temperature of the acid was maintained at or near − 12°. The precipitated nitration product had m. p. about 120°, and amounted to 78% of the theoretical quantity. A further 8% of neutral material, m. p. 110—115°, was obtained by extraction with ether, so that about 14% was hydrolysed or oxidised under the conditions used. The combined fractions were crystallised once from alcohol, and the product from the mother-liquors again crystallised from the same solvent; in this way 64% of the total was obtained as the practically pure *p*-isomeride, m. p. 151—152° (unaltered by admixture with the synthetic specimen). The remaining 36% had m. p. about 90° (Found: C, 55·6; H, 4·0. Calc.: C, 56·4; H, 4·3%), and was analysed by the bromination method. The bromination number was 2·332, whereas that of the pure *p*-isomeride was 2·313, which represents 3% of the *m*-isomeride. Since this applied to only 36% of the total, the corresponding value for the whole product is *1% meta-*. The above separation shows that the main product is para-.

Diacetylbenzylamine.—Various attempts were made to nitrate this substance, using the methods employed in the previous cases and those of Holmes and Ingold, but the results were erratic, varying mixtures of the *m*- and *p*-compounds being obtained. Also the analytical data were unsatisfactory, and it was ascertained that acetic acid is formed in the reaction, evidently by the destruction of the acylamino-grouping. It was therefore decided to change the reagent. A solution of the benzylamine (5 g.) in acetic anhydride (20 g.) was allowed to flow into a solution of nitric acid (1·8 g.; *d* 1·5) in acetic anhydride (8 g.) at − 14°. The mixture was kept below − 10° for 1 hour, and then evaporated in the cold in a good vacuum over potassium hydroxide (Found: C, 57·5; H, 4·8; N, 11·0. Calc.: C, 55·9; H, 5·1; N, 11·9%). These numbers indicate the presence of considerable amounts of impurity, but an approximate analysis by the bromination method showed the *m*-content to be small, and hydrolysis to the nitrobenzylamines indicated the main constituent to be the *p*-isomeride.

Benzylmethylamine.—The application of the bromination method to the nitration product of this substance was found to be affected by disturbances (probably elimination of the side chain) which rendered it impracticable, and the nitration product (conditions as for benzylamine) was therefore oxidised as described on p. 2455. The nitrobenzoic acids contained no benzoic acid (yield 78%) (Found: C, 50·0; H, 3·2%), and on separation by first washing with chloroform and then crystallising the barium salts of the soluble acids, gave 21% of *p*-nitrobenzoic acid (m. p. 234°) and 61% of *m*-nitrobenzoic acid (m. p. 131—138°), 18% being unseparated; from the solubilities it is estimated that this portion contained 8% of *m*-acid and 4% of *p*-acid. Nitration at 100° followed by similar treatment gave acids, not consisting wholly of mononitrobenzoic acids, which yielded 9% of nearly pure *p*-nitrobenzoic acid on separation by the use of chloroform.

Dibenzyldimethylammonium Picrate.—Dibenzylamine hydrochloride (15 g.) was added to a mixture of methyl iodide (30 g.), alcohol (10 c.c.) and dilute sodium hydroxide (20 c.c.). After keeping for 1 hour, the mixture was heated for 15 minutes on the steam-bath and poured into water. The iodide was collected (m. p. 193°) and converted into picrate, which was recrystallised from water; yellow prisms, m. p. 146° (Found: C, 57·9; H, 4·9. $C_{22}H_{23}O_7N_4$ requires C, 58·2; H, 4·8%).

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