CCXVI.—*The Orienting Influence of Free and Bound Ionic Charges on Attached Simple or Conjugated Unsaturated Systems. Part I. The Nitration of Some Derivatives of Benzylamine.*

By Harry Raymond Ing and Robert Robinson.

From the results obtained in the investigation of the directive powers of alkyloxy-groups in aromatic substitution (Allan, Oxford, Robinson, and Smith, this vol., p. 401), the hypothesis was developed that a general polar effect, *e.g.*, that associated with an ionic charge, can control the direction of polarisation of conjugated systems and consequently the orientation of entering substituents. On an electronic theoretical basis, it was shown that a group (A) which tends to repel electrons (*e.g.*, a negatively-charged ionic centre), when attached to an aromatic nucleus must assist the

entry of substituents * in the *op*-positions. Conversely, a group (B) which strongly attracts electrons (*e.g.*, a positively charged ionic centre) should lead to penultimate substitution which, in the benzene series, is *m*-substitution. Moreover, a group (C) which in some phases attracts electrons and in other phases repels them should favour *op*-substitution. Examples of the (B) effect are to be noted in the β-substitution of pyridinium salts and the well-known cases of *m*-substitution in salts of aniline derivatives, including phenyltrimethylammonium bromide, and in diazonium salts. The possibility obviously existed that the kationic charges of the various benzylammonium † ions might be near enough to the nucleus to exercise a similar influence and produce predominating *m*-substitution ‡ in the benzyl group.

Examples of the *m*-orienting effect of the benzylammonium salt grouping which have been previously recorded are the *m*-nitration of benzyldiethylammonium nitrate (Noelting and Kregezy, *Bull. Soc. chim.*, 1916, **19**, 335) and of phenylbenzylethylammonium sulphate (or nitrate) in the benzyl group (Schultz and Bosch, *Ber.*, 1902, **35**, 1292). The results of the latter authors have been confirmed, whilst those of Noelting and Kregezy are indirectly confirmed by our experiments on the nitration of benzylpiperidine. Holmes and Ingold (J., 1925, **127**, 1800) studied the nitration of benzylamine and of numerous derivatives of benzylamine and reached the following conclusions :

(1) Benzylamine salts nitrate mainly in the *op*-positions.

(2) Benzylamine derivatives containing a tervalent nitrogen

* We imply here substituents of the ordinary type having positive polarity (NO_2, N_2R, COR, Br from Br_2, etc.). For the entry of anions or anionoid complexes many of the statements in the text should be inverted.

† We are engaged in studying the nitration of β-phenylethyltrimethylammonium nitrate and of γ-phenylpropyltrimethylammonium nitrate in order to determine the influence of the length of the chain separating the nucleus and the nitrogen atom. Even in the former case, the substitution occurs chiefly in the para-position.

‡ In the course of the discussion at the Society's Meeting in May of 1925 on the paper of Holmes and Ingold the theory considered to be applicable to the nitration of benzylamines was clearly stated by the undersigned (compare *Chem. and Ind.*, 1925, **44**. 563). Subsequently, the probability that the observed *m*-nitration should be characteristic of the benzylammonium salts was reaffirmed (*ibid.*, p. 639), in spite of statements by Professor Ingold that the facts were opposed to these predictions. In a further letter to the editor of *Chemistry and Industry* (*ibid.*, p. 639), the assumption was made that the case of Holmes and Ingold, respecting the interpretation of their experiments, could be substantiated and, with this proviso twice clearly stated, the consequences were considered. This has been misconstrued by Dr. Flürscheim (*Chem. and Ind.*, 1926, **45**, 43) as an expression of the writer's own *a priori* views.—R. R.

atom and in which the formation of a salt is precluded nitrate mainly in the *m*-position.

(3) When primary or secondary benzylamines yield in fuming nitric acid a high proportion of the *m*-derivatives, the explanation is that the nitroamine, *e.g.*, $CH_2Ph{\cdot}NH{\cdot}NO_2$, is formed in the first place.*

These theories are, however, supported by very little direct experimental evidence and there is nothing in the work of Holmes and Ingold which is inconsistent with alternative views except the following. It is stated that diacetylbenzylamine is nitrated in the *m*-position and no by-products could be detected, whilst dibenzylmethylamine, the only tertiary base (excluding benzylamides) examined, yielded *p*- and *o*-nitro-derivatives and no *m*- by-product could be isolated.

The latter observation is definitely opposed to our view that the benzylamine salts exhibit a tendency to *m*-substitution. We have now found that diacetylbenzylamine is largely nitrated in the *p*-position, to some extent in the *o*-position, and possibly to some extent in the *m*-position. This has been shown by a method of degradation and not by isolation of the initially formed products. The case is an unsuitable one for detailed study by the latter method and we therefore directed our attention to the nitration of phthalbenzylimide. Here again, *p*- and *o*-derivatives were produced, but it was difficult to obtain the former in a state of purity. We are able to show that dibenzylmethylamine affords on nitration *mm'*-dinitrodibenzylmethylamine, but once again the case is an unsuitable one.

We have, accordingly, nitrated benzylpiperidine and isolated *m*-nitrobenzylpiperidine in about 50% yield. The chief by-product is the *p*-nitro-derivative. There can therefore be no doubt that

* It is not quite clear how the nitroamine is supposed to promote the *m*-substitution. The work of Bamberger (*Ber.*, 1895, **28**, 399) on phenylnitroamine is quoted by Holmes and Ingold as providing an analogy, but a study of Bamberger's papers has left us with the impression that this author contemplated the *migration* of the nitroxyl group to the *o*- and *p*-positions and not the further *nitration* of the nitroamine. If Holmes and Ingold consider that the nitro-group in the benzylnitroamines *migrates* to the *m*-position under the influence of mineral acid, their view, however inherently improbable, can logically be sustained as analogous to that of Bamberger; it could, however, be very readily tested by direct experiment. If, on the other hand, the view of Holmes and Ingold is that the benzylnitroamines are *nitrated* to *m*-nitrobenzylnitroamines, then it should be noted that there is no analogy with the case of phenylnitroamine and, moreover, it becomes necessary to assume the almost complete formation of a nitroamine as a preliminary to substitution and the complete hydrolysis of the nitroamine after substitution has occurred.

tertiary benzylamines exhibit a marked tendency towards *m*-nitration, and the nitroamine hypothesis becomes superfluous.

The question of the yield of *m*-nitrobenzylamine and of the *m*-nitro-derivatives of secondary benzylamines obtained in the nitration of the respective bases in the cold and at 100° must now be considered. According to Holmes and Ingold (*loc. cit.*, p. 1806, line 4), the yield of *m*-compound from benzylamine is about 80% at −10° and about 100% at 100°. We cannot confirm either of these statements and it is evident that the material regarded by Holmes and Ingold as pure *m*-nitrobenzylammonium nitrate contained a preponderating amount of *p*-nitrobenzylammonium nitrate. In the circumstances, no significance can be attached to the figures quoted by Holmes and Ingold in this case and we also find that the yield of *mm'*-dinitrodibenzylamine claimed by these authors is much too high. In the absence of an accurate method of analysis,* we are not prepared to submit precise statements at this stage, but our preliminary work has given us the impression that the tendency to *m*-substitution rises in the series benzylamine, dibenzylamine, benzylpiperidine. Really predominant *m*-substitution occurs when benzyltrimethylammonium nitrate is nitrated by means of cold fuming nitric acid. Unquestionably, therefore, it is the benzylammonium salts which undergo substitution in the *m*-position and the hypothesis regarding the orienting effect of the charge of the ionic centre in the side chain is amply confirmed.† In accordance with modern theory, we regard strong electrolytes as completely dissociated into ions; strictly speaking, our hypothesis only applies when the kationic charge exerts a field in the direction of the nucleus. It is early to discuss the various factors which may influence the distribution of this field, and it would obviously be necessary to consider such abstruse topics as the possibility of the existence of free base in concentrated nitric acid solution; the influence of surrounding atoms, perhaps in co-ordinating with the ammonium hydrogen; and even the possibility of the existence of undissociated salts or of a condition of the kation, produced by encounters with anions, which would correspond to that assumed to exist in the undissociated salt.

That bound as well as free ions can exert an orienting influence on the nucleus is clear from the case of phenylnitromethane, which

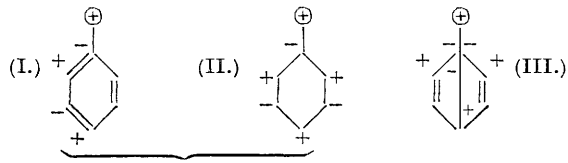
* We are now studying the composition of the products of the nitration of benzylpyridinium perchlorate by a method of reduction and bromination under standard conditions.

† The work of Vorländer and others has shown that a positively charged atom *directly* attached to the nucleus is *m*-derivative, and the novel feature of our hypothesis is the postulation of similar *m*-direction by a positively charged atom which is not directly attached to the ring.

was shown by Holleman (*Rec. trav. chim.*, 1895, **14**, 123) to nitrate in the *m*-position. Here it may be supposed that the semi-polar bond between oxygen and nitrogen confers on the nitrogen true kationic character * and the real, positive charge produces a field in the direction of the nucleus. When the nitro-group is directly attached to the nucleus, the effect is naturally enhanced but, in addition, the oxygen atom not concerned with the semi-polar bond renders possible the formation of a crotonoid conjugated system. The latter tends to promote *m*-substitution by inhibiting *op*-substitution to a relatively greater extent. It is proposed to study the behaviour of *m*-phenylene- and *m*-xylylene-bistrimethylammonium salts towards substituting agents in order to gain further information regarding the mechanism of the effect of a charged centre on the nucleus, since in these cases the various theoretical possibilities do not lead to quite the same predictions. In the absence of more precise information it will be sufficient at this stage to summarise the mechanisms which appear to provide an explanation of the effect.

(1) The penultimate substitution hypothesis to which reference has already been made.

(2) Electrostatic induction along the lines of Thomson's suggestions (*Phil. Mag.*, 1923, **46**, 497). This view may be applied to the Kekulé formula (I) or to the Dewar formula (III). (II) is an extreme form of (I) and is formulated in agreement with Lowry's view of the condition of a polarised benzene nucleus.



op-*Inhibition* and m-*activation*. op-*Inhibition*.

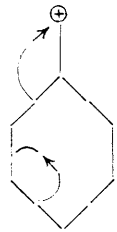
(3) Electrons may be drawn from the aromatic nucleus into the ammonium system. It appears that this is only possible if the ammonium ionic centre can accommodate an additional electron, possibly as a planetary electron analogous to that contained in

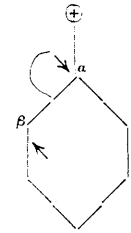
* An effect similar to that of the nitroxyl group in $CH_2Ph{\cdot}NO_2$ was anticipated in the case of the group $CH_2Ph{\cdot}N{\cdot}CO$ and especially in $CH_2Ph{\cdot}N(COMe)_2$. The neutralised system (compare Allan, Oxford, Robinson, and Smith, *loc. cit.*), $\overset{\curvearrowright}{N}$———$\overset{\curvearrowright}{C}$———O, with positively charged nitrogen is evidently not so fully polarised as the nitroxyl group and the above-mentioned substances containing it are in category (C) rather than in category (B) (compare p. 1656).

$NR_4\}e$ or in a neutral sodium atom. The figure (IV) illustrates the resulting changes.

(4) The attraction exerted by the kationic charge on the electrons in the aromatic nucleus may be so powerful that C_α—C_β covalency electrons are to some extent appropriated by C_α and break away from C_β. The resulting changes are illustrated in (V) and involve *m*-substitution by *op*-inhibition.

(IV.)





(V.)

This possibility was suggested to us by Professor Lapworth and it appeals to us as a satisfactory alternative to (I). There are intermediate possibilities combining these hypotheses in various ways. A curious feature of the substitutions in aniline and benzylamine salts is that the products are chiefly *m*- and *p*-derivatives. The combination of *o*- and *m*-derivatives is observed in many other cases, a striking example being the nitration of acetophenone. When we understand why the yield of *o*-nitroacetophenone in this process is relatively high, it is probable that the formation of the *p*-by-products in the substitutions of aniline and benzylamine salts will acquire theoretical significance. Finally, it should be pointed out that all the theories of the mechanism of the effect agree in recognising the fundamental hypothesis of polar activation * and once again it appears that a series of experiments, which were thought to provide evidence showing that polarity theories break down in their applications to organic chemistry, have in the sequel convincingly vindicated a basic assumption common to all these hypotheses.

EXPERIMENTAL.

In this section we do not claim that in any case we have *repeated* the work of Holmes and Ingold in exact detail.

Nitration of Benzylamine.—Benzylamine (20 g.) was added during 40 minutes to nitric acid (100 c.c., *d* 1·5) cooled to −10° and mechanically stirred. After 1·5 hours, the mixture was added to ice and water, and the salt collected, washed with water (total

* A conception which includes that of polar inhibition and does not imply any view of the degree of polarisation preceding reaction. We imagine that the degree of activation of the aromatic nucleus is in most cases very small.

filtrate, 500 c.c.), and dried in a vacuum (yield, 31·4 g. or 78%). The salt had m. p. about 200° (decomp.) with previous softening. The product was further examined as follows: (1) The salt (10 g.) was decomposed with sodium nitrite and dilute sulphuric acid on the steam-bath; the neutral or acid oil (A), isolated by means of chloroform, was then oxidised with potassium permanganate in alkaline solution. After separation through the barium salts, *m*-nitrobenzoic acid (0·35 g.) and *p*-nitrobenzoic acid (4·6 g.) were obtained. (The oxidation processes we have employed favour the detection of the *p*-isomerides. Professor Pyman has kindly informed us that in the oxidation of *o*-, *m*-, and *p*-nitrophenylglyoxalines by hot permanganate solution, the yields of the nitrobenzoic acids obtained were of the order 10%, 60%, and 90%, respectively.) (2) The oil (A) was again prepared (from 10 g.) and boiled for 2 hours with 40% nitric acid. On cooling, a mixture of *p*-nitrobenzaldehyde (1·5 g.) and *p*-nitrobenzoic acid (1·4 g.) separated and the constituents were isolated and identified. On dilution of the filtrate to 500 c.c., *m*-nitrobenzaldehyde (0·35 g.) crystallised, whilst the material extracted from the mother-liquor by chloroform gave, on oxidation with potassium permanganate, *m*-nitrobenzoic acid (0·7 g.) and *p*-nitrobenzoic acid (0·2 g.). (3) The salt (9·5 g.) was crystallised from water (70 c.c.) and 8·5 g., m. p. 200—203°, were obtained. This product was recrystallised from water (70 c.c.) and 4·6 g., m. p. 214°, were obtained. The method of preparation and the properties of the product thus obtained correspond with those of the material which Holmes and Ingold (*loc. cit.*) identified as *m*-nitrobenzylammonium nitrate. On oxidation with 40% nitric acid of the nitrobenzyl alcohols prepared from this specimen in the usual way, we obtained, however, *p*-nitrobenzaldehyde (1·6 g.) and *p*-nitrobenzoic acid (0·5 g.), but no *m*-nitro-derivatives. On standing, the mother-liquors from the above crystallisations deposited 1·5 g. of a salt, m. p. 180—185°, and this, together with the mother-liquors, was treated with sodium nitrite. The recovered crude nitrobenzyl alcohols were oxidised with 40% nitric acid and *m*-nitrobenzaldehyde (1·5 g.), but no *p*-nitrobenzaldehyde, was obtained.

Nitration of Benzylammonium Nitrate.—Benzylammonium nitrate (11 g.) was nitrated at −15° with nitric acid (*d* 1·5) and, after the addition of ice, the nitrobenzylammonium nitrates (10 g.) were collected. These were crystallised from water (90 c.c.), and 7 g., m. p. 210°, separated. Recrystallisation from 50 c.c. of water gave 5·0 g., m. p. 216° (decomp.). This material was converted into free base, which was acetylated with acetic anhydride. The diluted reaction mixture was heated and 2·8 g., m. p. 133° without further

purification, crystallised from the filtered solution. The m. p. was not lowered by admixture with a genuine specimen of aceto-*p*-nitrobenzylamide, m. p. 133° (Amsel and Hofmann, *Ber.*, 1886, **19**, 1286).

Summarising our results, it appears that crystallisation of the crude product gives the *p*-isomeride, not the *m*-isomeride as stated by Holmes and Ingold, and that consequently the experiments here described constitute the first clear indication that the *m*-nitro-derivative is produced in the reaction.

Nitration of Benzylamine at 100°.—Benzylamine (10 g.) was added to nitric acid (75 c.c., *d* 1·5), initially at 95°, so that the temperature was maintained between 95° and 105°. Ten minutes afterwards, water (100 c.c.), a solution of sodium nitrite (20 g.), and a few drops of cupric nitrate solution were added and the mixture was then boiled for 8 hours. *p*-Nitrobenzaldehyde (5·5 g.) was thus isolated and after oxidation of the residues with permanganate *m*- and *p*-nitrobenzoic acids were obtained and identified, but were accidentally lost before being weighed.

Nitration of Diacetylbenzylamine.—Diacetylbenzylamine (10 g.) obtained by the method of Holmes and Ingold (*loc. cit.*) was introduced drop by drop during 30—45 minutes into well-stirred nitric acid (100 g., *d* 1·5) cooled in a mixture of ice and salt. After a further hour, the product was mixed with ice, and 11·5 g. of a pale yellow oil were isolated by means of chloroform. In a similar experiment, the method of isolation suggested by Holmes and Ingold (*loc. cit.*) was used and only 5·0 g. of the oil were obtained.* Doubtless, therefore, substances other than the simple nitro-derivatives of diacetylbenzylamine are produced in the reaction. The material from the chloroform extraction was hydrolysed with boiling 25% hydrochloric acid for 9 hours, the product converted into the nitrobenzyl alcohols, and, after oxidation with boiling 40% nitric acid and permanganate oxidation of the residues, we obtained *p*-nitrobenzaldehyde (1·7 g.), *p*-nitrobenzoic acid (1·75 g.), and crude *o*-nitrobenzoic acid (0·17 g.). No evidence of the formation of *m*-nitro-derivatives was forthcoming at any stage. It is true that the isolated products were obtained in a yield which was only 40% of that theoretically possible, but we should nevertheless have difficulty in accepting the hypothesis that the *m*-nitro-compounds were present in considerable relative amount and completely eluded our observation.

Nitration of Phthalbenzylimide.—Phthalbenzylimide (Gabriel,

* Oxidation of this oil with permanganate in presence of pyridine gave *p*-nitrobenzoic acid, an unidentified acid, and a little *m*-nitrobenzoic acid (less than 0·05 g.).

Ber., 1887, **20**, 2227) was gradually added during 30 minutes to nitric acid (50 g., *d* 1·5) maintained below −15°. The red colour formed on each addition of the imide disappeared on shaking and, after 1 hour, the mixture was poured on ice, and the product collected, washed and dried (6·0 g.). Extraction with hot alcohol left a small, sparingly soluble residue which after crystallisation from acetic acid was identified as phthal-*o*-nitrobenzylimide (Gabriel, *loc. cit.*). The product soluble in hot alcohol was repeatedly crystallised from different solvents, namely, alcohol, ethyl acetate, acetic acid, and benzene, and fractions varying in m. p. from 150—154° to 162—164° were thus obtained. The m. p.'s of all these fractions were depressed by the addition of phthal-*m*-nitrobenzylimide (m. p. 165—166°; Gabriel, *loc. cit.*, p. 2869, gives m. p. 155°) and either raised or unaltered by the addition of pure phthal-*p*-nitrobenzylimide, m. p. 174°. Prolonged extraction of the nitration product (6 g.) with light petroleum in a Soxhlet apparatus afforded a rough separation, and the residue (1·5 g.), on extraction with alcohol and crystallisation from acetic acid, gave phthal-*o*-nitrobenzylimide (0·7 g.). The reunited material was boiled with a quantity of alcohol insufficient to dissolve one-half of it; the satiny, colourless crystals which separated from the cooled filtrate had m. p. 146—150°. A mixture of phthal-*o*-nitrobenzylimide and phthal-*p*-nitrobenzylimide was also boiled with alcohol in insufficient quantity to dissolve the whole of either of the constituents. The crystals which separated from the filtrate had m. p. 153—158° and resembled the mixture from the nitration in appearance and behaviour towards hot sodium hydroxide solution. A mixture of the two mixtures, m. p. 146—150° and m. p. 153—158°, had m. p. 151—153°.

The reactions of phthal-*p*- and -*m*-nitrobenzylimides towards moderately concentrated boiling aqueous sodium hydroxide differ greatly. The *p*-isomeride passes into a yellow solution which quickly becomes deep brownish-orange; a brown solid soon separates and on addition of water an almost clear orange solution is obtained. The *m*-isomeride also passes into solution, but this rapidly clouds and an oil makes its appearance without the development of intense colour.

Throughout this investigation we have studied the reactions of the various products with hot aqueous sodium hydroxide and methyl-alcoholic potassium hydroxide, but the details are not submitted in all cases. In the present instance the crude product and all the fractions gave the phthal-*p*-nitrobenzylimide type of reaction.

The crude nitration product from phthalbenzylimide was hydrolysed with acetic acid and fuming hydrochloric acid at 130—140° for 6 hours. Phthalic acid having been removed, the nitrobenzyl-

amines were converted into nitrobenzyl alcohols, and these were oxidised by boiling 40% nitric acid. In this way, only *p*-nitrobenzaldehyde and *p*-nitrobenzoic acid were obtained. The latter also resulted from a permanganate oxidation of a solution of the original nitration product in 0·5% aqueous sodium hydroxide.

The crude nitration product was also hydrolysed by means of hydrazine, in accordance with a general method which will shortly be described by Ing and Manske, and the nitrobenzylamines were then acetylated. There was no difficulty in isolating pure aceto-*p*-nitrobenzylamide, m. p. 133°, by crystallisation of the product.

Nitration of Benzylpiperidine.—Benzylpiperidine (15 g., b. p. 247—248°) was gradually added during 40 minutes to well-stirred nitric acid (80 c.c., *d* 1·5) cooled in a mixture of ice and salt. Nitric acid (20 c.c., *d* 1·5) was then used to wash the stirrer, etc., and after 15 minutes, the mixture was allowed to remain at room temperature for 1 hour and then diluted. The base set free by ammonia was extracted with ether, washed with aqueous sodium hydroxide and with water, and then removed by shaking with three successive volumes (100 c.c., 100 c.c., 50 c.c.) of 7% sulphuric acid, leaving about 0·5 g. of a neutral unidentified compound in the extract. A solution of potassium iodide (20 g.) in 100 c.c. of lukewarm water was added to the acid extract; a copious crystallisation then occurred and after 1 minute the salt was collected and dried (15 g.). 7·8 G. of a base (B) were isolated from the filtrate by means of ammonia and ether.

In another experiment, the same quantities were employed, but the mixture was allowed to remain in the ice-bath for 3 hours and then worked up as before. Only 0·07 g. of neutral product was isolated. Employing on this occasion potassium iodide (18 g.) dissolved in 200 c.c. of cold water and keeping the mixture for 3 hours, we isolated 16·5 g. of the hydriodide and 8·1 g. of the base (B). This corresponds to a total yield of 97%, whilst the hydriodide was obtained in 55% yield. The salt crystallises from water in almost colourless, roughly quadrilateral, micaceous plates, m. p. 221° (Found: I, 36·4. $C_{12}H_{17}O_2N_2I$ requires I, 36·5%).

The three nitrobenzylpiperidines were prepared by the methods of Lellmann and Pekrun (*Annalen*, 1890, **259**, 40). *o*-Nitrobenzylpiperidine is a yellow oil which dissolves in dilute sulphuric acid to a colourless solution; on addition of potassium iodide, the *hydriodide* separates in highly characteristic, *intensely yellow* crystals. *p*-Nitrobenzylpiperidine exhibits a colour reaction with hot alkaline solutions; its hydriodide is pale yellow. *m*-Nitrobenzylpiperidine hydriodide was identical in every respect with the once-crystallised salt obtained from the nitration of benzylpiperidine.

The crystallisation of the crude nitration product is effected with little loss in weight, and the absence of any considerable proportion (*e.g.*, 5—10%) of the *o*- or *p*-isomeride appears to be guaranteed by the very pale yellow colour of the salt and by its behaviour with boiling aqueous sodium hydroxide—the reaction observed was practically identical with that of the pure *m*-isomeride. This conclusion was confirmed by reducing the base from the hydriodide with tin and hydrochloric acid in the usual manner, when *m*-aminobenzylpiperidine, m. p. 112°, was obtained (*o*-aminobenzylpiperidine and *p*-aminobenzylpiperidine have m. p.'s 82° and 87°, respectively; compare Lellmann and Pekrun, *loc. cit.*).

The bases (B) consisted chiefly of *m*- and *p*-nitrobenzylpiperidine, although the presence of the *o*-isomeride in small relative amount was not excluded. The reaction with sodium hydroxide was that of *p*-nitrobenzylpiperidine, and the hydriodide was pale yellow. On oxidation with potassium permanganate at 70—90° in presence of pyridine *p*-nitrobenzoic acid was obtained.

The bases were converted into picrates and by fractional crystallisation from acetone and alcohol a sparingly soluble picrate, crystallising in deep yellow prisms, m. p. 198—200°, together with a somewhat more readily soluble picrate crystallising in large, canary-yellow prisms, m. p. 175°, was obtained. On decomposition with aqueous sodium hydroxide, the former gave *m*-nitrobenzylpiperidine, identified as its hydriodide, whilst the latter, which was difficult to purify, yielded *p*-nitrobenzylpiperidine as an oil which crystallised slowly in large, rectangular plates; after recrystallisation by almost complete evaporation of a solution in light petroleum, this substance had m. p. 34°, alone or mixed with an authentic specimen. From these results, it appears that the yield of *m*-nitrobenzylpiperidine in the nitration exceeds 60% of that theoretically possible.

Nitration of Dibenzylamine.—Dibenzylamine (14 g.) was added during 45 minutes to 80 c.c. of nitric acid (*d* 1·5), which was mechanically stirred and maintained at 0°. The mixture was then kept for 3 hours at the ordinary temperature. The salt obtained by the addition of ice was collected and oxidised with potassium permanganate in the presence of pyridine (250 c.c.) and 20% aqueous sodium hydroxide (100 c.c.) at as low a temperature as was convenient, but finally on the steam-bath. The solution was boiled for 1 hour in order to decompose amides, and *p*-nitrobenzoic acid (7·4 g.) and *m*-nitrobenzoic acid (7·5 g.) were then isolated by known methods and identified (total yield, 62·8%).

Acetylation of the nitrated bases gave a mixture of acetyl derivatives from which, by fractional crystallisation from alcohol,

pure aceto-*pp'*-dinitrodibenzylamide and pure aceto-*mm'*-dinitrodibenzylamide agreeing with the description of Holmes and Ingold (*loc. cit.*, p. 1820) were isolated and identified with genuine specimens. These substances were, however, isolated in very poor yield and the major product consisted of a more readily soluble mixture of substances which could not be separated.

The product of the nitration of dibenzylamine at 70—90° gave, on oxidation with permanganate, a 25% yield of *p*-nitrobenzoic acid. *m*-Nitrobenzoic acid also was produced, but the yield was small, doubtless owing to the fact that the oxidation was effected at 100°.

Nitration of Dibenzylmethylamine.—The amine (8·2 g.) was added during 45 minutes to stirred nitric acid (60 c.c., *d* 1·5) cooled in a freezing mixture. After 1·5 hours from the commencement, the product was kept at the ordinary temperature for 2 hours. The bases were isolated, warmed with acetic anhydride, recovered, and separated from 0·2 g. of a neutral product. The oil was boiled with 10% aqueous sodium hydroxide (350 c.c.) under reflux for 18 hours, a process which was calculated to destroy the *p*-nitro-compounds. The base was then again isolated, and on trituration with alcohol it crystallised (1·8 g.); after recrystallisation from ethyl alcohol, it was obtained in almost colourless needles which melted, alone or mixed with authentic *mm'*-dinitrodibenzylmethylamine (Holmes and Ingold, *loc. cit.*), at 83—84°. A considerable amount of base remaining in the mother-liquor could not be crystallised.

In another experiment, 10 g. of dibenzylmethylamine were nitrated, and the product was oxidised with alkaline potassium permanganate, *m*-nitrobenzoic acid (4·0 g.) and crude *p*-nitrobenzoic acid (3·0 g., mixed with a very sparingly soluble by-product which was not further investigated) being obtained.

Benzyltrimethylammonium Nitrate, $CH_2Ph{\cdot}NMe_3\}NO_3$.—A mixture of benzyl chloride (in small excess) and an absolute alcoholic solution (33 %) of trimethylamine was kept for several days, water and ether were then added and the aqueous solution was treated with potassium iodide. The crystalline benzyltrimethylammonium iodide produced was washed, dried, dissolved in water, and silver iodide exactly precipitated by means of silver nitrate. The colourless, neutral filtrate was evaporated to a small bulk; on cooling, the nitrate crystallised in glistening, hexagonal columns, m. p. 151—160°. As it was rather readily soluble, the process of separation was assisted by the addition of sodium nitrate to the filtrate. The crystals, dried for a short time in a vacuum, lost 0·4% at 120° (Found in material dried at 100°: C, 56·8; H, 7·6. $C_{10}H_{16}O_3N_2$ requires C, 56·6; H, 7·5%).

o-*Nitrobenzyltrimethylammonium Perchlorate*,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NMe_3\}ClO_4.$$

—A mixture of *o*-nitrobenzyl chloride and 33% alcoholic trimethylamine which had been kept for a week was treated with ether and the syrup which separated was washed with fresh ether and dissolved in water. The chloride was converted into nitrate by means of silver nitrate, but when the filtrate from the silver chloride was concentrated to a small bulk it did not deposit the nitrate even after saturation with sodium nitrate or addition of a few drops of nitric acid. Addition of perchloric acid caused the rapid separation of the *perchlorate*, which crystallised from very dilute perchloric acid in flat, colourless needles, m. p. 166° (Found: C, 40·6; H, 5·4. $C_{10}H_{15}O_6N_2Cl$ requires C, 40·8; H, 5·1%). On boiling with 20% aqueous sodium hydroxide, a clear yellow solution was obtained, but this soon clouded owing to the separation of an oil and the odour of *o*-nitrotoluene was observed.

m-*Nitrobenzyltrimethylammonium Nitrate*,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NMe_3\}NO_3.$$

—A careful comparison of specimens prepared by the following two methods showed them to be identical in every respect.

(A) Nitric acid was added to a solution of *m*-nitrobenzyltrimethylammonium chloride prepared in the usual way from *m*-nitrobenzyl chloride and alcoholic trimethylamine. The salt crystallised from very dilute nitric acid, in which it was very sparingly soluble, in frond-like aggregates of prisms or in hexagonal or rhombic plates or prisms according to the conditions. Crystallisation at a high temperature favoured the production of prisms, whilst the fern-like aggregates could always be obtained by slowly cooling a dilute aqueous solution to which a drop of dilute nitric acid had been added. When boiled with 20% aqueous sodium hydroxide, the salt did not dissolve and the solution remained almost colourless. After a short interval, a milkiness appeared and the solid acquired a dull brownish-crimson colour. The odour of a nitrotoluene was barely perceptible in the steam.

(B) Vacuum-dried benzyltrimethylammonium nitrate (10 g.) was added in the course of 20 minutes to 50 c.c. of nitric acid (*d* 1·5) * cooled in a mixture of ice and salt and mechanically stirred. Ten minutes after the addition, a further 10 c.c. of nitric acid (*d* 1·5) were employed to wash the stirrer (which was removed),

* Benzyltrimethylammonium nitrate was recovered unchanged from a solution in nitric acid (*d* 1·42) which had been kept for 12 hours. A portion of the solution was distilled under atmospheric pressure, and unchanged substance could be isolated from the concentrated residue. The operation of an inhibiting factor is unmistakable.

ice was added after 2·5 hours, and the precipitate collected 8 hours later (yield 10·5 g. or 86·6%; filtrate, 285 c.c.). The crude salt exhibited very feebly the reaction with sodium hydroxide characteristic of the *p*-isomeride. 4 G. were dissolved in 750 c.c. of hot water, and 10 c.c. of nitric acid (*d* 1·42) added; 3·4 g. of the salt, m. p. 251° (decomp.), crystallised on cooling and was free from the *p*-isomeride (Found: C, 46·8; H, 6·2; N, 16·4. $C_{10}H_{15}O_5N_3$ requires C, 46·7; H, 5·8; N, 16·3%). When a boiling solution of the salt (5 g.) in water (1000 c.c.) was treated with sodium carbonate and potassium permanganate, satisfactory oxidation could not be effected owing to the separation of the permanganate of the quaternary base as a deep crimson, crystalline precipitate.

p-*Nitrobenzyltrimethylammonium Nitrate*,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NMe_3\}NO_3.$$

—*p*-Nitrobenzyl bromide and trimethylamine afforded a quaternary salt which was changed to the iodide by means of potassium iodide and then to the nitrate by means of exact decomposition with silver nitrate. The clear filtrate from the silver iodide was concentrated and 2 or 3 drops of nitric acid were added, causing the crystallisation of the quaternary *nitrate*. The substance crystallises from dilute nitric acid in colourless, diamond-shaped prisms and prismatic needles, m. p. 211° (decomp.), which, air-dried, lose 2·5% at 120° in a vacuum (Found in material dried at 120°: C, 46·5; H, 5·9. $C_{10}H_{15}O_5N_3$ requires C, 46·7; H, 5·8%).

The salt is moderately readily soluble in hot water, sparingly soluble in dilute nitric acid, and readily soluble in more concentrated nitric acid. Its aqueous solutions resemble those of some other salts described in this communication in having the property of not wetting a glass surface. When boiled with 20% aqueous sodium hydroxide, this salt partially dissolves and the solution rapidly becomes milky; simultaneously the odour of *p*-nitrotoluene in the steam becomes marked. After a time a solid appears suspended in an orange liquid and on dilution a bright orange-yellow solution is obtained.

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