LXII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXX. The Nitration of Phenylbromocyanonitromethane, with Special Reference to an Alleged Example of Intramolecular meta-Rearrangement.*

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THE important part played by the nitration of phenylbromocyanonitromethane in the history of the theory of aromatic substitution led us to reinvestigate this reaction, with the result (J., 1926, 2462) that we had to controvert Flürscheim's original statement (*J. pr. Chem.*, 1902, **66**, 328) that the *p*-nitro-derivative alone is formed. Flürscheim and Holmes subsequently published (J., 1928, 453) a detailed examination of the reaction, and, whilst confirming our finding to the extent of showing that the principal product of nitration is the *m*-derivative (thus bringing this case into line with phenylnitromethane itself, and with β-phenyl-β-nitropropane and other derivatives of the form $C_6H_5 \cdot CR_2 \cdot NO_2$, all of which we had shown to yield large proportions of *m*-compound), investigated also a number of side reactions leading to products which when oxidised gave *p*-nitro- and *m*-bromo-benzoic acids. These side reactions (lateral decomposition) form the main subject of the present paper.

## (A) *Conditions of Occurrence of the Side Reactions.*

Since water, although it facilitates the ionisation $H^{\cdot}(O \cdot NO_2)'$, will oppose any tendency towards $(OH)'(NO_2)'$, nitration velocities must in general be strongly dependent on the water content of the nitric acid. It is consistent that the most important factor determining the conditions under which lateral decomposition tends to replace the normal (mainly meta) nitration of phenylbromocyanonitromethane is the concentration of the nitric acid. In order to indicate the magnitude and limits of this effect we have carried out a series of nitration experiments under identical conditions, namely, those previously employed, but with acid varying in strength from $d_4^{15°}$ 1·490 to $d_4^{15°}$ 1·517 (see E,* 2, *a*). The figures, which appear consistent with those published by Flürscheim and Holmes only in the regions where the result is relatively little dependent on the strength of the acid,† are in the first table, from

* Throughout, E refers to the experimental section.
† When phenylnitromethane is treated for 3 hours at −15° to 0° with nitric acid, *d* 1·52 (10 parts), mononitration proceeds without the formation of by-products. With acid, $d_4^{15°}$ 1·483, under conditions otherwise the same,

which Fig. 1 is plotted. The second table, which refers to nitration under other conditions (see E, 2, *b*), shows that the speed of the side reactions, unlike that of nitration, is comparatively slightly affected by the strength of the acid, at least within considerable limits; for longer contact with a weaker acid increases lateral decomposition (as measured by brominated products), but decreases direct nitration (as measured by meta-nitration) despite the increased

FIG. 1.

Density of $HNO_3 + H_2O$.
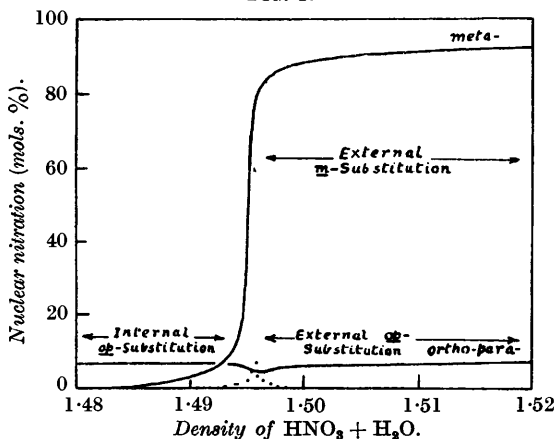
time. The *op*-nitro-derivatives arise partly by nitration and partly by side reactions.

Nitration No.	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Nitric acid, $d_4^{15°}$	1·490	1·494	1·494	1·495*	1·497	1·505	1·517
Acids by ⎧ Unni-							
KMnO₄ ⎱ trated	89·0	81·4	80·3	43·6	9·5	3·0	1·5
oxidation ⎰ *op*-Nitro-	7·5	6·5	7·0	3·7	5·7	7·0	6·2
(%). ⎩ *m*-Nitro-	3·5	12·1	12·7	52·7	84·8	90·0	92·3

nitration is not quantitative, but the proportion of *m*-derivative in the nitro-phenylnitromethanes is the same as before, namely, $66·8 \pm 1·0\%$, which figure should therefore replace the lower one given by us previously.

* This is the acid used by us formerly, the density of which was given in the uncorrected form *d* 1·49, as we were not then aware of the importance of the fourth figure. Flürscheim and Holmes, although aware of the notable influence of small density differences, stated that *m*-nitration does not occur appreciably under our conditions, but it will be seen that we have confirmed our previous estimate of the *m*-content almost exactly. Furthermore, they attribute to us a statement that the small amount of *p*-nitrobenzoic acid in the oxidation acids is not accompanied by a larger amount of benzoic acid, but we cannot find any such assertion : the only statement bearing on the point is that benzoic acid is present, and in quantity sufficient for isolation. Again, they refer to the ultimate analysis of the oxidation acids as proving the statement they attribute to us; but the conclusion is theirs, and is unjustified, if for no other reason than that the mixtures contain bromo-acids.
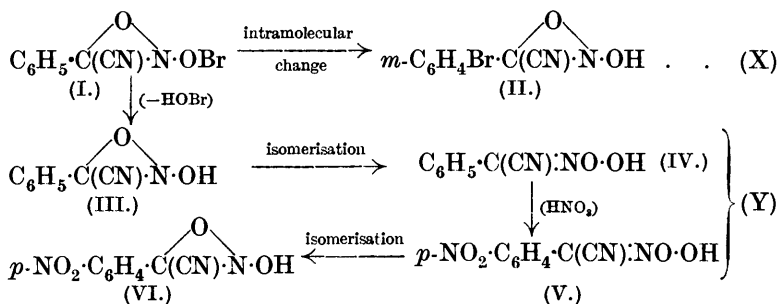
Acids by $KMnO_4$-oxidation (mols. %).

No.	HNO_3 $d_{4°}^{15°}$.	Time (days).	Unsub-stituted.	Bromo-.	op-Nitro-.	m-Nitro-.
8	1·482	10	0·0	38·1	20·1	41·8
{ 9	1·455	14	34·5	48·5	9·0	8·0
{ 10	1·455	33	4·6	59·1	22·6	13·6

The lateral decomposition takes place also in the absence of nitric acid (E, 10, 11, and 12), and the significance of this is discussed later (C, 1 and 2).

(B) *Nature of the Side Reactions. Section (i). A Criticism.*

(1) *Summary of Flürscheim and Holmes's Conclusions.*—The remarkable conclusions of these authors may be summarised by the statement that the process of lateral decomposition which leads, after oxidation, to *m*-bromobenzoic acid is an *intramolecular m*-migration of bromine, to be formulated * as at (X), whereas that which leads, after oxidation, to *p*-nitrobenzoic acid is dependent on an *extramolecular p*-nitration of the nucleus, and is to be represented as at (Y).

The following changes are stated to take place, in addition to the *m*-migration leading to (II), namely, reduction of the original substance (I), re-arrangement of the reduction product (III), nitration of the isomeride (IV) thus formed, and conversion of the nitration product (V) into its isomeride (VI) :

$$C_6H_5 \cdot C(CN) \cdot N \cdot OBr \xrightarrow[\text{change}]{\text{intramolecular}} m\text{-}C_6H_4Br \cdot C(CN) \cdot N \cdot OH \quad . \quad . \quad (X)$$
(I.) (—HOBr) (II.)

$$C_6H_5 \cdot C(CN) \cdot N \cdot OH \xrightarrow{\text{isomerisation}} C_6H_5 \cdot C(CN) \colon NO \cdot OH \quad (IV.)$$
(III.) (HNO$_3$)

$$p\text{-}NO_2 \cdot C_6H_4 \cdot C(CN) \cdot N \cdot OH \xleftarrow{\text{isomerisation}} p\text{-}NO_2 \cdot C_6H_4 \cdot C(CN) \colon NO \cdot OH \Bigg\} (Y)$$
(VI.) (V.)

Alleged changes omitted from this outline are referred to briefly under (B, 4).

(2) *Formation of* m-*Bromo-derivatives.*—Flürscheim and Holmes regard process (X) as " the first proved case of *intramolecular*

* The reproduction in this section of Flürscheim and Holmes's cyclic formulæ is for accuracy in quotation, and does not imply our acceptance of their arguments in favour of this method of formulation. For a discussion of the significance of " hypobromite reactions " in *C*- and *O*-halogen compounds, see Ingold and Shoppee, J., 1928, 382—383.

m-migration " of a substituent in a side chain.* Furthermore, taking it together with the " almost exclusive extramolecular *m*-nitration of phenylbromocyanonitromethane," they state that it " proves that the law governing direct and indirect *m*-substitution is the same—just as the same law has long been known to apply to direct and indirect substitution in the *o*- and *p*-positions." This *m*-migration from a *m*-orienting side chain is stated to agree with their " theory of affinity distribution."

We think we understand how a theory, which, for a *m*-orienting benzene derivative, $C_6H_5 \cdot R$, postulates a distribution giving an enhanced affinity-field to the *m*-position, can accommodate *m*-migration arising from the attraction by the enhanced meta-field of some loosely bound portion of R. We are, however, prepared to say that such an occurrence is scarcely possible on our theory, according to which the meta-field (electrostatic) is *permanently reduced by* R ($- I$ effect), without the possibility of relief from those momentary excitations (T effect) which may make the (normally also de-activated) *op*-positions the centres of instantaneous attracting fields extending to the side chain (compare Ingold and Shaw, J., 1927, 2918). Our view is, in short, that if any portion of R migrates internally to the nucleus it should reach the *op*-positions, never the *m*-position; that the chances of its reaching the *m*-position should be smaller the stronger the *m*-orienting power of R; and that there should be no common law applying to direct and to indirect *m*-substitution. We were accordingly disposed to question this " first proved case," despite the definite character of Flürscheim and Holmes's statements with regard to the evidence.

Three reasons are given for regarding the transference of bromine as taking place by an intramolecular process. Of these, the first two are the " observations " (*a*) that the progress of the reaction is " not affected by the addition of a substance containing a *m*-directing group," and (*b*) that the rate of migration of bromine is " independent of the concentration." Our experiments do not enable us to confirm either statement. As to (*a*), we find that the addition of a second substance containing a *m*-directing group *causes a large proportion (e.g., about 40%) of the bromine to be transferred to the* m*-position of that substance* (see E, 4).

Argument (*b*) would not in any case be cogent, because the invariance of the rate, even if established, would be capable of several explanations (as that it is determined by a pseudo-unimolecular change to a more rapidly brominated product, or that the brominating agent is volatile and that the medium becomes satur-

* The italics are theirs.

ated with it, etc.). Our experiments show (1) that the dynamics of the bromine transference are far from simple; for example, there is almost certainly a period of induction (see E, 5). Furthermore, we find (2) that factors foreign to homogeneous reaction-dynamics, such as the escape of gases from the reaction mixture, influence the accumulation of nuclear bromine (see E, 8). In the circumstances it is difficult to attach a definite numerical significance to the term " rate," and the translation of yields into rates is challengeable; nevertheless, we find (3) that the yields obtained after equal times at different concentrations are, contrary to the indications of Flürscheim and Holmes, so widely different as to show that their simple view of the dynamics of the process is far from adequate (see E, 3). The observations summarised under (1) and (2) above will be referred to again later; those summarised under (3) may be illustrated here by the following table, in which the brackets indicate groups of experiments in which all conditions were identical excepting the initial concentration of phenylbromo-cyanonitromethane (PBCN).

	(E, 3, a; 20 hours' nitration).			(E, 3, b; 240 hours' nitration).		
Nitration No.	11	12	13	14	15	16	17
Conc. PBCN, wt. %	100·0	66·7	33·3	9·1	11·1	5·9	4·0
m-Bromo-, mols. %	1·2	8·6	19·9	37·2	49·0	38·1	29·2

We have no doubt that the relationship here exhibited is part of a much more complicated connexion between the concentration and the rate of transference of bromine to the nucleus; it is obvious, nevertheless, that the rate is not *independent* of the concentration.

The remaining argument (*c*) is that the presence of the product (II) to be expected from the intramolecular rearrangement (X) has been " conclusively established." We think, however, that this statement is exaggerated. The reason for it is that, *in Flürscheim and Holmes's opinion*, *m*-bromophenylbromocyanonitromethane, which *is* present, is formed from (II) by the action of hypobromous acid, which they consider to be produced as shown at (Y), and to be present in quantities sufficient for detection in the spent nitric acid solutions. We shall show below that hypobromous acid is absent (see B, 4 and E, 5), and that there is a simpler explanation of the formation of *m*-bromophenylbromocyanonitromethane (compare C, 1).

Summarising our experiments, it appears that none of the reasons given by Flürscheim and Holmes for regarding the bromine-transference as intramolecular survives experimental re-examination; nor is there at present any proof that the initial product of such a change is formed at all.

(3) *Formation of* p-*Nitro-derivatives.*—The only direct argument advanced by Flürscheim and Holmes in support of their claim to have " quantitatively elucidated " the group of reactions (Y) is the statement that they have " conclusively established " the presence of two of the postulated compounds, namely (III) and (VI).

The presence of (III) is inferred from the presence amongst the products of a phenyl derivative which, when directly boiled with permanganate, gives *p*-nitrobenzoic acid and an excess of benzoic acid. This effect is *assumed* to be due to the decomposition of (III); but there is no other evidence that (III) is actually the substance responsible, and the same assumption might equally have been made with regard to any other hypothetical intermediate (still containing side-chain nitroxyl) possibly present during permanganate oxidation. We have, however, prepared (III) and find that it decomposes *by itself* with a considerable transference (more than 20%) of the nitro-group from the side chain to the *p*-position (see E, 13); so that even if the existence of (III) in the nitration solution were established (which is not yet the case) the fact would tell against, and not in favour of, the theory that the few units % of *p*-nitro-products formed by lateral decomposition arise from extramolecular nitration of the aromatic nucleus by nitric acid (compare C, 2).

Flürscheim and Holmes's " proof " that (VI) is present rests on their statement that *p*-nitrophenylbromocyanonitromethane is present in substantial excess of the quantity attributable to direct nitration of phenylbromocyanonitromethane, together with their opinion that this excess arises by the action of hypobromous acid (which, in reality, is absent) on (VI). Flürscheim and Holmes record, for instance, that the *op*-nitrophenylbromocyanonitromethanes formed on nitration with nitric acid $d_4^{15°}$ 1·480 amount to about 60% of the quantity of *m*-isomeride; and they attribute the excess (presumably over about the first 10%) to the action of hypobromous acid on the hypothetical intermediate (VI). We have carefully examined this matter, both by following Flürscheim and Holmes's experimental method for the estimation of the *op*- and *m*-compounds, and also by a more direct method. By both methods we find (see E, 9) that the quantity of *op*-nitrophenylbromocyanonitromethanes formed by acid of the strength given constitutes only about 10% of the nitro-derivatives possessing an unaltered side chain; and this is approximately the quantity which might be expected to arise by direct nitration of phenylbromocyanonitromethane.

We are therefore unable to agree with any of the evidence

advanced by Flürscheim and Holmes in favour of their theory of external nuclear nitration, and in the sequel we shall propose an alternative theory (C, 2 and D, 3).

(4) *Additional Details.*—The remaining reactions which Flürscheim and Holmes claim to have elucidated are contained in their paper in three somewhat elaborate schemes (*loc. cit.*, pp. 457, 458, 460), none of which requires further consideration, since each is fundamentally dependent on one or more of the points already discussed. The following matter is, however, of some importance.

Flürscheim and Holmes postulate the intervention of hypobromous acid and consider this substance to be present in the nitration solution in quantity corresponding to the production of a " very material precipitation of silver bromide "; it is stated, moreover, that the conditions of their tests were such as to indicate the practical absence of free bromine from their solutions. Contrary to both these statements, we have (*a*) been unable to convince ourselves of the presence of *any* hypobromous acid (see E, 5), and (*b*) have established the presence of a *large amount* of free bromine (see E, 6). The reliability of our negative result (*a*) is indirectly confirmed by the positive result (*b*) (compare also *c*, below) for the following reason. The equilibrium ratio $[\text{H}^{\cdot}][\text{Br}'][\text{HOBr}]/[\text{Br}_2]$ is known (Bray, *J. Amer. Chem. Soc.*, 1910, **32**, 938) to be of the order of 10^{-8}; it is also known that this equilibrium is established very rapidly. Therefore, even in a comparatively dilute acid solution, containing no *extraneous* bromide ions, the concentration of hypobromous acid could be only an almost infinitesimal fraction of that of the bromine; actually the solutions are strongly acid, which makes the fraction much smaller still. This conclusion is additionally enforced by our further observation (*c*) that a comparatively large amount of extraneous bromide ion in the form of free hydrobromic acid is present (see E, 6). This must further reduce the concentration of hypobromous acid to a minute fraction of the already infinitesimal trace which might have existed in its absence. Therefore, known thermodynamic relations, whilst they support the conclusions drawn from our tests, are at variance with those derived by Flürscheim and Holmes from theirs.

(C) *Nature of the Side Reactions. Section (ii). Constructive Suggestions.*

(1) *Formation of* m-*Bromo-derivatives.*—An observation by Flürscheim and Holmes, which we are able to confirm, is that, when phenylbromocyanonitromethane is nitrated with acid so weak that side reactions strongly predominate, *m*-bromophenylbromocyanonitromethane is the principal product having an unde-

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composed side chain. Flürscheim and Holmes's theory does not accommodate the direct formation of this major product, and they therefore postulate the following stages : (a) the original substance undergoes rearrangement, side-chain bromine passing to the nucleus ; (b) another portion of the original substance loses side-chain bromine as hypobromous acid ; (c) the hypobromous acid puts back bromine into the side chain of the rearrangement product. The inadequacy of this hypothesis will be clear from the foregoing criticism : thus (a) has been dealt with under (B, 2), (b) under (B, 3), and (c) under (B, 4). We suggest that m-*bromophenyl-bromocyanonitromethane is formed directly by nuclear attack of an external brominating agent, which either is, or depends on, free bromine.* Our reasons will now be summarised.

(i) m-Bromophenylbromocyanonitromethane is a major product (Flürscheim and Holmes ; see also E, 9) under the conditions stated above.

(ii) In the nitration solution *a brominating agent is present* which is capable of introducing bromine into the m-position of a competing m-orienting benzene derivative (see B, 2 ; also E, 4).

(iii) When phenylbromocyanonitromethane decomposes *in the absence of any added reagent*, the volatile products contain large amounts of bromine and hydrogen bromide, and also a quantity of nitrosyl bromide sufficient for liquefaction and redistillation (see E, 10). The first is a brominating agent, the second would be in the presence of concentrated nitric acid, and the third is a potential brominating agent since it is a source of nascent bromine (Trautz and Dalal, Z. anorg. Chem., 1920, **110**, 1). When these volatile products are drawn rapidly away by the use of a vacuum *there is practically no nuclear bromination* (see E, 11) ; wherefore the m-bromination is obviously far from being a simple intramolecular change ; that is, it must be an extramolecular change.

(iv) We find, contrary to Flürscheim and Holmes, that the rate of formation of m-bromo-products varies largely with the concentration of the original substance (see B, 2 ; also E, 3). Thus the external brominating agent shown by (ii) to be *present*, is by (iii) and (iv) shown to be *responsible* for the m-bromination.

(v) Bromine is present in large quantities *in the nitration solution*, since its vapour is a major constituent of the evolved gases (see E, 6).

(vi) Nitrosyl bromide and hydrobromic acid, similarly proved to be present in the solution (see E, 6), must be sources of nascent bromine. That is, *bromine*, both actually and *in statu nascendi*, is, by (v) and (vi), shown to be *present* in the nitration solutions.

(vii) The nuclear bromination occurring in nitric acid solution

is notably increased when the concentration of dissolved bromine is artificially augmented (see E, 7). Thus (Nitrations No. 31 and 32) the addition of one molecular proportion of bromine raised nuclear mono-bromination from 35·7 to 82·5%, and also gave rise to an appreciable amount of dibromination. Therefore, the bromine is evidently *capable* of effecting the nuclear bromination under the conditions obtaining.

(viii) The nuclear bromination occurring in nitric acid solution is notably decreased when the concentration of volatile substances is artificially decreased by aiding their escape (see E, 8). Thus the effect of aspiration with air, previously purified and saturated at the temperature of the experiment with the vapour of nitric

FIG. 2.

Time (hours).
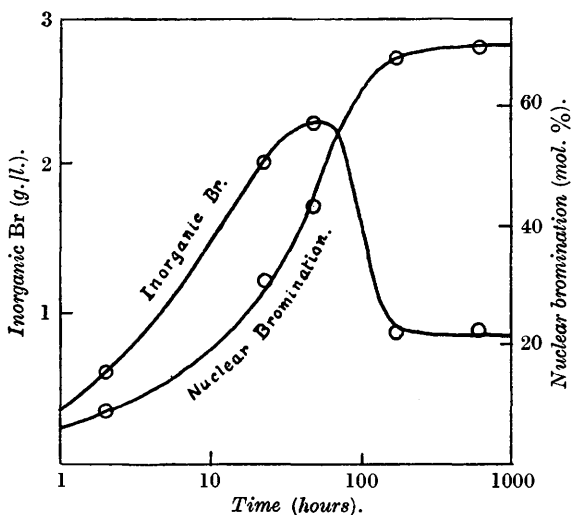
acid of the strength employed, was to reduce the *m*-bromination from 35·7 to 19·5% (Nitrations No. 32 and 33; compare 36). Aspiration with similarly treated oxygen-free nitrogen reduced the *m*-bromination from 43·1 to 23·3% (Nitrations No. 34 and 35). We conclude that the external brominating agent responsible for the *m*-bromination is a *volatile* substance.

(ix) During the reaction in nitric acid the concentration of inorganic bromine (that which is precipitable as silver bromide after removal of all organic material) first rises and then falls after the manner characteristic of an intermediate in consecutive reactions; meanwhile the concentration of nuclear bromination products rises to a maximum and then remains constant (see E, 5). This effect is shown in Fig. 2, which is drawn from the results

obtained in a group of experiments (Nitrations No. 22—26) in which the time-variation of the different bromination and nitration products was traced over a long period. Similar curves can be constructed from the results of Nitrations No. 27—30, which were similarly studied. We conclude that the external brominating agent responsible for the *m*-bromination is an *inorganic* substance.

Since the best known inorganic, volatile brominating agent is bromine, which has been proved both to be present and to be competent, we venture to connect it with the external brominating agent which has been shown to be responsible for the *m*-bromination.

(2) *Formation of* p-*Nitro-derivatives*.—The different orientation of the substituent in these derivatives shows that the mechanism of their formation must be radically different from that of the *m*-bromo-compounds. Flürscheim and Holmes, having postulated *intramolecular m*-migration of the bromine, fulfilled this obvious requirement by asserting that the *p*-nitro-compounds arise through the *extramolecular* substitution of a different aromatic compound. But this type of explanation will not serve; for we have shown that a brominating agent is present which, since it readily brominates even *m*-orienting compounds which undergo substitution comparatively slowly, would brominate to a still larger extent Flürscheim and Holmes's hypothetical intermediate, which undoubtedly would undergo *p*-substitution relatively very rapidly. Actually, very little *p*-bromination occurs. It would be beside the mark to argue that too little of the hypothetical intermediate is present; for then it would not explain what it was invented to explain, namely, the formation of a preponderance of *p*- over *m*-nitro-compounds, under conditions which also lead to a preponderance of *m*- over *p*-bromo-compounds. Thus the essential change leading to the formation of *p*-nitro-compounds is apparently *not* extra-molecular nitration by nitric acid, and once again we have to reverse Flürscheim and Holmes's conclusion and suggest that the *formation of* p-*nitro-compounds depends on an internal change involving group-migration*, in a sense to be considered later. Our reasons may be summarised as follows :

(i) The absence of any substantial quantity of *p*-bromo-products (see E, 4 and 9) appears to preclude the theory of ordinary substitution through a *p*-orienting intermediate.

(ii) Flürscheim and Holmes's hypothetical *p*-orienting intermediate is, in fact, instantly converted by bromine into a *m*-orienting compound (see E, 14).

(iii) Contrary to Flürscheim and Holmes, we find no product definitely attributable to ordinary nitration through a *p*-orienting intermediate. Excluding the small proportion of *op*-nitrophenyl-

bromocyanonitromethane conceivably arising from direct nitration of phenylbromocyanonitromethane (see B, 3), we cannot find in substantial quantity any derivative containing *two* nitro-groups, one in the *p*-position and the other in the side chain (see E, 9) (contrast bromination).

(iv) When nitric acid is *absent* during the progress of lateral decomposition, *op*-nitro-derivatives are still formed; and, moreover, they are formed in quantity (*e.g.*, 12%) sufficient to account, by means of a similar mechanism, for their production (*e.g.*, about 10%) by lateral decomposition in nitric acid solution (see E, 11).

By the phrase " internal change involving group-migration " we do not necessarily mean " intramolecular migration," although this would be included as a special case. A consideration of the mechanism of any real or so-called migration involves two major questions, namely, whether or no there is an internal change of structure, and, if there is, whether the group migrates within or without the molecule. To illustrate : In the " rearrangement " of *N*-chloroacetanilide there is neither an internal structural change * nor internal group-migration (Orton); in anionotropy the isomerisation of the kation is internal, but the group-migration is external (Burton, Ingold); in the rearrangement of imino-ethers both the structural change and the group-migration are internal (Chapman). An alternative expression of our suggestion is, therefore, that the formation of *p*-nitro-derivatives depends on a process belonging either to the second or to the third of the categories here exemplified (compare Ingold, Smith, and Vass, J., 1927, 1245). The matter is further discussed below.

(3) *Additional Details.*—The above attempt to elucidate the general character of the side reactions leaves several details undetermined, as, for instance, the form in which bromine is *originally* eliminated, later to become elementary bromine. It may be eliminated as nitrosyl bromide. This view would readily accommodate the formation of benzoyl cyanide as the main product of decomposition in the absence of nitric acid, and the presence in the gases of nitrosyl bromide, and the products of its dissociation, bromine and nitric oxide (E, 6 and 10) :

$$C_6H_5 \cdot CBr(NO_2) \cdot CN \longrightarrow C_6H_5 \cdot CO \cdot CN + NOBr;$$
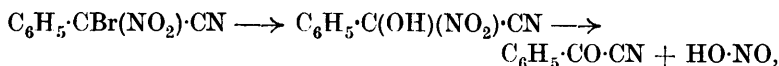$$2NOBr \rightleftharpoons Br_2 + 2NO.\dagger$$
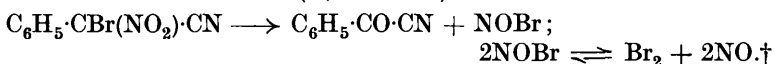
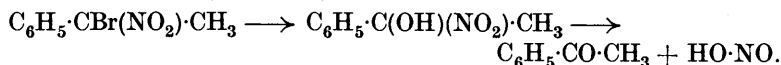Some of the eliminated bromine may also appear first as hydrogen

* Apart, of course, from the polarisations involved in any substitution by an external reagent.

† Nitrosyl tribromide, $NOBr_3$, would also be formed (reversibly), and its presence *may* be of importance in connexion with the intimate mechanism of bromination.

bromide, through the intervention of (subsequently regenerated) water, the organic product, α-nitro-α-cyanobenzyl alcohol, thus formed eliminating nitrous acid. Some hydrogen bromide and nitrogen peroxide are certainly evolved, in addition to bromine and nitric oxide (E, 6 and 10). This suggestion, which may be formulated thus,

$$C_6H_5 \cdot CBr(NO_2) \cdot CN \longrightarrow C_6H_5 \cdot C(OH)(NO_2) \cdot CN \longrightarrow$$
$$C_6H_5 \cdot CO \cdot CN + HO \cdot NO,$$

was made to us by Dr. H. Burton. The first stage appears a possible reaction for any benzyl halide, and we have illustrated the postulated elimination of nitrous acid by converting α-bromo-α-nitro-α-phenylethane into acetophenone by the action of silver oxide and water (see E, 17) :

$$C_6H_5 \cdot CBr(NO_2) \cdot CH_3 \longrightarrow C_6H_5 \cdot C(OH)(NO_2) \cdot CH_3 \longrightarrow$$
$$C_6H_5 \cdot CO \cdot CH_3 + HO \cdot NO.$$

Here we have used a methyl group in place of the cyano-group in order to avoid hydrolysis of the carbonyl compound.

Various questions arose in connexion with the internal change involving p-migration, such as .whether the group-migration is internal or external, and whether the displaced group is nitroxyl or nitrosyl. We have never observed a blue colour suggestive of the last hypothesis. In any event a concomitant oxidation must occur, either of the already displaced group, or of the residual side chain ; for it has not been found possible to isolate an earlier product of these changes than p-nitrobenzoyl cyanide, the formation of which must involve the absorption of one atom of oxygen. We have illustrated (see E, 15) the possibility of the mechanism represented by
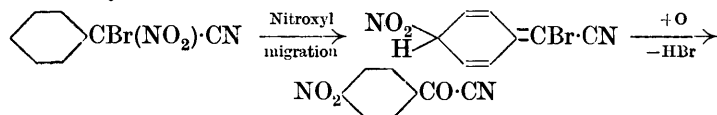
by demonstrating the formation of p-nitrobenzoyl cyanide (see also E, 16) by the action of reagents, known to be present in the above decomposition (namely, bromine and nitrogen peroxide), on a p-nitrophenyl derivative containing a reduced nitroxyl-free side chain (p-nitrophenylacetonitrile). The most probable view of the oxidation seems to be that the anion, p-NO_2 \cdot \overline{C_6H_4 \cdot CBr \cdot CN}$, intervening in the tautomerisation of the quinonoid product of nitroxyl-migration, achieves neutrality by ejecting a bromide ion, thus giving a bivalent carbon compound, p-NO_2 \cdot C_6H_4 \cdot C \cdot CN$ (electron sextet), which would be autoxidisable to p-nitrobenzoyl cyanide.

A variant of the first of the suggested mechanisms for the formation of benzoyl cyanide from phenylbromocyanonitromethane consists in the elimination of nitroxyl bromide, and then the immediate oxidation by this substance of the bivalent carbon compound, $C_6H_5 \cdot C \cdot CN$, so formed. The supposition that intermediates of this general type may arise by decomposition of the side chain in phenylbromocyanonitromethane renders intelligible the formation, not only of benzoyl cyanides, but also of stilbene derivatives—for the production of which we have obtained direct evidence by the isolation (see E, 12) of dicyanostilbene,

$$CPh(CN) \dot{:} CPh(CN).$$
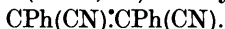
The suggestions contained in this section are necessarily tentative.

(D) Summary and Conclusions.

(1) *Phenylbromocyanonitromethane*.—It has been shown (*a*) that Flürscheim and Holmes's alleged evidence that this substance passes by intramolecular migration of bromine into *m*-bromophenylcyanonitromethane is valueless, (*b*) that free bromine is present under all conditions in which *m*-bromo-products, including *m*-bromophenylbromocyanonitromethane, are formed, and (*c*) that a large body of cogent evidence exists (nine reasons, C, 1) which points unmistakably to the conclusion that these *m*-bromo-products are formed by extramolecular bromination of the nucleus.

(2) *Intramolecular* m-*Migration*.—It follows from (1) that no " proved case " of the intramolecular *m*-migration of a substituent from a side chain has as yet been discovered.

(3) *Theories of Aromatic Substitution*.—The intramolecular *m*-migration of a side-chain substituent, and indirect *m*-substitution dependent on this mechanism, are conceptions foreign to a theory of aromatic substitution which postulates inductive *m*-deactivation in *m*-orientation. The formation of *op*-products through an internal change involving the migration of a substituent from a normally *m*-directing side chain is, however, possible on this theory, since it envisages tautomeric *op*-activation (but not *m*-). The available evidence favours the suggestion that in the lateral decomposition of phenylbromocyanonitromethane *p*-nitro-products are formed in this way, the alleged contrary evidence of Flürscheim and Holmes having been controverted.

EXPERIMENTAL.

Preparation of Phenylbromocyanonitromethane (E, 1).

(1) *Method* (a).—In the earlier part of the investigation this substance was obtained by Flürscheim's method (*loc. cit.*), the samples being freshly prepared as required and analysed before

use (Found : C, 39·8, 40·1, 40·3; H, 2·1, 2·15, 2·05; Br, 32·6. Calc. : C, 39·8; H, 2·1; Br, 33·2%); but later it was found that a more uniform and stable product could be obtained by a method permitting the exclusion of water throughout the process.

Method (b).—Dry bromine (slightly less than the theoretical quantity) was added gradually to a stirred suspension of the finely powdered dry sodium salt of phenylcyanonitromethane in dry ether, and the filtered solution was evaporated at the ordinary temperature in a vacuum over phosphoric oxide. The product, a very pale yellow liquid, did not darken in colour and did not develop any sharp smell of benzoyl cyanide on being kept in air for more than one month; it is therefore much more stable than the product obtained by method (a). Also, the new process is more expeditious, since only a small volume of ether requires evaporation in the vacuum. As a precaution against the adventitious decomposition of any sample, however, the material was always freshly prepared as required.

Nitration of Phenylbromocyanonitromethane (E, 2—9).

(2) *Effect of Nitric Acid of Different Concentrations.*—(Series *a*. Nitrations No. 1—7.) These nitrations were all carried out under our formerly described conditions—except that the strength of the acid was varied—the products being isolated and analysed as recommended by Flürscheim and Holmes (oxidation method C was used throughout). The density of the nitric acid, free or almost free from nitrous acid, was determined with a 5 c.c. pyknometer to five significant figures, but the fifth figure is not accurate and is not quoted. The results are in the first table under (A), and the analytical data refer to acids obtained by oxidation of the nitration products from which the acid by-products have been removed by extraction with potassium hydrogen carbonate. The figures represent, not molecular percentages, but percentages by weight, since the un-nitrated acids contained undetermined proportions of *m*-bromobenzoic acid. Other numerical data are given in the table below.

(Series *b*. Nitrations No. 8—10.) These protracted nitrations were carried out with 16 parts of nitric acid at room temperature, and owing to the length of time the proportion of bromination is high. In these experiments the whole nitration product was oxidised. The results are given in the second table under (A), in which the figures for the bromo-acids include any nitro-*m*-bromobenzoic acids calculated as bromobenzoic acid, except in No. 8, in which the actual proportions of these acids were 21·1 and 17·0 mols. % respectively. The densities were determined as above.

Other details in connexion with nitrations No. 1—10 are in the following table :

Series.	Nitration No.	PBCN used (g.).	Acid product (g.).	Neutral product (g.).	C (%).	H (%).	m-NO$_2$-PBCN separated (%).	Material oxidised (g.).	Acids formed (g.).
	1	4·490	—	4·045	41·1	2·2	None	3·185	1·751
	2	5·161	0·088	4·740	37·5	2·0	,,	3·610	2·092
	3	2·537	—	2·257	—	—	,,	1·940	1·081
(a)	4	3·027	—	3·215	36·6	1·7	0·94	1·746*	0·992
	5	2·594	0·124	2·658	34·7	1·6	None	0·694	0·352
	6	3·403	—	3·670	—	—	49·0†	2·422	1·328†
	7	8·214	—	9·580	34·5	1·6	47·0	1·850*	0·791
	8	4·00		3·360	—	—	None	3·260	2·588
(b)	9	2·00		1·455	—	—	,,	1·455	1·299
	10	7·63		6·680	—	—	,,	1·580	1·359

* After separation of stated proportion of m-NO$_2$-PBCN.

† From different portions of neutral product.

A bar signifies " not determined."

(3) *Effect of Concentration of Phenylbromocyanonitromethane.*—(Series a. Nitrations No. 11—14.) The nitric acid used had $d_4^{15°}$ 1·483. Four portions of the same specimen of phenylbromocyanonitromethane were simultaneously treated with the proportions of nitric acid indicated in the table under B, 2, and left in the same water-bath at room temperature for 20 hours. The solutions were worked up as under E, 2, the whole product being oxidised in each case. The yields and compositions are given below.

(Series b. Nitrations No. 15—17.) The nitric acid had $d_4^{15°}$ 1·482. Three portions of the same specimen of phenylbromocyanonitromethane were simultaneously treated with the proportions of acid recorded under B, 2, and kept for 240 hours in the same bath at room temperature. The solutions were evaporated for a few hours over potassium hydroxide in a vacuum to remove the more volatile products and then extracted with ether. The whole products were oxidised as before, with the results recorded below :

Series.	Nitration No.	PBCN (g.).	Nitration products (g.).	Oxidation acids (g.).	Composition of acids R·CO$_2$H (mols. %).				
					R = C$_6$H$_5$.	op- NO$_2$·C$_6$H$_4$.	m- NO$_2$·C$_6$H$_4$.	m- Br·C$_6$H$_4$.	NO$_2$-m- Br·C$_6$H$_3$.
	11	4·137	—	2·220	97·7	1·1	0·0	1·2	0·0
(a)	12	3·997	—	2·389	91·0	0·4	0·0	8·4	0·2
	13	4·009	—	2·324	78·0	0·7	1·4	19·0	0·9
	14	3·945	—	2·355	17·0	5·3	40·5	32·3	4·9
(b)	15	4·00	3·457	2·525	17·6	12·0	21·4	35·5	13·5
	16	4·00	3·360	2·588	0·0	20·1	41·8	21·1	17·0
	17	4·00	3·111	2·314	0·0	20·8	48·0	13·7	15·5

(*Note.*—A bar signifies " not weighed.")

(4) *Intramolecular Transference of Bromine.*—(Series a. Nitrations No. 18—20.) A specimen of nitric acid, $d^{18°}$ 1·45 (uncorr.), was used. Three nitrations were set up simultaneously, No. 18 with

1·90 g. of phenylbromocyanonitromethane and 16·0 g. of nitric acid, No. 19 with 3·00 g. of benzyltrimethylammonium picrate and 16·0 g. of nitric acid, and No. 20 with 1·90 g. of phenylbromocyano-nitromethane, 3·00 g. of benzyltrimethylammonium picrate, and 16·0 g. of nitric acid; they were allowed to proceed in the same desiccator at the ordinary temperature for 800 hours. Potassium hydroxide was used in the desiccator, and the pressure in the stoppered nitration flasks was released from time to time.

(No. 18.) A solid had separated (0·1728 g.) which was identified as pure *m*-bromobenzoic acid (m. p. 150°). A further quantity of the same acid in a crude condition (m. p. about 140°) was obtained by the addition of about 250 c.c. of ice-water. The ethereal extract yielded a neutral fraction, which was not investigated, and an acid fraction (0·857 g.), which contained bromine and had m. p. 152—161°. By repeated crystallisation of the less soluble portion of this, a small amount of a still impure bromo-acid was obtained, the m. p. (about 220°) of which was raised by admixture with *p*-bromobenzoic acid.

(No. 19.) No crystallisation had occurred, and the solution, on being poured into water, gave 2·154 g. of a picrate, m. p. about 167°. A further 0·846 g. was obtained by treatment of the evapor-ated solution with sodium picrate. On crystallisation from alcohol, these picrate fractions yielded pure benzyltrimethylammonium picrate, m. p. 171°, showing that no considerable amount of nitration had occurred.

(No. 20.) The solid which had separated (0·161 g.) had m. p. 232° and was identified as *p*-nitrobenzoic acid. By addition of water to the solution, evaporation, and addition of sodium picrate, 2·20 g. of a picrate were obtained which after crystallisation from dilute alcohol yielded a product containing, according to an estim-ation of the bromine content, 95% of bromobenzyltrimethyl-ammonium picrate. It had m. p. about 143° before purification and consisted essentially of the *m*-bromo-salt (below) (mixed m. p.).

(Series *b*.) Preparation of *m*-bromobenzyltrimethylammonium salts. *m*-Bromotoluene, prepared from *m*-toluidine, was bromin-ated at 170—175° with slightly more than the theoretical amount of bromine, and the crude product was mixed with an excess of 33% alcoholic trimethylamine. The salt precipitated by the addition of ether was decolorised by charcoal in alcohol, reprecipit-ated with ether, and crystallised from absolute alcohol–ligroin; *m-bromobenzyltrimethylammonium bromide* was then obtained as white triangular prisms, m. p. 216° (Found: Ionisable Br, 26·2. $C_{10}H_{15}NBr_2$ requires ionisable Br, 25·9%). When this salt was

heated in a vacuum at 220—225°, decomposition took place. The product, presumably a mixture of m-bromobenzyl bromide and m-bromobenzyldimethylamine, on oxidation with hot 3% potassium permanganate solution yielded m-bromobenzoic acid, m. p. 147—148° (mixed m. p.). The quaternary *picrate*, obtained from the bromide by treatment with saturated aqueous sodium picrate, separated from absolute alcohol in small prisms, m. p. 150° (Found : C, 42·4; H, 3·9. $C_{16}H_{17}O_7N_4Br$ requires C, 42·0; H, 3·9%). *Benzyltrimethylammonium bromide*, prepared in the usual way, crystallised from alcohol–ligroin in thick rectangular plates, m. p. 235°, which depressed the m. p. of the m-bromo-bromide on admixture.

(No. 21.) Phenylbromocyanonitromethane (8·00 g.) and benzyl-trimethylammonium picrate (12·60 g.) were nitrated together, with 35·4 c.c. of the nitric acid used for series (a), during 300 hours at room temperature. p-Nitrobenzoic acid, a neutral product (which had the odour of benzoyl cyanide and gave benzoic acid on oxidation), picric acid, and a series of picrate fractions (total, 11·46 g.) were isolated. A representative sample of the picrate fractions had a bromine content indicating the presence of 46% of m-bromo-benzyltrimethylammonium picrate. The least soluble fractions, m. p. 148—149°, 149—150°, consisted essentially of this substance (mixed m. p.'s); they were compared with the synthetic specimen and converted into the corresponding bromides, which were similarly compared, and decomposed by heating in a vacuum at 220° to products which, when oxidised, yielded m-bromobenzoic acid, m. p. 146—149° (mixed m. p.). The most soluble picrate fraction, m. p. about 163°, contained only a trace of bromine and consisted essentially of unchanged benzyltrimethylammonium picrate (mixed m. p.).

(5) *Variation with Time of Organic Products and Inorganic Bromine.*—(Series a. Nitrations No. 22—26.) These were set up together by leaving a solution of 14·28 g. of phenylbromocyano-nitromethane in 98 c.c. of nitric acid (d 1·46 uncorr.) at room temperature and withdrawing samples of 20 c.c. at intervals for analysis. Each sample was run on to ice prepared from distilled water, and the organic material extracted under standard conditions in halogen-free vessels with pure halogen-free ether. In the aqueous solution the bromine precipitable as silver bromide was estimated in the usual way. The organic product was separated into neutral and acid portions by extraction with potassium hydrogen carbonate solution. By weighing the two fractions separately it was shown that the acid portion was far too small to account for the proportion of m-brominated products, which are therefore proved to arise

by bromination of a neutral m-orienting substance. The neutral and the acid fractions were combined for analysis as under E, 2.

(Series b. Nitrations No. 27—30.) Phenylbromocyanonitromethane (24·26 g.) was nitrated with 166 c.c. of nitric acid (d 1·45 uncorr.) at the ordinary temperature. Samples of 20 c.c. were withdrawn at intervals as before, but in this series the order of addition of ether and silver nitrate was inverted, and the organic product was not separated into neutral and acid portions, but was weighed all together and oxidised as above. A qualitative test after 2·5 hours showed the presence of free bromide ions.

The results obtained in both series are recorded in the following table :

Series.	Nitr. No.	Time (hrs.).	Inorg. Br (g./l.).	Organic (g./c.c.). Neutral.	Organic (g./c.c.). Acid.	Acids by oxidn. (g./c.c.)	R = C_6H_5	op- $NO_2 \cdot C_6H_4$	m- $NO_2 \cdot C_6H_4$	m- $Br \cdot C_6H_4$	NO_2-m- $Br \cdot C_6H_3$	Nuclear by-products.
(a)	22	2	0·61	0·1215		0·0593	82·0	8·5(?)	0·3	9·1		9·1
	23	23	2·03	0·1105	0·0046	0·0578	63·5	3·1	1·6	31·8		31·8
	24	48	2·32	0·1112	0·0060	0·0877	51·6	4·0	1·0	41·0	2·4	43·4
	25	168	0·86	0·0946	0·0145	0·0919	24·5	5·0	2·3	63·8	4·4	68·2
	26	360	0·92	0·0600	0·0407	0·0897	22·3	3·8	3·9	60·3	9·7	70·0
(b)	27	23	1·19	0·1036		0·0654	61·0	5·4	1·8	29·2	2·3	31·5
	28	49	2·03	0·1000		0·0639	55·0	2·8	1·0	37·3	3·9	41·2
	29	144	2·29	0·1093		0·0773	26·6	1·2(?)	2·0	56·1	14·0	70·1
	30	312	1·19	0·1017		0·0759	24·8	3·1	5·0	49·8	17·3	67·1

The spent liquors of each of these nitrations were treated with silver nitrate under the conditions of Flürscheim and Holmes's recorded tests for hypobromous acid. For the first few seconds the silver bromide precipitate remained colloidal, and appeared as a haze by transmitted light; soon, however, it began to flocculate, and, as is usual with silver bromide precipitates, the process was greatly hastened by shaking. An artificial solution of redistilled bromine in halogen-free aqueous nitric acid, when treated with a little halogen-free ether and silver nitrate under the same conditions, behaved, contrary to Flürscheim and Holmes's statement, in exactly the same way.

(6) The Volatile Products.—Flürscheim and Holmes do not record the formation, in large quantity, of a number of volatile products of the action of nitric acid on phenylbromocyanonitromethane. Many of our nitrations, including the series 22—30, were carried out in an all-glass apparatus in which the volatile products could be drawn off and examined. The gases identified were bromine (formation of styrene dibromide, m. p. and mixed m. p. 68°, from styrene in carbon tetrachloride), hydrogen bromide (usual test, with halogen-free reagents, after removal of bromine), nitrogen peroxide (colour in absence of free bromine and oxygen;

formation of nitrite and nitrate with alkali; formation of deep blue nitrosite with tetramethylethylene in carbon tetrachloride), and nitric oxide (colour on addition of oxygen after removal of bromine and nitrogen peroxide). The presence of bromine and nitric oxide proves the presence of nitrosyl bromide.

(7) *Effect of Addition of Bromine.*—(Nitrations No. 31, 32.) These experiments were set up simultaneously, the same samples of phenylbromocyanonitromethane and nitric acid (10 parts; $d_4^{15°}$ 1·483) being used, and allowed to proceed in sealed tubes for 36 hours at the ordinary temperature. The whole products were oxidised in each case. In No. 31, bromine (1 mol.) was added, and the un-nitrated acids, recovered after oxidation with permanganate and reduction with titanous chloride, had a bromine content equivalent to more than 100% of monobromobenzoic acid; the composition of the mixture was therefore calculated as that of a mixture of mono- and di-bromobenzoic acids. In No. 32, no additional bromine was introduced, and the un-nitrated acids, which had a much lower bromine content, were taken as a mixture of benzoic and bromobenzoic acids. The following are the compositions of the acids R·CO₂H, calculated as mols. % on these assumptions :

Nitration.	PBCN (g.).	Acids (g.).	R = C₆H₅.	op- NO₂·C₆H₄.	m- NO₂·C₆H₄.	C₆H₄Br.	NO₂·C₆H₃Br.	Total mono-bromo-.	C₆H₃Br₂.
31	4·160	3·429	0·0	0·3	2·5	71·1	11·4	82·5	14·7
32	4·050	1·811	22·7	2·0	39·6	31·8	3·9	35·7	0·0

(8) *Effect of Aspiration with Air and Nitrogen.*—(Nitrations No. 32—36.) Simultaneously with No. 32, another nitration, No. 33, was set up with the same materials in the same proportion, but in an all-glass apparatus permitting the passage of a gas through the solution. The nitration was carried out at the same temperature and during the same period as No. 32, but throughout the whole time air, previously passed over decarbonating and drying agents and then through a sample of the same nitric acid, $d_4^{15°}$ 1·483, as that used for the nitration, was drawn through by a water-pump, a capillary tube being used as a precaution against back-diffusion and irregular flow.

Two more nitrations, No. 34 and 35, were set up simultaneously with each other, the same sample of phenylbromocyanonitromethane and the same nitric acid ($d_4^{15°}$ 1·483; 10 parts) being used —No. 34 in a loosely stoppered bottle, and No. 35 in the aspiration apparatus—and allowed to proceed at the same temperature (room) during the same time (36 hours). Nitrogen, taken from a cylinder, freed from oxygen by passage through alkaline pyrogallol, dried, and saturated with the vapour of the nitric acid used for nitration, was passed through the nitration solution throughout the period,

capillaries being used to buffer the stream, and slight suction from a water-pump serving to maintain the conditions of pressure the same as in No. 33.

Experiment No. 36 was a duplicate of No. 33, except that the temperature, and the rate of bubbling of the air, were only approximately repeated. Since the main object was to obtain an additional check on the reduced proportion of *m*-bromination, indicated by experiments 33 and 35, the analysis was shortened by estimating the small amount of nitro-*m*-bromo-acids as *m*-bromobenzoic acid along with the main portion of this substance. The error thus introduced makes the mols. % of *m*-bromo-products slightly high, so that the corresponding estimate of the reduction of *m*-bromination caused by aspiration is on the conservative side.

All analyses of this series were carried out on the *whole* nitration products, as under E, 2. The results are shown in the table, in which the brackets indicate pairs of experiments in which all conditions, other than those relating to the escape of volatile products, were identical :

Nitra-tion.	Aeration and aspiration.	PBCN (g.).	Oxidation acids (g.).	Composition of acids R·CO$_2$H (mols. %).				
				R = C$_6$H$_5$.	op- NO$_2$·C$_6$H$_4$.	m- NO$_2$·C$_6$H$_4$.	m- C$_6$H$_4$Br.	NO$_2$-m-C$_6$H$_3$Br.
32	Sealed tube	4·050	1·811	22·7	2·0	39·6	31·8	3·9
33	Air passed	5·040	2·097	51·2	4·6	24·7	14·6	4·9
34	Loosely stoppered	3·979	2·296	17·1	3·6	36·2	39·2	3·9
35	Nitrogen passed	4·014	1·762	22·9	3·8	50·0	21·8	1·5
36	Air passed	4·145	2·343	47·8	3·1	31·8	17·3	

(9) *Nuclear Substitution Products with an Unaltered Side Chain.* —(Nitration No. 37.) In this experiment we followed the procedure recommended by Flürscheim and Holmes for the separation and analysis of the products with an unaltered side chain, but, contrary to their statement, encountered no difficulty in estimating these substances by direct oxidation to the corresponding substituted benzoic acids; the results obtained by Flürscheim and Holmes's method were therefore checked by this more direct method.

Phenylbromocyanonitromethane (8·86 g.) was nitrated with 120 c.c. of nitric acid, d_4^{15} 1·480, for 120 hours at room temperature. Benzoic acids were removed from the ethereal extract of the product by shaking with 5% potassium hydrogen carbonate solution, and a portion (3·81 g.) of the neutral residue (7·35 g.) was shaken with ether and a solution of potassium iodide (12 g.) in water (60 c.c.). The aqueous solution was shaken for 1·5 hours with 10% aqueous potassium hydroxide, and then oxidised with boiling 3% potassium permanganate solution, that part of the iodine thus produced which did not escape from the solution being destroyed

by sulphur dioxide after the oxidation. The ethereal solution, when freed from iodine by washing with aqueous sodium thiosulphate, dried, and evaporated, left a residue weighing 1·534 g. The complete neutral product thus contains 59·8% of arylbromocyanonitromethanes and 40·2% of benzoyl cyanides, etc. In the following table the figures for *op*-nitro-derivatives may be slightly high (*e.g.*, 2%) and those for bromonitro-products correspondingly low, owing to incomplete hydrolysis under our conditions of the salts of the bromoaminobenzoic acids in acid solution. The row marked " calc." contains percentages indirectly calculated in accordance with Flürscheim and Holmes's procedure. The compositions of the acids $R \cdot CO_2H$, obtained from the various fractions of the nitration product, are in mols. %.

Product of nitration No. 37.	$R =$ C_6H_5.	*op*- $NO_2 \cdot C_6H_4$.	*m*- $NO_2 \cdot C_6H_4$.	*m*- C_6H_4Br.	$NO_2 \cdot C_6H_3Br$.
(*a*) Whole neutral (taken as 100% by weight)	1·5	7·1	43·0	39·7	8·7
(*b*) Bromocyanonitromethanes (59·8% by weight)	4·3	7·0	54·8	25·1	8·8
(*c*) Benzoyl cyanides, etc. (40·2% by weight)	0·3	4·3	16·7	71·0	7·7
(*d*) Bromocyanonitromethanes (calc.)	2·4	9·0	60·7	18·6	9·3

The non-nitrated benzoic acids recovered in the course of the analyses (*b*) and (*c*) were qualitatively examined. Each consisted of nearly pure *m*-bromobenzoic acid, which was obtained pure (m. p. and mixed m. p.) by one crystallisation from chloroform in both cases. This confirms the analogous result recorded under E, 4, and shows that, contrary to Flürscheim and Holmes's conclusion, *op*-orienting compounds are not present during these nitrations.

Lateral Decomposition of Phenylbromocyanonitromethane in the Absence of Nitric Acid (E, 10—12).

(10) *Decomposition at Atmospheric Pressure.*—(*a*. At the ordinary temperature.) Phenylbromocyanonitromethane (8·86 g., prepared by method *a* : see E, 1) was allowed to decompose at the ordinary temperature in an apparatus similar to that used for the examination of the gaseous products formed on nitration (see E, 6). Bromine, hydrogen bromide, nitric oxide, and nitrogen peroxide were identified, and the partly solid residue remaining after 3 months (6·78 g.) yielded benzoyl cyanide, *p*-nitrobenzoyl cyanide and *p*-nitrobenzoic acid as the main isolable products (m. p. and mixed m. p. in each case).

(*b*. At 75—80°.) Flürscheim and Holmes identified bromine and nitric oxide amongst the volatile products; we find that

hydrogen bromide, nitrogen peroxide, and nitrosyl bromide are also produced. The decomposition of phenylbromocyanonitromethane (17·0 g.) was allowed to proceed in an all-glass apparatus in which the volatile products condensable at $-35°$ were collected in a bulb (subsequently to be used as a distilling flask) cooled in liquid ammonia, whilst the products which were not thus condensable passed into an eudiometer. In the non-liquefied gaseous portion, hydrogen bromide and nitric oxide were identified as described previously. The deep brown liquefied product was distilled by applying a cooling bath to a series of sealed-on bulbs to be used as receivers, and placing around the distilling bulb a water-bath, which, initially at $0°$, was slowly heated. The bulbs were caused successively to function as receiver by a simple mechanism involving the rotation of a well-ground glass joint, and the fractionation was controlled by a thermometer, the very small bulb of which, touching the bottom of the distilling bulb, was totally immersed in the boiling liquid until near the end of the distillation. Finally, the bulbs were cut off, and their contents tested. The first fraction (small) had b. p. $-2°$ (constant), and on decomposition with distilled water gave a solution which, after being made alkaline with halogen-free potassium hydroxide, was proved to contain bromide and nitrite but no nitrate (recorded b. p. of nitrosyl bromide, $-2°$). The second fraction (large) had b. p. $20—24°$, and its solution in alkali yielded positive tests for nitrite and nitrate (recorded b. p. of nitrogen peroxide, $22°$). The third fraction (small) had b. p. up to $54°$, mostly above $50°$, and consisted of bromine containing a little nitrogen peroxide (proved as for second and fourth fractions). The fourth fraction (large), b. p. about $59°$, was proved to be bromine by its odour, volatility, the liberation of iodine from an iodide, and the formation of styrene dibromide (m. p. and mixed m. p.) from styrene.

The residue (13·0 g.) in the decomposition flask was placed in a vacuum to remove any further quantity of volatile material, and then distilled under reduced pressure; benzoyl cyanide (4·7 g.), m. p. $32—34°$, was obtained, together with an impure fraction (5·2 g.) from which p-nitrobenzoyl cyanide crystallised (m. p. $116°$ after recrystallisation from ligroin), and a residue which decomposed.

(11) *Decomposition in a Vacuum.*—The decomposition was carried out at $77—80°/20$ mm., and the residue oxidised by Flürscheim and Holmes's method C. The acids contained benzoic acid (86·4 mols. %), op-nitrobenzoic acid (11·9 mols. %), and m-bromobenzoic acid (1·7 mols. %), but no m-nitro- or nitro-m-bromo-acids. Despite the rapid removal in this experiment of any possible volatile nitrating agents, the proportion of op-nitro-products is similar to

(somewhat higher than) that found by Flürscheim and Holmes for decomposition at the ordinary pressure.

(12) *Decomposition in the Presence of Phosphoric Oxide.*—This experiment, although it represents an unsuccessful (and very crude) attempt to arrest the decomposition by drying, is of interest inasmuch as it led to the isolation of dicyanostilbene. A concentrated ethereal solution of phenylbromocyanonitromethane (prepared by method *b*; see E, 1) was dried with phosphoric oxide for 2 days, and then transferred to a dried bulb containing fresh pentoxide. The ether was removed by distillation and the residue decomposed at about 75°. After removal of most of the benzoyl cyanide from the product by distillation up to 100°/9 mm., the residue was extracted with ligroin. The crystalline substance thus obtained, after recrystallisation from the same solvent, had m. p. 155—156°, both alone and after admixture with an authentic specimen of dicyanostilbene.

Observations on Phenylcyanonitromethane (E, 13, 14).

(13) *Decomposition in the Absence of Reagents.*—(*a.* Isolation of benzoyl cyanide.) An ethereal extract of the nitro-compound, prepared from 4·0 g. of its purified sodium salt, was evaporated, and the residue warmed to assist decomposition and finally heated on the steam-bath for a short time. The residue on distillation yielded a small fraction, b. p. about 110°/24 mm., which solidified and was identified as benzoyl cyanide, m. p. 32—34°. Extensive decomposition occurred on continuing the distillation.

(*b.* Evidence of nitroxyl-migration.) The above experiment was repeated, but the residue, instead of being distilled, was shaken for 3 hours with 10% potassium hydroxide solution, and the product oxidised with permanganate. The acids thus obtained contained 10% by weight of an acidic gum which was insoluble both in ether and in hot hydrochloric acid. The remaining 90% of the acids had the following composition : benzoic acid 75·3 mols. %, *m*-nitrobenzoic acid 0·3 mol. % (?), and *op*-nitrobenzoic acids 24·4 mols. %.

(14) *Action of Bromine.*—An ethereal solution of the nitro-compound reacted instantly with one molecular proportion of bromine in freshly prepared ethereal solution. The product obtained from the ethereal solution, after washing with water and drying, had the properties of phenylbromocyanonitromethane.

Formation of Benzoyl Cyanide and its Analogues (E, 15—17).

(15) *Conversion of* p-*Nitrophenylacetonitrile into* p-*Nitrobenzoyl Cyanide.*—*p*-Nitrophenylacetonitrile (5 g.) was heated to 120° (bath temperature) until fused, and then at 100—110° during the

gradual addition of dry bromine (6 g.) by a delivery tube dipping under the surface. Heating at the same temperature was continued until the evolution of hydrogen bromide ceased, and the cooled product was shaken with about 200 c.c. of dry ether, which dissolved all but a small amount of viscous oil. The residue from the ether rapidly crystallised, and after a further crystallisation from ether–ligroin yielded p-*nitrophenylbromoacetonitrile* as small cubes, m. p. 96° (Found : C, 40·5; H, 2·2. $C_6H_5O_2N_2Br$ requires C, 39·8; H, 2·1%).

An attempt to effect the bromination at 140—150° by means of bromine vapour carried in a current of carbon dioxide led to the formation of di-p-nitrodicyanostilbene, which crystallised from acetone and then melted at 275°.

The ether-insoluble oil, the residue obtained on evaporation of the ethereal extract, and the pure bromo-compound were separately treated for 1 hour at 80—90° with the oxides of nitrogen evolved from arsenious acid and nitric acid (d 1·35, uncorr.). The products were distilled under diminished pressure, and, in the first two cases, distillates were obtained which solidified and after crystallisation from ligroin yielded pure p-nitrobenzoyl cyanide (m. p. and mixed m. p. 116—117°). The same substance was obtained when p-nitrophenylacetonitrile was treated at 100—110° for 1 hour with a mixture of bromine vapour and the oxides of nitrogen generated as above. In the later stages of the above distillations at 5 mm. extensive decomposition occurred, making it impossible to identify the remainder of the material.

(16) *Conversion of Mandelonitrile into Benzoyl Cyanide.*—When mandelonitrile was warmed on the steam-bath with a small proportion of bromine, hydrogen bromide was evolved and a very small quantity of a solid substance crystallised in the condenser. The liquid product was mixed with water and extracted with ether, and the acidic substances were removed from the ethereal extract by washing with potassium hydrogen carbonate solution. When the residue from the ethereal solution was distilled, the small fraction, b. p. 100—120°/24 mm., which was collected before the onset of decomposition, crystallised on cooling and yielded benzoyl cyanide, m. p. and mixed m. p. 32—34°.

(17) *Conversion of α-Bromo-α-nitro-α-phenylethane into Acetophenone.*—The bromonitro-compound (Baker and Ingold, *loc. cit.*) was first treated in the cold, and then gently warmed, with excess of moist silver oxide. The product was extracted with ether, freed from acids by washing with potassium hydrogen carbonate solution, and, after evaporation of the ether, distilled under diminished pressure. The initial portion of the distillate, b. p. about 120°/18

mm., on treatment with aqueous semicarbazide acetate, yielded a copious precipitate of acetophenonesemicarbazone (m. p. and mixed m. p.).

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