LXII.—*The Laws of Aromatic Substitution. Part VII. The Constitution and Substitution of Phenylnitromethane and Some of its Derivatives.*

By BERNHARD FLÜRSCHEIM and ERIC LEIGHTON HOLMES.

BAKER and INGOLD (J., 1926, 2462) nitrated phenylbromocyanonitromethane and obtained results differing materially from those which one of us had recorded (*J. pr. Chem.*, 1902, **66**, 321). They thereupon asserted that those early experiments had been carried out incorrectly. We have now completed an exhaustive examination of the reaction, with the following results :

1. Contrary to the statement of Baker and Ingold, the experimental observations published by one of us (*loc. cit.*) have been found correct throughout. Phenylbromocyanonitromethane yields, on *brief* treatment with nitric acid (*d* 1·480) and subsequent oxidation by the usual methods, practically only benzoic and *p*-nitrobenzoic acids (see Experimental, section III, 8, d; p. 480), exactly as stated in 1902.

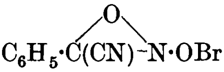
2. This *p*-nitrobenzoic acid—amounting usually to 34—38% of the weight of the total acids—arises essentially from the migration of the nitro-group during the oxidation. The occurrence of this migration, which can be prevented by prior treatment with alkali (see section IIIB; p. 463), has been quantitatively proved.

3. *m*-Nitration can occur under various conditions, as stated by Baker and Ingold, but it does not take place appreciably under the conditions, nor even approximately in the proportion, recorded by these authors (see sections IA and IV; pp. 456, 465).

4. The complex changes occurring on *prolonged* exposure of phenylbromocyanonitromethane to nitric acid (*d* 1·480) have been quantitatively elucidated. The main change—the migration of bromine into the *m*-position (see sections IB and IV; pp. 457, 466)—occurs to the extent of 54% in 10 days, and the rate of formation of the *m*-bromophenyl compound is independent of the concentration.

5. The correlated behaviour of phenylcyano*iso*nitromethane, benzoyl cyanide and *m*-bromobenzoic acid on nitration has also been quantitatively ascertained (see sections IB and IV; pp. 461, 466).

6. The following (primary) nitro-derivatives are formed *directly* by nitration of the compounds named :

Phenylbromocyanonitromethane,  $C_6H_5\cdot\overset{O}{C(CN)-N}\cdot OBr$ (in nitric acid, *d* 1·52) : 92—93% of *m*-nitrophenylbromocyanonitromethane and 8—7% of the corresponding *p*(and *o*)-nitro-compound.

Phenylcyano*iso*nitromethane, $C_6H_5\cdot C(CN){:}NO\cdot OH$ (in nitric acid, *d* 1·480) : more than 99% of *p*-nitrophenylcyano*iso*nitromethane.

Benzoyl cyanide, $C_6H_5\cdot CO\cdot CN$ (in nitric acid, *d* 1·52) : 87·6% of *m*-nitrobenzoyl cyanide and 12·4% of *o*- and *p*-nitrobenzoyl cyanides.

m-Bromobenzoic acid (in nitric acid, *d* 1·480): 96% of *o*- and *p*-nitro-*m*-bromobenzoic acids and 4% of *m*′-nitro-*m*-bromobenzoic acid.

7. The migration of the nitro-group during the oxidation of phenylcyanonitromethane has been discovered and quantitatively examined (see section IIIB; p. 464). It occurs to the extent of 14 mol.%.

8. The decomposition of phenylbromocyanonitromethane and its *m*-nitro-derivative by heat alone, by hot dilute nitric acid, and by concentrated sulphuric acid (see sections IIIA, IIIB, and II; pp. 462, 464) and also the rearrangement of phenylbromocyanonitromethane in ethereal solution (see Experimental, section III, 3; p. 476) have been quantitatively studied. For example, the decomposition of phenylbromocyanonitromethane by heat yields 92 mol.% of benzoyl cyanide and 8 mol.% of *p*-nitrobenzoyl cyanide.

9. Phenylbromocyanonitromethane has been found to be a hypobromite, with an oxygen bridge (see 6), in accordance with Willstätter and Hottenroth's formula for tertiary bromonitro-compounds—a formula which is now co-ordinated with other observations by certain suggestions concerning tautomerism (see section V; p. 467). Hypobromite reactions of phenylbromocyanonitromethane and its newly discovered *m*-nitro-derivative have been quantitatively examined. Phenylbromomalonic ester—a true bromide—does not display such reactions at the ordinary temperature; at 95°, however, there is equilibrium between the hypobromite form and the bromide form, the latter greatly preponderating.

In the nitration performed by one of us (*loc. cit.*), nitric acid of *d* 1·480 * (8 parts, in a freezing mixture) was used. Baker and Ingold, who employed nitric acid of *d* 1·49 (8 parts, in a freezing mixture) obtained acids which, according to their analysis, were almost free from benzoic acid and contained an average of about 52% of *m*-nitrobenzoic acid. Our present investigations prove that no *m*-nitration is produced by acid of *d* 1·480 and very little by acid of *d* 1·490. When, however, the strength or relative amount of the acid, or the temperature or time of nitration, is increased, phenylbromocyanonitromethane may be nitrated appreciably or even completely, the proportion of the *m*-isomeride formed in the latter

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* The work was done at Heidelberg in 1902 with "rauchende Salpetersäure." Reference to Blücher's "Auskunftsbuch," 1903, shows that "gelbe rauchende Salpetersäure" (usually called "rauchende" merely) was acid of *d* 1·480.

case being, not Baker and Ingold's 52%, but 92—93%. Whenever the nitration has not been carried to completion, the unchanged phenylbromocyanonitromethane partly undergoes re-arrangement during oxidation under the usual conditions and thus the percentage of the *p*-isomeride in the nitrobenzoic acids is increased, but, contrary to Baker and Ingold's statement, *p*-nitrobenzoic acid is in this case always accompanied by benzoic acid in preponderating amount.

The behaviour of phenylbromocyanonitromethane as a hypobromite enabled us to follow the course of the reactions occurring during nitration and the changes in the side chain and in the nucleus. The procedure is summarised as follows: A sample of the nitration product was treated with aqueous potassium iodide and the liberated iodine was titrated. What did not go into the potassium iodide solution (*i.e.*, products with *partly* altered side chain) was oxidised to the acids ($R·C_6H_4·CO_2H$) and the molecular composition of these was determined. The difference between this composition and the molecular composition of the acids obtained by oxidation of the initial nitration product (exclusive of acids formed during the nitration; see below) gave the molecular composition (which could not be determined directly) of the acids due to oxidation of the portion of the nitration product which was soluble in potassium iodide solution and therefore contained an unaltered hypobromite side chain. The acids formed during the nitration itself were separated initially by their solubility in potassium bicarbonate solution, and their molecular composition was determined directly. Migration during oxidation was prevented by prior treatment with alkali.

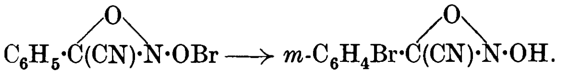
I. *Reactions of Phenylbromocyanonitromethane in Nitric Acid of Various Strengths and in Various Proportions.*

A. *In Kahlbaum's Nitric Acid* (d 1·52).—The nitromethane undergoes *m*-nitration (92—93%) and *p*(and *o* ?)-nitration (8—7%).

A large proportion of the *m*-nitrophenylbromocyanonitromethane was isolated in the pure state and analysed. The position of the nitro-group was proved by transformation into *m*-nitrobenzoyl cyanide and *m*-nitrobenzoic acid. That phenylbromocyanonitromethane and its *m*-nitro-derivative contain side chains having the same hypobromite constitution was shown by their giving the same reactions (see section V; p. 468). The composition of the remainder of the nitration product was ascertained by determining the percentages of the isomeric acids obtained by oxidation. The absence of benzoic acid proved that nitration was complete.

B. *In Nitric Acid* ($d^{15°}$ 1·480).—

(B1)



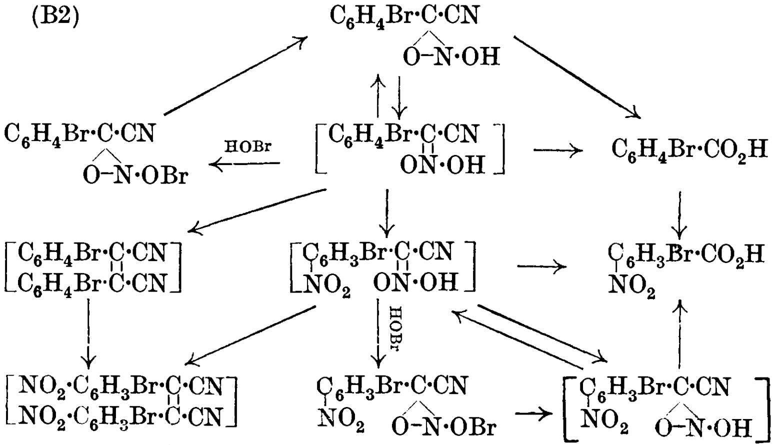
$$C_6H_5\cdot C(CN)\!\overset{O}{\frown}\!N\cdot OBr \longrightarrow m\text{-}C_6H_4Br\cdot C(CN)\!\overset{O}{\frown}\!N\cdot OH.$$

The transfer of bromine from the side chain to the *m*-position in the nucleus was quantitatively established by determining the bromine content of the acids obtained by oxidation, by isolating from these acids a large proportion of pure *m*-bromobenzoic acid, and by the fact that the portion of the nuclear bromo-compounds which had undergone nitration yielded, after oxidation, reduction, and bromination, nearly pure 2 : 4 : 6-tribromoaniline. That this transfer of bromine is an intramolecular migration—and not bromination of one molecule by another—follows from the observations that the rate of transfer is independent of concentration and is not affected by the addition of a substance containing a *m*-directing group. The latter fact was proved by adding to a solution of phenylbromocyanonitromethane in ether—in which also bromine was found to migrate—a large proportion of benzoyl cyanide. The migration of bromine, though slow, is the main change that occurs in nitric acid of *d* 1·480 : after 75 minutes, less than 3 mol.% had migrated; after 10 days, the nuclear bromine had increased to 54 mol.%.

The further changes undergone in nitric acid of *d* 1·480 by *m*-bromophenylcyanonitromethane (B2) and phenylbromocyanonitromethane (B3) are indicated in the following schemes.

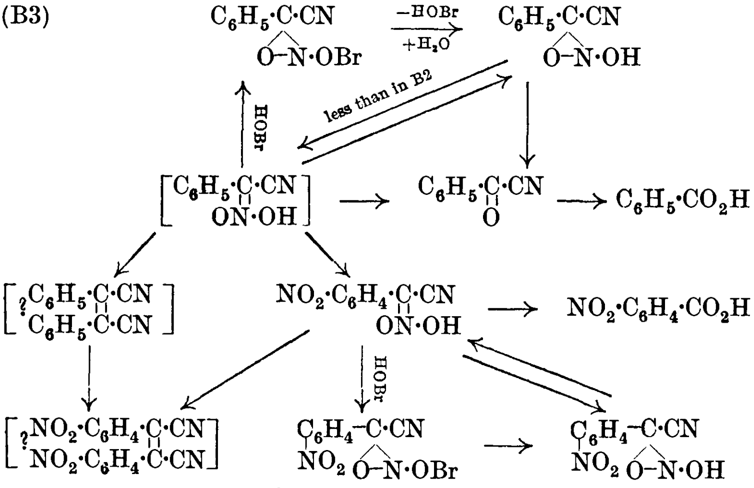
Names in square brackets denote products for the presence of which only indirect evidence was obtained.

(B2)



Br in position 3; NO_2 in position 4 (and 2?).

(B3)



NO$_2$ in position 4.

When *m*-nitration of phenylbromocyanonitromethane occurs, the *m*-nitro-derivative shows changes analogous to those given for the *p*-nitro-derivative in scheme B3.

The products represented in schemes B2 and B3 may be divided into three classes: (1) compounds with completely transformed side chain (benzoic acid and its nuclear-substituted derivatives); (2) compounds with intact side chain (phenylbromocyanonitromethane and its nuclear-substituted derivatives); and (3) compounds with partly transformed side chain (phenylcyanonitromethane, benzoyl cyanide, stilbene and their nuclear-substituted derivatives).

Transformation of the side chain to carboxyl does not—contrary to Baker and Ingold's indications—occur appreciably during the first few hours. At 13° and 15·5°, even after 6 days, only about 10% (by weight) of acids was formed. Compounds with a partly transformed side chain are, however, formed in a much higher proportion (see section IV, p. 465, Table I, for exact figures).

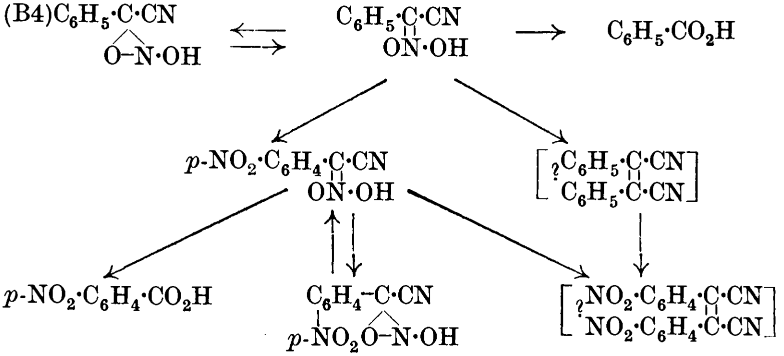
The nature of the partly transformed side chains. Benzoyl cyanide was detected by its unmistakable pungent odour.

The presence of phenylcyanonitromethane and its nuclear derivatives was conclusively established by the following facts: in some of the earlier experiments, the portion of the nitration product insoluble in potassium iodide solution was oxidised without precautions to prevent migration, and yielded many times more than the true amount of *p*-nitrobenzoic acid. This unique reaction (compare section IIIB; p. 464) leaves no doubt as to the presence of phenylcyanonitromethane. The presence of its nuclear derivatives follows from the proved presence of relatively large proportions of *m*-bromo-, *p*-nitro-, and 4-(2-)nitro-3-bromo-phenylbromocyanonitromethane among the compounds with an *unaltered* side chain after 6 days' nitration : the *m*-bromo- and 4-(2-)nitro-3-bromo-compounds can only arise from the lateral bromination of the initially produced corresponding compounds without side-chain bromine (compare formulæ B1; p. 457), and it is shown below that a similar explanation applies to the *p*-nitro-compound. Now we found that hypobromous acid reacts instantaneously with phenylcyano*iso*nitromethane to form phenylbromocyanonitromethane. Partial hydrolysis (see scheme B3; p. 458) of phenylbromocyanonitromethane to phenylcyanonitromethane in nitric acid of *d* 1·480 supplies hypobromous acid, which then combines with the *iso*-forms of phenylcyanonitromethane and of its nuclear derivatives.

Since the equilibrium between a nitro- and an *iso*nitro-form alters in favour of the latter with increasing "negative" substitution (Hantzsch), the proportion of *m*-nitrophenylcyanonitromethane finally present as hypobromite (*m*-nitrophenylbromocyanonitromethane) is found to be greater than for the un-nitrated compound. Similarly, for the *m*-bromo-derivative this proportion, after a 6 days' nitration, is found to be $\frac{1}{2}$ to $\frac{3}{4}$ as high as for the unsubstituted compound, notwithstanding that the latter was originally already present as hypobromite and the former was not. For the *p*-nitro-compound the final proportion of hypobromite is found to be higher than for the unsubstituted compound, although here again it cannot have been a hypobromite when first formed, as we shall now show.

Simple nitration of phenylbromocyanonitromethane (see A; p. 456) leads almost exclusively to the *m*-nitro-derivative. But in nitric acid of *d* 1·480 the *p*-nitro-compound predominates over the *m*-isomeride, at least when not more than 13 parts of acid are used. It follows that only a negligible portion of the *p*-compound can owe its production to nitration of phenylbromocyanonitromethane. Nor can the immediate hydrolytic product of phenylbromocyanonitromethane, *viz.*, phenylcyanonitromethane, account for *p*-nitration, because, whereas the concentration of this hydrolytic product increases as the reaction proceeds, the rate of *p*-nitration decreases. When, however, phenylcyano*iso*nitromethane in the nascent state is nitrated, whether by nitric acid of *d* 1·480 or of *d* 1·52 (*e.g.*, by nitrating its sodium salt), *p*-nitration occurs almost exclusively; a portion of the *p*-nitrophenylcyano*iso*nitromethane is then transformed into *p*-nitrobenzoic acid and the remainder isomerises to the "true" nitromethane (see p. 469) (and possibly some *pp'*-dinitrostilbene is formed; see below). And this is what also happens during the nitration of phenylbromocyanonitromethane—with the difference that the concentration of the *iso*-compound is relatively very low, and that hypobromous acid is present. The latter not only reacts with *p*-nitrophenylcyano*iso*nitromethane to form *p*-nitrophenylbromocyanonitromethane (compare above), but also, as it accumulates through the progressive initial hydrolysis of phenylbromocyanonitromethane, practically stops further *p*-nitration as a result of its exceedingly rapid reaction with the un-nitrated *iso*-compound. *m*-Bromophenylcyanonitromethane is similarly nitrated in its—somewhat more favoured—*iso*-form.

(B4)



The formation of the remainder of the compounds with a partly transformed side chain, *viz.*, stilbene and its nuclear-substituted derivatives (see schemes B2 and B3; pp. 457, 458), though not absolutely proved, is rendered probable by the following consideration :

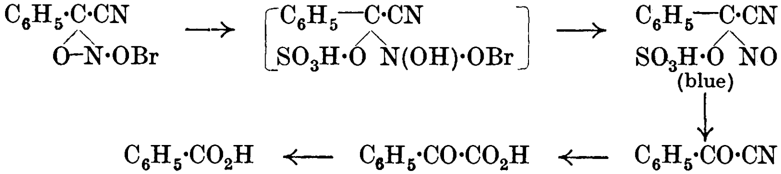
Wislicenus and Elvert (*Ber.*, 1908, **41**, 4126) found that *p*-bromophenylcyano*iso*nitromethane, by treatment with dilute sulphuric acid, yielded not only *p*-bromobenzoic acid but also *pp'*-dibromodicyanostilbene. (They also stated that concentrated mineral acids produce *p*-bromobenzoic acid, but apparently had not observed the characteristic blue colour reaction referred to below.) An indirect indication of the formation of stilbene derivatives was obtained in our case in the bromonitrophenyl series. These derivatives, after a 6 days' nitration, were found only or almost only amongst the acids and in the portion of the product insoluble in potassium iodide, the essential absence of the potassium iodide-soluble hypobromite, and therefore of the hydrolytic product in equilibrium therewith, thus being indicated. Moreover, the benzoyl cyanide of the series could hardly have survived, since we found that nitrobenzoyl cyanides are hydrolysed with extreme ease. Barring these normal constituents of a product insoluble in potassium iodide, there remained only the corresponding stilbene as a probable main constituent.

The mode of formation of the compounds with completely transformed side chains (*acids*). The above nitrations of *iso*-compounds show that, of each acid produced during the nitration of phenylbromocyanonitromethane, a portion must originate directly from the *corresponding iso*nitro-compound. That the *p*-nitro-acid is not formed by some reaction of the *iso*nitro-group *prior* to nitration follows from the consideration that the intermediate products of such reaction, benzoylformic and benzoic acids and, as we have ascertained, benzoyl cyanide also, would be nitrated chiefly in the *m*-position in so far as they were nitrated at all, and that some of the *p*-nitro-product always retains its side chain with the original nitro-group. In the case of bromonitrobenzoic acid, a second portion is derived from the nitration of *m*-bromobenzoic acid, since we have found that this acid is slowly nitrated in 86% nitric acid. The remaining portions of each acid are formed from the corresponding "true" nitrocyano-compounds (in their bridge form). This follows from the fact that the nitration of phenylbromocyanonitromethane produces much more benzoic acid than *p*-nitrobenzoic acid; since we found that the reverse held when phenylcyano*iso*nitromethane was nitrated, the excess of benzoic acid beyond what is attributable to the *iso*-form must arise from the "true" nitro-compound. This is confirmed by the analogous—but much quicker—action of concentrated sulphuric acid (I, 7 and 8; p. 455) on the bridge in phenylbromocyanonitromethane; here the expected intermediate nitroso-derivative (which can also isomerise to the hydroxamic acid in the case of primary nitro-compounds) attains such a concentration that it can be detected by its intense blue colour (see formulæ, section II; p. 462).

The *kinetics* of the process, for a given temperature, expressed by the molecular percentage yields obtained with various times and concentrations (section IV; p. 466), agree with the above considerations. Only approximate kinetic calculations are, of course, possible in this complicated case, but the ratio, for instance, of *p*-nitrophenyl produced to the mean of the unsubstituted phenyl initially and finally present shows a definite increase with increasing relative volume of acid; obviously because the rate of nitration of the *iso*nitro-compounds remains unaffected, whereas the competing recombination with hypobromous acid is retarded. At the same time the ratio of total *m*-bromination to average phenyl present remains constant (unimolecular change). The rate of decrease of side-chain bromine, as indicated by titrations with potassium iodide, after the first until the sixth day is much slower than the kinetics of the bromine-migration would require; it is explained by the formation of *m*-bromophenylbromocyanonitromethane from the corresponding *iso*nitro-compound and hypobromous acid.

II. *Reactions in Concentrated Sulphuric Acid.*

(1) Phenylbromocyanonitromethane :



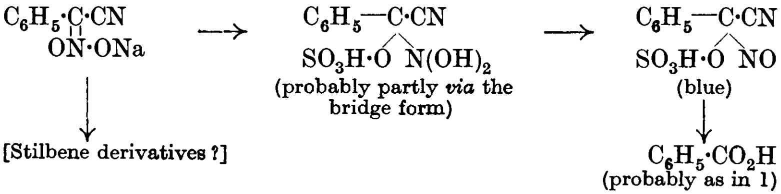
$$C_6H_5\cdot\overset{\displaystyle C\cdot CN}{} \; O{-}N\cdot OBr \longrightarrow \left[C_6H_5{-}C\cdot CN \;\; SO_3H\cdot O\;\; N(OH)\cdot OBr\right] \longrightarrow C_6H_5{-}C\cdot CN \;\; SO_3H\cdot O\;\; NO$$

(blue)

$$C_6H_5\cdot CO_2H \longleftarrow C_6H_5\cdot CO\cdot CO_2H \longleftarrow C_6H_5\cdot CO\cdot CN$$

(2) *m*-Nitrophenylbromocyanonitromethane: Reactions analogous to those in (1).

(3) Phenylcyano*iso*nitromethane (sodium derivative) :



$$C_6H_5\cdot C\cdot CN \;\; ON\cdot ONa \longrightarrow C_6H_5{-}C\cdot CN \;\; SO_3H\cdot O\;\; N(OH)_2 \longrightarrow C_6H_5{-}C\cdot CN \;\; SO_3H\cdot O\;\; NO \longrightarrow C_6H_5\cdot CO_2H$$

(probably partly *via* the bridge form)

(blue)

[Stilbene derivatives ?]

(probably as in 1)

The formation of a nitroso-compound in all three cases was indicated by the production of a blue colour. Benzoyl cyanide was identified in (1) by its odour. Benzoic acid was isolated in (1) and (3), and *m*-nitrophenylglyoxylic acid in (2). The latter compound (m. p. 144·5—145°) was also obtained from *m*-nitrobenzoyl cyanide by treatment with cold concentrated hydrochloric acid, and its nature confirmed by analysis and the thiophen test. The acid, m. p. 77—78° (after softening at 65°), described in Beilstein's " Organische Chemie " as *m*-nitrophenylglyoxylic acid must therefore, to say the least, have been very impure.

III. *Re-arrangements produced by Heating.*

A. *Re-arrangements by Dry Heating.*—(1) Phenylbromocyanonitromethane gives bromine, nitric oxide, benzoyl cyanide (92 mol.% found; more than 72 mol.% isolated) and *p*-nitrobenzoyl cyanide (8 mol.% found; 7·5 mol.% isolated).

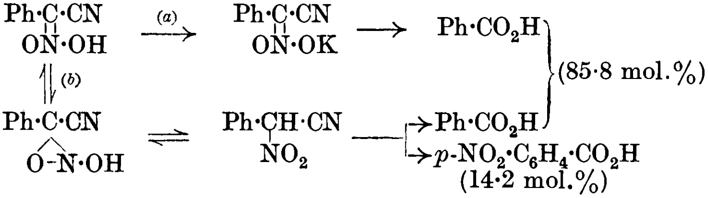
(2) *m* - Nitrophenylbromocyanonitromethane gives *m* - nitrobenzoyl cyanide (93·5 mol.% isolated) and a brominated mixture (8% of the weight of *m*-nitrophenylbromocyanonitromethane used).

When phenylbromocyanonitromethane was prepared for the first time (by one of us, *loc. cit.*), its decomposition by heat, and two substances produced thereby, were described. One of these substances was later identified by Wislicenus and Schäfer (*Ber.*, 1908, **41**, 4169) as benzoyl cyanide. They isolated the other, still impure and not analysed, in a yield of 1·6 mol.%, and hydrolysed it to *p*-nitrobenzoic acid; they thought it "might possibly be *p*-nitrobenzoyl cyanide." We have now isolated it in a yield of 7·5 mol.% and proved it to be *p*-nitrobenzoyl cyanide by obtaining a constant melting point agreeing with Zimmermann's (*J. pr. Chem.*, 1902, **66**, 353) and by analysis. Since the total migration of NO_2, determined by oxidation, exceeded this 7·5 mol.% by only 0·5 mol.%, *o*-migration must be negligible.

m-Nitrobenzoyl cyanide, similarly obtained from *m*-nitrophenylbromocyanonitromethane, was identified by its properties, by analysis, and by hydrolysis to *m*-nitrobenzoic acid.

B. *Re-arrangements by Heating with an Oxidising Agent in Aqueous Solution.*—(a) *With permanganate.*

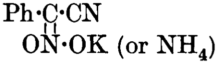
(1)



$$\underset{\mathrm{ON\cdot OH}}{\mathrm{Ph\cdot C\cdot CN}} \xrightarrow{(a)} \underset{\mathrm{ON\cdot OK}}{\mathrm{Ph\cdot C\cdot CN}} \longrightarrow \mathrm{Ph\cdot CO_2H}$$

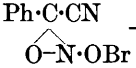
$$\underset{\mathrm{O{-}N\cdot OH}}{\mathrm{Ph\cdot C\cdot CN}} \rightleftharpoons \underset{\mathrm{NO_2}}{\mathrm{Ph\cdot CH\cdot CN}} \longrightarrow \mathrm{Ph\cdot CO_2H}\ (85{\cdot}8\ \text{mol.\%});\ \longrightarrow p\text{-}\mathrm{NO_2\cdot C_6H_4\cdot CO_2H}\ (14{\cdot}2\ \text{mol.\%})$$

(2)



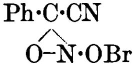
$\underset{\mathrm{ON\cdot OK}}{\mathrm{Ph\cdot C\cdot CN}}$ (or NH_4) $\longrightarrow$ Ph·CO_2H; $\longrightarrow$ hydrolysis, then reactions as in 1*b* (mol.% of *p*-nitro-acid = 2·8 for NH_4-salt and 0·1 for K-salt).

(3)



$\underset{\mathrm{O{-}N\cdot OBr}}{\mathrm{Ph\cdot C\cdot CN}} \longrightarrow$ *p*-NO_2·C_6H_4·CO_2H (12·5 mol.%) + Ph·CO_2H (87·5 mol. %).
= 30% thermal decomposition, yielding 8 mol.% of *p*-nitro-compound (see III A1; p. 462), + 70% hydrolysis, yielding 14·2 mol.% of *p*-nitro-compound (see 1*b* above).

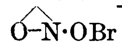
(4)



$\underset{\mathrm{O{-}N\cdot OBr}}{\mathrm{Ph\cdot C\cdot CN}}$ in presence of 0·93 times its weight of Ph·CO·CN, whereby reaction 1*a* (above) is retarded, but 1*b* is unaffected, $\longrightarrow$ *p*-NO_2·C_6H_4·CO_2H (21·5 mol.%) + Ph·CO_2H (78·5 mol.%).

(b) *With nitric acid*, d 1·125.

(5)



$\underset{\mathrm{O{-}N\cdot OBr}}{\mathrm{Ph\cdot C\cdot CN}} \longrightarrow$ *p*-NO_2·C_6H_4·CO_2H (11—12 mol.%) + Ph·CO_2H (89—88 mol.%), which corresponds to about half hydrolysis (III B1, above) and half thermal decomposition (III A1; p. 462).

The scheme for III B1 (p. 463) is proved by the fact that hardly any migration occurs when the potassium salt of phenylcyano*iso*-nitromethane is oxidised (III B2). The *iso*nitro-group is stabilised in the order $\colon NO{\cdot}OK > \colon NO{\cdot}ONH_4 > \colon NO{\cdot}OH$, so that *p*-migration is observed in the inverse order. In a substance containing the group $\colon NO{\cdot}OK$ hardly any migration occurs, and in agreement with this we found that such a substance was only very slightly hydrolysed in aqueous solution. III B3 follows immediately, and III B5 approximately, from III A1 (p. 462) and III B1. An admixture of an alkali-insoluble material, as in III B4, hinders the transformation of phenylbromocyanonitromethane into the potassium salt and therefore favours *p*-migration. This explains why, when phenylbromocyanonitromethane in presence of the only partly alkali-insoluble products of its reaction with 86% nitric acid is heated with permanganate (without first converting it into the potassium salt), much more *p*-nitrobenzoic acid is found than in III B3. And when —as in the 1902 experiment of one of us—such heating is carried out after a nitration of brief duration, then, apart from traces of *m*-bromo- and (possibly) *o*-nitro-benzoic acid too small for detection by separation, only *p*-nitrobenzoic and benzoic acids can be found—exactly as one of us had recorded (*loc. cit.*).

Although this migration of a nitro-group during a permanganate oxidation appears to be unique, it is quite intelligible, since it occurs in the following phases : (1) (in the case of phenylbromocyanonitromethane) Hydrolysis to phenylcyanonitromethane, with participation of the aqueous permanganate solution. (2) Decomposition and re-arrangement of that portion of the phenylcyanonitromethane which does *not* go into solution as *iso*-ion. This decomposition and re-arrangement occur in the suspended oil *without* participation of the aqueous permanganate solution. (3) Oxidation of the products of re-arrangement and decomposition, with participation of the permanganate solution.

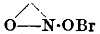
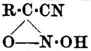
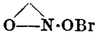
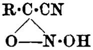
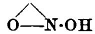
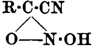
It should further be pointed out that in oxidation method A (see Experimental, p. 471), which produces re-arrangement, boiling is carried out with solutions of alkali of a somewhat higher concentration than in method C (p. 471), which precludes re-arrangement; only the *initial* heating to the boiling point is performed in the presence of alkali in the one case and in its absence in the other. It is therefore not possible to argue that the *p*-nitrobenzoic acid obtained by method A is derived from a *p*-nitro-derivative originally present and that this derivative, if treated as in method C, would be destroyed by the alkali. Quite apart from this, alkali has no such effect under our conditions, as is shown by the identical yields obtained in the oxidation of *p*-nitrobenzaldehyde with and without alkali (Experimental, III 8 g; p. 481). Further, the facts that the oxidation of phenylcyanonitromethane and of its *iso*ammonium salt, each in the *absence* of added alkali, yields 14·2 mol.% of *p*-nitrobenzoic acid in the former case but only 2·8 mol.% in the latter, and that in the complete nitrations (acid of *d* 1·52) No. 17 (oxidation by method A) and No. 18 (oxidation by method C) identical yields of *p*-nitrobenzoic acid are obtained (no re-arrangement being possible in the absence of un-nitrated product), show conclusively that the portion of the *p*-nitrobenzoic acid produced by method A, but not produced by method C, can only arise by a re-arrangement.

IV. *Nuclear and Lateral (Side-chain) Changes during Nitration, expressed as Molecular Percentages.*

PBCN denotes phenylbromocyanonitromethane. The nitration numbers in Table I refer to the corresponding numbers in Table II.

TABLE I.

Lateral decomposition, mol.%.

Substance.	Products of nitration.	R = *m*-C_6H_4Br.	NO_2-*m*-C_6H_3Br.	*p*-(*o*-) $C_6H_4{\cdot}NO_2$.	*m*-$C_6H_4{\cdot}NO_2$.	C_6H_5.	Total.
1. PBCN (nitration No. 10) :							
KHCO$_3$-soluble :	$R{\cdot}CO_2H$	3·70	0·95	1·61	0·85	8·69	15·80
KI-soluble :		10·79	0	2·32	3·39	23·38*	39·88
Insoluble	 $R{\cdot}CO{\cdot}CN$ $[R{\cdot}C(CN){:}]_2$	14·09	8·25	0·90	0·68	20·40	44·32
2. PBCN (nitration No. 11) :							
KHCO$_3$-soluble :	$R{\cdot}CO_2H$	3·49	0·84	1·34	0·69	7·74	14·10
KI-soluble :		8·72	1·07	1·99	3·48	23·42*	38·68
Insoluble	 $R{\cdot}CO{\cdot}CN$ $[R{\cdot}C(CN){:}]_2$	19·81	8·24	1·15	0·79	17·23	47·22
3. $C_6H_5{\cdot}C(CN){:}NO{\cdot}ONa$ (nitration No. 22) :							
KHCO$_3$-soluble :	$R{\cdot}CO_2H$	—	—	8·80	0·03	0·84	9·67
KHCO$_3$-insoluble	 $R{\cdot}CO{\cdot}CN$ $[R{\cdot}C(CN){:}]_2$	—	—	80·93	4·05	5·35	90·33
4. $C_6H_5{\cdot}C(CN){:}NO{\cdot}ONa$ (nitrations Nos. 23, 24) :							
KHCO$_3$-soluble :	$R{\cdot}CO_2H$	—	—	14·34	0·04	1·36	15·74
KOH-soluble less KHCO$_3$-soluble		—	—	61·55	0·39	7·94	69·88
Insoluble	$R{\cdot}CO{\cdot}CN$ $[R{\cdot}C(CN){:}]_2$	—	—	4·23	0·09	10·06	14·38

* Original substance.

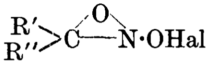
TABLE II.

Nitration No.	Parts of acid and density.	Temp. and time.	Nuclear substitution, mol. %. Unsubstit.	m-Br.	Nitro-m-Br.	p(o-)-NO_2.	m-NO_2.
(1) PBCN.							
1, 2	52; 1·480	15°; 15 mins.	94·0	2·4	3·4		0·2
3, 4	13 „	15°; 75 „	93·55	3·35	2·75		0·35
5, 6	52 „	15°; 75 „	93·7	3·7	3·45		0·4
7	13 „	13°; 24 hrs.	72·75	16·45	4·45	4·45	1·9
8	13 „	room; 24 „	73·6	17·05	4·4	4·45*	0·5
9	52 „	12·6°; 24 „	62·45	15·25	4·1	5·35	12·85
10	13 „	13°; 6 days	52·5	28·85	8·95	4·8	4·9
11	13 „	15·5°; 6 „	48·4	32·0	10·15	4·5	4·95
12	8 „	room; 10 „	45·0	34·65	15·25	3·8	1·3
13	8 „	„ „	41·95	53·65		3·8*	0·6
14	13 „	„ „	37·4	34·9	19·25	5·1	3·35
15	13 „	„ „	37·55	36·35	17·35	5·1*	3·65
16	52; 1·4805	12·6°; 24 hrs.	43·95	14·4	3·4	4·95	33·3
17	8; 1·52	15°; 15 mins.	0	0	7·15		92·85
18	8; 1·52	−10°; 1 hr., then room; 15 mins.	0	0	8·0		92·0
19	8; 1·500	15°; 2 hrs.	38·45		5·75		55·8
20	8; 1·490	Baker and Ingold's	96·7		1·65		1·65
21	8; 1·490	„ „	96·35		1·60		2·05
(2) $C_6H_5\cdot C(CN){:}NO\cdot ONa$.							
22	8; 1·52	−10°; 1 hr., then room; 15 mins.	6·2	—	—	89·7	4·1
23	17·4; 1·480	+14°; 60 „	19·35	—	—	80·1	0·55
24	13; 1·480	+15°; 60 „	19·45	—	—	80·0	0·55
(3) $C_6H_5\cdot CO\cdot CN$.							
25	13; 1·480	−10°; 1 hr., then room; 15 mins.	99·9	—	—	0	0·1
26	8; 1·52	−10°; 1 hr., then room; 1 hr.	19·2	—	—	10·0	70·8
(4) m-$C_6H_4Br\cdot CO_2H$.			Unchanged.			Nitrated in p(o).	m.
27	148; 1·480	16·2°; 7 days	0	—	—	96·2	3·8
28	119 „	room; 5 weeks	0	—	—	95·6	4·4
29	148 „	16·2°; 24 hrs.	48·9	—	—	49·1	2·0

The corresponding yields by weight, together with explanatory remarks, will be found in the experimental part.

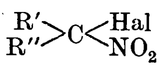
V. *The Constitution of Phenylbromocyanonitromethane and Other Acylmethyl Halides.*

The surprising reactivity of bromine in bromomalonic esters, compared with bromonitroacetic esters, led Willstätter and Hottenroth (*Ber.*, 1904, **37**, 1775) to propose formula (I) for the halides of secondary nitro-compounds and (III) for polynitro-compounds, (II; $R'' = H$) being retained for the halides of primary nitro-compounds.



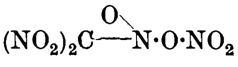
$\begin{matrix}R'\\R''\end{matrix}{>}C\overset{O}{\text{—}}N\cdot OHal$

(I.)



$\begin{matrix}R'\\R''\end{matrix}{>}C{<}\begin{matrix}Hal\\NO_2\end{matrix}$

(II.)



$(NO_2)_2C\overset{O}{\text{—}}N\cdot O\cdot NO_2$

(III.)

(IV.) $(NO_2)_3C\cdot O\cdot NO$

$C(NO_2)_4$ (V.)

Schmidt (*Ber.*, 1919, **52**, 402) then substituted for (III) an equilibrium formula (III $\rightleftharpoons$ IV), but later (with Ascherl and Knilling, *Ber.*, 1926, **59**, 1876) reverted to (V) for polynitro-compounds and to (II) for all halogenonitro-compounds, following their discovery that methyl hypobromite is added to *cyclo*hexene in methyl-alcoholic solutions, not only of brominated secondary nitro-compounds, but also of tribromophenol bromide, etc., and that in particular dibromo- and bromonitro-malonic esters behave similarly. Now this similarity ("gleichartiges Verhalten") was found in the fact that, *ceteris paribus*, the dibromo-ester gave 11·2% of hypobromite addition in 72 hours, whereas the bromonitro-ester gave 78·8% in 24 hours (thus reacting, roughly, at a fifty times higher bimolecular rate). Assuming, however, that in spite of such differences these authors' uniform formulation of all the compounds was justified, then they would all be *O*-bromides (hypobromites), since for one of them, tribromophenol bromide, this constitution may now be regarded as definitely proved (compare Lauer, *J. Amer. Chem. Soc.*, 1926, **48**, 442); a conclusion which would be extremely improbable in the case of, *e.g.*, dibromomalonic ester.

Willstätter and Hottenroth thought that *both* forms of bromonitromalonic esters might be accessible. We suggest that sometimes only the *C*-bromide may be stable, sometimes only the hypobromite form; in other cases both forms may exist in appreciable quantities in equilibrium—the relative stability of either being determined by the usual three factors (*p*, *q*, and *s*; compare previous papers). *Ceteris paribus*, *C*-Hal and *C*-NO_2 are much more stable than *O*-Hal and *O*-NO_2 (*p*). "Negative" substitution of *C* reduces this advantage (*p*), in the order $NO_2 > CN > CO$. Steric obstruction at *C* (*e.g.*, by C_6H_5) also reduces it (*s*). But if these effects happen to coincide with the possibility of a better affinity exchange in the *O*-form (*q*), then the resulting advantage may be more or less completely shifted to the *O*-form. For instance, the *O*-form of tribromophenol bromide, being benzenoid, has a better affinity exchange than the quinonoid isomeride. Conversely, transition of dibromomalonic ester into its *O*-form produces, in an ethylenic bond, a new centre of unsaturation. In a bromonitro-compound, however, a "double" bond is obviated in the *O*-form by means of an oxygen bridge. Similar considerations apply, *mutatis mutandis*, to transitions of the ketonic into the enolic forms of the corresponding hydrogen compounds. This may explain the observation of Thorpe and his co-workers (J., 1921, **119**, 1203; 1922, **121**, 1898), that from a *C*-bromide a hypobromite reaction was obtained in proportion to the tendency towards tautomerism exhibited by the corresponding hydrogen compound.* Examining the results of Schmidt's experiments,† we found that the hypobromites (*e.g.*, tribromophenol bromide, bromonitromalonic ester) reacted most quickly, *C*-bromides incapable of tautomerism (*e.g.*, carbon tetrabromide, tribromoacetic ester) did not react, and other *C*-bromides reacted at relative rates parallel to the relative rates of partial transition into hypobromites which the considerations we have outlined would lead one to expect. In Willstätter and Hottenroth's case, a solution of bromonitroacetic ester should contain, not form (II) only as they assume, but both *C*- and *O*-forms. We find that their own experiments confirm this view. Whereas one of their comparative tests—substitution of hydrogen for bromine by means of dry ammonia or amines—was not conclusive, similar abnormal reduction by potassium iodide took place not only with bromonitromalonic, but also with bromonitroacetic ester; completely with the former (*O*-bromide), but only partly with the latter (*O*- + *C*-bromides).

We have applied Willstätter's tests to phenylbromocyanonitromethane and its *m*-nitro-derivative, in both of which dry ammonia rapidly and completely replaces bromine by hydrogen. *m*-Nitrophenylbromocyanonitromethane, a well-defined crystalline material, can, as such, be a hypobromite *only*. Semi-quantitative measurements of the rate of reduction of phenylbromocyanonitromethane, an oil, prove that it also consists of only one form, unless the rate of isomerisation of any *C*-bromide present were almost infinitely greater than Schmidt's and Willstätter's experiments indicate. Both compounds are also—instantaneously and quantitatively—reduced by potassium iodide. For comparison, an undoubted *C*-bromide of perfectly analogous composition, *viz.*, phenylbromomalonic ester, was examined. It gave a measurable reaction neither with ammonia nor with potassium iodide, thus placing the hypobromite structure of phenylbromocyanonitromethane beyond doubt. By heating with aniline, bromine was slowly replaced, the

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* Several authors have failed to distinguish between the *abnormal* reduction of halogen compounds (by alkali iodides, amines, etc.), and *normal* reactions, such as their reduction by ordinary reducing agents (hydriodic acid, hydrazine, etc.) or the replacement by hydrogen of CO_2R, CO_2H, or CN (*via* CO_2H). Although in the latter replacements *reactivity* depends on the same three factors, the *nature* of the reactions is normal, carbonate being normally formed in preference to formate. Accordingly they can occur when not only these groups, but also the hydrogen which replaces them, is incapable of tautomeric migration (*e.g.*, elimination of carbonic acid from 2 : 4 : 6-trinitrobenzoic acid by mere boiling with water).

† Schmidt and his co-workers have recognised the existence of a hydrolytic equilibrium, but their formulation of it, *e.g.*, (in alcohol) $(NO_2)_3CBr + ROH \rightleftharpoons (NO_2)_3CH + ROBr$, is inadequate, since it ignores the real reactants on either side—the bridged *O*-bromide and the *iso*nitro-compound.

ratio of bromide to hypobromite reaction being about 6 : 1. Taking into account the much greater reactivity of the *O*-bromide, it is again obvious that its concentration in equilibrium with the *C*-bromide must be exceedingly small.

Our finding that the " true " form of phenylcyanonitromethane, for which we postulate an equilibrium between the usual nitro- and the bridge formulation, can change to benzoic acid without passing through the *iso*nitro-form supports our conception of the presence of a bridged constituent. More conclusive proof which we have obtained will be presented in connexion with other work.*

VI. *Interpretation by Theories of Aromatic Substitution.*

The transformation of phenylbromocyanonitromethane into its *m*-bromo-isomeride constitutes, we believe, the first proved case of *intramolecular m*-migration of a lateral *substituent.* It makes it probable that the change of benzoyl nitrate into *m*-nitrobenzoic acid observed by Francis (*Ber.*, 1906, **39**, 3798) and of tribromophenol bromide into tetrabromophenol (Benedikt, *Annalen*, 1879, **199**, 132) are also intramolecular and, together with the almost exclusive extramolecular *m*-nitration of phenylbromocyanonitromethane, proves that the law governing direct and indirect *m*-substitution is the same—just as one and the same law has long been known to apply to direct and indirect substitution in the *o*- and *p*-positions. *m*-Substitution in these cases agrees with our theory of affinity distribution, as well as with Robinson's electronic theory; with the former because of the postulated inversion of the directive effect of methyl through the affinity demand of tervalent nitrogen; and with the latter in view of the postulated electron shift toward the " negative " groups.

Again, the essentially exclusive *p*-substitution of phenylcyano-*iso*nitromethane follows, according to our theory, from the greatly enhanced residual affinity of the methyl carbon. It can also be reconciled with Robinson's views on the assumption that nitration (even with acid of *d* 1·52) occurs essentially only in a—temporary—conjugated phase, and not in the—relatively permanent—normal phase in which the electron shift would cause *m*-substitution as above.

Lastly, several mechanisms in accordance with either theory can be devised for the partial oxidation of phenylcyanonitromethane to

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* Branch and Jaxon-Deelman (*J. Amer. Chem. Soc.*, 1927, **49**, 1765) allot the bridge form to the *iso*nitro-compound, and the nitronic formula to its salt (ion). In Part X of this series we shall give definite experimental proof that this view is untenable, and shall show that these authors' experiments afford valuable proof for our own formulation.

p-nitrobenzoic acid and for the partial thermal decomposition of phenylbromocyanonitromethane into *p*-nitrobenzoyl cyanide; but none can be proved at present.

EXPERIMENTAL.

In the first series of nitrations, the old tedious method of separating the acids by fractional crystallisation was used. When it was found that bromo- and nitrobromo-acids were present, and that these precluded strictly quantitative separations, our new method was evolved and applied in a further series of nitrations. Then the unexpected discovery that oxidation was accompanied by further *p*-nitration made it necessary to repeat all the nitrations and oxidise the products by a new method, so that altogether 61 nitrations and separations were carried out. We shall—apart from a few special cases—confine ourselves to recording *full* data of the final series only.

I. *Methods.*—(1) *Preparation of phenylbromocyanonitromethane.* (a) To an ice-cooled solution of sodium phenylcyano*iso*nitromethane (1 part) in water (5—6 parts), bromine (0·86 part; 0·99 equiv.) in saturated, ice-cooled aqueous solution was added all at once, with stirring. Average yield = 1·275 parts of phenylbromocyanonitromethane = 97 mol.%.

(b) To the salt (1 part) in water (20 parts), bromine (0·7 part; 0·8 equiv.) in water (70 parts) was added at 0° during 45 minutes with mechanical stirring.

(c) With hypobromous acid: To the salt (3·68 parts) in water (100 parts), a solution of potassium hydroxide (2·24 parts) and bromine (3·20 parts) in water (180 parts) was added at 0°, followed rapidly, with mechanical stirring, by concentrated sulphuric acid (1·96 parts) in water (50 parts). Yield 4·43 parts of phenylbromocyanonitromethane = 92 mol.%.

In all cases the precipitated oil was extracted with pure ether, and the dried ethereal solution evaporated without heating. Beyond variations in the yellow colour, no differences could be detected between these different preparations, but method (A) was used throughout, except for nitration No. 18, where method (C) was employed. An attempt to prepare phenylbromocyanonitromethane from the free *iso*nitro-compound by adding, at 0° and with good stirring, 0·367 g. of 10% sulphuric acid to 1·38 g. of the salt in 138 c.c. of water, and then at once, to the still clear solution, 120 c.c. of 1% aqueous bromine, yielded a product containing only 27·4% of bromine instead of 33·2%.

(2) *Nitration.* During addition of phenylbromocyanonitromethane to the nitric acid the temperature was not allowed to rise more than 1°. The mixture was poured on 270 parts of chopped

ice per part of phenylbromocyanonitromethane used and was extracted with 54 parts, then again with 27 parts, of pure ether, and the extract was washed four times with 18 parts of water—or, where the acids were extracted, only twice with water and twice with an excess of concentrated aqueous potassium bicarbonate—then at once dried and evaporated at the ordinary temperature.

(3) *Determination of bromine.* (a) In the side chain: 1 Part of nitrated oil in 20 parts of benzene was shaken with 4 parts of potassium iodide in 20 parts of water and immediately titrated with *N*/10-thiosulphate, starch being added when the solution had become very light brown, and the mixture being well shaken during titration. With pure phenylbromocyanonitromethane and *m*-nitrophenylbromocyanonitromethane there was no need to dissolve the product in benzene before treatment. (b) In the nucleus: In the acids obtained by oxidation, bromine was determined by the Carius method.

(4) *Oxidation.* Method A: 1 Part of the nitrated material was heated with 1·13 parts of permanganate in 34 parts of water; as soon as the mixture boiled, 0·38 part of caustic soda in 9·5 parts of water was added. On decolorisation, further permanganate was added in lots of 0·38 part until the colour persisted after 3 hours' boiling.

Method B: 1 Part of the nitrated material was treated on a shaking machine with 7·76 parts of 10% aqueous caustic potash and 7·76 parts of water for 1 hour, and then, after dilution to 120 parts, boiled with 2 parts of permanganate. The end-point was reached as in method A.

Method C: Exactly as B, except that shaking was continued for 3 hours.

Method D: The same, but with 6 hours' shaking.

Throughout, the acids were brought to constant weight at 50°.

(5) *Determination of the different nitro-acids.* The method we have evolved is so simple, accurate, and of such general applicability that we describe it in a separate communication (Part VI; preceding paper). Here it suffices to say that benzoic and *m*-bromobenzoic acids are together recovered as such (see Part VI for calculation of their molecular percentages); that *p*- and *o*-nitrobenzoic acids are together weighed as 2 : 4 : 6-tribromoaniline, and *m*-nitrobenzoic acid as 2 : 4 : 6-tribromo-3-aminobenzoic acid, whereas 4-(and/or 2-)nitro-3-bromobenzoic acid is weighed as tribromoaniline derived from a separate fraction.

II. *Results of the Nitrations.*—Table III contains the actual weighings in connexion with all nitrations where oxidation was carried out by a method precluding re-arrangement. This applies to all oxidations by methods C and D, also by method B when applied to 10-day nitrations (where little material capable of rearrangement survived), and by method A in the case of complete nitration. Beside these, nitrations 4, 8, 13, and 15, where oxidation involved some, but relatively little, migration, have been included for comparison; the corresponding yields of tribromoaniline (marked with asterisks), when compared, respectively, with those of Nos. 3, 7, 12, and 14, show the amount of migration during oxidation. In Table II, the corresponding figures with asterisks represent the *true* molecular *p*(*o*)-nitration as determined by Nos. 7, 12, and 14, respectively, and have been used in calculating the remaining molecular yields in Nos. 8, 13, and 15. A bar in the tables signifies that a determination was not carried out. The experimental conditions for each nitration in Table III are to be found under the corresponding numbers in Table II.

The recovery of material after nitration was practically quantitative throughout; but since the time during which the viscous oils produced from phenylbromocyanonitromethane by treatment with nitric acid of *d* 1·480 could be kept in a vacuum desiccator was limited by their tendency to lateral decomposition, traces of ether were sometimes retained, and therefore the potassium iodide determinations of lateral bromine in the nitration products are only approximately quantitative; all other determinations are unaffected, since they depend only on the acids.

The purity of the compounds obtained by reduction and bromination of the acids was always checked by melting- and " mixed " melting-point determinations. For tribromoaniline from *p*(*o*)-nitrobenzoic acid, melting points ranged between 113—117° and 118—119° (m. p. of pure substance, 119—120°); for tribromoaniline from bromonitrobenzoic acid, between 105—110° and 114 to 117°; and for tribromoaminobenzoic acid (when more than traces were obtained), between 164—167° and 170—171° (m. p. of pure acid, 170·5°). The m. p. of the benzoic acid naturally varied with its content of bromobenzoic acid; for example, in No. 4 (brief nitration) the acid melted at 117—119° (m. p. of pure acid, 121°).

The percentages of nuclear bromine for Nos. 1 and 5 were obtained, respectively, from duplicate nitrations 2 and 6.

In No. 17, 5·300 g. of pure *m*-nitrophenylbromocyanonitromethane were first separated by recrystallisation of the solid portion (9·063 g.) of the nitration product, and corresponding fractions of the oily portion (0·669 g.) and the material from the mother-liquors were then oxidised together. In a duplicate nitration, 0·400 g. of oil and 3·856 g. of solid (m. p. 67—69°) were obtained, yielding 2·086 g. of pure *m*-nitrophenylbromocyanonitromethane. From the

TABLE III.

							Reduction and bromination of acids.						
								Found (g.).					
Nitration No.	Material used (g.).	Yield (g.).	Acids extracted by $KHCO_3$.	Oxidised (g.).	Yield of acids (g.).	Br in acids (%).	Used (g.).	Benzoic + bromobenzoic acids.	Tribromoaniline from *p*(*o*)-nitro-acid.	Tribromo-*m*-aminobenzoic acid.	Tribromoaniline from nitrobromobenzoic acid.	Lateral Br in nitration product (% of theory by weight).	Oxidation method.
1. PBCN.													
1, 2	5·567	5·501	—	4·033	1·970	1·58	1·000	0·901	0·092	0·006	—	94·1	C
3	6·792	6·801	—	6·142	2·941	2·28	1·000	0·915	0·073	0·015	—	94·8	D
4	11·770	11·809	—	10·410	5·061	2·02	1·500	1·340	0·254*	0·007	—	90·7	B
							1·000	0·880	0·155*	0·005	—		
5, 6	5·260	5·140	+ 0·017	4·477	2·212	2·4	1·000	0·905	0·085	0·020	0·006	92·4	C
7	6·500	6·329	+ 0·149	5·448	2·889	11·69	1·000	0·818	0·102	0·044	0·103	69·0	D
8	8·232	8·284	—	7·681	4·146	11·97; N = 1·18	1·000	0·703	0·162*	0·012	0·101	62·0	B
9	5·322	5·334	+ 0·044	4·624	2·554	10·5	1·000	0·685	0·120	0·325	0·092	64·1	C
10	8·310	7·201	+	3·037	1·820	19·51	0·500	0·350	0·039	0·056	0·097	46·7	D
			0·811	—	—	15·2	0·554	0·373	0·120	0·072	0·071	0	—
11	9·130	7·878	+	2·365	1·485	21·29	1·000	0·773	0·073	0·112	0·216	44·9	C
			0·812	—	—	15·8	0·500	0·344	0·101	0·059	0·063	0	—
12	6·189	5·883	—	4·160	2·514	23·4; N = 2·04	1·000	0·713	0·075	0·030	0·301	31·8	B
							0·800	—	0·058	0·021	0·231		
13	2·521	2·403	—	1·927	1·107	25·4; N = 2·04	0·465	0·390	0·088*	0·006	—	—	A
14	6·070	5·500	—	4·924	2·983	24·8; N = 2·5	0·900	0·524	0·086	0·064	0·326	23·6	B
15	9·800	9·091	—	7·340	4·925	24·3; N = 2·61	1·000	0·605	0·114*	0·080	0·307	19·6	A
							1·000	0·582	0·128*	0·075	0·335		
16	5·060	5·170	—	4·392	2·311	9·17	1·000	0·502	0·105	0·827	0·072	73·0	C
							0·800	0·357	0·085	0·623	0·058		
17	8·340	9·732	—	4·099	1·865	—	1·000	0	0·301	1·830	—	—	A
18	8·900	10·411	+ 0·149	2·602	1·352	—	1·000	01	0·154	2·003	—	—	C
19	5·011	5·448	+ 0·176	3·604	1·752	—	1·000	0·308	0·125	1·372	—	—	C
20	8·925	8·669	+ 0·148	3·088	—	—	1·000	—	0·044	0·051	—	—	C
21	5·011	4·872	+ 0·064	1·645	0·771	—	0·700	0·624	0·030	0·044	—	—	C
2. $C_6H_5\cdot C(CN){:}NO\cdot ONa$.													
22	3·000	Oil	+ 0·277	Whole oil	2·221	0	1·000	0·044	1·800	0·102	0	0	C
23	5·000	5·262	KOH-soluble oxid.		3·357	0	1·000	0·076	1·804	0·012	0	0	C
			KOH-insol. oxidised.		0·564	0	0·400	0·217	0·287	0·007	0		
24	6·000	5·029	+	2·330	1·569	0	1·000	0·169	1·634	0·015	0	0	C
			0·739	—	—	0	0·700	0·041	1·290	0·004	0		
3. $C_6H_5\cdot CO\cdot CN$.													
25	4·436	4·293	—	0·642	0·552	0	0·545	0·519	—	0·008	0	0	See text
26	5·410	7·051	—	6·600	5·189	0	1·000	0·102	0·207	1·673	0	0	
4, *m*-$C_6H_4Br\cdot CO_2H$.													
27	0·500	0·610	—	—	—	—	0·610	0	0	0·043†	0·794	0	—
28	0·500	0·613	—	—	—	—	0·400	0	0	0·030†	0·498	0	—
29	0·500	0·546	—	—	—	—	0·546	0·243	0	0·022†	0·401	0	—

oxidation-acids of the remainder, 15·9% of *p*-nitrobenzoic acid was isolated, corresponding to 7—8 mol.% of pure *p*-acid on the whole nitration product. *o*-Nitration must therefore be negligible.

In No. 22, the composition of the acids (only 0·277 g., m. p. 227—231°) given had to be based on the analysis of the acids in No. 24, of equal melting point.

No. 22 was duplicated, but with addition of 1 g. of sodium nitrite to the nitric acid to see whether the proportion of acids produced during nitration was due to the content of nitrous acid. This is not the case, since only 0·253 g. of acids (m. p. 222—227°) was formed. In a duplicate of No. 9, but at 16·2° instead of 12·6°, and with 0·3 g. of sodium nitrite per g. of phenylbromocyanonitromethane added, there was a slightly higher acid formation (2·4% of the weight of phenylbromocyanonitromethane, against 0·8% in No. 9).

In a triplicate of No. 22 and in a duplicate of No. 23, after removal of acids in bicarbonate, the remainder, in benzene, yielded a precipitate of ammonium salt, and its KOH-soluble portion gave a KI-soluble hypobromite; the presence of much material with an unaltered side chain (see Table II) thus being confirmed.

In No. 24, to correlate the molecular percentages of the acid fractions produced during nitration and by oxidation, a normal oxidation yield of 85% of the theoretical was taken as a basis.

In Nos. 25 and 26, oxidations were carried out with a 1 : 60 permanganate solution as described in Part V of this series.

In No. 25, the yield of 4·293 g. was separated into 3·651 g. of pure unchanged benzoyl cyanide (m. p. 33—34°) and a partly oily fraction, only the latter being submitted to oxidation.

In Nos. 20 and 21, the nitration products, instead of being shaken with bicarbonate, were extracted five times with sodium carbonate according to Baker and Ingold's directions, but even so, not 10% as they state, but only 1 to 2% of acids were obtained.

In Nos. 27, 28, and 29, the traces of *m*-nitro-compound (marked †) were presumably recovered as tetrabromo-*m*-aminobenzoic acid. The percentage of this in No. 29 had to be deduced from Nos. 27 and 28. The *m*-bromobenzoic acid used, after repeated crystallisation, always had the (*usually* obtained) m. p. of 152—153° (not 155°; Wheeler and McFarland).

In No. 13, the 0·390 g. of benzoic, etc., acids yielded, by fractional recrystallisation from water, 0·160 g. of *m*-bromobenzoic acid (m. p. 143—145°; mixed m. p. 152·5—153°) and, on further recrystallisation, 0·045 g. melting at 148—156° (nitrobromo-acids; m. p. depression with *m*-bromobenzoic acid). The 0·160 g. of *m*-bromo-acid isolated, although not quite pure, represents quite

75% of the total unnitrated bromo-acid formed. In a duplicate of No. 13, on 8·353 g. of phenylbromocyanonitromethane, the oily nitration product, on standing, deposited first nitration acids, from which, by 50% methyl alcohol, 0·2 g. of *m*-bromobenzoic acid (m. p. 147—150°; mixed m. p.) was obtained, and then crystals, m. p. 167—180°, yielding on treatment with benzene 0·1 g. of *p*-nitrobenzoic acid (m. p. 190—200°; mixed m. p.).

In Nos. 10 and 11 (figures for No. 11 in brackets), the KI-insoluble portion from 3·986 (4·475) g. of the nitration product yielded, by method D(C), 1·259 (1·545) g. of acids containing 23·44 (26·1)% of bromine. Of these, 0·900 (1·000) g. gave 0·581 (0·693) g. of benzoic+bromobenzoic acids, 0·035 (0·045) g. of tribromoaniline from *p*-nitro-acid, 0·331 (0·322) g. of tribromoaniline from nitrobromo-acid, and 0·030 (0·035) g. of tribromo-*m*-aminobenzoic acid. Before oxidation, the material smelled strongly of benzoyl cyanide.

The diluted spent acids from two nitrations with 13 parts of nitric acid of *d* 1·480, one at 15° for 24 hours, the other at 16·2° for 4 days, gave with silver nitrate at first only a faint cloudiness, but in the course of several minutes a very material precipitation of silver bromide. Since bromine reacts instantaneously under similar conditions, this test appeared to confirm the postulated presence of hypobromous acid.

III. *Other Observations.*—1. *Purity of phenylbromocyanonitromethane.* Repeated oxidations of phenylbromocyanonitromethane by method C (p. 471) yielded benzoic acid containing from 0·40 to 0·57% of halogen, calculated as bromine, so that phenylbromocyanonitromethane (prepared by method A; p. 471) contains 0·20 to 0·29%. This is, at least partly, due to re-arrangement in ethereal solution (see below) during its preparation, but there may, in addition, be a trace of nuclear bromination during the action of bromine on the sodium salt. The salt we used contained only 0·066% of chlorine (derived from a trace of nuclear chlorine in the benzyl chloride from which it was made), which accounts for 0·085% in phenylbromocyanonitromethane, calculated as bromine.

The potassium iodide method showed an average content of hypobromite-bromine of 99·2% of the theoretical for the samples of phenylbromocyanonitromethane used in the recorded experiments, with variations between 98·8 and 99·4%—except in No. 18 (phenylbromocyanonitromethane made by means of hypobromous acid: KI-soluble Br, 98·0%).

2. *Volatility and stability of phenylbromocyanonitromethane.* The substance (3·623 g.) was dissolved in 45 c.c. of commercial "absolute" ether (*d* 0·717) and, after the ether had been removed by a current of dry air, was brought to constant weight in a vacuum;

loss, 0·019 g. = 0·52%. The percentage of mobile bromine, originally 99·4, was finally 98·6.

When phenylbromocyanonitromethane was left for 1 week in a desiccator over caustic potash, at atmospheric pressure, the mobile bromine decreased by 2%, but the percentage of nuclear bromine determined after oxidation showed no measurable change.

3. *Re-arrangement of phenylbromocyanonitromethane in ether.* The substance (6·330 g.), in 63·2 c.c. of ether (carefully dried over sodium), was left for 48 hours at room temperature. Whereas initially 2·133 g. of the phenylbromocyanonitromethane had yielded 0·954 g. of acids containing 0·40% of bromine, 5·080 g. of the recovered phenylbromocyanonitromethane gave on oxidation by method C 2·356 g. of acids containing 1·60% of bromine, corresponding to a migration of 0·6% of bromine, involving a re-arrangement of 1·8% of the phenylbromocyanonitromethane. Simultaneously the mobile bromine decreased from 98·8% to 97·0%.

When phenylbromocyanonitromethane was treated in exactly the same way, except that 93% of its weight (= 1·7 equivs.) of benzoyl cyanide was initially added to the solution in ether, 0·48% of the bromine migrated in 48 hours; there was therefore no bromination of benzoyl cyanide.

4. m-*Nitrophenylbromocyanonitromethane.* The solid portion, amounting to over 90% of the total nitration products, obtained with nitric acid of *d* 1·52, and melting usually at 67—69°, was dissolved in a little cold benzene and allowed to crystallise after addition of petrol; 55—60% of the solid was thus recovered as pure m-*nitrophenylbromocyanonitromethane*, white needles, m. p. 70—70·5°, which did not change on further recrystallisation (Found : N, 14·90; Br by the Carius method, 27·78; Br by treatment with potassium iodide, 27·5, 27·6. $C_8H_4O_4N_3Br$ requires N, 14·69; Br, 27·96%). For proof of the position of the nitro-group, see below.

5. *Reduction of phenylbromocyanonitromethane and its* m-*nitro-derivative by potassium iodide, potassium hydroxide, or ammonia.* That treatment with potassium iodide (see I, 3; p. 471) actually yields the potassium salt of the corresponding *iso*nitro-compound was proved by reconverting this salt into the hypobromite. For example, the aqueous solution of the salt obtained from *m*-nitrophenylbromocyanonitromethane by treatment with sodium iodide gave, after removal of the iodine in benzene and gradual addition of a little less than the theoretical amount of a 1% bromine solution at 0°, a precipitate of *m*-nitrophenylbromocyanonitromethane (m. p. 67—68°; mixed m. p.) amounting to 85% of the theoretical quantity, calculated on the bromine used.

With an excess of 10% aqueous caustic potash, phenylbromocyanonitromethane and its *m*-nitro-derivative rapidly gave, on shaking, solid *iso*nitro-potassium-salt, which dissolved on addition of water.

Sodium carbonate in concentrated solution did not react immediately with phenylbromocyanonitromethane on shaking, but reacted partly on standing for a week.

Phenylbromocyanonitromethane in ether, when shaken with an excess of 10% aqueous ammonia, reacted rapidly with a strong evolution of gas (presumably nitrogen). Solid *m*-nitrophenylbromocyanonitromethane reacted similarly with aqueous ammonia, practically everything going into solution.

Baker and Ingold, who used potassium hydroxide to nearly neutralise their nitration mixture, thereby presumably reduced some of the supernatant material; this would account for their low nitration yields, which they attributed to oxidation.

Dry ammonia gas, passed into a benzene solution of phenylbromocyanonitromethane, precipitates most, but not nearly all, of the material in the form of the *iso*nitro-ammonium salt, together with some ammonium bromide derived from the decomposition of nitrogen bromide, entirely in accordance with Willstätter and Hottenroth's observations on bromonitromalonic esters. We found, however, that the incompleteness of the precipitation is merely due to solubility or dissociation of the ammonium salt in benzene, since separation from petrol is practically complete. The precipitate was removed at intervals of 4 minutes, and the filtrate brought to its original volume, dry apparatus of approximately constant dimensions being used throughout. The precipitates were brought to nearly constant weight in a vacuum, and the bromide ion in each was determined and deducted as ammonium bromide. Thus 2·063 g. of phenylbromocyanonitromethane in 60 c.c. of petrol (b. p. 30—50°) gave 0·889, 0·348, 0·269, and 0·114 g. at 4-minute intervals and finally 0·112 g. in 30 minutes: total, 1·732 g. of ammonium salts; the excess of 0·209 g. over the theoretical quantity being due to occluded solute. The ammonium bromide precipitates amounted to 0·372 g., and the petrol finally retained 0·078 g. of solute. In two other experiments, 2·026 g. of phenylbromocyanonitromethane gave 1·859 g. of ammonium salt (theory requires 1·505 g.), and 1·686 g. gave 1·481 g. (theory, 1·252 g.), whereas 0·604 g. of phenylbromocyanonitromethane made with hypobromous acid gave 0·438 g. (theory, 0·448 g.) in 30 minutes. For a two-phase reaction, and allowing for occlusions, the rate of change follows the mass law sufficiently to preclude the initial presence of an appreciable proportion of a relatively inert isomeride.

m-Nitrophenylbromocyanonitromethane (0·500 g.), dissolved in

10 c.c. of dry benzene, gave with dry ammonia in 2 minutes 0·365 g. of ammonium salt and 0·052 g. of ammonium bromide. The filtrate, evaporated in a vacuum and redissolved in 3 c.c. of benzene, gave 0·013 g. of ammonium salt and 0·010 g. of ammonium bromide : total ammonium salt, 0·378 g. (theory requires 0·389 g.).

0·50 G. of crude *m*-nitrophenylbromocyanonitromethane (m. p. 67—69°) in 10 c.c. of benzene, after prolonged treatment with ammonia gas, gave 0·455 g. of precipitate; the filtrate retained 0·027 g. of an oil. A filtered solution of the 0·455 g. in 20 c.c. of water, treated at 0° with an excess of 3% aqueous bromine, gave 0·372 g. of *m*-nitrophenylbromocyanonitromethane (shrinking at 67°, m. p. 69—70°; mixed melting point), thus proving that dry ammonia produces the ammonium salt of *m*-nitrophenylcyano*iso*-nitromethane.

6. *Decomposition of phenylbromocyanonitromethane by heat alone.* One of us (*loc. cit.*) had stated that phenylbromocyanonitromethane decomposes "at water-bath temperature"; Wislicenus and Schäfer (*loc. cit.*) then gave "about 55°" as the decomposition point with strong gas evolution. A number of samples prepared by methods (a) and (b) (p. 470) have now been examined. All the samples gradually darkened, but evolution of gas first occurred at 72—78° with slow heating, and at 80—83° in a bath pre-heated to 75°; a further rise of 2—3° made the evolution violent.

Quantitative tests: (a) Phenylbromocyanonitromethane (3·740 g.) was heated at 90—100° until the gas evolution had ceased, and the residue was shaken for 1 hour with 60 c.c. of cold 5% aqueous potassium hydroxide, and oxidised with a 1 : 60 permanganate solution. The acids (1·739 g.) contained 0·47% of bromine, that is, no more than acids obtained from phenylbromocyanonitromethane by oxidation method C (p. 471), so that no bromine had migrated during decomposition. 1 G. of the acids gave on reduction, etc., 0·869 g. of benzoic acid and 0·209 g. of tribromoaniline.

(b) Phenylbromocyanonitromethane (24 g.), similarly heated, left a residue of 12·50 g. At 4 mm. pressure this gave a distillate of 9·38 g. of benzoyl cyanide (m. p. 32—34°) and a residue of 2·30 g., which, on recrystallisation from petrol (b. p. 100—120°), yielded 1·150 g. of *p*-nitrobenzoyl cyanide (m. p. 114—115°) + 0·173 g. (m. p. 104—108°); the mother-liquor contained some benzoyl cyanide.

(c) Phenylbromocyanonitromethane (19 g.) was treated as under (b), but the residue in the flask was distilled (at 100—120°/4 mm.) before recrystallisation from petrol (b. p. 60—80°). Distillate, 0·9 g.; m. p. 103—108° before and 115—116° after recrystallisation.

(d) Phenylbromocyanonitromethane (15 g.) was treated as under (c), except that decomposition was effected in an atmosphere of carbon dioxide. The crude distilled *p*-nitrobenzoyl cyanide (m. p. 101—106°) weighed 0·8 g. The constant m. p. after recrystallisation was 115·5—116° (Found : N, 16·28, 16·08. Calc. for $C_8H_4O_3N_2$: N, 15·91%). The result shows that the oxygen needed for the formation of *p*-nitrobenzoyl cyanide does *not* come from the air.

p-Nitrobenzoyl cyanide has already been obtained, by another method, by Zimmermann (*loc. cit.*), who gives the melting point as 116·5°. We found that atmospheric moisture gradually changes it to *p*-nitrobenzoic acid.

7. *Decomposition of* m-*nitrophenylbromocyanonitromethane by heat alone.* This substance begins to evolve gas slightly above its melting point, or, on prolonged heating, even at its melting point. Quantitative tests : 8·00 g. heated to constant weight, at about 95°, in a long-necked flask provided with a calcium chloride tube, showed a loss of 2·70 g. The product, distilled at 7 mm. pressure, gave 4·60 g. of *m*-nitrobenzoyl cyanide, distilling at 144—146°, and 0·65 g. of residue, from which alcohol extracted 0·468 g. of a semi-solid of high bromine content, leaving 0·106 g. of a bromine-free solid melting above 200°.

m-Nitrobenzoyl cyanide was obtained by us as a light yellow oil (Found : N, 15·98. Calc. for $C_8H_4O_3N_2$: N, 15·91%). Like its *p*-isomeride, it is gradually hydrolysed to the corresponding nitrobenzoic acid by atmospheric moisture. 1·116 G., when boiled with 24 c.c. of 10% sulphuric acid for 3 hours, gave 1·058 g. (quantitative yield) of *m*-nitrobenzoic acid (m. p. 138·5—139° ; mixed m. p.).

8. *Changes in presence of heated aqueous permanganate.* (a) Phenylbromocyanonitromethane (4·255 g.) was heated with 4 g. of permanganate in 240 c.c. of water for 1 hour, then with a further 2 g. of permanganate for 3 hours. The acids formed (1·776 g.) contained 0·85% of bromine ; 1 g. thereof gave on reduction, etc., 0·794 g. of benzoic + bromobenzoic acids and 0·316 g. of tribromoaniline, and therefore consisted of 2·1% (by weight) of bromobenzoic, 16·0% of *p*(*o*)-nitrobenzoic, and 81·9% (by difference) of benzoic acids. In a parallel test, 5·530 g. of phenylbromocyanonitromethane gave 2·369 g. of acids containing 0·91% of bromine, of which 1 g. yielded 0·804 g. of benzoic + bromobenzoic acids and 0·334 g. of tribromoaniline.

(b) Phenylcyanonitromethane, obtained from 2 g. of its sodium salt, dissolved in water, and 10·9 c.c. of *N*-sulphuric acid, was, after dilution to 120 c.c., boiled with 2 g. of permanganate until this was decolorised, and then with a further 2 g. for 2 hours. The acids

(1·503 g.) yielded 1·147 g. of benzoic acid and 0·549 g. of tribromoaniline, corresponding to 18·5% (by weight) of *p*(*o*)-nitrobenzoic acid.

(c) The ammonium salt of phenylcyano*iso*nitromethane, obtained by passing dry ammonia for 20 minutes through a petrol solution of phenylbromocyanonitromethane, gave with a 1 : 60 solution of permanganate 0·403 g. of acids yielding 0·030 g. of tribromoaniline, corresponding to 3·75% (by weight) of *p*(*o*)-nitrobenzoic acid.

(d) The potassium salt of phenylcyano*iso*nitromethane, obtained by completely dissolving 3·228 g. of phenylbromocyanonitromethane by shaking it for 15 minutes with 50 c.c. of 5% aqueous potassium hydroxide and diluting the solution to 240 c.c., was oxidised by boiling with 4 g. of permanganate. The 1·434 g. of acids obtained yielded, besides benzoic acid of 0·57% bromine content, only 0·005 g. of tribromoaniline, corresponding to 0·17% (by weight) of *p*(*o*)-nitrobenzoic acid.

(e) Phenylbromocyanonitromethane in the presence of foreign matter gave on treatment with permanganate a higher degree of *p*-migration than phenylbromocyanonitromethane alone. For example, the phenylbromocyanonitromethane–benzoyl cyanide mixture recovered from the experiment described under (3) (p. 476) was oxidised (5·345 g.), as in 8 a (p. 479), to 3·763 g. of acids, 1 g. of which yielded 0·881 g. of benzoic acid and 0·200 g. of tribromoaniline, corresponding to 27·4% (by weight) of *p*(*o*)-nitrobenzoic acid calculated on the proportion of the acids corresponding to the phenylbromocyanonitromethane in the original mixture.

Again, the earlier nitration mixtures, oxidised by method A (p. 471) (oxidation of phenylbromocyanonitromethane in presence of products with an altered side chain), gave yields of tribromoaniline, of which the following are examples : nitration analogous to No. 1, 0·667 g. of tribromoaniline per g. of acid; analogous to No. 3, 0·671 g. of tribromoaniline; analogous to No. 3, 0·700 g. of tribromoaniline; analogous to No. 8, 0·513 g. of tribromoaniline. Phenylcyanonitromethane also gave more tribromoaniline when oxidised by method A in presence of admixtures; for instance, the benzene layer from the potassium iodide reaction of a nitration product obtained according to No. 8 gave, after oxidation by method A, 0·596 g. of tribromoaniline per g. of acid, and 0·850 g. in the case of a nitration with 13 parts of nitric acid of *d* 1·480 at — 11° for 1 hour and then at 15° for 15 minutes. The latter nitration yielded a nitration product giving, by method A, acids containing 38·2% of *p*(*o*)-nitrobenzoic acid, from which 26·2% (by weight) of *p*-nitrobenzoic acid (m. p. 228—232°) was isolated; 22%, m. p. 225—230°, was obtained in a duplicate nitration, and

18·2% (m. p. 230—235°) in another similar experiment (nitration, however, being effected with only 8 parts of nitric acid).

(f) *m*-Nitrophenylbromocyanonitromethane (0·500 g.), oxidised by method C (p. 471), yielded 0·252 g. of bromine-free *m*-nitrobenzoic acid (m. p. 139°; mixed m. p.). By method A, 0·610 g. yielded impure *m*-nitrobenzoic acid which gave the thiophen test of the corresponding glyoxylic acid.

To show that the mere trace of re-arrangement of the potassium salt of phenylcyano*iso*nitromethane corresponds to a mere trace of hydrolysis of the salt, 2 g. of the corresponding sodium salt, in 40 c.c. of water, were shaken for 15 minutes with 40 c.c. of benzene. On evaporation the benzene layer left only 0·015 g. of extracted hydrolysed material.

(g) *p*-Nitrobenzaldehyde (1·000 g.) was boiled for 3 hours with 1 g. of permanganate in 60 c.c. of water. Another 1·000 g. of the aldehyde was shaken for 3 hours with 8 c.c. of 5% potassium hydroxide, then diluted to 60 c.c. and, after addition of 1 g. of permanganate, boiled for 3 hours. The yield of *p*-nitrobenzoic acid in the first case was 0·942 g., m. p. 234—236°, and in the second case 0·941 g., m. p. 235—236°. Addition of potassium hydroxide according to method C, therefore, diminishes neither the yield nor the degree of purity of *p*-nitrobenzoic acid.

9. *Changes in presence of hot dilute nitric acid.* 1·645 G. of the nitration product of No. 21 (obtained according to Baker and Ingold's directions) were boiled, also according to their directions, with nitric acid (13·6 c.c.; *d* 1·125; 2 hours). The yield of acids was 0·904 g. From 0·900 g. of this, 0·688 g. of benzoic acid, 0·288 g. of tribromoaniline, and 0·077 g. of tribromo-*m*-aminobenzoic acid were obtained, corresponding to 16·2% (by weight) of *p*-nitrobenzoic acid and 3·82% of *m*-nitrobenzoic acid. On repetition, the yields were 15·75% and 3·62%, respectively (nitration No. 20). But here again, the true amount of *p*-nitrobenzoic acid due to nitration, as ascertained by method C (see Tables II and III), was only a small fraction of the above. The nitric acid used by Baker and Ingold, who found quite 52% of *m*-nitrobenzoic acid, must obviously have been substantially stronger than they indicate. Even at a higher temperature, relatively little *m*-nitration occurs with 8 parts of nitric acid of *d* 1·490. For instance, at + 15°, 4·400 g. of phenylbromocyanonitromethane yielded in 4 hours 4·426 g., including 0·062 g. soluble in bicarbonate, 2·840 g. of which, when oxidised with nitric acid as described above, gave 1·663 g. of acids; 1 g. of these yielded 0·655 g. of benzoic acid, 0·339 g. of tribromoaniline, and 0·399 g. of tribromo-*m*-aminobenzoic acid, corresponding to 17·2% (by weight) of *p*-nitro- and 17·8% of

m-nitro-benzoic acid. Since the amount of benzoic acid was found considerably to exceed that of its *p*-nitro-derivative, it appears difficult to account for Baker and Ingold's analysis of their oxidation product (49·6% of carbon, nitrobenzoic acid requiring 50·3, and benzoic acid 68·8%).

10. *Changes in concentrated sulphuric acid.* (a) *m*-Nitrophenylbromocyanonitromethane (0·4 g.), dissolved in 5 c.c. of concentrated sulphuric acid, immediately turned pale blue and became brown after 5 minutes. A solution of 1 g. in 10 c.c. of concentrated sulphuric acid, after being left for 24 hours at room temperature, was poured on ice (gas evolution) and extracted with ether; 0·711 g. was obtained which yielded, by two recrystallisations from benzene, 0·172 g. (m. p. 143—144°; depression with *m*-nitrobenzoic acid) (Found : N, 7·4. Calc. for *m*-nitrophenylglyoxylic acid, $C_8H_5O_5N$: N, 7·2%). In another similar experiment, 33% (by weight) of the *m*-nitrophenylbromocyanonitromethane was recovered as *m*-nitrophenylglyoxylic acid, m. p. 141—143°, and 144—145° after one recrystallisation from benzene containing a little alcohol. The acid gave the characteristic thiophen test. We obtained the same acid by leaving 1·970 g. of *m*-nitrobenzoyl cyanide with 10 c.c. of hydrochloric acid (*d* 1·195) at room temperature for 48 hours and filtering off the crystals. Yield 1·710 g., m. p. 139—143°; by recrystallisation from benzene + 20% of alcohol, 1·32 g. of colourless prisms, m. p. 144·5—145°, were obtained. The pure acid had hitherto not been obtained. *p*-Nitrobenzoyl cyanide, when similarly treated with hydrochloric acid, yields, not *p*-nitrophenylglyoxylic acid, but pure *p*-nitrobenzoic acid.

(b) Phenylbromocyanonitromethane (0·34 g.) in 5 c.c. of concentrated sulphuric acid was red at first and changed within 5 minutes through deep purple to deep blue, in another 15 minutes to greenish-blue, in another 20 to deep green, in a further 50 minutes to deep brown. 0·502 G. of phenylbromocyanonitromethane in 5 c.c. of concentrated sulphuric acid gave after a few hours a distinct test for benzoyl cyanide (odour on diluting a few drops of the solution); after 22 hours, 0·271 g., m. p. 60—65°, was extracted by ether from the solution, poured on ice. 1·017 G. of phenylbromocyanonitromethane in 8 c.c. of concentrated sulphuric acid was left for 18 days, and water was then slowly added without cooling (gas evolution). Filtration of the cold liquid left 0·441 g. of benzoic acid (m. p. 105—110°; mixed m. p.) and extraction of the filtrate with ether gave 0·111 g. of less pure benzoic acid (m. p. 95—102°). Since, on similar treatment, some benzoic acid (m. p. 112—114°) was obtained from the above product of m. p. 60—65°, the latter consisted, no doubt, essentially of phenylglyoxylic acid (m. p. 65—66°).

(c) The sodium salt of phenylcyano*iso*nitromethane (0·5 g.) in 5 c.c. of concentrated sulphuric acid gave at once a bright blue colour, changing within 5 minutes to purple, blue-green, green and olive-green, and within an hour to brown. On pouring the liquid into water after 48 hours and extracting the solution with ether, 0·312 g. of a dark brown, oily substance was obtained which, by sublimation at 90—100°, gave impure benzoic acid (m. p. 93—105°; mixed m. p.).

11. *Reactions of ethyl phenylbromomalonate.* This was prepared according to Wheeler and Johnson (*J. Amer. Chem. Soc.*, 1902, **24**, 688) and distilled at 135—136° (2 mm.) (Found: Br, 25·2. Calc. for $C_{13}H_{15}O_4Br$: Br, 25·4%).

(a) Potassium iodide test: 0·309 g. of the ester in 20 c.c. of benzene was mechanically shaken with 2 g. of potassiun iodide in 20 c.c. of water for 45 minutes. A mere trace of iodine was liberated, the colour developed with starch being discharged by a single drop of *N*/10-thiosulphate.

(b) Ammonia test: 0·691 g. of the ester, dissolved in 60 c.c. of dry petrol (b. p. 30—50°), was treated with dry ammonia during 22 minutes. An immediate slight unfilterable opalescence was produced, but no further change. After the solution had been shaken with dilute aqueous ammonia, the latter gave a very slight positive bromine test.

(c) Aniline test: 1·055 g. of the ester were heated at about 95°, for 2 hours, with 3·165 g. of aniline in an atmosphere of carbon dioxide. The product was shaken with 100 c.c. of cold 5% nitric acid and the solution obtained was freed from insoluble semi-oil by means of benzene and treated with silver nitrate, 0·1958 g. of silver bromide, corresponding to 31·2 mol.% of hydrogen bromide, being precipitated. The filtrate was made alkaline with ammonia and shaken with ether, and the extract was washed once with water and evaporated. The residue contained 0·47% of bromine (Carius), corresponding to approximately 5·3 mol.% of bromoaniline, calculated on the ester used.

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