169. *The Nitration and Hydroxylation of Aromatic Compounds by Pernitrous Acid.*

By E. Halfpenny and P. L. Robinson.

The reaction between pernitrous acid and a number of simple aromatic compounds is described. Both hydroxylation and nitration occur and diphenyl derivatives have been isolated. The products are mainly *m*-nitro-compounds, *o*- and *p*-hydroxy-compounds, or derivatives of *o*-nitrophenol.

Hydroxylation is considered to be due to hydroxyl radicals produced by the homolytic fission of pernitrous acid, and nitration to be due to nitrogen dioxide reacting with the free aryl radicals present in the solution.

Trifonow (*Z. anorg. Chem.*, 1922, **124**, 123, 136) observed that when benzene is shaken with nitrous acid and hydrogen peroxide both the organic and the aqueous layer become yellow. Alkali changed the colour to red, from which he assumed the formation of *o*-nitrophenol, and he suggested this reaction for detection of benzene in other hydrocarbons. Ficklen and Cook (*ibid.*, 1933, **211**, 141) determined the sensitivity of this test.

We have reported (preceding paper) that the decomposition of pernitrous acid releases free hydroxyl radicals, the evidence being the polymerisation of methyl acrylate and the hydroxylation of benzene. We believe that the radicals arise from the homolytic fission of the unstable pernitrous acid. In addition to phenolic compounds, benzene yielded appreciable quantities of nitrobenzene. Nitration in aqueous media of very low acidity (approximately N/30) at room temperature seemed sufficiently remarkable to call for further investigation. The reaction proves to be of considerable generality. Nearly always the nitro-group enters the ring at the *meta*-position relative to an existing substituent. When both hydroxyl and nitro-group enter the ring together, the hydroxyl appears, almost without exception, *ortho* and *para* in respect to an original substituent, with the nitro group adjacent to the hydroxyl. A compound of particular interest found among the products is diphenyl: although it occurs in small quantity, its formation evidently has an important bearing on any explanation which may be advanced to account for these hydroxylations and nitrations.

We show that acidity decreases during the reaction and that the decrease is quantitatively related to the extent of nitration.

We believe the first stage in this nitration process to be an attack by the hydroxyl radical on the aromatic compound with the formation of a free aryl radical; and the second to be a combination of this aryl radical with nitrogen dioxide, the other radical produced by the rupture of the pernitrous acid. Unsuccessful attempts have been made to identify the aryl radicals by having either iodine or nitric oxide present in the reaction system.

The yield of nitrated and hydroxylated compounds, based on the nitrite used, is less than 10%, except for anisole. With some compounds appreciable tar appears in the product. Various changes in conditions, made to increase the yield, were unsuccessful.

Experimental

The Reaction with Toluene, Nitrobenzene, Dimethylaniline, Phenol, Anisole, and Chlorobenzene.—Aromatic compounds were brought into contact with decomposing pernitrous acid by vigorously agitating them with a slightly acid solution of hydrogen peroxide and adding sodium nitrite solution. To compare products and yields with those from benzene already reported, the same quantities, concentrations, and methods of mixing were used throughout. The aromatic compound (100 c.c.) was emulsified with 5% hydrogen peroxide solution (100 c.c.), 3N-hydrochloric acid (5 c.c.), and water (250 c.c.) in a 750-c.c. round-bottomed flask. 5% Sodium nitrite solution (150 c.c.) was added dropwise to the rapidly stirred mixture. With phenol, the quantity of nitrite was reduced to avoid the evolution of oxides of nitrogen. Only the organic phase was examined and, since the yields are small, many runs were necessary to get sufficient material for examination. The products from the various experiments are listed in Tables 1 and 2 (p. 942).

Toluene. A light yellowish-brown colour developed in both the aqueous and the organic layer. The organic material from fifty runs, on redistilled toluene, was extracted with dilute sodium hydroxide solution and, after being washed with water, further extracted with saturated sodium hydrogen sulphite solution. After being further washed with water and dried (Na_2SO_4), the toluene was removed by vacuum-distillation, to leave a dark liquid (9·5 g., equiv. to 0·2 g. per run). Distilled at 5 mm. this gave a yellow liquid and a tarry residue (1 g.). The distillate, from infra-red analysis, appeared to consist of nitrotoluene 20, halogeno-compounds (probably benzyl chloride) 30, benzaldehyde 7, and nitrocresol 9%. (The last two are present owing to incomplete extractions by sodium hydroxide and sodium hydrogen sulphite.)

The bisulphite solution was treated with excess of sodium carbonate and extracted with ether. The dried ethereal extract, on evaporation, left a residue (2·0 g., equiv. to 0·04 g. per run). The residue gave a colourless distillate (1·5 g.; b. p. 179°), identified as benzaldehyde by the preparation of its phenylhydrazone (m. p. 156—158°; lit., 158°) and 2 : 4 dinitrophenylhydrazone (m. p. 236°; lit., 235°) and of benzoic acid (m. p. 121°; lit., 121°).

The alkaline extract, washed with ether to remove traces of toluene, was acidified and extracted with ether. The extract after drying and removal of the ether, left a residue of phenolic compounds (12·5 g., equiv. to 0·25 g. per run); this on steam-distillation gave a semi-solid, separable by filtration into a yellow crystalline solid (3 g.) and a light brown oil (7·5 g.). The first, recrystallised from aqueous alcohol, had m. p. 69°, and was identified as 2-methyl-6-nitrophenol by mixed m. p. and by its acetate (m. p. 41·5°; lit., 42°). The oil (m. p. *ca.* 10°) was a mixture. Attempts at separation failed, but the benzoate (Schotten–Baumann) crystallised from alcohol as fine needles, m. p. 98—99°, and served to identify the chief constituent of the oil as 4-methyl-2-nitrophenol (benzoate, m. p. 100—101°). The tarry residue from the steam-distillation, when distilled in a vacuum, gave a small amount of white material. This crystallised from water in an unstable form which melted at a low temperature and then resolidified, suggesting that it was 2-methyl-4-nitrophenol, a deduction rendered probable by the stable phase melting at 95° (lit., 96°).

Nitrobenzene. The deep yellowish-orange organic material from twenty runs on AnalaR nitrobenzene was extracted with sodium hydroxide solution, washed, dried, and distilled in a vacuum. The residue (15·8 g., equiv. to 0·8 g. per run), on steam-distillation, gave 14·6 g. of crude *m*-dinitrobenzene. Infra-red analysis showed that it contained *m*- 91, *p*- 5, and *o*-dinitrobenzene 4%. The black, tarry residue from the steam-distillation, when heated in a vacuum, gave a small crystalline sublimate (m. p. 198—199° when recrystallised from alcohol) which was probably 3 : 3′-dinitrodiphenyl.

The phenolic substances (14·5 g., equiv. to 0·7 g. per run) from the alkaline extract gave, on steam-distillation, *o*-nitrophenol (2·0 g.; m. p. 45° after recrystallisation from aqueous alcohol; m. p. not depressed by authentic *o*-nitrophenol). The residual solution from the steam-distillation, treated with concentrated sodium hydroxide solution, precipitated the sodium salts of *m*- and *p*-nitrophenol which were fractionally crystallised from 10% sodium hydroxide solution to yield crude *p*- (2·8 g.) and *m*-nitrophenol (0·66 g.). By recrystallisation from dilute hydrochloric acid (charcoal), the *m*-nitrophenol had m. p. 96—97° (lit., 96°) and the *p*-nitrophenol, m. p. 112—114° (lit., 114°). The respective benzoates had m. p.s 93—95° and 142°. This (somewhat crude) separation indicated that the three isomeric nitrophenols are present in the approximate proportions *p*- 51, *o*- 37, and *m*-nitrophenol 12%.

On acidification of the strongly alkaline filtrate from the sodium salts of *m*- and *p*-nitrophenol, a black precipitate formed which was separated and dissolved in alcohol. The mother-liquor was extracted with ether, and the ethereal extract was added to the alcoholic solution. Removal of the solvents left a black, tarry residue which, when heated, yielded a very small sublimate (m. p. 171—172°), possibly 4-hydroxy-3 : 4′-dinitrodiphenyl.

Dimethylaniline. Nine runs were made on AnalaR dimethylaniline (commercial dimethylaniline gave a purple colour due to crystal-violet), and the organic material, after extraction with sodium hydroxide, was dried and distilled, leaving a residue (12 g., equiv. to 1·3 g. per run). This was distilled at 22 mm. and gave, at 125°, a distillate (4·5 g.) which was steam-distilled to remove any dimethyl-*p*-nitroaniline, and then extracted with ether from a slightly acid aqueous solution to remove most of the remaining dimethylaniline. The yellow oil thus obtained was crude dimethyl-*o*-nitroaniline (hydrochloride, decomp. 172—173°; lit., 173—174°). Reduction of the nitro-compound yielded a diamine giving the characteristic colour reactions of *o*-aminodimethylaniline.

The residue remaining after distillation of the dimethyl-*o*-nitroaniline was extracted with alcohol, and the extract freed from tar by boiling it with animal charcoal. Removal of the alcohol left a mixture which was separated by fractional precipitation from an acid solution by means of alkali. The two fractions, subsequently recrystallised from alcohol, gave dimethyl-*p*-nitroaniline (0·32 g.; m. p. 163·5°) and fairly pure tetramethylbenzidine (0·46 g.; m. p. 189—191°) respectively. Both compounds were further characterised by colour reactions.

The phenolic material (0·87 g., equiv. to 0·1 g. per run) from the alkaline extract, when extracted with ether, left a yellow, unidentified, insoluble solid (0·16 g.) which, after recrystallisation from acetone, melted at 210° with vigorous decomposition.

Phenol. Ten runs were made, each with 10 g. of phenol. The acidified phenol–hydrogen peroxide mixture was at 40°, whereby the former was kept almost completely in solution. Only 50 c.c. of 5% sodium nitrite solution were used in each run because more caused vigorous evolution of nitrous fumes. The brown aqueous solution from ten runs was extracted with ether, and the ethereal solution was dried. This ethereal solution, distilled to remove the ether and unchanged phenol, left a semi-solid, tarry residue (25·5 g., equiv. to 2·5 g. per run). The residue, dissolved in hot 6N-sodium hydroxide, yielded on cooling a small amount of a crystalline yellow sodium salt which, reconverted into the phenol and recrystallised, proved to be *p*-nitrophenol (m. p. 110°) (benzoate, m. p. 142°).

The alkaline filtrate from the sodium salt of *p*-nitrophenol was acidified and extracted with ether. The dried ethereal solution on evaporation left a residue which was fractionally distilled in a vacuum. The first fraction, a low-melting, yellow solid (possibly *o*-nitrophenol and phenol), was reduced with alkaline sodium dithionite (hydrosulphite) and gave a benzoate which, after recrystallisation melted partly at 65° and completely at 155°, suggestive of a mixture of the benzoates of phenol (m. p. 68°) and *o*-aminophenol (m. p. 182°). The second fraction, a light yellow solid (2·5 g.) becoming almost white (m. p. 102—104°) after recrystallisation from dilute hydrochloric acid, was identified as catechol by preparation of the dibenzoate (m. p. 85—86°; lit., 86°), a mixed m. p. with authentic catechol (101—104°), the green colour with ferric chloride, and an immediate white precipitate with lead acetate. The third fraction, a very pale yellow solid (2·0 g.) becoming white (m. p. 170—171°) when recrystallised, was identified as quinol by preparation of the diacetate (m. p. 122—123°; lit., 123°).

Anisole. The yellow-orange organic material from twenty runs was extracted with sodium hydroxide solution, dried, and distilled, leaving a trace of tar from which nothing significant was isolated.

The sodium hydroxide solution, after acidification, was extracted with ether which when dried and evaporated left a residue (60 g., equiv. to 3 g. per run). This, distilled in a vacuum, gave three fractions (*a*), (*b*), and (*c*). The first, (*a*), a light yellow solid (30 g.), gave on recrystallisation colourless needles (m. p. 41°) from which a benzoate (m. p. 68°) was prepared, proving that it was phenol with, perhaps, traces of *o*-nitrophenol. Fraction (*b*), a low-melting yellow solid (8·0 g.), was, from qualitative tests, evidently mainly *o*-nitrophenol, a view confirmed by the dibenzoate derivative (m. p. 181—182°; lit., 182°), made by reduction with alkaline sodium dithionite to *o*-aminophenol and treatment thereof with benzoyl chloride. Fraction (*c*), an orange semi-solid material (7·7 g.), gave, when recrystallised, 4-methoxy-2-nitrophenol (5 g.; m. p. 80°), identified by its benzoate (m. p. 89—90°; lit., 89°). The mother-liquor yielded a small amount of another crystalline substance (m. p. 55—60°) probably impure 6-methoxy-2-nitrophenol.

Chlorobenzene (Experimental work by J. J. HILLARY). Redistilled chlorobenzene (100 c.c.), 2·5% hydrogen peroxide solution (380 c.c.), and 2·5N-hydrochloric acid (5 c.c.) were mechanically mixed, and 5% sodium nitrite solution (150 c.c.) was added dropwise. The bright yellow, organic material from seventy-two such runs, after extraction with sodium hydroxide solution, drying, and removal of the chlorobenzene, left a residue (29·5 g., equiv. to 0·4 g. per run). This residue, when distilled in a vacuum, gave a distillate (24 g.) which solidified on cooling and was proved to be crude *m*-chloronitrobenzene (m. p. 44—45° after recrystallisation) by reduction to *m*-chloroaniline and preparation of the benzoyl derivative (m. p. 122°). By fractionally crystallising the crude *m*-chloronitrobenzene from aqueous alcohol, a small amount of *p*-chloronitrobenzene (m. p. 83°) was separated and identified by reduction to *p*-chloroaniline (m. p. 68°).

The phenolic material from the alkaline extract (21 g., equiv. to 0·3 g. per run) gave, when distilled, a quantity of light yellow, volatile liquid distillate with the properties of crude *o*-chlorophenol. The residue, recrystallised from benzene, gave a bright yellow crystalline substance (m. p. 86—87°) identified as 4-chloro-2-nitrophenol by the acetate (m. p. 48°).

Change in Acidity during the Reaction and its Quantitative Relation to the Product.—Our view of the nitration brought about by this reaction (see p. 943) implies a fall in acidity during its course. This assumption has been confirmed experimentally for nitrobenzene, chlorobenzene, and benzene.

TABLE 1. *Non-phenolic products.*

Starting material	Major products	Minor products
C_6H_6	$PhNO_2$	Ph_2, *p*-$C_6H_4(NO_2)_2$
PhMe	$C_6H_4Me\cdot NO_2$, PhCHO, halogeno-compounds	—
$PhNO_2$	*m*-$C_6H_4(NO_2)_2$	*o*- and *p*-$C_6H_4(NO_2)_2$, $(3\text{-}NO_2\cdot C_6H_4\cdot)_2$
$PhNMe_2$	*o*- and *p*-$NO_2\cdot C_6H_4\cdot NMe_2$ (*p*-$Me_2N\cdot C_6H_4)_2$	—
PhCl	*m*-$C_6H_4Cl\cdot NO_2$	*p*-$C_6H_4Cl\cdot NO_2$

TABLE 2. *Phenolic products.*

Starting material	Major products	Minor products
C_6H_6	*o*-$NO_2\cdot C_6H_4\cdot OH$	3 : 1 : 4-$NO_2\cdot C_6H_3Ph\cdot OH$ PhOH, *p*-$NO_2\cdot C_6H_4\cdot OH$ [2 : 4 : 1-$(NO_2)_2C_6H_3\cdot OH$]
PhMe	6 : 2 : 1- and 2 : 4 : 1-$NO_2\cdot C_6H_3Me\cdot OH$	4 : 2 : 1-$NO_2\cdot C_6H_3Me\cdot OH$
$PhNO_2$	*o*-, *m*-, and *p*-$NO_2\cdot C_6H_4\cdot OH$	3 : 4-$NO_2\cdot C_6H_3(OH)\cdot C_6H_4\cdot NO_2$-*p*
$PhNMe_2$	—	Unidentified substance (m. p. 210°, decomp.)
PhCl	*o*-$C_6H_4Cl\cdot OH$ 2 : 4 : 1-$NO_2\cdot C_6H_3Cl\cdot OH$	—
PhOH	*o*- and *p*-$C_6H_4(OH)_2$	*o*- and *p*-$NO_2\cdot C_6H_4\cdot OH$
PhOMe	PhOH, *o*-$NO_2\cdot C_6H_4\cdot OH$, 2 : 4 : 1-$NO_2\cdot C_6H_3(OMe)\cdot OH$	2 : 6 : 1-$NO_2\cdot C_6H_3(OMe)\cdot OH$

Nitrobenzene. 5% Sodium nitrite solution (150 c.c.) was added dropwise to an emulsion of 6% hydrogen peroxide solution (100 c.c.), water (250 c.c.), 2·46N-hydrochloric acid (5 c.c.), and nitrobenzene (100 c.c.). Afterwards the pH of the aqueous layer was measured at a glass electrode. In three experiments, the hydrogen-ion concentration changed from 0·012 g.-ion per 500 c.c. at the beginning to 0·007 g.-ion at the end, *i.e.*, 0·005 g.-ion of hydrogen had been used per run.

If it is assumed that the fall in acidity is related to nitration as $HCl \equiv HO_2\cdot NO \equiv C_6H_4(NO_2)_2$ and that the relation is reasonably quantitative, then the weight of *m*-dinitrobenzene to be expected would be 0·84 g. per run, which is remarkably close to the 0·80 g. actually isolated.

Chlorobenzene. By similar measurement and calculation for chlorobenzene, the significant product from which is *m*-chloronitrobenzene (the *o*-chlorophenol does not affect the issue), the hydrogen ion used proved to be equivalent to 0·35 g. of this compound. The actual yield of *m*-chloronitrobenzene was 0·4 g.

Benzene. The formation of both nitrobenzene and *o*-nitrophenol would be expected to contribute to the reduction in acidity. It being borne in mind that they are found in the proportion 2 : 1, the calculated weight of nitrated material should have equalled 1·0 g. which, again, is not remote from the 0·76 g. found under corresponding conditions.

Factors Influencing Yields.—In view of preparative possibilities the relation between yield and conditions was examined for nitrobenzene.

Hydrogen-ion concentration. Increasing the acidity reduces yields of both phenolic and non-phenolic products :

	Non-phenols (g.)		Phenols (g.)	
Initial [H^+] (g.-ion/l.)	Run 1	Run 2	Run 1	Run 2
0·291	0·35	0·32	0·50	0·28
0·063	0·91	0·86	0·66	0·63

Hydrogen peroxide. The reaction is not very sensitive to this reagent, but a twelve-fold increase in concentration showed evident reduction in yield :

Initial [H_2O_2] (g./l.)	20·2	253·0
Non-phenols (g.)	0·91	0·42
Phenols (g.)	0·68	0·50

Sodium nitrite. (*a*) Rate of addition. Three runs, with nitrite of different concentrations but with the same amount of reagent in every case, showed that the changes were without appreciable influence :

[$NaNO_2$] (g./l.)	300	150	50
Non-phenols (g.)	0·92	0·92	0·91
Phenols (g.)	0·63	0·58	0·66

(*b*) Total amount used. The yields of both hydroxylated and nitrated compounds appear to be proportional to nitrite added, provided that hydrogen peroxide is in excess throughout :

5% $NaNO_2$ added (c.c.)	150	100	50
Non-phenols (g.)	0·82	0·66	0·21
Phenols (g.)	0·70	0·57	0·16

Temperature. The yield of hydroxylated and nitrated material increases with temperature, but a greater amount of tar is formed :

	Non-phenols (g.)		Phenols (g.)	
Temp.	Run 1	Run 2	Run 1	Run 2
8—13°	0·94	0·86	0·59	0·71
50—55°	1·60	1·50	0·91	0·95
98°	1·77	1·81	1·17	1·25

Hydrogen, nitrogen, air. When blown through the reactants hydrogen appeared to reduce the yield of hydroxylated material; neither nitrogen nor air had significant effect :

	Non-phenols (g.)		Phenols (g.)	
Conditions	Run 1	Run 2	Run 1	Run 2
Rapid air stream	0·99	0·88	0·69	0·61
Rapid H_2 stream	1·05	1·03	0·41	0·48
Rapid N_2 stream	1·17	1·16	0·56	0·56
Normal	1·04 1·07 *	1·13	0·67 0·63 *	0·69

* Run 3.

Order of addition of reagents. Yields did not differ appreciably when (*a*) a mixture of hydrogen peroxide and sodium nitrite was added to acidified nitrobenzene or (*b*) sodium nitrite was added to a mixture of nitrobenzene and acidified hydrogen peroxide. They did differ considerably, however, when (*c*) hydrogen peroxide was added to acidified nitrite and nitrobenzene (table below). With nitrite in excess throughout, the products were all greatly reduced in amount and associated with more tar.

	Non-phenols (g.)		Phenols (g.)	
Method of mixing	Run 1	Run 2	Run 1	Run 2
(*a*)	0·76	0·83	0·76	0·76
(*b*)	0·87	0·71	0·80	0·78
(*c*)	0·27	0·16	0·31	0·21

Emulsifiers. The various types used (fatty alcohol–polyethylene oxide condensates and polyglyceryl ricinoleate), although they increased the dispersion, did not increase the yield of either hydroxylated or nitrated material.

DISCUSSION

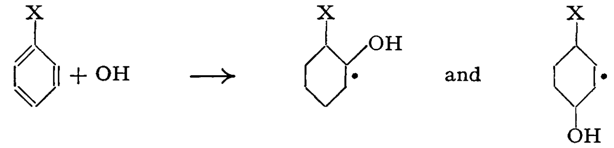
We showed (preceding paper) that a typical aromatic compound, benzene, is nitrated and hydroxylated by dilute solutions of pernitrous acid, whether prepared by using hydrogen peroxide or not, and further that these reactions take place at low acidity and laboratory temperatures. We concluded that the reactions resulted from the presence of two free radicals—hydroxyl and nitrogen dioxide—and experimental work described above has tended throughout to confirm these inferences. At an early stage we were led to dismiss any idea of the nitronium ion NO_2^+ on account, first, of its being a highly improbable species in acidities of the order of N/30, and, secondly, because the products of certain nitrations, for example, *m*-chloronitrobenzene from chlorobenzene, are not those formed in nitrations which may, with certainty, be ascribed to the action of the nitronium ion. We have satisfactory evidence that the nitration does not proceed through the formation of a nitroso-compound, by the action of the nitrosyl ion NO^+, and its subsequent oxidation to a nitro-compound.

In the nitrous acid–hydrogen peroxide reaction with aromatic compounds the hydroxylation is nearly always *ortho* and *para* to the original substituent which appears to be in accord with recent views on radical substitution in aromatic compounds (Augood, Hey, Nechvatal, and Williams, *Nature*, 1951, **167**, 725). Exceptions are *m*-nitrophenol from nitrobenzene (but the amounts found are much smaller than those for either *o*- or *p*-nitrophenol) and some of the other minor products from this and other starting materials. Nitration, on the other hand, except for dimethylaniline, is almost exclusively *meta* to the original substituent. When, however, there is simultaneous hydroxylation and nitration the incoming groups occupy adjacent positions in all the major products. Attempts to account for the above facts have led us to choose radical addition rather than hydrogen replacement as a basis of the general scheme, albeit speculative, advanced below. This or any other interpretation must start from the point that our reaction products cannot be due to ionic-substitution processes.

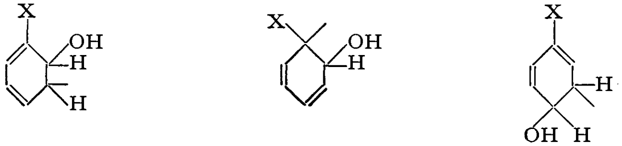
(*a*) The pernitrous acid undergoes homolytic fission :

$$HO_2{\cdot}NO \longrightarrow HO + NO_2$$

(*b*) The hydroxyl radical enters the aromatic nucleus (almost exclusively) in the *ortho* and the *para*-position :

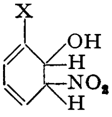


In the radicals formed, the unpaired electron will probably be localised in the position adjacent to the hydroxyl group :



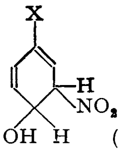
but the possibility of the formation of quinonoid structures is not excluded :

(*c*) By reaction between these free aryl radicals and nitrogen dioxide, for which the activation energy will be practically zero, the nitro-group is attached :



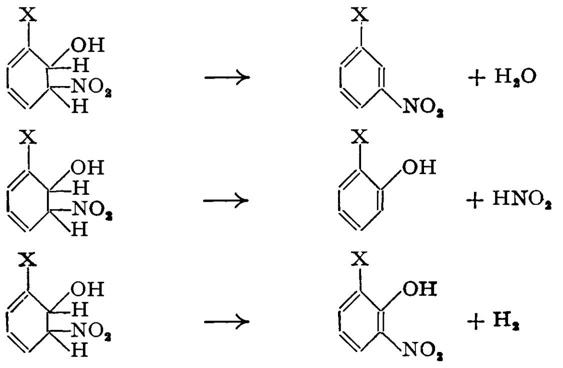
(*A*)

(*B*)

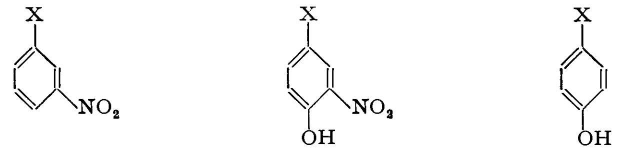


(*C*)

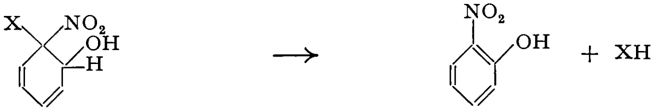
(*d*) These addition compounds are unstable and liable to break down by the elimination of water, of nitrous acid, or of hydrogen, *e.g.*, in (*A*) :



Similarly (*C*) will give



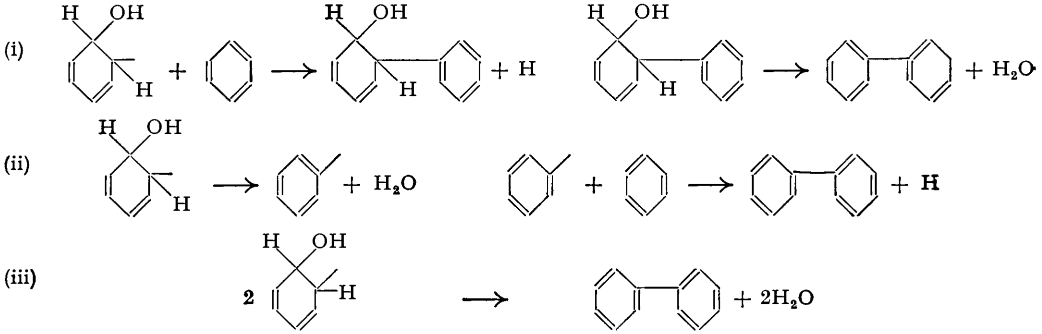
But in the case of (*B*) the same type of reaction renders possible the elimination of the original substituent X :



The purely hydroxylated products may result from a more direct process, *e.g.* :

By such means hydroxyl and nitro-groups may be introduced, individually or together, into the aromatic molecule. The hydroxyl group will always enter in the *ortho-* or *para-*position, and the nitro-group in the *meta*-position, relative to the original substituent. When both hydroxylation and nitration occur, hydroxyl and nitro-groups will be adjacent to one another, unless the intermediate aryl radical should adopt the quinonoid structure, when the nitro-group will take up a position *para* to the hydroxyl. The course of the decomposition of the addition compound depends somewhat on the nature of the original substituent which thus determines the product.

With benzene these suggestions account satisfactorily for the major products nitrobenzene and *o*-nitrophenol, and also for the two minor products, phenol and *p*-nitrophenol. The diphenyl isolated may result from one or more of the following sequences (owing to the presence of nitrogen dioxide concurrently with the aryl radical it is not to be expected that diphenyl will occur in more than a small quantity) :



Speculation as to the way in which the minor products *p*-dinitrobenzene and 4-hydroxy-3-nitrodiphenyl are formed is perhaps not profitable at this stage.

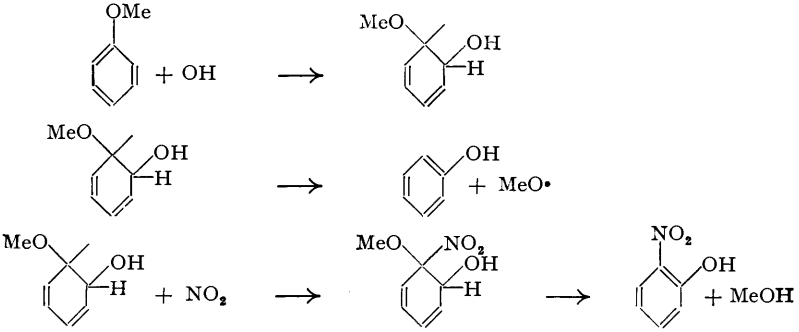
Of the toluene products the nitrotoluene, 2-methyl-6-nitrophenol and 4-methyl-2-nitrophenol may well result from the operation of such a scheme as that outlined above. The benzaldehyde probably springs from the direct oxidation of toluene by the pernitrous acid. Formation of the halogeno-compound suggests the presence of chlorine atoms, presumably from the discharge of chloride ions.

The formation of some *m*-nitrophenol from nitrobenzene indicates that here, at least, the hydroxyl radical does not enter the aromatic nucleus exclusively in the *ortho-* and *para*-positions. The probable mode of formation of the other major products from nitrobenzene comes readily within the general scheme outlined above.

The compounds derived from dimethylaniline are anomalous, but may be explained in view of the fact that Bamburger and Tschirner (*Ber.*, 1899, **32**, 1897) obtained the same product simply by the action of nitrous acid on dimethylaniline oxide. It is conceivable that the hydrogen peroxide oxidised the dimethylaniline to the oxide which in turn reacted with the nitrous acid.

The major products obtained from chlorobenzene and phenol present no anomalies. Phenol is interesting in that the dominant compounds are catechol and quinol, not nitrophenols.

Anisole provides an example in which the original substituent is eliminated. The reactions involved are probably :



In the presence of iodine the yield from benzene is much reduced but the hope that it would successfully compete with nitrogen dioxide for aryl radicals, and thus serve to identify them, was not realised. One halogeno-compound, 6-iodo-2-nitrophenol, was isolated but the manner of its formation is unknown.

Nitric oxide, also sent on the same quest, when present during the reaction with benzene, led to the formation of some nitrosophenol. This may be caused by the gas combining with either the phenolic products or the aryl radicals. A possibility, regarded as unlikely, is the concurrent formation of the nitrosyl ion and hydroxyl radical, $NO + H_2O_2 \longrightarrow NO^+ + OH + OH^-$, followed by nitrosation of the aromatic compounds.

The presence of nitroso-compounds here, and the fact that they are not immediately oxidised to nitro-compounds, taken with the absence of any evidence of nitroso-compounds in the normal reaction, goes far to establish that the nitro-compounds are not the result of the oxidation of nitroso-compounds.

It appears that pernitrous acid provides a general method for nitration and hydroxylation of aromatic compounds and especially for the preparation of *m*-nitro-compounds and derivatives of *o*-nitrophenol. Unfortunately the yields are very small and in many cases the products include species which are difficult to separate and may be associated with tars. Of the aromatic compounds used, nitrobenzene and anisole gave the best yields, based on the nitrite used ; with nitrobenzene about 8% of the nitrite was effective, and with anisole about 30%. For benzene, toluene, and chlorobenzene the corresponding figure is less than 6%. Phenol gives a comparatively high yield of hydroxylated product, but this is most probably due to its relatively high solubility. It has been shown that the yield in the case of nitrobenzene (the only compound fully investigated) cannot be improved by altering the concentration or the method of mixing. Raising the temperature increased the yield, but the product contained considerably more tar.

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