CCXLVIII.—*The Direct Formation of Quinones from 2 : 6-Disubstituted Derivatives of 4-Nitrophenol.*

By EDWARD CHARLES SNELL JONES and JAMES KENNER.

IN extension of previous researches in the diphenyl series, it was desired to examine the behaviour of triphenyl derivatives, and in this connexion 4-nitro-2 : 6-diphenylphenol (I) was selected as a suitable material for exploratory purposes. When, however, the compound was dissolved in hot glacial acetic acid solution, the originally colourless concentrated solution rapidly became red, oxides of nitrogen were evolved, and, after completion of the reaction, red needles of pure 2 : 6-diphenyl-1 : 4-benzoquinone (II) were deposited on cooling.

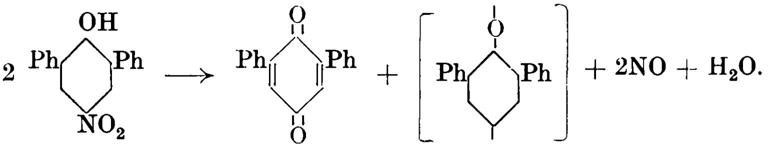
The conditions requisite for this remarkable reaction, and its nature, have therefore been studied more closely. In the first place, it is very liable to inhibition by small amounts of impurity, *e.g.*, hydrochloric acid, and, possibly for this reason, was not quantitative in a number of the instances to be referred to later. Acetic acid plays no part in the change, since this also occurs when the nitrophenol is heated alone, and also when its solution in benzene is exposed to the light from a mercury vapour lamp.

Then, in considering the mechanism of the decomposition by heat alone, or in solution, it was natural to assume that the nitrophenol reacted in the *aci*- or quinonoid form, particularly when it was observed that the yellow sodium salt of 4-nitro-2 : 6-diphenylphenol became scarlet when its temperature was slightly raised. We were thus led to compare the reaction with the formation of aldehydes or ketones, together with nitrous oxide, on acidification of solutions of the sodium salt of aliphatic nitro-compounds (Nef, *Annalen*, 1894, **280**, 266; *Ber.*, 1896, **29**, 1223) :

$$2\left[{}^{X}_{Y}\!\!>\!C\cdot NO_2\right]H \longrightarrow 2\,{}^{X}_{Y}\!\!>\!C{=}O + N_2O + H_2O.$$

But when the gaseous products were examined in the present instance, by carrying out the reaction in an atmosphere of carbon dioxide, nitric oxide was found to be the sole gaseous product from 4-nitro-2 : 6-diphenylphenol, and the quinone was accompanied by an equimolecular proportion of a colourless material. The latter was readily isolated, since it crystallised when the reaction was carried out in acetic acid solution. Analysis and molecular-weight determinations indicated it to be a six-fold polymeride of (III) in combination with two extra oxygen atoms.

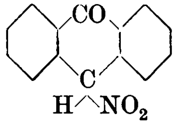
Apparently the oxygen atoms of (III) serve to connect aromatic nuclei, since the polymeride is very easily oxidised to 2 : 6-diphenylbenzoquinone by chromic acid. In a special experiment, water was actually collected as a product of the decomposition of 4-nitro-2 : 6-diphenylphenol by heat.

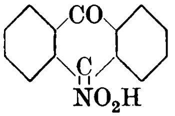


(I.) (II.) (III.)

The probable dependence of the reaction on the *aci*-form is illustrated in an interesting manner by the work of Meisenheimer and Connerade (*Annalen*, 1903, **329**, 133), who obtained nitroanthrone in two forms, to which they assigned the formulæ (IV) and (V), which both undergo decomposition when heated.

(IV.)





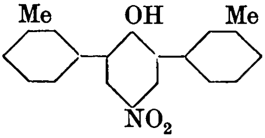
(V.)

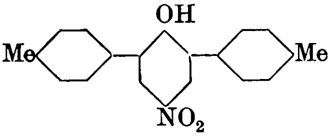
A. G. Perkin and Mackenzie, who first isolated nitroanthrone, recorded its decomposition by heat into anthraquinone and oxides of nitrogen (J., 1892, **61**, 869). These instances, therefore, appear to conform to the type now under discussion, but we have not yet examined them more closely, and we have so far confined ourselves to simpler derivatives of *p*-nitrophenol.

Apparently at least two substituents are necessary, at any rate for facility of reaction, and these should occupy the 2- and 6-positions. The synthesis of 3 : 5-diphenylphenol having only recently been achieved (Kenner and Shaw, this vol., p. 769), we have not yet examined its 2-nitro-derivative, but 2-nitro-*s*.-xylenol proved to be quite stable, whereas 2 : 6-dimethyl-, -methylethyl-, and -diethyl-4-nitrophenols all underwent smooth decomposition in acetic acid solution. On the other hand, the 2-phenyl and 2-ethyl derivatives only yielded oxides of nitrogen when heated alone and somewhat strongly, and no odour of quinone was detected. Pursuing this line of inquiry, it was found that Armstrong and Brown (*Ber.*, 1874, **7**, 926) had studied the thermal decomposition of 2 : 6-dichloro- and -dibromo-4-nitrophenols (Brunck, *Z. Chem.*, 1867, 204) just above their melting points, and recorded the production of nitrogen, nitric oxide, and nitrogen peroxide as gaseous products, together with quinones and other substances (compare Post and Brackebusch, *Annalen*, 1880, **205**, 91). In our experiments, a certain amount of nitrosyl chloride and bromide were respectively obtained, and relatively somewhat drastic thermal conditions were necessary before 2 : 6-dichloroquinone was obtained. Further, Armstrong recorded the decomposition of 4 : 6-dichloro-2-nitrophenol, with formation of gases composed of 98·6% of nitric oxide and 1·4% of nitrogen, surmising also the formation of 4 : 6-dichloro-*o*-benzoquinone (J., 1871, **24**, 477). We were unable to bring about a similar change in the case of 2 : 6-*dicarbethoxy*-4-*nitrophenol*, and it would seem that *o,p*-directive substituents are requisite.

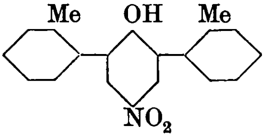
The manner in which the character of the second product may vary with the nature of the substituents in the 2- and 6-positions was well illustrated by the behaviour of the 2 : 6-*di*-m- and -p-*tolyl*-4-*nitrophenols* (VI) and (VII), whether heated alone or in glacial acetic acid solution.

(VI.)





(VII.)



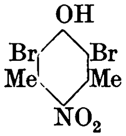
(VIII.)

In the latter case 2 : 6-*di*-p-*tolylbenzoquinone* was only separated with difficulty from the resulting mixture, and in the former, purification could not be achieved. In both cases the second product also appeared to be red and possibly (though this remains to be demonstrated) a tetratolyl derivative of diphenoquinone. The reaction could not be induced in 2 : 6-*di*-o-*tolyl*-4-*nitrophenol* (VIII), whether by heating alone or in glacial acetic acid solution, and correspondingly the sodium salt of this compound does not undergo a change of colour when warmed. We therefore sought to overcome the difficulty in the last case by introducing a hydrogen acceptor. Lead tetra-acetate was selected for this purpose, since Dimroth had demonstrated the efficiency of a suspension of this reagent in glacial acetic acid for the oxidation of quinols to quinones (*Ber.*, 1920, **53**, 484, 487; 1921, **54**, 3058; 1922, **55**, 1231; 1923, **56**, 1375). The device proved to be valuable, since it not only renders possible the decomposition of the *oo'*-derivative just mentioned, but also causes that of 4-nitro-2 : 6-diphenylphenol, and of the other compounds already mentioned, to occur quantitatively even at a temperature a little above the ordinary. Under these conditions also, halogen was eliminated from 2 : 6-dichloro- and -dibromo-nitro-phenols, and this prevented us from isolating the corresponding quinones in these cases.

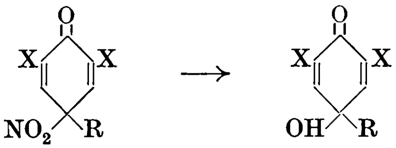
Remarkably enough, however, 2 : 6-dibromo-4-nitro-3 : 5-dimethylphenol (IX) is readily converted by this means into the corresponding quinone, so that the two methyl groups exert a well-marked protective effect on the halogen atoms. Our attention was drawn to this compound, because Lindemann had shown it (as well as 1-nitro-β-naphthol and its 3 : 5-dibromo-derivative) to undergo decomposition in glacial acetic acid solution, and to furnish quinones in presence of nitric acid (compare Fries and Oehmke, *Annalen*, 1928, **462**, 1).

Qualitative experiments have also shown that lead tetra-acetate causes the elimination of oxides of nitrogen from *o*- and *p*-nitrophenols and from picric acid as well as from 2-phenyl- and -ethyl-4-nitrophenols, but reaction occurred much less readily than in the other cases and the mixture in each case required to be heated.

The formation of nitric oxide, whilst apparently suggesting a fundamental difference between the reaction now discussed and that already cited in the aliphatic series, provided a basis for a second comparison—with the formation of quinols (XI) from quinitrols (X)—of which numerous instances were recorded by Zincke and by Auwers and their collaborators :—



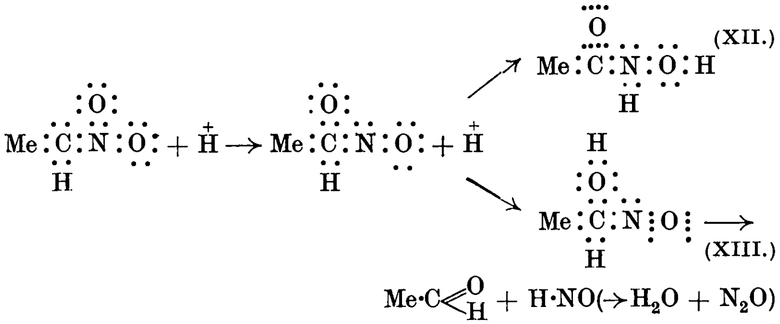
(IX.)



(X.) (XI.)

Although this change proceeds when the quinitrols are heated above their melting point, alone or with a solvent (which need not be glacial acetic acid, but can be an indifferent medium) (Auwers and Rapp, *Annalen*, 1898, **302**, 156), it is evident that hydrogen must be provided from some external source, and the reaction has therefore been regarded as essentially one of hydrolysis (compare, for example, Auwers, *Ber.*, 1902, **35**, 454). The gaseous products appear never to have been examined, and when mentioned are somewhat vaguely referred to as " Stickoxyde " (compare, for example, Fries, *Ber.*, 1906, **39**, 437, 445, 448). In the case of the quinitrol from 3 : 5-dichloro-*p*-cresol, however, we found the gas evolved from its decomposition in glacial acetic acid solution to be nitric oxide, as in the case of the nitrophenols, but accompanied by a very small proportion of nitrogen. The second comparison was thus justified, and the two reactions are therefore closely connected. Incidentally confirmatory evidence is supplied in favour of the nitro- as against the nitrite formula for the quinitrols.

Fries and Oehmke (*loc. cit.*) also refer to the connexion between quinitrol and quinone formation, surmising in the latter case a primary formation of the quinol. In our view, however, and in spite of the divergence already indicated, these reactions are related to those of the aliphatic series. The latter were regarded by Nef as instances of "intramolecular oxidation," and the same process is exemplified by the isolation of acethydroxamic acid (XII) (Bamberger, *Ber.*, 1902, **35**, 45) and of its mono- and di-benzoyl derivatives (Nef, *loc. cit.*) from the decomposition of the sodium salt of *aci*-nitroethane by acid and by benzoyl chloride, respectively. These changes are simply explained in terms of Kuhn and Albrecht's formula for the *aci*-nitroethane anion (*Ber.*, 1927, **60**, 1297) as due in the first place to the transference of a co-ordinated oxygen atom from a positive nitrogen to the adjoining negative carbon atom; a more satisfactory distribution of electrons is thus achieved :

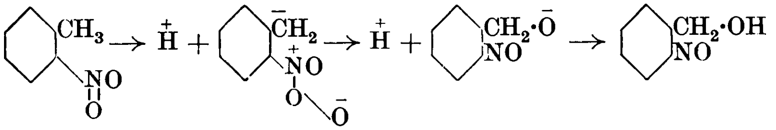


(XII.)

(XIII.)

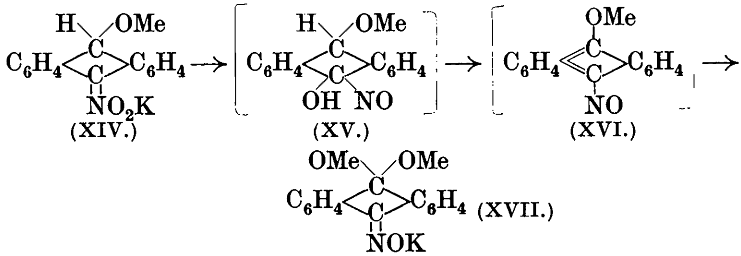
$$Me{\cdot}C{<}^{O}_{H} + H{\cdot}NO(\rightarrow H_2O + N_2O)$$

Nef also compared his results with the formation of dinitrosostilbene from *p*-nitrotoluene (Fischer and Hepp, *Ber.*, 1893, **26**, 2231; compare Green and Baddiley, J., 1908, **93**, 1722) and with Baeyer's synthesis of indigotin from *o*-nitrobenzaldehyde and acetone. These reactions involve a transference of co-ordinated oxygen to the fifth carbon atom from the nitro-group, whilst the formation of *o*-nitrosobenzyl alcohol from *o*-nitrotoluene (Kalle and Co., D.R.-P. 194811) depends on transference to the third carbon atom (compare also B.A.S.F., D.R.-P. 114839; Bamberger and Elger, *Annalen*, 1910, **371**, 322; 1929, **475**, 288) :—



The necessity of postulating a mechanism of this kind also becomes clear when it is remembered that the familiar condensation reactions of *p*-nitro-, 2 : 4-dinitro-, and 2 : 4 : 6-trinitro-toluenes all involve replacement of hydrogen by a kationoid, rather than by an anionoid group like hydroxyl.

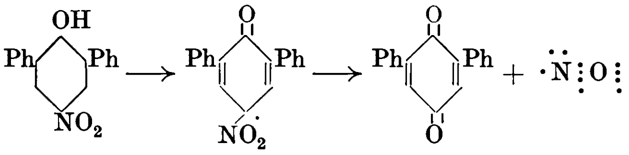
On the other hand, hydroxylation or alkoxylation occurs on the fourth, rather than on the third or fifth carbon atom, in the formation of 4-nitroso-α-naphthol-2 : 5-disulphonic acid from α-nitronaphthalene-3 : 8-disulphonic acid in presence of boiling aqueous sodium hydroxide (Friedlaender, *Ber.*, 1895, **28**, 1535; compare D.R.-P., 127295; Graebe, *Ber.*, 1899, **32**, 2876; Friedlaender, *ibid.*, p. 3526), and of the potassium salt of anthraquinoneoxime dimethylacetal (XVII) from methylanthracene nitrate (XIV) in presence of methyl-alcoholic potassium hydroxide (Meisenheimer, *Annalen*, 1902, **323**, 205) :—



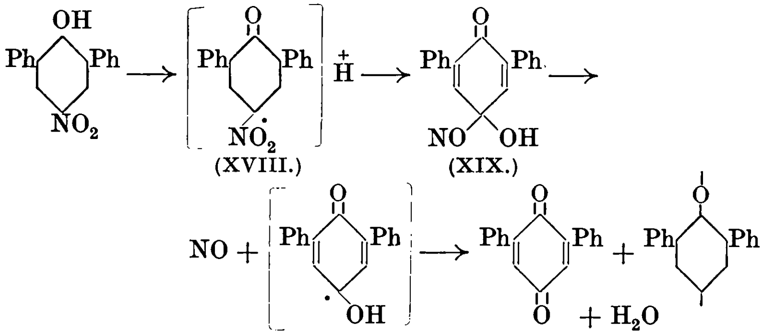
(XIV.) (XV.) (XVI.) (XVII.)

Now the additive compound of trinitrobenzene with potassium methoxide is analogously constituted to (XIV) (Meisenheimer, *loc. cit.*) and is converted into 3 : 5-dinitroanisole when boiled with methyl alcohol (Lobry de Bruyn and van Leent, *Rec. trav. chim.*, 1890, **9**, 214, 218; 1894, **13**, 148; 1895, **14**, 150). The formation of 3 : 5-dinitro-oxazine from 2 : 4 : 6-trinitro-2-hydroxydiphenylamine (Turpin, J., 1891, **59**, 722; Kehrmann, *Ber.*, 1899, **32**, 2605) is an essentially similar reaction, and it seems possible to reconcile the results of these three reactions only by postulating in each case an intermediate product of the type (XV), in which migration of an oxygen to the adjacent carbon atom has occurred. In the instance illustrated, this appears preferable to the assumption made by Meisenheimer of a direct conversion of (XIV) into (XVI).

This body of evidence in regard to aromatic nitro-compounds renders it highly probable that the initial course of the decomposition of the nitrophenols is analogous to that of the aliphatic *aci*-nitro-compounds, and in the case of the oxidation by lead tetra-acetate the following scheme shows that the observed evolution of nitric oxide would be an almost necessary consequence of migration of the co-ordinated oxygen atom :—



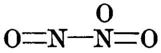
The fact that this does not depend on transition to the *aci*-form explains its applicability to 4-nitro-2 : 6-di-*o*-tolylphenol. The series of changes in absence of an oxidising agent would be represented as follows :—

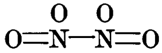

(XVIII.) (XIX.)

Acceptance of this scheme is, however, conditional on an explanation of the production of nitric oxide by the decomposition of (XIX), which is the formal analogue of (XIII).

In our opinion, this is to be found in the " heterogeneity " of the conjugation in (XIX) (Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, 7; Allan, Oxford, Robinson, and Smith, J., 1926, 404). The cases of the hexa-arylethanes, tetra-arylhydrazines, and similar compounds, of the sulphonium iodide, $(Et_2S{\cdot}SEt)I$ (Hilditch and Smiles, J., 1907, **91**, 1394; compare Davis, *Ber.*, 1891, **24**, 3548; Jackson, *Annalen*, 1875, **179**, 18), of hydrazoethane dihydrochloride (Harries, *Ber.*, 1894, **27**, 2276) and the benzidine change (compare Robinson and Robinson, J., 1918, **113**, 639), and of β-amino-ketones and -hydroxy-acids all illustrate the tendency of heterogeneous systems to seek relief by such dissociation as is postulated for (XIX). This reaction thus appears as the organic analogue of the dissociation of the oxides of nitrogen, and the diminishing tendency to dissociation of the structures (XX), (XXI), and (XXII) (compare Wieland, *Ber.*, 1921, **54**, 1776; Battegay and Kern, *Bull. Soc. chim.*, 1928, **41**, 1336) in the order given is in accord with the greater affinity of the nitroso- than of the nitro-group for proton :

$$O{=}N{-}N{=}O$$
(XX.)


$$O{=}N{-}\overset{O}{N}{=}O$$
(XXI.)


$$O{=}\overset{O}{N}{-}\overset{O}{N}{=}O$$
(XXII.)

The mutual agreement of these various facts suggests it is no longer true that, in nitric oxide and nitrogen peroxide, nitrogen exhibits valencies which " cannot be explained in the present state of our knowledge " (Sidgwick, " Theory of Valency," 1927, 279; compare

G. N. Lewis, "Valence and the Structure of Atoms and Molecules," 1923, 128).

These considerations further indicate that decomposition of the nitrophenols might also proceed directly by dissociation of nitrogen peroxide from their *aci*-forms. Not only, however, would such a mechanism differentiate this reaction from all the others which have been cited, but in another communication it will be shown that dissociation of this character probably occurs among the quinitrols, in a reaction the outcome of which differs essentially from the results now communicated.

Although the constitution of the quinitrols prevents any assumption of complete ionisation corresponding to (XVIII), their conversion into quinols can be adequately explained in terms of a similar mechanism involving incipient ionisation. A close parallel is provided by comparing the oxidation of tertiary hydrocarbons to the corresponding alcohols, with the formation of *o*-nitrosobenzyl alcohol already discussed.

EXPERIMENTAL.

(*A*) *Preparation of Materials.*

Ketones.—*Di*-o-*tolylacetone* resulted from the dry distillation of calcium *o*-tolylacetate (95 g.) previously dried at 140°. From the crude product (59 g.) the pure ketone was isolated by distillation at 201°/16 mm.; it melted at 50—52° (Found: C, 85·8; H, 7·7. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%). Its *semicarbazone* was obtained in fine white prisms, m. p. 142—143° (Found: N, 14·8. $C_{18}H_{21}ON_3$ requires N, 14·6%).

Di-m-*tolylacetone* was prepared from calcium *m*-tolylacetate in 70% yield, b. p. 204/16 mm., and could not be obtained in the solid state (Found: C, 85·4; H, 7·6%). Its *semicarbazone* crystallised in well-formed prisms, m. p. 92—93° (Found: N, 14·6%).

Di-*p*-tolylacetone, previously described by Errera (*Gazzetta*, 1891, **21**, 102), was characterised by its *semicarbazone*, white needles, m. p. 84—85° (Found: N, 14·5%).

Nitrophenols.—Certain of the 2-mono- and 2 : 6-di-substituted 4-nitrophenols required for this investigation had been obtained previously by other workers, indicated in the notes appended to the table below, but for our purpose it was more convenient to employ the general method of condensing the appropriate derivative of acetone with the sodium salt of nitromalonaldehyde according to the method of Hill (*Amer. Chem. J.*, 1900, **24**, 1). The product was conveniently isolated, after removal of alcohol by distillation from a steam-bath, by collecting the sodium salt from the cooled residue, and gradually adding an aqueous solution of the salt to ice-cold dilute hydrochloric acid. The product was purified by crystallisation, usually from alcohol, and finally from glacial acetic acid to which a drop of concentrated hydrochloric acid had been added to inhibit decomposition. The actual proportions of material employed in the various preparations are summarised in Table I.

TABLE I.

Substituents. Derivatives of 4-nitrophenol.	Derivative of acetone, g.	Alcohol, c.c.	Sodionitromalonaldehyde, g.	Water, c.c.	Sodium hydroxide, g.	Water, c.c.	Time of condensation.	Yield, %.	M. p.
1. 2 : 6-Diphenyl-	Diphenyl- 60	300	42	400	21·4	100	5 days	81	137°
2. 2 : 6-Di-*o*-tolyl-	Di-*o*-tolyl- 42	500	27·7	140	14·4	40	20 hrs. 30—35°	74·4	192—193
3. 2 : 6-Di-*m*-tolyl-	Di-*m*-tolyl- 36	150	24	210	12	60	4 days	86·5	145
4. 2 : 6-Di-*p*-tolyl-	Di-*p*-tolyl- 25	500	17	175	10	50	4 days	92·5	137
5. 2 : 6-Dimethyl-	Dimethyl- 5	15	7·8	45	0·4	45	1 day	94	171
6. 2-Methyl-6-ethyl-	Methylethyl 15	120	18·8	170	2	10	1 day	74·2	135—136
7. 2 : 6-Diethyl	Diethyl 10	40	14	190	1·6	10	1 day	77	130—131
8. 2 : 6-Dicarbethoxy-	Ethyl acetonedicarboxylate 10·8	42	8·3	40	0·55	10	1 day	84·6	61
9. 2-Ethyl	Ethyl 5·5	40	10	90	1	10	1 day	69·5	79—80

Description and Analysis.—With the exception of 4-nitro-2 : 6-di-*o*-tolylphenol and 2 : 6-dicarbethoxy-4-nitrophenol, the sodium salts of the following nitrophenols are either red at the ordinary temperature, or if yellow, rapidly become bright red on warming. The sodium salt of the di-*o*-tolylnitrophenol is colourless even at 100°, and the nitrophenol when heated alone tends to distil rather than undergo decomposition.

1. 4-Nitro-2 : 6-diphenylphenol has been described by Hill (*loc. cit.*).

2. 4-*Nitro*-2 : 6-*di*-o-*tolylphenol* was obtained in vitreous prisms, moderately easily soluble in alcohol, chloroform, and benzene, sparingly in ether and ligroin (Found : C, 75·2; H, 5·5. $C_{20}H_{17}O_3N$ requires C, 75·2; H, 5·4%).

3. 4-*Nitro*-2 : 6-*di*-m-*tolylphenol*, well-formed needles, moderately easily soluble in alcohol, chloroform, and glacial acetic acid (Found : C, 75·1; H, 5·3; N, 4·5. $C_{20}H_{17}O_3N$ requires C, 75·2; H, 5·4; N, 4·4%).

4. 4-*Nitro*-2 : 6-*di*-p-*tolylphenol*, feathery white needles, very soluble in ether and chloroform, moderately easily in alcohol (Found : C, 75·3; H, 5·3; N, 4·5%).

5. 5-Nitro-*m*-2-xylenol was also prepared from *m*-2-xylenol, and we are able to supplement the account given by Auwers and Markovits (*Ber.*, 1908, **41**, 2335) by recording as a subsidiary

product of the operation of nitration, 2 : 6-xyloquinone. This was identified by its melting point, 72—73°, and conversion into the corresponding quinol, m. p. 149—151°, and the agreement of these data with those recorded by Noelting and Baumann (*Ber.*, 1885, **18**, 1150) (Found : C, 70·5; H, 6·0. Calc. for $C_8H_8O_2$: C, 70·6; H, 5·9%).

6. Auwers and Wittig (*Ber.*, 1924, **57**, 1273) prepared 4-nitro-2-methyl-6-ethylphenol by oxidation of the nitrosophenol with alkaline potassium ferricyanide, recording the melting point 133—134°. The composition of our product was confirmed by analysis (Found : N, 7·8. Calc. for $C_9H_{11}O_3N$: N, 7·7%).

7. 4-*Nitro*-2 : 6-*diethylphenol* is very soluble in most organic solvents. It was obtained in crisp, pale yellow needles from glacial acetic acid (Found : N, 7·2. $C_{10}H_{13}O_3N$ requires N, 7·2%).

8. 2 : 6-*Dicarbethoxy*-4-*nitrophenol* separated as the sodium salt within a few minutes of the preparation of the condensation mixture as a mass of light yellow needles. The free nitrophenol crystallised from alcohol in long lustrous needles, moderately easily soluble in the usual organic solvents (Found : N, 5·3. $C_{12}H_{13}O_7N$ requires N, 5·0%).

9. 4-*Nitro*-2-*ethylphenol*, minute needles very soluble in all the usual organic solvents, crystallised most satisfactorily from a very small amount of formic acid (Found : N, 8·4. $C_8H_9O_3N$ requires N, 8·4%).

Other nitrophenols used in this work were prepared as follows :—

2-Nitro-*s*.-xylenol was prepared by the method of Auwers and Borsche (*Ber.*, 1915, **48**, 1714). Careful addition of light petroleum to a solution of the crude material caused the precipitation of uncrystallisable gummy material. The nitrophenol then separated in a pure condition, m. p. 110—111°. Auwers and Borsche (*loc. cit.*) record m. p. 107—108°.

4 : 6-Dibromo-*m*-5-xylenol (Mühlhaus, *Dissert.*, Brunswick, 1924; compare Fries, *Annalen*, 1928, **462**, 1) was readily prepared by adding bromine (32 g.), drop by drop, to a solution of 2-nitro-*s*.-xylenol (16·7 g.) in chloroform (170 c.c.) and cooling the mixture in ice. Long clear needles crystallised, m. p. 175—178°. This was raised to 182—183° by recrystallisation from glacial acetic acid (Found : N, 4·4. Calc. for $C_8H_7O_3NBr_2$: N, 4·3%). Mühlhaus records m. p. 177°.

(*B*) *Preparation of* 2 : 6-*Disubstituted* p-*Quinones by Oxidation of the Nitrophenols with Lead Tetra-acetate.*

The method consists in treating the nitrophenol in the presence of glacial acetic acid with lead tetra-acetate ($\frac{1}{2}$ mol.), prepared by the method of Dimroth and Schweisse (*Ber.*, 1923, **56**, 1377). It was found to be unnecessary either to effect solution or to apply heat. The reaction proceeded smoothly when the reactants were mixed and was not accompanied by the development of heat, the undissolved material going gradually into solution. In some cases it was possible to isolate the quinone directly from the reaction mixture, but generally the mixture was treated with ether and water, acid and lead salt being removed by aqueous extraction, and any unchanged nitrophenol by means of sodium hydroxide solution. The pure quinone remained in the ether, from which it was isolated by evaporation of the solvent.

Excellent yields were obtained in the following seven instances :—

2 : 6-Diphenyl-1 : 4-benzoquinone, m. p. 135°, did not depress the melting point of a specimen prepared by oxidation of the corresponding aminophenol (Hill, *loc. cit.*).

2 : 6-*Di*-o-*tolylbenzoquinone*, yellow needles from alcohol, m. p. 124°, very soluble in ether and chloroform, sparingly in benzene and alcohol (Found : C, 83·3 ; H, 5·7. $C_{20}H_{16}O_2$ requires C, 83·3 ; H, 5·6%). This quinone was also prepared in the usual manner.

4-*Amino*-2 : 6-*di*-o-*tolylphenol* was obtained by treating a solution of the nitro-compound (12·5 g.) in glacial acetic acid (120 c.c.) with a solution of stannous chloride (56 g.) in concentrated hydrochloric acid (42 c.c.). After the mixture had been boiled under reflux for 30 minutes, the tin salt of the hydrochloride of the base separated when the liquid was cooled in a freezing mixture. Tin was removed from a solution of the salt in hot water (1000 c.c.) by treatment with hydrogen sulphide, and the aminophenol (8·5 g.) isolated by pouring the liquor into ice-cold dilute sodium carbonate solution. The substance, m. p. 215°, crystallised from chloroform in pure white needles which assumed a purplish tint on exposure to air (Found : C, 83·2; H, 6·6. $C_{20}H_{19}ON$ requires C, 83·0; H, 6·6%). A solution of the aminophenol (8·5 g.) in water (55 c.c.) and sulphuric acid (11 g.) was oxidised by addition of a solution of sodium dichromate (5 g.) in water (14 c.c.). After prolonged heating on the water-bath, the deep red intermediate indamine gave place to the yellow quinone, which was isolated in excellent yield, m. p. 124°.

2 : 6-*Di*-p-*tolylbenzoquinone*, bright red needles from alcohol, m. p. 161°, soluble in ether and chloroform, sparingly soluble in cold alcohol, benzene, and glacial acetic acid, but moderately easily in the hot solvents (Found : C, 83·1 ; H, 5·6. $C_{20}H_{16}O_2$ requires C, 83·3 ; H, 5·6%). It was converted by reduction into the corresponding *quinol*, m. p. 105°, stellate clusters of prismatic needles from benzene (Found : C, 82·8 ; H, 6·4. $C_{20}H_{18}O_2$ requires C, 82·7 ; H, 6·2%).

2 : 6-Dimethylbenzoquinone, m. p. 72—73°, as described by Nöelting and Baumann (*loc. cit.*), identical with the product obtained from the nitration of *m*-2-xylenol.

2-*Methyl*-6-*ethylbenzoquinone*, bright yellow needles from light petroleum (b. p. below 40°), m. p. 40—41°, freely soluble in most organic solvents (Found : C, 71·9; H, 6·7. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%). The corresponding *quinol*, m. p. 99—100°, obtained by reduction of the quinone with sulphurous acid, crystallised from benzene in long needles (Found : C, 71·0; H, 7·9. $C_9H_{12}O_2$ requires C, 71·0; H, 7·9%).

2 : 6-Diethylbenzoquinone, fine yellow needles from light petroleum (b. p. below 40°), m. p. 35°, freely soluble in most organic solvents. On reduction it yielded the corresponding *quinol*, m. p. 102—103° after crystallisation from ether (Found : C, 72·4; H, 8·6. $C_{10}H_{14}O_2$ requires C, 72·2; H, 8·5%).

2 : 6-Dibromo-3 : 5-dimethylbenzoquinone, m. p. 174°, as recorded by Mühlhaus (*loc. cit.*) (Found : C, 32·6; H, 2·1. Calc. for $C_8H_6O_2Br_2$: C, 32·7; H, 2·1%).

2 : 6-*Di*-m-*tolylbenzoquinone* was prepared in a similar manner to the above. Although the reaction seemed to pursue the normal course, the quinone was only isolated in a pure condition with some difficulty, by triturating the crude product with glacial acetic acid and finally crystallising it from this solvent. It formed orange-red needles, m. p. 103—105°, moderately easily soluble in the usual organic solvents (Found : C, 83·2; H, 5·6. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·6%).

Unsuccessful attempts were made to obtain quinones by means of this reaction from 2 : 6-dichloro-4-nitrophenol and from 2 : 6-dicarbethoxy-4-nitrophenol. In the former case, reaction proceeded with more than customary vigour, and was accompanied by removal of halogen, whilst in the latter instance there was no reaction.

(*C*) *Decomposition of* 2 : 6-*Disubstituted*-4-*nitrophenols in Boiling Glacial Acetic Acid Solution.*

For the purpose of determining the nature and proportion of the gaseous products of the reaction, definite quantities of the nitrophenol and glacial acetic acid were placed in a small flask, connected on the one side to a carbon dioxide generator, and on the other through a reflux condenser and a Wöhler tube containing potassium bicarbonate solution to a nitrometer charged in the normal manner with potassium hydroxide solution. The washing tube was inserted in order to remove any higher oxides of nitrogen, but it was found at the end of the reaction that, except in the cases of the halogenated nitrophenols, where to a certain extent the nitrosyl halide was formed, no iodine was liberated when a mixture of the bicarbonate solution with potassium iodide was acidified. It thus appeared that higher oxides of nitrogen were not produced by the reaction.

Air having been completely displaced from the apparatus, the flask was heated by means of an oil-bath. The purity of the nitric oxide collected was in all cases checked by transference to a eudiometer and then, in the first experiments, by its complete absorption in aqueous ferrous sulphate solution, and in later experiments by its complete solubility in water when oxygen was gradually added. The results of the typical experiments are summarised in Table II.

TABLE II.

Substituents.	Concentration.	NO evolved percentage.	Remarks.
2 : 6-Diphenyl-	2·91 g./10 c.c.	80	
2 : 6-Di-*m*-tolyl-	3·19 g./10 c.c.	45·5	
,,	6·4 g./5 c.c.	91·6	
2 : 6-Di-*o*-tolyl-	—	—	No reaction.
2 : 6-Di-*p*-tolyl-	3·19 g./10 c.c.	67	
2 : 6-Dimethyl-	0·83 g./5 c.c.	30	
2-Methyl-6-ethyl-	Nitric oxide evolved, quantitative experiment not carried out.		
2 : 6-Diethyl-	,, ,,	,,	,, ,,
2 : 6-Dichloro-	4·2 g./5 c.c.	23	Brown fumes also evolved.
2 : 6-Dibromo-	2·97 g./10 c.c.	40	,, ,,
3 : 5-Dimethyl-	—	—	No reaction.
2 : 6-Dicarbethoxy-	—	—	,, ,,
2 : 6-Dibromo-3 : 5-dimethyl-	Nitric oxide evolved, quantitative experiment not carried out.		

General Remarks.—Isolation of the products of reaction was achieved by the method used in the case of the lead tetra-acetate decomposition. In the case of 4-nitro-2 : 6-diphenylphenol, decomposition was accompanied by the separation of a white microcrystalline neutral substance, m. p. above 500°. This was almost insoluble in alcohol and ethyl acetate, sparingly in ether and glacial acetic acid, though remarkably soluble in benzene and nitrobenzene. It could not be crystallised from these solvents, and precipitation was effected by diluting the solutions with glacial acetic acid. However, alteration of the substance resulted from this treatment, since the precipitated material was no longer soluble in that solvent. The material used for analysis was that obtained directly from decomposition of the nitrophenol in acetic acid solution. It was collected on a hardened filter paper, and washed first with glacial acetic acid, and then with pure ether to remove the last traces of quinone. It consisted of an almost white, sandy powder (Found : C, 86·5, 86·7, 86·3; H, 4·9, 4·9, 4·7; *M*, 1665, 1581, 1950, using chloroform). The following results of microanalysis were communicated by Dr. Schoeller:—C, 87·0; H, 4·9%; *M*, 1360, 1640. These results agree best with a molecular formula $C_{108}H_{72}O_8$, which requires C, 86·6; H, 4·85%; *M*, 1496·6.

The material was immediately converted into 2 : 6-diphenylbenzoquinone by treatment with aqueous sodium dichromate solution and dilute sulphuric acid.

4-Nitro-2 : 6-di-*p*-tolylphenol yielded a red mass which was obviously a mixture. The second constituent was precipitated in a gummy condition by suitable dilution with water of a solution of the mixture in glacial acetic acid, and the pure quinone could then be isolated from the solution. The same general phenomena were observed in the decomposition of 4-nitro-2 : 6-di-*m*-tolylphenol, but in this case the quinone could not be isolated from the resulting orange-red mixture. In each instance, therefore, the second product seemed to differ in character from the compound described above, and its colour suggested the possibility that diphenoquinone derivatives might have been produced.

In each case the amount of neutral material (quinone and second product) was found to be proportional to the percentage of nitric oxide evolved, the residue consisting of unchanged nitrophenol. Careful examination of this residue, both in the case of 2 : 6-diphenyl- and 2 : 6-di-*p*-tolyl-4-nitrophenols, gave no indication that quinol was formed.

From 2 : 6-dichloro- and 2 : 6-dibromo-4-nitrophenols, no quinone could be isolated, and steam distillation of the neutral fraction in the former case failed to yield the quinone. Not merely were the proportions of nitric oxide evolved somewhat small, but decomposition in these cases was not confined to the formation of this gas. The red fumes of nitrosyl halide were readily observed, and in both cases the bicarbonate solution liberated iodine from acidified potassium iodide solution. Reduction of the acidified bicarbonate washings by means of sulphurous acid, and titration of the neutralised solution with *N*/10-silver nitrate solution, showed that from the dichloro-compound 5·5%, and from the dibromo-compound 9·0%, of the available halogen had been removed.

The products from the nitroxylenol were not closely examined.

The reactive nitrophenols also lose nitric oxide quite readily when heated with benzoic acid, but the reaction is less facile in the presence of propionic or *n*-butyric acid, and decomposition did not occur in presence of formic acid. Positive results were obtained in adipic acid solution, no doubt by virtue of its high boiling point, but charring occurred in all cases.

(*D*) *Thermal Decomposition of Dry* 2 : 6-*Disubstituted* 4-*Nitrophenols.*

This was studied in the apparatus employed for the acetic acid decomposition.

TABLE III.

Substituents.	Quantity.	Temp.	Percentage of NO.	Remarks.
2 : 6-Diphenyl	2·91 g.	180°	94	
,, ...	8·7 g.	160	90·5	Apparatus adapted to detect water.
2 : 6-Di-*m*-tolyl- ...	3·19 g.	200	32	,, ,, ,,
2 : 6-Di-*p*-tolyl-	6·4 g.	160	97·7	,, ,, ,,
2 : 6-Dichloro-	2·08 g.	140	54	Nitrophenol somewhat volatile.
2 : 6-Dimethyl-	1·67 g.	200	25·2	Nitrophenol and quinone both volatile.

The products from the typical experiments above were isolated in the manner previously described.

In the first three cases the formation of water as a product of reaction was demonstrated by modifying the apparatus. The reflux condenser was removed and the substance was heated in a small flat-bottomed distillation flask, with its side tube as low as possible. The water was collected in a tube, protected from access of water vapour from the bicarbonate washer by means of a calcium chloride tube, and immersed in a freezing mixture. In each case the water collected was identified by its behaviour towards anhydrous copper sulphate, and by its freezing point.

No quinone could be obtained from the 2 : 6-dichloro-4-nitrophenol under the conditions outlined in Table III, but when the compound was strongly heated in a test-tube, the quinone vaporised as described by Armstrong (*loc. cit.*) and was identified by its melting point, 120°, odour, and crystalline form, as well as by direct comparison with an authentic specimen.

The volatility of 4-nitro-2 : 6-dimethylphenol was inimical to its complete decomposition under the experimental conditions employed. The greater volatility of the xyloquinone, however, permitted it to be easily isolated and identified as a product of the reaction by its odour and melting point, 72—73°, and comparison with an authentic specimen.

(*E*) *Decomposition of* 3 : 5-*Dichloro*-4-*methylquinitrol.*

3 : 5-Dichloro-*p*-cresol was prepared by the method of Zincke (*Annalen*, 1903, **328**, 278), but was more conveniently isolated by distillation under diminished pressure, b. p. 125°/16 mm. The fraction thus obtained crystallised immediately.

By the action of nitric acid (very slight excess over the calculated quantity) on 3 : 5-dichloro-*p*-cresol (1 part) in glacial acetic acid (5 parts), 3 : 5-dichloro-4-methylquinitrol was readily prepared and crystallised at once : after dilution with an equal amount of water, the product was filtered and washed first with dilute acetic acid, then with water, and obtained in a yield amounting to 92% of the theoretical. Under Zincke's conditions (*loc. cit.*), using 1 c.c. of nitric acid per gram of cresol, the yields are lower, and negligible if the mixture is kept for ½ hour. The melting point of this reactive substance, 74—76°, was raised to 80—82° when taken in a warm bath.

When treated under the conditions described under section (*C*), the quinitrol evolved nitric oxide, to the extent of 58·5%, whilst at 85° (external temp.) 45% of the gas was liberated. Also, as in the case of the halogenated nitrophenols, nitrosyl halide was evolved, in both experiments the amount of chlorine removed amounting to 9·8% of that available.

(*F*) *Qualitative Examination of Other Nitrophenols.*

4-Nitro-2-phenylphenol (Hill, *Amer. Chem. J.*, 1905, **33**, 8; compare also Borsche and Scholten, *Ber.*, 1917, **50**, 596, 600), 4-nitro-2-ethylphenol, *p*-nitrophenol, *o*-nitrophenol, and picric acid each yielded oxides of nitrogen (identified by means of starch-iodide paper) when treated in hot glacial acetic acid solution with lead tetra-acetate, but the reaction took place much less readily than in the cases described above. The first three compounds gave a similar result when heated alone, but the boiling point of *o*-nitrophenol is apparently too low to permit the reaction to occur under atmospheric pressure. *m*-Nitrophenol does not react when heated in the dry state, but in glacial acetic acid reaction with lead tetra-acetate ensues. It is, however, preceded by effervescence, which indicates that there is a prior reaction.

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