488. *The Oxidation of Phenylhydrazine.*

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A new method of phenylation is described, namely, oxidation of phenylhydrazine with metallic oxides (preferably silver) in an aromatic solvent. Phenyl radicals are the active species. Similar reactions have been effected with four other arylhydrazines. Diaryls are also formed by the oxidation of phenylhydrazine with air, and with benzoquinones, in aromatic solvents, and with silver oxide and cupric sulphate in aqueous media.

It is well known that phenylhydrazine is extremely sensitive to oxidation and this phenomenon was the subject of numerous early investigations. Many different oxidising agents [1] have been used and a variety of products is formed according to the reagent and the conditions. Nearly all previous oxidations have been conducted in aqueous media, although Fischer and Ehrhard [2] oxidised phenylhydrazine with mercuric oxide in ether, obtaining aniline, diphenyl, mercury, and nitrogen, and Chattaway examined the effect of oxygen [3] and certain metallic oxides,[4] in the absence of a solvent, obtaining nitrogen, benzene, a little diphenyl, and traces of other substances. This paper is mainly concerned with the oxidation of phenylhydrazine in aromatic solvents, which has not been studied hitherto.

The oxidations were effected by gradual addition of the equivalent amount of silver oxide to a solution of phenylhydrazine in an aromatic solvent. Yellow mercuric oxide is a more vigorous oxidant but the reaction is complicated by the formation of arylmercury compounds; in both cases it is necessary to control the reaction by cooling, indeed on one occasion an uncontrolled oxidation mixture with mercuric oxide in benzene caught fire. Cupric oxide and lead dioxide are much less effective and heating is necessary to start the reaction. The principal oxidation products are nitrogen, water, and a mixture of diaryls. The latter are of most interest and the minor products were not isolated in every experiment but we found that benzene was formed when the oxidation was done in bromobenzene and in nitrobenzene, and this is doubtless a normal product. A similar oxidation of 2-naphthylhydrazine in benzene gave naphthalene as well as 2-phenylnaphthalene. Usually a trace of azobenzene was isolated by chromatography and in reactions on a larger scale (15 g. of phenylhydrazine) diphenyl was detected. Mercuric oxide gave diphenylmercury in addition and, if used in excess, some phenylmercuric chloride. This probably arose from a trace of mercuric chloride in the sample of oxide and when mercuric chloride was deliberately added phenylmercuric chloride was the major product. The oxidations are not quantitative. A series of nitrogen determinations carried out on the oxidation of phenylhydrazine with silver oxide in bromobenzene showed that only 65—70% of the theoretical volume was liberated, and acid extraction of the reaction mixture yielded unchanged phenylhydrazine (*ca.* 10%). Attempts to improve the efficiency of the oxidation by raising the temperature at the end of reaction are hampered by the thermal instability of phenylhydrazine. Aniline is formed and the amount of azobenzene increases. It seems likely that the azobenzene usually obtained arises from a little aniline in the phenylhydrazine but we were unable to obtain a sample of the latter which gave no trace of azobenzene. Probably slight decomposition occurs during distillation, even at very low pressure. A little *p*-nitroaniline was isolated on oxidation of *p*-nitrophenylhydrazine in warm benzene; in this case heating is necessary as the hydrazine is rather insoluble in benzene and the reaction is very slow in cold suspension.

The diaryls obtained in different solvents are listed in Table 1; a mixture of isomers was obtained in all cases (except in benzene) but on the usual scale of operation (5 g. of

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[1] Seide, Scherlin, and Bras, *J. prakt. Chem.*, 1933, **138**, 55, and references therein.
[2] Fischer and Ehrhard, *Annalen*, 1879, **199**, 332.
[3] Chattaway, *J.*, 1907, **91**, 1323.
[4] Chattaway, *J.*, 1908, **93**, 270.

phenylhydrazine) it was only possible to isolate a few individual compounds as indicated. The formation of these compounds suggests that the oxidation of phenylhydrazine under these conditions produces phenyl radicals which then attack the solvent, and this is strongly supported by the following evidence. (1) The products formed by oxidation of phenylhydrazine with silver oxide in *iso*propylbenzene include 2 : 3-dimethyl-2 : 3-diphenylbutane. This arises by the abstraction of an α-hydrogen atom from *iso*propylbenzene and dimerisation of the resulting radical, and its formation establishes the homolytic nature of this reaction.[5] (2 : 3-Dimethyl-2 : 3-diphenylbutane is not formed by the action of silver oxide alone on *iso*propylbenzene.) (2) Infrared analysis [6] of the mixture of chlorodiphenyls obtained by oxidising phenylhydrazine with silver oxide in chlorobenzene shows that the ratio of isomers formed is in agreement, having regard to the accuracy of the analytical method, with those obtained by Augood, Hey, and Williams [6] for the phenylation of chlorobenzene by benzoyl peroxide, and by means of the Gomberg reaction, and by Bryce-Smith and Clarke [7] using silver iodide dibenzoate (see Table 2). We conclude that the active species, namely, the phenyl radical, is the same in each case and the silver oxide oxidation of phenylhydrazine therefore joins the growing list [8] of methods available for the phenylation of aromatic compounds. The reaction can be most simply represented as follows :

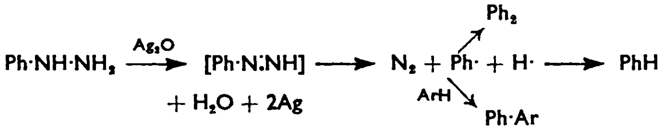
TABLE 1. *Oxidation of phenylhydrazine with silver and mercuric oxides.*

Solvent	Phenylation products isolated
Benzene	Diphenyl
Toluene	Mixed methyldiphenyls
*iso*Propylbenzene *	Mixed *iso*propyldiphenyls
Nitrobenzene	2- and 4-Nitrodiphenyl
Chlorobenzene	2-Chlorodiphenyl
Bromobenzene	4-Bromodiphenyl
Anisole †	Mixed methoxydiphenyls
Pyridine	2-, 3-, and 4-Phenylpyridines ‡

* Silver oxide only in this solvent.
† Mercuric oxide only in this solvent.
‡ Isolated as their picrates.

TABLE 2. *Phenylation of chlorobenzene. Isomer ratios* (%).

Method	*ortho*	*meta*	*para*
Benzoyl peroxide [6]	60·3	25·9	13·75
Gomberg [6]	64·55	21·7	13·7
Silver iodide dibenzoate [7]	60·0	24·0	16·0
Phenylhydrazine–silver oxide	64·9	22·1	13·0



$$\mathrm{Ph{\cdot}NH{\cdot}NH_2 \xrightarrow{Ag_2O} [Ph{\cdot}N{:}NH] \longrightarrow N_2 + Ph{\cdot} + H{\cdot} \longrightarrow PhH}$$

$$\mathrm{+ H_2O + 2Ag \qquad Ph{\cdot} \nearrow Ph_2 \qquad Ph{\cdot} \xrightarrow{ArH} Ph{\cdot}Ar}$$

The formation of diphenyl is shown as arising by dimerisation of phenyl radicals. This minor product was first detected in oxidation products obtained in bromobenzene and in this instance it could conceivably be formed by phenyl radicals attacking the bromobenzene with displacement of bromine. To test this, phenylhydrazine was oxidised with silver oxide in [^{14}C]bromobenzene. The diphenyl obtained was very feebly active, which seems to imply that a very small proportion of the phenyl radicals do behave in this way.

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[5] Kharasch, McBay, and Urry, *J. Org. Chem.*, 1945, **10**, 401.
[6] Augood, Hey, and Williams, *J.*, 1953, 45.
[7] Bryce-Smith and Clarke, *J.*, 1956, 2264.
[8] References to five methods are given by Hey, Nechvatal, and Robinson, *J.*, 1951, 2892. For others see Hey, Stirling, and Williams, *J.*, 1954, 2747; 1956, 1475; Sandin and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 2253; and ref. 7.

In addition to the reaction scheme postulated above it is possible that oxidation of the phenylhydrazine may lead to the diazo-compound, Ph·N:N·OH, homolysis of which would yield hydroxyl as well as phenyl radicals. As yet we have obtained no definite evidence in favour of this. The formation of hydroxyl radicals in the presence of aromatic solvents has usually been detected by isolation of the appropriate phenols but this method is not very suitable under the present conditions as the phenols, if formed, would also be susceptible to oxidation. We have shown that *p*-cresol is oxidised to a tetrahydro-oxodibenzofuran derivative with silver oxide in benzene, and such products would of course react further with phenylhydrazine. In practice alkaline extraction of oxidation mixtures usually gave a few mg. of solid having a definite phenolic odour but we have not been able to identify any of these products. Phenol was obtained on oxidation of phenylhydrazine in benzene when the mixture was boiled after the reaction but this in inconclusive. In these circumstances phenol could arise by interaction of phenyl radicals and hot water.

Yields of phenylated products are usually low and as a preparative method there is no advantage over older procedures, but where a substituted phenylhydrazine is available it may occasionally be useful. Some examples are shown in Table 3.

TABLE 3. *Oxidation of arylhydrazines with silver oxide in benzene.*

Hydrazine	Product	Yield (%)
p-Bromophenyl	4-Bromodiphenyl	36
p-Nitrophenyl	4-Nitrodiphenyl	28
2 : 4-Dinitrophenyl	2 : 4-Dinitrodiphenyl	39
2-Naphthyl	2-Phenylnaphthalene	9·5
p-Nitrophenyl (in thiophen solution)	2-*p*-Nitrophenylthiophen	13

It has long been known that phenylhydrazine does not react normally with benzoquinones, *i.e.*, phenylhydrazones are not formed. Instead the quinone is reduced to a quinol with the liberation of nitrogen and the reaction, using phenylhydrazine "carbamate," was adapted by Willstätter and Cramer[9] for use as a gasometric method for the estimation of quinones. This reaction, in aromatic solvents, appears to take the same course as the silver oxide oxidation, producing phenyl radicals which then attack the solvent. When benzene solutions of phenylhydrazine and benzoquinone (or chloranil) were mixed at room temperature there was a vigorous evolution of nitrogen and the quinol separated. Diphenyl and a trace of azobenzene were isolated from the benzene solution. Similarly 4-nitrodiphenyl was obtained on oxidation of phenylhydrazine with chloranil in nitrobenzene at room temperature, and in *iso*propylbenzene 2 : 3-dimethyl-2 : 3-diphenylbutane and diphenyl were detected in addition to the *iso*propyldiphenyls.

Aerial oxidation of phenylhydrazine is of a similar character to those described above. This reaction was studied by Chattaway[3] who exposed filter paper saturated with phenylhydrazine to oxygen. Nitrogen was evolved readily but the only other product isolated was benzene. On bubbling oxygen through a solution of phenylhydrazine in *iso*propylbenzene much tar is produced from which we have been able to isolate a little 2 : 3-dimethyl-2 : 3-diphenylbutane besides azobenzene and mixed *iso*propyldiphenyls. A similar oxidation in pyridine afforded 4-phenylpyridine.

From the nature of the products isolated most of the oxidations of phenylhydrazine which have been effected in aqueous solution seem to be ionic. Intermediate diazo-compounds are probably formed which then decompose in the expected fashion. In some cases there is definite evidence for the formation of diazonium salts, *e.g.*, in oxidations with chlorine or bromine,[10] or with iodate in acid solution.[11] Most of these reactions are of theoretical interest only, but the use of cupric sulphate in boiling aqueous solution is of practical value[12] for the removal of hydrazino-groups, $\mathrm{Ar{\cdot}NH{\cdot}NH_2} \longrightarrow \mathrm{ArH}$. A brief

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[9] Willstätter and Cramer, *Ber.*, 1910, **43**, 2976.

[10] Chattaway, *J.*, 1908, **93**, 852.

[11] Miller and Furman, *J. Amer. Chem. Soc.*, 1937, **59**, 161.

[12] Cf. Schofield and Swain, *J.*, 1950, 392.

examination has shown that this oxidation, and possibly others in neutral aqueous solution, are, at least in part, homolytic reactions : for diphenyl (and benzene) was formed when phenylhydrazine was oxidised with cupric sulphate in hot water, and phenylpyridines (the 2- and the 4-isomer were isolated as their picrates) when the same oxidation was conducted in aqueous pyridine. Similar oxidations of phenylhydrazine with silver oxide in water, and in aqueous pyridine, yielded small amounts of diphenyl and 4-phenylpyridine, respectively.

EXPERIMENTAL

Solvents were purified as described by Hey *et al.*[6, 13] and Bryce-Smith and Clarke.[7] Chromatographic separations were done on alumina with light petroleum (b. p. 50—60°) as solvent. Products were identified by mixed m. p. determinations unless otherwise indicated.

Oxidation of Phenylhydrazine with Silver Oxide.—General procedure. To a vigorously stirred solution of phenylhydrazine (5 g.) in an aromatic solvent (150 ml.), cooled in ice-water, silver oxide (11 g.) was added gradually. Stirring was continued for 30 min., by which time the reaction had subsided, and the mixture was then left overnight at room temperature. The silver residue was filtered off and washed with the solvent, and the combined filtrates were dried ($MgSO_4$). Unless otherwise stated, the solvent was removed by distillation *in vacuo* through a helix-packed column, and the residual oil worked up as detailed below.

(i) *In benzene.* (*a*) Hydrochloric acid extraction of the reaction mixture (from 10 g. of phenylhydrazine) yielded unchanged phenylhydrazine (1·2 g.). Chromatography of the residue after removal of the solvent gave diphenyl (0·8 g.), m. p. 69°, and azobenzene (0·3 g.), m. p. 68°. (*b*) The above experiment was repeated and the oxidation mixture finally boiled under reflux for 30 min. Extraction of the benzene solution with 2N-aqueous sodium hydroxide then gave phenol (0·14 g.) (benzoate, m. p. 69°). Further extraction with dilute hydrochloric acid yielded a mixture of phenylhydrazine (0·4 g.) and aniline (0·2 g.) (benzanilide, m. p. 161°), separated by fractional distillation.

(ii) *In chlorobenzene.* (*a*) Distillation gave a light red oil (2·5 g.), b. p. 120—150°/7 mm., which was chromatographed, yielding azobenzene (0·13 g.) and a yellow oil (1·1 g.), crystallisation of which from alcohol gave 2-chlorodiphenyl (0·36 g.), m. p. 34°. (*b*) The oxidation was repeated on a larger scale (4 × 15 g. of phenylhydrazine) to obtain a mixture of isomeric chlorodiphenyls for infrared analysis. Azobenzene was removed from the initial light red oil by catalytic reduction and extraction of aniline with dilute hydrochloric acid. Distillation then gave diphenyl and a light yellow oil, b. p. 82—100°/0·2 mm., which was further purified by chromatography.

(iii) *In bromobenzene.* (*a*) 15 G. of phenylhydrazine were used. Before being worked up the reaction mixture was extracted with hydrochloric acid which gave unchanged phenylhydrazine (1·2 g.) but no aniline. Carbon tetrachloride (60 ml.) was then added to the solution and a fraction, b. p. 70—80°, was collected by distillation. This was nitrated by dropwise addition of a mixture of fuming nitric acid (10 ml.) and concentrated sulphuric acid (10 ml.). After being heated under reflux for 15 min. the solution was poured on ice. Crystallisation of the precipitate from aqueous alcohol gave *m*-dinitrobenzene, m. p. 90° (1·6 g., equiv. to 0·74 g. of benzene). The mixture was then filtered and worked up in the usual way. Chromatography of the initial oil (2·9 g.; b. p. 100—125°/1·5 mm.) gave a light yellow oil (1·8 g.) which on distillation yielded diphenyl (0·55 g.) and mixed bromodiphenyls (0·95 g.), b. p. 90—100°/0·03 mm., which crystallised from alcohol, yielding 4-bromodiphenyl (0·3 g.), m. p. 89°. (*b*) The reaction was repeated with phenylhydrazine (15 g.) in [^{14}C]bromobenzene (200 ml.; activity 1·5 μc/mole). The solutions from four such oxidations were combined and the diphenyl was isolated as in (*a*). It was freed from radioactive solvent by repeated chromatography, distillation, and final crystallisation from light petroleum (b. p. 30—40°). The activity was $2 \cdot 7 \times 10^{-7}$ μc/mole.

(iv) *In nitrobenzene.* (*a*) Extraction of the reaction mixture (from 10 g. of phenylhydrazine) with dilute hydrochloric acid yielded unchanged phenylhydrazine (1 g.). Benzene was isolated by distillation with carbon tetrachloride and converted into *m*-dinitrobenzene (1 g., equiv. to 0·46 g. of benzene). The crude product obtained on removal of the solvent distilled to a light red oil (4·2 g.), b. p. 90—150°/0·2 mm. Chromatography gave diphenyl (0·3 g.), azobenzene (0·3 g.), mixed nitrodiphenyls as a yellow oil (1·7 g.), and the 4-isomer (0·9 g.). (*b*) The combined products from several oxidations (60 g. of phenylhydrazine in all) were distilled, giving a red oil

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[13] Hey, Pengilly, and Williams, *J.*, **1956**, **1463**; Hey, Stirling, and Williams, *J.*, **1955**, **3963**.

(11·8 g.), b. p. 100—140°/8 mm., and a fraction (5 g.), b. p. 150—160°/8 mm., which solidified. The latter, 4-nitrodiphenyl, crystallised from alcohol in light yellow needles, m. p. 113°. A chromatogram of the red oil yielded (1) diphenyl (1·2 g.), (2) azobenzene (0·9 g.), (3) 2-nitrodiphenyl (1·2 g.), m. p. 36° (from alcohol), (4) a yellow oil (1·5 g.) (mixed nitrodiphenyls), and (5) 4-nitrodiphenyl (2·7 g.).

(v) *In* iso*propylbenzene*. The crude product from phenylhydrazine (15 g.) in *iso*propylbenzene (150 ml.) distilled as a light yellow oil (4·8 g.), b. p. 85—150°/2·5 mm. Chromatography then yielded (1) diphenyl (0·3 g.), (2) 2 : 3-dimethyl-2 : 3-diphenylbutane (0·5 g.), m. p. 118° (Found : C, 90·7; H, 9·1. Calc. for $C_{18}H_{22}$: C, 90·75; H, 9·25%), and (3) mixed *iso*propyldiphenyls as a light yellow oil, b. p. 80—100°/0·15 mm. (0·9 g.) (Found : C, 91·5; H, 8·0. Calc. for $C_{15}H_{16}$: C, 91·8; H, 8·2%).

(vi) *In pyridine*. Distillation gave a mixture of phenylpyridines (0·95 g.), b. p. 110—130°/0·2 mm., and azobenzene (0·1 g.). Conversion of the phenylpyridines into their picrates and fractional crystallisation from acetone gave the 2-isomer (0·14 g.), m. p. 175°, the 3-isomer (0·08 g.), m. p. 160°, and the 4-isomer (0·13 g.), m. p. 195°.

(vii) *In toluene*. The crude product from the oxidation of phenylhydrazine (10 g.) in toluene (200 ml.) distilled as a light yellow oil (2 g.), b. p. 90—120°/3 mm. A chromatogram yielded diphenyl (50 mg.) and a mixture of methyldiphenyls (1·5 g.), b. p. 77—84°/0·3 mm. (Found : C, 92·5; H, 7·2. Calc. for $C_{13}H_{12}$: C, 92·85; H, 7·15%).

Oxidation of Phenylhydrazine with Mercuric Oxide.—General procedure. Mercuric oxide (10 g.) was added gradually to a vigorously stirred solution of phenylhydrazine (5 g.) in an aromatic solvent (150 ml.), cooled in ice-water. A brisk evolution of nitrogen took place and mercury and water separated. The mixture was left overnight at room temperature, the mercury residue was filtered off and washed with solvent, and the combined filtrates were dried ($MgSO_4$). The solvent was then removed by distillation *in vacuo* through a helix-packed column, and the product worked up as indicated below.

(1) *In benzene*. (*a*) The residue crystallised from alcohol, yielding diphenylmercury (1·35 g.) as plates, m. p. 125°. Steam-distillation of the concentrated alcohol mother-liquor gave diphenyl (0·7 g.). (*b*) The reaction was repeated with the addition of mercuric chloride (1 g.). After being kept overnight, the mixture was boiled under reflux for 10 min. and filtered hot. On cooling, phenylmercuric chloride (3 g.), m. p. 254°, separated. The solvent was removed by distillation and extraction of the residue with ether left more ether-insoluble phenylmercuric chloride (1·5 g.). Working up the ethereal solution as above gave diphenylmercury (1·5 g.) and diphenyl (0·5 g.).

(ii) *In chlorobenzene*. Extraction of the residue with light petroleum (b. p. 50—60°) left the insoluble diphenylmercury (1·45 g.). The red oil obtained on removal of the light petroleum was distilled, yielding a light red oil (0·6 g.), b. p. 120—150°/7 mm. When crystallised from ethanol it gave 2-chlorodiphenyl (0·13 g.) as light yellow prisms, m. p. 34°.

(iii) *In bromobenzene*. Diphenylmercury (0·9 g.) was isolated as in (i). Removal of the light petroleum and distillation of the residue gave a light red oil (2·0 g.), b. p. 100—140°/7 mm. Chromatography of this afforded azobenzene (0·1 g.) and a yellow oil (0·8 g.) (mixed bromodiphenyls) (Found : C, 62·6; H, 4·25. Calc. for $C_{12}H_9Br$: C, 61·8; H, 3·9%).

(iv) *In nitrobenzene*. The residue on distillation gave a light red oil (2·9 g.), b. p. 100—160°/0·05 mm. Chromatography yielded phenylmercuric chloride (0·1 g.), azobenzene (0·22 g.), and a mixture of nitrodiphenyls (1·1 g.) which, on fractional crystallisation from alcohol, yielded the 2- and the 4-isomer.

(v) *In pyridine*. Diphenylmercury (1·28 g.) was isolated as above. Distillation of the residue gave a mixture of phenylpyridines (0·95 g.), b. p. 115—120°/0·15 mm. All three isomers were isolated, as their picrates, by fractional crystallisation.

(vi) *In anisole*. The initial products were diphenylmercury (1·5 g.) and a light red oil (0·98 g.), b. p. 130—140°/7 mm. Chromatography of this gave azobenzene (0·15 g.) and mixed methoxydiphenyls as a faintly yellow oil (0·5 g.) (Found : C, 84·7; H, 6·4. $C_{13}H_{12}O$ requires C, 84·8; H, 6·4%).

Oxidation of Phenylhydrazine with Other Metallic Oxides.—Cupric oxide. The oxide (11 g.) was added to a solution of phenylhydrazine (5 g.) in pyridine (200 ml.) and the suspension warmed to 50—60° until reaction began. Working up as before gave a mixture of phenylpyridines (0·8 g.), b. p. 120—130°/0·2 mm. All three isomers were separated by fractional crystallisation of their picrates.

Lead dioxide. Repetition of the above experiment, but with lead dioxide (8 g.), gave a mixture of the three phenylpyridines (1·5 g.) which were separated as their picrates.

Oxidation of Other Arylhydrazines with Silver Oxide.—(i) To a vigorously stirred solution of *p*-bromophenylhydrazine (1·8 g.) in benzene (100 ml.), silver oxide (4 g.) was added gradually. Then the mixture was boiled under reflux for 30 min. and left overnight. Working up in the usual way and distillation of the crude product gave a colourless oil, b. p. 100—120°/2 mm., which solidified. Crystallisation from alcohol gave 4-bromodiphenyl as colourless needles, m. p. 88° (0·7 g.) (Found : C, 62·1; H, 4·0; Br, 33·5. Calc. for $C_{12}H_9Br$: C, 61·8; H, 3·85; Br, 34·3%).

(ii) (*a*) Oxidation of a warm suspension of *p*-nitrophenylhydrazine (5 g.) in benzene (200 ml.) as in (i) gave, after removal of the solvent, a solid residue. Crystallisation from alcohol gave 4-nitrodiphenyl as light yellow needles, m. p. 113° (1·8 g.). (*b*) In another experiment using 10 g. of *p*-nitrophenylhydrazine, extraction of the benzene solution with dilute hydrochloric acid gave *p*-nitroaniline (0·3 g.) (acetyl derivative, m. p. 216°).

(iii) Oxidation of a warm suspension of 2 : 4-dinitrophenylhydrazine (5 g.) in benzene (200 ml.) and working up as above gave a solid product. Extraction with ether left a little unchanged 2 : 4-dinitrophenylhydrazine. Removal of the ether yielded 2 : 4-dinitrodiphenyl which crystallised from alcohol as orange plates, m. p. 110° (2 g.) (Found : C, 59·0; H, 3·6; N, 11·6. Calc. for $C_{12}H_8O_4N_2$: C, 59·0; H, 3·3; N, 11·5%).

(iv) Oxidation of *p*-nitrophenylhydrazine (10 g.) in thiophen (200 ml.) and chromatography of the product using ether–light petroleum (1 : 1) gave 2-*p*-nitrophenylthiophen, m. p. 138° (1·7 g.) (Found : C, 58·2; H, 3·4; N, 6·5. Calc. for $C_{10}H_7O_2NS$: C, 58·3; H, 3·4; N, 6·8%). From two other bands were obtained (1) orange *leaflets*, m. p. 210° (0·3 g.), possibly 2 : 5-di-*p*-nitrophenylthiophen (Found : C, 57·8; H, 3·2. $C_{16}H_{10}O_4N_2S$ requires C, 58·8; H, 3·05%), and (2) a bright red solid, m. p. 258° (0·1 g.) (from alcohol).

(v) (*a*) Oxidation of 2-naphthylhydrazine (6 g.) in benzene (200 ml.) in the usual way gave a crude product which yielded on distillation naphthalene (1·4 g.), b. p. 60—70°/2·5 mm., m. p. 79° (from alcohol), and 2-phenylnaphthalene (0·7 g.), b. p. 120—125°/2·5 mm., m. p. 101° (from alcohol). (*b*) A similar oxidation using an excess of mercuric oxide and 2-naphthylhydrazine (3·5 g.) gave naphthalene (0·8 g.), 2-phenylnaphthalene (0·4 g.), and 2-naphthylmercuric chloride (0·6 g.), m. p. 268°.

Oxidation of Phenylhydrazine with Quinones.—*General procedure.* To a vigorously stirred solution of phenylhydrazine (5 g.) in an aromatic solvent (200 ml.) was added an equivalent quantity of the quinone. Vigorous evolution of nitrogen took place and immediate separation of the quinol. The mixture was boiled under reflux for 1 hr., cooled, and filtered. The solvent was then removed by distillation *in vacuo* and the residue worked up in the usual way.

(i) *Benzoquinone in benzene.* Quinol (4·5 g.) was collected and the benzene solution yielded diphenyl (0·4 g.) and a trace of azobenzene.

(ii) *Chloranil in benzene.* The products were tetrachloroquinol (11 g.), diphenyl (0·6 g.), and a trace of azobenzene.

(iii) *Chloranil in nitrobenzene.* 10 G. of phenylhydrazine were used (the mixture was *not* heated after the addition of the quinone). Tetrachloroquinol separated and distillation of the residue obtained on removal of the solvent gave 4-nitrodiphenyl (0·2 g.), m. p. 113°.

(iv) *Chloranil in* iso*propylbenzene.* The volatile product from 15 g. of phenylhydrazine distilled at 80—130°/2 mm. (1·1 g.) and was separated by chromatography into diphenyl (0·05 g.), 2 : 3-dimethyl-2 : 3-diphenylbutane (0·1 g.), and a light yellow oil (0·6 g.) (mixed *iso*propyldiphenyls).

Oxidation of Phenylhydrazine in Aqueous Media.—(i) *Silver oxide in water.* The oxide (30 g.) was added gradually to a vigorously stirred suspension of phenylhydrazine (15 g.) in water (200 ml.) cooled in ice-water. The mixture was then kept at 60—70° for 30 min. Benzene was isolated by distillation with carbon tetrachloride and was converted into *m*-dinitrobenzene (5·0 g., equiv. to 2·3 g. of benzene). Subsequent steam-distillation of the reaction mixture yielded diphenyl (60 mg.).

(ii) *Silver oxide in aqueous pyridine.* Silver oxide (20 g.) was added to a vigorously stirred solution of phenylhydrazine (10 g.) in pyridine (100 ml.) and water (100 ml.). Next day the mixture was refluxed for 30 min. and filtered. Removal of the solvents left a residue which distilled as a yellow oil (2·3 g.), b. p. 90—120°/0·1 mm., and from this 4-phenylpyridine was isolated as its picrate (0·3

(iii) *Cupric sulphate in water.* A solution of cupric sulphate (40 g.) in water (300 ml.) was added gradually with stirring to a solution of phenylhydrazine (15 g.) in boiling water (200 ml.). Boiling under reflux was continued for 30 min. after the addition was complete. Benzene was isolated as the dinitro-derivative (equiv. to 1·2 g. of benzene) as in (i), and diphenyl (0·17 g.) was obtained by steam-distillation.

(iv) *Cupric sulphate in aqueous pyridine.* As in (iii) cupric sulphate solution was added to phenylhydrazine (10 g.) in aqueous pyridine at 60—70°. Distillation as before yielded benzene (1·9 g.; isolated as the dinitro-derivative). Removal of the solvent and distillation of the residue gave a yellow oil (0·7 g.), b. p. 90—120°/0·1 mm., from which 2- and 4-phenylpyridine were isolated as their picrates.

Oxidation of Phenylhydrazine with Oxygen.—(i) *In* iso*propylbenzene.* A slow stream of oxygen was passed through a solution of phenylhydrazine (20 g.) in *iso*propylbenzene (300 ml.) for 40 hr. Removal of the solvent left a tar which distilled to a red oil (2·7 g.), b. p. 70—110°/0·7 mm. Chromatography gave azobenzene (0·5 g.) and a light yellow oil (0·7 g.) from which 2 : 3-dimethyl-2 : 3-diphenylbutane (20 mg.) was precipitated on addition of nitromethane. Removal of the nitromethane and distillation of the residue gave a light yellow oil (0·4 g.), b. p. 80—100°/0·15 mm. (Found: C, 91·7; H, 8·0. Calc. for $C_{15}H_{16}$: C, 91·8; H, 8·2%).

(ii) *In pyridine.* The reaction was carried out as in (i). The product was a yellow oil (0·9 g.), b. p. 80—115°/0·05 mm., from which 4-phenylpyridine was isolated as its picrate.

Oxidation of p-*Cresol.*—Silver oxide (10 g.) was added to a solution of *p*-cresol (5 g.) in benzene (100 ml.), and the mixture left overnight, then boiled under reflux for 15 min., cooled, and filtered. The product, after removal of the solvent, was steam-distilled to remove unchanged cresol (3·1 g.). Extraction of the residue with ether and then distillation gave a gum (0·5 g.), b. p. 210—230°/0·5 mm. Treatment of the latter with 5% sodium hydroxide solution precipitated the ketone [14] which formed a phenylhydrazone, m. p. 181° (0·15 g.).

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[14] Pummerer, Melamed, and Puttfarcken, *Ber.*, 1922, **55**, 3116; Pummerer, Puttfarcken, and Schopflocher, *Ber.*, 1925, **58**, 1808.