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FURTHER STUDIES ON THE CYCLISATION OF 3-HYDROXY-2'-NITRODIPHENYL ETHERS AND RELATED COMPOUNDS

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Abstract—The reductive cyclisation of 4,6-dimethyl and 4,6-dichloro derivatives of 3-hydroxy-2'-nitrodiphenyl ethers has been examined as a potential route to 1H-phenoxazinones. Unexpectedly, cyclisation of the dichloro compound proceeded with loss of a Cl and yielded 2-chloro-3H-phenoxazin-3-one. The cyclisation of a range of analogous substrates has been investigated and shown to provide novel and convenient syntheses of 3-aminophenoxazine, 3H-phenothiazin-3-one and 8-hydroxy-5,10-dihydro-11H-dibenzo[b, e][1, 4]diazepin-11-one.

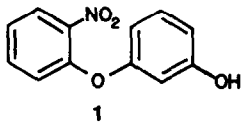
A recent paper[1] described a new synthetic route to the 3H-phenoxazin-3-one ring system which was based upon the *in situ* generation of the nitroso species (**2**) by reduction of **1** with zinc and aqueous ammonium chloride, and its subsequent intramolecular cyclisation to **3**. The reductive conditions employed also effected the subsequent conversion of **3** to **4**. The basic concept of this cyclisation procedure should be capable of much wider synthetic exploitation and this paper presents some pertinent observations in that respect.

Although cyclisation of the nitroso intermediate **2** might have been expected to occur both *ortho* and *para* to the OH group, no product resulting from the former mode of coupling has yet been encountered. However, it was anticipated that introduction of a substituent at C6, and for synthetic convenience at C4, would ensure that cyclisation would occur at C2 thus providing an entrée into the little known 1H-phenoxazin-1-one system. Unexpectedly reductive cyclisation of the dichlorodiphenyl ether **5** with zinc and ammonium chloride in aqueous dimethoxyethane at 30–40° proceeded with expulsion of the blocking Cl atom and gave a 79% yield of 3H-2-chlorophenoxazin-3-one (**12**). Similar treatment of the dimethyldiphenyl ether **6** provided a mixture of the derived amine and the desired 1-hydroxyphenoxazine (**15**). Thus far attempts to oxidise this compound to the corresponding orthoquinonoid 1H-phenoxazinone (**16**) have been unsuccessful. Only ferric chloride in acetic acid has provided a well-defined product to which either structure **17** or **18** may be assigned on the basis of its spectroscopic properties. Thus the IR spectrum exhibited bands for CO groups at 1745 and 1680 cm^{-1}, and for N–H at 3320 cm^{-1}. The NMR spectrum was comprised of three singlets for Me groups at δ 1.35, 1.95 and 2.2, together with another singlet at δ 6.1 for an olefinic proton, a broad D_2O exchangeable band for N–H at δ 4.8 and a four proton multiplet between δ 6.6 and 7.3 for the aromatic protons.

While the success of these cyclisations depends upon appropriate activation of the non-nitro group bearing aromatic ring it appeared possible that the synthetically more versatile amino group could serve the same function. Normally nitroso groups are directly attacked by primary amino groups, thereby generating an azo linkage, but in the present situation where intramolecular attack of this sort was sterically precluded, it appeared possible that reaction might occur at the carbon *para* to the amino function. In practice reduction of the aminodiphenyl ether **19** gave 3-aminophenoxazine (**20**) in 88% yield. This two-step synthesis is clearly far more convenient and proceeds in much better yield than previously described[5] routes.

Replacement of the O atom of the diphenyl ether by other groupings and subsequent reductive cyclisation was expected to provide new synthetic routes to a variety of other heterocycles. Not surprisingly, the sulphide (**7**) provided an excellent yield of 3H-phenothiazin-3-one (**13**). However, the diphenylamine **8** gave only the corresponding amine and none of the anticipated phenazine was detected. This was particularly surprising as *o*-nitrodiphenylamines have been successfully cyclised to phenazines by treatment with sodium ethoxide and borohydride in refluxing ethanol.[2]

The reductive cyclisation has also been examined of three systems in which the aromatic nuclei were separated by two atom bridges. The benzanilide **9** gave a reasonable yield of the dibenzodiazepinone **21**, but the isomeric benzanilide **10** yielded only the corresponding amine. The benzyl phenyl ether **11** also failed to yield any of the anticipated dibenzo-oxazepin **22**, the major product being the hydrazobenzene **23**, formed by intermolecular coupling.



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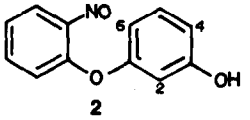

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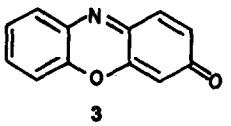

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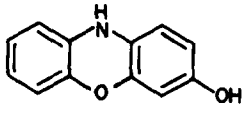

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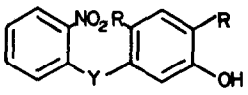
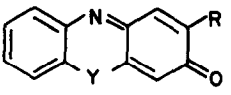
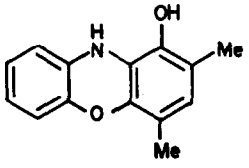


5: Y = O, R = Cl
6: Y = O, R = Me
7: Y = S, R = H
8: Y = NH, R = H
9: Y = CONH, R = H
10: Y = NHCO, R = H
11: Y = CH_2O, R = H



12: Y = O, R = Cl
13: Y = S, R = H
14: Y = NH, R = H



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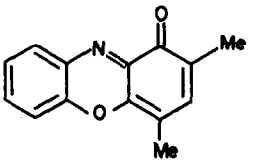

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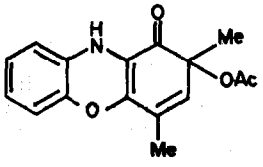

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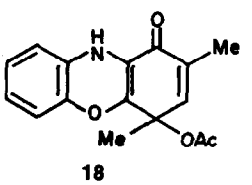

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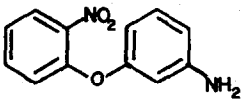

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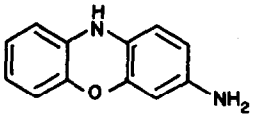

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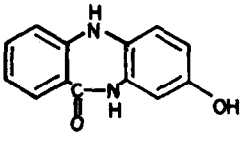

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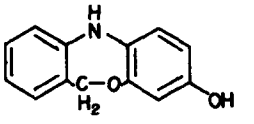

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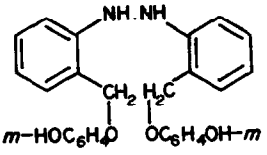

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EXPERIMENTAL

Unless otherwise stated, NMR spectra were measured at 60 MHz on a Perkin-Elmer R12B spectrometer for $CDCl_3$ solns with internal TMS. UV spectra were recorded for ethanol solns on a Unicam SP 800 spectrophotometer and IR spectra for Nujol or hexachlorobutadiene mulls on a Unicam SP 200 instrument. Mass spectra were recorded on an MS 30 by the U. of L. Mass Spectrometry Service at Q.E.C.

Preparation of 4,6-*dichloro*-3-*hydroxy*-2'-*nitrodiphenyl ether*

o-Nitrochlorobenzene (15.8 g) was heated at 120–130° for 2 hr in N,N-dimethylformamide (200 ml) containing cuprous oxide (14.3 g) and the monopotassium salt of 4,6-dichlororesorcinol. The latter was prepared by dissolving the resorcinol (17.9 g) in a soln of KOMe (from 3.9 g metal) in MeOH (100 ml) and evaporating to dryness. The cooled mixture was treated with 4N HCl (200 ml) and diluted with water. The crude products were isolated by ether extraction and chromatographed on silica gel in 60/80° petroleum ether–benzene (1:1).

Elution with the same solvents but increasing the benzene content gave firstly 1,3bis(*o*-nitrophenoxy)-4,6-dichlorobenzene (1.5 g, 7%) m.p. 128–129° from EtOH. (Found: C, 51.0; H, 2.5; N, 6.6; Cl, 16.8. Calc. for $C_{18}H_{10}Cl_2N_2O_6$: C, 51.3; H, 2.4; N, 6.7; Cl, 16.9%). Further elution gave 4,6-dichloro-3-hydroxy-2'-nitrodiphenyl ether as a viscous liquid. (Found: C, 48.3; H, 2.7; N, 4.4; Cl, 23.4. Calc. for $C_{12}H_7Cl_2NO_4$: C, 48.0; H, 2.3; N, 4.7; Cl, 23.7%). IR 3475, 1610, 1535 cm^{-1}; NMR δ 4.6 (br, 1H, OH), 6.4–8.2 (m, 6H, ArH); MS *m/e* 301 (15), 300 (5), 299 (25), 179 (20), 177 (30), 151 (20), 149 (40), 122 (100).

Preparation of 3-(*o*-*nitrobenzyloxy*)*phenol*

o-Nitrobenzyl chloride was reacted with resorcinol as in the preceding experiment. Two products were isolated by chromatography on silica gel in benzene–EtOAc (19:1). The first eluted was 1,3-bis(*o*-nitrobenzyloxy)benzene (30%) m.p. 115–116° from *n*-hexanol (Found: C, 63.2; H, 4.2; N, 7.1. Calc. for $C_{20}H_{16}N_2O_6$: C, 63.2; H, 4.2; N, 7.4%); NMR δ 5.4 (s, 4H, CH_2), 6.4–8.0 (m, 12H, ArH); MS *m/e* 380 (30), 245 (100), 215 (10), 214 (20), 186 (13), 136 (20). The second was 3-(*o*-nitrobenzyloxy)phenol (35%) m.p. 81–83° from benzene (Found: C, 63.6; H, 4.6; N, 5.6. Calc. for $C_{13}H_{11}NO_4$: C, 63.7; H, 4.5; N, 5.7%); IR 3500, 3400, 1600, 1520 cm^{-1}; NMR δ 5.4 (s, 1 H, OH), 5.45 (s, 2 H, CH_2), 6.3–8.4 (m, 8 H, ArH); MS *m/e* 245 (40), 136 (100), 110 (18).

Preparation of 3-*hydroxy*-4,6-*dimethyl*-2'-*nitrodiphenyl ether*

o-Nitrochlorobenzene was reacted with 4,6-dimethylresorcinol[3] using the foregoing procedure except that N-methylpyrrolidone was substituted for the dimethylformamide. The product (24%) was separated from unreacted *o*-chloronitrobenzene and tarry materials by chromatography on silica gel in benzene and crystallised from cyclohexane, m.p. 88–89°. (Found: C, 64.7; H, 5.0; N, 5.5. Calc. for $C_{14}H_{13}NO_4$: C, 64.9; H, 5.0; N, 5.4%); IR 3420, 1600, 1520, 1500 cm^{-1}; NMR δ 2.05 (s, 3 H, CH_3), 2.17 (s, 3 H, CH_3), 5.1–5.7 (br, 1 H, OH), 6.4–8.1 (m, 6 H, ArH); MS *m/e* 259 (60), 137 (100), 123 (15), 122 (10).

Preparation of 3-*hydroxy*-2'-*nitrodiphenyl sulphide*

KOH (1.4 g) was moistened with a few drops of water and heated to give a clear melt. *m*-Hydroxybenzenethiol[4] (3.15 g) was added followed immediately by *o*-nitrochlorobenzene (3.9 g) and the mixture stirred at 90–100° for 1 hr. The mixture was diluted with water, acidified and ether extracted. The ethereal soln was extracted with 20% NaOH aq. The aqueous alkaline extract was acidified and the product isolated by ether extraction. The crude material thus obtained was chromatographed on silica gel in benzene–$CHCl_3$ (1:1), which eluted pure 3-hydroxy-2'-nitrodiphenyl sulphide (2.5 g, 40%) m.p. 107–108° from benzene-petroleum ether (1:1). (Found: C, 58.4; H, 3.7; N, 5.6. Calc. for $C_{12}H_9O_3NS$: C, 58.3; H, 3.6; N, 5.7%); IR 3420, 1590, 1580, 1560, 1505 cm^{-1}; MS *m/e* 247 (40), 230 (25), 200 (20), 184 (15), 183 (50), 182 (30), 172 (20), 171 (40), 155 (30), 154 (100), 141 (15), 139 (25), 138 (13), 131 (10), 129 (15), 128 (20), 127 (14), 115 (18), 108 (20), 93 (20).

Reaction of o-*chloronitrobenzene with* m-*aminophenol.* *m*-Aminophenol (5.5 g), *o*-chloronitrobenzene (3.9 g) and sodium carbonate (5.3 g) were heated together under N_2 in dry refluxing dimethylformamide for 3 hr. The mixture was then diluted with water and the products isolated by ether extraction. Chromatography of the product mixture on silica gel with benzene–$CHCl_3$ (1:1) provided firstly 3-hydroxy-2'-nitrodiphenylamine (~3%) m.p. 139–141° from benzene–petroleum ether. (Found: C, 62.8; H, 4.5; N; 11.9. Calc. for $C_{12}H_{10}N_2O_3$: C, 62.6; H, 4.3; N, 12.2%); IR 3390, 3320, 1618, 1600, 1560, 1500 cm^{-1}; MS *m/e* 230 (100), 213 (10), 196 (20), 184 (30), 183 (40), 170 (20), 169 (10), 168 (20), 167 (10), 157 (12), 156 (10), 154 (40), 149 (80), 141 (16), 128 (10), 127 (10), 121 (20), 120 (15), 96 (20).

Further elution provided 3-amino-2'-nitrodiphenyl ether (29%) as a viscous liquid which on diazotisation and coupling with β-naphthol gave an orange-red dye. (Found: C, 62.7; H, 4.4; N, 12.1. Calc. for $C_{12}H_{10}N_2O_3$: C, 62.6; H, 4.3, N, 12.2%); IR 3450, 3375, 1625, 1602, 1582, 1530 cm^{-1}; MS *m/e* 230 (100), 213 (20), 200 (5), 197 (12), 186 (5), 185 (25), 184 (30), 183 (35), 158 (10), 157 (12), 156 (20), 154 (15), 139 (10), 128 (15), 127 (12), 124 (10), 122 (10), 115 (10), 109 (20), 108 (15), 106 (10), 92 (15).

Attempts to improve the yield of the diphenylamine by carrying out the reaction using Cu powder in place of Na_2CO_3 were unsuccessful, as was heating the reactants together in the presence of anhyd $ZnCl_2$ at 130–140°.

Preparation of 3'-hydroxy-2-nitrobenzanilide. o-Nitrobenzoic acid (8.4 g) and thionyl chloride (4.5 ml) were heated together with stirring in o-dichlorobenzene (100 ml). The temp. was gradually raised to 120° over 2 hr and this was maintained for a further hr. The soln was cooled to 80°, a soln of *m*-aminophenol (5 g) in o-dichlorobenzene (100 ml) added and the stirred mixture heated at 100–120° for 2 hr. The hot mixture was filtered and most of the o-dichlorobenzene evaporated *in vacuo*. The residue was washed with a small quantity of cyclohexane and dissolved in the minimum quantity of EtOH. This soln was diluted with 10% NaOH aq and the di-(o-nitrobenzoyl) derivative of *m*-aminiphenol extracted with ether. The aqueous soln was acidified with HCl and extracted with EtOAc. The dried (Na_2SO_4) extract was evaporated and the residue chromatographed on silica gel. The required 3'-hydroxy-2-nitrobenzanilide (9.5 g) was eluted with benzene: EtOAc: EtOH (7:2:1) and crystallised from benzene–EtOH (9:1), m.p. 174–176° (Found: C, 60.8, H, 3.9, N, 10.7. Calc. for $C_{13}H_{10}NO_4$: C, 60.5; H, 3.9; N, 10.9%); IR 3340, 1658, 1605, 1560, 1530 cm^{-1}; NMR δ 3.13 (br, 2 H, OH and NH), 6.5–8.4 (m, 8 H, ArH); MS *m/e* 258 (20), 228 (2), 212 (5), 150 (100). The di(o-nitrobenzoyl) derivative of *m*-aminophenol (1.5 g, 7%) had m.p. 143–145° from benzene-EtOH (9:1). (Found: C, 59.4; H, 3.2; N, 10.3. Calc. for $C_{20}H_{13}N_3O_7$: C, 59.0; H, 3.2; N, 10.3%); IR, 3350, 1750, 1680, 1615, 1538 cm^{-1}; NMR δ 2.8 (br, 1 H, NH), 6.8–8.4 (m, 12 H, ArH); MS *m/e* 407 (3), 393 (4), 214 (60), 186 (100), 172 (40), 158 (20), 146 (10), 131 (12), 101 (20).

Preparation of 3-hydroxy-2'-nitrobenzanilide. PCl_3 (9 ml) was added dropwise to a hot soln of o-nitroaniline (13.8 g) and *m*-hydroxybenzoic acid (13.8 g) in o-dichlorobenzene (150 ml). The mixture was heated under reflux for 4 hr and the solvent distilled off *in vacuo*. The residue was washed with a small volume of 60–80° petroleum ether and then partitioned between ether (400 ml) and 10% NaOH aq (800 ml). The alkaline soln was washed with ether, acidified and the crude product obtained by ether extraction. Pure 3-hydroxy-2'-nitrobenzanilide (16.3 g) was obtained by crystallization of the crude product from 50% aq EtOH, m.p. 168–171° (Found: C, 60.6; H, 3.9; N, 10.5. Calc. for $C_{13}H_{10}N_2O_4$: C, 60.5; H, 3.9; N, 10.9%); IR 3500, 3400, 1690, 1610, 1598, 1510 cm^{-1}; NMR δ 6.9–8.3 (m, 8 H, ArH), 10.8 (br, 1 H, NH or OH); MS *m/e* 258 (10), 212 (5), 121 (100).

Reductive cyclisations

(a) 4,6-Dichloro-3-hydroxy-2'-nitrodiphenyl ether (1 g) and ammonium chloride (0.5 g) were dissolved in 60% aqueous 1.2-dimethoxyethane (25 ml) and Zn dust (1.2 g) added with stirring over a period of 15 min keeping the temp. from exceeding 40°. After a further 20 min stirring, the mixture was filtered and the residue washed with the above solvent mixture (30 ml). The combined filtrates were stirred for 4 hr at room temp. when the initially colourless soln became orange-red and a product precipitated. The mixture was diluted with water and the product isolated by $CHCl_3$ extraction. The crude product was chromatographed on silica gel and elution with benzene–EtOAc (9:1) gave 2-chloro-3H-phenoxazin-3-one (0.6 g, 79%) m.p. 233–235° from benzene (Found: c, 62.3; H, 2.6; Cl, 15.4; N, 6.1. Calc. for $C_{12}H_6ClNO_2$: C, 62.2; H, 2.6; Cl, 15.3; N, 6.1%); UV 364 (10,900); 455 (6,900) nm; IR 1638, 1590 cm^{-1}; MS *m/e* 233 (35), 231 (100), 205 (20), 203 (60), 196 (40), 168 (22), 140 (28), 113 (10).

(b) Following the same procedure 4,6-dimethyl-3-hydroxy-2'-nitrodiphenyl ether (1 g) gave two products in order of elution:– (i) 2,4-dimethyl-1-hydroxyphenoxazine (0.22 g) m.p. 120–123° from benzene (Found: C, 74.3; H, 5.6; N, 6.0. Calc. for $C_{14}H_{13}NO_2$: C, 74.0; H, 5.7; N, 6.2%. IR 3400, 3250 cm^{-1}; MS *m/e* 227 (100), 212 (60), 197 (5), 184 (12), 183 (8), 154 (4), 149 (6), 133 (5), 123 (13), 109 (12), 108 (15), 93 (20). The compound (0.15 g) in AcOH (40 ml) was mixed with a sat. $FeCl_3$ aq (1.5 g), stirred for 10 min and diluted with water. The product (0.13 g) was isolated by $CHCl_3$ extraction, purified by elution through a silica gel column with benzene–EtOAc (4:1) and crystallised from aqueous EtOH, m.p. 174–175°. (Found: C, 67.5; H, 5.3; N, 4.9. Calc. for $C_{16}H_{15}NO_4$: C, 67.4; H, 5.3; N, 4.9%); IR 3320, 1745, 1680 cm^{-1}; NMR δ 1.35 (s, 3 H, CH_3), 1.95 (s, 3 H, CH_3), 2.2 (s, 3 H, CH_3), 4.78 (br, 1 H, NH), 6.1 (s, 1 H, –CH=), 6.6–7.3 (m, 4 H, ArH); MS *m/e* 285 (12), 270 (6), 243 (20), 228 (100). (ii) 2'-amino-4,6-dimethyl-3-hydroxydiphenyl ether (45%) m.p. 176–180° from benzene. (Found: C, 73.0; H, 6.4; N, 6.1. Calc. for $C_{14}H_{15}NO_2$: C, 73.4; H, 6.6; N, 6.1%); IR 3360, 3280 cm^{-1}; NMR δ 2.1 (s, 6 H, 2 × CH_3), 2.8 (br, 2 H, NH_2), 6.2–7.5 (m, 6 H, ArH); MS *m/e* 229 (100), 214 (30), 213 (30), 212 (30), 197 (10), 136 (10), 133 (15), 123 (55), 121 (40), 109 (40), 108 (60).

(c) Similarly, 3'-hydroxy-2-nitrobenzanilide yielded, following chromatography of the crude product on silica gel with benzene–EtOAc (7:3), 8-hydroxy-5, 10-dihydro-11H-dibenzo[b, e]-[1, 4]diazepin-11-one (40%) m.p. 253–256° from acetone–benzene (3:7). (Found: C, 66.6; H, 4.4; N, 11.5. Calc. for $C_{13}H_{10}N_2O_2$ $\frac{1}{2}H_2O$: C, 66.4; H, 4.7; N, 11.9%); IR 3340, 3200, 1670, 1630, 1615 cm^{-1}; NMR δ 3.3 (br, 2 H, NH/OH), 6.3–8.0 (m, 7 H, ArH), 9.45 (br, 1 H, NH/OH); MS *m/e* 226 (21), 199 (21), 198 (42), 197 (100), 182 (12), 169 (33), 156 (21), 129 (12), Refluxing with AcOH-Ac_2O (1:1) gave after purification by elution through silica gel in $CHCl_3$ the 0-acetyl derivative (71%) m.p. 226–228° from $CHCl_3$ (Found: C, 60.9, H, 4.4; N, 9.4. Calc. for $C_{15}H_{12}N_2O_3$ $1\frac{1}{2}$ H_2O: C, 61.0, H, 5.1; N, 9.5%); IR 3360, 3330, 1740, 1690 cm^{-1}; NMR δ 2.26 (s, 3 H, CH_3), 3.3 (br, 2 H, NH), 6.5–8.5 (m, 7 H, ArH); MS *m/e* 268 (45), 236 (100), 231 (30), 225 (12), 204 (18), 181 (12), 169 (15), 131 (90), 119 (60), 109 (15), 100 (15).

(d) The product from reduction of 3-hydroxy-2'-nitrobenzanilide was purified by elution through a silica gel column with cyclohexane-EtOAc (3:7) and identified as 2'-amino-3-hydroxybenzanilide (44%), m.p. 250–253° from acetone. (Found: C, 65.7; H, 5.4; N, 11.6. Calc. for $C_{13}H_{12}N_2O_2$ $\frac{1}{2}H_2O$: C, 65.8; H, 5.5; N, 11.8%; IR 3390, 3300, 1680 cm^{-1}; NMR δ 3.4 (br, 2 H, NH_2), 6.8–8.2 (m, 8 H, ArH), 8.9 (br, 1 H, NH or OH), 10.8 (br, 1 H, NH or OH); MS *m/e* 228 (13), 212 (6), 210 (13), 122 (12), 121 (100), 107 (8), 93 (30).

(e) Reduction of 3-(o-nitrobenzyloxy)phenol gave as the principal identifiable product the corresponding hydrazobenzene (35%) which was obtained as a glass solid m.p. 60–62° after chromatography of the crude reaction product on silica gel and elution with benzene–EtOAc (19:1). (Found: C, 69.9; H, 5.4; N, 5.9. Calc. for $C_{26}H_{24}N_4O_2.H_2O$; C, 70.0; H, 5.8; N, 6.3%); IR 3400 cm^{-1}; NMR δ 5.29 (s, 2 H, CH_2) 5.48 (s, 2 H, CH_2), 6.3–8.5 (m, 20 H, of which 4 H disappear on addition of D_2O, 16 × ArH, 4 × OH and/or NH), MS *m/e* 428 (50), 335 (50), 318 (25), 225 (5), 208 (50), 181 (5), 149 (10), 110 (100).

(f) The reductive cyclisation of 3-hydroxy-2'-nitrodiphenyl sulphide was conducted as described above except that 60% aq EtOH was used as the reaction medium. Prolonged aerial oxidation was necessary to maximise the yield (81%) of 3H-phenothiazinone m.p. 158–161° from MeOH–benzene–cyclohexane (1:4:5) (lit. m.p. 160–165°). (Found: C, 67.9; H, 3.5; N, 6.2. Calc. for $C_{12}H_7NOS$: C, 67.6; H, 3.3; N, 6.6%); UV 500 (15340), 365 (26400) nm.: IR 1638, 1605 cm^{-1}; MS *m/e* 213 (100), 185 (90).

(g) The reduction of 2-nitro-3'-hydroxydiphenylamine was also conducted in 60% aq EtOH. The principal product 2-amino-3'-hydroxydiphenylamine was isolated by column chromatography on silica gel and elution with benzene–EtOAc (9:1) followed by crystallisation from benzene, m.p. 100–103° (77%). (Found: C, 71.7; H, 6.0; N, 13.9. Calc. for $C_{12}H_{12}N_2O$: C, 72.0; H, 6.0; N, 14.0%); IR 3400, 3300 cm^{-1}; MS *m/e* 200 (100), 185 (30), 184 (8), 183 (20), 182 (15), 181 (10), 172 (8), 159 (10), 158 (8), 157 (10), 132 (33).

(h) The filtered aqueous ethanolic soln resulting from reduction of 3-amino-2'-nitrodiphenyl ether was concentrated *in vacuo* and allowed to stand in the cold under N_2 to allow the product to crystallise. Recystallisation from EtOH–water containing 2%

sodium dithionite gave 3-aminophenoxazine (88%) m.p. 170–173° (lit.[5] m.p. 172–173°) (Found: C, 72.9; H, 4.9; N, 14.4. Calc. for $C_{12}H_{10}N_2O$: C, 72.7; H, 5.1; N, 14.1%).

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