The Smiles Rearrangement of 2-Aryloxy-5-nitrophenoxides. Attempted Routes to Benzoxirens and Tribenzo[*b*,*e*,*h*]trioxonins

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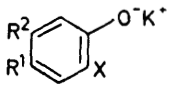
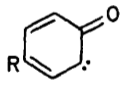
Formation of dibenzo-*p*-dioxins by the pyrolysis of 2-halogenophenoxides does not appear to involve intermediate benzoxirens. Thermal self-condensation of potassium 2-bromo-5-nitrophenoxide (1b) gave a mixture of 2,7- and 2,8-dinitrodibenzo-*p*-dioxins (6d) and (6e). The mechanism of formation of the 2,8-isomer (6e) is shown to involve Smiles rearrangement of potassium 2-(2-bromo-5-nitrophenoxy)-5-nitrophenoxide (9a). Further examples of Smiles rearrangements of 2-aryloxy-5-nitrophenoxides and an attempted synthesis of the tribenzo-[*b*,*e*,*h*]trioxonin derivatives (16) are described.

Our interest in the antiaromatic character of three-membered heterocyclic rings [1] led us to investigate the possibility that thermolysis of the 2-halogenophenoxides



(1)

a; R^1 = Me, R^2 = H, X = Cl
b; R^1 = H, R^2 = NO_2, X = Br
c; R^1 = NO_2, R^2 = H, X = Br



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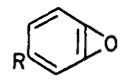
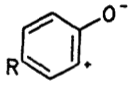


(4)

a; R = Me
b; R = NO_2



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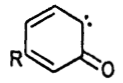
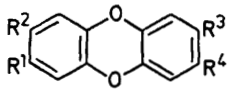


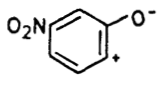
(5)

a; R = Me
b; R = NO_2



(6)

a; R^1 = R^2 = R^3 = R^4 = H
b; R^1 = R^3 = Me, R^2 = R^4 = H
c; R^1 = R^4 = Me, R^2 = R^3 = H
d; R^1 = R^3 = H, R^2 = R^4 = NO_2
e; R^1 = R^4 = H, R^2 = R^3 = NO_2



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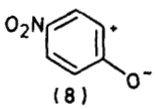
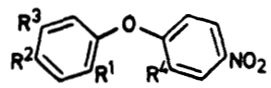


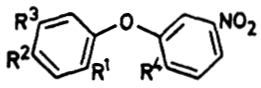
(8)

(1) might result in the transient formation of the benzoxirens (4). We have found that thermolysis of potassium 2-chloro-4-methylphenoxide (1a), under a variety of conditions, gave only 2,7-dimethyldibenzo-*p*-dioxin (6c). The absence of the isomeric 2,8-dimethyldibenzo-*p*-dioxin (6b) in the reaction product excluded the possibility that the benzoxiren (4a) was a reaction intermediate or that during the reaction the intermediate α-oxo-carbene (2; R = Me) rearranges to the isomeric species (5a). In a similar study using sodium 2-bromo-4- and -5-methylphenoxide, Cadogan and his co-workers have also eliminated the possibility that a benzoxiren (4) is generated during the formation of the dibenzo-*p*-dioxins (6) and they have presented evidence that α-oxo-carbenes [*e.g.* (2)] are the reaction intermediates.[2] Although these investigations did not encourage us in our quest for the benzoxirens (4), it was interesting to speculate that if the 1,3-dipolar canonical-form (3) makes an important contribution to the structure of the α-oxo-carbenes then the presence of a *m*-nitro-substituent may provide a strong driving force for rearrangement to the isomer [*i.e.* (7)→(8)]. In order to investigate



(9)

	R^1	R^2	R^3	R^4
a;	Br	H	NO_2	OK
b;	OMe	H	NO_2	OH
c;	OEt	H	NO_2	OH
d;	OMe	H	NO_2	OK
e;	H	H	H	OK
f;	H	Me	H	OK



(10)

g;	Br	H	NO_2	OH
h;	H	H	H	OH
i;	H	Me	H	OMe
j;	H	Me	H	OH
k;	H	H	H	OMe
l;	Br	H	NO_2	OMe

this possibility, thermolysis of potassium 2-bromo-5-nitrophenoxide (1b) (see the Scheme) was examined. When the salt (1b) was heated in dimethylformamide (DMF) (150 °C) over several days, it was indeed found that a mixture of 2,7- and 2,8-dinitrodibenzo-*p*-dioxins (6d) and (6e) was formed. We demonstrate herein that the rearranged product (6e) is formed *via* a Smiles rearrangement [3,4] of the intermediate potassium nitrophenoxide (9a) and not by formation of 3-nitrobenzoxiren (4b), or by the rearrangement of an α-oxo-carbene (5b).

The mixture of the dioxins (6d) (12%), m.p. 267—269 °C, and (6e) (16%), m.p. 212—215 °C, obtained by thermolysis of potassium 2-bromo-5-nitrophenoxide (1b) was conveniently separated by extraction with hot ethanol; whereas compound (6d) was virtually insoluble in this solvent, the 2,8-isomer (6e) readily dissolved and crystallised as pale yellow needles when

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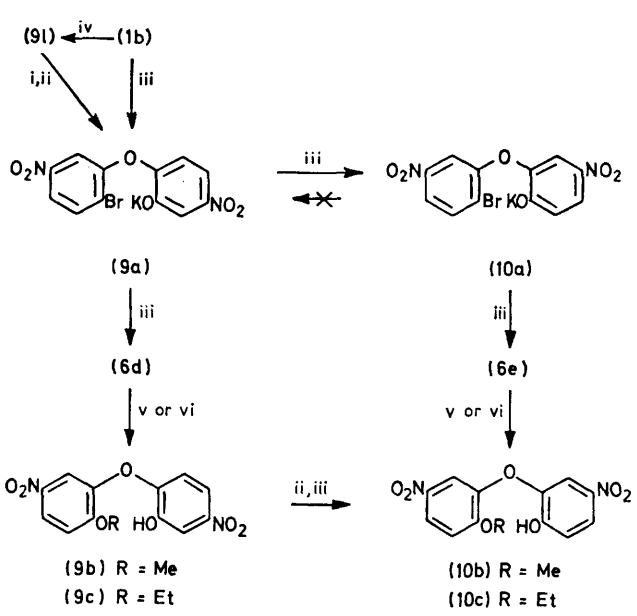
cooled. The isomeric dinitrodibenzo-*p*-dioxins (6d) and (6e), prepared in this way, were identical with samples obtained by nitration of dibenzo-*p*-dioxin (6a). Although the spectroscopic properties of compounds (6d) and (6e) are similar and fully consistent with the proposed structures, they do not provide a method of distinguishing between the isomeric structures of (6d) or (6e). We have measured the dipole moment of compound (6e) in benzene solution and the value of 3.96D ± 0.03 is good evidence that this isomer has C_{2v} symmetry.



SCHEME *Reagents:* i, HBr–AcOH; ii, KOH–EtOH; iii, DMF, 150 °C; iv, 2-bromo-5-nitroanisole; v, MeONa–MeOH, dilute HCl; vi, EtONa–EtOH, dilute HCl

Recent crystallographic studies have shown that the dibenzo-*p*-dioxin ring system is planar.[5-7] If it is assumed that the dipole moment of compound (6e) is the resultant of the C–NO_2 bond moments (4.08D; the dipole moment of nitrobenzene), the calculated moment (Figure) is 4.08D which is in good agreement with the experimental value (3.96D). A similar analysis shows that the 2,7-isomer (6d) (C_{2h} symmetry) should have a zero moment; the low solubility of compound (6d) precluded investigation of its dipole moment.

The formation of the products (6d) and (6e) by pyrolysis of the salt (1b) almost certainly proceeds *via* the intermediate biaryl ether (9a). This possibly occurs by initial generation of the carbene (7) which is then trapped by the salt (1b) or, alternatively, by nucleophilic attack of the 2-bromo-5-nitrophenoxide ion on the salt (1b). The intermediate (9a) may then either cyclise to give compound (6d) or undergo a Smiles rearrangement to give the isomeric ether (10a). It is interesting to note that potassium 2-bromo-4-nitrophenoxide (1c) remains unchanged in hot DMF, even over a long period of time. In order to provide support for these mechanistic proposals (see the Scheme) we have synthesised the biaryl ether intermediates (9a) and (10a) and have investigated their thermal cyclisation.

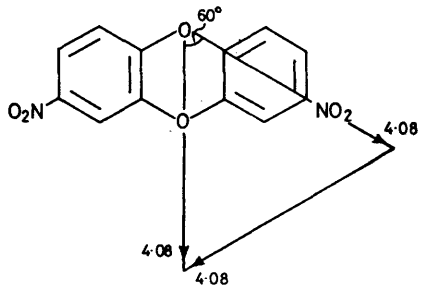


FIGURE The calculated dipole moment of 2,8-dinitrodibenzo-*p* dioxin (6e)

Reaction of equimolar amounts of 2-bromo-5-nitroanisole and the salt (1b), in hot DMF solution did not yield the desired diphenyl ether (9l); only the dioxins (6d) and (6e) were formed. Presumably, demethylation of the ether (9l) followed by cyclisation occurred rapidly under these conditions. This problem was avoided by using a large excess of 2-bromo-5-nitroanisole and the resultant ether (9l) was then converted into the diphenyl ether (9g) using hydrobromic acid. Subsequent treatment of the phenol (9g) with potassium hydroxide (1 equiv.) in ethanol gave the salt (9a) as a deep red solid. When this salt was heated in DMF solution the dioxins (6d) (37%) and (6e) (56%) were formed and isolated as pure products. The product ratio for this reaction {[(6e)] : [(6d)] 1.51} is similar to that found for thermal self-condensation of the salt (1b) {[(6e)] : [(6d)] 1.33} and this observation provides good evidence that compound (9a) is an intermediate in the reaction (1b)→(6d) + (6e).

The biaryl ether (10a) is a *p*-nitrophenol derivative and the parent phenol (10g) was conveniently prepared in good yield by treatment of the salt (1b) with chloroacetone followed by condensation of the resultant 1-(2-bromo-5-nitrophenoxy)propan-2-one with sodium nitromalonaldehyde.[8-10] The phenol (10g) and ethanolic potassium hydroxide (1 equiv.) gave the potassium salt (10a), upon evaporation, as an orange solid. In hot DMF solution the salt (10a) gave, exclusively, the dioxin (6e) (91%), indicating that the Smiles rearrangement (9a)→(10a) (Scheme) is not reversible.

A particularly interesting feature of the mechanism described in the Scheme is that the Smiles rearrangement (9a)→(10a) competes favourably with nucleophilic displacement of the activated bromo-substituent (9a)→(6d) (Scheme). The relative ease of the rearrangement (9a)→(10a) (Table 1) can be attributed to conjugated

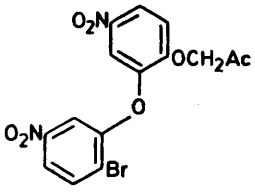
TABLE 1

Smiles rearrangement of 2-aryloxy-5-nitrophenoxides in DMF at 150 °C

Reactants	Products	Yield (%)
(9a)	(10a)	56
(9d)	(10d)	72
(9e)	(10e)	63
(9f)	(10f)	75

interaction between the phenoxide anion and the *p*-nitro-substituent in the rearranged product (10a); the increased thermodynamic stability of the product (10a) with respect to the precursor (9a) (Table 1) lowers the activation energy for the interconversion, in accord with the Hammond postulate.[11] It is interesting to compare this system (Scheme) with recently described systems in which there is rapid interconversion of diaryl ethers by Smiles rearrangement, prior to dioxin formation.[12,13]

We describe three further examples of the Smiles rearrangement of 2-aryloxy-5-nitrophenoxides (Table 1). Treatment of the dioxin (6d) with hot methanolic sodium methoxide solution gave, after acidic work-up, the diphenyl ether (9b), m.p. 129 °C. Similar treatment of the dioxin (6e) gave the isomeric phenol (10b), m.p. 148—150 °C. In analogous experiments using ethanolic sodium ethoxide, the biaryl ethers (9c), m.p. 127—129 °C, and (10c), m.p. 147—149 °C were also prepared. When the potassium salt of the phenol (9b) was heated



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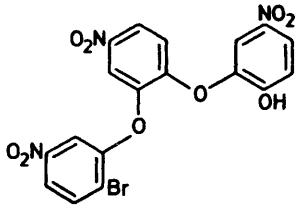
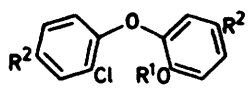


(12)

in DMF solution, Smiles rearrangement occurred to give, after acidic work-up, the isomeric phenol (10b) in 72% yield. Since the driving force of this reaction [(9d)→(10d); Table 1] is the formation of a *p*-nitrophenolate, this rearrangement provides further confirmation of the structures assigned to the isomers (6d) and (6e).

The two Smiles rearrangements which are described above [(9a)→(10a) and (9d)→(10d); Table 1] are both associated with electron-withdrawing groups in the migrating aryl substituent. We were interested to discover if an unsubstituted phenyl group would undergo a similar migration. Treatment of 2-bromo-5-nitroanisole with potassium phenoxide gave the diphenyl ether (9k) which was converted into the phenol (9h) using hydrobromic acid. When the potassium salt (9e) of this phenol was heated in DMF, Smiles rearrangement occurred and the isomeric product (10e) was isolated as its phenol (10h) in 63% yield and fully characterised by conversion into the methyl ether (10k), which was identical with an authentic sample. As far as we are aware, the reaction (9e)→(10e) (Table 1) is the first example of a Smiles rearrangement of a 2-hydroxy-biaryl ether in which the migrating group is an unsubstituted phenyl ring.[3,4] In a similar sequence using the *p*-tolyl derivative [(9f)→(10f) (Table 1)], the absence of any positional isomerism in the migrating aryl group was demonstrated.

Investigations of the Synthesis of Tribenzo[b,f,h]*trioxonins* (16).—During the preparation of the dioxin (6a) by thermal condensation of 2-chlorophenol in the presence of potassium carbonate,[14] we encountered two additional products. After isolation of compound (6a) by distillation, an ethanolic solution of the residue gave, with time, tiny crystals which were identified as the pentakis(phenoxy)phenol (15b) (2%), m.p. 86—90 °C. This compound was converted into its methyl ether (15c), m.p. 180—183 °C, using methyl iodide. Evaporation of the ethanol solution gave a syrup which was shown to be the bis(phenoxy)phenol (14b) (40%). No other products were encountered. It would appear that during thermolysis the biaryl ether (13a) is initially formed. This intermediate, which was not isolated, may then either cyclise to the dioxin (6a) or, alternatively, react with an excess of 2-chlorophenol to give the potassium phenoxide (14a). This salt did not appear to cyclise to tribenzo[*b*,*e*,*h*]trioxonin (16; R = H) under these conditions, but a small amount of dimerisation did occur to give compound (15a). The possibility that the intermediate biaryl ether (13a) undergoes a Smiles rearrangement under these conditions can be eliminated since the



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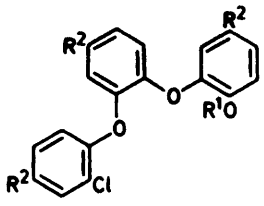

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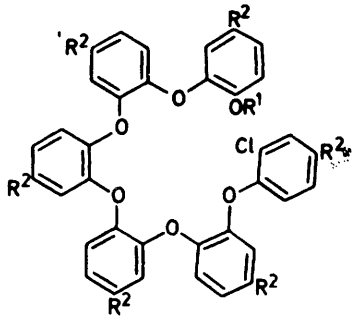
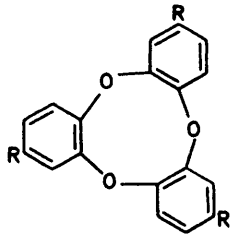


(15)

a; R^1 = K, R^2 = H
b; R^1 = R^2 = H
c; R^1 = Me, R^2 = H
d; R^1 = K, R^2 = Me
e; R^1 = H, R^2 = Me
f; R^1 = R^2 = Me

methyl derivative (13d) gave only the dioxin (6b), together with compound (14e).

Tribenzo[*b*,*e*,*h*]trioxonins (16) are of some interest



(16)

because of their rigid structure and the possibility that they may co-ordinate to small metal cations. The parent system (16; R = H) has been prepared in low yield (10%) by Ullmann reaction between 1,2-dibromobenzene and 2,2′-dihydroxydiphenyl ether.[15] No other investigations of this ring system have been reported. We have investigated the possibility of preparing rings of type (16) by thermal cyclisation of salts of the phenol (12). The phenol derivative (12), as a precursor to tribenzo[*b*,*e*,*h*]trioxonins (16), has several attractive features: (i) the *p*-nitrophenol function will prevent Smiles rearrangement leading to a mixture of isomers; (ii) the *p*-nitro-bromophenyl function will greatly facilitate ring closure; and (iii) the nitro-substituents in the product can be readily converted into other functional groups.

We have attempted to prepare the phenol (12) by treatment of the ketone derivative (11) with sodium nitromalonaldehyde in a manner analogous to the formation of the *p*-nitrophenol (10g). The propan-2-one (11) was prepared by treatment of the potassium salt (10a) with chloroacetone. When the ketone (11) was treated with sodium nitromalonaldehyde in ethanolic alkali solution the only significant product isolated was the diphenyl ether (10g). Presumably nucleophilic displacement of the *p*-nitrophenoxy-substituent of the ketone (11) occurs much more readily than deprotonation; this is clearly attributable to the stability of *p*-nitrophenoxide anions. The use of hindered bases to catalyse this condensation could possibly avoid this problem, but this has not been investigated in this study.

EXPERIMENTAL

I.r. and n.m.r. (60 MHz) spectra were determined with Perkin-Elmer 257 and R12 instruments, respectively. U.v. spectra were determined with a Unicam SP800A instrument. Unless otherwise stated, i.r. spectra were measured for solutions in chloroform, u.v. spectra in ethanol, and n.m.r. spectra in deuteriochloroform (tetramethylsilane as internal reference). Only significant bands from i.r. spectra are quoted. Mass spectra were measured with a Hitachi-Perkin-Elmer RMU-6E mass spectrometer.

Evaporation refers to the removal of volatile materials under diminished pressure. When substances are stated to be identical, this refers to their m.p.s, mixed m.p.s, and i.r. spectra. Separations by column chromatography were carried out using BDH Silica gel (60—120 mesh). Merck Kieselgel 60 PF_{254} was used for thick- and thin-layer chromatography (t.l.c.).

TABLE 2

Experimental results for the determination of the dipole moment of compound (6e) [a]

10^6W	ϵ	V
553	2.2805	1.1445
1 100	2.2854	1.1442
1 696	2.2927	1.1436
2 297	2.2991	1.1432
2 828	2.3030	1.1429

[a] α, the slope of the dielectric constant-weight fraction graph, 6.25; β, the slope of the specific volume-weight fraction graph, 0.46; R_D 51.84 cm³; T^P 396 cm³; μ 3.96 ± 0.03 D.

The dipole moment of compound (6e) was determined by measuring the dielectric constant of dilute solution in pure benzene at 25 °C using a Wayne-Kerr Autobalance Universal Bridge. Specific volumes were determined with a Sprengel–Ostwald pyknometer. This method of calculation is that recommended by Everard, Hill, and Sutton.[16] The experimental results are shown in Table 2.

Potassium 2-Bromo-5-nitrophenoxide (1b).—A solution of potassium hydroxide (7.7 g) in ethanol (40 ml) was added with stirring to a solution of 2-bromo-5-nitrophenol [17] (30 g) in ethanol (180 ml). The deep red solution was then concentrated under reduced pressure and the orange crystalline mass which precipitated was collected. Recrystallisation from ethanol gave the *nitrophenoxide* (1b) (29 g, 84%) as deep red prisms, m.p. >300 °C (decomp.) (Found: C, 27.4; H, 0.9; N, 5.2. $C_6H_3BrKNO_3$ requires C, 28.1; H, 1.2; N, 5.5%); $\lambda_{max.}$ (H_2O) 226, 264, 298, and 365sh nm (ε 9 870, 8 350, 5 880, and 1 700); $\nu_{max.}$ (KBr disc) 1 500 and 1 340 cm^{-1}; τ (D_2O) 2.1—2.9 (m, Ar-H).

Potassium 2-Bromo-4-nitrophenoxide (1c).—2-Bromo-4-nitrophenol [18] (3 g) in ethanol (25 ml) was mixed with a solution of potassium hydroxide (1.3 g) in ethanol (10 ml). A yellow, crystalline precipitate separated almost immediately. After 1 h at room temperature, the product was collected, dried under reduced pressure (80 °C), and identified as the *nitrophenoxide* (1c) (3.5 g, 99%), orange prisms, m.p. >300 °C (Found: C, 27.8; H, 1.0; N, 5.7. $C_6H_3BrKNO_3$ requires C, 28.1; H, 1.2; N, 5.5%); $\lambda_{max.}$ (H_2O) 270, 307, and 400 nm (ε 4 430, 2 770, and 15 790); $\nu_{max.}$ (KBr disc) 1 570 (NO_2), 1 490, and 1 290 cm^{-1}; τ (D_2O) 2.19 (d, *J* 3 Hz, 3-H), 2.55 (dd, *J* 3 and 8 Hz, 5-H), and 3.92 (d, *J* 8 Hz, 6-H).

Thermolysis of the Nitrophenoxide (1b).—A solution of compound (1b) (10 g) in dimethylformamide (DMF) (20 ml) was heated at 150 °C (4 d) with stirring. The solution was cooled, poured into ice–water, and the aqueous mixture was then boiled to coagulate the precipitated solid. This solid product was collected and extracted with hot ethanol (95%). Evaporation of the ethanol extract gave a yellow solid which was purified by t.l.c. (chloroform as eluant) and identified as 2,8-dinitrodibenzo-*p*-dioxin (6e) (425 mg, 16%). This sample was recrystallised from ethanol to give pale yellow needles, m.p. 212—215 °C (lit.,[19] 190 °C) (Found: C, 52.1; H, 2.8; N, 10.2. Calc. for $C_{12}H_6N_2O_6$: C, 52.6; H, 2.2; N, 10.2%); $\lambda_{max.}$ 211, 259, 305, and 356 nm (ε 33 930, 35 732, 8 740, and 9 250); $\nu_{max.}$ 1 530, 1 490, 1 350, 1 325, and 1 300 cm^{-1}; τ ($CDCl_3$ + CF_3CO_2H) 2.08 (dd, *J* 2.5 and 9 Hz, 3- and 7-H), 2.15 (d, *J* 2.5 Hz, 1- and 9-H), and 2.95 (d, *J* 9 Hz, 4- and 6-H); *m/e* 274 ($M^{+\cdot}$)→228($M^{+\cdot}$ − NO_2), *m** 190; identical with a sample prepared by nitration of dibenzo-*p*-dioxin (6a).

The residue, which was insoluble in ethanol, was also purified by t.l.c. (chloroform as eluant) and identified as 2,7-dinitrodibenzo-*p*-dioxin (6d) (300 mg, 12%). This sample was recrystallised from 1-methyl-2-pyrrolidone to give orange-brown flakes, m.p. 267—269 °C (lit.,[19] 256 °C) (Found: C, 52.3; H, 2.3; N, 10.3. Calc. for $C_{12}H_6N_2O_6$: C, 52.6; H, 2.2; N, 10.2%); $\lambda_{max.}$ 215, 243, 294, and 334 nm (ε 29 540, 23 420, 15 820, and 12 130); $\nu_{max.}$ 1 525, 1 495, 1 360, 1 340, 1 325, and 1 300 cm^{-1}; τ (1-methyl-2-pyrrolidone) 2.40 (dd, *J* 2.5 and 7.5 Hz, 3- and 8-H), 2.58 (d, *J* 2.5 Hz, 1- and 6-H), and 3.00 (d, *J* 7.5 Hz, 4- and 9-H); *m/e* 274 ($M^{+\cdot}$)→228 ($M^{+\cdot}$ − NO_2), *m** 190; identical with a sample prepared by nitration of dibenzo-*p*-dioxin (6a).

Thermolysis of the Nitrophenoxide (1c).—A solution of

compound (1c) (3.5 g) in DMF (10 ml) was heated at 150 °C (14 d). The solvent was evaporated and the residue shown to be the starting material (pure by n.m.r. analysis).

*Nitration of Dibenzo-*p*-dioxin* (6a).—Compound (6a) (3 g) [14] and acetic anhydride (50 ml) were mixed and chilled to 0 °C. Concentrated nitric acid (15 ml) (S.G. 1.43) was added slowly with stirring and the temperature was maintained at 0 °C. The reaction was vigorous. When addition was complete, the stirring was continued (15 min), and the solid product was then collected. Extraction of this solid with hot ethanol and evaporation of the alcoholic solution gave pale yellow crystals which were recrystallised from ethanol to give the dioxin (6e) (1.5 g, 33%) as pale yellow needles, m.p. 212—215 °C, identical with a sample prepared by thermolysis of compound (1b).

The insoluble residue was recrystallised from 1-methyl-2-pyrrolidone to give the dioxin (6d) (0.8 g, 18%) as brown prisms, m.p. 267—269 °C, identical with a sample prepared by thermolysis of compound (1b).

Reactions of the Dioxin (6d).—(a) *With sodium methoxide.* Compound (6d) (0.5 g) and sodium methoxide (0.5 g) in methanol (25 ml) were heated at reflux temperature (16 h). Evaporation gave a residue which was dissolved in water (20 ml) and acidified (dilute HCl). The solid precipitate was collected, dried, and recrystallised from light petroleum (b.p. 60—80 °C) to give 2-(2-*methoxy*-5-*nitrophenoxy*)-5-*nitrophenol* (9b) (0.42 g, 75%) as fine needles, m.p. 129 °C (Found: C, 50.9; H, 3.4; N, 9.1. $C_{13}H_{10}N_2O_7$ requires C, 51.0; H, 3.3; N, 9.2%); $\lambda_{max.}$ 212, 227sh, and 303 nm (ε 19 400, 16 100, and 12 800); $\nu_{max.}$ (KBr) 3 500, 1 600, 1 520, 1 350, 1 285, and 1 215 cm^{-1}; τ ($CDCl_3$ + CF_3CO_2H) 1.5—2.4 (m, 3-, 4′-, 5-, and 6′-H), 2.8 (d, *J* 8 Hz, 3′- or 6-H), 3.2 (d, *J* 8 Hz, 3′- or 6-H), and 6.05 (s, OMe); *m/e* 306 ($M^{+\bullet}$).

(b) *With sodium ethoxide.* Compound (6d) (0.5 g) and sodium ethoxide (0.5 g) in ethanol (25 ml) were heated at reflux temperature (17 h). The reaction mixture was worked up in the manner described above and recrystallised from light petroleum (b.p. 60—80 °C) to give 2-(2-*ethoxy*-5-*nitrophenoxy*)-5-*nitrophenol* (9c) (0.45 g, 77%) as pale yellow needles, m.p. 127—129 °C (Found: C, 52.3; H, 4.0; N, 8.4. $C_{14}H_{12}N_2O_7$ requires C, 52.5; H, 3.8; N, 8.7%); $\lambda_{max.}$ 214, 231, and 305 nm (ε 15 900, 16 300, and 13 600); $\nu_{max.}$ (KBr) 3 300, 1 590, 1 520, 1 340, 1 285, and 1 270 cm^{-1}; τ 1.6—2.4 (m, 3-, 4′-, 5, and 6′-H), 2.89 (d, *J* 8 Hz, 3′- or 6-H), 3.20 (d, *J* 8 Hz, or 3′-H), 3.60 (br s, OH), 5.85 (q, *J* 6 Hz, OCH_2), and 8.69 (t, *J* 6 Hz, Me); *m/e* 320 ($M^{+\bullet}$)→291 ($M^{+\bullet}$ − Et), *m** 266 and 274 ($M^{+\bullet}$ − EtOH).

Reactions of the Dioxin (6e).—(a) *With sodium methoxide.* Compound (6e) (0.3 g) was treated with sodium methoxide (0.3 g) in methanol solution (25 ml) in the manner described for compound (6d) above. Recrystallisation of the solid product from light petroleum (b.p. 60—80 °C) gave 2-(2-*methoxy*-5-*nitrophenoxy*)-4-*nitrophenol* (10b) (0.22 g, 66%) as tiny, buff needles, m.p. 148—150 °C (Found: C, 50.4; H, 3.6; N, 9.0. $C_{13}H_{10}N_2O_7$ requires C, 51.0; H, 3.3; N, 9.2%); $\lambda_{max.}$ 212, 232, and 314 nm (ε 15 000, 14 300, and 12 200); $\nu_{max.}$ 3 400br, 1 600, 1 510, 1 345, and 1 285 cm^{-1}; τ ($CDCl_3$ + CF_3CO_2H) 1.78 (dd, *J* 3 and 8 Hz, 4- or 4′-H), 1.92 (d, *J* 3 Hz, 6 or 6′-H), 1.96 (dd, *J* 3 and 8 Hz, 4′- or 4-H), 2.34 (d, *J* 3 Hz, 6′- or 6-H), 2.83 (2 superimposed d, *J* 8 Hz, 3- and 3′-H), and 6.03 (s, OMe); *m/e* 306 ($M^{+\bullet}$).

(b) *With sodium ethoxide.* Compound (6e) (0.3 g) was treated with sodium ethoxide (0.3 g) in ethanol solution in the manner described for compound (6d) above. Recrystallisation of the solid product from light petroleum (b.p. 60—80 °C) gave 2-(2-*ethoxy*-5-*nitrophenoxy*)-4-*nitrophenol* (10c) (0.2 g, 57%) as tiny, cream prisms, m.p. 147—149 °C (Found: C, 52.0; H, 4.3; N, 8.4. $C_{14}H_{12}N_2O_7$ requires C, 52.5; H, 3.8; N, 8.7%); $\lambda_{max.}$ 234 and 317 nm (ε 14 300 and 14 500); $\nu_{max.}$ 3 360br, 1 600, 1 505, and 1 340 cm^{-1}; τ ($CDCl_3$ + CF_3CO_2H) 1.6—2.1 [m, 4-, 4′-, and 6- (or 6′-) H], 2.29 [d, *J* 3 Hz, 6′- (or 6-) H], 2.83 [d, *J* 8 Hz, 3- (or 3′-) H], 2.86 [d, *J* 8 Hz, 3′ (or 3-) H], 5.83 (q, *J* 6 Hz, OCH_2), and 8.68 (t, *J* 6 Hz, Me); *m/e* 320 ($M^{+\bullet}$)→291 ($M^{+\bullet}$ − Et), *m** 266 and 274 ($M^{+\bullet}$ − EtOH).

1-*Bromo*-2-(2-*methoxy*-4-*nitrophenoxy*)-4-*nitrobenzene* (9l).—A solution of the nitrophenoxide (1b) (1.1 g) and 2-bromo-5-nitroanisole (10 g) in DMF (50 ml) was heated at 150 °C (2 h). The solution was cooled, poured onto ice–water, and the solid product collected and crystallised from ethanol. This crystalline product was identified as starting material. The ethanolic solution, upon concentration, gave a second crop of 2-bromo-5-nitroanisole which was removed and the mother liquor was evaporated to give a solid residue which was shown to be a two-component mixture. This mixture was separated by column chromatography (benzene as eluant). The first component was collected and recrystallised from light petroleum (b.p. 60—80 °C) to give the *diphenyl ether* (9l) (0.35 g, 23%) as tiny, cream crystals, m.p. 173—175 °C (Found: C, 41.8; H, 2.7; N, 7.6. $C_{13}H_6BrN_2O_6$ requires C, 42.3; H, 2.5; N, 7.6%); $\lambda_{max.}$ 225, 279, and 315sh nm (ε 18 600, 15 400, and 9 000); $\nu_{max.}$ (KBr) 1 530, 1 500, and 1 345 cm^{-1}; τ 1.9—3.1 (m, 6 Ar-H) and 6.06 (s, OMe); *m/e* 368 [$M^{+\bullet}$ (^{79}Br)].

2-(2-*Bromo*-5-*nitrophenoxy*)-5-*nitrophenol* (9g).—Compound (9l) (0.5 g) was added to a mixture of hydrobromic acid (47%) (5 ml) and glacial acetic acid (5 ml) and the solution was heated under reflux (*ca.* 110 °C) (24 h). The acid solution was then cooled and poured onto ice–water to give a precipitate which was collected and dried. Recrystallisation from light petroleum (b.p. 80—100 °C) gave the *diphenyl ether* (9g) (0.35 g, 73%) as fine, cream needles, m.p. 139—140 °C (Found: C, 40.0; H, 2.3; N, 7.5. $C_{12}H_7BrN_2O_6$ requires C, 40.6; H, 2.0; N, 7.9%); $\lambda_{max.}$ 215, 230, 280, and 320sh nm (ε 14 000, 13 500, 11 800, and 6 400); $\nu_{max.}$ (KBr) 3 000—3 600br, 1 520, 1 350, and 1 280 cm^{-1}; τ 1.9—2.5 [m, 3-, 4-, 6′-, and 6- (or 3′-) H], 2.78 [s, 3′- (or 6-) H], 3.21 (d, *J* 7 Hz, 5′-H), and 4.65 (br s, OH); *m/e* 354 [$M^{+\bullet}$ (^{79}Br)]→275 ($M^{+\bullet}$ − Br) and 274 ($M^{+\bullet}$ − HBr), *m** 213.

Thermal Cyclisation of Potassium 2-(2-*Bromo*-5-*nitrophenoxy*)-5-*nitrophenoxide* (9a).—The diphenyl ether (9g) (0.4 g) in ethanol (10 ml) was mixed with potassium hydroxide (1 equiv., 63 mg) in ethanol (5 ml) to give an orange solution. Evaporation at ≤40 °C gave the potassium salt (9a) as a deep red residue which was used directly, without characterisation.

The salt (9a) in DMF (10 ml) was heated at 150 °C (1 h). The red colouration rapidly disappeared and potassium bromide was deposited. The reaction mixture was cooled and then poured onto ice–water and the pale yellow precipitate was collected and dried. This crude product (300 mg) was shown by t.l.c. (chloroform as eluant) to be a mixture of the dioxins (6d) and (6e). Extraction with hot ethanol and purification of the soluble and insoluble fractions by t.l.c. (chloroform as eluant) gave the dioxins (6e) (174 mg, 56%), m.p. 212—215 °C, and (6d) (114 mg, 37%), m.p. 267—269 °C. Both samples were identical with authentic specimens.

2-(2-Bromo-5-nitrophenoxy)-4-nitrophenol (10g).—1-(2-Bromo-5-nitrophenoxy)propan-2-one (5.5 g) in ethanol (100 ml) was added to a solution of sodium nitromalonaldehyde (3.14 g) [9] in water (33 ml). 1M-Sodium hydroxide (75 ml) was added and the red solution was stirred overnight at room temperature. Evaporation gave a residue which was dissolved in water, extracted with ether, and acidified with 2M-hydrochloric acid The solid product which formed was extracted into ether (200 ml) and the ethereal solution dried (Na_2SO_4). The dark solid, obtained upon evaporation, was purified by passage through a short column of silica gel (chloroform as eluant). Recrystallisation from light petroleum (b.p. 60—80 °C) gave the *diphenyl ether* (10g) (5.1 g, 72%) as fine needles, m.p. 162—164 °C (Found: C, 40.5; H, 1.9; N, 7.6. $C_{12}H_7BrN_2O_6$ requires C, 40.6; H, 2.0; N, 7.9%); $\nu_{max.}$ (KBr) 3 200—3 600br, 1 590, 1 510, 1 340, and 1 300 cm^{-1}; τ 1.8—3.0 (m, 6 Ar-H) and 3.7 (br s, OH); *m/e* 354 [$M^{+\bullet}$ (^{79}Br)] and 275 ($M^{+\bullet}$ — Br).

Thermal Cyclisation of Potassium 2-(2-Bromo-5-nitrophenoxy)-4-nitrophenoxide (10a).—Compound (10g) (0.4 g) in ethanol (10 ml) was mixed with potassium hydroxide (1 equiv., 63 mg) in ethanol (5 ml) to give a deep yellow solution. Evaporation at 40 °C gave the potassium salt (10a) as an orange residue which was used immediately.

The salt (10a) in DMF (10 ml) was heated at 150 °C (1 h). The yellow colouration faded and potassium bromide was deposited. The reaction mixture was cooled and then poured onto ice–water, and the yellow product was collected and dried. The product (280 mg, 91%), m.p. 212—215 °C was shown by t.l.c. (chloroform as eluant) to be the pure dioxin (6e). This sample was recrystallised from ethanol and shown to be identical with an authentic specimen.

2-Methoxy-4-nitro-1-phenoxybenzene (9k).—A solution of 2-bromo-5-nitroanisole (23 g) and potassium phenoxide (13 g) in DMF (100 ml) was heated under reflux (10 h). The solution was left at room temperature overnight and then poured onto ice–water, and the aqueous mixture heated (*ca.* 50 °C) in order to coagulate the oily precipitate; it was then cooled (0 °C) A brown oil was deposited. The aqueous solution was decanted off and the residual oil was washed with water and dissolved in a minimum volume of hot ethanol. Upon refrigeration, the ethanolic solution gave a light brown oil which was collected and further purified by column chromatography (chloroform as eluant) to give the diphenyl ether (9k) (10 g, 41%) as a yellow oil which would not crystallise. Distillation (141—142 °C at 0.3 mmHg) gave a crystalline sample, m.p. 43 °C (lit.,[20] 59 °C) (Found: N, 5.6. Calc. for $C_{13}H_{11}NO_4$: N, 5.7%); $\lambda_{max.}$ 212, 233sh, 300, and 329 nm (ε 18 600, 10 900, 6 250, and 7 250); $\nu_{max.}$ 1 585, 1 525, 1 490, 1 350, and 1 275 cm^{-1}; τ 2.14 (d, *J* 3 Hz, 3-H), 2.23 (dd, *J* 3 and 8 Hz, 5-H), 2.5—3.3 (m, 6-H and Ph), and 6.07 (s, OMe); *m/e* 245 ($M^{+\bullet}$).

A similar procedure was used to prepare the derivatives (9i), (10i), and (10k). 2-Bromo-5-nitroanisole and the potassium salt of *p*-cresol gave *2-methoxy-1-(4-methylphenoxy)-4-nitrobenzene* (9i) (35%) as orange-yellow prisms from ethanol, m.p. 79—80 °C (Found: C, 64.5; H, 4.9; N, 5.5. $C_{14}H_{13}NO_4$ requires C, 64.8; H, 5.0; N, 5.4%); $\lambda_{max.}$ 218, 233sh, 290, and 333 nm (ε 3 000, 9 450, 5 200, and 7 250); $\nu_{max.}$ 1 595, 1 525, 1 500, 1 350, and 1 275 cm^{-1}; τ 2.1—2.4 (m, 3- and 5-H), 2.7—3.4 (m, 6-H and C_6H_4), 6.07 (s, OMe), and 7.67 (s, Me); *m/e* 259 ($M^{+\bullet}$). 2-Bromo-4-nitroanisole and potassium phenoxide gave 1-methoxy-2-phenoxy-4-nitrobenzene (10k) (48%) as large, grey needles from ethanol, m.p. 69—70 °C (lit.,[21] m.p. 72 °C) (Found: C, 63.7; H, 4.7; N, 6.0. Calc. for $C_{13}H_{11}NO_4$: C, 63.7; H, 4.5; N, 5.7%); $\lambda_{max.}$ 212, 230sh, and 307 nm (ε 12 000, 10 800, and 7 700); $\nu_{max.}$ 1 585, 1 525, 1 490, 1 350, and 1 275 cm^{-1}; τ 1.97 (dd, *J* 2.5 and 7 Hz, 4-H), 2.23 (d, *J* 2.5 Hz, 6-H), 2.5—3.2 (m, Ph and 3-H), and 6.09 (s, OMe); *m/e* 245 ($M^{+\bullet}$). 2-Bromo-4-nitroanisole and the potassium salt of *p*-cresol gave *1-methoxy-2-(4-methylphenoxy)-4-nitrobenzene* (10i) (40%) as hexagonal rods from ethanol, m.p. 112—115 °C (Found: C, 65.1; H, 5.4; N, 5.2. $C_{14}H_{13}NO_4$ requires C, 64.8; H, 5.0; N, 5.4%); $\lambda_{max.}$ 215, 235sh, and 313 nm (ε 11 250, 8 400, and 5 200); $\nu_{max.}$ (KBr) 1 590, 1 510, 1 500, 1 335, 1 270, and 1 230 cm^{-1}; τ 1.9—3.5 (m, 7 Ar-H), 6.05 (s, OMe), and 7.68 (s, Me).

5-Nitro-2-phenoxyphenol (9h).—Compound (9k) (1 g) was mixed with glacial acetic acid (10 ml) and hydrobromic acid (47%) (10 ml). The mixture was heated at 110 °C (24 h) and poured onto ice–water to give a solid which was collected and dried. The crude phenol was purified by t.l.c. (chloroform as eluant) and recrystallised from light petroleum (b.p. 60—80 °C) to give the *diphenyl ether* (9h) (0.4 g, 42%) as yellowish brown flakes, m.p. 96—97 °C (Found: C, 62.7; H, 4.0; N, 5.9. $C_{12}H_9NO_4$ requires C, 62.3; H, 3.9; N, 6.1%); $\lambda_{max.}$ 217, 236, 298, and 334 nm (ε 11 900, 7 200, 4 850, and 5 100); $\nu_{max.}$ 3 520, 1 590, 1 520, 1 490, 1 350, and 1 270 cm^{-1}; τ 2.13 (d, *J* 3 Hz, 3-H), 2.32 (dd, *J* 3 and 8 Hz, 5-H), 2.4—3.0 (m, Ph), 3.21 (d, *J* 8 Hz, 6-H), and 3.75 (br s, OH); *m/e* 231 ($M^{+\bullet}$).

A similar procedure using compound (9i) gave 2-(4-methylphenoxy)-5-nitrophenol (9j) as a pale yellow oil, $\lambda_{max.}$ 220, 238sh, 300, and 335 nm (ε 12 800, 8 300, 5 450, and 6 050); $\nu_{max.}$ 3 540, 1 610, 1 530, 1 495, 1 350, and 1 280 cm^{-1}; τ 2.0—4.0 (m, 7 Ar-H and OH) and 7.64 (s, Me).

Smiles Rearrangements of the Potassium 5-Nitrophenoxides.—(a) *Pyrolysis of potassium 5-nitro-2-phenoxyphenoxide* (9e). Compound (9h) (300 mg) in ethanol (10 ml) was mixed with a solution of potassium hydroxide (1 equiv., 73 mg) in ethanol (10 ml). A red colouration developed and evaporation at 40 °C gave the potassium salt (9e) as a deep red oil which was used without purification. The salt (9e) in DMF (10 ml) was heated at 150 °C (24 h). The reaction mixture was cooled and then poured into ice–water and acidified (dilute HCl) to give an oily precipitate. The product was extracted into chloroform and purified by t.l.c. (silica gel; chloroform as eluant) to give *4-nitro-2-phenoxyphenol* (10h) (190 mg, 63%) as an oil (Found: M^+, 231.0498. $C_{12}H_9NO_4$ requires *M*, 231.0532); $\nu_{max.}$ 3 530, 1 595, 1 525, 1 505, 1 495, 1 350, and 1 305 cm^{-1}; τ 2.10 (dd, *J* 2 and 7.5 Hz, 4-H), 2.31 (d, *J* 2 Hz, 6-H), 2.5—3.2 (m, Ph and 3-H), and 4.0 (br s, OH).

Treatment of an ethanol solution of compound (10h) with an ethereal solution of diazomethane gave compound (10k), m.p. 69—70 °C, identical with an authentic sample.

(b) *Pyrolysis of potassium 2-(4-methylphenoxy)-5-nitrophenoxide* (9f). Compound (9j) (400 mg) was converted into its potassium salt (9f) in a manner analogous to that described above. The deep red semi-solid salt in DMF (10 ml) was heated at 150 °C (24 h). Work-up as described for the previous experiment gave 2-(4-methylphenoxy)-4-nitrophenol (10j) (300 mg, 75%) as a pale yellow oil (Found: M^+, 245.0685. $C_{13}H_{11}NO_4$ requires *M*, 245.0688); $\lambda_{max.}$ 218, 237sh, and 330 nm (ε 11 700, 8 450, and 6 000); $\nu_{max.}$ 3 530, 1 600, 1 530, 1 505, 1 350, and 1 305 cm^{-1}; τ 2.07 (dd, *J* 2.5 and 7 Hz, 4-H), 2.33 (d, *J* 2.5 Hz, 6-H), 2.5—3.5 (m, C_6H_4, 3-H, and OH), and 7.64 (s, Me).

Treatment of an ethanol solution of compound (10j) with

an ethereal solution of diazomethane gave compound (10i), m.p. 112—115 °C, identical with an authentic sample.

(c) *Pyrolysis of potassium* 2-(2-*methoxy*-5-*nitrophenoxy*)-5-*nitrophenoxide* (9d). In the manner described above, compound (9b) (0.4 g) was converted into the potassium salt (9d) which, in DMF (10 ml) at 150 °C (24 h) gave, when poured into water, acidified, and recrystallised from light petroleum (b.p. 60—80 °C), 2-(2-methoxy-5-nitrophenoxy)-4-nitrophenol (10b) (0.29 g, 72%), m.p. 148—150 °C, identical with an authentic sample prepared from the dioxin (6e).

2-*Bromo*-5-*nitroanisole*.—An ethanol solution of 2-bromo-5-nitrophenol [17] was treated with ethereal diazomethane (1 equiv.). Evaporation and recrystallisation of the product from ethanol gave 2-bromo-5-nitroanisole (87%) as prisms, m.p. 103—104 °C (lit.,[22] 104 °C) (Found: C, 36.2; H, 2.8; N, 6.1. Calc. for $C_7H_6BrNO_3$: C, 36.2; H, 2.6; N, 6.0%); $\lambda_{max.}$ 213, 233, 282, and 324 nm (ε 9 000, 8 300, 6 900, and 4 150); $\nu_{max.}$ 1 535, 1 480, 1 350, and 1 265 cm^{-1}; τ 2.28 (s, 3 Ar-H) and 6.01 (s, OMe).

In a similar manner, 2-bromo-4-nitrophenol [18] gave 2-bromo-4-nitroanisole (82%) as prisms, m.p. 105—106 °C (lit.,[23] 108 °C) (Found: C, 36.1; H, 2.8; N, 6.2. Calc. for $C_7H_6BrNO_3$: C, 36.2; H, 2.6; N, 6.0%); $\lambda_{max.}$ 214, 235, and 310 nm (ε 8 750, 6 800, and 6 100); $\nu_{max.}$ 1 590, 1 525, 1 490, 1 350, and 1 280 cm^{-1}; τ 1.55 (d, *J* 2.5 Hz, 3-H), 1.78 (dd, *J* 2.5 and 8 Hz, 5-H), 3.03 (d, *J* 8 Hz, 6-H), and 6.00 (s, OMe).

1-(2-*Bromo*-5-*nitrophenoxy*)*propan*-2-*one*.—Potassium 2-bromo-5-nitrophenoxide (1b) (10 g) and chloroacetone (4.3 g) in dry acetone (100 ml) were heated under gentle reflux (3 h). After evaporation the residue was treated with water (50 ml) and the aqueous mixture extracted with chloroform (3 × 75 ml). The combined chloroform extracts were washed with water (2 × 50 ml), dried (Na_2SO_4), and evaporated. The residue was recrystallised from ethanol to give 1-(2-*bromo*-5-*nitrophenoxy*)*propan*-2-*one* (7.7 g, 72%) as needles, m.p. 94—96 °C (Found: C, 39.4; H, 2.9; N, 5.1. $C_9H_8BrNO_4$ requires C, 39.4; H, 2.9; N, 5.1%); $\nu_{max.}$ (KBr) 1 720 cm^{-1}; τ 2.1—2.5 (m, 3 Ar-H), 5.25 (s, CH_2), and 7.60 (s, Me).

In a similar manner, compound (10a) and chloroacetone gave 2-(2-*bromo*-5-*nitrophenoxy*)-4-*nitrophenoxypropan*-2-*one* (11) (55%) as prisms, m.p. 170—172 °C (Found: C, 43.8; H, 2.6; N, 7.0. $C_{15}H_{11}BrN_2O_7$ requires C, 43.8; H, 2.7; N, 6.8%); $\nu_{max.}$ (KBr) 1 730 cm^{-1}; τ ([$^2H_6$]dimethyl sulphoxide) 1.65—2.80 (6 H, m, Ar-H), 4.90 (2 H, s, CH_2), and 7.93 (3 H, s, Me).

Thermal Condensation of 2-*Chlorophenols*. (*WARNING: Some Dibenzo*-p-*dioxin Derivatives are extremely Toxic* [12]).—(a) *Pyrolysis of* 2-*chlorophenol*. An extension of the method described by Shine and Shade [14] was employed. 2-Chlorophenol (136 g), anhydrous potassium carbonate (73 g), and copper powder (8 g) were heated at 170—200 °C (6 h) with mechanical stirring. Aqueous potassium hydroxide (150 ml; 20%) was added to the cold reaction mixture and the mixture was heated at reflux temperature (3 h). The aqueous solution was cooled, filtered through a glass-wool plug, and thoroughly extracted with ether. Evaporation of the combined ethereal extracts gave a crystalline residue which was distilled under diminished pressure. The distillate (b.p. 140—160 °C at 3 mmHg) solidified and recrystallised from ethanol to give dibenzo-*p*-dioxin (6a) (11 g, 11%) as needles, m.p. 118—119 °C (lit.,[14] 120—121 °C); $\lambda_{max.}$ 210, 227, and 290 nm (ε 7 326, 13 020, and 3 793); $\nu_{max.}$ 1 590, 1 490, 1 295, and 1 280 cm^{-1}; τ 3.18 (s, Ar-H).

The residue obtained after vacuum distillation was dissolved in hot ethanol and the solution was allowed to stand at 0 °C (16 h). A fine, crystalline precipitate which had formed was collected and shown to be a single compound of high purity by t.l.c. (silica gel; chloroform as eluant). Recrystallisation of the product from a large volume of ethanol gave 2-[2-(2-{2-[2-(2-*chlorophenoxy*)*phenoxy*]*phenoxy*}*phenoxy*)*phenoxy*]*phenol* (15b) (2 g, 2%, before recrystallisation) as tiny prisms, m.p. 86—90 °C (Found: C, 73.4; H, 4.7. $C_{36}H_{25}ClO_6$ requires C, 73.4; H, 4.3%); $\lambda_{max.}$ 215, 273, and 278sh nm (ε 47 500, 9 800, and 9 250); $\nu_{max.}$ (KBr) 1 610, 1 590, 1 495, 1 265, 1 195, and 750 cm^{-1}; τ 3.04 (m, Ar-H).

The ethanolic mother liquor was evaporated to give a residual syrup which was a single spot by t.l.c. (silica gel; chloroform as eluant). Column chromatography gave a viscous oil, identified as 2-[2-(2-*chlorophenoxy*)*phenoxy*]-*phenol* (14b) (44 g, 40%) (Found: C, 70.0; H, 4.6%; $M^{+\bullet}$, 312.0593. $C_{18}H_{13}ClO_3$ requires C, 69.1; H, 4.2%; *M*, 312.0553); $\lambda_{max.}$ 218 and 274 nm (ε 30 000 and 7 100); $\nu_{max.}$ 3 550, 1 610, 1 590, 1 500, 1 480, 1 265, and 1 190 cm^{-1}; τ (CCl_4) 2.5—3.5 (m, Ar-H) and 4.5 (br s, OH).

(b) *Pyrolysis of* 2-*chloro*-p-*cresol*. In the manner described above, 2-chloro-*p*-cresol (143 g) was heated with anhydrous potassium carbonate (70 g) and copper powder (8 g) at 170—200 °C (7.5 h). Treatment with aqueous alkali, extraction with ether, and vacuum distillation gave a distillate (b.p. 162 °C at 5 mmHg) which rapidly crystallised. Recrystallisation from ethanol gave 2,7-dimethyldibenzo-*p*-dioxin (6c) (13.8 g, 13%) as needles, m.p. 113 °C (lit.,[24] 109—110 °C) (Found: C, 79.1; H, 5.8. Calc. for $C_{14}H_{12}O_2$: C, 79.2; H, 5.7%); $\lambda_{max.}$ 228 and 293 nm (ε 24 500 and 3 450); $\nu_{max.}$ (KBr) 1 590, 1 500, 1 445, 1 300, 1 220, and 1 120 cm^{-1}; τ 3.38 (m, 6 Ar-H) and 7.83 (s, 2 × Me).

The residue from the distillation was dissolved in ethanol, but no product crystallised with time. Evaporation gave a thick syrup which was a single compound (t.l.c.). Column chromatography (silica gel; chloroform as eluant) gave a viscous oil which was identified as 2-[2-(2-*chloro*-4-*methylphenoxy*)-4-*methylphenoxy*]-4-*methylphenol* (14e) (30 g, 37%) (Found: Cl, 9.4; $C_{21}H_{19}ClO_3$ requires Cl, 10.0%); $\lambda_{max.}$ 226 and 281 nm (ε 17 500 and 6 200); $\nu_{max.}$ 3 520, 3 000, 2 920, 1 600, 1 510, 1 490, 1 270, and 1 220 cm^{-1}; τ (CCl_4) 2.8—3.6 (m, 9 Ar-H), 4.55 (br s, OH), 7.79 (s, 2 × Me), and 7.88 (s, Me).

2-[2-(2-{2-[2-(2-*Chlorophenoxy*)*phenoxy*]*phenoxy*}*phenoxy*)-*phenoxy*]-2-*methoxybenzene* (15c).—Potassium hydroxide (0.2 g) was added to a suspension of compound (15b) (1 g) in ethanol (50 ml) and the mixture was heated under reflux (30 min). The mixture was cooled, methyl iodide (25 ml) added, and the mixture was reheated at reflux temperature (48 h). Evaporation gave a residue which was dissolved in chloroform and washed with water. The product was dried ($MgSO_4$), evaporated, and then purified by t.l.c. (silica gel; chloroform as eluant). Recrystallisation from ethanol gave *compound* (15c) (0.3 g, 29%) as tiny crystals, m.p. 180—183 °C (Found: C, 73.2; H, 4.3. $C_{37}H_{27}ClO_6$ requires C, 73.7; H, 4.5%); $\lambda_{max.}$ 228, 272, and 277sh nm (ε 31 460, 10 200, and 9 500); $\nu_{max.}$ 1 580, 1 500, 1 260, and 1 110 cm^{-1}; τ 2.9—3.3 (m, 24 Ar-H) and 6.28 (s, OMe).

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REFERENCES

[1] M. J. S. Dewar and C. A. Ramsden, *J. Chem. Soc., Chem. Commun.*, 1973, 688.
[2] J. I. G. Cadogan, J. T. Sharp, and M. J. Trattles, *J. Chem. Soc., Chem. Commun.*, 1974, 900.
[3] W. E. Truce, E. M. Kreider, and W. W. Brand, *Org. React.*, 1970, **18**, 99.
[4] J. Skarzewski and Z. Skrowaczewska, *Wiad. Chem.*, 1974, **28**, 155.
[5] F. P. Boer, F. P. Van Remoortere, P. P. North, and M. A. Neuman, *Acta Crystallogr., Sect. B*, 1972, **28**, 1023.
[6] M. Senma, Z. Taira, T. Taga, and K. Osaki, *Cryst. Struct. Commun.*, 1973, **2**, 311.
[7] A. W. Cords and C. K. Fair, *Acta Crystallogr., Sect. B*, 1974, **30**, 1621.
[8] P. E. Fanta, *Org. Synth.*, 1952, **32**, 95.
[9] P. E. Fanta and R. A. Stein, *Chem. Rev.*, 1960, **60**, 261.
[10] T. R. Govindachari, S. Prabhakar, P. S. Santhanam, and V. Sudarsanam, *Indian J. Chem.*, 1966, **4**, 433.
[11] G. S. Hammond, *J. Am. Chem. Soc.*, 1955, **77**, 334.
[12] A. P. Gray, S. P. Cepa, and J. S. Cantrell, *Tetrahedron Lett.*, 1975, 2873.
[13] A. S. Kende and M. R. DeCamp, *Tetrahedron Lett.*, 1975, 2877.
[14] H. J. Shine and L. R. Shade, *J. Heterocycl. Chem.*, 1974, **11**, 139.
[15] T. Weiss, P. Schulz, and G. Klar, *Z. Naturforsch., Teil B*, 1974, **29**, 156.
[16] K. B. Everard, R. A. W. Hill, and L. E. Sutton, *Trans. Faraday Soc.*, 1950, **46**, 417.
[17] R. V. Henley and E. E. Turner, *J. Chem. Soc.*, 1930, 938.
[18] M. H. van Erp, *Recl. Trav. Chim. Pays-Bas Belq.*, 1910, **29**, 218.
[19] M. Tomita, *J. Pharm. Soc. J. pn.*, 1935, **55**, 1060.
[20] F. Lions and A. M. Willison, *J. Proc. Roy. Soc. New South Wales*, 1938, **72**, 257.
[21] R. Q. Brewster and H. S. Choguill, *J. Am. Chem. Soc.*, 1939, **61**, 2702.
[22] W. E. Hanford and R. Adams, *J. Am. Chem. Soc.*, 1935, **57**, 1592.
[23] J. Burns, H. McCombie, and H. A. Scarborough, *J. Chem. Soc.*, 1928, 2928.
[24] B. Anjaneyulu, T. R. Govindachari, S. S. Sathe, N. Viswanathan, K. W. Gopinath, and B. R. Pai, *Tetrahedron*, 1969, **25**, 3091.