

## Intramolecular Cyclisation of Substituted Phenoxyethanols and Related Compounds with Mercury(II) Oxide and Iodine

By André Goosen\* and Cedric W. McClelland, Organic Chemistry Research Laboratories, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth, South Africa

Electron-donating substituents have been shown to promote intramolecular cyclisation of 2-phenoxyethanols to form Ar<sub>1</sub>-5 and Ar<sub>2</sub>-6 cyclisation products. The *meta*-iodo-substituent promotes Ar<sub>2</sub>-6 cyclisation to form 2,3-dihydro-1,4-benzodioxins. The Ar<sub>2</sub>-6 cyclisation product from 3-phenylpropan-1-ols has been shown to be formed by rearrangement of an Ar<sub>1</sub>-5 intermediate in which carbon migrates in preference to oxygen. Ar<sub>1</sub>-6 cyclisation of 3-phenoxypropan-1-ols is shown to occur less readily than the corresponding Ar<sub>1</sub>-5 cyclisation of 2-phenoxyethanols.

2-PHENOXYETHANOL (1), upon refluxing with lead(IV) acetate, has been reported to produce a small amount of 2,3-dihydro-1,4-benzodioxin (28; R = H) as the only intramolecular cyclisation product.<sup>1</sup> Similar cyclisations to form 2,3-dihydro-1,4-benzopyran have been found during lead(IV) acetate<sup>2</sup> and cerium(IV) ammonium nitrate<sup>3</sup> oxidations of 3-phenylpropan-1-ol. In none of these investigations was any evidence of Ar<sub>1</sub>-5 spiro-cyclisation reported. In contrast, intramolecular addi-

tion of radicals,<sup>4</sup> including alkoxy radicals,<sup>5</sup> to multiple bonds generally leads to preferential formation of five- rather than six-membered cyclic adducts, and both Ar<sub>1</sub>-5 and Ar<sub>2</sub>-6 products or intermediates have been reported during intramolecular cyclisations of alkyl,<sup>6</sup> acyl,<sup>7</sup> aryl,<sup>8</sup> amidyl,<sup>8a,9</sup> and acyloxy<sup>10</sup> radicals onto aromatic rings.

We recently reported<sup>11</sup> a novel synthesis of *p*-benzoquinone monoethylene acetal (21) from the photo-reaction of 2-(*p*-iodophenoxy)ethanol (12) in the presence of mercury(II) oxide-iodine. While this substrate underwent efficient Ar<sub>1</sub>-5 cyclisation to the virtual

<sup>1</sup> M. Lj. Mihailovic and M. Miloradovic, *Tetrahedron*, 1966, **22**, 723.

<sup>2</sup> M. Lj. Mihailovic, L. Zivkovic, Z. Maksimovic, D. Jeremic, Z. Cekovic, and R. Matic, *Tetrahedron*, 1967, **23**, 3095; S. Moon and P. R. Clifford, *J. Org. Chem.*, 1967, **32**, 4017.

<sup>3</sup> M. P. Doyle, L. J. Zuidema, and T. R. Bade, *J. Org. Chem.*, 1975, **40**, 1454.

<sup>4</sup> J. W. Wilt, 'Free Radicals,' ed. J. K. Kochi, Interscience, New York, 1973, vol. 1, p. 333; M. Julia, *Accounts Chem. Res.*, 1971, **4**, 386; C. Walling and A. Cioffari, *J. Amer. Chem. Soc.*, 1972, **94**, 6059; A. L. J. Beckwith, I. A. Blair, and G. Phillipou, *Tetrahedron Letters*, 1974, 2251; Y. L. Chow, R. A. Perry, and B. C. Burnaby, *Tetrahedron Letters*, 1972, 531; E. Flesia, A. Croatto, P. Tordo, and J. M. Surzur, *ibid.*, p. 535; M. E. Kuehne and D. A. Horne, *J. Org. Chem.*, 1975, **40**, 1287; J. M. Surzur, L. Stella, and P. Tordo, *Tetrahedron Letters*, 1970, 3107; J. M. Surzur, L. Stella, and R. Nouguier, *ibid.*, 1971, 903; J. M. Surzur and L. Stella, *Tetrahedron Letters*, 1974, 2191; Y. L. Chow, R. A. Perry, B. C. Menon, and S. C. Chen, *ibid.*, 1971, 1545; Y. L. Chow, R. A. Perry, and B. C. Menon, *ibid.*, p. 1549.

<sup>5</sup> R. D. Rieke and N. A. Moore, *J. Org. Chem.*, 1972, **37**, 413; B. C. Gilbert, H. A. H. Laue, and R. O. C. Norman, *J.C.S. Perkin II*, 1976, 1047; J. M. Surzur, M. P. Bertrand, and R. Nouguier, *Tetrahedron Letters*, 1969, 4197; P. Tordo, M. P. Bertrand, and J. M. Surzur, *ibid.*, 1970, 3399; J. M. Surzur, and R. Nouguier, *Bull. Soc. chim. France*, 1973, 2399.

<sup>6</sup> S. Winstein, R. Heck, S. Lapporte, and R. Baird *Experientia* 1956, **12**, 138; P. S. Dewar, A. R. Forrester, and R. H. Thomson, *J. Chem. Soc. (C)*, 1971, 3950; J. W. Wilt and C. F. Dockus, *J. Amer. Chem. Soc.*, 1970, **92**, 5813.

<sup>7</sup> W. H. Urry, D. J. Trecker, and H. D. Hartzler, *J. Org. Chem.*, 1964, **29**, 1663.

<sup>8</sup> (a) D. H. Hey, G. H. Jones, and M. J. Perkins, *J. Chem. Soc. (C)*, 1971, 116; S. A. Glover, A. Goosen, and H. A. H. Laue, *J.C.S. Perkin I*, 1973, 1647; (b) D. H. Hey, J. A. Leonard, C. W. Rees, and A. R. Todd, *J. Chem. Soc. (C)*, 1967, 1513; D. H. Hey, C. W. Rees, and A. R. Todd, *ibid.*, p. 1518; D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 113; B. S. Thyagarajan, N. Kharasch, H. B. Lewis, and W. Wolf, *Chem. Comm.*, 1967, 614.

<sup>9</sup> D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 118; A. R. Forrester, A. S. Ingram, and R. H. Thomson, *ibid.*, p. 2847; S. A. Glover and A. Goosen, *ibid.*, 1974, 2353.

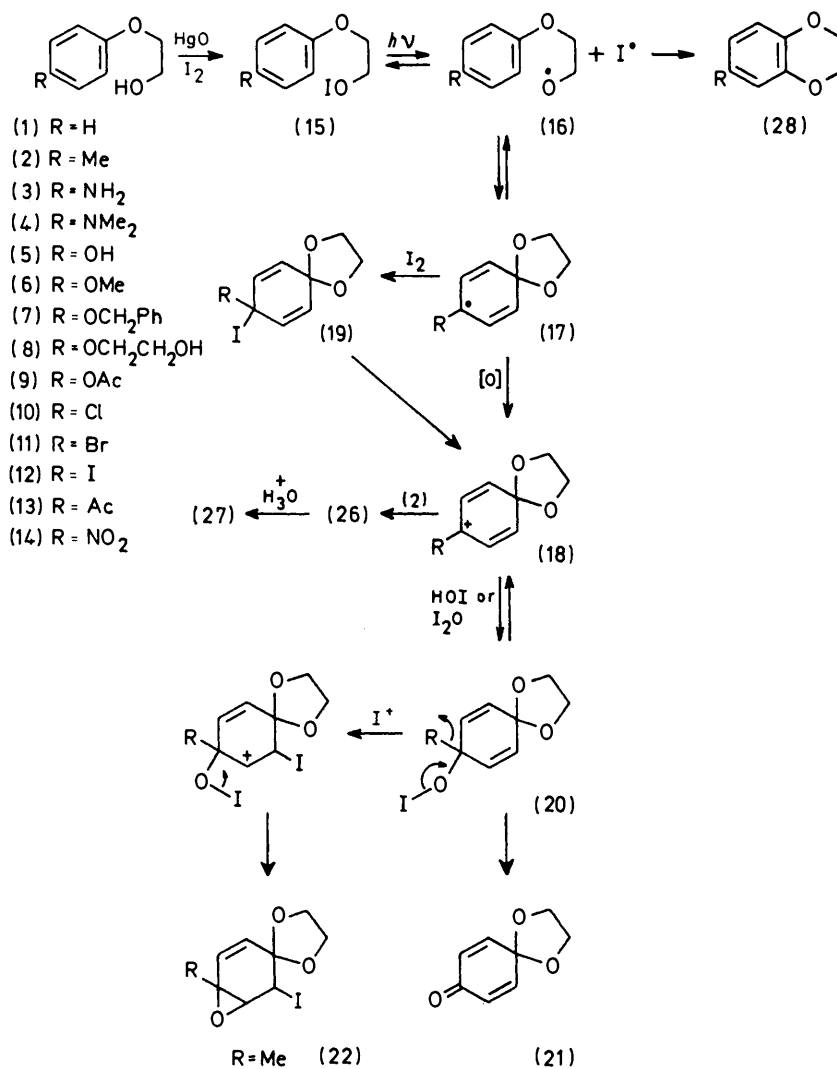
<sup>10</sup> J. W. Wilt and D. D. Oathoudt, *J. Org. Chem.*, 1958, **23**, 218; J. W. Wilt and J. L. Finnerty, *ibid.*, 1961, **26**, 2173; W. Rickatson and T. S. Stevens, *J. Chem. Soc.*, 1963, 3960; W. H. Starnes, jun., *J. Amer. Chem. Soc.*, 1963, **85**, 3708.

<sup>11</sup> A. Goosen and C. W. McClelland, *J.C.S. Chem. Comm.*, 1975, 665.

exclusion of Ar<sub>2</sub>-6 cyclisation, the *p*-chloro- and *p*-bromo-substituted substrates [(10) and (11)] reacted less efficiently and underwent more Ar<sub>2</sub>-6 than Ar<sub>1</sub>-5 cyclisation. In this paper, the effect of various aryl substituents on the reactions of 2-phenoxyethanols, 3-phenylpropan-1-ols, and 3-phenoxypropan-1-ols, with

to produce the monoacetal (21) probably takes place *via* a polar process involving the hypiodite (23).

It is unlikely that the substantial amounts of *p*-benzoquinone, formed from 2-(*p*-hydroxyphenoxy)ethanol (5), are due to hydrolysis of the acetal (21) since the acetal was recovered in high yield from the reactions



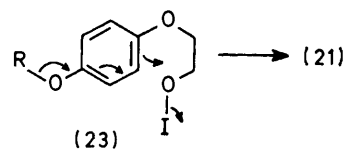
particular reference to Ar<sub>1</sub>-5 and Ar<sub>2</sub>-6 cyclisation products, is outlined.

#### RESULTS AND DISCUSSION

The products from *p*-substituted 2-phenoxyethanols [(1)–(14)] with mercury(II) oxide and iodine in the dark are given in Table I. When, with the exception of *p*-amino substituents, the ring was highly activated towards S<sub>E</sub> reactions, cyclisation occurred to give the monoacetal (21) as the major product. Less activated systems gave nuclear iodinated products and when a deactivating substituent was present the substrate was relatively inert.

The Ar<sub>1</sub>-5 cyclisation which occurs in the dark reaction

of other substrates. It is more likely that it is formed from the intermediate phenoxy-iodide (24). The inter-



mediate quinone (25), analogous to quinone methiodides<sup>12</sup> formed during the oxidation of phenols, could also contribute to the formation of the monoacetal (21).

<sup>12</sup> K. Schofield, R. S. Ward, and A. M. Choudhury, *J. Chem. Soc. (C)*, 1971, 2834.

The products from the photoreactions of 2-phenoxyethanol and its *p*-substituted derivatives in the presence

TABLE 1

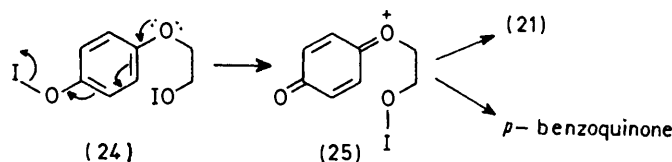
Dark reactions of *p*-substituted 2-phenoxyethanols with mercury(II) oxide-iodine

Substrate	Reaction time (h)	Starting material	Products [%]	
			(21)	Other
(1)	4	0	0	(12) [95]
(2)	6	Trace	0	2-(2-Iodo-4-methylphenoxyethanol) [87]
(3)	6	0	0	Polymer
(4)	6	0	0	Polymer
(5)	6	0	44	<i>p</i> -Benzoquinone [25]
(6)	6	Trace	80	
(7)	7.5		70	Benzyl alcohol [49] benzaldehyde [8] <i>p</i> -benzoquinone [6]
(8)	6		16	<i>p</i> -Benzoquinone bisethylene acetal [27] unreacted and iodinated alcohol [48]
(9)	6	90	4	
(10)	22	88	Trace	2-( <i>p</i> -Chlorophenoxy)ethyl formate [7], (28; R = Cl) [4]
(11)	22	85	Trace	2-( <i>p</i> -bromophenoxy)ethyl formate [6], (28; R = Br) [5]
(12)	6	100	0	
(13)	9	93	0	
(14)	6	100	0	

of mercury(II) oxide and iodine are summarised in Table 2. Only in the case of the *p*-chloro- and *p*-bromo-substituted 2-phenoxyethanols [(10) and (11)] did more

is concluded that in these cases at least, the spirodienone is formed *via* an Ar<sub>1</sub>-5 cyclisation of the alkoxy radical (16).

The monoacetal (21) was present in the reaction mixture prior to work-up and is thus formed from the



carbenium ion (18), derived from either the radical (17) by oxidation, or the iodide (19). The carbonyl oxygen in the monoacetal (21) is not derived from water or oxygen since the yield of the spirodienone was unaffected when the reaction with 2-(*p*-iodophenoxy)ethanol (12) was carried out in the presence of anhydrous calcium sulphate, and insufficient oxygen was present to account for its high yield. Isolation of the dienyl ethers (26) and (27) and the epoxide (22; R = Me) from the reaction of 2-(*p*-methylphenoxy)ethanol (2) affords further evidence for the intermediacy of the carbenium ion (18). As expected the presence of good leaving groups mitigated against the formation of the dienyl ethers and they could thus not be isolated from the 2-phenoxyethanols [(9)–(12)].

2-[*p*-(2-Hydroxyethoxy)phenoxy]ethanol (8) gave a good yield of the spirodienone (21) while the amount of bisacetal was about half that formed in the dark re-

TABLE 2

Photoreactions of *p*-substituted 2-phenoxyethanols with mercury(II) oxide-iodine

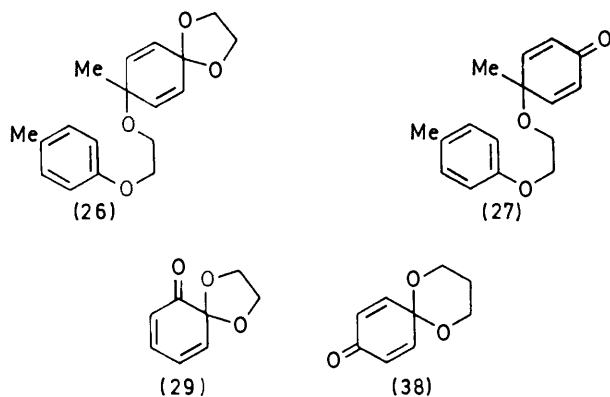
Substrate	Reaction time (h)	Starting material	Products [%]			
			(21)	(28)	Starting material formate	Other
(1)	6	0	43	R = I, 8 R = H, 14	0	(6) [13]
(2)	0.5	41	2	18	0	(26) [7], (27) [5], (22) [5]
(3)	6	0	0	0	0	Polymer
(4)	6	0	0	0	0	Polymer
(5)	5	0	54	0	0	<i>p</i> -Benzoquinone [22]
(6)	6	0	85	0	0	
(8)	6	0	80	0	0	<i>p</i> -Benzoquinone bisethylene acetal [15]
(9)	6	0	60	0	0	<i>p</i> -Benzoquinone [8], 2-( <i>p</i> -acetoxyphenoxy)ethyl acetate [25]
(10)	6	36	19	28	6	
(11)	6	38	20	26	6	
(12)	0.5	12	77	6		
	6	5	88	5	1	
(12) + CaSO <sub>4</sub>	6.75	Trace	81	5		
(13)	6	72	0	8	8	
(14)	6.5	95	0	0	0	

Ar<sub>2</sub>-6 than Ar<sub>1</sub>-5 cyclisation occur. The reaction mixtures from those substrates with *p*-oxy-substituents [(5)–(9)] were devoid of products arising from Ar<sub>2</sub>-6 cyclisation.

In contrast to the dark reactions, the photoreactions of 2-phenoxyethanols containing *p*-acetoxy- (9), *p*-chloro- (10), *p*-bromo- (11) and *p*-iodo-groups (12) all produced significant amounts of the monoacetal (21). Hence it

action. If the intermediate spirodienyl radical were to be oxidised to the carbenium ion in this substrate a much higher yield of bisacetal would be expected on the basis of the intramolecular reaction predominating over the intermolecular trapping by oxygen species. Hence it is suggested that in this substrate the intermediate spirodienyl radical (17) undergoes β-fragmentation to produce the spirodienone (21).

In addition to a good yield of spirodienone (21), 2-(*p*-acetoxyphenoxy)ethanol (9) afforded some acetylated starting material. The stability of the starting alcohol (9) towards the reagent in the dark, and also in the presence of acetic acid, shows that the formation of the



diacetate is due to neither a transesterification process nor a Lewis-acid-catalysed esterification with acetic acid. Hence it is proposed that it is formed from the reaction of the alcohol (9) with acetyl iodide which is generated from the spirodienyl intermediate (17) or (18).

No 2,3-dihydro-1,4-benzodioxins (28) were formed from any of the *p*-oxy-substrates [(5)–(9)] indicating that Ar<sub>1</sub>-5 cyclisation is much faster than Ar<sub>2</sub>-6, and the resulting spirodienyl radical (17) or carbenium ion (18) reacts much more rapidly than either is able to rearrange to an Ar<sub>2</sub>-6 species.

The small quantities of formate esters isolated are most probably formed *via* a Lewis-acid (*e.g.* I<sub>2</sub>O) catalysed formylation of the starting alcohol by formaldehyde<sup>13</sup> liberated by  $\beta$ -cleavage of the alkoxy-radical (16). The other fragment could not be isolated. The low yield of formate esters relative to intramolecular cyclisation products in all the substrates investigated indicates that, in contrast to hydroxy- and keto-groups,<sup>14</sup> the phenoxy substituent inhibits  $\beta$ -cleavage.

In contrast to 2-(*p*-methoxyphenoxy)ethanol (6) which, in the dark underwent exclusive Ar<sub>1</sub>-5 cyclisation, the *ortho*-isomer afforded a complex mixture which consisted mainly of aryl-iodinated starting alcohol. An n.m.r. spectrum of the crude product showed that the methoxy group was retained, which indicates that a polar Ar<sub>1</sub>-5 cyclisation to the linear spirodienone (29) does not occur readily. The photoreaction gave an even more complex mixture of products which contained no significant dienone i.r. absorptions.

2-(*o*-Iodophenoxy)ethanol with mercury(II) oxide and iodine was relatively stable in the dark, but when irradiated gave 2-iodo-1,4-benzoquinone 1-ethylene acetal and a small amount of 5-iodo-2,3-dihydro-1,4-benzodioxin.

In an effort to induce Ar<sub>2</sub>-6 cyclisation, the dark and light reactions of 2-(*m*-methoxyphenoxy)ethanol and 2-(*m*-iodophenoxy)ethanol were investigated. In the dark the methoxylated substrate was quantitatively converted into 2-(2,4-di-iodo-5-methoxyphenoxy)ethanol whereas the iodo-substituted substrate gave an intractable mixture. The mixture from the photoreaction of the methoxylated substrate contained di-iodinated starting alcohol and a small amount of the Ar<sub>2</sub>-6 cyclisation product. In contrast the irradiated reaction mixture from 2-(*m*-iodophenoxy)ethanol contained more of the Ar<sub>2</sub>-6 cyclisation products (*i.e.* equal amounts of the 5- and 6-iodo-2,3-dihydro-1,4-benzodioxins) than 3-iodo-1,4-benzoquinone 1-ethylene acetal. The yield of the Ar<sub>2</sub>-6 cyclisation products was increased when the irradiation was carried out at a higher temperature. These results show that the *m*-iodo-substituent activates the *ortho*-position leading to a considerably larger proportion of Ar<sub>2</sub>-6 cyclisation.

In order to assess the role played by the ether oxygen in the cyclisation process, *p*-iodo- and *p*-methoxy-3-phenylpropan-1-ol were treated with mercury(II) oxide and iodine. The mixture from the photoreaction of 3-(*p*-iodophenyl)propan-1-ol (30) contained 1-oxaspiro-[4.5]deca-6,9-dien-8-one (31) (5%), Ar<sub>2</sub>-6 cyclisation products [(32)–(34)] (54%), and oxidation (37) (8%), fragmentation (35) (13%), and formylation (36) (5%) products. 6,8-Di-iodochroman (34) was shown to be formed from the mono-iodochroman (32) with mercury(II) oxide and iodine in the dark. Irradiation of the mono-iodochroman (32) in the presence of mercury(II) oxide and iodine gave the chromanone (33) presumably *via* a benzylic abstraction followed by oxidation and reaction with an oxygen species. Since the chromanone (33) was present in the reaction mixtures prior to work-up, its formation *via* hydrolysis of 4,4,6-tri-iodochroman may be discounted. The structures of the chromans (32) and (34) as well as the chromanone (33) exclude the possibility of direct Ar<sub>2</sub>-6 cyclisation and hence afford evidence for a spirodienyl intermediate. These results are in accord with dienone-phenol rearrangements where alkyl groups have been found to migrate in preference to an ether oxygen.<sup>15</sup>

In comparison with the rapid high-yield conversion of 2-(*p*-methoxyphenoxy)ethanol in the dark, 3-(*p*-methoxyphenyl)propan-1-ol underwent mainly aryl iodination with Ar<sub>1</sub>-5 cyclisation occurring to a minor extent (9%). The photoreaction afforded the spirodienone (31) in synthetically useful yield (56%) and a mixture of minor products with no evidence of any significant amount of Ar<sub>2</sub>-6 cyclisation.

The effect of ring size on the formation of the spiro system was ascertained by irradiating 3-(*p*-iodophenoxy)propan-1-ol with mercury(II) oxide and iodine as before. The reaction mixture contained mainly starting material

<sup>13</sup> A. Goosen and C. W. McClelland, *J.C.S. Perkin I*, 1976, 383.

<sup>14</sup> A. Goosen and H. A. H. Laue, *J. Chem. Soc. (B)*, 1969, 995; *J. Chem. Soc. (C)*, 1969, 388; *J. S. African Chem. Inst.*, 1971, 24, 126.

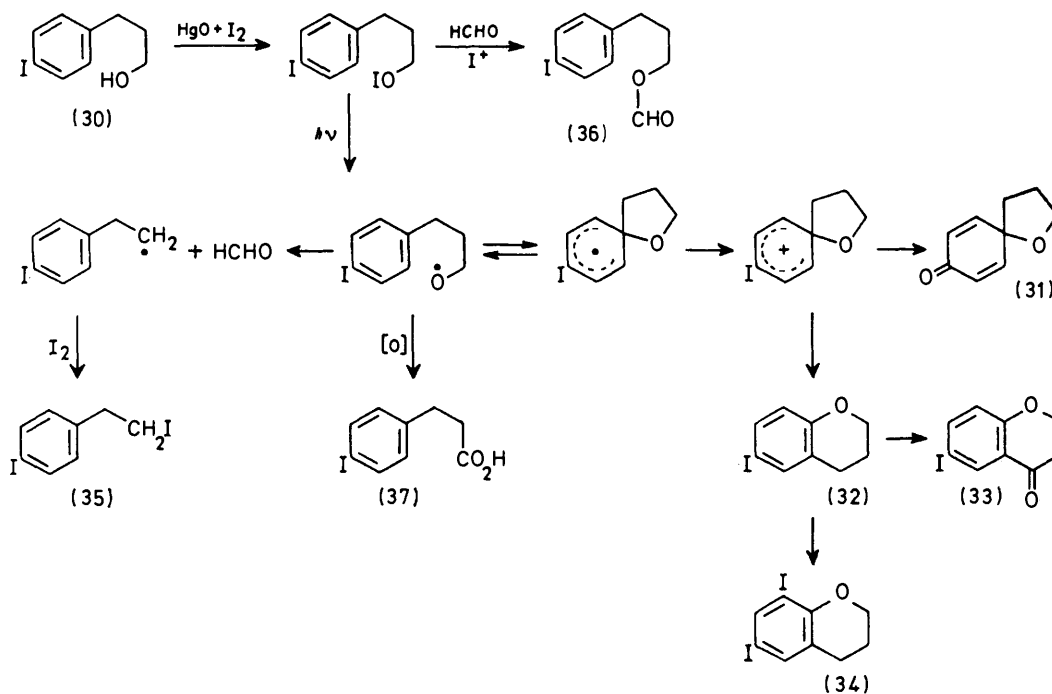
<sup>15</sup> S. Goodwin and B. Witkop, *J. Amer. Chem. Soc.*, 1957, 79, 179; E. Hecker and E. Meyer, *Chem. Ber.*, 1964, 97, 1926; A. M. Choudhury, K. Schofield, and R. S. Ward, *J. Chem. Soc. (C)*, 1970, 2543.

with a small amount of 1,5-dioxaspiro[5.5]undeca-7,10-dien-9-one (38). No cyclisation products were obtained when the reaction was repeated at 49–50 °C. In the dark 3-(*p*-methoxyphenoxy)propan-1-ol reacted with mercury(II) oxide and iodine to produce mainly iodinated alcohol and a small amount of the dienone (38). However when the reaction mixture was irradiated the dienone (38) was the major product.

These results are in accordance with previous evidence<sup>16</sup> that Ar<sub>1</sub>-6 cyclisations do not occur as readily

analysed (n.m.r., i.r.) and subsequently chromatographed. The results are given in Tables 1 and 2. [Only those experiments which gave products which were not characterised (i.r., n.m.r., and g.l.c.) by comparison with authentic specimens are reported.]

(a) *Dark reactions.* 2-(*p*-Methylphenoxy)ethanol (2). Chromatography (silica with chloroform) afforded 2-(2-iodo-4-methylphenoxy)ethanol (0.30 g),  $\delta(\text{CDCl}_3)$  2.21 (3 H, s), 2.82 (1 H, s, OH), 4.00 (4 H, m), 6.70 [1 H, d,  $J(\text{BA})$  8.5 Hz], 7.08 [1 H, dd,  $J(\text{AB})$  8.5,  $J(\text{AX})$  2 Hz], and 7.59 [1 H, d,  $J(\text{XA})$  2 Hz];  $\nu_{\text{max.}}$  (CHCl<sub>3</sub>) 3 600, 3 460,



as the Ar<sub>1</sub>-5 process, and further that in most cases Ar<sub>1</sub>-5 cyclisation occurs more readily than Ar<sub>2</sub>-6.

#### EXPERIMENTAL

G.l.c. analyses were carried out with a Becker Packard 420 chromatograph fitted with an Autolab 6300 digital integrator. I.r. spectra were run on Unicam SP 200G and SP 1 000 spectrometers. 60 MHz <sup>1</sup>H N.m.r. spectra were recorded on a Perkin-Elmer R12A spectrometer with Me<sub>4</sub>Si as internal standard. Carbon-13 n.m.r. and mass spectra were recorded on Varian CFT-20 and A.E.I. M59 spectrometers, respectively, at the N.C.R.L./C.S.I.R. laboratories in Pretoria.

*Reaction of 2-Phenoxyethanol and its Aryl-substituted Derivatives with Mercury(II) Oxide-Iodine. General Procedure.*—A mixture of the appropriate 2-phenoxyethanol (1.75 mmol), iodine (2.60 g, 10 mmol), and red mercury(II) oxide (1.10 g, 5 mmol) in benzene (20 ml) was stirred at room temperature either in the dark or under irradiation (1 000 W tungsten lamp). After 6 h the reaction was quenched (aqueous sodium thiosulphate) and the product dried (sodium sulphate) and concentrated. The residue was

1 290, 1 265, 1 083, and 1 057 cm<sup>-1</sup> (Found: C, 39.0; H, 4.0%; M<sup>+</sup> 278. C<sub>9</sub>H<sub>11</sub>IO<sub>2</sub> requires C, 38.9; H, 4.0%; M<sup>+</sup> 278).

2-(*p*-Methoxyphenoxy)ethanol (6). This gave a trace of starting material and mainly *p*-benzoquinone monoethylene acetal (21) which was purified by sublimation from the crude product, followed by recrystallisation from benzene–light petroleum; m.p. 52–53 °C (lit.<sup>17</sup> m.p. 52–53 °C);  $\delta(\text{CDCl}_3)$  4.10 (4 H, s) 6.12 (2 H, d,  $J$  10 Hz), and 6.61 (2 H, d,  $J$  10 Hz);  $\nu_{\text{max.}}$  (CHCl<sub>3</sub>) 1 697, 1 681, 1 641, and 1 120 cm<sup>-1</sup> (identical with reported data<sup>17</sup>), M<sup>+</sup> 152.

2-[*p*-(2-Hydroxyethoxy)phenoxy]ethanol (8). When the residue was diluted with chloroform, starting material precipitated out and was filtered off (m.p. 103–105 °C). Analysis (n.m.r., i.r.) of the filtrate revealed *p*-benzoquinone monoethylene acetal (21), *p*-benzoquinone bisethylene acetal [identified<sup>17</sup> on the basis of two singlets at  $\delta(\text{CDCl}_3)$  4.00 and 5.90 with an integral ratio of 2 : 1], and a number of iodinated alcoholic compounds.

2-(*m*-Methoxyphenoxy)ethanol. This gave a solid residue (0.77 g) which crystallised from benzene as 2-(2,4-di-iodo-

<sup>16</sup> M. R. Crampton and M. J. Willison, *J.C.S. Perkin II*, 1976, 155; J. W. Wilt and J. A. Lundquist, *J. Org. Chem.*, 1964, 29 921.

<sup>17</sup> J. E. Heller, A. S. Dreiding, B. R. O'Connor, H. E. Simmons, G. L. Buchanan, R. A. Raphael, and R. Taylor, *Helv. Chim. Acta*, 1973, 56 272.

5-methoxyphenoxy)ethanol, m.p. 125–127 °C;  $\delta(\text{CDCl}_3)$  2.45 (OH, broad), 3.83 (3 H, s), 4.05 (4 H, m), 6.38 (1 H, s), and 8.02 (1 H, s) (Found: C, 26.0; H, 2.45%;  $M^+$  420.  $\text{C}_9\text{H}_{10}\text{I}_2\text{O}_3$  requires C, 25.7; H, 2.4%;  $M$  420).

2-(*m*-Iodophenoxy)ethanol. This gave a mixture of starting material and one other component which could not be separated by chromatography (silica with benzene), but was suspected to be 2-(3,4-di-iodophenoxy)ethanol on the basis of its n.m.r. spectrum;  $\delta(\text{CDCl}_3)$  6.55 [1 H, dd,  $J(\text{AB})$  8.8,  $J(\text{AX})$  2.9 Hz], 1.37 [1 H, d,  $J(\text{XA})$  2.9 Hz], and 7.60 [1 H, d,  $J(\text{BA})$  8.8 Hz].

3-(*p*-Methoxyphenyl)propan-1-ol. This gave after chromatography (silica with chloroform) 1-oxaspiro[4.5]deca-6,9-dien-8-one (31), (0.052 g);  $\delta(\text{CDCl}_3)$  2.08 (4 H, m), 4.06 (2 H, t), 6.10 (2 H, d,  $J$  10 Hz), and 6.82 (2 H, d,  $J$  10 Hz),  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 1 698, 1 679, and 1 638  $\text{cm}^{-1}$  (Found:  $M^+$ , 150. Calc. for  $\text{C}_9\text{H}_{10}\text{O}_2$ :  $M$ , 150), and 3-(3-iodo-4-methoxyphenoxy)propan-1-ol (0.126 g),  $\delta(\text{CDCl}_3)$  1.81 (2 H, quintet), 2.20 (OH, s), 2.60 (2 H, t), 3.62 (2 H, t), 3.81 (3 H, s), 6.71 [1 H, d,  $J(\text{BA})$  8.5 Hz], 7.12 (1 H, dd,  $J(\text{AB})$  8.5,  $J(\text{AX})$  2 Hz], and 7.61 (1 H, d,  $J(\text{XA})$  2 Hz) (Found:  $M^+$ , 292. Calc. for  $\text{C}_{10}\text{H}_{13}\text{IO}_2$ :  $M$ , 292).

(b) Photoreactions. 2-(*p*-Methylphenoxy)ethanol (2). This gave after chromatography (alumina with benzene–light petroleum, benzene–chloroform) starting alcohol; *p*-benzoquinone monoethylene acetal (21), identical with an authentic specimen (n.m.r., i.r.); 6-methyl-2,3-dihydro-1,4-benzodioxin (28; R = Me),  $\delta(\text{CDCl}_3)$  2.24 (3 H, s), 4.20 (4 H, s), and 6.70 (3 H, m) (Found:  $M^+$ , 150. Calc. for  $\text{C}_9\text{H}_{10}\text{O}_2$ :  $M$ , 150); 8-methyl-8-[2-(*p*-methylphenoxy)ethoxy]-1,4-dioxaspiro[4.5]deca-6,9-diene (26), m.p. 75.5–77 °C (light petroleum),  $\delta(\text{CDCl}_3)$  1.33 (3 H, s, CMe), 2.23 (3 H, s, ArMe), 3.54 (2 H, t, MeC–O–CH<sub>2</sub>), 3.95 (4 H, s, O–CH<sub>2</sub>–CH<sub>2</sub>–O), 4.06 (2 H, t, CH<sub>2</sub>OAr), 5.83 (4 H, s, CH=CH–C–CH=CH–C), 6.71 (2 H, d, *o*-MeArH), and 7.00 (2 H, d, *m*-MeArH),  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 1 678 and 1 617  $\text{cm}^{-1}$  (Found:  $M^+$ , 302. Calc. for  $\text{C}_{18}\text{H}_{22}\text{O}_4$ :  $M$ , 302); 4-methyl-4-[2-(*p*-methylphenoxy)ethoxy]cyclohexa-2,5-dienone (27), m.p. 75–76 °C (light petroleum),  $\delta(\text{CDCl}_3)$  1.46 (3 H, s, CMe), 2.27 (3 H, s, ArMe), 3.62 (2 H, t, MeC–O–CH<sub>2</sub>), 4.01 (2 H, t, CH<sub>2</sub>OAr), 6.28 (2 H, d,  $J$  9.3 Hz, CO–CH=C), and 6.63–7.20 (6 H, m, CO–C=CH and ArH),  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 1 679, 1 634, and 1 099  $\text{cm}^{-1}$  (Found C, 74.25; H, 7.1%;  $M^+$ , 258;  $\text{C}_{16}\text{H}_{18}\text{O}_3$  requires C, 74.4; H, 7.0%;  $M$ , 258); and the relatively unstable 6-iodo-7,8-epoxy-8-methyl-1,4-dioxaspiro[4.5]dec-9-ene (22), m.p. 93–95 °C (light petroleum)  $\delta(\text{CDCl}_3)$  1.54 (3 H, s, Me), 3.76 (1 H, d,  $J$  2.5 Hz, CHI), 4.00 (4 H, s, OCH<sub>2</sub>CH<sub>2</sub>O), 4.53 (1 H, m, CHI), 5.70 [1 H, dd,  $J(\text{AB})$  10,  $J(\text{AX})$  1 Hz, C=CHCMe]; decoupled <sup>13</sup>C n.m.r. (intensity, carbon) 132.56 (27, C-10), 129.78 (28, C-9), 65.76 (26, C-2 or C-3), 65.18 (29, C-3 or C-2), 62.40 (29, C-7), 29.40 (24, Me), and 20.46 (28, C-6) p.p.m. (no quaternary carbons were observed owing to low concentrations) (Found:  $M^+$ , 294. Calc. for  $\text{C}_9\text{H}_{11}\text{IO}_3$ ;  $M$ , 294).

2-(*p*-Chlorophenoxy)ethanol (10). This gave after chromatography (silica with light petroleum, benzene) starting alcohol, *p*-benzoquinone monoethylene acetal (21) (identical with an authentic specimen), 6-chloro-2,3-dihydro-1,4-benzodioxin (28; R = Cl),  $\delta(\text{CCl}_4)$  4.14 (4 H, s), and 6.65–6.85 (3 H, m),  $\nu_{\text{max.}}$  ( $\text{CCl}_4$ ) 1 306, 1 294, 1 253, 1 197, 1 120, and 1 071  $\text{cm}^{-1}$  (Found:  $M^+$ , 170/172.  $\text{C}_8\text{H}_7\text{ClO}_2$  requires  $M$ , 170/172), and 2-(*p*-chlorophenoxy)ethyl formate, m.p. 55 °C (light petroleum),  $\delta(\text{CDCl}_3)$  4.12 (2 H, t), 4.51 (2 H, t), 6.81 (2 H, d), 7.25 (2 H, d), and 8.11 (1 H, s),  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ )

1 729 and 1 178  $\text{cm}^{-1}$  (Found: C, 53.9; H, 4.5%;  $M^+$  200/202.  $\text{C}_9\text{H}_9\text{ClO}_3$  requires C, 53.9; H, 4.5%;  $M$  200/202).

2-(*p*-Bromophenoxy)ethanol (11). This gave after chromatography (silica with light petroleum, benzene) starting alcohol, *p*-benzoquinone monoethylene acetal (21) (identical with an authentic specimen), 6-bromo-2,3-dihydro-1,4-benzodioxin (28; R = Br),  $\delta(\text{CDCl}_3)$  4.22 (4 H, s), 6.75–7.10 (3 H, m),  $\nu_{\text{max.}}$  ( $\text{CCl}_4$ ) 1 303, 1 290, 1 253, 1 197, 1 125, and 1 069  $\text{cm}^{-1}$  (Found C, 45.2; H, 3.2%;  $M^+$ , 214/216.  $\text{C}_8\text{H}_7\text{BrO}_2$  requires C, 44.7; H, 3.3%;  $M$ , 214/216), and 2-(*p*-bromophenoxy)ethyl formate, m.p. 72.5–73.5 °C (light petroleum),  $\delta(\text{CDCl}_3)$  4.20 (2 H, t), 4.50 (2 H, t), 6.83 (2 H, d), 7.43 (2 H, d), and 8.15 (1 H, s),  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 1 730 and 1 179  $\text{cm}^{-1}$  (Found: C, 44.1; H, 3.6%;  $M^+$  244/246.  $\text{C}_9\text{H}_9\text{BrO}_3$  requires C, 44.1; H, 3.7%;  $M$  244/246).

2-(*p*-Iodophenoxy)ethanol (12). This gave after chromatography (silica with benzene–light petroleum 7 : 3) starting alcohol, *p*-benzoquinone monoethylene acetal (21) (identical with an authentic specimen), 6-iodo-2,3-dihydro-1,4-benzodioxin (28; R = I),  $\delta(\text{CDCl}_3)$  4.18 (4 H, s), 6.57 (1 H, d), 7.09 (1 H, d), and 7.16 (1 H, s),  $\nu_{\text{max.}}$  ( $\text{CCl}_4$ ) 1 301, 1 289, 1 253, 1 197, 1 129, and 1 061  $\text{cm}^{-1}$  (Found:  $M^+$  262. Calc. for  $\text{C}_8\text{H}_7\text{IO}_2$ :  $M$ , 262), and 2-(*p*-iodophenoxy)ethyl formate, m.p. 89–90 °C (light petroleum),  $\delta(\text{CDCl}_3)$  4.11 (2 H, t), 4.48 (2 H, t), 6.58 (2 H, d), 7.52 (2 H, d), and 8.05 (1 H, s),  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 1 728 and 1 180  $\text{cm}^{-1}$  (Found: C, 37.3; H, 3.1%;  $M^+$ , 292.  $\text{C}_9\text{H}_9\text{IO}_3$  requires C, 37.0; H, 3.1%;  $M$ , 292). The reaction was repeated in the presence of anhydrous calcium sulphate (50 mmol) and the crude mixture was shown (n.m.r., i.r., t.l.c.) to be almost identical with that obtained in the previous case.

2-(*m*-methoxyphenoxy)ethanol. Analysis (n.m.r., t.l.c.) revealed a complex mixture (0.61 g) from which only 2-(2,4-di-iodo-5-methoxyphenoxy)ethanol (0.16 g) and the 5,7- or 5,8-di-iodo-isomer of 6-methoxy-2,3-dihydro-1,4-benzodioxin (0.01 g),  $\delta(\text{CDCl}_3)$  3.82 (3 H, s), 4.31 (4 H, s), and 7.24 (1 H, s),  $\nu_{\text{max.}}$  ( $\text{CCl}_4$ ) 1 289, 1 264, 1 229, 1 108, and 1 070  $\text{cm}^{-1}$  (Found:  $M^+$ , 418. Calc. for  $\text{C}_9\text{H}_8\text{I}_2\text{O}_3$ : 418), could be separated by chromatography (silica with benzene).

2-(*m*-Iodophenoxy)ethanol. This gave after chromatography (silica with light petroleum, benzene) starting alcohol (0.120 g), 5-iodo-2,3-dihydro-4,5-benzodioxin (0.032 g) and 6-iodo-2,3-dihydro-4,5-benzodioxin (28; R = I) (0.070 g) (identical with authentic specimens), 3-iodo-1,4-benzoquinone 1-ethylene acetal (0.030 g),  $\delta(\text{CDCl}_3)$  4.12 (4 H, s), 6.28 [1 H, d,  $J(\text{BA})$  10 Hz], 6.67 [1 H, dd,  $J(\text{AB})$  10,  $J(\text{AX})$  2.6 Hz], and 7.39 [1 H, d,  $J(\text{XA})$  2.6 Hz],  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 1 682, 1 650, 1 605, and 1 149  $\text{cm}^{-1}$  (Found:  $M^+$ , 278. Calc. for  $\text{C}_8\text{H}_7\text{IO}_3$ :  $M$ , 278), and 2-(*m*-iodophenoxy)ethyl formate (0.020 g)  $\delta(\text{CDCl}_3)$  4.15 (2 H, t), 4.51 (2 H, t), 6.92 (2 H, m), 7.27 (2 H, s), and 8.10 (1 H, s),  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 1 730 and 1 180  $\text{cm}^{-1}$ .

2-(*o*-Iodophenoxy)ethanol. This gave after chromatography (silica with benzene–chloroform 1 : 1) 5-iodo-2,3-dihydro-1,4-benzodioxin (0.020 g),  $\delta(\text{CDCl}_3)$  4.26 (4 H, m), 6.54 [1 H, t,  $J(\text{AB})$  8.5 Hz], 6.83 [1 H, dd,  $J(\text{BA})$  8.5,  $J(\text{XA})$  2 Hz], and 7.27 [1 H, dd,  $J(\text{AB})$  8.5,  $J(\text{AX})$  2 Hz],  $\nu_{\text{max.}}$  ( $\text{CCl}_4$ ) 1 302, 1 290, 1 260, 1 249, 1 230, 1 140, and 1 089  $\text{cm}^{-1}$  (Found:  $M^+$ , 262. Calc. for  $\text{C}_8\text{H}_7\text{IO}_2$ :  $M$ , 262), and 2-iodo-1,4-benzoquinone 1-ethylene acetal (0.022 g),  $\delta(\text{CDCl}_3)$  3.87–4.28 (2 H, m), 4.28–4.69 (2 H, m), 6.17 [1 H, dd,  $J(\text{AB})$  10,  $J(\text{AX})$  2 Hz], 6.82 [1 H, d,  $J(\text{BA})$  10 Hz], and 6.99 [1 H, d,  $J(\text{XA})$  2 Hz],  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 1 679, 1 638, 1 602, and 1 151  $\text{cm}^{-1}$  (Found: C, 35.1; H, 2.4%;  $M^+$ , 278.  $\text{C}_8\text{H}_7\text{IO}_3$  requires C, 35.6; H, 2.5%;  $M$ , 278).

3-(*p*-Iodophenyl)propan-1-ol (30). This gave after chromatography (silica with light petroleum, benzene, chloroform) 2-(*p*-iodophenyl)ethyl iodide (35) (13%),  $\delta(\text{CDCl}_3)$  3.05—3.40 (4 H, m), 6.95 (2 H, d), and 7.68 (2 H, d), identical with an authentic specimen (g.l.c.); 6,8-di-iodochroman (34) (15%), m.p. 80—81.5 °C (light petroleum),  $\delta(\text{CDCl}_3)$  1.97 (2 H, quintet), 2.73 (2 H, t), 4.26 (2 H, t), 7.33 (1 H, d,  $J$  1.3 Hz), and 7.87 (1 H, d,  $J$  1.3 Hz),  $\nu_{\text{max.}}$  ( $\text{CCl}_4$ ) 1 285, 1 244, 1 158, and 1 058  $\text{cm}^{-1}$  (Found:  $M^+$ , 385. Calc. for  $\text{C}_9\text{H}_8\text{I}_2\text{O}$ :  $M$ , 385); 6-iodochroman (32) (21%),  $\delta(\text{CDCl}_3)$  1.92 (2 H, quintet), 2.70 (2 H, t), 4.10 (2 H, t), 6.48 (1 H, d), and 7.20—7.50 (2 H, m), identical with an authentic specimen (g.l.c.); 3-(*p*-iodophenyl)propyl formate (36) (5%),  $\delta(\text{CDCl}_3)$  2.02 (2 H, quintet), 2.68 (2 H, t), 4.15 (2 H, t), 6.96 (2 H, d), 7.76 (2 H, d), and 8.07 (1 H, s) (Found:  $M^+$ , 290. Calc. for  $\text{C}_{10}\text{H}_{11}\text{IO}_2$ :  $M$ , 290), identical with an authentic specimen (g.l.c.); 6-iodochroman-4-one (33) (18%), m.p. 90—91 °C (light petroleum),  $\delta(\text{CDCl}_3)$  2.81 (2 H, t), 4.57 (2 H, t), 6.80 [1 H, d,  $J(\text{BA})$  8.5 Hz], 7.77 [1 H, dd,  $J(\text{AB})$  8.5,  $J(\text{AX})$  2 Hz], and 8.22 [1 H, d,  $J(\text{XA})$  2 Hz],  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 1 696 and 1 281  $\text{cm}^{-1}$  (Found: C, 39.7; H, 2.6%;  $M$ , 274. Calc. for  $\text{C}_9\text{H}_7\text{IO}_2$ : C, 39.4; H, 2.6%;  $M$ , 274), identical with an authentic specimen; 1-oxa-spiro[4.5]deca-6,9-dien-8-one (31) (5%),  $\delta(\text{CDCl}_3)$  2.08 (4 H, m), 4.06 (2 H, t), 6.10 (2 H, d,  $J$  10 Hz), and 6.82 (2 H, d,  $J$  10 Hz),  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 1 698, 1 679, and 1 638  $\text{cm}^{-1}$  (Found:  $M^+$ , 150. Calc. for  $\text{C}_9\text{H}_{10}\text{O}_2$ :  $M$ , 150), identical (n.m.r., i.r., and t.l.c.) with an authentic specimen; 3-(*p*-iodophenyl)propanoic acid (37) (8%), m.p. 140—142 °C (light petroleum) (lit.<sup>18</sup> m.p. 140—141 °C),  $\delta(\text{CDCl}_3)$  2.66 (2 H, t), 2.90 (2 H, t), 6.98 (2 H, d), and 7.65 (2 H, d),  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 3 600—2 300 (broad), 1 718, and 1 406  $\text{cm}^{-1}$  (Found:  $M^+$ , 276. Calc. for  $\text{C}_9\text{H}_9\text{IO}_2$ :  $M$ , 276), and starting alcohol (30) (16%).

3-(*p*-Methoxyphenoxy)propan-1-ol. This gave after chromatography (silica with benzene-chloroform 1:1) *p*-benzoquinone, identical with an authentic specimen (n.m.r., i.r., and m.p.), and 1,5-dioxaspiro[5.5]undeca-7,10-dien-9-one (38) (56%), m.p. 74—75 °C (benzene-light petroleum),  $\delta(\text{CDCl}_3)$  1.88 (2 H, quintet), 4.07 (4 H, t), 6.15 (2 H, d,  $J$  10.5 Hz), and 7.11 (2 H, d,  $J$  10.5 Hz),  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 1 690, 1 678sh, 1 644, 1 121, and 1 000  $\text{cm}^{-1}$  (Found: C, 64.8; H, 6.0%;  $M^+$ , 166.  $\text{C}_9\text{H}_{10}\text{O}_3$  requires C, 65.1; H, 6.1%;  $M$ , 166).

3-(*p*-Iodophenoxy)propan-1-ol. (i) Analysis (n.m.r., i.r., and t.l.c.) revealed mainly starting alcohol (80%) and 1,5-dioxaspiro[5.5]undeca-7,10-dien-9-one (38) (6%) by comparison with an authentic specimen. (ii) The reaction was repeated at 49—50 °C. Chromatography of the reaction

mixture (silica with light petroleum, benzene, chloroform) afforded 2-(*p*-iodophenoxy)ethyl iodide (16%), m.p. 48 °C (light petroleum),  $\delta(\text{CDCl}_3)$  3.37 (2 H, t), 4.20 (2 H, t), 6.65 (2 H, d), and 7.55 (2 H, d) (Found:  $M^+$ , 374. Calc. for  $\text{C}_8\text{H}_8\text{I}_2\text{O}$ :  $M$ , 374); bis-1,3-(*p*-iodophenoxy)propane (6%), m.p. 158—159 °C (benzene-light petroleum),  $\delta(\text{CDCl}_3)$  2.21 (2 H, quintet), 4.19 (4 H, t), 6.62 (4 H, d), and 7.50 (4 H, d),  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 1 256  $\text{cm}^{-1}$  (Found:  $M^+$ , 480. Calc. for  $\text{C}_{15}\text{H}_{14}\text{I}_2\text{O}_2$ :  $M$ , 480); 3-(*p*-iodophenoxy)propyl 3-(*p*-iodophenoxy)propanoate (15%), m.p. 86—87.5 °C (benzene-light petroleum),  $\delta(\text{CDCl}_3)$  2.10 (2 H, t), 2.76 (2 H, t), 3.85—4.40 (6 H, m), 6.62 (4 H, d), and 7.51 (4 H, d),  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 1 740 and 1 183  $\text{cm}^{-1}$  (Found:  $M^+$ , 552. Calc. for  $\text{C}_{18}\text{H}_{18}\text{I}_2\text{O}_4$ :  $M$ , 552); 3-(*p*-iodophenoxy)propanoic acid (14%), m.p. 165 °C (benzene),  $\delta(\text{CDCl}_3)$  2.84 (2 H, t), 4.20 (2 H, t), 6.67 (2 H, d), and 7.55 (2 H, d),  $\nu_{\text{max.}}$  (Nujol) 3 300—2 400br 1 698, and 1 242  $\text{cm}^{-1}$  (Found:  $M^+$ , 292. Calc. for  $\text{C}_9\text{H}_9\text{IO}_3$ :  $M$ , 292), and starting alcohol (29%).

*Dark Reaction of 6-Iodochroman with Mercury(II) Oxide-Iodine.*—A mixture of 6-iodochroman (0.084 g, 0.30 mmol), iodine (5.40 g, 21.1 mmol) and red mercury(II) oxide (2.20 g, 10.2 mmol) in benzene (15 ml) was stirred in the dark at room temperature for 22 h. The reaction was quenched (aqueous sodium thiosulphate), and the organic layer separated, dried (sodium sulphate), and concentrated to an oil. Analysis (n.m.r., g.l.c.) revealed starting material (45%) and 6,8-di-iodochroman (34) (52%), identical with a specimen isolated from an earlier reaction.

*Photoreaction of 6-Iodochroman with Mercury(II) Oxide-Iodine.*—A mixture of 6-iodochroman (0.395 g, 1.43 mmol), iodine (7.9 g, 31.1 mmol) and red mercury(II) oxide (3.1 g, 14.3 mmol) in benzene (20 ml) was irradiated (1 000 W tungsten lamp) at room temperature for 6 h. I.r. analysis of a portion, prior to work-up, showed the presence of a carbonyl absorption (1 702  $\text{cm}^{-1}$ ). The reaction, worked up as above, gave an oil (0.41 g). Analysis (n.m.r., i.r., and t.l.c.) revealed starting material (40%) and 6-iodochroman-4-one (33) (38%) (comparison with an authentic specimen).

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