

[Bis(aryloxyacetoxy)iodo]benzenes

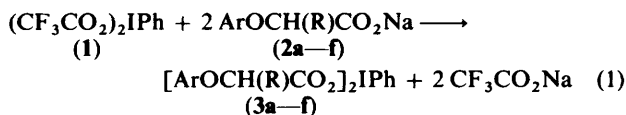
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The title compounds (3) have been prepared and their chemical properties studied. With iodine they give aryloxymethyl aryloxyacetates (4) through the intermediacy of aryloxyacetyl hypoiodites and α -iodoanisoles. The former are unstable but have been trapped with pyridine to give *N*-iodopyridinium aryloxyacetates, whereas the latter are stable and react independently with compounds (3) to afford the acetates (4). The thermolysis of (3) has been studied and, besides esters (4), aryl aryloxyacetates are also formed. The mechanism of the thermolysis is briefly discussed.

Diacyloxyiodobenzenes, $(\text{RCO}_2)_2\text{IPh}$ (hereafter DIBs), constitute a well-studied class of hypervalent iodine compounds.¹ The majority of their representatives contain simple acyloxy groups, such as acetoxy, trifluoroacetoxy, and benzyloxy. The strong herbicidal properties of several aryloxyacetic acids or derivatives thereof such as 2,4-D and Diclofop methyl,² in conjunction with the biocidal properties of hypervalent iodine compounds in general,³ made it desirable to synthesize a series of [bis(aryloxyacetoxy)iodo]benzenes of type (3) and study their chemical and biological properties. We report here on the chemistry of these compounds.

Compounds (3a–f) have been obtained in good yields from the reaction of [bis(trifluoroacetoxy)iodo]benzene (1) with the sodium salts of aryloxyacetic acids (2a–f) [Equation (1)].

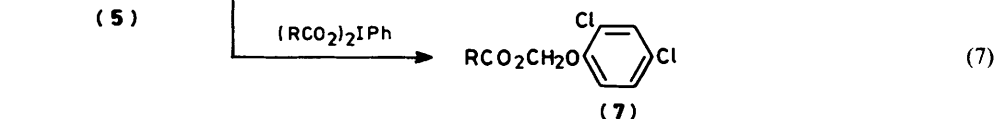
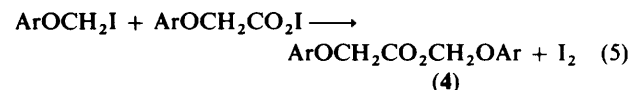
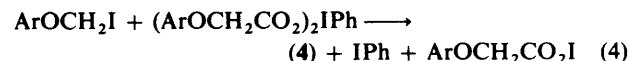
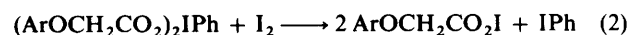


a; Ar = Ph, R = H d; Ar = 2,4-Me₂C₆H₃, R = H
b; Ar = *p*-BrC₆H₄, R = H e; Ar = 2,4-Cl₂C₆H₃, R = H
c; Ar = *p*-MeC₆H₄, R = H f; Ar = *p*-(2,4-Cl₂C₆H₃O)C₆H₄,
R = Me

This new method⁴ is more convenient than conventional methods and has been found suitable for the synthesis of the hitherto unknown mixed DIBs, with two different acyloxy groups. However, compounds (3; R = H, Ar = *p*-NO₂C₆H₄ or *p*-MeOC₆H₄) were too unstable to be isolated; among the stable analogues only (3a) withstood recrystallization, the other compounds being insoluble in ordinary solvents. Compounds (3) show the expected weak oxidizing properties of DIBs and can add two acyloxy groups to an alkene or substitute a hydrogen atom by an acyloxy group in acetophenone; they

react also with β -diketones such as dimedone to afford phenyliodonium ylides in non-alkaline media.⁵

One interesting reaction of DIBs is with halogens⁶ (excluding fluorine), where an unstable acyl hypoiodite is thought to be initially formed; when compound (1) is used, trifluoroacetyl hypoiodites can halogenate *in situ* a variety of aromatic substrates. We found that addition of iodine to a refluxing solution of (3) in methylene chloride led to the formation of aryloxymethyl aryloxyacetates, (4), in 10–50% yields. Other products formed are phenyl iodide and variable quantities of aryloxyacetic acids. Esters of type (4) may be regarded as esters of the hemiacetals of formaldehyde (acetaldehyde) and were not common until recently, when a series of mainly alkoxyacetic acids in the presence of mercury(II) oxide and iodine.⁷ The esters (4) have been characterized by elemental analysis, spectral data and hydrolysis, the latter giving aryloxyacetic acids, phenols, and formaldehyde (acetaldehyde). A characteristic feature of these esters is the carbonyl stretching vibration, which appears at 1755–1775 cm⁻¹. The reaction of compound (3) and iodine leading to the formation of compound (4) is the result of a series of distinct reactions, represented by Equations (2)–(5). From these reactions, Equation (2) has already been mentioned⁶ and Equation (3) is well known⁸ for derivatives of simple carboxylic

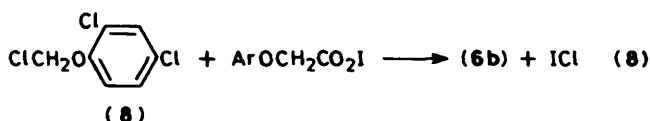


(6) a; Ar = Ph, R = H
b; Ar = *p*-BrC₆H₄, R = H
c; Ar = *p*-(2,4-Cl₂C₆H₃O)C₆H₄, R = Me

(7) a; R = Ph
b; R = *o*, *p*-Cl₂C₆H₃
c; R = Me

acids. Equation (4) has been the subject of a detailed study between DIBs and alkyl iodides,⁹ where reaction (5) has been suggested as a subsequent step. The decarboxylation products of $\text{ArOCH}_2\text{CO}_2\text{I}$ are stable compounds and therefore we made independently 2,4-dichloro- α -iodoanisole (5) and found that it reacts not only with compound (3e) to afford compound (4e) but also with other DIBs of type (3) providing access to mixed 2,4-dichlorophenoxymethyl aryloxyacetates (6) [Equation (6)]. The reaction can be extended to the preparation of 2,4-dichlorophenoxy carboxylates, (7) [Equation (7)], by using simple DIBs.

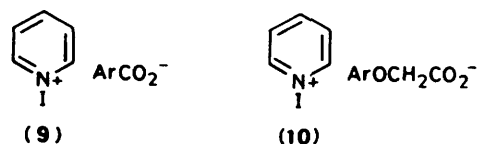
DIBs arising from acids with $\text{p}K_a$ values in the range 3–4 have a rather weakly electrophilic hypervalent iodine and react only with alkyl iodides possessing a highly nucleophilic iodine, such as benzyl and *t*-butyl iodides.⁹ The more reactive [bis(trifluoroacetoxy)iodo]benzene, (1) reacts not only with all kinds of iodides but also with benzyl and *t*-butyl chlorides. DIBs of type (3) do not react with α ,2,4-trichloroanisole (8) but if an equimolar quantity of iodine is added, the acyl hypoiodite initially formed, $\text{ArOCH}_2\text{CO}_2\text{I}$, reacts with (8) before decarboxylation occurs to afford esters of type (6) [Equation (8)].



In the above reaction iodine monochloride is also produced; it has been identified by the addition of cyclohexene to the reaction mixture, when 1-chloro-2-iodocyclohexane was formed, identical with the product from an independent reaction of cyclohexene and ICl. The same chloroanisole (8) also reacts with compound (1) to give 2,4-dichlorophenoxy-methyl trifluoroacetate, which could not be isolated on account of its high sensitivity to moisture but was identified from its i.r. spectrum (ν_{CO} at 1805 cm^{-1} , in CH_2Cl_2). The reactivity of compound (8) with $\text{ArOCH}_2\text{CO}_2\text{I}$ compared with its inertness towards compound (3) suggests that any of the product (5) formed reacts with $\text{ArOCH}_2\text{CO}_2\text{I}$ rather than with compound (3), i.e. step (5) predominates over step (4).

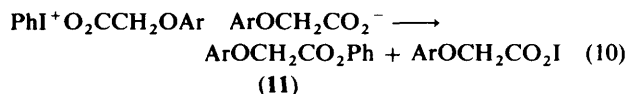
Both homolytic and heterolytic processes probably take place in the reaction of compound (3) with iodine. The decarboxylation of hypoiodites [Equation (3)] to α -iodoanisoles is likely to be homolytic, by analogy with simple acyl hypoiodites.⁸ This stage plays an important role to the overall reaction, as judged by the observation that best yields are obtained by using benzene as the solvent, whereas with chloroform the main products are the acids $\text{ArOCH}_2\text{CO}_2\text{H}$, obviously arising from the interaction of the solvent with the free radical $\text{ArOCH}_2\text{CO}_2^\cdot$. Most of our esters are easily hydrolysed during chromatographic separation, using silica gel, so that the actual amounts isolated are moderate. However, the reaction of the dichloride (5) with [bis(2,6-dichlorobenzoyloxy)iodo]benzene afforded the ester (7b) in 84% yield, no doubt because of steric inhibition to hydrolysis.

Acyl hypoiodites are relatively unstable and have never been isolated or detected spectroscopically. It has been reported¹⁰ that the reaction of silver carboxylates and iodine in the presence of pyridine gives stable 'complexes' of the type $\text{RCO}_2\text{I}\cdot\text{pyridine}$, however, silver trifluoroacetate under similar conditions gave *N*-iodopyridinium trifluoroacetate.¹¹ Since several iodine compounds containing an electrophilic iodine atom afford crystalline charge transfer complexes,¹² and the trifluoroacetate salt might present a special case, the reaction of several silver benzoates as well as aryloxyacetates with iodine in pyridine was performed and it was found that in all cases the *N*-iodopyridinium salts (9) and (10) were formed.

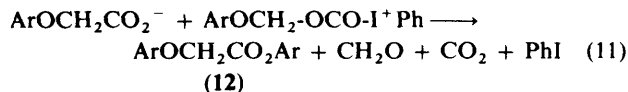


The assignment of these structures was based on the carbonyl absorptions at $1660\text{--}1690\text{ cm}^{-1}$, typical of carboxylate ions. By contrast, acetyl hypobromite¹³ has a high carbonyl absorption at 1790 cm^{-1} . The same compounds (10) were obtained when the reaction of compound (3) and iodine was performed in the presence of pyridine; this finding corroborates that aryloxyacetyl hypoiodites are true intermediates, which can be trapped by pyridine. The unsubstituted compound (10; $\text{Ar} = \text{Ph}$) was not formed from the reaction of either (3a) or the silver salt (2a) and iodine; instead, *p*-iodophenoxyacetic acid was isolated, the iodinating species being the pyridinium salt (10), as an independent reaction between compound (10); $\text{Ar} = p\text{-BrC}_6\text{H}_4$ and anisole has proved, where *p*-iodoanisole was produced. Slightly deactivated aromatic compounds were not iodinated by compound (10).

Mechanistic studies on the thermolysis of dibenzoyloxyiodobenzenes¹⁴ have shown that concurrent heterolytic and homolytic decomposition occurs. The main products are phenyl benzoates and benzoyl hypoiodites, which are further transformed. The analogy of this thermal decomposition with the reaction of DIBs (including compound (3)) and iodine has led us to study the thermolysis of (3). Although brief heating of molten (3b) at 200°C gave phenyl iodide in large quantities, the ester (4b) (in 49% yield), and a further ester, $\text{ArOCH}_2\text{CO}_2\text{Ar}$ (12; $\text{Ar} = p\text{-BrC}_6\text{H}_4$) (8% yield) none of the expected compound $\text{ArOCH}_2\text{CO}_2\text{Ph}$ (11)¹⁴ was obtained. Despite this it is suggested that the thermolysis starts according to the generally proposed scheme [Equations (9) and (10)].



As soon as it is formed, $\text{ArOCH}_2\text{CO}_2\text{I}$ is decarboxylated into α -iodoanisole which reacts with still available (3) to give the ester (4) and iodine [as in Equation (4)]. Iodine reacts then with compound (2) [Equation (2)] to produce further $\text{ArOCH}_2\text{CO}_2\text{I}$, so that the reactions of Equations (3), (4), and (2) alternate and the ester (11) must be produced in trace amounts only. The other ester (12) is presumably the result of the alternative nucleophilic attack by $\text{ArOCH}_2\text{CO}_2^-$ to the aromatic carbon atom linked with I^+ of the iodonium ion $\text{ArOCH}_2\text{-OCO-I}^+\text{Ph}$.



This reaction is favoured over that of Equation (10), because of the higher electrophilic character of the aromatic C in Ar than in Ph. The thermolysis of compound (3e; $\text{Ar} = 2,4\text{-Cl}_2\text{C}_6\text{H}_3$) would be expected to promote the reactions of Equations (9) and (11), as well as those of Equations (3), (4), and (2). Indeed, after heating for only 3 min at 200°C , both esters (4e) and (12e) were produced in greater amounts than (4b) and (12b).

The thermolysis of compound (3b) in *p*-phenylene dichloride at 174°C gave essentially the same results as the thermolysis of the melt, as distinct from dibenzoyloxyiodobenzene, with which

both phenylation and benzoyloxylation of the solvent were observed.¹⁵ The lack of solvent participation in the thermolysis of compound (**3b**) may be attributed to the fast decarboxylation of the free radical $\text{ArOCH}_2\text{CO}_2^\cdot$ into ArOCH_2^\cdot , which reacts preferentially with iodine rather than with the solvent.

Experimental

I.r. spectra were recorded with a Perkin-Elmer 257 spectrometer. Mass spectra were obtained from a Hitachi-Perkin-Elmer RMU-6L (single focusing) spectrometer at 70 eV. ^1H N.m.r. spectra were recorded on a Varian A-60A spectrometer. All aryloxyacetic acids were known compounds and were prepared from chloroacetic acid and sodium phenolates, with the exception of 2-[p-(2,4-dichlorophenoxy)phenoxy]propionic acid, which was prepared by hydrolysis of its methyl ester, the active constituent of the herbicide Illoxan[®] (kindly supplied by Hoechst). α ,2,4-Trichloroanisole and α ,4-dichloroanisole were prepared by chlorination of 2,4-dichloroanisole and 4-chloroanisole respectively with chlorine. 2,4-Dichloro- α -iodoanisole¹⁶ was prepared from α ,2,4-trichloroanisole and sodium iodide and the same method was used for the preparation of 4-chloro- α -iodoanisole, which was obtained in 40% yield, m.p. 56–58 °C (from light petroleum); $\delta(\text{CDCl}_3)$ 6.06 (2 H, s), 7.00 (2 H, d), and 7.36 (2 H, d) (Found: C, 31.1; H, 2.1. $\text{C}_7\text{H}_6\text{ClIO}$ requires C, 31.28; H, 2.23%). Both α -iodoanisoles decompose at room temperature and must be kept under refrigeration. [Bis-(2,6-dichlorobenzoyloxy)iodo]benzene was prepared from sodium 2,6-dichlorobenzoate (4.26 g, 20 mmol) in acetonitrile (20 ml) which was treated with [bis(trifluoroacetoxy)iodo]benzene (4.3 g, 10 mmol) in acetonitrile (10 ml) and stirred at room temperature for 5 h. The precipitate formed was washed with acetonitrile and gave crystals (5.25 g, 90% yield), m.p. 182–184 °C, $\nu_{\text{max.}}$ (Nujol) 1 670 cm^{-1} ; $\delta(\text{CDCl}_3)$ 7.23 (6 H, s) and 7.46–8.38 (5 H, m) (Found: C, 41.1; H, 1.9. $\text{C}_{20}\text{H}_{11}\text{Cl}_4\text{IO}_4$ requires C, 40.96; H, 1.83).

[Bis(aryloxyacetoxy)iodo]benzenes (**3**): General Procedure.—A suspension of dried sodium aryloxyacetate (20 mmol) in acetonitrile (20 ml) was treated with a solution of [bis(trifluoroacetoxy)iodo]benzene (10 mmol) in acetonitrile (10 ml) and the mixture was stirred for 12–24 h at room temperature. After this fine reaction was complete and compounds (**3b**–**e**) which are insoluble in acetonitrile were collected by filtration, washed with acetonitrile, which dissolves sodium trifluoroacetate, and used without further purification, since all attempts at crystallisation led to extensive decomposition. However, the compounds were reasonably pure and gave acceptable elemental analyses with the exception of (**3d,f**). Compound (**3a**) is soluble in MeCN, so that after removal of the solvent the residue was extracted with warm CHCl_3 and was the only compound which was able to be crystallized. Compounds (**3d**) and (**3f**) were the most unstable; these were formed at 0 °C and could be stored only under refrigeration.

[Bis(phenoxyacetoxy)iodo]benzene (**3a**) was obtained in 60% yield, m.p. 156–159 °C (from chloroform–hexane); $\nu_{\text{max.}}$ (Nujol) 1 670 cm^{-1} ; $\delta(\text{CDCl}_3)$ 4.53 (4 H, s) and 6.73–7.48 (15 H, m); m/z 204 and 152 (Found: C, 51.9; H, 3.6. $\text{C}_{22}\text{H}_{19}\text{IO}_6$ requires C, 52.17; H, 3.75%).

[Bis(p-bromophenoxyacetoxy)iodo]benzene (**3b**) was obtained in 95% yield, m.p. 179–181 °C; $\nu_{\text{max.}}$ (Nujol) 1 680 cm^{-1} ; $\delta[(\text{CD}_3)_2\text{SO}]$ 4.81 (4 H, s), 7.00 (4 H, d, J 8 Hz), and 7.24–8.00 (9 H, m); m/z 228–230 and 204 (Found: C, 39.5; H, 2.3. $\text{C}_{22}\text{H}_{17}\text{BrIO}_6$ requires C, 39.77; H, 2.56%).

[Bis(p-tolyloxyacetoxy)iodo]benzene (**3c**) was obtained in 94% yield, m.p. 127–129 °C; $\nu_{\text{max.}}$ (Nujol) 1 670 cm^{-1} ; $\delta(\text{CDCl}_3)$ 2.03 (6 H, s), 4.63 (4 H, s), and 6.73–8.00 (13 H, m); m/z 204 and

165 (Found: C, 53.4; H, 4.6. $\text{C}_{24}\text{H}_{23}\text{IO}_6$ requires C, 53.93; H, 4.31%).

[Bis-(2,4-xylyloxyacetoxy)iodo]benzene (**3d**) was obtained in 67% yield, m.p. 137–140 °C; $\nu_{\text{max.}}$ (Nujol) 1 680 cm^{-1} ; $\delta(\text{CDCl}_3)$ 2.18 (6 H, s), 2.26 (6 H, s), 4.58 (4 H, s), 6.51–7.01 (6 H, m), and 7.46–8.11 (5 H, m); m/z 204 and 180 (Found: C, 55.9; H, 4.6. $\text{C}_{26}\text{H}_{27}\text{IO}_6$ requires C, 55.52; H, 4.80%).

[Bis(2,4-dichlorophenoxyacetoxy)iodo]benzene (**3e**) was obtained in 62% yield, m.p. 142–144 °C; $\nu_{\text{max.}}$ (Nujol) 1 675 cm^{-1} ; $\delta(\text{CDCl}_3)$ 4.61 (4 H, s), 6.63 (2 H, d, J 8 Hz), 7.00–7.15 (2 H, dd, J 8, 3 Hz), 7.33 (2 H, d, J 3 Hz), and 7.10–8.03 (5 H, m); m/z 395, 365, and 204 (Found: C, 41.1; H, 2.2. $\text{C}_{22}\text{H}_{15}\text{Cl}_4\text{IO}_6$ requires C, 40.99; H, 2.33%).

[Bis{2-[p-(2,4-dichlorophenoxy)phenyl]propionyloxy}iodo]benzene (**3f**) was obtained in 74% yield, m.p. 48–51 °C; $\nu_{\text{max.}}$ (Nujol) 1 680 cm^{-1} ; $\delta(\text{CDCl}_3)$ 1.52 (6 H, d), 4.63 (4 H, q), and 6.75–7.55 (19 H, m); m/z 326 and 204 (Found: C, 49.6; H, 3.1. $\text{C}_{36}\text{H}_{27}\text{Cl}_4\text{IO}_8$ requires C, 50.46; H, 3.15%).

Reactions of Compound (**3**) with Iodine.—A solution of iodine (1–2 mmol) in methylene chloride (15 ml) was added to a solution of (**3**) (1–2 mmol) in methylene chloride (10 ml) and kept under reflux for 3–6 h. The reaction mixture was treated with 5% aqueous NaHSO_3 , then 3% aqueous Na_2CO_3 , and finally water. After drying (Na_2SO_4), the solvent was removed and the residue was chromatographed on a silica gel column, using mixtures of chloroform–light petroleum as the eluant. After phenyl iodide, the esters (**4**) were eluted.

Compound (**3a**) (506 mg) gave phenoxymethyl phenoxyacetate (**4a**) (85 mg, 33%); $\nu_{\text{max.}}$ (film) 1 775 (lit.,⁷ 1 780) cm^{-1} ; $\delta(\text{CDCl}_3)$ 4.70 (2 H, s), 6.0 (2 H, s), and 7.0–7.8 (10 H, m); m/z 258 (M^+).

Compound (**3b**) (2 mmol, 1 326 mg) gave p-bromophenoxy-methyl p-bromophenoxyacetate (**4b**) (308 mg, 37%), m.p. 87–89 °C (from chloroform–light petroleum); $\nu_{\text{max.}}$ (Nujol) 1 775 cm^{-1} ; $\delta(\text{CDCl}_3)$ 4.58 (2 H, s), 5.75 (2 H, s), 6.68 (2 H, d, J 9 Hz), 6.78 (2 H, d, J 9 Hz), 7.30 (2 H, d, J 9 Hz), and 7.33 (2 H, d, J 9 Hz); m/z 416–414 (M^+) (Found: C, 43.6; H, 2.6. $\text{C}_{15}\text{H}_{12}\text{Br}_2\text{O}_4$ requires C, 43.29; H, 2.88%). When the reaction was carried out in chloroform the yield was found to be 22%, whereas in benzene it was 50%.

Compound (**3c**) (2 mmol, 1 070 mg) gave p-methylphenoxy-methyl p-tolyloxyacetate (**4c**) (85 mg, 29%), non crystallizable oil; $\nu_{\text{max.}}$ (film) 1 775; $\delta(\text{CCl}_4)$ 2.25 (6 H, s), 4.42 (2 H, s), 5.63 (2 H, s), and 6.45–6.96 (8 H, m); m/z 286 (M^+) (Found: C, 71.7; H, 6.5. $\text{C}_{17}\text{H}_{18}\text{O}_4$ requires C, 71.32; H, 6.29%).

Compound (**3d**) (2 mmol, 1 120 mg) gave 2,4-xylyloxymethyl 2,4-xylyloxyacetate (**4d**) (80 mg, 25%), m.p. 45–47 °C (from light petroleum); $\nu_{\text{max.}}$ (film) 1 760 cm^{-1} ; $\delta(\text{CDCl}_3)$ 2.16 (6 H, s), 2.21 (6 H, s), 4.58 (2 H, s), 5.78 (2 H, s), 6.52 (2 H, d, J 8 Hz), 6.90 (2 H, d, J 8 Hz), and 7.17 (2 H, s); m/z 314 (M^+) (Found: C, 72.8; H, 7.1. $\text{C}_{19}\text{H}_{22}\text{O}_4$ requires C, 72.61; H, 7.00%).

Compound (**3e**) (1 mmol, 644 mg) gave 2,4-dichlorophenoxy-methyl 2,4-dichlorophenoxyacetate (**4e**) (160 mg, 40%), m.p. 111–112 °C (from hexane); $\nu_{\text{max.}}$ (Nujol) 1 760 cm^{-1} ; $\delta(\text{CDCl}_3)$ 4.70 (2 H, s), 5.81 (2 H, s), and 6.60–7.10 (6 H, m); m/z 395–397 (M^+) (Found: C, 45.25; H, 2.4. $\text{C}_{15}\text{H}_8\text{Cl}_4\text{O}_4$ requires C, 45.49; H, 2.54%).

Compound (**3f**) (1 mmol, 856 mg) gave p-(2,4-dichlorophenoxy)phenoxy-methyl 2-[p-(2,4-dichlorophenoxy)phenoxy]propionate (**4f**) (60 mg, 10%), m.p. 82–83 °C (from chloroform–hexane); $\nu_{\text{max.}}$ (film) 1 755 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.45 (3 H, d, J 7 Hz), 1.61 (3 H, d, J 7 Hz), 4.56 (1 H, q, J 7 Hz), 6.43 (1 H, q, J 7 Hz), and 6.70–7.40 (14 H, m); m/z no M^+ (Found: C, 57.1; H, 3.7. $\text{C}_{29}\text{H}_{22}\text{Cl}_4\text{O}_6$ requires C, 57.23; H, 3.62%).

Reactions of Compound (**3**) with 4-Chloro- α -iodoanisole and 2,4-Dichloro- α -iodoanisole (**5**).—A solution of the iodo compound (**3**) (0.5 mmol) in methylene chloride (20 ml) was mixed

with a solution of the anisole (1 mmol) in methylene chloride (10 ml) and the mixture was set aside at room temperature in the dark for 2–6 h. After this the solvent was removed and the residue chromatographed on a silica gel column, using mixtures of chloroform–light petroleum as the eluant. In order of elution, phenyl iodide and iodine, 2,4-dichlorophenol and the esters compound (6) were obtained.

Compounds (3a) and (5) gave 2,4-dichlorophenoxyethyl phenoxycetate (6a) (285 mg, 75%), m.p. 33–35 °C (from chloroform); ν_{\max} (film) 1 780 and 1 760 cm^{-1} ; $\delta(\text{CDCl}_3)$ 4.66 (2 H, s), 5.83 (2 H, s), and 6.83–7.38 (8 H, m); m/z 327–326 (M^+) (Found: C, 55.2; H, 3.5. $\text{C}_{15}\text{H}_{12}\text{Cl}_2\text{O}_4$ requires C, 55.04; H, 3.67%).

Compounds (3b) and (5) gave 2,4-dichlorophenoxyethyl *p*-bromophenoxyacetate (6b) (190 mg, 47%), m.p. 104–105 °C (from chloroform–hexane); ν_{\max} (Nujol) 1 765 cm^{-1} ; $\delta(\text{CDCl}_3)$ 4.63 (2 H, s), 5.83 (2 H, s), and 6.63–7.55 (7 H, m); m/z 406 (M^+) (Found: C, 44.5; H, 2.7. $\text{C}_{15}\text{H}_{11}\text{BrCl}_2\text{O}_4$ requires C, 44.33; H, 2.71%).

Compounds (3f) and (5) gave 2,4-dichlorophenoxyethyl 2-[*p*-(2,4-dichlorophenoxy)phenoxy]propionate (6c) (270 mg, 54%), non-crystallisable oil; ν_{\max} (film) 1 765 cm^{-1} ; $\delta(\text{CDCl}_3)$ 1.56 (3 H, d, J 7 Hz), 4.53–4.88 (1 H, q, J 7 Hz), 5.68 (1 H, d, J 6 Hz), 5.95 (1 H, d, J 6 Hz), and 6.68–7.43 (10 H, m); m/z 502 (M^+) (Found: C, 52.45; H, 3.1. $\text{C}_{22}\text{H}_{16}\text{Cl}_4\text{O}_5$ requires C, 52.59; H, 3.18%).

Compounds (3e) and (5) gave the ester (4e) in 43% yield, identical with that obtained from compound (3e) and iodine.

Compound (3f) and 4-chloro- α -iodoanisole gave *p*-chlorophenoxyethyl 2-[*p*-(2,4-dichlorophenoxy)phenoxy]propionate (210 mg, 45%), m.p. 81–83 °C (from chloroform–hexane); ν_{\max} (film) 1 770 cm^{-1} ; $\delta(\text{CDCl}_3)$ 1.61 (3 H, d, J 7 Hz), 4.60–4.95 (1 H, q, J 7 Hz), 5.76 (1 H, d, J 6 Hz), 5.90 (1 H, d, J 6 Hz), and 6.72–7.48 (11 H, m); m/z 467 (M^+) (Found: C, 57.0; H, 3.7. $\text{C}_{22}\text{H}_{17}\text{Cl}_3\text{O}_5$ requires C, 56.50; H, 3.64%).

Reactions of Diacyloxyiodobenzenes with 2,4-Dichloro- α -iodoanisole (5).—The conditions were similar to those described for the reactions between compounds (3) and (5). Dibenzoyloxyiodobenzene and compound (5) gave 2,4-dichlorophenoxy-methylbenzoate in 35% yield; m.p. 63–65 °C (lit.,¹⁶ m.p. 65–66 °C) and 2,4-dichlorophenol in 45% yield.

Bis-(2,6-dichlorobenzoyloxy)iodobenzene and compound (5) gave 2,4-dichlorophenoxyethyl 2,6-dichlorobenzoate (7b) (307 mg, 84%), m.p. 64–66 °C (from chloroform–hexane); ν_{\max} (film) 1 755 cm^{-1} ; $\delta(\text{CDCl}_3)$ 6.06 (2 H, s), and 7.16–7.35 (6 H, m); m/z 366 (M^+) (Found: C, 45.6; H, 2.3. $\text{C}_{14}\text{H}_8\text{Cl}_4\text{O}_3$ requires C, 45.90; H, 2.18%).

Diacetoxyiodobenzene and compound (5) gave 2,4-dichlorophenoxyethyl acetate (7c) in only 8% yield, whereas bis-(trifluoroacetoxy)iodobenzene and compound (5) produced the corresponding ester (ν_{\max} 1 805 cm^{-1}) which could not be isolated. In both cases 2,4-dichlorophenol was obtained in 66 and 75% yield, respectively.

N-Iodopyridinium *p*-bromophenoxyacetate.—A suspension of compound (3b) (730 mg, 1.1 mmol) in methylene chloride (15 ml) was mixed with a solution of iodine (280 mg, 11 mmol) in methylene chloride (15 ml), and pyridine (0.17 ml, 2.2 mmol) was then added. The reaction mixture was refluxed for 2 h, filtered and to the filtrate hexane was added. The precipitate (500 mg, 52% yield) (10; Ar = *p*-bromophenyl) had m.p. 118–120 °C (from light petroleum); ν_{\max} (Nujol) 1 690 cm^{-1} ; $\delta(\text{CDCl}_3)$ 4.73 (2 H, s), 6.96 (2 H, d, J 9 Hz), 7.65 (2 H, d, J 9 Hz), and 7.80–8.96 (5 H, m) (Found: C, 36.4; H, 2.4; N, 3.1. $\text{C}_{13}\text{H}_{11}\text{BrINO}_3$ requires C, 35.78; H, 2.52; N, 3.21%). The same compound was also obtained from silver *p*-bromophenoxyacetate and iodine in chloroform–pyridine, in 69% yield. With

time, it liberated iodine so the elemental analysis was not satisfactory.

Thermal Decomposition of Bis(*p*-bromophenoxyacetoxy)-iodobenzene (3b).—A solid sample of (3b) (1 g, 1.5 mmol) was heated in an oil-bath at 200 °C for 30 min. After cooling, the residue was washed with chloroform and the undissolved solid was identified as *p*-bromophenoxyacetic acid (21% yield). The chloroform solution was evaporated and the residue subjected to chromatography on a silica gel column using mixtures of light petroleum–chloroform as the eluant. After phenyl iodide (200 mg, 65%), *p*-bromophenyl *p*-bromophenoxyacetate (12b) was eluted (50 mg, 8%), m.p. 123–125 °C (from chloroform–hexane); ν_{\max} (Nujol) 1 785 and 1 765 cm^{-1} ; $\delta(\text{CDCl}_3)$ 4.76 (2 H, s), 6.75 (2 H, d), 6.91 (2 H, d), and 7.13–7.41 (4 H, two d); m/z 386 (M^+) (Found: C, 43.8; H, 2.6. $\text{C}_{14}\text{H}_{10}\text{Br}_2\text{O}_3$ requires C, 43.52; H, 2.59%). The final product to be eluted was the ester (4b) (300 mg, 49%). When the thermolysis was carried out in *p*-phenylene dichloride, after reflux at 174 °C for 30 min. the same products were obtained [(12b) and (4b) in 20% and 58% yield, respectively].

Thermal Decomposition of Bis-(2,4-dichlorophenoxyacetoxy)-iodobenzene (3e).—A solid sample of compound (3e) (1.25 g, 2 mmol) was heated in an oil-bath at 200 °C for 3 min. The separation procedure as described for compound (3b) was followed and besides 2,4-dichlorophenoxyacetic acid (130 mg, 15%) and phenyl iodide (290 mg, 71%), 2,4-dichlorophenyl 2,4-dichlorophenoxyacetate (12e) was obtained (110 mg, 15%), m.p. 93–95 °C (from chloroform–hexane); ν_{\max} (Nujol) 1 765 cm^{-1} ; $\delta(\text{CDCl}_3)$ 4.86 (2 H, s), and 6.75–7.41 (6 H, m); m/z 367, 366, 365 (M^+) (Found: C, 45.6; H, 2.2. $\text{C}_{14}\text{H}_{10}\text{Cl}_4\text{O}_3$ requires C, 45.90; H, 2.18%). Finally, the ester (4e) was also obtained (495 mg, 64%).

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Received 3rd July 1985; Paper 5/1125