Formation and synthetic use of oxygen-centred radicals with (diacetoxyiodo)arenes

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***o*-Alkyl- or *o*-aryl-benzenecarboxylic acids and alcohols containing an aromatic ring are treated with a (diacetoxyiodo)arene–iodine system to give the corresponding cyclized products such as phthalide, benzocoumarin and chromane derivatives in moderate to good yields *via* the corresponding oxygen-centred radicals. For the carboxylic acids, [bis(trifluoroacetoxy)iodo]benzene functions effectively, while (diacetoxyiodo)benzene is effective for the alcohols. Chromane and its derivatives are obtained as iodinated compounds by hypoiodite species derived from (diacetoxyiodo)benzene and iodine.**

Many natural products have lactone and cyclic ether skeletons and, in particular, phthalide, coumarin and chromane skeletons are commonly found in such compounds (taiwanin C, vitamin E, *etc*.); furthermore, an anti HIV-1 reagent (calanolide A) also has such structural elements. In view of this, there have been extensive studies on the preparation of such skeletons.[1] Most preparation methods use ionic reactions or the Diels–Alder reaction, radical cyclizations being rare. Generally, peroxides are used for the generation of oxygen-centred radicals,[2] although these reactions are not easy to handle and control. In spite of its toxicity, lead tetraacetate is a very useful reagent in such work because it is both an excellent oxidant and easy to handle.[3] Although the oxygen-centred radicals generated by this reagent from aromatic carboxylic acids and alcohols have been used to prepare phthalide, coumarin, and chromane skeletons,[3] the product yields were very low. Recently, the chemistry of trivalent iodine compounds has been widely studied because of the potential of these compounds to act as oxidants[4] and radical precursors:[5] for instance (diacyloxyiodo)arenes can generate alkyl[5] and alkoxy radicals.[6] In this methodology, alkyl radicals were used for C–C bond formation; for example, the alkylation of π-deficient heteroaromatic compounds and the addition to the activated olefins having electron-withdrawing groups, and functionalization. Suárez *et al*. has reported the fragmentation of steroidal alcohols *via* alkoxy radicals. Although carbonyloxy radicals generated from (diacyloxyiodo)arenes have not been used for organic synthesis, we planned to use such reactions for the direct cyclization of aromatic carboxylic acids and alcohols containing an aromatic ring. We now report full details of these experiments together with an extension of the methodology.[7]

Results and discussion

Synthesis of lactones

Since aliphatic carbonyloxy radicals undergo rapid decarboxylation to give the corresponding alkyl radicals,[5] we focused on the formation and use of their aromatic counterparts. Initially, we attempted to generate *p*-methylbenzenecarbonyloxy radicals from [bis(*p*-methylphenylcarbonyloxy)iodo]benzene and to convert them into phenyl *p*-methylbenzenecarboxylate by trapping with benzene in the presence of iodine and with irradiation from a tungsten lamp (500 W). The reaction was followed by NMR spectroscopy and the results are shown in Fig. 1.

Irradiation of [bis(*p*-methylphenylcarbonyloxy)iodo]benzene in benzene gave phenyl *p*-methylbenzenecarboxylate, *p*-methylbenzenecarboxylic acid and iodobenzene. One of the two carbonyloxy groups in (diaroyloxyiodo)benzene gives rise to an ester and the other to a carboxylic acid. Here, carboxylic acid and iodobenzene might be formed by the oxidation of the addition intermediate of *p*-methylphenylcarbonyloxy radical and benzene. Irradiation of [bis(*o*-alkylphenylcarbonyloxy)iodo]benzene and [bis(*o*-phenylphenylcarbonyloxy)iodo]benzene in the presence of iodine gave the corresponding phthalide and benzocoumarin *via* oxygen-centred radicals in good yields (see Table 1). The addition of [bis(trifluoroacetoxy)iodo]benzene is needed to oxidize the hydrogen iodide formed (entries 3 and 4), which acts as an effective reducing agent of the starting (diaroyloxyiodo)benzene; in fact, the yields were improved by the addition in compounds **1a**, **1b** and **1c**. The poor yield of **4a** from **1a** can be explained in terms of the abstraction of methyl hydrogen by the carbonyloxy radical formed being slower than in the other compounds.[8] In entry 3, the presence of an isocoumarin analogue suggests that 2-isopropenyl-5-isopropylbenzenecarboxylic acid might be formed, since lactones are known to be formed from γ- or δ-pentenoic acids in the presence of iodine.[9] Although the described reaction proceeded with only fluorescent lighting (40 W), the product yield was low and a prolonged reaction time was required as compared with reactions carried out with tungsten lamp irradiation (entries 7, 8 and 9). In entries 6, 10 and 11, the corresponding seven-membered lactones were not formed. [Bis(*o*-phenoxyphenylcarbonyloxy)iodo]benzene gave phenyl *o*-hydroxybenzoate (phenyl salicylate) alone (entry 10), by intramolecular ipso-

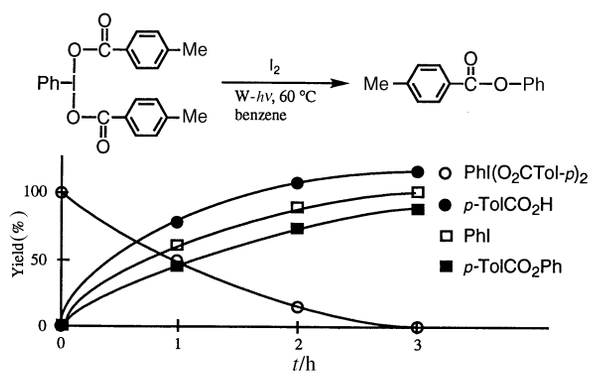


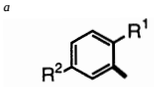
Fig. 1 Formation of phenyl *p*-methylbenzoate. Yields were calculated based on [bis(*p*-methylphenylcarbonyloxy)iodo]benzene.

Table 1 Reaction of (diaroyloxyiodo)benzene

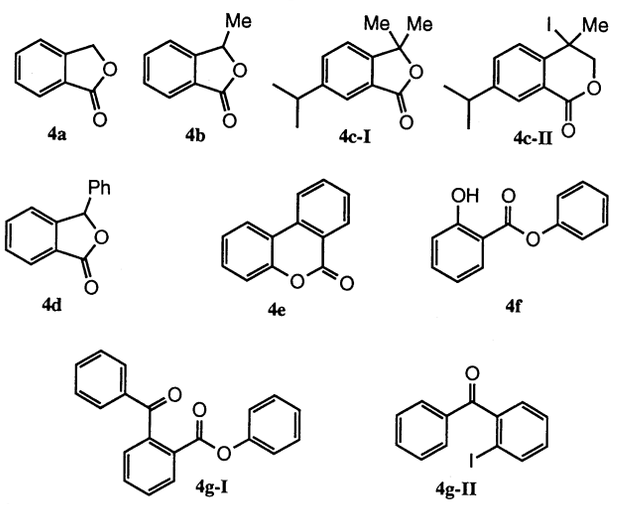
$$PhI(O_2CAr)_2 \xrightarrow[h\nu]{I_2\ \mathbf{2},\ PhI(O_2CCF_3)_2\ \mathbf{3}} \text{Product}$$

1 **4**

Entry	Ar[a]	Ratio (**1**:**2**:**3**)	Conditions[b]	Product[c]	Yield (%)[d]
1	**1a**	1.0:0.2:0.5	**A**	**4a**	19
2	**1b**	1.0:0.2:0.5	**A**	**4b**	72
3	**1c**	1.0:0.2:0.5	**A**	**4c-I/4c-II**	71/10
4	**1c**	1.0:0.2:0	**A**	**4c-I/4c-II**	60/0
5	**1d**	1.0:0.2:0	**A**	**4d**	77
6	**1d**	1.0:0.2:0	**B**	**4d**	70
7	**1e**	1.0:0.2:0	**A**	**4e**	93
8	**1e**	1.0:0.2:0	**B**	**4e**	90
9	**1e**	1.0:0.2:0	**C**	**4e**	68
10	**1f**	1.0:0.2:0	**B**	**4f**	54
11	**1g**	1.0:1.0:0	**B**	**4g-I/4g-II**	41/28

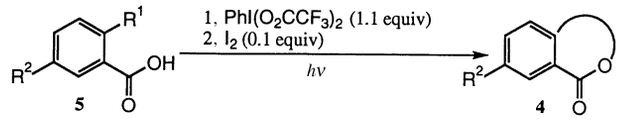
[a] 
1a: R^1 = **Me**, R^2 = **H**; **1b**: R^1 = **Et**, R^2 = **H**; **1c**: R^1 = R^2 = **Pr**^{i}; **1d**: R^1 = **PhCH$_2$**, R^2 = **H**; **1e**: R^1 = **Ph**, R^2 = **H**; **1f**: R^1 = **PhO**, R^2 = **H**; **1g**: R^1 = **PhCO**, R^2 = **H**.

[b] **A**: Irradiation of **1** (0.5 mmol) with a high-pressure mercury lamp (400 W) for 5 h in CH_2Cl_2 (5–10 cm^3) at 15–25 °C. **B**: Irradiation of **1** (0.5 mmol) with a tungsten lamp (500 W) for 2 h in a mixture of C_6H_6 (13 cm^3) and CH_2Cl_2 (3 cm^3) at 60–70 °C. **C**: Stirring of **1** (0.5 mmol) under room light (fluorescent lighting, 40 W) for 28 h in $ClCH_2CH_2Cl$ (10 cm^3) at 15–25 °C. [c] Structure of products:



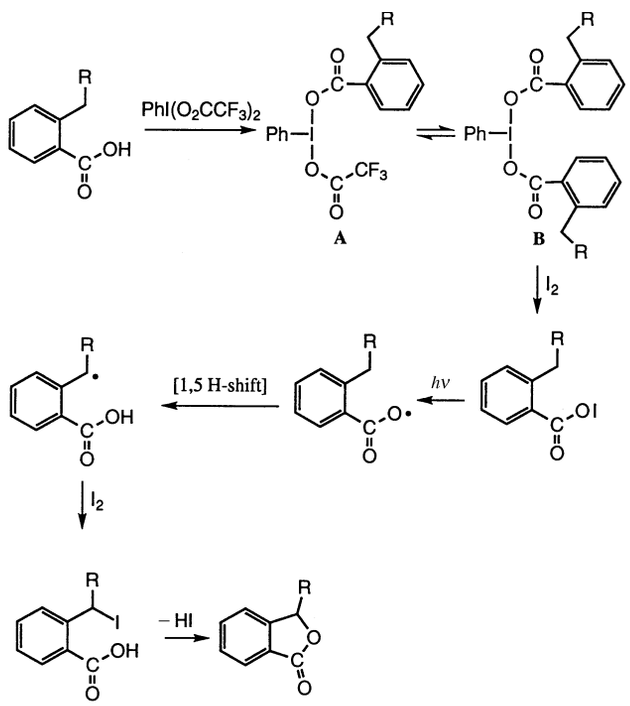
[d] Yields were calculated based on compound **1**.

Table 2 Direct conversion of aromatic carboxylic acids to lactones



Entry	R^1	R^2	Conditions[a]	Lactone	Yield (%)[b]	
1	Me	H	**A**	**4a**	5	(24)[c]
2	Et	H	**A**	**4b**	40	(80)
3	Pr^i	Pr^i	**A**	**4c-I/4c-II**	36/4	(63/7)
4	Bn	H	**A**	**4d**	62	(91)
5	Ph	H	**B**	**4e**	90	(99)

[a] **A**: Irradiation of **5** (1.0 mmol) with a high-pressure mercury lamp for 5 h in CH_2Cl_2 (5–10 cm^3) at 15–25 °C. **B**: Irradiation of **5** (1.0 mmol) with a tungsten lamp for 2 h in a mixture of C_6H_6 (13 cm^3) and CH_2Cl_2 (3 cm^3) at 60–70 °C. [b] Yields were calculated based on **5**. [c] Conversion yield.



Scheme 1 Plausible reaction mechanism for γ-lactone formation

substitution on the phenoxy carbon atom by the carbonyloxy radical, and [bis(*o*-benzoylphenylcarbonyloxy)iodo]benzene gave phenyl *o*-benzoylbenzenecarboxylate, which was formed by the reaction of *o*-benzoylbenzoyloxy radical and benzene, together with a decarboxylative iodination product, 2-iodobenzophenone (entry 11).[10]

Direct cyclization of an aromatic carboxylic acid, without preparation of (diaroyloxyiodo)benzene, proceeded effectively in the presence of [bis(trifluoroacetoxy)iodo]benzene and iodine to give the corresponding lactones. The results and reaction conditions are shown in Table 2.

The results indicate that most of the compounds give the corresponding lactones in moderate to good yields, except for entry 1. The reason for the poor yield in this case is similar to that given above for the low product yield of **4a** from **1a**. We attempted to determine whether this direct lactonization proceeded *via* a monosubstituted or a disubstituted trivalent iodine compound. Use of a monosubstituted compound, [(2-ethylphenylcarbonyloxy)(trifluoroacetoxy)iodo]benzene gave 3-methylphthalide **4b** in 33% yield (conversion yield was 52%); use of [bis(2-ethylphenylcarbonyloxy)iodo]benzene resulted in a 50% reduction in the yield (entry 2, Table 1). This result suggests that the arylcarbonyloxy radical is formed *via* a disubstituted one, **B** (see Scheme 1), and that there is an equilibrium state between **A** and **B**. *o*-Phenylbenzoic acid was treated with mercury diacetate–iodine or lead tetraacetate–iodine systems to give **4e** in good yield (92% or 99%). In contrast, *N*-(2-biphenylcarbonyloxy)pyridine-2-thione (Barton ester) gave **4e** in only 13% yield. In these reactions, (diacetoxyiodo)benzene failed to work well; moreover, the reactions do not proceed in the dark.

A plausible mechanism for the present reaction is shown in Scheme 1. The hypoiodite species are generated from a disubstituted trivalent iodine compound **B**. Homolytic bond cleavage of the I–O bond occurs to form a carbonyloxy radical which then abstracts a hydrogen atom *via* a six-membered transition state (1,5 H-shift) to give a benzyl carbon radical. This is further trapped by iodine, with subsequent cyclization by way of an ionic pathway. However, the carbon radical intermediate may be oxidized by a trivalent iodine compound to give a carbocation. In fact, when lead tetraacetate was used for this type of cyclization, the carbon radical was oxidized to a carbocation.

The X-ray structure of [bis(*o*-methylbenzoyloxy)iodo]benzene **1a** is shown in Fig. 2. This molecule adopted a T-shaped structure as in (diacetoxyiodo)benzene and [bis(1-adamantylcarbonyloxy)iodo]arenes.[11] However, since there are no big differences in bond angles and bond lengths between the compounds, we were unable to obtain any information on

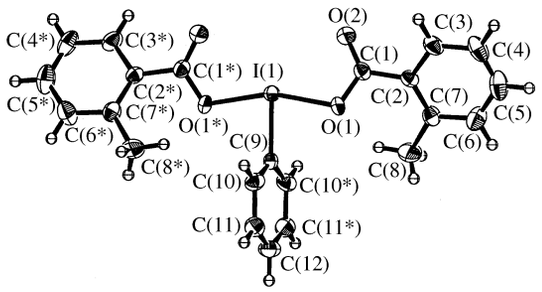
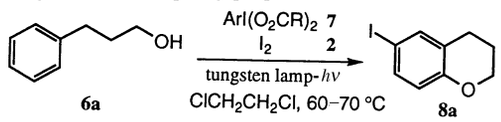


Fig. 2 X-Ray crystal structure of [bis(*o*-methylbenzoyloxy)iodo]-benzene **1a**. Selected bond lengths (Å) and angles (°): I(1)–O(1) 2.136(3), I (1)–C(9) 2.095(6), O(1)–I(1)–O(1*) 161.0(2), O(1)–I(1)–C(9) 80.49(8). Starred atoms are related to their unstarred equivalents by a two-fold operation ($1 - x$, y, $1.5 - z$).

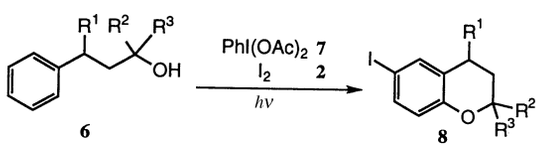
Table 3 Cyclization of 3-phenylpropanol



Entry	Ar	R	Yield (%)
1	Ph	CF_3	0
2	C_6H_4Me-*p*	Me	63
3	Ph	Me	64
4	C_6H_4Cl-*p*	Me	64

Molar ratio of **6a**:**7**:**2** was 1.0:2.2:1.0.

Table 4 Cyclization of 3-phenylpropanol and its derivatives to cyclic aromatic ethers



Entry	Alcohol	R^1	R^2	R^3	Conditions[a]	Cyclic ether	Yield (%)
1	**6a**	H	H	H	**B-1**	**8a**	42
2	**6a**	H	H	H	**B-2**	**8a**	47
3	**6a**	H	H	H	**B-3**	**8a**	64[b]
4	**6a**	H	H	H	**C**	**8a**	48
5	**6b**	Me	H	H	**B-3**	**8b**	68
6	**6c**	H	Me	H	**B-4**	**8c**	52[b]
7	**6d**	H	Bu	H	**C**	**8d**	34
8	**6e**	H	$C_{13}H_{27}$	H	**B-4**	**8e**	5
9	**6e**	H	$C_{13}H_{27}$	H	**C**	**8e**	31
10	**6f**	H	Ph	H	**B-4**	**8f**	20[c]
11	**6f**	H	Ph	H	**C**	**8f**	48[d]
12	**6g**	H	Me	CH_3	**C**	**8g**	41
13	**6h**	H	Bu	CH_3	**C**	**8h**	22
14	**6i**	H	$C_{13}H_{27}$	CH_3	**C**	**8i**	10

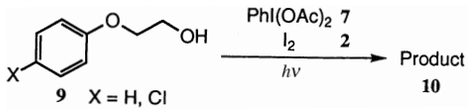
[a] Molar ratios of **6**:**7**:**2** were **B-1** (1.0:1.1:0.5), **B-2** (1.0:1.1:1.1), **B-3** (1.0:2.2:1.1), **B-4** (1.0:1.5:1.1) and irradiation was carried out with a tungsten lamp (500 W) at 60–70 °C. **C**: Molar ratio of **6**:**7**:**2** was 1.0:1.1:1.1 and the reaction was carried out under room light (fluorescent lighting, 40 W) at 15–25 °C. [b] β-Phenethyl iodide was not formed. [c] β-Phenethyl iodide was obtained in 48% yield. [d] β-Phenethyl iodide was obtained in 10% yield.

reactivity differences between (diaroyloxyiodo)benzene and (diacyloxyiodo)benzene.

Synthesis of cyclic aromatic ethers

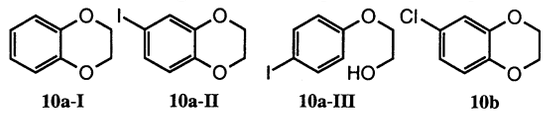
Next, we attempted to cyclize alcohols containing an aromatic ring to the corresponding cyclic aromatic ethers. Initially, 3-phenylpropanol and its analogues were treated with bis(trifluoroacetoxyiodo)benzene and iodine as for the aromatic carboxylic acids. However, cyclic aromatic ethers were not formed; instead, the corresponding aldehydes were obtained.[12]

Table 5 Cyclization of phenoxyethanol



Entry	Alcohol[a]	Ratio (**9**:**7**:**2**)	Conditions[b]	Product[c]	Yield (%)
1	**9a**	1.0:0.5:1.1	**B**	**10a-I**/**10a-II**	16/0
2	**9a**	1.0:1.1:1.1	**B**	**10a-I**/**10a-II**	39/12
3	**9a**	1.0:2.2:1.1	**B**	**10a-I**/**10a-II**	6/22
4	**9a**	1.0:1.1:1.1	**C**	**10a-III**	77
5	**9b**	1.0:1.1:1.0	**B**	**10b**	23

[a] **9a** 2-phenoxyethanol; **9b** 2-(*p*-chlorophenoxy)ethanol. [b] **B**: Irradiation was carried out with a tungsten lamp at 60–70 °C. **C**: Reaction was carried out under room light at room temp. [c] Structure of products:



Further study on the reactivity of (diacetoxyiodo)arenes was carried out as shown in Table 3. The same yields of 6-iodochromane were obtained with 4-methyl-1-(diacetoxyiodo)-benzene, (diacetoxyiodo)benzene and 4-chloro-1-(diacetoxyiodo)benzene. Accordingly, (diacetoxyiodo)benzene was used for the preparation of cyclic aromatic ethers with other alcohols; the results are shown in Table 4. Here, the iodination of the cyclized product, chromane, occurred to give 6-iodochromane with a hypoiodite species derived from (diacetoxyiodo)benzene and iodine. Iodination of electron-rich aromatic rings with [bis(trifluoroacetoxy)iodo]benzene and iodine is known.[13] In primary alcohols such as **6a**, conditions **B** gave the compound **8a** in the best yield. However, secondary and tertiary alcohols such as **6d–i** gave the corresponding cyclized products in better yield under conditions **C** than conditions **B** (entries 7–14); this is because the alcohols were easily oxidized and the corresponding alkoxy radicals undergo facile β-fragmentation. Since reaction conditions **C** were much milder than conditions **B**, the oxidation and β-fragmentation were reduced. The compounds **8f** and **8i** obtained were flavan and tocopherol analogues, respectively.

Thus, various alcohols containing an aromatic ring at γ-position were cyclized to the corresponding 6-iodo cyclic aromatic ethers. However, 2-phenylethanol gave solely benzyl iodide in 43% yield by way of β-fragmentation and 4-phenylbutan-1-ol gave solely 1-phenyltetrahydrofuran in 70% yield by way of a 1,5 H-shift (Barton type reaction), under the same conditions. Even at room temperature, 2-phenylethanol failed to cyclize to 2,3-dihydrobenzofuran.

The same cyclization with lead tetraacetate is known.[3] However, examples of this cyclization are limited and the yields were extremely low. The same cyclization with 2-phenoxyethanol **9a** and a derivative was then studied as shown in Table 5. Use of **9a** gave a mixture of two cyclized products **10a-I** and **10a-II** together with the iodination product **10a-III** (*ca.* 20%, entries 1-3). The reason why a mixture of compounds **10a-I** and **10a-II** was obtained under the same conditions is that the iodine was consumed by the direct iodination of compound **9a** to form compound **10a-III**. A similar reaction with 2-(*p*-chlorophenoxy)-ethanol **9b** gave a low yield of the cyclized product.

An NMR experiment was carried out to elucidate the reaction pathway and to observe the formation of the single or double acetate-exchanged intermediate of (diacetoxyiodo)benzene **7** by 3-phenylpropanol **6a**. When a solution ($CDCl_3$) of **7** and **6a** was examined by ^1H NMR spectroscopy, new signals appeared at δ 8.01 (2 H, d, J 7.9, *ortho*-H), 3.84 (2 H, t, J 6.2, CH_2O) and 2.55 (2 H, t, J 7.3, $PhCH_2$). These signals come from the single acetate-exchanged intermediate **11a**. This equi-

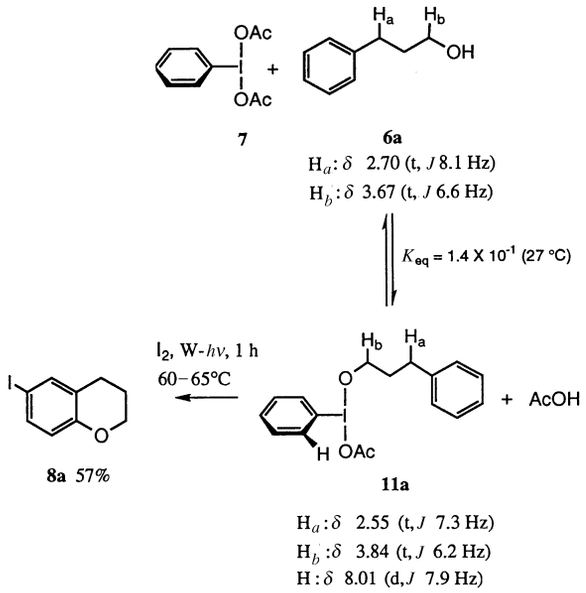


Fig. 3 Formation of single acetate-exchanged intermediate **11a**

librium state was achieved within 15 min after mixing of compounds **7** and **6a**.

The equilibrium constant was determined to be 1.4×10^{-1} at 27 °C. Compound **11a** is the first intermediate to produce the hypoiodite species which generates the corresponding alkoxy radical rapidly even with only irradiation with room light. Meanwhile, the isolation of the single acetate-exchanged intermediate was attempted. The molar ratio of (diacetoxyiodo)benzene–3-phenylpropanol was 2.2:1.0. After a solution of (diacetoxyiodo)benzene and 3-phenylpropanol had been stirred for 30 min, it was evaporated under reduced pressure. The residue dissolved in $CDCl_3$ was examined by ^{1}H NMR, and its spectrum agreed with that of **11a**. After this, the residue was dissolved in 1,2-dichloroethane and when irradiated with a tungsten lamp in the presence of iodine for 1 h at 60–65 °C, gave 6-iodochromane in 57% yield. These results indicated that the new signals belong to compound **11a** which is the first intermediate to produce hypoiodite which generates the corresponding alkoxy radical upon irradiation with room light (fluorescent lighting) or a tungsten lamp.

A plausible reaction mechanism is shown in Scheme 2. After stirring of a mixture of the (diacetoxyiodo)benzene and 3-phenylpropanol in 1,2-dichloroethane, iodine was added to form a hypoiodite species. Cleavage of the I–O bond of the hypoiodite species took place under irradiation with light, to generate the alkoxy radical. This alkoxy radical attacks the aromatic ring, and oxidative aromatization occurs. After the iodination by the hypoiodite species which is formed from (diacetoxyiodo)benzene and iodine, 6-iodochromane is produced.

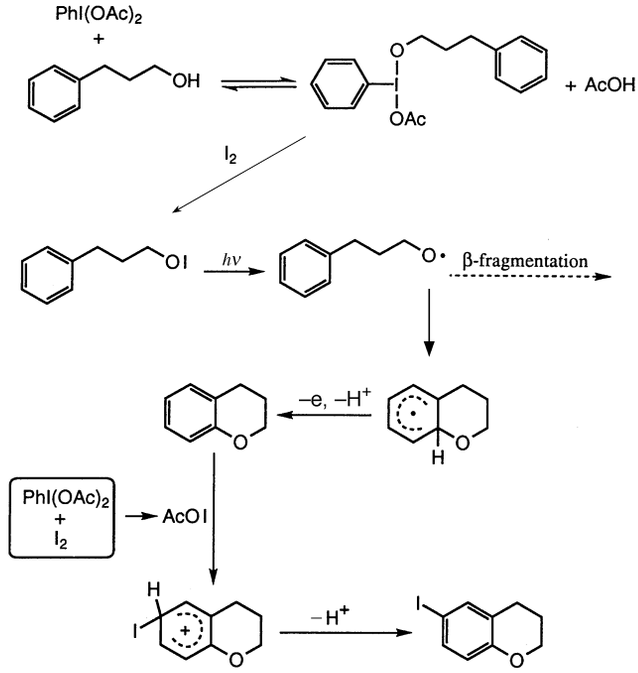
The driving force of the present two types of reaction is the difference in bond dissociation energy of O–H (BDE_{OH} = ~ 110 kcal mol^{-1}) and C–H (BDE_{CH} = ~ 89–96 kcal mol^{-1}).[14]

In conclusion, this method is useful for the photochemical cyclization of aromatic carboxylic acids and alcohols containing an aromatic ring to the corresponding lactones and cyclic ethers under mild reaction conditions in a simple experimental procedure. Furthermore, the (diacyloxyiodo)arene–iodine system has attractive advantages such as lower toxicity and affords better yields than previous methods using lead tetraacetate.

Experimental

General

Microanalyses were performed with a Perkin-Elmer 240B and 240 elemental analysers at the Chemical Analysis Center of



Scheme 2 Plausible reaction mechanism for 6-iodochromane

Chiba University. X-Ray crystallographic data were collected on a Rigaku AFC5S diffractometer with graphite monochromated Cu-Kα radiation. IR Spectra were recorded on a Hitachi-215 spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured with JEOL-JNM-FX270 and JEOL-JNM-GSX-400 spectrometers. Chemical shifts are expressed in ppm downfield from $SiMe_4$ in δ units. *J* Values are given in Hz. Mass spectra were measured with Hitachi M-60 (EI) and JEOL-HX 110A (FAB) mass spectrometers. 3-Nitrobenzyl alcohol was used in the matrix of mass spectra (FAB). Melting points were determined on a Yamato MP-211 melting point apparatus. Wakogel C-200 and C-300 were used for column chromatography, Kieselgel 60 F254 (Merck) was used for TLC, and Wakogel B-5F was used for pTLC.

Materials

[Bis(trifluoroacetoxy)iodo]benzene, (diacetoxyiodo)benzene and most of the aromatic carboxylic acids, primary alcohols and 2-phenoxyethanol are commercially available. 2-Ethylbenzoic acid, 2,5-diisopropylbenzoic acid, and other secondary and tertiary alcohols were prepared by the Grignard reaction. (Diaroyloxyiodo)benzenes were prepared by the acyloxy exchange reaction of (diacetoxyiodo)benzene and aromatic carboxylic acids.[15] 4-Methyl-1-(diacetoxyiodo)benzene and 4-chloro-1-(diacetoxyiodo)benzene were prepared by the literature method.[16] 4-Phenylpropan-2-ol and 2-(4-chlorophenoxy)-ethanol were prepared by the reduction of benzylacetone and 4-chlorophenoxyacetic acid with lithium aluminium hydride.

General conversion of (diaroyloxyiodo)benzenes to the corresponding lactones

A solution of **1** (0.5 mmol), [bis(trifluoroacetoxy)iodo]benzene (0.11 g, 0.25 mmol) and iodine (0.025 g, 0.1 mmol) in dry dichloromethane (5 cm^3) in a Pyrex vessel was irradiated with a high-pressure mercury lamp (400 W) for 5 h at 15–25 °C; the distance between the Hg lamp and the reaction vessel was *ca*. 10 cm. The reaction mixture was poured into sat. aq. $NaHCO_3$ and extracted with dichloromethane (×3). The combined extracts were poured into sat. aq. Na_2SO_3 and extracted with dichloromethane. The extract was dried (Na_2SO_4) and evaporated under reduced pressure and the residual oil was purified by preparative TLC on silica gel using hexane–EtOAc (4:1) as eluent.

General conversion of aromatic carboxylic acids to the corresponding lactones

After a solution of [bis(trifluoroacetoxy)iodo]benzene (0.47 g, 1.1 mmol) and **5** (1.0 mmol) in dry dichloromethane (5 cm^3) had been stirred for 2 h in the dark, iodine (0.025 g, 0.1 mmol) was added to it. The solution was irradiated with a tungsten lamp (500 W) for 2 h at 60–70 °C. The reaction mixture was then poured into sat. aq. $NaHCO_3$, extracted with dichloromethane (×3), and the combined extracts were poured into sat. aq. Na_2SO_3 and extracted with dichloromethane. Finally, the extract was dried (Na_2SO_4) and evaporated under reduced pressure and the residual oil was purified by preparative TLC on silica gel using benzene–EtOAc (30:1) as eluent.

Phthalide 4a. Mp 74.0–75.0 °C. The product was identical with a commercial sample.

3-Methylphthalide 4b. Oil; ν_{max}(neat)/cm^{-1} 2940, 1740, 1590, 1450, 1210, 1030, 760 and 740; δ_H(400 MHz, $CDCl_3$) 1.64 (3 H, d, *J* 6.5, CH_3), 5.57 (1 H, q, *J* 6.5, CH), 7.64 (1 H, d, *J* 7.7, 4-H), 7.53 (1 H, t, *J* 7.7, 6-H), 7.68 (1 H, t, *J* 7.3, 5-H), 7.89 (1 H, d, *J* 7.7, 7-H); δ_C(100 MHz, $CDCl_3$) 20.39 (Cp, CH_3), 77.76 (Ct, CH), 125.75 (Cq, Ar), 121.59, 125.65, 129.07, 134.09 (Ct, Ar) and 151.21 (Cq, CO) [Found (HRMS; FAB): $(M + H)^+$, 149.0627. Calc. for $C_9H_9O_2$: M + H, 149.0603].

3,3-Dimethyl-6-isopropylphthalide 4c-I. Oil; ν_{max}(neat)/cm^{-1} 2930, 1750, 1580, 1490, 1290, 1200, 1035, 800 and 740; δ_H(400 MHz, $CDCl_3$) 1.29 (6 H, d, *J* 7.0, isopropyl-CH_3), 1.65 (6 H, s, CH_3), 3.02 (1 H, septet, *J* 7.0, isopropyl-CH), 7.31 (1 H, d, *J* 8.1, 4-H), 7.53 (1 H, d, *J* 8.1, 5-H) and 7.72 (1 H, s, 7-H); δ_C(100 MHz, $CDCl_3$) 23.92 (Cp, CH_3), 27.40 (Cp, CH_3), 33.98 (Ct, CH), 85.32 (Cq), 120.47 (Ct, Ar), 123.07 (Ct, Ar), 125.48 (Cq, Ar), 133.09 (Ct, Ar), 150.25 (Cq, Ar), 152.75 (Cq, Ar) and 170.17 (Cq, CO) [Found (HRMS; FAB): $(M + H)^+$, 205.1229. Calc. for $C_{13}H_{17}O_2$: *M* + H, 205.1227].

3,4-Dihydro-4-iodo-4-methyl-7-isopropylisocoumarin 4c-II. Oil; ν_{max}(neat)/cm^{-1} 2925, 1750, 1585, 1485, 1290, 1200, 1110, 1030, 800 and 730; δ_H(400 MHz, $CDCl_3$) 1.30 (6 H, d, *J* 7.0, isopropyl-CH_3), 1.85 (3 H, s, CH_3), 3.03 (1 H, septet, *J* 7.0, isopropyl-CH), 3.58 (1 H, d, *J* 11.0, CH_2), 3.64 (1 H, d, *J* 11.0, CH_2), 7.39 (1 H, d, *J* 8.1, 5-H), 7.56 (1 H, d, *J* 8.1, 6-H) and 7.75 (1 H, s, 8-H); δ_C(100 MHz, $CDCl_3$) 12.50 (Cs, CH_2), 23.82 (Cp, CH_3), 25.10 (Cp, CH_3), 33.97 (Ct, CH), 83.95 (Cq), 120.98 (Ct, Ar), 123.23 (Ct, Ar), 126.32 (Cq, Ar), 133.25 (Ct, Ar), 149.42 (Cq, Ar) and 151.21 (Cq, Ar) [Found (HRMS; EI): M^+, 330.0117. Calc. for $C_{13}H_{15}IO_2$: *M*, 330.0117].

3-Phenylphthalide 4d. Mp 113.0–114.0 °C; ν_{max}(KBr)/cm^{-1} 3000, 1740, 1580, 1455, 1280, 1060, 970 and 740; δ_H(400 MHz, $CDCl_3$) 6.41 (1 H, s, CH), 7.27–7.40 (6 H, m, phenyl and 4-H), 7.56 (1 H, t, *J* 7.3, 6-H), 7.65 (1 H, t, *J* 7.3, 5-H) and 7.97 (1 H, d, *J* 7.3, 7-H) [Found (HRMS; EI): M^+, 210.0678. Calc. for $C_{14}H_{10}O_2$: M, 210.0680].

3,4-Benzocoumarin 4e. Mp 91.0–92.0 °C; ν_{max}(KBr)/cm^{-1} 1720, 1600, 1480, 1300, 1205, 1100, 900, 760 and 730; δ_H(400 MHz, $CDCl_3$) 7.31–7.36 (2 H, m, 8- and 10-H), 7.47 (1 H, t, *J* 7.7, 9-H), 7.57 (1 H, t, *J* 8.0, 4-H), 7.81 (1 H, t, *J* 8.0, 5-H), 8.04 (1 H, d, *J* 7.7, 7-H), 8.10 (1 H, d, *J* 8.0, 6-H) and 8.39 (1 H, d, *J* 8.0, 3-H); δ_C(100 MHz, $CDCl_3$) 117.75 (Ct, Ar), 118.02 (Cq, Ar), 121.23 (Cq, Ar), 121.67 (Ct, Ar), 122.76 (Ct, Ar), 124.54 (Ct, Ar), 128.86 (Ct, Ar), 130.42 (Ct, Ar), 130.54 (Ct, Ar), 134.74 (Cq, Ar), 134.83 (Ct, Ar), 151.27 (Cq, Ar) and 161.16 (Cq, CO) (Found: C, 79.63; H, 3.98%. Calc. for $C_{13}H_8O_2$: C, 79.58; H, 4.11%) [Found (HRMS; FAB): $(M + H)^+$, 197.0610. Calc. for $C_{13}H_9O_2$: M + H, 197.0603].

Phenyl salicylate 4f. Oil; ν_{max}(neat)/cm^{-1} 3150, 1680, 1580, 1480, 1300, 1190 and 750; δ_H(400 MHz, $CDCl_3$) 6.97 (1 H, t, *J* 7.0, Ar), 7.04 (1 H, d, *J* 7.7, Ar), 7.22 (2 H, d, *J* 7.7, Ar), 7.31 (1 H, t, *J* 7.7, Ar), 7.45 (2 H, t, *J* 7.7, Ar), 7.52 (1 H, t, *J* 7.0, Ar), 8.08 (1 H, d, *J* 7.0, Ar) and 10.51 (1 H, br s, OH); δ_C(100 MHz, $CDCl_3$) 111.81 (Cq, Ar), 117.81 (Ct, Ar), 119.44 (Ct, Ar), 121.68 (Ct, Ar), 126.38 (Ct, Ar), 129.62 (Ct, Ar), 130.33 (Ct, Ar), 136.46 (Ct, Ar), 150.06 (Cq, Ar), 162.18 (Cq, Ar) and 168.94 (Cq, CO) [Found (HRMS; EI): M^+, 214.0623. Calc. for $C_{13}H_{10}O_3$: *M*, 214.0630].

Phenyl 2-benzoylbenzoate 4g-I. Oil; ν_{max}(neat)/cm^{-1} 3030, 1730, 1670, 1590, 1480, 1270, 1190 and 720; δ_H(400 MHz, $CDCl_3$) 6.79 (2 H, d, *J* 9.0, Ar), 7.15 (1 H, t, *J* 7.5, Ar), 7.26 (2 H, dd, *J* 9.0, 7.5, Ar), 7.42 (2 H, t, *J* 7.3, Ar), 7.49 (1 H, d, *J* 6.0, Ar), 7.56 (1 H, t, *J* 7.3, Ar), 7.63–7.73 (2 H, m, Ar), 7.78 (2 H, d, *J* 7.3, Ar) and 8.21 (1 H, d, *J* 7.7, Ar) [Found (HRMS; FAB): $(M + H)^+$, 303.1019. Calc. for $C_{20}H_{15}O_3$: *M* + H, 303.1021].

General conversion of alcohols into cyclic ethers

With heat. A solution of (diacetoxyiodo)benzene (0.71 g, 2.2 mmol) and **6** (1.0 mmol) was stirred in dry 1,2-dichloroethane (10 cm^3) for 0.25 h, after which iodine (0.28 g, 1.1 mmol) was added to it. The solution was irradiated with a tungsten lamp (500 W) for 2 h at 60–70 °C and then poured into sat. aq. Na_2SO_3 and extracted with EtOAc (×3). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure and the residual oil was purified by preparative TLC on silica gel using hexane–benzene (5:1) as eluent.

Under room light conditions. A solution of (diacetoxyiodo)-benzene (0.35 g, 1.1 mmol) and **6** (1.0 mmol) was stirred in dry 1,2-dichloroethane (10 cm^3) for 0.25 h, after which iodine (0.28 g, 1.1 mmol) was added to it. The solution was stirred with exposure to room light (fluorescent lighting, 40 W) at 15–25 °C for 2 h after which it was poured into sat. aq. Na_2SO_3 and extracted with EtOAc (×3). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure and the residual oil was purified by preparative TLC on silica gel using hexane–benzene (5:1) as eluent.

6-Iodochromane 8a. Oil; ν_{max}(neat)/cm^{-1} 2900, 2850, 1560, 1480, 1230, 1120 and 810; δ_H(400 MHz, $CDCl_3$) 1.97 (2 H, tt, *J* 6.4 and 5.1, 3-H), 2.74 (2 H, t, *J* 6.4, 4-H), 4.16 (2 H, t, *J* 5.1, 2-H), 6.56 (1 H, d, *J* 9.2, 8-H), 7.33 (1 H, d, *J* 9.2, 7-H) and 7.34 (1 H, s, 5-H); δ_C(100 MHz, $CDCl_3$) 21.87 (Cs, CH_2), 24.53 (Cs, CH_2), 66.40 (Cs, CH_2), 81.99 (Cq, Ar), 119.01 (Ct, Ar), 124.99 (Cq, Ar), 135.91 (Ct, Ar), 138.21 (Ct, Ar) and 154.79 (Cq, Ar) (Found: C, 41.65; H, 3.39. Calc. for C_9H_9OI: C, 41.57; H, 3.49%) [Found (HRMS; EI): M^+, 259.9689. Calc. for C_9H_9OI: *M*, 259.9698].

2-Phenyltetrahydrofuran. Oil; ν_{max}(neat)/cm^{-1} 3000, 2950, 2850, 1600, 1490, 1445, 1360, 1060, 760 and 700; δ_H(270 MHz, $CDCl_3$) 1.78–1.88 (1 H, m, 3-H), 1.95–2.08 (2 H, quint, *J* 5.3, 4-H), 2.25–2.40 (1 H, m, 3-H), 3.93 (1 H, q, *J* 6.6, 5-H), 4.09 (1 H, q, *J* 6.6, 5-H), 4.89 (1 H, t, *J* 7.3, 2-H) and 7.22–7.34 (5 H, m, phenyl) [Found (HRMS; EI): M^+, 148.0886. Calc. for $C_{10}H_{12}O$: *M*, 148.0888].

4-Methyl-6-iodochromane 8b. Oil; ν_{max}(neat)/cm^{-1} 2920, 2840, 1560, 1480, 1260, 1220, 1130, 1120, 1040 and 810; δ_H(400 MHz, $CDCl_3$) 1.31 (3 H, d, *J* 7.0, CH_3), 1.70 (1 H, ddd, *J* 15.8, 7.0 and 3.3, 3-H), 2.05 (1 H, ddd, *J* 15.8, 7.0 and 2.2, 3-H), 2.91 (1 H, sextet, *J* 7.0, 4-H), 4.17 (2 H, td, *J* 7.0 and 3.3, 2-H), 6.56 (1 H, d, *J* 8.4, 8-H), 7.34 (1 H, dd, *J* 8.4 and 1.5, 7-H) and 7.43 (1 H, d, *J* 1.5, 5-H); δ_C(100 MHz, $CDCl_3$) 22.04 (Cp, CH_3), 28.37 (Ct, CH), 29.79 (Cs, CH_2), 63.90 (Cs, CH_2), 82.23 (Cq, Ar), 119.11 (Ct, Ar), 130.42 (Cq, Ar), 135.97 (Ct, Ar), 137.27 (Ct, Ar) and 154.27 (Cq, Ar) [Found (HRMS; FAB): M^+, 273.9860. Calc. for $C_{10}H_{11}OI$: *M*, 273.9855].

2-Methyl-6-iodochromane 8c. Mp 43.0–44.0 °C; ν_{max}(KBr)/cm^{-1} 2920, 1550, 1460, 1240, 1110 and 820; δ_H(400 MHz, $CDCl_3$) 1.38 (3 H, dd, *J* 6.2 and 2.9, CH_3), 1.63–1.73 (1 H, m, 3-H), 1.97 (1 H, ddd, *J* 13.5, 7.5 and 2.9, 3-H), 2.67–2.85 (2 H, m, 4-H), 4.07–4.13 (1 H, m, 2-H), 6.56 (1 H, d, *J* 8.0, 8-H), 7.34 (1 H, d, *J* 8.0, 7-H) and 7.35 (1 H, s, 5-H); δ_C(100 MHz, $CDCl_3$) 21.20 (Cs, CH_3), 24.50 (Cs, CH_2), 28.72 (Cs, CH_2), 72.32 (Ct, CH), 81.85 (Cq, Ar), 119.01 (Ct, Ar), 124.64 (Cq, Ar), 135.88 (Ct, Ar), 137.98 (Ct, Ar) and 154.95 (Cq, Ar)

(Found: C, 43.65; H, 3.93. Calc. for $C_{10}H_{11}OI$: C, 43.82; H, 4.04%) [Found (HRMS; EI): M^+, 273.9840. Calc. for $C_{10}H_{11}OI$: *M*, 273.9855].

2-Butyl-6-iodochromane 8d. Oil; ν_{max}(neat)/cm^{-1} 2900, 2830, 1560, 1470, 1240, 1120 and 820; δ_H(400 MHz, $CDCl_3$) 0.92 (3 H, t, *J* 7.1, CH_3), 1.32–2.00 (8 H, m, CH_2 and 3-H), 2.70 (1 H, ddd, *J* 16.7, 5.5 and 3.3, 4-H), 2.79 (1 H, ddd, *J* 16.7, 10.6 and 5.1, 4-H), 3.94 (1 H, tdd, *J* 10.3, 5.5 and 2.2, 2-H), 6.56 (1 H, d, *J* 8.2, 8-H), 7.33 (1 H, d, *J* 8.2, 7-H) and 7.34 (1 H, s, 5-H); δ_C(100 MHz, $CDCl_3$) 14.04 (Cp, CH_3), 22.65 (Cs, CH_2), 24.46 (Cs, CH_2), 26.87 (Cs, CH_2), 27.39 (Cs, CH_2), 34.92 (Cs, CH_2), 76.11 (Ct, CH), 81.71 (Cq, Ar), 119.05 (Ct, Ar), 124.93 (Cq, Ar), 135.82 (Ct, Ar), 137.94 (Ct, Ar) and 155.00 (Cq, Ar) [Found (HRMS; EI): M^+, 316.0323. Calc. for $C_{13}H_{17}OI$: *M*, 316.0324].

2-Tridecyl-6-iodochromane 8e. Mp 31.0–32.0 °C; ν_{max}(KBr)/cm^{-1} 2890, 2810, 1560, 1470, 1230, 1120 and 815; δ_H(400 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 6.8, CH_3), 1.20–1.34 (22 H, br s, tridecyl-CH_2), 1.47–1.73 (3 H, m, tridecyl-CH_2 and 3-H), 1.93–1.99 (1 H, m, 3-H), 2.69 (1 H, ddd, *J* 17.7, 8.2 and 3.3, 4-H), 2.79 (1 H, ddd, *J* 17.7, 11.3 and 5.7, 4-H), 3.91–3.97 (1 H, m, 2-H), 6.56 (1 H, d, *J* 8.4, 8-H), 7.33 (1 H, d, *J* 8.4, 7-H) and 7.34 (1 H, s, 5-H); δ_C(100 MHz, $CDCl_3$) 14.11 (Cp, CH_3), 22.68, 24.46, 25.23, 26.88, 29.35, 29.58, 29.64, 31.90 and 35.23 (Cs, CH_2), 76.12 (Ct, CH), 81.70 (Cq, Ar), 119.06 (Ct, Ar), 124.93 (Cq, Ar), 135.83 (Ct, Ar), 137.94 (Ct, Ar) and 155.01 (Cq, Ar) (Found: C, 59.47; H, 7.95. Calc. for $C_{22}H_{35}OI$: C, 59.73; H, 7.97%) [Found (HRMS; EI): M^+, 442.1736. Calc. for $C_{22}H_{35}OI$: *M*, 442.1733].

2-Phenyl-6-iodochromane 8f. Mp 70.0–73.0 °C; ν_{max}(KBr)/cm^{-1} 2870, 1550, 1460, 1220, 1120, 810, 750 and 700; δ_H(400 MHz, $CDCl_3$) 2.02–2.11 (1 H, m, 3-H), 2.17–2.23 (1 H, m, 3-H), 2.75 (1 H, dt, *J* 15.8 and 4.4, 4-H), 2.94 (1 H, ddd, *J* 15.8, 10.5 and 5.1, 4-H), 5.05 (1 H, dd, *J* 10.3 and 2.6, 2-H), 6.68 (1 H, d, *J* 8.4, 8-H), 7.31–7.36 (5 H, m, phenyl), 7.39 (1 H, d, *J* 8.4, 7-H) and 7.40 (1 H, s, 5-H); δ_C(100 MHz, $CDCl_3$) 24.65 (Cs, CH_2), 29.35 (Cs, CH_2), 77.77 (Ct, CH), 82.30 (Cq, Ar), 119.22 (Ct, Ar), 124.64 (Cq, Ar), 125.89 (Ct, Ar), 127.95 (Ct, Ar), 128.55 (Ct, Ar), 136.08 (Ct, Ar), 137.99 (Ct, Ar), 141.15 (Cq, Ar) and 155.03 (Cq, Ar) (Found: C, 53.46; H, 3.75. Calc. for $C_{15}H_{13}OI$: C, 53.59; H, 3.90%) [Found (HRMS; EI): M^+, 336.0011. Calc. for $C_{15}H_{13}OI$: *M*, 336.0011].

2,2-Dimethyl-6-iodochromane 8g. Oil; ν_{max}(neat)/cm^{-1} 2950, 2900, 1560, 1470, 1260, 1220, 1160, 1120 and 820; δ_H(400 MHz, $CDCl_3$) 1.31 (6 H, s, CH_3), 1.77 (2 H, t, *J* 6.6, 3-H), 2.73 (2 H, t, *J* 6.6, 4-H), 6.54 (1 H, d, *J* 8.6, 8-H), 7.34 (1 H, d, *J* 8.6, 7-H) and 7.34 (1 H, s, 5-H); δ_C(100 MHz, $CDCl_3$) 22.14 (Cs, CH_2), 26.75 (Cp, CH_3), 32.34 (Cs, CH_2), 74.50 (Cq), 81.44 (Cq, Ar), 119.60 (Ct, Ar), 123.79 (Cq, Ar), 135.99 (Ct, Ar), 137.91 (Ct, Ar) and 153.96 (Cq, Ar) (Found: C, 45.46; H, 4.46. Calc. for $C_{11}H_{13}IO$: C, 45.85; H, 4.55%) [Found (HRMS; EI): M^+, 288.0027. Calc. for $C_{11}H_{13}OI$: *M*, 288.0011].

2-Butyl-2-methyl-6-iodochromane 8h. Oil; ν_{max}(neat)/cm^{-1} 2900, 2830, 1560, 1470, 1230, 1120 and 815; δ_H(400 MHz, $CDCl_3$) 0.90 (3 H, t, *J* 7.1, butyl-CH_3), 1.25 (3 H, s, CH_3), 1.28–1.40 (4 H, m, CH_2), 1.51–1.62 (2 H, m, butyl-CH_2), 1.69–1.84 (2 H, m, 3-H), 2.71 (2 H, t, *J* 6.6, 4-H), 6.54 (1 H, d, *J* 8.4, 8-H), 7.33 (1 H, d, *J* 8.4, 7-H) and 7.35 (1 H, s, 5-H) [Found (HRMS; FAB): M^+, 330.0486. Calc. for $C_{14}H_{19}OI$: *M*, 330.0481].

2-Methyl-2-tridecyl-6-iodochromane 8i. Oil; ν_{max}(neat)/cm^{-1} 2890, 2820, 1560, 1470, 1250, 1120 and 820; δ_H(400 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 7.0, tridecyl-CH_3), 1.25–1.29 (27 H, br s, tridecyl-CH_2 and CH_3), 1.72 (1 H, dt, *J* 7.0 and 6.6, 3-H), 1.78 (1 H, dt, *J* 7.0 and 6.6, 3-H), 2.70 (2 H, t, *J* 6.6, 4-H), 6.54 (1 H, d, *J* 8.4, 8-H), 7.34 (1 H, d, *J* 8.4, 7-H) and 7.35 (1 H, s, 5-H); δ_C(100 MHz, $CDCl_3$) 14.11 (Cp, CH_3), 21.85, 22.68 and 23.54 (Cs, CH_2), 24.09 (Cp, CH_3), 29.35, 29.58, 29.64, 30.06, 30.43, 31.92, 39.58 (Cs, CH_2), 76.74 (Cq), 81.29 (Cq, Ar), 119.62 (Ct, Ar), 124.07 (Cq, Ar), 135.95 (Ct, Ar), 137.85 (Ct, Ar) and 153.99 (Cq, Ar) [Found (HRMS; FAB): M^+, 456.1882. Calc. for $C_{23}H_{37}OI$: *M*, 456.1889].

2,3-Dihydro-1,4-benzodioxine 10a-I. Oil; the product was identical with a commercial sample.

6-Iodo-2,3-dihydro-1,4-benzodioxine 10a-II. Oil; ν_{max}(neat)/cm^{-1} 2950, 1570, 1480, 1250, 1120 and 810; δ_H(270 MHz, $CDCl_3$) 4.23 (4 H, s, CH_2), 6.61 (1 H, d, *J* 8.4, 8-H), 7.11 (1 H, dd, *J* 8.4, 2.3, 7-H), 7.18 (1 H, d, *J* 2.3, 5-H) [Found (HRMS; FAB): M^+, 261.9485. Calc. for $C_8H_7O_2I$: *M*, 261.9491].

6-Chloro-2,3-dihydro-1,4-benzodioxine 10b. Oil; ν_{max}(neat)/cm^{-1} 2950, 2900, 1580, 1480, 1245, 1120, 1060 and 800; δ_H(400 MHz, $CDCl_3$) 4.24 (4 H, s, CH_2), 6.78 (1 H, d, *J* 8.4, 8-H), 6.80 (1 H, d, *J* 8.4, 7-H) and 6.87 (1 H, s, 5-H) [Found (HRMS; EI): M^+, 170.0129. Calc. for $C_8H_7O_2{}^{35}Cl$: *M*, 170.0135].

2-(4-Iodophenoxy)ethanol 10a-III. Mp 73.5–74.5 °C; ν_{max}(KBr)/cm^{-1} 3300, 2900, 1580, 1480, 1240, 1080, 1050 and 800; δ_H(400 MHz, $CDCl_3$) 2.10 (1 H, br d, *J* 8.1, OH), 3.96 (2 H, t, *J* 4.0, OCH_2), 4.03 (2 H, dt, *J* 8.1 and 4.0, CH_2OH), 6.69 (2 H, d, *J* 8.8, Ar) and 7.55 (2 H, d, *J* 8.8, Ar) [Found (HRMS; FAB): M^+, 263.9656. Calc. for $C_8H_9O_2I$: *M*, 263.9647].

Determination of equilibrium constant with (diacetoxyiodo)-benzene 7 and 3-phenylpropanol 6a

The reaction of (diacetoxyiodo)benzene (0.142 g, 0.44 mmol) and 3-phenylpropanol (0.027 g, 0.2 mmol) in $CDCl_3$ (0.6 cm^3), with dichloromethane as an internal standard, was followed by ^{1}H NMR spectroscopy (JEOL-GSX-400) at 27 °C. An equilibrium state was achieved within 15 min at 27 °C after mixing of 3-phenylpropanol and (diacetoxyiodo)benzene, since the ratio of 3-phenylpropanol and the single-acetate exchanged intermediate **11a** remained unchanged in each NMR spectrum after 15, 45 and 90 min; **11a**: δ_H(400 MHz, $CDCl_3$) 1.73 (2 H, tt, *J* 7.3 and 6.2, CH_2), 2.00 (3 H, s, CH_3), 2.55 (2 H, t, *J* 7.3, CH_2), 3.84 (2 H, t, *J* 6.2, OCH_2), 7.13–7.30 (5 H, br s, Ph), 7.44–7.60 [3 H, m, Ph(*m* and *p*)] and 8.01 [2 H, d, *J* 7.9, Ph(*o*)].

X-Ray crystal structure determination

A crystal was mounted on a glass fibre and transferred to the diffractometer.

Crystal data

$C_{22}H_{19}O_4I$, $M = 474.29$; monoclinic, $a = 16.912(3)$, $b = 10.6794(8)$, $c = 10.760(4)$ Å, $\beta = 96.11(2)°$, $V = 1932.3(7)$ Å^3 [from 2θ values of 20 centred reflections ($39.3 \leq 2\theta \leq 44.3°$, $\lambda = 1.541\,84$ Å, $T = 298$ K)], space group *C*2/*c* (No. 15), $Z = 4$, $D_x = 1.630$ g cm^{-3}, colourless prismatic crystal 0.4 × 0.2 × 0.2 mm, μ(Cu-Kα) = 13.23 mm^{-1}.

Data collection and processing

Rigaku AFC5S four-circle diffractometer, graphite-monochromated Cu-Kα X-radiation, ω–2θ scans with ω scan width (1.47 + 0.30 tan θ)°; 1587 reflections measured ($2\theta_{max} = 120°$), 1529 unique (merging $R = 0.048$), giving 1342 with $F \geq 6\sigma(F)$ which were retained in all calculations. No crystal decay was observed.

Structure solution and refinement

The structure was solved by heavy-atom methods and expanded by Fourier techniques. At isotropic convergence calculated corrections (min. 0.739, max. 1.000) for absorption were applied using DIFABS.[17] Full-matrix least-squares refinement on *F* with all non-H atoms anisotropic and hydrogen atoms included at calculated positions. The weighting scheme gave satisfactory agreement analyses. Final $R = 0.028$, $R_w = 0.038$, $S = 1.13$ for 124 refined parameters. The final ΔF synthesis showed no peaks outside the range −0.47 to 0.41 e Å^{-3}. All calculations were performed using TEXSAN.[18]

Full crystallographic details for this study have been

deposited with the Cambridge Crystallographic Data Centre.† Any request for this material should be accompanied by a full bibliographic reference together with the reference number CCDC 207/73.

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† For details of the scheme, see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1.

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