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# Synthesis of lithium ω-(*m*- and *p*-lithiophenoxy)alkoxides modified with magnesium 2-ethoxyethoxide. Crystal structures of bis[4-(2-hydroxyethoxy)phenyl]mercury and bis[4-(3-hydroxypropoxy)phenyl]mercury

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**Abstract**

*m*- and *p*-Chlorinated ω-phenoxyalcohols **1**, were transformed into the corresponding lithium ω-(*m*- and *p*-lithiophenoxy)alkoxides **4**, respectively, by successive deprotonation with *n*-butyllithium and subsequent chlorine–lithium exchange by lithium naphthalene radical anion in THF–methylcyclohexane. Lithium 2-(4-lithiophenoxy)ethoxide (**4a′**) was also prepared by bromine–lithium exchange of 2-(4-bromophenoxy)ethanol (**2a′**) with two equivalents of *n*-butyllithium. The organolithiums were modified with magnesium 2-ethoxyethoxide in order to avoid *ortho*-metallation of the above-mentioned substituted arenes. Subsequent reaction of these intermediates with the electrophiles carbon dioxide, benzophenone, benzonitrile and 0.5 equivalents of mercuric chloride yielded the expected *m*- and *p*-substituted (ω-hydroxyalkoxy)benzenes in yields ranging from 50 to 75%. The crystal structures of the organomercurials **8a′** and **8b′** have been determined and revealed the Hg atom to occupy a crystallographic center of symmetry in a linear C–Hg–C arrangement. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Phenoxyalcohols; Lithium naphthalene; Lithium; Magnesium; Mercury; Crystal structure

## 1. Introduction

An additional functionality on lithium reagents considerably increases the synthetic utility of the organolithium compounds and a number of such reagents have already been reported [1]. The latter reagents may be classified into two broad categories. The first category includes those lithium reagents that derive from displacement of a heteroatom or a heteroatom-bearing group by lithium, while the second includes organometallic reagents derived from 'directed metallation'. Both categories suffer from certain limitations. The synthesis of organolithiums belonging to the first category usually requires reductive conditions with which the additional functional group should therefore be compatible. Reagents derived from directed metallation are usually aryllithiums possessing special functionalities which are responsible for directing the site of metallation of the aromatic rings [1b]. Recently, we reported the *ortho*-directed lithiation of ω-phenoxyalcohols and ω-phenoxyalkanethiols [2]. The present report provides information on the lithiation of the analogous *m*- and *p*-halogenated ω-phenoxyalcohols **1**, **2** by halogen–lithium exchange using *n*-butyllithium or by reductive lithiation with lithium naphthalene radical anion. The applications and advantages of lithium arene radical anions and arene-catalyzed lithiation reactions have been previously reported [1c,3].

One of the possible competing reactions to the halogen–lithium exchange of *m*- or *p*-halogenated ω-phenoxyalcohols is the *ortho*-lithiation of the aromatic

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ring. Organoalkali reagents form complexes with magnesium 2-ethoxyethoxide that exhibit normal organometallic behavior but diminished reactivity compared with the uncomplexed compounds [4], and so, in order to suppress the undesired reactions, we decided to carry out the halogen–lithium displacements in the above-mentioned systems in the presence of magnesium 2-ethoxyethoxide. This reagent has previously been successfully used in other similar cases [5].

The synthetic utility of these new reagents for carbon–carbon or carbon–metal bond formation has been demonstrated by their reaction with various electrophiles. In addition, the crystal structures of two organomercurials, prepared via the above-mentioned intermediates, are reported.

## 2. Results and discussion

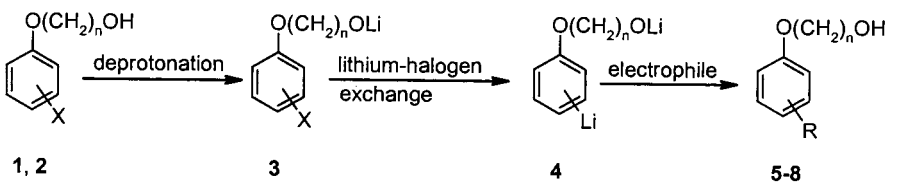
### 2.1. General considerations

The general synthetic strategy employed in the present work is outlined in Scheme 1.

Displacement of a chlorine atom in a *meta* position can be considered as something of a challenge since the originally formed organolithium **4** could also metallate the *meta*-chloro derivative at the highly activated site between the two *ortho*-directing groups with the formation of a benzyne precursor **9** (Scheme 2). Thus, application of conventional reductive lithiation for the displacement of the chlorine atom in **3** should lead to more than one lithiated product.

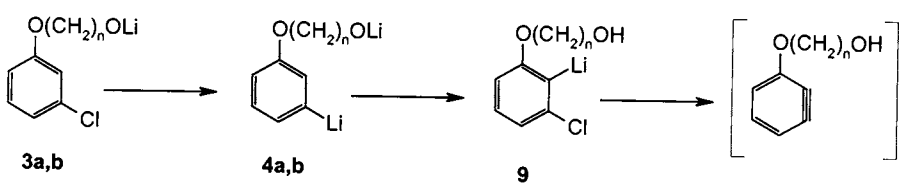
The same could be said for the reaction involving bromine–lithium exchange in cases such as **4′** (Scheme 3).

Indeed, **3′** presents more than one site for attack by the lithiating agent and the situation is complicated further by the instability of *para* compared with *ortho* lithiated products. We reasoned that in order to suppress or even eliminate the undesired reactions, both in the reductive lithiation or in the halogen–metal interchange reactions, we should suppress the metallating abilities of **4**, **4′** and of butyllithium. This can be achieved by carrying out these reactions in the presence of magnesium 2-ethoxyethoxide [5]. Evidently in this case, the BuLi–$Mg(OCH_2CH_2OEt)_2$ complex exhibits a reactivity profile analogous to that of the organomagnesium reagent, although it retains the ability to undergo halogen–metal interchange that is characteristic of organolithium compounds.

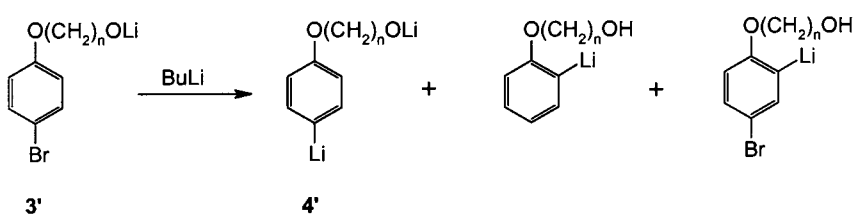



**1a:** X = *m*-Cl, n = 2; **1b:** X = *m*-Cl, n = 3
**1a'**: X = *p*-Cl, n = 2; **1b'**: X = *p*-Cl, n = 3
**2a'**: X = *p*-Br, n = 2

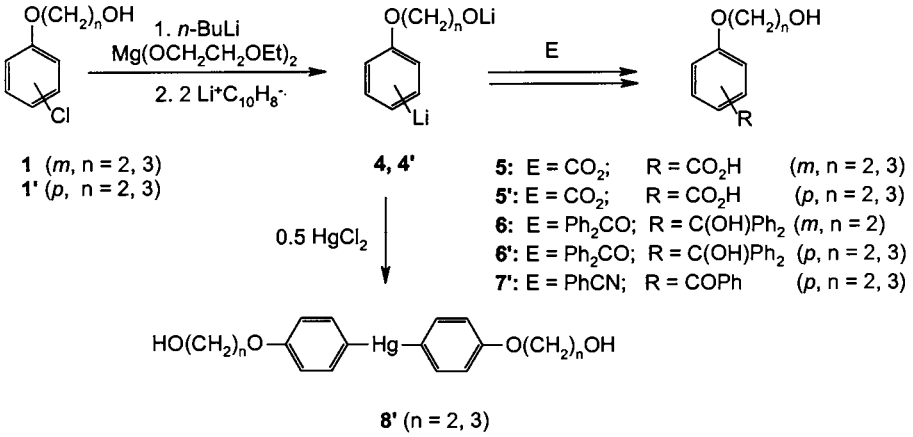
Scheme 1.




Scheme 2.




Scheme 3.




Scheme 4.

Table 1
Reductive cleavage of ω-(*m*- and *p*-chlorophenoxy)alcohols **1**, **1′** and bromine–lithium exchange of 2-(4-bromophenoxy)ethanol (**2a′**). Reactions of organolithiums **4**, **4′** with electrophiles

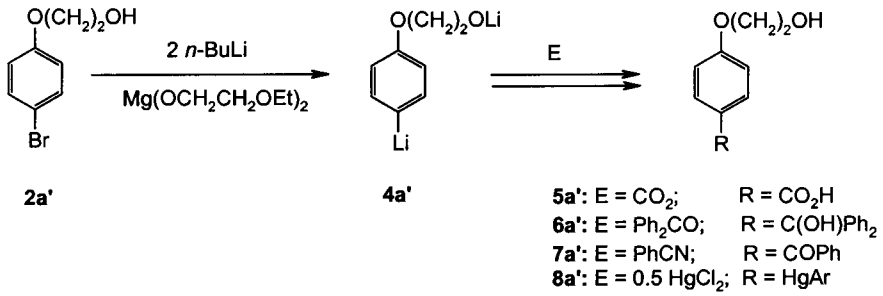
| Haloalcohol | Organolithium | Electrophile | Product | Yield (%) | M.p. (°C) (recr. solv.) |
|---|---|---|---|---|---|
| **1a**: *m*, *n* = 2 | **4a** | $CO_2$ | **5a** | 50 | 106–108 (toluene) [a] |
| **1b**: *m*, *n* = 3 | **4b** | $CO_2$ | **5b** | 63 | 105–108 (toluene) |
| **1a′**: *p*, *n* = 2 | **4a′** | $CO_2$ | **5a′** | 72 | 173–175 (toluene) [b] |
| **2a′** | **4a′** | $CO_2$ | **5a′** | 66 | 173–175 (toluene) [b] |
| **1b′**: *p*, *n* = 3 | **4b′** | $CO_2$ | **5b′** | 73 | 136–138 ($CH_2Cl_2$–hexane) |
| **1a**: *m*, *n* = 2 | **4a** | $Ph_2CO$ | **6a** | 57 | 123–125 (toluene–hexane) |
| **1a′**: *p*, *n* = 2 | **4a′** | $Ph_2CO$ | **6a′** | 74 | 104–105 (toluene) |
| **2a′** | **4a′** | $Ph_2CO$ | **6a′** | 72 | 104–105 (toluene) |
| **1b′**: *p*, *n* = 3 | **4b′** | $Ph_2CO$ | **6b′** | 68 | 68–70 (toluene–hexane) |
| **1a′**: *p*, *n* = 2 | **4a′** | PhCN | **7a′** | 60 | 80–82 (toluene–hexane) [c] |
| **2a′** | **4a′** | PhCN | **7a′** | 55 | 80–82 (toluene–hexane) |
| **1b′**: *p*, *n* = 3 | **4b′** | PhCN | **7b′** | 58 | 73–75 (ether) |
| **1a′**: *p*, *n* = 2 | **4a′** | $HgCl_2$ | **8a′** | 75 | 168–170 (acetone) |
| **2a′** | **4a′** | $HgCl_2$ | **8a′** | 75 | 168–170 (acetone) |
| **1b′**: *p*, *n* = 3 | **4b′** | $HgCl_2$ | **8b′** | 67 | 150–152 (isopropanol) |

[a] Lit. [9], m.p. 111°C.
[b] Lit. [9], m.p. 177°C.
[c] Lit. [11], m.p. 84–85°C.

### *2.2. Chlorine–lithium exchange of m- and p-chlorinated ω-phenoxyalcohols **1**, **1′** by lithium naphthalene radical anion*

Attempted conversion of lithium *m*- and *p*-chlorinated ω-phenoxyalcoholates **3**, **3′** to the corresponding lithium derivatives with lithium metal, under various reaction conditions, or by conventional reductive lithiation with lithium naphthalene radical anion, led to very low yields of the corresponding organolithiums, due to reasons discussed in the previous section. However, when reductive lithiation was carried out in the presence of one equivalent of magnesium 2-ethoxyethoxide and the organolithium was subsequently carboxylated, yields of the expected substituted benzoic acids **5**, **5′** ranging between 50 and 73% were realized. On the other hand, chlorine–lithium exchange of the chlorinated ω-phenoxyalcohols **1**, **1′** proceeded in good yields using two equivalents of lithium naphthalene radical anion, after initially treating the starting materials with *n*-butyllithium in order to form the corresponding phenoxyalkoxides (Scheme 4). Chlorine–lithium exchange is very fast and is complete after 10–30 min at temperatures between −70 and −20°C. The completion of the reaction was clearly indicated by the disappearance of the dark green colour of the radical anion solution.

The yields of lithiated products **4**, **4′** were determined by carboxylation and subsequent acidic hydrolysis forming 3- and 4-(ω-hydroxyalkoxy)benzoic acids **5**, **5′**, respectively, in yields ranging between 50 and 73% (Table 1). The derivatisation of **4**, **4′** with benzophenone yielded the primary–tertiary diols **6**, **6′**, respectively. Reaction of **4′** with benzonitrile following by acidic hydrolysis yielded the ω-(4-benzoylphe-




Scheme 5.

noxy)alcohols **7′**. In addition to C–C bond formation, dilithiated species **4′** were also applied to C–metal bond formation by their reaction with 0.5 equivalent of mercury chloride, yielding hydroxy-substituted organomercurials **8′**.

### 2.3. Bromine–lithium exchange of 2-(4-bromophenoxy)ethanol (2a′) by n-butyllithium

Lithium 2-(4-lithiophenoxy)ethoxide (**4a′**) was also prepared by bromine–lithium exchange of 2-(4-bromophenoxy)ethanol (**2a′**) with two equivalents of *n*-butyllithium in THF–methylcyclohexane, in the presence of magnesium 2-ethoxyethoxide (Scheme 5). It should be stressed that, in the absence of magnesium alkoxide, the analogous bromine–lithium exchange of *p*-bromoanisole in THF, using *n*-butyllithium, yielded virtually no *para*-substituted aryllithium [5a].

Organolithium **4a′** prepared from **2a′** using this method was quenched with the electrophiles carbon dioxide, benzophenone, benzonitrile and 0.5 equivalents of mercury chloride, yielding the compounds **5a′**, **6a′**, **7a′** and **8a′**, respectively (Table 1). The yields range between 55 and 75%, and they are close to the corresponding yields of compounds **5a′**–**8a′**, prepared using the lithium naphthalene radical anion.

### 2.4. Crystal structures of the organomercurials 8a′ and 8b′

Suitable crystals of **8a′** and **8b′** for X-ray crystal structure determination were obtained by recrystallization from acetone and isopropanol, respectively. The structures of molecules **8a′** and **8b′** (Fig. 1) are as shown with coplanar phenyl rings and the Hg atom to occupy a crystallographic center of symmetry, similarly to the structures of the analogues bis[*o*-(ω-hydroxyalkoxy)phenyl]mercury compounds [2a]. The C(1)–Hg distances in molecules **8a′** and **8b′** of 2.067 and 2.072 Å, respectively, are normal for these types of molecules. Selected bond distances, angles and torsion angles for **8a′** and **8b′** are presented in Table 2.

## 3. Experimental

### 3.1. General

The chlorinated ω-phenoxyalcohols **1**, **1′** were prepared by the reaction of chlorinated sodium phenoxide, prepared from *m*- or *p*-chlorophenol and aqueous NaOH, with the appropriate ω-haloalcohol according to a known procedure [6]. 2-(4-Bromophenoxy)ethanol (**2a′**) was synthesized by acidic hydrolysis of 2-(4-bromophenoxy)ethyl acetate, which in turn was prepared by *para*-bromination of 2-phenoxyethanol in the presence of glacial acetic acid, following a known procedure [7]. The halogenated phenoxyalcohols **1a**, **1b**, **1a′**, **1b′** and **2a′** are known compounds [8]. The lithium naphthalene radical anion used for lithiation reactions was freshly prepared in THF in a concentration of 1.0 M, according to a known procedure [3d]. *n*-BuLi was

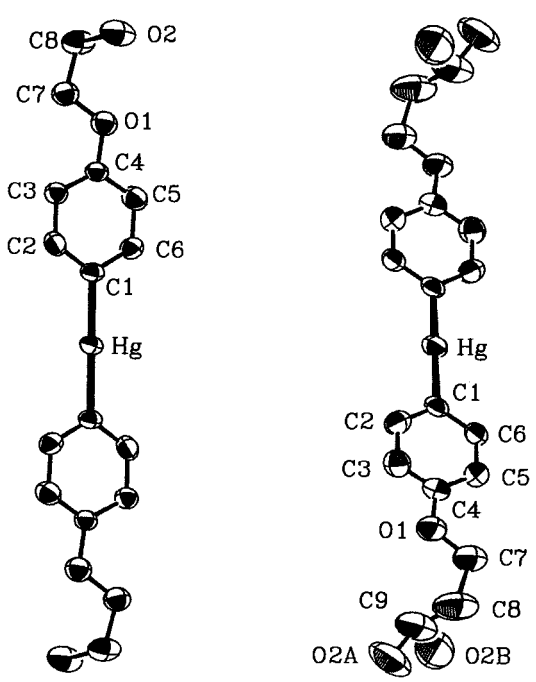



Fig. 1. ORTEP drawings of **8a′** and **8b′** at the 50% probability level. The hydrogen atoms are omitted for clarity.

Table 2
Selected bond distances (Å), bond angles (°) and torsion angles (°) for **8a′** and **8b′**

| | **8a′** | **8b′** |
|---|---|---|
| *Bond distances* | | |
| HG–C(1) | 2.067(6) | 2.072(7) |
| C(4)–O(1) | 1.376(7) | 1.360(8) |
| O(1)–C(7) | 1.411(1) | 1.420(1) |
| C(8)–O(2) | 1.430(9) | |
| C(9)–O(2A) | | 1.310(1) |
| C(9)–O(2B) | | 1.310(1) |
| *Bond angles* | | |
| HG–C(1)–C(2) | 123.5(5) | 120.6(5) |
| C(3)–C(4)–O(1) | 124.6(6) | 114.9(6) |
| C(7)–C(8)–O(2) | 109.6(6) | |
| C(8)–C(9)–O(2A) | | 133.0(1) |
| C(8)–C(9)–O(2B) | | 109.0(1) |
| *Torsion angles* | | |
| C(3)–C(4)–O(1)–C(7) | 7 | −179 |
| C(4)–O(1)–C(7)–C(8) | 171 | 179 |
| O(1)–C(7)–C(8)–O(2) | 75 | |
| O(1)–C(7)–C(8)–C(9) | | −62 |
| C(7)–C(8)–C(9)–O(2) | | 171(−75) |

[a] In the case of disorder of the hydroxyl group the second value is given in parentheses.

prepared from lithium metal and *n*-BuCl in methylcyclohexane. Lithiation reactions were performed in standard glassware with ground joints under argon. THF was distilled from $LiAlH_4$. The organic extracts of all compounds prepared in this paper were dried over $Mg_2SO_4$. NMR: Bruker AC 300 or Varian FT 80; $^1$H- and $^{13}$C-NMR shifts were referenced to the solvents. DEI MS: Finnigan MAT 95Q. Melting points were measured on a Büchi melting point apparatus and were not corrected.

### 3.2. Reductive lithiations of *1*, *1′* by lithium naphthalene radical anion

#### 3.2.1. Typical procedure

*3.2.1.1. Lithium 2-(3-lithiophenoxy)ethoxide (**4a**).* To a suspension of magnesium 2-ethoxyethoxide (4 g, 19.8 mmol) in THF (10 ml) under argon was added *n*-BuLi (10.9 ml of 1.86 M solution in methylcyclohexane, 20.3 mmol) at −78°C, and the mixture stirred for 15 min at this temperature and then for 2 h at room temperature (r.t.). A solution of 2-(3-chlorophenoxy)ethanol (**1a**) (3.45 g, 20 mmol) in THF (15 ml) was then added at −78°C and the mixture stirred for 15 min, after which a solution of freshly prepared lithium naphthalene radical anion (40 mmol) in THF (40 ml) was added slowly over 20 min. The addition was carried out at such a rate that the temperature did not rise above −50°C. During the addition, the dark green color of lithium naphthalene solution turned to red–brown. The mixture was then warmed slowly to r.t. and the organolithium **4a** quenched with a given electrophile (vide infra).

### 3.3. Bromine–lithium exchange of *2a′* by *n*-butyllithium

#### 3.3.1. Lithium 2-(4-lithiophenoxy)ethoxide (*4a′*)

To a suspension of magnesium 2-ethoxyethoxide (2 g, 9.9 mmol) in THF (5 ml) under argon was added *n*-BuLi (10.9 ml of 1.86 M solution in methylcyclohexane, 20.3 mmol) at −78°C, and the mixture stirred for 15 min at this temperature and for 2 h at r.t. A solution of 2-(4-bromophenoxy)ethanol (**2a′**) (2.2 g, 10 mmol) in THF (10 ml) was then added at −78°C and the mixture stirred for 30 min at this temperature and for 1 h with ice–water bath cooling. The organolithium **4a′** was then quenched with a given electrophile (vide infra).

### 3.4. Carboxylation of dilithiated species *4*, *4′*. Synthesis of *m*- and *p*-(ω-hydroxyalkoxy)benzoic acids *5*, *5′*

#### 3.4.1. Typical procedure

*3.4.1.1. 3-(2-Hydroxyethoxy)benzoic acid (**5a**).* The mixture of **4a** in THF, prepared from **1a** (20 mmol) as described above, was poured rapidly into a beaker containing a slurry of crushed dry ice and anhydrous ether. When the carboxylation mixture had reached r.t., water was added and the volume was reduced by evaporation. After filtration, the aqueous phase was washed with toluene and hexane and acidified with 20% $H_2SO_4$. The product was extracted with ether (4 × 50 ml) and dried. After removing the drying agent, the extract was evaporated yielding **5a** (1.82 g, 50%) as a white solid which was recrystallized from toluene, m.p. 106–108°C (lit. [9] m.p. 111°C). $^1$H-NMR ($CD_3OD$): δ 7.77–6.80 (m, 4H, Ar), 4.85 (s, 2H, OH and COOH), 4.20–3.87 (m, 4H, $(CH_2)_2$). $^{13}$C{$^1$H}-NMR ($CD_3OD$): δ 167.76 (C=O), 158.38, 131.19, 128.55, 121.23, 118.69 and 114.32 (Ar), 68.77 and 59.64 ($OCH_2$ and $CH_2OH$).

*3.4.1.2. 3-(3-Hydroxypropoxy)benzoic acid (**5b**).* $^1$H-NMR ($CD_3OD$): δ 7.64–6.90 (m, 4H, Ar), 4.87 (s, 2H, OH and COOH), 4.10 (t, $^3J = 6.2$ Hz, 2H, $OCH_2$), 3.74 (t, $^3J = 6.2$ Hz, 2H, $CH_2O$), 2.12-1.83 (m, 2H, $CH_2$). $^{13}$C{$^1$H}-NMR ($CD_3OD$): δ 167.70 (C=O), 158.30, 131.09, 128.59, 121.19, 118.60 and 114.40 (Ar), 67.70 and 58.58 ($OCH_2$ and $CH_2OH$), 32.25 ($CH_2$). Anal. Calc. for $C_{21}H_{20}O_3$: C, 61.22; H, 6.16. Found: C, 61.05; H, 6.31%.

*3.4.1.3. 4-(2-Hydroxyethoxy)benzoic acid (**5a′**) [9].* $^1$H-NMR ($CD_3OD$): δ 7.98 and 7.01 (sym. dd, 4H, Ar), 4.85 (s, 2H, OH and COOH), 4.20–3.84 (m, 4H,

$(CH_2)_2$). $^{13}C\{^1H\}$-NMR ($CD_3OD$): $\delta$ 168.05 (C=O), 160.10, 134.27, 125.62 and 116.74 (Ar), 71.28 and 61.98 ($OCH_2$ and $CH_2OH$).

*3.4.1.4. 4-(3-Hydroxypropoxy)benzoic acid (**5b′**) [10].* $^1H$-NMR ($CD_3OD$): $\delta$ 7.91 and 6.98 (sym. dd, 4H, Ar), 4.74 (s, 2H, OH and COOH), 4.15 (t, $^3J = 6.2$ Hz, 2H, $OCH_2$), 3.74 (t, $^3J = 6.2$ Hz, 2H, $CH_2O$), 2.15–1.84 (m, 2H, $CH_2$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 167.91 (C=O), 162.41, 130.84, 121.91 and 113.21 (Ar), 64.08 and 57.49 ($OCH_2$ and $CH_2OH$), 31.14 ($CH_2$).

### *3.5. Reaction of **4**, **4′** with benzophenone. Synthesis of carbinols **6**, **6′***

#### *3.5.1. Typical procedure*

*3.5.1.1. Diphenyl-[m-(2-hydroxyethoxy)phenyl]methanol (**6a**).* To a mixture of **4a** in THF, prepared from **1a** (20 mmol) as described above, was added a solution of benzophenone (3 g, 16.5 mmol) in THF (10 ml), with ice–water bath cooling, after which the reaction mixture was stirred at r.t. for 1 h. Water was then added and after filtration to remove $Mg(OH)_2$, the product was extracted with toluene and dried. After filtration, the solvent was removed by evaporation and the residue was heated under vacuum to remove naphthalene and the liberated 2-ethoxyethanol. The remaining viscous oil was treated with hexane yielding **6a** (3 g, 57%) as a white solid, which was recrystallized from toluene–hexane, m.p. 123–125°C. $^1H$-NMR ($CD_3OD$): $\delta$ 7.38–6.79 (m, 14H, Ar), 4.07–3.80 (m, 4H, $(CH_2)_2$), 2.06 and 1.67 (brs, 2H, $2 \times$ OH). $^{13}C\{^1H\}$-NMR ($CD_3OD$): $\delta$ 157.94, 148.46, 146.69, 127.57, 127.24, 126.60, 125.97, 120.07, 114.15 and 112.04 (Ar), 80.90 (CHOH), 68.53 and 59.70 ($OCH_2$ and $CH_2OH$). Anal. Calc. for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.59; H, 6.31%.

*3.5.1.2. Diphenyl-[4-(2-hydroxyethoxy)phenyl]methanol (**6a′**).* $^1H$-NMR ($CDCl_3$): $\delta$ 7.44–6.80 (m, 14H, Ar), 4.04–3.90 (m, 4H, $(CH_2)_2$), 3.00 and 2.22 (brs, brs, 2H, $2 \times$ OH). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 157.84, 147.21, 139.90, 129.39, 127.92, 127.19 and 114.01 (Ar), 81.78 (CHOH), 69.39, 61.43 ($OCH_2$ and $CH_2OH$). Anal. Calc. for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.55; H, 6.36%.

*3.5.1.3. Diphenyl-[4-(3-hydroxypropoxy)phenyl]methanol (**6b′**).* $^1H$-NMR ($CDCl_3$): $\delta$ 7.44–6.80 (m, 14H, Ar), 4.09 (t, $^3J = 5.8$ Hz, 2H, $OCH_2$), 3.80 (t, $^3J = 5.9$ Hz, 2H, $CH_2O$), 2.21–1.85 (m, 4H, $CH_2$ and $2 \times$ OH). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 157.79, 147.29, 139.76, 129.30, 127.98, 127.10 and 114.10 (Ar), 81.67 (CHOH), 68.5 and 61.58 ($OCH_2$ and $CH_2OH$), 32.43 ($CH_2$). Anal. Calc. for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 78.85; H, 6.67%.

### *3.6. Reaction of **4′** with benzonitrile. Synthesis of ω-(4-benzoylphenoxy)alcohols (**7′**)*

#### *3.6.1. Typical procedure*

*3.6.1.1. 2-(4-Benzoylphenoxy)ethanol (**7a′**).* To a mixture of **4a′** in THF, prepared from **1a′** (10 mmol) as described above, was added a solution of benzonitrile (1 g, 9.7 mmol) in THF (10 ml), with ice–water bath cooling, after which the reaction mixture was stirred at r.t. overnight. Water was then added and, after filtration, the product was extracted with toluene. The organic phase was treated with 3.6 N aqueous solution HCl (15 ml), the aqueous phase was separated and refluxed for 2 h. The product was extracted with toluene, washed with water and dried. After filtration, the solvent was removed by evaporation. The remaining viscous oil was treated with hexane, yielding **7a′** (1.4 g, 60%) as a white solid, which was recrystallized from toluene–hexane, m.p. 80–82°C (lit. [11] m.p. 84–85°C). The $^1H$- and $^{13}C$-NMR spectra were in accordance with those previously reported [11].

*3.6.1.2. 3-(4-Benzoylphenoxy)propanol (**7b′**).* $^1H$-NMR ($CDCl_3$): $\delta$ 7.90–6.88 (m, 9H, Ar), 4.17 (t, $^3J = 6.1$ Hz, 2H, $OCH_2$), 3.91 (t, $^3J = 6.2$ Hz, 2H, $CH_2O$), 2.20–1.94 (m, 2H, $CH_2$), 2.55 (brs, 1H, OH). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ 195.76 (C=O), 162.80, 138.29, 132.56, 131.96, 130.04, 129.67, 128.23 and 114.16 (Ar), 65.47 and 59.29 ($OCH_2$ and $CH_2OH$), 32.06 ($CH_2$). Anal. Calc. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.69; H, 6.34%.

### *3.7. Reaction of **4′** with mercury chloride. Synthesis of bis[4-(ω-hydroxyalkoxy)phenyl]mercuric compounds **8′***

#### *3.7.1. Typical procedure*

*3.7.1.1. Bis[4-(2-hydroxyethoxy)phenyl]mercury (**8a′**).* To a mixture of **4a′** in THF, prepared from **1a′** (20 mmol) as described above, was added dropwise a solution of mercury chloride (2.3 g, 8.5 mmol) in THF (20 ml), with ice–water bath cooling, after which the reaction mixture was stirred at r.t. overnight. The work-up procedure was as described for **6a**. Purification of the crude product was carried out by recrystallization from acetone yielding **8a′** (3.03 g, 75%) as a white solid, m.p. 168–170°C. $^1H$-NMR (DMSO-$d_6$): $\delta$ 7.49 and 6.99 (sym. dd, 4H, Ar), 4.87 (t, $^3J = 5.5$ Hz, 1H, OH), 4.01 (t, $^3J = 5.1$ Hz, 2H, $OCH_2$), 3.79–3.74 (m, 2H, $CH_2O$). $^{13}C\{^1H\}$-NMR (DMSO-$d_6$): $\delta$ 162.46, 157.96, 138.75 and 114.10 (Ar), 69.04 and 59.62 ($OCH_2$ and $CH_2OH$). DEI MS: $m/z$ (relative intensity) 476 ($M^+$; $C_{16}H_{18}^{202}HgO_4$, 100), 431 (5), 388 (34), 339 (5), 293 (14),

137 (59), 93 (52), 65 (39). HRMS: Anal. Calc. for $C_{16}H_{18}HgO_4$ 476.0930. Found 476.0921.

*3.7.1.2. Bis[4-(3-hydroxypropoxy)phenyl]mercury (**8b′**).* $^1$H-NMR (DMSO-$d_6$): $\delta$ 7.48 and 6.98 (sym. dd, 4H, Ar), 4.58 (s, 1H, OH), 4.06 (t, $^3J = 6.20$ Hz, 2H, $OCH_2$), 3.64–3.38 (m, 2H, $CH_2O$), 1.93–1.89 (m, 2H, $CH_2$). $^{13}$C{$^1$H}-NMR (DMSO-$d_6$): $\delta$ 162.14, 157.70, 138.49 and 113.80 (Ar), 63.83 and 57.08 ($OCH_2$ and $CH_2OH$), 31.92 ($CH_2$). DEI MS: $m/z$ (relative intensity) 504 ($M^+$; $C_{18}H_{22}^{202}HgO_4$, 100), 446 (13), 388 (36), 293 (12), 151 (32), 94 (68), 65 (32). HRMS: Anal. Calc. for $C_{18}H_{22}HgO_4$ 504.1226. Found 504.1225.

Table 3
Numerical data of the structure determination for **8a′** and **8b′**

| Compound | **8a′** | **8b′** |
|---|---|---|
| Formula | $Hg(C_8H_9O_2)_2$ | $Hg(C_9H_{11}O_2)_2$ |
| Formula weight | 474.9 | 502.96 |
| $a$ (Å) | 13.645(3) | 11.279(2) |
| $b$ (Å) | 5.000(1) | 4.9039(8) |
| $c$ (Å) | 11.203(2) | 31.551(9) |
| $\beta$ (°) | 99.77(2) | 95.96(2) |
| $V$ (Å$^3$) | 753.3(3) | 1735.7(6) |
| $Z$ | 2 | 4 |
| $D_{calc.}$ (Mg m$^{-3}$) | 2.093 | 1.924 |
| $D_{measd.}$ (Mg m$^{-3}$) | 2.00 | 1.91 |
| Space group | $P2_1/c$ | $A2/n$ |
| Crystal dimensions (mm) | $0.1 \times 0.03 \times 0.38$ | $0.03 \times 0.31 \times 0.42$ |
| $\mu$ (mm$^{-1}$) | 10.195 | 8.851 |
| Transmission factors | 0.7366/0.3465 | 0.7403/0.1376 |
| Scan speed (deg min$^{-1}$) | 1.5–15.0 | 1.8–18.0 |
| Scan range (°) | 1.6 plus $\alpha_1$–$\alpha_2$ | 1.7 plus $\alpha_1$–$\alpha_2$ |
| 2θ limit (°) | 53.0 | 50.0 |
| Data collected | 1449 | 2296 |
| Data unique | 1324 | 1810 |
| Data used | 1324 | 1292 |
| $F_o >$ | | $3.0\sigma(F_o)$ |
| $R_{int}$ | 0.0116 | 0.0157 |
| Range of $h$ | −16–16 | 0–14 |
| Range of $k$ | −5–0 | 0–5 |
| Range of $l$ | 0–13 | −36–36 |
| Weighting scheme | (unit) | [e] |
| With $g$ | | 0.00017 |
| $F(000)$ | 452 | 968 |
| Nr [a] | 133 | 124 |
| $\lvert\Delta/\sigma\rvert_{max}$ | 0.168 | 0.006 |
| $(\Delta\rho)_{max}$ (e Å$^{-3}$) | 0.629 | 1.128 |
| $(\Delta\rho)_{min}$ (e Å$^{-3}$) | −0.588 | −0.994 |
| $S$ [b] | 1.69 | 1.58 |
| $R$ [c] (observed) | 0.0294 | 0.0328 |
| $R$ [c] (all data) | 0.0298 | 0.0486 |
| $R_w$ [d] (observed) | 0.0311 | 0.0350 |
| $R_w$ [d] (all data) | 0.0323 | 0.0371 |

[a] Nr = number of refined parameters.
[b] $S = [\Sigma w(\Delta F)^2/(N-P)]^{1/2}$; $P$ = no. of parameters; $N$ = no. of observed reflections.
[c] $R = \Sigma|\Delta F|/\Sigma|F_o|$.
[d] $R_w = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$.
[e] $w = (\sigma^2(F_o) + gF_o^2)^{-1}$.

*3.8. X-ray structure determinations of **8a′** and **8b′***

Numerical data on the structure determinations have been collected in Table 3. Intensity data were obtained at 297 K on a Syntex $P2_1$ automatic diffractometer by variable-rate $\theta - 2\theta$ scans with Nb-filtered Mo–$K_\alpha$ radiation ($\lambda = 0.71069$ Å). Lattice parameters were obtained by a least-squares analysis of 15 reflections scattered in reciprocal space. Three reflections monitored periodically showed a $< 3\%$ intensity fluctuation. Lp and numerical absorption corrections were applied. The density was measured by flotation, and the position of the Hg atom was located from a Patterson map. Subsequent Fourier synthesis revealed the positions of all the other non-H atoms. Refinement proceeded by full-matrix least-squares in which $\Sigma w\Delta^2$ was minimized with SHELX76 [12]. The non-H atoms were refined using anisotropic temperature factors and the hydrogen atoms isotropic. The hydroxyl group was disordered over two positions with occupancy 0.5 in **8b′**. Atomic scattering factors were taken from International Tables for X-ray Crystallography [13].

## 4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 125123 for compound **8a′** and CCDC no. 125124 for compound **8b′**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax. +44-1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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