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Synthesis and Structures of Isomerically Pure Bis-(Alkylbenzo) Crown Ethers

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ABSTRACT: A convenient method for the synthesis of bis-(4-alkyl-2-hydroxyphenoxy) alkoxy ethers, precursors to highly lipophilic, alkylbenzo-substituted crown ethers, is described. Thirteen isomerically-pure, bis-*t*-alkylbenzo crown ethers were prepared. The solid-state structures of three representative, bis-*t*-octylbenzo crown ethers are reported, representing the first structures ever reported for *t*-octylbenzocrown ethers.
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INTRODUCTION

Crown ethers have been known and studied for the complexation and transport of ionic species for nearly thirty years.[1] It is well-established that substituent groups on the macrocyclic ring influence the properties of these macrocycles.[2,3] Solubility properties,[1,4] as well as binding strength[2] and selectivity,[5] are affected by the nature of the substituent. Addition of hydrocarbon groups generally increases the lipophilicity of crown ethers relative to their unsubstituted analogs.[3,6] Of the two most common substituents, benzo and cyclohexano, the benzo crown ethers are generally more lipophilic than the corresponding cyclohexano derivatives, but are typically less soluble in nonpolar organic diluents.[6] To counter this effect, alkyl-substituted benzo crown ethers have been utilized,[1,7,8] with the most common alkyl substituent being *t*-butyl (1,1-dimethylethyl). Recent reports have indicated that, in certain cases, larger substituents,[9] such as *t*-octyl (2,2,4-trimethylpentyl),[10,11] are required to provide lipophilicity and solubility sufficient for practical use. Of course, alkyl substituents increase the lipophilicity of the corresponding cyclohexano crown ethers as well.[8]

One of the attractive features of these two types of crown ethers, benzo and cyclohexano, are their ease of synthesis; the benzo crown ethers are readily prepared from catechol, while the cyclohexano crown ethers are prepared by reduction of the corresponding benzo crown ethers.[1] Bis-alkylbenzocrown ethers are usually synthesized from substituted catechols as a mixture of positional isomers; the even-numbered bis-alkylbenzocrown ethers (12C4, 18C6, 24C8, etc.) are obtained as a mixture of two compounds (4,4' and 4,5'), while the odd-numbered crown ethers (15C5, 21C7, etc.) generate three isomers (see Figure 1). Since dicyclohexano crown ethers are prepared from dibenzocrown ethers, they will exhibit the same regioisomerism as their dibenzo precursors, in addition to the syn/anti isomerism that results from the reduction process.[1] The existence of isomers does not usually interfere with the study of these compounds for catalysis, ion-exchange, transport, or extraction. However, the assumption that the various positional isomers have the same complexation properties has not been tested. In fact, there is evidence that the 4,4' and 4,5' positional isomers of cis-syn-cis and/or cis-anti-cis bis-*t*-butylcyclohexano-18-crown-6 do not extract cations with the same efficiency.[12] In addition, the presence of mixtures of positional isomers interferes with physical and structural studies, such as single-crystal structure determination by X-ray diffraction and solution complexation studies by ^{1}H and ^{13}C NMR.

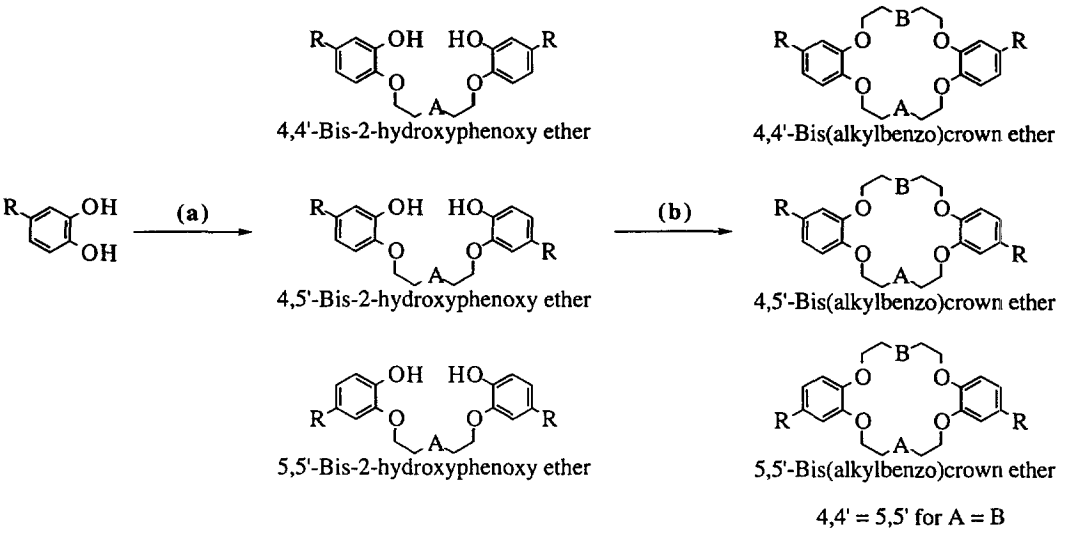


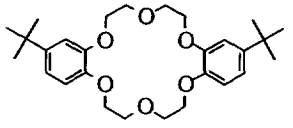
Fig. 1. Traditional synthesis of bis-alkylbenzocrown ethers yields a mixture of positional isomers. (a) MOH, Cl-CH_2CH_2-A-CH_2CH_2-Cl, (b) MOH, Cl-CH_2CH_2-B-CH_2CH_2-Cl

As a part of our continuing studies of crown ethers as solvent extraction reagents, we have developed a synthesis of isomerically pure 4,4'-substituted bis-2-hydroxyphenoxy ethers. We have used these precursors to prepare isomerically pure bis-*t*-butylbenzo and bis-*t*-octylbenzo-substituted crown ethers (Figure 2), and have determined the crystal structures of several of these, specifically, 4,4'-bis-*t*-octylbenzo-21-crown-7 (**4**), 4,4'-bis-*t*-octylbenzo-24-crown-8 (**10**), and the acetonitrile complex of 4,4'-bis-*t*-octylbenzo,furano-21-crown-7 (**13**).

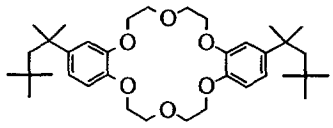
RESULTS AND DISCUSSION

Synthesis

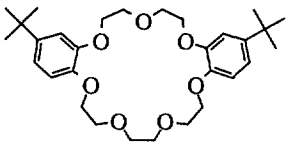
The traditional synthesis of benzo-substituted crown ethers involves the condensation of catechol, or a substituted catechol, with an α,ω-polyethyleneglycol dichloride.[1] For 4-substituted catechols this generates the mixture of positional isomers shown in Figure 1. Monoprotection of a 4-substituted catechol also produces an isomer mixture. In order to avoid a tedious isomer separation, we evaluated the alternative approaches outlined in Scheme 1 for the synthesis of bis-4-alkyl-2-hydroxyphenoxy ethers, precursors to the desired crown ethers. In our hands, the condensation (Step 1b) of *o*-nitrophenol (X = NO_2), salicylaldehyde (X = CHO), or *o*-hydroxyacetophenone (X = $COCH_3$) with either 2-chloroethyl ether (A = O) or bis-1,2-(2'-chloroethoxy)ethane (A = OCH_2CH_2O) failed to provide the desired diaryl ethers in acceptable yield or purity. Nitration and Friedel-Crafts acylation of a diaryl ether (Step 2b, A = OCH_2CH_2O) also failed, except in one case[11] where a modest yield of bis-2-formylphenoxy ether (X = CHO, A = OCH_2CH_2O) was obtained. However, the reproducibility of this reaction was less than satisfactory. Therefore, we considered alternative synthons (X) for the hydroxy group. The approach we settled on, outlined in Scheme 2, provided the desired bis-4-alkyl-2-hydroxyphenoxy ethers in good yield. This synthesis is convenient, highly reproducible, amenable to scale-up, and requires no chromatographic separations. Bis-*t*-butylbenzo (BbB) and bis-*t*-octylbenzo (BoB) crown ethers were readily prepared from these precursors.



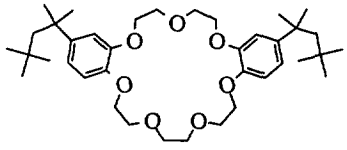
(**1**) 4,4'-Bis-*t*-butylbenzo-18-crown-6



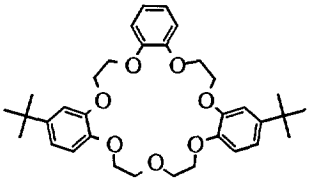
(**2**) 4,4'-Bis-*t*-octylbenzo-18-crown-6



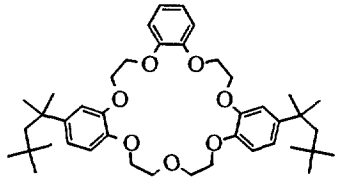
(**3**) 4,4'-Bis-*t*-butylbenzo-21-crown-7



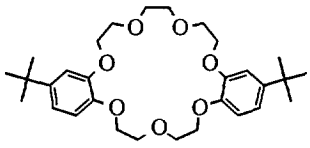
(**4**) 4,4'-Bis-*t*-octylbenzo-21-crown-7



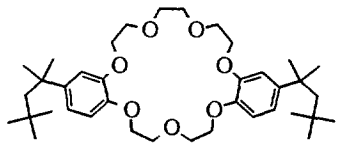
(**5**) 4,4'-Bis-*t*-butylbenzo,benzo-21-crown-7



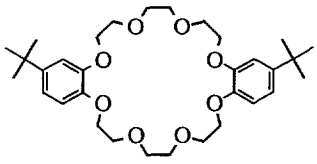
(**6**) 4,4'-Bis-*t*-octylbenzo,benzo-21-crown-7



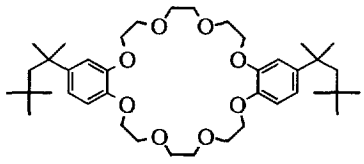
(**7**) 5,5'-Bis-*t*-butylbenzo-21-crown-7



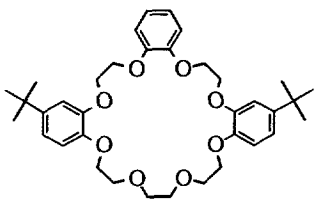
(**8**) 5,5'-Bis-*t*-octylbenzo-21-crown-7



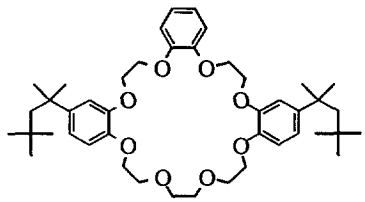
(**9**) 4,4'-Bis-*t*-butylbenzo-24-crown-8



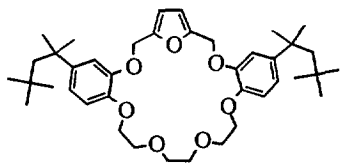
(**10**) 4,4'-Bis-*t*-octylbenzo-24-crown-8



(**11**) 4,4'-Bis-*t*-butylbenzo,benzo-24-crown-8

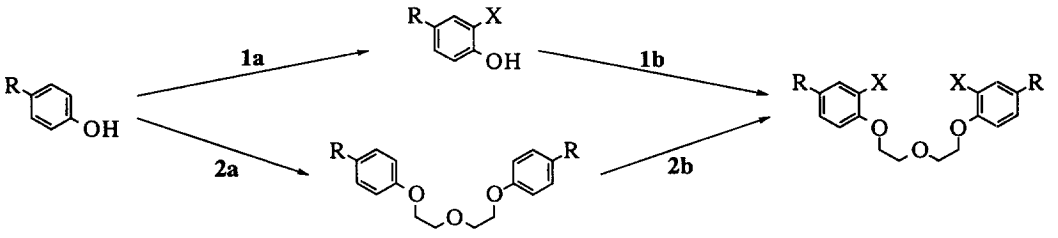


(**12**) 4,4'-Bis-*t*-octylbenzo,benzo-24-crown-8

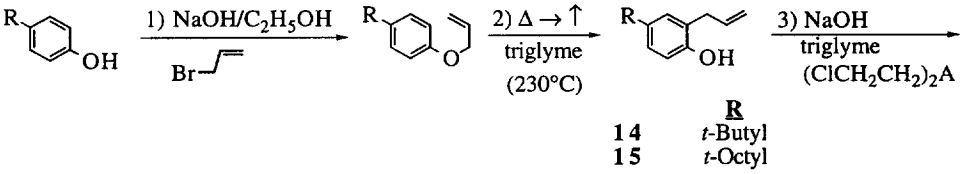


(**13**) 4,4'-Bis-*t*-octylbenzo,furano-21-crown-7

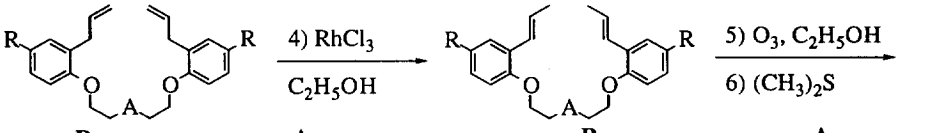
Fig. 2. Isomerically pure bis-alkylbenzocrown ethers.



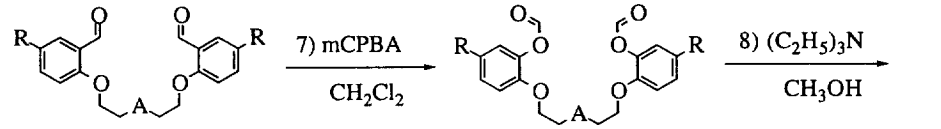
Scheme 1. Synthetic approaches to isomerically pure bis-4-alkyl-2-hydroxyphenoxy ethers.



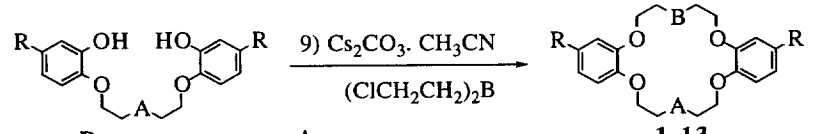
	R
14	*t*-Butyl
15	*t*-Octyl



	R	A		R	A
16	*t*-Butyl	O	17	*t*-Butyl	O
21	*t*-Octyl	O	22	*t*-Octyl	O
26	*t*-Butyl	$CH_2CH_2OCH_2CH_2$	27	*t*-Butyl	$CH_2CH_2OCH_2CH_2$
31	*t*-Octyl	$CH_2CH_2OCH_2CH_2$	32	*t*-Octyl	$CH_2CH_2OCH_2CH_2$



	R	A		R	A
18	*t*-Butyl	O	19	*t*-Butyl	O
23	*t*-Octyl	O	24	*t*-Octyl	O
28	*t*-Butyl	$CH_2CH_2OCH_2CH_2$	29	*t*-Butyl	$CH_2CH_2OCH_2CH_2$
33	*t*-Octyl	$CH_2CH_2OCH_2CH_2$	34	*t*-Octyl	$CH_2CH_2OCH_2CH_2$



	R	A
20	*t*-Butyl	O
25	*t*-Octyl	O
30	*t*-Butyl	$CH_2CH_2OCH_2CH_2$
35	*t*-Octyl	$CH_2CH_2OCH_2CH_2$

1-13
(see Figure 1)

Scheme 2. Synthesis of isomerically pure bis-4-alkyl-2-hydroxyphenoxy ethers.

Solid State Structures

Few crystal structures of large (>crown-6), uncomplexed, benzo-substituted crown ethers are reported in the literature[13,14,15,16] The structural work presented here was performed to address this shortfall and to study the structural effects of alkyl substitution on these crown ethers. Additionally, we wish to determine what effect on the structure of the crown ring, if any, is achieved by substituting various groups onto the crown ether ring. Specifically, we focused on the bis-*t*-octylbenzo crown ethers and determined the crystal structures of 4,4'-bis-*t*-octylbenzo-21-crown-7 (**4**, Fig 3), 4,4'-bis-*t*-octylbenzo-24-crown-8 (**10**, Fig 4), and the acetonitrile complex of 4,4'-bis-*t*-octylbenzo,furano-21-crown-7 (**13**, Fig 5). A summary of X-ray diffraction data is presented in Table I.

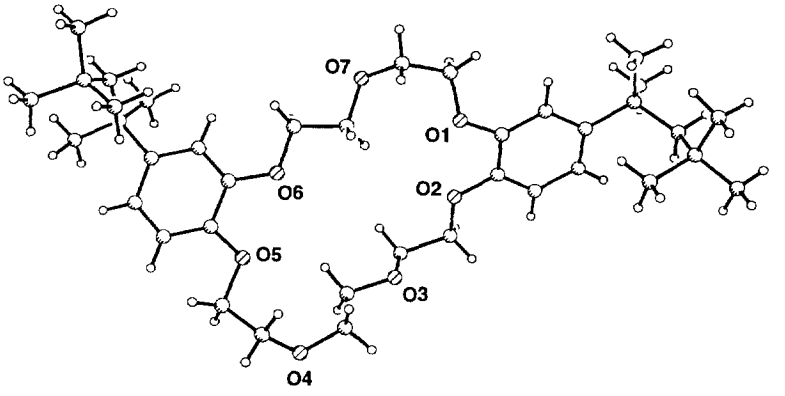


Figure 3. Crystal structure of 4,4'-bis-*t*-octylbenzo-21-crown-7 (**4**). Oxygen atoms are labeled, carbon atoms are represented by shaded spheres, and hydrogen atoms are represented as open spheres.

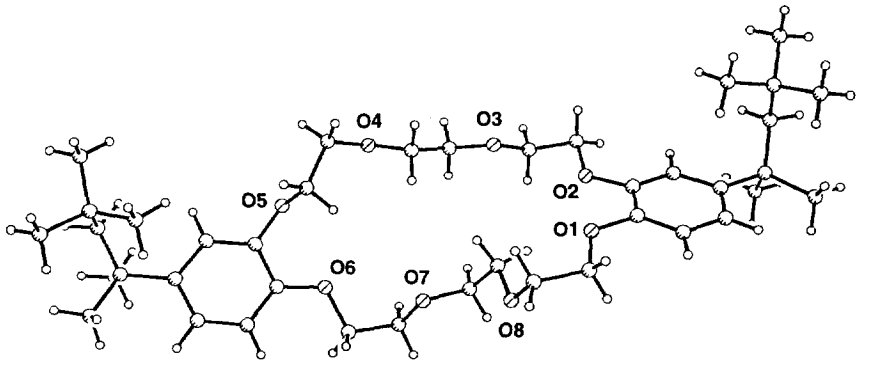


Figure 4. Crystal structure of 4,4'-bis-*t*-octylbenzo-24-crown-8 (**10**). Oxygen atoms are labeled, carbon atoms are represented by shaded spheres, and hydrogen atoms are represented as open spheres.

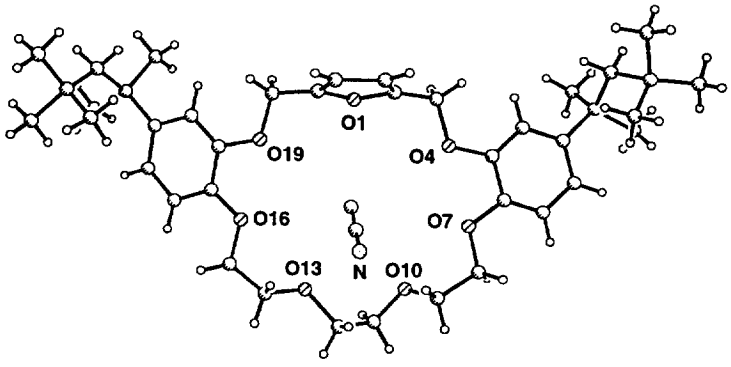


Figure 5. Crystal structure of 4,4'-bis-*t*-octylbenzo,furano-21-crown-7 (**13**). Heteroatoms are labeled, carbon atoms are represented by shaded spheres, and hydrogen atoms are represented as open spheres. Hydrogen atoms on the acetonitrile molecule are not pictured since they were not located.

Table I. Summary of X-ray Diffraction Data[a]

compound	**4**	**10**	**13**
empirical formula	$C_{38}H_{60}O_7$	$C_{40}H_{64}O_8$	$C_{40}H_{58}O_7 \cdot CH_3CN$
formula weight	628.98	672.91	650.98
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$(No. 2)	$P2_1/c$ (No. 14)
a, Å	18.318(12)	7.537(3)	18.551(5)
b, Å	15.488(7)	12.691(4)	9.629(3)
c, Å	13.044(7)	21.322(8)	24.885(7)
α, deg		93.25(2)	
β, deg	91.58(3)	97.81(2)	108.412(11)
γ, deg		102.35(2)	
V, Å^3	3699(4)	1966.0(13)	4218(2)
Z	4	2	4
density (calcd), g•cm^{-3}	1.13	1.14	1.03
R	0.057	0.045[b]	0.080

[a] Data were collected using Mo Kα radiation (λ = 0.71073 Å) at room temperature for **4** and **13**, and at -110 °C for **10**. The atomic coordinates for these structures have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ UK.

[b] The *R* value for **10** is based on $F^2 > 2\sigma(F^2)$, and is presented here for comparison purposes only.[19]

All three structures exhibit the expected 4,4' regiochemistry. These are the first reported structures of benzocrown ethers containing *t*-octyl substituents on the benzene rings. They clearly demonstrate that these bulky groups are oriented well away from the crown ether cavity and are not expected to hinder nor otherwise influence the coordination of guest molecules. This is particularly well illustrated in **13** (Fig 5) which experiences no steric difficulties in accommodating an acetonitrile guest, forming weak hydrogen bonds between the acetonitrile methyl group and the crown oxygen atoms. These C···O separations vary from 3.35 to 3.70 Å and average 3.5 Å in complex **10**, which is longer than most reported distances in acetonitrile-crown ether inclusion complexes, which average 3.4 Å.[17] Acetonitrile complexes only to one face of the crown, the other face is occupied by part of a neighboring crown (primarily the crown atoms between O7 and O16), although no hydrogen bonds are observed between crown ether molecules. The complexed acetonitrile holds open the crown ether cavity in **13**, illustrating how this crown might accommodate other guests (e.g. large alkali metal ions). It is worth noting that the furan oxygen is oriented roughly 90° away from the crown ether ring, similar to nitromethane complexes of closely related furanotribenzo-21-crown-7,[18] but in contrast to metal ion complexes of other furan-containing crown ethers.[19,20] This suggests that incorporation of the furan group into this crown will have a deleterious effect on its ability to bind to electropositive guests. The uncomplexed crowns **4** and **10** collapse in on the crown ether cavity, as is generally observed for uncomplexed crown ethers, adopting conformations similar to those observed for closely related dimethyldibenzo-21-crown-7 and dibenzo-24-crown-8.[13,14]

EXPERIMENTAL

All reagents were obtained from commercial sources and used as received unless otherwise noted. 3-Chloroperoxybenzoic acid, obtained from Aldrich Chemical Company, Inc., was stated to be of 57-86% purity; molar equivalents were calculated based on a nominal 50% purity. The progress of all of the reactions was monitored by TLC on Silica Gel 60 using ether/hexanes eluent, unless otherwise noted. All preparative chromatography was performed on Silica Gel 60 (60-200 mesh) using ether/hexanes eluent. NMR spectra were obtained at 9.4 T in $CDCl_3$ solvent. All coupling constants are given in Hz. The synthesis of **4** and **13** have ben reported previously.[11] X-ray data collection, reduction, solution and refinement were performed as described previously.[21]

Preparation of 2-Allyl-4-*t*-butylphenol[22] (14) in Triglyme. A solution of 4-*t*-butylphenol (50.0 g, 0.333 mol) and sodium hydroxide (15.0 g, 0.375 mol) in ethanol (200 ml) was prepared under an Argon atmosphere in a 500 mL round-bottom flask equipped with a magnetic stirring bar, solvent-recovery distillation head,[23] and a condensor. 3-Bromo-1-propene (35 ml, 0.40 mol) was added and the solution was heated with stirring at reflux for 30 minutes. Triglyme (150 mL) was added and the flask was heated in an oil bath, the temperature of which was raised to 230 °C over one hour as the ethanol was collected in the distillation head. The resulting solution was heated for two hours while maintaining a gentle reflux of triglyme.[24] Upon cooling to ~100-120 °C, a solution of **14** sufficient for use in the subsequent reaction was obtained.

Preparation of 2-Allyl-4-*t*-octylphenol[25] (15) in Triglyme. A solution of **15** in triglyme was prepared from 4-*t*-octylphenol (50 g, 0.25 mol) in the same manner as for the preparation of **14**.

Bis-2-(2'-allyl-4'-*t*-butylphenoxy)ethyl Ether (16). Sodium hydroxide (13.3 g, 0.33 mol) was added to the triglyme solution of **14** and the mixture was heated with stirring under Argon at 150 °C until all of the sodium hydroxide was dissolved.[26] A solution of 2-chloroethyl ether (19 ml, 0.16 mol) in triglyme (50 mL)

was added in one portion and the solution was heated with stirring under Argon overnight (~18 hours) at 150 °C. The triglyme was evaporated *in vacuo*[23] and the residue was partitioned between hexanes (500 mL) and water (200 mL). The hexanes phase was extracted twice with a solution of 0.5 M NaOH in 1/1 (v/v) methanol/water (1 x 500 mL, then 1 x 100 mL), twice with water (2 x 100 mL), dried over sodium sulfate, and evaporated *in vacuo* to obtain **16** (65 g, 90%) of sufficient purity for the subsequent reaction. The crude product was determined to be >95% pure by ^{1}H NMR. A small sample (~100 mg) was purified by chromatography for analysis. IR: (CCl_4): 3080 ($C=CH_2$), 2965 ($C(CH_3)_3$), 1639 (C=C), 1248 (Ar-O-C), 1138 (C-O-C), 1065 (Ar-O-C) cm^{-1}; ^{1}H (400.13 mHz; $CDCl_3$): δ 1.29 (s, 18 H, $C(C\underline{H}_3)_3$), 3.39 (d, 4 H, J = 6.7, $PhC\underline{H}_2CH=CH_2$), 3.92 (t, 4 H, J = 5.0, $-CH_2OCH_2-$), 4.12 (t, 4 H, J = 5.0, $ArOCH_2-$), 5.01 (d/d, 2 H, J_{cis} = 10.0/1.6, $HC\underline{H}=CH-$), 5.05 (d/d, 2 H, J_{trans}=17.0/1.6, $\underline{H}CH=CH-$), 6.00 (d/d/t, 2 H, J = 10.0, 17.0, 6.7, $-C\underline{H}=CH_2$), 6.78 (2 H, d, J = 8.2, ArH^6), 7.15 (d, 2 H, J = 2.6, ArH^3), 7.17 (2 H, d/d, J = 2.6/8.2, ArH^5); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.6, 34.1, 34.7, 68.1, 70.2, 111.4, 115.1, 123.8, 127.0, 128.4, 137.4, 143.6, 154.3. Anal. Calcd for $C_{30}H_{42}O_3$: C, 79.96; H, 9.39. Found: C, 79.8; H, 9.4.

Bis-2-(2'-propenyl-4'-*t*-butylphenoxy)ethyl Ether (17). $RhCl_3$ (0.5 g) was added to a solution of crude **16** (65 g, ~0.14 mol) in ethanol (400 ml). The solution was heated with stirring at reflux for 5 hours, at which time a second portion of $RhCl_3$ (0.25 g) was added. The solution was stirred at reflux for an additional two hours to obtain a solution of **17** of sufficient purity for the subsequent reaction. A sample (1 ml) was removed for analysis; the ethanol was removed *in vacuo* and the residue was partitioned between hexanes and water, dried over sodium sulfate, and evaporated *in vacuo* to obtain **17** as a pale yellow oil which was purified by chromatography. IR: (CCl_4): 3036 (ArCH=CH-), 2964 ($C(CH_3)_3$), 1687 (C=C), 1248 (Ar-O-C), 1137 (C-O-C), 1063 (Ar-O-C) cm^{-1}; ^{1}H (400.13 mHz $CDCl_3$): δ 1.30 (s, 18 H, $C(C\underline{H}_3)_3$), 1.87 (d/d, 6 H, J = 6.6/1.3, $ArCH=CHC\underline{H}_3$), 3.95 (t, 4 H, J = 5.1, $-CH_2OCH_2-$), 4.15 (t, 4 H, J = 5.1, $ArOCH_2-$), 6.25 (d/q, 2 H, J = 15.7/6.6, $ArCH=C\underline{H}CH_3$), 6.73 (d/q, 2 H, J=15.7/1.3, $ArC\underline{H}=CHCH_3$), 6.79 (2 H, d, J = 8.5, ArH^6), 7.15 (d/d, 2 H, J = 8.5/2.4, ArH^5), 7.41 (2 H, d, J = 2.4, ArH^3); ^{13}C (100.63 mHz, $CDCl_3$): δ 18.8, 31.5, 34.1, 68.5, 70.1, 112.4, 123.6, 124.5, 126.0, 126.24, 126.4, 143.7, 153.5. Anal. Calcd for $C_{30}H_{42}O_3$: C, 79.96; H, 9.39. Found: C, 79.3; H, 9.3.

Bis-2-(2'-formyl-4'-*t*-butylphenoxy)ethyl Ether (18). Dichloromethane (100 mL) was added to the ethanol solution of **17** (~0.14 mol) from the previous reaction. The mixture was cooled to -78 °C in a dry ice/acetone bath and treated with a stream of ozone (~1% O_3 in O_2) until the reaction was complete by TLC analysis (~3 hours). The solution was purged with a stream of O_2 for 5 minutes to remove excess ozone. Dimethyl sulfide (35 ml, 0.48 mol) was added, the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. After one hour, the solvent was evaporated *in vacuo* and the residue was partitioned between dichloromethane and water. The organic phase was washed once with saturated aqueous $NaHCO_3$, dried over sodium sulfate, and filtered through a short column of silica gel (~20 g) to obtain a solution of **18** of sufficient purity for the subsequent reaction. A small sample (~100 mg) was purified by chromatography for analysis. IR: (CCl_4): 2965 ($C(CH_3)_3$), 1688 (C=O), 1248 (Ar-O-C), 1136 (C-O-C), 1066 (Ar-O-C) cm^{-1}; ^{1}H (400.13 mHz $CDCl_3$): δ 1.31 (s, 18 H, $C(C\underline{H}_3)_3$), 3.98 (t, 4 H, J = 4.6, $-CH_2OCH_2-$), 4.25 (t, 4 H, J = 4.6, $ArOCH_2-$), 6.94 (2 H, d, J = 8.8, ArH^6), 7.85 (d, 2 H, J = 2.6, ArH^3), 7.57 (2 H, d/d, J = 2.6/8.8, ArH^5), 10.50 (s, 2H, ArCHO); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.3, 34.3, 68.6, 70.0, 112.9, 124.7, 124.9, 133.0, 144.2, 159.2, 189.9. Anal. Calcd for $C_{26}H_{34}O_5$: C, 73.21; H, 8.03. Found: C, 73.2; H, 8.4.

Bis-2-(2'-formyloxy-4'-*t*-butylphenoxy)ethyl-Ether (19). 3-Chloroperoxybenzoic acid (50 g, 0.15 mmol) was added to the solution of **18** (~0.14 mol) in dichloromethane from the previous reaction. The reaction warmed spontaneously to a gentle reflux. Additional 3-chloroperoxybenzoic acid (50 g, 0.15 mmol) was added in 10 g portions at 30 minute intervals. Following the final addition of 3-chloroperoxybenzoic acid, the reaction mixture was heated at reflux for one hour. After cooling in an ice bath, dimethyl sulfide (10 ml) was added and the solution was stirred for 30 minutes. The reaction mixture was filtered and the filtrant was washed twice with hexanes (100 mL). The filtrates were washed (separately) three times each with saturated aqueous $NaHCO_3$. The combined organic phases were dried over sodium sulfate and the solvent was evaporated *in vacuo* to obtain **19** (79 g, 123 %) of sufficient purity for the subsequent reaction.[27]

Bis-2-(2'-hydroxy-4'-*t*-butylphenoxy)ethyl Ether (20). Crude **19** (79 g) was dissolved in methanol (300 ml) and triethylamine (10 ml) was added. The mixture was allowed to stand at room temperature for 30 minutes, after which the solvent was evaporated *in vacuo*. The residue was dissolved in hexanes (500 mL), washed with 1 N HCl, and decanted into a beaker. A voluminous white solid precipitated upon standing. After cooling in an ice bath, the solution was filtered to obtain **20** (32 g, 50% from 2-chloroethyl ether) as a white solid. Recrystallization from methanol yielded pure **20** (26.0 g, 40.4%). mp 106.0-106.5 °C; IR: (CCl_4): 3402 (br, OH), 2966 ($C(CH_3)_3$), 1248 (Ar-O-C), 1140 (C-O-C), 1063 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz $CDCl_3$): δ 1.28 (s, 18 H, $C(C\underline{H}_3)_3$), 3.83 (t, 4 H, J = 4.4, $-CH_2OCH_2$-), 4.18 (t, 4 H, J = 4.4, $ArOCH_2$-), 6.82 (2 H, d/d, J = 8.3/2.0, ArH^5), 6.85 (d, 2 H, J = 8.3, ArH^6), 7.03 (2 H, d, J = 2.0, ArH^3), 7.49 (s, 2H, ArOH); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.4, 34.3, 69.6, 69.9, 113.6, 115.4, 116.5, 116.7, 119.7, 123.9, 146.9. Anal. Calcd for $C_{24}H_{34}O_5$: C, 71.61; H, 8.51. Found: C, 72.0; H, 8.7.

Bis-2-(2'-allyl-4'-*t*-octylphenoxy)ethyl Ether (21). **21** (52 g, 74%) of sufficient purity for the subsequent reaction was prepared from **15** (~0.25 mol), sodium hydroxide (10 g, 0.25 mol), and 2-chloroethyl ether (14 ml, 0.12 mol) in the same manner as described for the synthesis of **16**. A small sample (~100 mg) was purified by chromatography for analysis. IR: (CCl_4): 3080 ($C=CH_2$), 2955 ($C(CH_3)_3$), 1248 (Ar-O-C), 1137 (C-O-C), 1061 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz $CDCl_3$): δ 0.70 (s, 18 H, $C(C\underline{H}_3)_3$), 1.33 (s, 12 H, $C(C\underline{H}_3)_2$), 1.68 (s, 4 H, C-$C\underline{H}_2$-, 3.39 (d, 4 H, J = 6.4, $PhC\underline{H}_2CH=CH_2$), 3.92 (t, 4 H, J = 4.9, $-CH_2OCH_2$-), 4.12 (t, 4 H, J = 4.9, $ArOCH_2$-), 4.97-5.06 (m, 4 H, $\underline{H}_2C=CH$-), 5.98 (d/d/t, 2 H, J = 10.1/16.89/6.4, -$C\underline{H}=CH_2$), 6.75 (2 H, d, J = 9.1, ArH^6), 7.12 (d, 2 H, J = 2.5, ArH^3), 7.13 (2 H, d/d, J = 2.5/9.1, ArH^5); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.7, 31.8, 32.3, 34.6, 37.9, 57.0, 68.0, 70.2, 110.9, 115.0, 124.6, 127.8, 128.1, 137.4, 142.2, 154.2. Anal. Calcd for $C_{38}H_{58}O_3$: C, 81.09; H, 10.39. Found: C, 81.3; H, 10.6.

Bis-2-(2'-propenyl-4'-*t*-octylphenoxy)ethyl Ether (22). A solution of **21** (52 g, 93 mmol) and $RhCl_3$ (0.20 g) in ethanol (200 ml) was refluxed for two hours. A white crystalline solid formed upon cooling to room temperature. **22** (41 g, 80%) was obtained as white crystals after cooling in an ice bath and filtration. IR: (CCl_4): 3036 (ArCH=CH-), 2956 ($C(CH_3)_3$), 1247 (Ar-O-C), 1133 (C-O-C), 1064 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz $CDCl_3$): δ 0.72 (s, 18 H, $C(C\underline{H}_3)_3$), 1.34 (s, 12 H, $C(C\underline{H}_3)_2$), 1.70 (s, 4 H, C-$C\underline{H}_2$-, 1.88 (d/d, 6 H, J = 1.7/6.7, $PhCH=CHC\underline{H}_3$), 3.96 (t, 4 H, J = 5.1, $-CH_2OCH_2$-), 4.15 (t, 4 H, J = 5.1, $ArOCH_2$-), 6.23 (d/q, 2 H, J = 15.8/6.7, $ArCH=C\underline{H}$-CH_3), 6.73 (d/q 2 H, J = 15.8/1.7 $PhC\underline{H}=CHCH_3$), 6.77 (2 H, d, J = 8.6, ArH^6), 7.13 (2 H, d/d, J = 2.3/8.6, ArH^5), 7.38 (d, 2 H, J = 2.3, ArH^3); ^{13}C (100.63 mHz, $CDCl_3$): δ 18.9,

31.7, 31.8, 32.4, 38.0, 57.0, 68.2, 70.0, 111.7, 113.0, 124.5, 125.4, 125.9, 126.4, 142.4. Anal. Calcd for $C_{38}H_{58}O_3$: C, 81.09; H, 10.39. Found: C, 80.9; H, 10.6.

Bis-2-(2'-formyl-4'-*t*-octylphenoxy)ethyl Ether (23). A solution of **23** in dichloromethane was prepared from **22** (41 g, 73 mmol) in the same manner as described for the conversion of **17** to **18**. A small sample (~100 mg) was purified by chromatography for analysis. IR: (CCl_4): 2956 ($C(CH_3)_3$), 1686 (C=O), 1255 (Ar-O-C), 1135 (C-O-C), 1061 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz $CDCl_3$): δ 0.71 (s, 18 H, $C(C\underline{H}_3)_3$), 1.35 (s, 12 H, $C(C\underline{H}_3)_2$), 1.72 (s, 4 H, $C\text{-}C\underline{H}_2$-, 3.98 (t, 4 H, J = 4.8, $-CH_2OCH_2$-), 4.25 (t, 4 H, J = 4.8, $ArOCH_2$-), 6.92 (2 H, d, J = 8.7, ArH^6), 7.55 (d/d, 2 H, J = 2.6/8.7, ArH^5), 7.83 (d, 2 H, J = 2.6, ArH^3), 10.51 (s, 2H, ArCHO); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.5, 31.8, 32.3, 38.1, 56.7, 68.4, 70.0, 112.4, 124.3, 125.6, 133.9, 143.1, 159.1, 190.0. Anal. Calcd for $C_{34}H_{50}O_5$: C, 75.80; H, 9.35. Found: C, 75.3 ; H, 9.6.

Bis-2-(2'-formyloxy-4'-*t*-octylphenoxy)ethyl-Ether (24). **24** was prepared from **23** in the same manner as described for the conversion of **18** to **19**.

Bis-2-(2'-hydroxy-4'-*t*-octylphenoxy)ethyl Ether (25). **25** was prepared from **24** in the same manner as described for the conversion of **19** to **20**. The crude product was recrystallized from methanol/water to obtain **25** (36 g, 58% from 2-chloroethyl ether) as a white solid. mp 102-103 °C; IR: (CCl_4): 3557 (sh, OH), 3400 (br, OH), 2955 ($C(CH_3)_3$), 1248 (Ar-O-C), 1141 (C-O-C), 1066 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz $CDCl_3$): δ 0.73 (s, 18 H, $C(C\underline{H}_3)_3$), 1.33 (s, 12 H, $C(C\underline{H}_3)_2$), 1.69 (s, 4 H, $C\text{-}C\underline{H}_2$-, 3.84 (t, 4 H, J = 4.3, $-CH_2OCH_2$-), 4.19 (t, 4 H, J = 4.3, $ArOCH_2$-), 6.72-6.88 (4 H, m, ArH^5/ArH^6), 6.92-7.08 (2 H, m, ArH^3), 7.40 (s, 2H, ArOH); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.6, 31.7, 32.4, 38.2, 56.9, 69.6, 69.8, 114.4, 115.0, 117.7, 143.3, 145.8, 146.7. Anal. Calcd for $C_{32}H_{50}O_5 \cdot 1/2CH_3OH$: C, 73.55; H, 9.88. Found: C, 73.6; H, 10.1.

Bis-1,2-[2'-(2''-allyl-4''-*t*-butylphenoxy)ethoxy]ethane (26). **26** (79 g, 100%) of sufficient purity for the subsequent reaction was prepared from **14**, bis-2-chloroethoxyethane (25 ml, 0.16 mol) and sodium hydroxide (13.3 g, 0.33 mol) in the same manner as for **16**, except that the reaction was complete after 2 hours at 150 °C. A small sample (~100 mg) was purified by chromatography for analysis. IR: (CCl_4): 3077 ($C=CH_2$), 2964 ($C(CH_3)_3$), 1249 (Ar-O-C), 1139 (C-O-C), 1065 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz $CDCl_3$): δ 1.28 (s, 18 H, $C(C\underline{H}_3)_3$), 3.39 (d, 4 H, J = 6.7, $PhC\underline{H}_2CH=CH_2$), 3.74 (s, 4H, $-OCH_2CH_2O$-), 3.86 (t, 4 H, J = 5.0, $-CH_2O$-R), 4.11 (t, 4 H, J = 5.0, $ArOCH_2$-), 5.01 (d/d/t, 2 H, J_{cis} = 10.1/1.2/1.9, $HC\underline{H}$=CH-), 5.06 (d/d, 2 H, J_{trans}=16.9/1.7/1.9, $\underline{H}CH$=CH-), 6.00 (d/d/t, 2 H, J = 10.1, 16.9, 6.7, $-C\underline{H}=CH_2$), 6.77 (2 H, d, J = 8.7, ArH), 7.15 (d, 2 H, J = 2.5, ArH), 7.17 (2 H, d/d, J = 2.5/8.7, ArH); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.6, 34.1, 34.7, 68.1, 70.0, 71.0, 111.4, 115.1, 123.8, 127.0, 128.4, 137.4, 143.5, 154.4. Anal. Calcd for $C_{32}H_{46}O_4$: C, 77.69; H, 9.37. Found: C, 77.3; H, 9.4.

Bis-1,2-[2'-(2''-propenyl-4''-*t*-butylphenoxy)ethoxy]ethane (27). $RhCl_3$ (0.30 g) was added to a solution of crude **26** (79 g, 0.16 mol) in ethanol (500 ml). The solution was heated with stirring at reflux; additional $RhCl_3$ (0.10 g) was added after one hour and again after two hours. After a total reaction time of 4.5 hours, the solution was cooled to obtain a solution of **27** of sufficient purity for the subsequent reaction. A sample (0.5 ml) was removed for analysis and purified, as described for **17**, to obtain **27** as a pale yellow oil. IR: (CCl_4): 3038 (Ar-CH=CH-), 2964 ($C(CH_3)_3$), 1249 (Ar-O-C), 1137 (C-O-C), 1066 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz $CDCl_3$): δ 1.29/1.30 (2 singlets, 18 H, $C(C\underline{H}_3)_3$), [cis: 1.84 (d/d, J = 1.9/7.0), trans: 1.89 (d/d, J = 1.7/6.5), total 6H, $PhCH=CHC\underline{H}_3$], 3.75/3.76/3.78 (3 singlets, total 4 H, $-OCH_2CH_2O$-), 3.84-3.91 (m,

4 H, -CH_2OR), 4.09-4.15 (m, 4 H, ArOCH_2-), [5.79 (d/q, J = 11.5/6.9, cis-PhCH=C<u>H</u>CH_3), 6.24 (d/q, J = 15.7/6.6, trans-PhCH=C<u>H</u>CH_3), total 2H], [6.57 (d/q, J = 11.5/1.9, cis- PhC<u>H</u>=$CHCH_3$), 6.72 (d/q, J = 15.7/1.7, trans-PhC<u>H</u>=$CHCH_3$), total 2H], [6.78 (d, J = 8.5, trans-ArH^6), 6.80 (d, J = 8.5, cis-ArH^6) total: 2H], [7.15 (d/d, J = 2.5/8.5, trans-ArH^5), 7.19 (d/d, J = 2.5/8.5, cis-ArH^5), total 2H], [7.29 (d, 2 H, J = 2.5, cis-ArH^3), 7.40 (d, J = 2.5, trans-ArH^3), total 2H]; ^{13}C (100.63 mHz, $CDCl_3$): δ 18.9, 31.5, 34.1, 68.3, 70.0, 71.0, 112.4, 123.6, 124.5, 126.0, 126.4, 143.7, 153.5. Anal. Calcd for $C_{32}H_{46}O_4$: C, 77.69; H, 9.37. Found: C, 77.3; H, 9.0.

Bis-1,2-[2'-(2"-formyl-4"-*t*-butylphenoxy)ethoxy]ethane (28). **28** was prepared from **27** in the same manner as described for the conversion of **17** to **18**. A small sample (~100 mg) was purified by chromatography for analysis. IR: (CCl_4): 2965 ($C(CH_3)_3$), 1687 (C=O), 1247 (Ar-O-C), 1135 (C-O-C), 1066 (Ar-O-C) cm^{-1}; ^{1}H (400.13 mHz $CDCl_3$): δ 1.30 (s, 18 H, $C(C\underline{H}_3)_3$), 3.74 (s, 4 H, -OCH_2CH_2O-), 3.90 (t, 4 H, J = 4.6, -CH_2OR), 4.23 (t, 4 H, J = 4.6, ArOCH_2-), 6.93 (2 H, d, J = 8.6, ArH^6), 7.84 (d, 2 H, J = 2.6, ArH^3), 7.56 (2 H, d/d, J = 2.6/8.6, ArH^5), 10.50 (s, 2H, ArCHO); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.3, 34.3, 68.5, 69.7, 71.1, 112.9, 124.7, 124.8, 133.0, 144.1, 159.3, 190.0. Anal. Calcd for $C_{28}H_{38}O_6$: C, 71.46; H, 8.14. Found: C, 72.0; H, 8.4.

Bis-1,2-[2'-(2"-formyloxy-4"-*t*-butylphenoxy)ethoxy]ethane (29). **29** (86.3 g) was prepared from **28** in the same manner as described for the conversion of **18** to **19**.

Bis-1,2-[2'-(2"-hydroxy-4"-*t*-butylphenoxy)ethoxy]ethane (30). **30** was prepared from **29** in the same manner as described for the conversion of **19** to **20**. The crude product was dissolved in 10% ether in hexanes (500 mL), washed once each with 1 N HCl, saturated aqueous NaCl, and saturated aqueous $NaHCO_3$ (100 mL each). The organic phase was dried over sodium sulfate and cooled in a freezer overnight to obtain impure **30** (40 g, 56% from bis-2-chloroethoxyethane) as an oily, yellow solid, which was recrystallized once from isopropyl ether (30 g, 42%), then from 90% aqueous methanol to obtain pure **30** (26.1 g, 36.5 %). mp 70.0-70.5 °C; IR: (CCl_4): 3557 (sh, OH), 3418 (br, OH), 2966 ($C(CH_3)_3$), 1283 (Ar-O-C), 1138 (C-O-C), 1066 (Ar-O-C) cm^{-1}; ^{1}H (400.13 mHz $CDCl_3$): δ 1.27 (s, 18 H, $C(C\underline{H}_3)_3$), 3.75 (s, 4 H, -OCH_2CH_2O-), 3.81 (m, 4 H, -CH_2OR), 4.14 (m, 4 H, ArOCH_2-), 6.79 (2 H, d/d, J = 8.2/1.9, ArH^5), 6.82 (d, 2 H, J = 8.2, ArH^6), 6.99 (2 H, d, J = 1.9, ArH^3), 6.99 (br s, 2H, ArOH); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.5, 34.3, 69.7, 70.1, 70.6, 113.2, 114.8, 116.5, 143.6, 146.4 146.8. Anal. Calcd for $C_{26}H_{38}O_6$•1/2 H_2O: C, 68.55; H, 8.63. Found: C, 68.7; H, 8.8.

Bis-1,2-[2'-(2"-allyl-4"-*t*-octylphenoxy)ethoxy]ethane (31). **31** (71 g, 100%) of sufficient purity for the subsequent reaction was prepared from **15** (~0.25 mol), sodium hydroxide (10 g, 0.25 mol), and bis-2-chloroethoxyethane (18.0 ml, 0.115 mol) in the same manner as described for the synthesis of **26**. A small sample (~100 mg) was purified by chromatography for analysis. IR: (CCl_4): 3079 (C=CH_2), 2956 ($C(CH_3)_3$), 1249 (Ar-O-C), 1135 (C-O-C), 1065 (Ar-O-C) cm^{-1}; ^{1}H (400.13 mHz $CDCl_3$): δ 0.70 (s, 18 H, $C(C\underline{H}_3)_3$), 1.33 (s, 12 H, $C(C\underline{H}_3)_2$), 1.68 (s, 4 H, C-$C\underline{H}_2$-, 3.38 (d, 4 H, J = 6.4, Ph$C\underline{H}_2$CH=CH_2), 3.75 (s, 4H, -OCH_2CH_2O-), 3.86 (t, 4 H, J = 4.9, -CH_2OCH_2-), 4.10 (t, 4 H, J = 4.9, ArOCH_2-), 4.99 (d/d, 2 H, J_{cis} = 10.1/1.8, HC<u>H</u>=CH-), 5.02 (d/d, 2 H, J_{trans}=16.8/1.8, <u>H</u>CH=CH-), 5.98 (d/d/t, 2 H, J = 10.1/16.8/6.4, -C<u>H</u>=CH_2), 6.75 (2 H, d, J = 7.2, ArH^6), 7.11 (d, 2 H, J = 2.4, ArH^3), 7.12 (2 H, d/d, J = 2.4/7.2, ArH^5); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.7, 31.8, 32.4, 34.6, 38.0, 57.1, 68.0, 70.1, 71.0, 111.2,

115.0, 124.7, 128.0, 128.1, 137.5, 142.3, 154.3. Anal. Calcd for $C_{40}H_{62}O_4$: C, 79.16; H, 10.30. Found: C, 77.5; H, 10.2.

Bis-1,2-[2'-(2"-propenyl-4"-*t*-octylphenoxy)ethoxy]ethane (32). $RhCl_3$ (0.20 g) was added to a solution of crude **31** (68 g, 0.11 mol) in ethanol (500 ml). The solution was heated with stirring at reflux overnight; additional $RhCl_3$ (0.20 g) was added and heating was continued until the next day. The solution was cooled to obtain a solution of **32** of sufficient purity for the subsequent reaction. A sample (0.5 ml) was removed for analysis and purified in the same manner as for **17.** IR: (CCl_4): 3036 (ArCH=CH-), 2956 ($C(CH_3)_3$), 1249 (Ar-O-C), 1133 (C-O-C), 1064 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz $CDCl_3$): δ 0.70/0.71/0.73 (3 singlets, total 18H, $C(C\underline{H}_3)_3$), 1.34 (s, 12 H, $C(C\underline{H}_3)_2$), 1.70 (s, 4 H, C-$C\underline{H}_2$-), [1.84 (d/d, J = 1.9/7.0, cis-PhCH=CHC$\underline{H}_3$), 1.89 (d/d, J = 1.6/6.6, trans- PhCH=CHC$\underline{H}_3$), total 6H], 3.74/3.76/3.77 (3 singlets, total 4 H, -OCH_2CH_2O-), 3.84-3.91 (m, 4 H, -CH_2OR), 4.08-4.16 (m, 4 H, $ArOCH_2$-), [5.78 (d/q, J = 11.4/7.0, cis-PhC$\underline{H}$=CHCH_3), 6.22 (d/q, J = 15.7/7.0, trans-PhCH=CHC$\underline{H}_3$) total 2H], [6.58 (d/q, J = 11.4/1.7, cis-PhCH=C$\underline{H}$CH_3), 6.71 (d/q, J = 15.7/1.6, trans-PhCH=C$\underline{H}$CH_3), total 2H], [6.75 (d, J = 8.5, trans-ArH^6), 6.78 (d, J = 8.5, cis-ArH^6) total: 2H], [7.12 (d/d, J = 2.4/8.5, trans-ArH^5), 7.16 (d/d, J = 2.4/8.5, cis-ArH^5), total 2H], [7.37 (d, J = 2.4, trans-ArH^3), 7.40 (d, 2 H, J = 2.4, cis-ArH^3), total 2H]; ^{13}C (100.63 mHz, $CDCl_3$): Trans: δ 18.9, 31.6, 31.8, 32.4, 38.0, 57.1, 68.2, 70.0, 71.0, 111.9, 124.6, 125.4, 125.8, 126.1, 126.6, 142.5, 153.4; Cis: δ 14.7, 31.6, 31.8, 32.3, 38.0, 57.1, 68.2, 70.0, 71.0, 111.5, 112.0, 124.6, 125.4, 125.8, 126.1, 126.7, 128.2, 153.4. Anal. Calcd for $C_{40}H_{62}O_4$: C, 79.16; H, 10.30. Found: C, 75.3; H, 9.9.

Bis-1,2-[2'-(2"-formyl-4"-*t*-octylphenoxy)ethoxy]ethane (33). A solution of **33** in dichloromethane was prepared from **32** in the same manner as described for the conversion of **17** to **18.** A small sample (~100 mg) was purified by chromatography for analysis. IR: (CCl_4): 2956 ($C(CH_3)_3$), 1686 (C=O), 1255 (Ar-O-C), 1131 (C-O-C), 1064 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz $CDCl_3$): δ 0.71 (s, 18 H, $C(C\underline{H}_3)_3$), 1.35 (s, 12 H, $C(C\underline{H}_3)_2$), 1.72 (s, 4 H, C-$C\underline{H}_2$-), 3.74 (s, 4 H, -OCH_2CH_2O-), 3.89 (t, 4 H, J = 4.8, -CH_2OR), 4.23 (t, 4 H, J = 4.8, $ArOCH_2$-), 6.92 (2 H, d, J = 8.7, ArH^6), 7.83 (d, 2 H, J = 2.7, ArH^3), 7.53 (2 H, d/d, J = 2.7/8.7, ArH^5), 10.50 (s, 2H, ArCHO); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.5, 31.9, 32.4, 38.2, 56.8, 68.4, 69.7, 71.1, 112.6, 124.6, 125.6, 133.8, 143.1, 159.2, 190.1. Anal. Calcd for $C_{36}H_{54}O_6$: C, 74.19; H, 9.34. Found: C, 73.8; H, 9.7.

Bis-1,2-[2'-(2"-formyloxy-4"-*t*-octylphenoxy)ethoxy]ethane (34). 34 (79 g, 118 %) was prepared from **33** in the same manner as described for the conversion of **18** to **19.**

Bis-1,2-[2'-(2"-hydroxy-4"-*t*-octylphenoxy)ethoxy]ethane (35). 35 was prepared from **24** (79 g) in the same manner as described for the conversion of **19** to **20.** The crude product was dissolved in hexanes (500 mL), washed once each with 1 N HCl, saturated aqueous NaCl, and saturated aqueous $NaHCO_3$ (100 mL each). The organic phase was dried over sodium sulfate and evaporated *in vacuo.* Recrystallization from methanol gave **35** (29.0 g, 45.1% from bis-2-chloroethoxyethane) as a white solid. mp 69-71 °C (begins losing solvent ~65 °C); IR: (CCl_4): 3557 (sh, OH), 3412 (br, OH), 2955 ($C(CH_3)_3$), 1276 (Ar-O-C), 1140 (C-O-C), 1060 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz $CDCl_3$): δ 0.73 (s, 18 H, $C(C\underline{H}_3)_3$), 1.31 (s, 12 H, $C(C\underline{H}_3)_2$), 1.67 (s, 4 H, C-$C\underline{H}_2$-, 3.75 (s, 4 H, -OCH_2CH_2O-), 3.81 (t , 4 H, J = 4.6, -CH_2OR), 4.14 (t , 4 H, J = 4.6, $ArOCH_2$-), 6.66 (br s, 2 H, -OH), 6.75-6.82 (m, 4H, ArH^5/ArH^6), 6.97 (br, 2 H, ArH^3); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.6, 31.8, 32.4, 38.2, 69.7, 70.1, 70.6, 114.1, 114.5, 117.5, 143.5, 145.3 146.6. Anal. Calcd for $C_{34}H_{54}O_6 \cdot CH_3OH \cdot 1/2H_2O$: C, 70.08; H, 9.91. Found: C, 69.8; H, 10.0.

General Procedure for the Synthesis of Crown Ethers

A mixture of bisphenol (2.5 mmol of **20**, **25**, **30**, or **35**), α,ω-dichloride or ditosylate (2.6 mmol), and cesium carbonate (1.0 g, 3.0 mmol) in anhydrous acetonitrile was stirred at reflux under Argon. When the presence of starting diphenol was no longer evident by TLC, the solvent was removed *in vacuo* and the residue was partitioned between dichloromethane and 1N NaOH. The organic phase was washed once with 1N HCl, dried over sodium sulfate and evaporated *in vacuo*.

The crown ethers that solidified upon evaporation were recrystallized from an appropriate solvent (see below). Products obtained as an oil were purified by chromatography on silica gel and recrystallized as appropriate.

Bis-*t*-butylbenzo-18-crown-6 (1). 317 mg (27%): mp 94 °C (MeOH); IR: (CCl_4): 1266 (Ar-O-C), 1147 (C-O-C), 1064 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz; $CDCl_3$): δ 1.29 (s, 18 H, $C(C\underline{H}_3)_3$), 4.01 (4H, t, J=4.7, $-CH_2OCH_2-$), 4.06 (4H,t, J=4.7, $-CH_2OCH_2-$), 4.16 (4H, t, J=4.7, $ArOCH_2-$), 4.21 (4H, t, J=4.7, $ArOCH_2-$), 6.80 (2 H, d, J = 8.3, ArH^6), 6.92 (2H, d/d, J=2.2/8.3, ArH^5), 6.94 (2H, d, J=2.2, ArH^3); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.5, 34.3, 69.8, 70.1, 70.4, 113.5, 114.8, 118.4, 145.1, 147.4, 149.0. Anal. Calcd for $C_{28}H_{40}O_6$: C 71.16; H 8.53. Found: C, 71.6; H 8.8.

Bis-*t*-octylbenzo-18-crown-6 (2). 720 mg (49.1%): mp 117 °C (MeOH); IR: (CCl_4): 1265 (Ar-O-C), 1149 (C-O-C), 1062 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz; $CDCl_3$): δ 0.71 (s, 18 H, $C(C\underline{H}_3)_3$), 1.33 (s, 12 H, $C(C\underline{H}_3)_2$), 1.68 (s, 4 H, $C\text{-}C\underline{H}_2-$), 4.01 (4H, t, J=4.7, $-CH_2OCH_2-$), 4.05 (4H,t, J=4.7, $-CH_2OCH_2-$), 4.16 (4H, t, J=4.7, $ArOCH_2-$), 4.20 (4H, t, J=4.7, $ArOCH_2-$), 6.78 (2 H, d, J = 8.4, ArH^6), 6.88 (2H, d/d, J=2.1/8.4, ArH^5), 6.92 (2H, d, J=2.1, ArH^3); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.6, 31.7, 32.2, 38.1, 57.0, 68.9, 69.6, 70.1, 70.2, 113.3, 113.7, 119.0, 143.4, 146.7, 148.1. Anal. Calcd for $C_{36}H_{56}O_6$: C 73.93; H 9.65. Found: C 73.9; H 9.9.

Bis-*t*-butylbenzo-21-crown-7 (3). 0.480 g (37.2%): mp 114.5 °C (MeOH); IR: (CCl_4): 1266 (Ar-O-C), 1147 (C-O-C), 1061 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz; $CDCl_3$): δ 1.29 (s, 18 H, $C(C\underline{H}_3)_3$), 3.84 (4 H, s, $-OCH_2CH_2O-$), 3.89 (4H, t, J=4.3, $-CH_2OCH_2-$), 4.04 (4H,t, J=4.3, $-CH_2OCH_2-$), 4.13 (4H, t, J=4.3, $ArOCH_2-$), 4.22 (4H, t, J=4.3, $ArOCH_2-$), 6.80 (2 H, d, J = 8.3, ArH^6), 6.92 (2H, d/d, J=2.0/8.3, ArH^5), 6.98 (2H, d, J=2.20, ArH^3); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.4, 34.2, 69.5, 69.7, 70.1, 70.3, 71.1, 113.5, 113.7, 118.3, 144.6, 147.0, 148.2. Anal. Calcd for $C_{30}H_{44}O_7$: C 69.74; H 8.58. Found: C 69.9; H 8.9.

Bis-*t*-butylbenzo,benzo-21-crown-7 (5). 1.06 g (75.5%): mp 127 °C (MeOH); IR: (CCl_4): 1263 (Ar-O-C), 1146 (C-O-C), 1062 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz; $CDCl_3$): δ 1.31 (s, 18 H, $C(C\underline{H}_3)_3$), 3.93 (4H, t, J=4.2, $-CH_2OCH_2-$), 4.16 (4H,t, J=4.7, $-CH_2OCH_2-$), 4.35-4.40 (8H, m, $ArOCH_2-$), 6.84 (2 H, d, J = 8.3, ArH^6), 6.89-7.01 (8H, m, ArH); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.5, 34.3, 69.2, 70.0, 70.2, 114.6, 115.7, 116.9, 118.9, 122.1, 124.8, 145.3, 147.6, 148.9, 149.9. Anal. Calculated for $C_{34}H_{44}O_7 \cdot 1/2CH_3OH$: C 71.35; H 7.98. Found: C 71.5; H 7.9.

Bis-*t*-octylbenzo,benzo-21-crown-7 (6). 0.848 g (50%): mp 130 °C (EtOH); IR: (CCl_4): 1256 (Ar-O-C), 1147 (C-O-C), 1062 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz; $CDCl_3$): δ 0.71 (s, 18 H, $C(C\underline{H}_3)_3$), 1.32 (s, 12 H, $C(C\underline{H}_3)_2$), 1.69 (s, 4 H, $C\text{-}C\underline{H}_2-$), 3.93 (4H, t, J=4.2, $-CH_2OCH_2-$), 4.16 (4H,t, J=4.7, $-CH_2OCH_2-$), 4.35-4.40 (8H, m, $ArOCH_2-$), 6.81 (2 H, d, J = 8.3, ArH^6), 6.85-7.02 (8H, m, ArH); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.6, 31.7, 32.3, 38.1, 57.0, 68.5, 69.6, 70.1, 114.6, 114.8, 116.0, 119.6, 121.8, 122.0, 143.7, 147.0, 148.0, 149.2. Anal. Calculated for $C_{42}H_{60}O_7$: C 74.52; H 8.93. Found: C, 74.2; H 9.3.

Bis-*t*-butylbenzo-21-crown-7 (7). 582 mg (45%): mp 97-98 °C (MeOH); IR: (CCl_4): 1265 (Ar-O-C), 1146 (C-O-C), 1060 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz; $CDCl_3$): δ 1.29 (s, 18 H, $C(C\underline{H}_3)_3$), 3.86 (4 H, s, $-OCH_2CH_2O-$), 3.92 (4H, t, J=4.2, $-CH_2OCH_2-$), 4.00 (4H,t, J=4.7, $-CH_2OCH_2-$), 4.15-4.19 (8H, m, $ArOCH_2-$), 6.84 (2 H, d, J = 8.3, ArH^6), 6.91 (2H, d/d, J=2.0/8.3, ArH^5), 6.93 (2H, d, J=2.20, ArH^3); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.5, 34.3, 69.8, 70.1, 70.5, 71.2, 113.3, 115.7, 118.4, 145.4, 147.4, 149.1. Anal. Calcd for $C_{30}H_{44}O_7$: C 69.74; H 8.58. Found: C 69.9; H 8.9.

Bis-*t*-octylbenzo-21-crown-7 (8). 775 mg (49.1%): mp 89-90 °C (MeOH); IR: (CCl_4): 1264 (Ar-O-C), 1147 (C-O-C), 1061 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz; $CDCl_3$): δ 0.70 (s, 18 H, $C(C\underline{H}_3)_3$), 1.32 (s, 12 H, $C(C\underline{H}_3)_2$), 1.67 (s, 4 H, $C-C\underline{H}_2-$), 3.86 (4 H, s, $-OCH_2CH_2O-$), 3.92 (4H, t, J=4.2, $-CH_2OCH_2-$), 3.99 (4H,t, J=4.7, $-CH_2OCH_2-$), 4.15-4.17 (8H, m, $ArOCH_2-$), 6.80 (2 H, d, J = 8.4, ArH^6), 6.88 (2H, d/d, J=2.0/8.4, ArH^5), 6.90 (2H, d, J=2.0, ArH^3); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.6, 31.7, 32.2, 38.1, 57.0, 69.6, 69.8, 70.3, 71.2, 113.5, 114.4, 119.2, 143.7, 146.7, 148.1. Anal. Calcd for $C_{38}H_{60}O_7$: C 72.58; H 9.62. Found: C 72.5; H 9.7.

Bis-*t*-butylbenzo-24-crown-8 (9). 0.44 g (35%): mp 80 °C (MeOH); IR: (CCl_4): 1266 (Ar-O-C), 1148 (C-O-C), 1060 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz; $CDCl_3$): δ 1.28 (s, 18 H, $C(C\underline{H}_3)_3$), 3.81 (4 H, s, $-OCH_2CH_2O-$), 3.83 (4 H, s, $-OCH_2CH_2O-$), 3.90 (4H, t, J=4.4, $-CH_2OCH_2-$), 3.92 (4H,t, J=4.4, $-CH_2OCH_2-$), 4.13 (4H,t, J=4.4, $ArOCH_2-$), 4.18 (4H,t, J=4.4, $ArOCH_2-$), 6.80 (2 H, d, J = 8.3, ArH^6), 6.90 (2H, d/d, J=2.2/8.3, ArH^5), 6.93 (2H, d, J=2.2, ArH^3); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.4, 34.2, 69.3, 69.5, 69.9, 71.0, 112.4, 113.5, 117.8, 144.4, 146.7, 148.1. Anal. Calculated for $C_{32}H_{48}O_8$: C 68.55; H 8.63. Found: C 68.7; H 8.6.

Bis-*t*-octylbenzo-24-crown-8 (10). 0.325 g (19.6%): mp 79 °C (MeOH); IR: (CCl_4): 1264 (Ar-O-C), 1147 (C-O-C), 1060 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz; $CDCl_3$): δ 0.70 (s, 18 H, $C(C\underline{H}_3)_3$), 1.31 (s, 12 H, $C(C\underline{H}_3)_2$), 1.67 (s, 4 H, $C-C\underline{H}_2-$), 3.81 (4 H, s, $-OCH_2CH_2O-$), 3.83 (4 H, s, $-OCH_2CH_2O-$), 3.85-3.92 (8 H, m, $-CH_2OCH_2-$), 4.12 (4H,t, J=4.3, $ArOCH_2-$), 4.16 (4H,t, J=4.3, $ArOCH_2-$), 6.76 (2 H, d, J = 8.3, ArH^6), 6.88 (2H, d/d, J=2.0/8.3, ArH^5), 6.90 (2H, d, J=2.0, ArH^3); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.6, 31.7, 32.2, 38.1, 56.9, 69.2, 69.6, 69.9, 71.1, 113.1, 113.6, 119.0, 143.2, 146.7, 148.0. Anal. Calculated for $C_{40}H_{64}O_8$: C 71.39; H 9.59. Found: C 71.6; H 9.8.

Bis-*t*-butylbenzo,benzo-24-crown-8 (11). 1.02 g (79.0%): mp 110 °C (MeOH); IR: (CCl_4): 1265 (Ar-O-C), 1256 (Ar-O-C), 1146 (C-O-C), 1060 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz; $CDCl_3$): δ 1.29 (s, 18 H, $C(C\underline{H}_3)_3$), 3.67 (4 H, s, $-OCH_2CH_2O-$), 3.81 (4H, t, J=4.2, $-CH_2OCH_2-$), 4.11 (4H,t, J=4.7, $-CH_2OAr-$), 4.30-4.45 (8H, m, $ArOCH_2-$), 6.82 (2 H, d, J = 8.3, ArH^6), 6.89-7.05 (8H, m, ArH); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.4, 34.2, 68.6, 68.8, 69.5, 69.6, 70.9, 114.1, 114.3, 115.9, 118.6, 121.9, 144.7, 147.1, 148.2, 149.2. Anal. Calculated for $C_{36}H_{48}O_8 \cdot 1/2CH_3OH$: C 70.17; H 8.07. Found: C 70.3; H 8.1.

Bis-*t*-octylbenzo,benzo-24-crown-8 (12). 0.92 g (71%): oil (SiO_2, acetone/toluene gradient); IR: (CCl_4): 1255 (Ar-O-C), 1147 (C-O-C), 1063 (Ar-O-C) cm^{-1}; ^1H (400.13 mHz; $CDCl_3$): δ 0.72 (s, 18 H, $C(C\underline{H}_3)_3$), 1.33 (s, 12 H, $C(C\underline{H}_3)_2$), 1.69 (s, 4 H, $C-C\underline{H}_2-$), 3.68 (4 H, s, $-OCH_2CH_2O-$), 3.81 (4H, t, J=4.3, $-CH_2OCH_2-$), 4.11 (4H,t, J=4.3, $-CH_2OAr-$), 4.35-4.45 (8H, m, $ArOCH_2-$), 6.79 (2 H, d, J = 8.4, ArH^6), 6.92 (2H, d/d, J=2.1/8.4, ArH^5), 6.93-6.98 (2H, m, ArH), 6.99 (2H, d, J=2.1, ArH^3), 7.00-7.05 (2H, m, ArH); ^{13}C (100.63 mHz, $CDCl_3$): δ 31.6, 31.7, 32.2, 38.0, 56.9, 68.6, 68.9, 69.4, 69.7, 70.9, 114.0, 115.2, 115.9, 119.7, 121.9, 143.5, 147.2, 148.0, 149.2. Anal. Calculated for $C_{44}H_{64}O_8$: C 73.30; H 8.95. Found: C 74.8; H 9.7.

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23. The solvent recovery distillation head serves conveniently as an addition funnel and for solvent removal.

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27. The bis-formyl ester hydrolized sufficiently upon work-up and chromatography to preclude obtaining good spectral data or elemental analysis. The NMR spectra of the crude product were consistant with the proposed structure.

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