(4.05 mmol) in Me_2SO (15 mL) was prepared from a solution of sodium methylsulfinyl carbanion (4.05 mmol) in Me_2SO and isopropyltriphenylphosphonium iodide (1.75 g, 4.05 mmol). Reaction of the ylide solution with **3** (500 mg, 3.12 mmol) according to the general procedure afforded a yellow oil containing a white solid (PPh_3). Analysis of the crude product mixture by ^1H NMR showed that **1,1-dimethyldispiro[2.2.5.2]trideca-4,12-diene (9)** was obtained in ca. 64% yield and that **4** was obtained in less than 1% yield. Purification of the crude product mixture by Kugelrohr distillation [70–75 °C (0.2 mm)] and GLC (6 ft × 0.25 in. 20% SE-30 column, 155 °C) provided **9** as a colorless liquid: ^1H NMR ($CDCl_3$) δ 5.74 (d, J = 9.9 Hz, 2 H, vinyl CH β to the cyclopropane), 5.27 (d, J = 9.9 Hz, 2 H, vinyl CH α to the cyclopropane), 1.44 (br s, 10 H), 1.07 (s, 6 H, CH_3), 0.70 (s, 2 H, cyclopropyl H); ^{13}C NMR ($CDCl_3$) δ 133.7 (C-5 and C-12), 128.0 (C-4 and C-13), 40.1 (C-7 or C-11), 38.8 (C-7 or C-11), 36.2 (C-6), 31.4 (C-2), 29.5 (C-1 or C-3), 26.0 (C-9), 25.4 (C-1 or C-3), 22.6 (CH_3), 21.6 (C-8 or C-10), 21.4 (C-8 or C-10); IR (CCl_4) 3040, 2990, 2930, 2860, 1620, 1450, 1380, 1125, 975, 950, 920, 905, 845 cm^{-1}; exact mass calcd for $C_{15}H_{22}$ 202.172, found 202.169. Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.99; H, 10.99.

Reaction of 3 with Isopropylidenetriphenylphosphorane in Tetrahydrofuran. A solution of n-butyllithium in hexane (1.4 mL, 2.8 mmol) was added dropwise to a stirred suspension of isopropyltriphenylphosphonium iodide (1.32 g, 3.05 mmol) in dry tetrahydrofuran (45 mL) under argon at room temperature. The resulting yellow solution was stirred at room temperature for 3 h. A solution of **3** (350 mg, 2.18 mmol) in dry THF (12 mL) was injected, and the reaction mixture was heated at reflux for 20 h. The reaction mixture was then cooled to 0 °C and quenched with water (30 mL). The layers were separated, and the aqueous phase was extracted with pentane (4 × 25 mL). The combined organic extracts were washed with water (2 × 25 mL) and saturated aqueous sodium chloride (1 × 25 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure yielded a yellow oil which by ^1H NMR analysis contained ca. 333 mg (75% yield) of **9**.

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Registry No. **3**, 87482-33-5; **4**, 87482-34-6; **5**, 87482-38-0; **6**, 4729-21-9; **7**, 87482-39-1; **8**, 87482-35-7; **9**, 87482-36-8; **12**, 87482-37-9; $CH_3SOCH_2^-$, 13810-16-7; methylenetriphenylphosphorane, 3487-44-3; ethylidenetriphenylphosphorane, 1754-88-7; isopropylidenetriphenylphosphorane, 16666-80-1; spiro[5.5]undec-1-en-3-one, 30834-42-5.

Synthesis of Highly Lipophilic Crown Ether Carboxylic Acids[1]

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Synthetic routes to eight highly lipophilic crown ether carboxylic acids are described. Structural variations within this series of crown ether carboxylic acids include changes in the crown ether cavity size, the lipophilic group attachment site, and the basicity of the crown ether oxygens.

Lipophilic crown ether carboxylic acids have been utilized for the solvent extraction of alkali and alkaline earth cations from aqueous solutions as well as for the transport of these metals cations across bulk liquid and liquid surfactant (emulsion) membranes.[2-11] Such ionizable crown ethers possess the distinct advantage over neutral crown compounds in that transport of the metal cation from the aqueous phase into the organic medium does not involve concomitant transfer of the aqueous phase anion.[4]

Previously we have described the preparation of lipophilic benzo and dibenzo crown ether carboxylic acids **1–6**.[9,12,13] All of these compounds are sufficiently lipophilic to avoid loss of the complexing agent from an organic phase into a contacting, highly alkaline, aqueous phase during the solvent extraction of metal ions. However, this series of lipophilic crown ether carboxylic acids provides only for a very limited variation of the crown ether cavity size.

We now report the synthesis of eight additional lipophilic crown ether carboxylic acids **7–14** (see Chart I). In combination with **3** and **4**, these new compounds provide for systematic variation of several structural features of lipophilic crown ether carboxylic acids.

Results and Discussion

Compounds **7**, **3**, **8**, and **9** are dibenzo crown ether carboxylic acids in which the lipophilic and carboxylic groups remain constant while the crown ether cavity size is varied from 14-crown-4 to 16-crown-15 to 19-crown-6 to 22-crown-7. A more limited variation of the crown ether cavity size for a somewhat different type of dibenzo crown ether carboxylic acid is provided by **11** and **13**. Compounds **3**, **4**, and **11** are a series of structural isomers in which the

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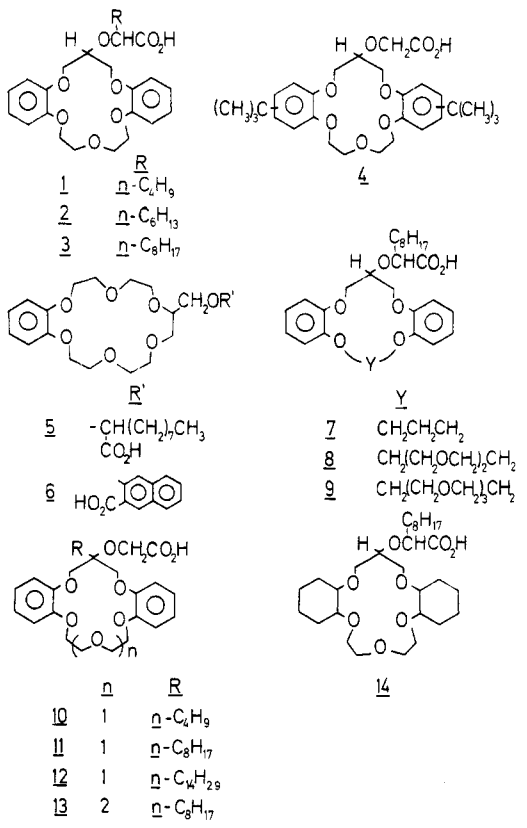
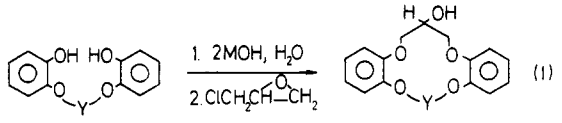
Chart I



attachment site for the lipophilic group(s) is changed. Since cation complexation by crown ethers increases when alkyl aryl ether oxygens are replaced by dialkyl ether oxygens,[14] the primary structural difference between **3** and **14** should be an increase of the oxygen basicity in the latter.

Synthesis of Crown Ether Alcohols. Dibenzo crown ether alcohols are key synthetic intermediates for the preparation of lipophilic crown ether carboxylic acids **7–14**.

The dibenzo crown ether alcohols **19–22** were produced by reactions of the corresponding diphenols **15–18** with epichlorohydrin in alkaline aqueous media (eq 1).[15] In



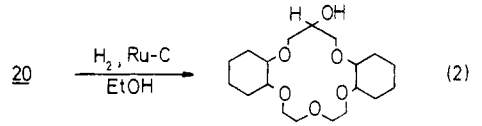
(1)

	Y	M		Yield (%)
15	$CH_2CH_2CH_2$	Li	19	51
16	$CH_2CH_2OCH_2CH_2$	Na	20	60
17	$CH_2(CH_2OCH_2)_2CH_2$	K	21	39
18	$CH_2(CH_2OCH_2)_3CH_2$	Cs	22	35

these reactions, the alkali hydroxide metal cation was varied to take advantage of the template effect.[16] The general procedure for the synthesis of **19–21** which has been reported earlier[15] was utilized for the reaction of bisphenol **18**, CsOH, and epichlorohydrin in water to produce *sym*-hydroxydibenzo-22-crown-7 (**22**) in 35% yield. Use of KOH as the base was found to be much less effective. Compared with the formation of dibenzo crown ether alcohols **19** and **20**, the yields obtained in the cyclization of bisphenols **17** and **18** with epichlorohydrin were somewhat lower and indicate a decreased efficiency of the reaction for producing larger-ring crown ether alcohols.

Although procedures for the preparation of bisphenols **16–18** have been published,[17,18] the reported yields of **17** and **18** are very low.[18] Alternative methods for the synthesis of **17** and **18** are recorded in the Experimental Section together with the preparation of the new bisphenol **15**.

High-pressure catalytic hydrogenation of *sym*-hydroxydibenzo-16-crown-5 (**20**) produced the corresponding saturated crown ether alcohol *sym*-hydroxydicyclohexano-16-crown-5 (**23**) in good yield (eq 2). Analysis

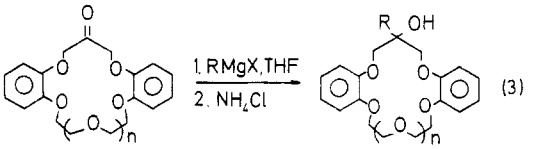


(2)

of **23** by thin-layer chromatography (TLC) indicated the presence of at least two diastereomers.

When subjected to Jones oxidation, crown ether alcohol **20** was converted into *sym*-ketodibenzo-16-crown-5 (**24**) in 75–80% yield. Oxidations with pyridinium chlorochromate[19] or chromium trioxide–pyridine–water (Cornforth reagent)[20] were less effective and an attempted oxidation with sodium hypochlorite[21] gave only ring chlorination of **20**. A 49% yield of *sym*-ketodibenzo-19-crown-6 (**25**) was obtained by the Jones oxidation of the corresponding dibenzo crown ether alcohol **21**.

Reactions of the crown ether ketones **24** and **25** with Grignard reagents in THF provided good to excellent yields of lipophilic dibenzo crown ether tertiary alcohols **26–29** (eq 3).



(3)

	n		n	R
24	1	26	1	n-C_4H_9
25	2	27	1	n-C_8H_{17}
		28	1	n-$C_{14}H_{29}$
		29	2	n-C_8H_{17}

Synthesis and Spectra of Lipophilic Crown Ether Carboxylic Acids. Crown ether alcohols **19, 21, 22,** and **23** were transformed into the corresponding lipophilic crown ether carboxylic acids **7, 8, 9,** and **14** by reaction with NaH and then 2-bromodecanoic acid in THF at room temperature. Yields of 35–46% were obtained. In some cases, rather specialized procedures were required to purify the highly lipophilic crown ether carboxylic acids.

Lipophilic crown ether carboxylic acids **10–12** were prepared by reactions of the corresponding lipophilic crown ether alcohols **26–28** with NaH and then bromoacetic acid in THF at room temperature. The use of excess bromoacetic acid produced quantitative conversions and eliminated the problematic separation of the lipophilic reaction product from any unconsumed lipophilic crown ether al-

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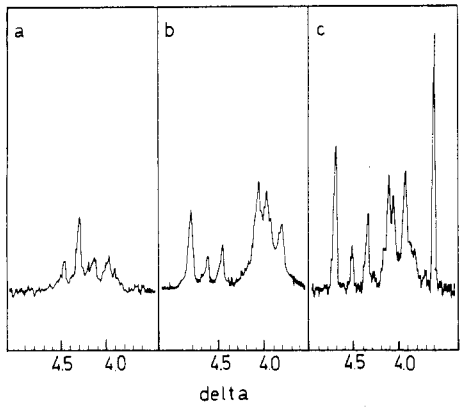


Figure 1. Proton magnetic resonance specta (60 MHz) in $CDCl_3$ for (a) *sym*-dibenzo-16-crown-5-oxyacetic acid (**30**), (b) *sym*-(*n*-octyl)dibenzo-16-crown-5-oxyacetic acid (**11**), and (c) methyl *sym*-(*n*-octyl)dibenzo-16-crown-5-oxyacetate.

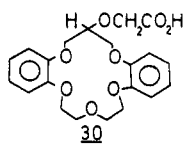
cohol. For the transformation of the crown ether alcohol **29** into crown ether carboxylic acid **13** even the use of excess bromoacetic did not produce complete conversion. Compound **13** was prepared in 78% yield by reaction of lipophilic crown ether alcohol **29** with NaH at room temperature and then with methyl bromoacetate at reflux followed by basic hydrolysis of the resultant ester.

Identities of lipophilic crown ether carboxylic acids **7–14** were verified by infrared (IR) and proton magnetic resonance (^{1}H NMR) spectroscopy and by elemental analysis. When taken in conjunction with the previously reported spectrum for **3**,[12] the IR spectra of lipophilic crown ether carboxylic acids **7–9** exhibit some interesting similarities and differences. For all four compounds, two carbonyl absorption bands are observed which are separated by 25–35 cm^{-1}. With **7** and **3** these are two sharp carbonyl absorptions and the O–H stretching absorption for the carboxylic acid groups is very broad and ill-defined. For **8** and **9**, the higher frequency carbonyl absorption is dominant and the lower one appears as a distinct shoulder. The O–H stretching absorption for the carboxylic acid group is well-defined for these compounds. We suggest that the IR spectral differences between **7** and **3** on the one hand and **8** and **9** on the other are due to enhanced intramolecular hydrogen bonding of the carboxylic acid group of the former with their polyether oxygens.[15]

The IR spectra of lipophilic crown ether carboxylic acids **13** and **14** exhibit single carbonyl absorption at 1740 and 1750 cm^{-1}, respectively, and pronounced O–H stretching absorptions for the carboxylic acid group, which suggest that intramolecular hydrogen bonding is unimportant.

For the series of *sym*-(*n*-alkyl)dibenzo-16-crown-5-oxyacetic acids **10–12**, the carbonyl absorptions consist of a dominant peak at 1730 cm^{-1}, which is flanked by a smaller peak at 1770 cm^{-1} and a definite shoulder at 1700 cm^{-1}. Only for **12** is the O–H stretching absorption for the carboxylic acid group found to be very pronounced.

Figure 1 records the ^{1}H NMR spectra in the region of 3.5–5.0 ppm for *sym*-dibenzo-16-crown-5-oxyacetic acid (**30**), *sym*-(*n*-octyl)dibenzo-16-crown-5-oxyacetic acid (**11**),



30

and methyl *sym*-(*n*-octyl)dibenzo-16-crown-5-oxyacetate. The two proton singlet at δ 4.46 (Figure 1a) is assigned to the methylene protons in the oxyacetic acid group of **30**. For **11** (Figure 1b) this two proton singlet is shifted downfield to 4.81 ppm. In addition, two apparent singlets with a total integrated area corresponding to two protons appear at 4.63 and 4.47 ppm. From the area of these two absorptions and the observation that their separation was unaffected by a change of external magnetic field strength from 60 to 100 MHz, they are assigned as the lower field portion of an "AB quartet" pattern[22] for the two methylene groups on either side of the tertiary carbon in the polyether ring. The two hydrogens of each methylene group are rendered nonequivalent by the deshielding effect of the carboxylic acid group which is positioned over one face of the polyether ring. The observed coupling constant of 10 Hz is consistent with geminal coupling.

One conceivable explanation for a restriction of the carboxylic acid group to one polyether ring face in **11** is intramolecular hydrogen bonding of the carboxylic acid group to the polyether ring oxygens. To probe this possibility, the ^{1}H NMR spectrum of the corresponding methyl ester was measured (Figure 1c). Close correspondence of the spectra for **11** and its methyl ester reveals that intramolecular hydrogen bonding interactions are not required.

Examination of a CPK space-filling model for *sym*-(*n*-octyl)dibenzo-16-crown-5-oxyacetic acid (**11**) reveals that the oxyacetic acid group will be oriented over one face of the polyether ring when the lipophilic *n*-octyl group extends away from the more polar polyether portion of the molecule. Therefore the unusual ^{1}H NMR spectral features of **11** may be attributed to a spatial restriction of the carboxylic acid group which arises when an alkyl group is attached to the crown ring carbon that bears the pendant oxyacetic acid function. In earlier reports from other laboratories, similar spatial restrictions of nonionizable crown ether pendant groups have been proposed to rationalize the increased efficiency in cation complexation which results from alkyl group attachment to the carbon that joins the pendant group to the polyether ring.[23,24]

Spatial restriction of the carboxylic acid groups of *sym*-(*n*-butyl)dibeno-16-crown-5-oxyacetic acid (**10**), *sym*-(*n*-tetradecyl)dibenzo-16-crown-5-oxyacetic acid (**12**), and *sym*-(*n*-octyl)dibenzo-19-crown-6-oxyacetic acid (**13**) is also readily apparent from their ^{1}H NMR spectra. The ^{1}H NMR absorptions for **10** and **12** in the region of 3.5–5.0 ppm are identical with that for **11** (Figure 1b). The two proton singlet for the oxyacetic acid group of **13** appears at 4.51 ppm and the downfield peaks of the "AB quartet" for the diastereotopic methylene hydrogens are at 4.47 and 4.29 ppm (J = 11 Hz).

Experimental Section

Melting points were taken with either a Mel-Temp of Fisher-Johns melting point apparatus and are uncorrected. IR spectra were obtained with a Nicolet MX-S or a Beckman Acculab 8 spectrometer and are recorded in reciprocal centimeters. ^{1}H NMR spectra were recorded with Varian EM360, EM360A, and XL100 spectrometers, and chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. Elemental analysis was performed by Galbraith Laboratories, Inc. of Knoxville, TN.

Chemicals. Unless specified otherwise reagent grade reactants and solvents were obtained from commercial suppliers and used as received. THF and *n*-pentane were purified by distillation from $LiAlH_4$. Pyridine was dried over KOH pellets. The crown ether alcohols **19–21** were available from earlier work.[15] Catechol mono-2-tetrahydropyranyl ether,[25] 2-bromodecanoic acid,[26] and

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1,5-bis(2-hydroxyphenoxy)-3-oxapentane[17] (16) were prepared by the literature methods.

1,3-Bis(2-hydroxyphenoxy)propane (15). Under nitrogen, a solution of NaOH (5.0 g, 125 mmol) in water (5 mL) was added during 1 h to a mechanically stirred solution of catechol (11.0 g, 100 mmol) and 1,3-dibromopropane (6.0 mL, 59 mmol) which had been heated to 120–140 °C. When the addition was completed, the reaction mixture was heated at this temperature and stirred for 8 h. While still fluid, the mixture was poured into water and a 5 N NaOH solution (50 mL) and CH_2Cl_2 were added. Solid material was removed by filtration and the aqueous layer of the filtrate was separated, neutralized with concentrated HCl and extracted with CH_2Cl_2. (Additional product was recovered by suspending the filtered solid in methylene chloride and adding concentrated HCl with stirring until the solid dissolved.) The CH_2Cl_2 solutions were combined, dried with $MgSO_4$ and passed through a short column of silica gel to remove polymeric contaminants. Evaporation of the CH_2Cl_2 in vacuo gave the title compound **15** (4.5 g, 35%); mp 130–131 °C; IR (KBr) 3350 (OH); ^1H NMR (CD_3COCD_3) 2.25 (m, 2), 4.22 (t, 4), 5.93 (br s, 2), 6.80 (s, 8). Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.23; H, 6.15. Found: C, 68.99; H, 6.27.

1,8-Bis(2-hydroxyphenoxy)-3,6-dioxaoctane (17). Under nitrogen, a mixture of catechol (110 g, 1.0 mol), KOH (42.0 g, 0.75 mol), and 600 mL of water was heated at reflux with stirring until a solution was obtained. Then 1,2-bis(2-chloroethoxy)ethane (33.7 g, 0.18 mol) was added dropwise over 4 h. Upon completion of the addition, the reaction mixture was refluxed for an additional 48 h and allowed to cool to room temperature. The oily layer which formed at the bottom of the flask was separated, dissolved in CH_2Cl_2, and washed with 5 N NaOH solution (2 × 100 mL) to separate the phenolic and nonphenolic products.[27] The pH of the resultant dark alkaline solution was adjusted to 9 with concentrated HCl and the solution was extracted with CH_2Cl_2.[28] The CH_2Cl_2 solution was dried with $MgSO_4$ and evaporated in vacuo. The resultant oil was dissolved in Et_2O (50 mL), 5 mL of water was added, and the mixture was stirred vigorously and placed in a refrigerator for 1 h. The solid hydrate of **17** which formed was filtered and dried to produce 40.0 g of crude product. The crude product was purified by chromatography on silica gel columns with Et_2O as eluent to provide 36.0 g (56%) of **17** hydrate: mp 54–55 °C (lit.[18] mp 33–35 °C); IR (KBr) 3580–3000 (OH, with maxima at 3480 and 3170), 1640 (hydrate OH); ^1H NMR ($CDCl_3$) 2.70 (br s, 2), 3.70 (s, 4), 3.56–4.00 (m, 4), 4.00–4.80 (m, 4), 6.87 (m, 8), 7.20 (br s, 2).

Tetraethylene glycol ditosylate (31) was prepared by adapting a published procedure for the synthesis of hexaethylene glycol ditosylate.[29] To a solution of 19.4 g (0.10 mol) of tetraethylene glycol in 250 mL of pyridine which had been cooled to −4 °C was added dropwise a solution of 57.2 g (0.30 mol) of *p*-toluenesulfonyl chloride in 250 mL of pyridine over 3 h under nitrogen. The reaction solution was stirred at −4 °C for an additional 3 h and was placed in a refrigerator overnight. The reaction mixture was poured into 1 L of ice–water and the resultant mixture was extracted with CH_2Cl_2 (3 × 350 mL). The combined CH_2Cl_2 extracts were washed with 6 N HCl (3 × 350 mL) and then with saturated aqueous ammonium chloride. After drying of the CH_2Cl_2 solution over $MgSO_4$, the solvent was removed in vacuo to yield 46.9 g (93%) of **31** as a pale brown oil, which was of sufficient purity for use in subsequent synthesis: ^1H NMR ($CDCl_3$) 2.42 (s, 6), 3.3–3.9 (m, 12), 4.17 (t, 4), 7.15–7.9 (m, 8).

1,11-Bis(2-hydroxyphenoxy)-3,6,9-trioxaundecane (18). After removing the protecting mineral oil from 10.0 g (0.21 mol) of NaH by washing with *n*-pentane under nitrogen, 31.1 g (0.16 mol) of catechol mono-2-tetrahydropyranyl ether[25] in 250 mL of THF was added. The mixture was stirred at room temperature for 0.5 h and heated to reflux, and 40.2 g (0.080 mol) of **31** in 200 mL of THF was added dropwise over 1 h. The reaction mixture was refluxed under nitrogen for 18 h, cooled, and filtered. Evaporation of the solvent from the filtrate in vacuo gave an oil which was chromatographed on silica gel with CH_2Cl_2:EtOH (96:4) as the eluent to produce, after evaporation of the solvent, 30.2 g of crude tetrahydropyranyl protected **18** as a yellow oil.

To a solution of 10.2 g (18.7 mmol) of this yellow oil dissolved in 100 mL of CH_2Cl_2:EtOH (1:1) was added 0.6 g of Amberlite IR-120 (SO_3H resin). The mixture was refluxed for 24 h, filtered, and evaporated in vacuo to yield a yellow oil. This oil was purified by column chromatography on silica gel with Et_2O as eluent, and 3.3 g (47%) of **18** was obtained as an oil which was used without further purification for the preparation of crown ether alcohol **22**: ^1H NMR ($CDCl_3$) 3.2–4.2 (m, 16), 6.4–7.0 (m, 10).

***sym*-Hydroxydibenzo-22-crown-7 (22).** A mixture of bisphenol **18** (1.00 g, 2.6 mmol), CsOH (0.80 g, 5.3 mmol), and 200 mL of water was stirred under nitrogen at 90–95 °C until the bisphenol dissolved. The solution was cooled to 50 °C and epichlorohydrin (0.25 mL, 3.2 mmol) was added over 15 min. Stirring and heating at 50 °C were continued for an additional 17 h. The cooled reaction mixture was extracted with CH_2Cl_2 (3 × 100 mL), and the combined CH_2Cl_2 layers were washed with water (5 × 200 mL), dried over $MgSO_4$, and evaporated. The residual oil was purified by column chromatography on silica gel with Et_2O:acetone (90:10) as eluent to provide 0.40 g (35%) of **22** as an oil: IR (neat) 3460 (OH); ^1H NMR ($CDCl_3$) 3.3–4.5 (m, 21), 6.88 (s, 8). Anal. Calcd for $C_{23}H_{30}O_8H_2O$: C, 61.05; H, 7.13. Found: C, 61.30; H, 6.97.

A larger scale synthesis which used 18.2 g of crude **18** gave a 23% yield of **22**.

***sym*-Hydroxydicyclohexano-16-crown-5 (23).** A 300-mL stainless steel stirred reactor was charged with **20** (4.85 g, 14 mmol), 5% Ru on carbon (0.50 g), and 100 mL of absolute EtOH. Hydrogenation was carried out at 100 °C and 1200 psi of hydrogen for 15 h.[30] After filtering the catalyst, the solvent was evaporated in vacuo. The resulting dark solid residue was purified by column chromatography on silica gel with Et_2O as eluent, which yielded 2.50 g (50%) of **23** as a white solid:[31] mp 90–95 °C; IR (KBr) 3420 (OH); ^1H NMR ($CDCl_3$) 1.0–2.0 (m, 16), 3.12 (br s, 1), 3.2–4.1 (m, 17). Anal. Calcd for $C_{19}H_{34}O_6$: C, 63.70; H, 9.50. Found: C, 63.57; H, 9.66.

***sym*-Ketodibenzo-16-crown-5 (24) (Improved Synthesis).**[32] With mechanical stirring, 20.0 g (57.8 mmol) of crown ether alcohol **20** was dissolved in 400 mL of purified acetone (refluxed over and distilled from $KMnO_4$). To the cooled (water bath) and vigorously stirred solution was added 60 mL of Jones reagent (26.7 g of CrO_3, 23 mL of concentrated H_2SO_4, and sufficient H_2O to make a 100 mL volume)[33] over a 10 min period. After an additional 2 h of stirring the reaction mixture consisted of a tan solution and a green precipitate. The tan solution was decanted and the green precipitate was washed with acetone (2 × 20 mL). The acetone washings were combined with the tan solution and 2.0 g of $NaHSO_3$ was added to decolorize the solution. Then up to 20 g of $NaHCO_3$ was added to consume the remaining acid. After filtration, the solution was partially evaporated in vacuo. The creamy white precipitate that formed was filtered, washed with cold acetone, and allowed to dry, which provided 55–65% yields of **24** with mp 138–139 °C (lit.[33] mp 138–139 °C).

***sym*-Ketodibenzo-19-crown-6 (25).** To a mechanically stirred solution of crown ether alcohol **21** (10.0 g, 25.8 mmol) dissolved in 150 mL of purified acetone (refluxed over and distilled from $KMnO_4$), 22 mL of Jones reagent[33] (vide supra) was added during 10 min. After stirring for an additional 3.5 h, the liquid phase was decanted and evaporated in vacuo to 70 mL. This solution was poured into 450 mL of water and allowed to stand overnight. The resulting solid was collected by filtration and recrystallized

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(27) From the resulting CH_2Cl_2 solution, 5.5 g of oil which contained several side products was isolated.
(28) Only a small amount of catechol is extracted at this pH.
(29) Newcomb, M.; Moore, S. S.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6405.
(30) This hydrogenation was performed by Dr. J. B. Kimble of Phillips Petroleum Company (Bartlesville, OK).
(31) The purified product showed two spots upon TLC analysis (silica gel plates, Et_2O) which indicated the presence of diastereomers.
(32) Eastman, M. P.; Patterson, D. E.; Bartsch, R. A.; Liu, Y.; Eller, P. G. *J. Phys. Chem.* **1982**, *86*, 2052.
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from *n*-hexane to afford 4.90 g (49%) of white solid: mp 80–80.5 °C; IR (neat) 1739 (C=O); ^{1}H NMR ($CDCl_3$) 3.8–4.5 (m, 12), 4.93 (s, 4), 6.93 (s, 8). Anal. Calcd for $C_{21}H_{24}O_7$: C, 64.62; H, 6.25. Found: C, 64.79; H, 6.30.

General Method for the Preparation of 26–28. To 0.28 g (11.5 mmol) of magnesium turnings in a flame-dried apparatus under nitrogen was added to 40 mL of THF and 11.5 mmol of the 1-bromoalkane. The mixture was refluxed until most of the magnesium had been consumed. Then 5.8 mmol of crown ether ketone **24** or **25** was added and refluxing was continued for 5 h. After cooling the reaction mixture to room temperature, 30 mL of 5% aqueous NH_4Cl solution was added and the mixture was stirred for 10 h. The THF was evaporated in vacuo and the residue was extracted with 50 mL of Et_2O. The Et_2O solution was dried with $CaCl_2$ and evaporated to afford a white solid which was stirred with 100 mL of *n*-pentane for 1 h. The solid was filtered and dissolved in a small amount of CH_2Cl_2 and loaded onto a silica gel column. Elution with CH_2Cl_2 and then Et_2O afforded colorless solids **10–12**.

sym-(*n*-Butyl)hydroxydibenzo-16-crown-5 (**26**): mp 103–103.5 °C); 58–65% yield; IR (neat) 3460 (OH); ^{1}H NMR ($CDCl_3$) 0.7–2.2 (m, 9), 3.26 (s, 1), 3.7–4.4 (m, 12), 6.90 (s, 8). Anal. Calcd for $C_{23}H_{30}O_6$: C, 68.66; H, 7.46. Found: C, 68.87; H, 7.59.

sym-(*n*-Octyl)hydroxydibenzo-16-crown-5 (**27**): mp 92–93 °C; 70–100% yield; IR (neat) 3450 (OH); ^{1}H NMR ($CDCl_3$) 0.7–2.1 (m, 17), 3.30 (s, 1), 3.7–4.4 (m, 12), 6.90 (s, 8). Anal. Calcd for $C_{27}H_{38}O_6$: C, 70.74; H, 8.30. Found: C, 70.57; H, 8.30.

sym-(*n*-Tetradecyl)hydroxydibenzo-16-crown-5 (**28**): mp 94–95 °C; 70–90% yield; IR (neat) 3445 (OH); ^{1}H NMR 0.7–2.1 (m, 29), 3.30 (s, 1), 3.8–4.3 (m, 12), 6.90 (s, 8). Anal. Calcd for $C_{33}H_{50}O_6$: C, 73.06; H, 9.23. Found: C, 73.01; H, 9.37.

***sym*-(*n*-Octyl)hydroxydibenzo-19-crown-6 (29).** A solution of crown ether ketone **25** (4.38 g, 11.3 mmol) in 20 mL of THF was added to a Grignard reagent which was prepared by the general method (vide supra) from 1-bromooctane (4.34 g, 22.5 mmol) and magnesium turnings (0.58 g, 23.9 mmol) in 40 mL of THF. After the reaction mixture had been stirred for 15 min, 20 mL of 5% aqueous NH_4Cl solution was added, and the mixture was stirred for an additional 20 min. The THF was evaporated in vacuo and the residue was extracted with 100 mL of CH_2Cl_2. The aqueous layer was reextracted with 30 mL of CH_2Cl_2. Evaporation of the combined CH_2Cl_2 layers in vacuo produced a brown oil which was purified by column chromatography on silica gel with CH_2Cl_2 as the eluent to give 4.20 g (74%) of **29** as a colorless oil: IR (neat) 2466 (OH); ^{1}H NMR ($CDCl_3$) 0.7–2.3 (m, 17), 3.57 (s, 1), 3.6–4.5 (m, 16), 6.87 (s, 8). Anal. Calcd for $C_{29}H_{42}O_7$: C, 69.32; H, 8.37. Found: C, 69.04; H, 8.51.

General Procedure for the Preparation of 10–12. After removal of the protecting mineral oil from 0.63 g (13.1 mmol) of NaH by washing with *n*-pentane under nitrogen, 2.2 mmol of crown ether alcohol **26–28** in 10 mL of THF was added. The mixture was stirred for 0.5 h at room temperature and then bromoacetic acid (0.66 g, 4.7 mmol) in 4 mL of THF was added dropwise. The reaction mixture was stirred for 45 h at room temperature. Careful addition of ice (to decompose the excess NaH) and then 20 mL of H_2O was followed by evaporation of the THF in vacuo. To the oily residue was added 20 mL of CH_2Cl_2 and the mixture was acidified to pH 1 with 6 N HCl. The organic layer was separated, washed with 10 mL of H_2O, dried over $CaCl_2$, and evaporated in vacuo to give quantitative yields of solids **10–12**. Further purification by column chromatography on silica gel with CH_2Cl_2 as the eluent gave colorless crystals.

sym-(*n*-Butyl)dibenzo-16-crown-5-oxyacetic acid (**10**): mp 145–146 °C; IR (neat) 3400–3000 (weak) (COOH), 1770, 1730, 1700 (sh) (C=O); ^{1}H NMR ($CDCl_3$) 0.7–2.1 (m, 9), 3.6–4.2 (m, 10), 4.55 (d, 2, J = 10 Hz), 4.81 (s, 2), 6.87 (s, 8), 9.20 (s, 1). Anal. Calcd for $C_{25}H_{32}O_8 \cdot 0.5H_2O$: C, 63.96; H, 7.03. Found: C, 64.02; H, 7.14.

sym-(*n*-Octyl)dibenzo-16-crown-5-oxyacetic acid (**11**): mp 95.5–97.5 °C; IR (neat) 3400–3000 (weak) (COOH), 1770, 1730, 1700 (sh) (C=O); ^{1}H NMR ($CDCl_3$) 0.7–2.2 (m, 17), 3.6–4.3 (m, 10), 4.55 (d, 2, J = 10 Hz), 4.81 (s, 2), 6.87 (s, 8), 9.40 (s, 1). Anal. Calcd for $C_{29}H_{40}O_8$: C, 67.44; H, 7.75. Found: C, 67.14; H, 7.73.

sym-(*n*-Tetradecyl)dibenzo-16-crown-5-oxyacetic acid (**12**): mp 107–108 °C; IR (neat) 3400–2400 (COOH), 1770, 1730, 1700 (sh) (C=O); ^{1}H NMR ($CDCl_3$) 0.8–2.2 (m, 29), 3.6–4.2 (m, 10), 4.55 (d, 2, J = 10 Hz), 4.81 (s, 2), 6.89 (s, 8) 9.60 (s, 1). Anal. Calcd for $C_{35}H_{52}O_8$: C, 70.00; H, 8.67. Found: C, 70.12; H, 8.55.

***sym*-(*n*-Octyl)dibenzo-19-crown-6-oxyacetic Acid (13).** After removal of the protecting mineral oil from 1.20 g (25 mmol) of NaH by washing with *n*-pentane under nitrogen, 4.20 g (8.4 mmol) of crown ether alcohol **29** in 10 mL of THF was added, and the mixture was stirred for 30 min at room temperature. Methyl bromoacetate (3.42 g, 22 mmol) in 10 mL of THF was added and the reaction mixture was refluxed for 20 h. Water (10 mL) was carefully added and the THF was evaporated in vacuo. After adding 100 mL of EtOH and 20 mL of 5 N NaOH to the residue, the solution was refluxed for 2 days. The solvent was evaporated in vacuo to a volume of 10 mL, and 100 mL of water was added. The solution was acidified to pH 1 with 6 N HCl and was extracted with CH_2Cl_2 (100 mL). The organic layer was separated, washed with water, and evaporated in vacuo to afford 3.66 g (78%) of **13** as a hydroscopic oil: IR (neat) 3700–2200 (COOH), 1740 (C=O); ^{1}H NMR ($CDCl_3$) 0.7–2.3 (m, 17), 3.5–4.3 (m, 14), 4.38 (d, 2, J = 11 Hz), 4.51 (s, 2), 6.86 (s, 8), 7.50 (s, 1). Anal. Calcd for $C_{31}H_{44}O_9 \cdot 1.8H_2O$: C, 62.79; H, 8.04. Found: C, 62.83; H, 7.81.

2-(*sym*-Dibenzo-14-crown-4-oxy)decanoic Acid (7). The protecting mineral oil was removed from 5.34 g (111 mmol) of NaH by washing with *n*-pentane under nitrogen and 50 mL of THF was added. After stirring the mixture for 15 min at room temperature, 7.30 g (22.3 mmole) of crown ether alcohol **19** dissolved in 120 mL of THF was added dropwise during 0.5 h. The reaction mixture was stirred for 1 h at room temperature and 8.38 g (33.4 mmol) of 2-bromodecanoic acid dissolved in 80 mL of THF was added dropwise over 4 h. After stirring the reaction mixture for 47 h at room temperature, an additional 2.0 g (8.0 mmol) of 2-bromodecanoic acid dissolved in 20 mL of THF was added during 1 h, and the reaction mixture was stirred for 40 h at room temperature. Careful addition of water destroyed the unconsumed NaH, after which the THF was evaporated in vacuo. The residue was dissolved in 75 mL of formamide which contained 2.3 g of NaOH. This formamide solution was successively extracted with 25 mL portions of Et_2O until unconsumed **19** was no longer evident in the ether extract by TLC. The formamide layer was acidified with 10% HCl and extracted with 100 mL of $CHCl_3$. The $CHCl_3$ layer was dried over $MgSO_4$ and evaporated in vacuo. The residue was a pale yellow oil to which 60 mL of *n*-hexane was added, and the mixture was placed in a refrigerator overnight. The resultant white solid was filtered and dried under vacuum to yield 5.0 g (46%) of 7: mp 74.5–76.5 °C; IR (KBr) 3200–2800 (COOH), 1725 and 1700 (C=O); ^{1}H NMR 0.7–2.5 (m, 19), 4.0–4.8 (m, 10), 6.95 (s, 8), 9.07 (s, 1). Anal. Calcd for $C_{28}H_{38}O_7$: C, 69.11; H, 7.87. Found: C, 69.25; H, 8.04.

2-(*sym*-Dibenzo-19-crown-6-oxy)decanoic Acid (8). After removal of the protecting mineral oil from 4.0 g (83 mmol) of NaH by washing with *n*-pentane under nitrogen, 40 mL of THF was added, and the mixture was stirred for 0.5 h at room temperature. Crown ether alcohol **21** (10.0 g, 26.7 mmol) dissolved in 50 mL of THF was added dropwise during 1 h and the reaction mixture was stirred for 0.5 h. Then 7.38 g (29.4 mmol) of 2-bromodecanoic acid dissolved in 100 mL of THF was added dropwise over 12 h, and the reaction mixture was stirred at room temperature for 48 h. Water was carefully added to destroy the excess NaH. The THF was evaporated in vacuo and the residue was added to 100 mL of water which was subsequently extracted with $CHCl_3$ (1 × 100 mL and then 2 × 25 mL). The combined $CHCl_3$ layers were acidified with 10% HCl, filtered, dried over $MgSO_4$, and evaporated in vacuo. The residue was dissolved with stirring in 80 mL of formamide which contained 5.0 g of NaOH. The formamide solution was extracted repeatedly with Et_2O:CCl_4 (1:3) until unreacted **21** could no longer be detected in the extract by TLC. The formamide layer was acidified with 10% HCl and extracted with $CHCl_3$ (1 × 100 mL and then 2 × 25 mL). The combined $CHCl_3$ extracts were dried over $MgSO_4$ and evaporated in vacuo to give 5.30 g (35%) of **8** as a hygroscopic heavy oil: IR (neat) 3350–2900 (COOH), 1740 and 1708 (C=O); ^{1}H NMR ($CDCl_3$) 0.7–2.2 (m, 17), 3.6–4.7 (m, 18), 6.90 (s, 8), 8.50 (s, 1). Anal. Calcd for $C_{31}H_{44}O_9 \cdot H_2O$: C, 64.34; H, 7.91. Found: C, 64.15; H, 7.82.

2-(*sym*-Dibenzo-22-crown-7-oxy)decanoic Acid (9). The protecting mineral oil was removed from 2.28 g (48 mmol) of NaH by washing with *n*-pentane under nitrogen and 40 mL of THF was added. After the mixture was stirred for 0.5 h at room

temperature, 4.30 g (9.5 mmol) of crown ether alcohol **22** dissolved in 50 mL of THF was added dropwise during 1 h. The reaction mixture was stirred for 1 h and 3.10 g (12.3 mmol) of 2-bromodecanoic acid dissolved in 50 mL of THF was added dropwise over a 3-h period. The reaction mixture was stirred for 62 h at room temperature and the THF was evaporated in vacuo. Water was carefully added to the residue to destroy unconsumed NaH and then more water (200 mL total) was added. The resulting alkaline aqueous solution was acidified to pH 2 with 6 N HCl and extracted with CH_2Cl_2 (4 × 100 mL). The combined organic layers were dried over $MgSO_4$ and evaporated in vacuo to afford 7.0 g of brown oil. Purification by column chromatography on silica gel eluting with acetone as eluent to remove impurities and then with MeOH provided 2.6 g of crude product as a yellow solid which was contaminated with 2-bromodecanoic acid. The yellow solid was dissolved in 100 mL of $CHCl_3$ and washed with 0.02 N NaOH (4 × 100 mL) and then with 100 mL of 0.1 N HCl. The $CHCl_3$ layer was dried over $MgSO_4$ and evaporated in vacuo to afford 2.30 g (38%) of **9** as a very viscous oil: IR (neat) 3450–3000 (COOH), 1745 and 1715 (sh) (C=O); ^1H NMR ($CDCl_3$) 0.6–2.1 (m, 17), 3.5–4.6 (m, 22), 6.90 (s, 8), 9.45 (br s, 1). Anal. Calcd for $C_{33}H_{48}O_{10}$: C, 65.54; H, 8.00. Found: C, 65.55; H, 7.89.

2-(*sym*-Dicyclohexano-16-crown-5-oxy)decanoic Acid (14). NaH (8.0 g, 167mmol) was washed with *n*-pentane under nitrogen to remove the protecting mineral oil. THF (80 mL) was added and after the mixture had been stirred for 0.5 h at room temperature, 12.0 g (33.5 mmol) of crown ether alcohol **23** dissolved in 50 mL of THF was added dropwise during 1.5 h. The reaction mixture was stirred for 1 h and 12.04 g (47.9 mmol) of 2-bromodecanoic acid dissolved in 100 mL of THF was added during a 2 h period. After the reaction mixture had been stirred for 10 h, a second portion of 2-bromodecanoic acid (3.1 g, 12.3 mmol) was added and stirring was continued for another 15 h. Water was carefully added to destroy the unconsumed NaH and the THF was evaporated in vacuo. The residue was dissolved in CH_2Cl_2 and acidified with 4 M HCl. The separated CH_2Cl_2 layer was dried over $MgSO_4$ and evaporated in vacuo. The residue was loaded onto a column of basic alumina (Brockman Activity 1). Unreacted 2-bromodecanoic acid and **23** were removed by elution with Et_2O and THF, respectively. Compound **14** was eluted with MeOH which contained 3% concentrated HCl (by volume). The methanolic eluent was evaporated in vacuo and extracted with $CHCl_3$. The $CHCl_3$ extract was dried over $MgSO_4$ and evaporated to yield 7.20 g (41%) of **14** as an oil: IR (neat) 3500–3000 (COOH), 1753 (C=O), 1107 (COC); ^1H NMR ($CDCl_3$), 0.7–2.8 (m, 33), 3.1–4.9 (m, 18), 8.2 (br s, 1). Anal. Calcd for $C_{29}H_{52}O_8$: C, 65.88; H, 9.91. Found: C, 65.73; H, 9.88.

Registry No. **7**, 87598-60-5; **8**, 87598-61-6; **9**, 87598-62-7; **10**, 87598-63-8; **11**, 87598-64-9; **12**, 87598-65-0; **13**, 87598-66-1; **14**, 87598-67-2; **15**, 42397-72-8; **17**, 68822-97-9; **18**, 68822-98-0; **18** tetrahydropyranyl derivative, 87598-68-3; **19**, 78328-81-1; **20**, 78328-78-6; **21**, 78328-79-7; **22**, 87655-07-0; **23**, 87598-69-4; **24**, 81633-82-1; **25**, 87598-70-7; **26**, 87598-71-8; **27**, 87598-72-9; **28**, 87598-73-0; **29**, 87598-74-1; **31**, 37860-51-8; catechol, 120-80-9; 1,3-dibromopropane, 109-64-8; 1,2-bis(2-chloroethoxy)ethane, 112-26-5; tetraethyl glycol, 112-60-7; catechol mono-2-tetrahydropyranyl ether, 21645-25-0; cesium hydroxide, 21351-79-1; epichlorohydrin, 106-89-8; bromoacetic acid, 79-08-3; methyl bromoacetate, 96-32-2; 2-bromodecanoic acid, 2623-95-2; 1-bromobutane, 109-65-9; 1-bromooctane, 111-83-1; 1-bromotetradecane, 112-71-0.

Inverse Electron Demand Diels–Alder Reactions of 4,6-Dimethyl-2-oxo-2*H*-pyran-5-carboxylic Acid Esters and Morpholino Enamines: Regiospecific Preparation of 3- or 4-Substituted-2,6-dimethylbenzoates[1]

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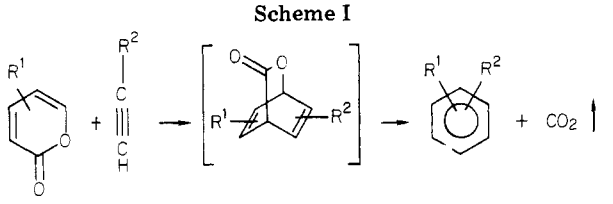
Previously, α-pyrones have been used as dienes in cycloaddition reactions with enamines to form adducts that, upon elimination of carbon dioxide via a cycloreversion reaction and concomitant aromatization through amine elimination, provided substituted aryl derivatives; however, the regioselectivity of this reaction was not determined. We report that the Diels–Alder reaction of methyl or ethyl 4,6-dimethyl-2-oxo-2*H*-pyran-5-carboxylate with morpholino enamines is regiospecific. By proper choice of enamine either of the isomeric 2,6-dimethylbenzoates may be obtained as a single product. In several cases a single regioisomeric dihydrobenzoate, which results from elimination of carbon dioxide from the initial cycloadduct, was isolated and characterized.

Introduction

The discovery in these laboratories that pyrethroid esters derived from cyclopropane and closely related carboxylic acids coupled with substituted biphenyl-3-methanols were highly effective insecticides[2] prompted us to investigate regiospecific synthesis routes to highly substituted benzyl alcohols, including biphenylmethanols, that would be practical in terms of allowing the preparation of the alcohols in sufficient yield and purity to make the derived esters commercially attractive.

Scheme I



Conceptually, we were intrigued by earlier investigations of α-pyrones being used as dienes in cycloaddition reactions with alkynes[3] to form adducts which, upon elimina-

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(2) (a) Plummer, E. L. U.S. Patent 4 130 657 to FMC Corporation, Dec 19, 1978. (b) Plummer, E. L. U.S. Patent 4 214 004 to FMC Corporation, July 22, 1980. (c) Engel, J. F. U.S. Patent 4 238 505 to FMC Corporation, Dec 9, 1980. (d) Plummer, E. L.; Pincus, D. S. *J. Agric. Food Chem.* **1981**, *19*, 1118. (e) Plummer, E. L. U.S. Patent 4 329 518 to FMC Corporation, May 11, 1982. (f) Engel, J. F.; Plummer, E. L.; Stewart, R. R.; Van Saun, W. A.; Montogomery, R. E.; Cruickshank, P. A.; Harnish, W. N.; Nethery, A. A. and Crosby, G. A. In "IUPAC Pesticide Chemistry"; J. Miyamoto et al., Eds.; Pergamon Press: New York, 1983; pp 101–106. (g) Cardis, A. B. U.S. Patent 4 375 476 to FMC Corporation, March 1, 1983.

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