Table IV, no. 9 and 10 were prepared in the same way but the products did not liquefy during drying.

Competitive Complex Formation. A methanol solution containing 0.97 g (0.01 mol) of potassium thiocyanate and 0.955 g (0.005 mol) of cesium thiocyanate in 20 ml of solvent was prepared by warming. To this solution fibrous crystals of dibenzo-18-crown-6 (3.6 g, 0.01 mol) were gradually added with stirring. The first portion dissolved instantly but when more than half had been added, crystals of a different appearance began to come out. The rest of the polyether and 25 ml of methanol were added and the slurry was warmed and agitated. It was then cooled in ice–water, filtered, washed with cold methanol, and dried. The crystals weighed 3.3 g, yield 72%. The product melted at 244–254° and had the following composition. *Anal.* Calcd for $C_{20}H_{24}O_6(KCNS)$: C, 55.1; H, 5.2; N, 3.1; S, 7.0; Cs, nil. Found: C, 55.4; H, 5.0; N, 3.3; S, 7.3; Cs, 1.0.

The filtrate and the methanol washing were combined (total volume 60 ml), added to 3.6 g (0.01 mol) of dibenzo-18-crown-6, and warmed at which nearly all the polyether dissolved. The mixture was filtered hot and allowed to stand at room temperature. Large crystals had formed by the next day, and they were isolated by decantation, washed with cold methanol, and dried. The crystals weighed 2.7 g, yield 59%. The product melted at 145–152° and had the following composition. *Anal.* Calcd for $(C_{20}H_{24}O_6)_2(CsCNS)$: C, 54.0; H, 5.3; N, 1.5; S, 3.5; K, nil. Found: C, 53.9; H, 5.0; N, 1.7; S, 3.6; K, 0.03.

The first crystals to come out are those of the 1:1 complex of potassium thiocyanate contaminated with some cesium compound. This would seem to indicate that this complex is more stable than the 2:1 complex of cesium thiocyanate which is formed subsequently. Although this conclusion is probably correct, the relative solubilities of the two complexes in methanol must also be involved.

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New Macrocyclic Polyethers

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Abstract: Nine new macrocyclic polyethers have been synthesized including acetals, a carbonate, and a derivative of 1,8-dihydroxynaphthalene. Dicyclohexyl-15-crown-5 is the best complexing agent for Na^+ found to date, and dicyclohexyl-16-crown-5 the most specific for Na^+ *vs.* the other alkali cations. The acetal polyethers are less effective complexing agents than similar compounds in which $-OCH_2O-$ has been replaced by $-OCH_2CH_2O-$.

The preparation and properties of a number of macrocyclic polyethers derived from aromatic vicinal diols have been previously reported.[1] It was shown that certain of these compounds, particularly those containing five to ten oxygen atoms, form stable complexes with the alkali and alkaline earth cations, and that the most favorable linkage for complexation is $-OCH_2CH_2O-$, followed by $-O(CH_2)_3O-$ and becoming ineffective beyond $-O(CH_2)_4O-$, but the effect of $-OCH_2O-$ had not been determined. It was further demonstrated that saturated compounds are better complexing agents than the corresponding aromatic compounds from which they are obtained by catalytic hydrogenation. The dibenzo polyethers containing five oxygen atoms were found to have a special affinity for the sodium ion, but they had not yet been hydrogenated to improve their effectiveness.

In a continuation of this work, nine new macrocyclic polyethers were synthesized: three contain the $-OCH_2-O-$ link to test the effect of this group on complex formation; two are saturated compounds derived from dibenzo-5-oxygen compounds; one is a product obtained from a dibenzo compound by hydrogenating only one of the atomatic rings; one is a derivative of 1,8-dihydroxynaphthalene which is not a vicinal diol; and two were prepared by ring-closing 1,17-dihydroxy-4,5,:13,14-dibenzo-3,6,9,12,15-pentaoxaheptadeca-4,13-diene, an intermediate which is well adapted to this process.

The code numbers and the structural formulas of the new compounds are shown in Figure 1. The digits within the diagrams indicate the total number of atoms in the polyether ring. The code numbers continue the series started in the original paper,[1] and the abbreviated nomenclature described therein will be used whenever applicable without ambiguity; otherwise, the compounds will be identified by their code numbers. L is dicyclohexyl-15-crown-5, LI is dicyclohexyl-16-crown-5, LII is benzocyclohexyl-18-crown-6, and LVIII is 1,8-naphthyl-16-crown-5; the others cannot be named in this way without using too many numbers. The full names of all these compounds are given in the Experimental Section. LVI is a cyclic polyether and a carbonate, but it is included here because it might be considered derived from LIV by the oxidation of the methylene to the carbonyl group. XXI is dibenzo-16-crown-5, XXV is dibenzo-15-crown-5, XXVIII is dibenzo-18-crown-6, and XXXI is dicyclohexyl-18-crown-6. The first three are mentioned in Table I and the last in Table IV. The structures of these compounds are shown in the original reference[1] but they should be discernible from their abbreviated names.

Results and Discussion

The methods used for and other information pertinent to the synthesis of these polyethers are shown in Table I, the melting points and the analytical data are given in Table II, and the ultraviolet spectra are summarized in Table III. Note that LIII, LIV, and LVII contain at

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(1) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

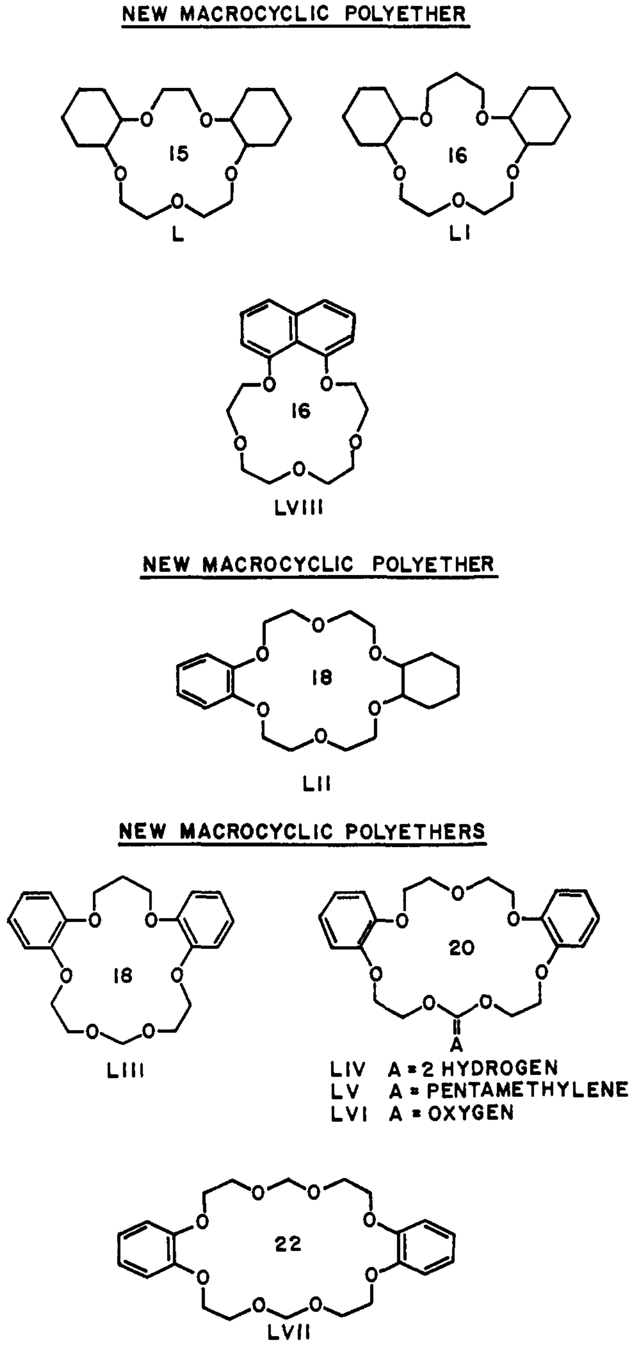

Figure 1. Structural formulas of cyclic polyethers.

least one formal linkage, $-OCH_2O-$, which makes them susceptible to acid hydrolysis (see Experimental Section), and LVIII is not a derivative of an aromatic vicinal diol.

The infrared spectra of all the compounds showed the absence of OH and the presence of the appropriate ether linkages. The nmr spectra of all except those discussed below were consistent with the proposed structures. The nmr spectra of LIV and LVII could not be determined because of insufficient solubility in deuteriochloroform, and the identity of LII was confirmed by high-resolution mass spectrometry.[2] Dibenzo-18-crown-6 (XXVIII) gave a strong molecular ion of mass 360.1561 (theory 360.1573). The most prominent fragment was $C_{12}H_{16}O_4$ from the loss of $C_8H_8O_2$. There was no evidence for any fragment between $C_{12}H_{16}O_4$ and the molecular ion $C_{20}H_{24}O_6$. Dicyclohexyl-18-crown-6 (XXXI) showed a weak molecular ion of mass 372.2504 (theory 372.2512) confirming its structure. The weak molecular ion is, undoubtedly, the result of decreased stabilization due to the loss of aromaticity upon saturation. The most prominent large fragment observed was $C_{18}H_{30}O_4$ from the loss of $C_2H_6O_2$. No fragment from the loss of $C_8H_8O_2$ but a fragment from the loss of $C_8H_{14}O_2$ was observed which corresponds to the same cleavage as for dibenzo-18-crown-6. However, its abundance was much less because of the loss of aromatic stabilization. Benzocyclohexyl-18-crown-6 (LII) gave a medium strong peak at a mass of 366.2013 (theory 366.2042), thus confirming the half-saturated structure. The fragmentation pattern was somewhat intermediate between the unsaturated and the fully saturated compounds.

The complexing properties of these cyclic polyethers were not investigated in detail, but some of the results obtained are shown in Table IV. The spectral criterion has been previously explained,[1] and can be applied only to aromatic compounds. The extraction method described below is a convenient way of comparing the relative complexing powers for different cations. This method has these advantages over the spectral method: complexing efficiencies can be ranked numerically, and saturated polyethers that do not absorb in the region of 275 mμ can also be evaluated.

When an aqueous solution of an alkali metal hydroxide or salt containing a very low concentration of the picrate of the same cation is mixed with an equal volume of an immiscible organic solvent, nearly all the picrate is present in the yellow aqueous phase and the organic phase remains substantially colorless. If a cyclic polyether is added to the system (by dissolving it in the organic solvent), the complexed picrate transfers to the organic phase, the extent depending on the effectiveness of the polyether as a complexing agent for the cation (assuming no complication due to lack of solubility). If the polyether is ineffective, the organic phase will be colorless; if the polyether is very powerful, most of the color will be in the organic phase. The efficiencies of the polyethers will lie between these two limits, and can be expressed as percentage extracted. The stoichiometry of the extractable complex is 1:1 in respect to alkali cation and picrate anion; hence, the maximum extraction is limited by the component present at the lowest concentration. For this reason, per cent extraction always means per cent of the extractable maximum.

The data in Table IV were obtained under these conditions: equal volumes of water and methylene chloride, picrate and polyethers at 7×10^{-5} M, alkali hydroxides at 0.1 M, and at room temperature. For the purpose of a comparison, the extraction data for dicyclohexyl-18-crown-6 (XXXI)[1] are included. This compound is the best complexing agent for potassium and also, in general, the most effective for the other cations.

Attempts to prepare crystalline complexes of LIII, LIV, and LVII with potassium thiocyanate by a method which always gives the complex of dibenzo-18-crown-6

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(2) Kindly examined by T. K. Beukelman, Jackson Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours and Co.

Table I. Synthetic Methods for Cyclic Polyethers. Reactants,[a] Solvents, and Yields

Compd	Method[1]	Reactant 1	Reactant 2	Solvent	Yield, %
L	Z	Hydrogenation of XXV[1]		1-Butanol	28
LI	Z	Hydrogenation of XXI[1]		1-Butanol	66
LII	Z	Partial hydrogenation of XXVIII[1]		Methanol[b]	8
LIII	W	1,3-Bis[*o*-hydroxyphenoxy]propane	Bis(2-chloroethoxy)methane	1-Butanol	31
LIV	W	Bis[2-(*o*-hydroxyphenoxy)ethyl] ether	Same as LIII	1-Butanol	62
LV	Special[c]	1,17-Dihydroxy-4,5,13,14-dibenzo-3,6,9,12,15-pentaoxaheptadeca-4,13-diene	Cyclohexanone	Benzene	16[d]
LVI	Special[c]	Same as LV	Phosgene	Benzene	48[d]
LVII	X	Catechol	Same as LIII	1-Butanol	8
LVIII	V	1,8-Dihydroxynaphthalene	1,11-Dichloro-3,6,9-trioxaundecane	2-Butanol	28

[a] Potassium hydroxide was used for the preparation of LIII, sodium hydroxide for LIV, LVII, and LVIII. [b] In the presence of sodium chloride. [c] See Experimental Section. [d] Yield on conversion: LV 28% reacted; LVI 31% reacted.

Table II. Analytical Data and Melting Points

Compd	Formula	Mp, °C[a]	Carbon, % Found	Carbon, % Calcd	Hydrogen, % Found	Hydrogen, % Calcd
L	$C_{18}H_{32}O_5$	62–63	66.2	65.9	9.9	9.8
LI	$C_{19}H_{34}O_5$	Below 26	66.6	66.7	9.9	9.9
LII	$C_{20}H_{30}O_6$	Below 26	65.4	65.6	8.2	8.2
LIII	$C_{20}H_{24}O_6$	118	66.6	66.7	6.7	6.7
LIV	$C_{21}H_{26}O_7$	151–152	64.7	64.6	6.6	6.7
LV	$C_{26}H_{34}O_7$	162	67.8	68.1	7.1	7.4
LVI	$C_{21}H_{24}O_8$	122–125	62.1	62.4	6.0	5.9
LVII	$C_{22}H_{28}O_8$	166–167	63.0	62.8	6.8	6.7
LVIII	$C_{18}H_{22}O_5$	112–115	68.2	68.0	6.9	6.9

[a] Melting points were taken on a Fisher–Johns apparatus and are uncorrected.

Table III. Ultraviolet Spectra in Methanol

Compd	Wavelength, mμ	Extinction coefficient
L	No absorption above 210	
LI	No absorption above 210	
LII	277	1600
LIII	275	4600
LIV	276	4800
LV	276	4900
LVI	275	3800
LVII	276	4200
LVIII	300	6900
	316.5	5900
	331	5600

Table IV. Evidence for Complex Formation

Compd	Ultraviolet spectrum in methanol	Extraction with water–methylene chloride, % Li^+	Na^+	K^+	Ca^+
L		3	45	23	12
LI		1	20	2	1
LIII	Negative with Li^+, Na^+, K^+, Ca^+, Ba^{2+}				
LIV	Positive with K^+, Cs^+ Negative with Li^+, Na^+, Mg^{2+}, Sr^{2+}, Ba^{2+}				
LV	Negative with all tested				
LVI	Positive with Na^+, NH_4^+, K^+, Cs^+ Negative with Li^+, Ag^+, Ba^{2+}				
LVII	Negative with all tested				
LVIII	Positive with Na^+, K^+, Ag^+, Sr^{2+}, Ba^{2+} Negative with Cs^+		6	25	
XXXI[1]		3	26	78	44

(XXVIII) were unsuccessful. This is particularly interesting in connection with LIII because it is a geometrical isomer of XXVIII, suggesting the importance of the correct location of the oxygen atoms in the polyether ring for complex formation. It also seems that $-OCH_2O-$ is a less favorable linkage than $-OCH_2CH_2O-$ for complexation.

As expected dicyclohexyl-15-crown-5 and dicyclohexyl-16-crown-5 are good complexing agents for sodium, L being the best found to date and LI being the most specific for sodium. Apparently, the size of the holes in these polyethers is just right for the sodium ion, and the difference in the complexing properties of the compounds is most likely due to the different effects of $-OCH_2CH_2O-$ and $-O(CH_2)_3O-$ on complex formation.

1,8-Naphtho-16-crown-5, LVIII, shows that macrocyclic polyethers capable of complexing cations can be prepared from aromatic diols other than vicinal.

1,17-Dihydroxy-4,5,13,14-dibenzo-3,6,9,12,15-pentaoxaheptadeca-4,13-diene, obtained by the acid hydrolysis of LIV, is interesting in two respects: it forms a dihydrate from which water is removed only with difficulty (melting under vacuum), and ultraviolet spectra indicate that it forms complexes in methanol with sodium and potassium cations. This seems to indicate that the molecule tends to assume a circular conformation and, possibly, because of this, it can be ring-closed with relative ease.

Work is continuing in this field and future plans include further study of the effects of changes in structure and composition on complexing power and a thermodynamic investigation of complex formation in different solvents and the species present in such solutions.

Experimental Section

The following instruments were used: Varian Model A-60 for nmr spectra, Perkin-Elmer Infracord Model 137 for infrared spectra, and Perkin-Elmer ultraviolet-visible spectrophotometer Model 202 for ultraviolet spectra.

All inorganic compounds were reagent grade, and all solvents and available organic materials were commercial products used without purification.

All phenolic reactants (reactant 1 in Table I), except catechol, and 1,8-dihydroxynaphthalene, were synthesized by treating 2 mol of the sodium salt of 2-(*o*-hydroxyphenoxy)tetrahydropyran or of *o*-hydroxyphenoxymethyl methyl ether with 1 mol of the dihalides, and obtaining the free dihydric phenols by acid hydrolysis. 2-(*o*-Hydroxyphenoxy)tetrahydropyran was prepared according to Parham and Anderson.[3]

All evaporations were made with a rotary vacuum evaporator.

Preparation of 2,5,12,15,18-Pentaoxatricyclo[17.4.0.0^{6,11}]tricosane (L). Method Z. A mixture of 10 g of 2,3,8,9-dibenzo-1,4,7,10,13-pentaoxacyclopentadeca-2,8-diene (XXV), 150 ml of 1-butanol, and 2.5 g of ruthenium catalyst (5% ruthenium on alumina) was hydrogenated in a 400-ml stainless steel bomb at 100° and 1000 psig with very good agitation until no more hydrogen was absorbed.

The catalyst was filtered off and the solvent was removed under vacuum. The residue weighing 9.8 g was placed on a column of alumina and eluted with 600 ml of benzene to give 2.8 g of product. Analytically pure compound was obtained by recrystallization from petroleum ether: molecular weight, calcd 328; found 321. Under proper conditions, the yield should be much higher.

Preparation of 2,6,13,16,19-Pentaoxatricyclo[18.4.0.0^{7,12}]tetracosane (LI). Method Z. This compound was prepared in the same way as L. Twenty grams of 2,3,9,10-dibenzo-1,4,8,11,14-pentaoxacyclohexadeca-2,9-diene (XXI) gave 13.6 g of the product as a viscous liquid which was not yet crystallized in about a year. Here too, the yield should be higher.

Preparation of 9,10-Benzo-2,5,8,11,14,17-hexaoxabicyclo[16.4.0-docosa-9-ene (LII). Method Z. A mixture of 154 g (0.43 mol) of 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (XXVIII), 250 ml of methanol, 28 g of sodium chloride in 80 ml of water, and 20 g of ruthenium catalyst was hydrogenated in a 1-l. stainless steel autoclave at 100° and 1000 psig with good agitation until about 2.4 mol of hydrogen had been absorbed.

The catalyst was filtered off and the filtrate was evaporated. The residue weighing 164 g was extracted twice with 300 ml of hot *n*-hexane and gave 41.8 g of viscous liquid which was put on a column of alumina (4.2 × 9.5 in.) with *n*-hexane. The column was eluted 5 times with 70 ml of *n*-hexane and 3 times with 70 ml of benzene and gave the following fractions in order (in grams): 0.1, 12.9, 5.0, 1.5, 0.8, 5.6, 0.8, and 0.3. Infrared spectra showed that fractions 1 and 2 contained no aromatic compounds, and 7 and 8 contained compounds with hydroxyl groups. Fractions 3, 4, 5, and 6 (12.9 g) consisted of the desired compound.

By underhydrogenating, say a quarter of total hydrogenation, a mixture should result from which the desired product should be more readily recovered at a higher yield.

Preparation of 2,3,9,10-Dibenzo-1,4,8,11,14,16-hexaoxacyclooctadeca-2,9-diene (LIII). Method W. A mixture of 21.5 g (0.083 mol) of 1,3-bis[*o*-hydroxyphenoxy]propane, 600 ml of 1-butanol, 10.7 g (0.166 mol) of 85% potassium hydroxide pellets, and 14.4 g (0.083 mol) of bis(2-chloroethoxy)methane was refluxed under nitrogen for 23 hr during which time the temperature was 116–118°.

The liquid was decanted and evaporated. The residue weighing 20.9 g was dissolved in 300 ml of methylene chloride, washed twice with 200 ml of 2% aqueous sodium hydroxide, dried with sodium sulfate, and evaporated. The residue weighing 15.2 g was recrystallized from methanol and gave 9.2 g of the product: molecular weight, calcd 360; found 378.

1,15-Dihydroxy-4,5,11,12-dibenzo-3,6,10,13-tetraoxapentadeca-4,11-diene was obtained by boiling LIII with methanolic hydrochloric acid containing a little water.

Anal. Calcd: C, 65.5; H, 6.9; mol wt, 348. Found: C, 65.2; H, 7.0; mol wt, 319.

Preparation of 2,3,11,12-Dibenzo-1,4,7,10,13,16,18-heptaoxacycloeicosa-2,11-diene (LIV). Method W. A mixture of 14.5 g (0.05 mol) of bis[2-(*o*-hydroxyphenoxy)ethyl] ether, 150 ml of 1-butanol, and 4 g (0.1 mol) of sodium hydroxide in 5 ml of water was heated to reflux temperature (105°) under nitrogen; a solution of 9 g (0.052 mol) of bis(2-chloroethoxy)methane in 50 ml of 1-butanol was added and refluxed for 18 hr.

The white crystals that precipitated on cooling were filtered, washed with water, dried, and proved to be the desired product (12.1 g). Analytically pure compound was obtained by recrystallization from 1,4-dioxane: molecular weight, calcd 390; found 387.

1,17-Dihydroxy-4,5,13,14-dibenzo-3,6,9,12,15-pentaoxaheptadeca-4,13-diene dihydrate was obtained by boiling LIV with methanolic hydrochloric acid containing a little water.

Anal. Calcd for $C_{20}H_{30}O_9$ (the dihydrate): C, 58.0; H, 7.2; mol wt, 414. Found: C, 58.8; H, 7.3; mol wt, 427; mp 73–91°.

It is difficult to remove the water from the dihydrate. Boiling with xylene does not accomplish it but melting the compound under vacuum will gradually eliminate the water.

Preparation of 2,3,13,14-Dibenzo-8-pentamethylene-1,4,7,9,12,15,18-heptaoxacycloeicosa-2,13-diene (LV). A mixture of 4.14 g (0.01 mol) of 1,17-dihydroxy-4,5,13,14-dibenzo-3,6,9,12,15-pentaoxaheptadeca-4,13-diene, 9.8 g (0.1 mol) of cyclohexanone, 0.2 g of *p*-toluenesulfonic acid monohydrate, and 550 ml of benzene was warmed on a steam bath for 5.5 hr during which time benzene was allowed to evaporate slowly until the volume had decreased to about 100 ml. The benzene solution was washed while still warm with 200 ml of water containing 5 g of sodium bicarbonate, then with 200 ml of water. White crystals (3 g) which came out during the night were found to be the starting diol: reacted, 4.14 − 3 = 1.14 g.

The benzene filtrate was evaporated and the residue was triturated with cold methanol, filtered, and dried. Two-tenths gram of the desired compound was recovered. Analytically pure material was obtained by recrystallization from methanol.

Preparation of 2,3,13,14-Dibenzo-1,4,7,9,12,15,18-heptaoxacycloeicosa-2,13-dien-8-one (LVI). Through a solution consisting of 200 ml of benzene, 1.89 g (0.005 mol) of 1,17-dihydroxy-4,5,13,14-dibenzo-3,6,9,12,15-pentaoxaheptadeca-4,13-diene, and 1.58 g (0.02 mol) of pyridine, phosgene, 122 ml at room temperature (0.005 mol), was passed at 36° and then warmed to 70°. On cooling, crystals formed. They were collected, warmed with 20 ml of methanol, cooled in ice, filtered, and dried. The white crystals, 0.3 g, were those of the desired compound. Unreacted starting diol, 1.3 g, was recovered from the filtrates.

Preparation of 2,3,13,14-Dibenzo-1,4,7,9,12,15,18,20-octaoxacyclodocosa-2,13-diene (LVII). Method X. A mixture of 22 g (0.2 mol) of catechol, 150 ml of 1-butanol, and 8 g (0.2 mol) of sodium hydroxide was refluxed (112.5°) under nitrogen, and to it were added dropwise in 67 min 18 g (0.104 mol) of bis(2-chloroethoxy)methane diluted with 20 ml of 1-butanol. The mixture was refluxed for 5.5 hr and cooled slightly, 8 g of sodium hydroxide added and the mixture was refluxed for 30 min; to it was added dropwise in 60 min 18 g of bis(chloroethoxy)methane diluted with 20 ml of 1-butanol, and the mixture was refluxed for 16 hr.

The hot solution was filtered and evaporated. The residue, 38.1 g, was dissolved in 400 ml of chloroform and washed with 200 ml of 5% aqueous sodium hydroxide. Much trouble with emulsion was encountered and it was finally overcome by the addition of calcium chloride. The chloroform layer was dried and evaporated, and the semisolid residue, 25.6 g, was crystallized from benzene. The desired product, 3.3 g, was recovered as white crystals. Analytically pure compound was obtained by recrystallization from 1,4-dioxane: molecular weight, calcd 420; found 435.

Preparation of 2,4-(1′,8′-Naphthylene)-1,5,8,11,14-pentaoxacyclohexadeca-2-ene (LVIII). Method V. A mixture of 16 g (0.1 mol) of 1,8-dihydroxynaphthalene, 250 ml of 2-butanol, 4 g (0.1 mol) of sodium hydroxide dissolved in 5 ml of water, and 23.1 g (0.1 mol) of 1,11-dichloro-3,6,9-trioxaundecane was refluxed with good agitation for 5 hr. Sodium hydroxide, 4 g dissolved in 25 ml of water, was added dropwise and the mixture was refluxed under nitrogen for 16 hr more. It was then cooled, acidified with 4.5 ml of concentrated hydrochloric acid, filtered, and evaporated.

The viscous, oily residue weighing 30.6 g was dissolved in 350 ml of chloroform and extracted twice with 150 ml of 5% aqueous sodium hydroxide. The chloroform layer was dried with magnesium sulfate and evaporated. The residue weighing 23.9 g crystallized on standing, and it was placed on a column of alumina with benzene and eluted with 1 l. of benzene. On evaporation, 8.8 g of white crystals were obtained.

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[3] W. E. Parham and E. L. Anderson, *J. Amer. Chem. Soc.*, **70**, 4187 (1948).