eV) m/e 452 (M^+), 410, 381, 363, and 350. Anal. Calcd for $C_{32}H_{20}O_3$: C, 84.94; H, 4.45. Found: C, 84.94; H, 4.30.

The acetylated product **15** was also obtained analogously from **14** in a 69% yield.

Alkylation of 12 with Alkyl Iodide and Sodium Methoxide in Methanol. The procedure employed for alkylation was similar to that of **10a**. 7-Ethoxy-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrone (**17a**) was obtained as yellow microcrystals in a 35% yield: mp 300–301 °C; IR (KBr) 1672 cm^{-1} (ArCOAr C=O); NMR ($CDCl_3$) δ 1.65 (t, 3, J = 7.5 Hz, CH_3), 4.30 (q, 2, J = 7.5 Hz, CH_2), 6.08 (d, 1, J = 10 Hz, CH=CHAr), 7.80 (d, 1, J = 10 Hz, CHAr), and 6.7–8.2 (m, 15, aromatic **H**); mass spectrum (76 eV) m/e 438 (M^+), 410, 409, 350, 276, and 274. Anal. Calcd for $C_{32}H_{22}O_2$: C, 87.65; H, 5.06. Found: C, 87.44; H, 5.00.

Methylation of **12** gave 7-methoxy-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrone (**17b**, 30%) as yellow microcrystals: mp 305 °C; IR (KBr) 1670 cm^{-1} (ArCOAr C=O); NMR ($CDCl_3$) δ 4.18 (s, 3, CH_3), 6.10 (d, 1, J = 10 Hz, CH=CHAr), 7.82 (d, 1, J = 10 Hz, CHAr), and 6.7–8.2 (m, 15, aromatic **H**); mass spectrum (75 eV) m/e 424 (M^+) and 409. Anal. Calcd for $C_{31}H_{20}O_2$: C, 87.71; H, 4.75. Found: C, 87.54; H, 4.87.

Oxidation of 2 with Chromium Trioxide. A solution of chromium trioxide (10.0 g, 0.100 mol) in water (30 mL) was added to 4.12 g (10.0 mmol) of **2** suspended in 160 mL of acetic acid, and the resulting dark red-brown mixture was stirred and heated under reflux for 2 h. The hot mixture was filtered, the filtrate was diluted with water (1.5 L), and the solid that separated was recovered by filtration. The solid then weighed 2.51 g and melted at 290–294 °C. Two recrystallizations of the product from acetic acid gave 2.14 g (46.7%) of 10-(1-anthraquinonyl)-10-carboxymethylanthrone (**18**) as yellow microcrystals: mp 295–296 °C; IR (KBr) 1760 (acid C=O), 1668, 1640 cm^{-1} (ArCOAr and quinone C=O, respectively); NMR (DMSO-d_6) δ 3.50 (s, 2, CH_2), and 6.8–8.8 (m, 16, aromatic **H**, COOH); mass spectrum (75 eV) m/e 458 (M^+), 399, 313, and 206. Anal. Calcd for $C_{30}H_{18}O_5$: C, 78.59; H, 3.96. Found: C, 78.38 H, 3.99.

The oxidation product **18** was obtained in ca. 45–50% yields on similar oxidations of **8**, **10**, **11**, and **12**, respectively.

Esterification of 18. Methyl Ester (19a). A solution of 1.00 g (2.18 mmol) of **18** in methanol (60 mL) containing 5 g of hydrogen chloride was refluxed for 2 h; removal of excess reagents in vacuo and a recrystallization of the product from methanol gave 0.78 g (76%) of the methyl ester of **18** as yellow microcrystals: mp 251 °C; IR (KBr) 1745 (ester C=O), 1680, 1675, 1660 cm^{-1} (ArCOAr and quinone C=O); NMR ($CDCl_3$) δ 3.17 (s, 3, CH_3), 3.35 (s, 2, CH_2), and 6.6–8.7 (m, 15, aromatic **H**); mass spectrum (75 eV) m/e 472 (M^+), 399, 313, and 256. Anal. Calcd for $C_{31}H_{20}O_5$: C, 78.80; H, 4.27. Found: C, 78.87; H, 4.47.

Ethyl Ester (19b). The oxidation product **18** was esterified with ethanol in the manner described above for methyl ester. A recrystallization of the product from ethanol gave the ethyl ester of **18** as yellow microcrystals in a 80% yield: mp 253 °C; IR (KBr) 1740 (ester C=O), 1674, 1658 cm^{-1} (ArCOAr and quinone C=O, respectively); NMR ($CDCl_3$) δ 0.81 (t, 3, J = 7.5 Hz, CH_3), 3.36 (s, 2, CH_2), 3.63 (q, 2, J = 7.5 Hz, CH_2CH_3), and 6.7–8.8 (m, 15, aromatic **H**); mass spectrum (75 eV) m/e 486 (M^+), 399, 312, and 279. Anal. Calcd for $C_{32}H_{22}O_5$: C, 79.00; H, 4.56. Found: C, 78.90; H, 4.6.

Registry No.—**1**, 4159-04-0; **2**, 65252-91-7; **8**, 65252-92-8; **9**, 65252-93-9; **10a**, 24165-82-0; **10b**, 24215-76-7; **11**, 65252-94-0; **12**, 65252-95-1; **13**, 65252-96-2; **14**, 65252-97-3; **15**, 65252-98-4; **16**, 58382-11-9; **17a**, 65252-99-5; **17b**, 65253-00-1; **18**, 65253-01-2; **19a**, 65253-02-3; **19b**, 65253-03-4; ethyl iodide, 75-03-6; methyl iodide, 74-88-4; diethyl sulfate, 64-67-5; dimethyl sulfate, 77-78-1; 1,2-bis(9-acetoxy-10-anthryl)ethane, 58382-04-0.

References and Notes

(1) (a) British Patent 373 129 (May 12, 1932); (b) British Patent 379 798 (September 8, 1932).
(2) (a) A. B. Turner, *Q. Rev., Chem. Soc.*, **18**, 347 (1964); (b) I. T. Millar and K. E. Richards, *J. Chem. Soc. C*, 855 (1967); (c) A. N. Al-Kafaji, Ph.D. Dissertation, University of Texas, Austin, Texas, 1966.
(3) (a) A. Mustafa and A. N. Islam, *J. Chem. Soc.*, S 81 (1949); (b) W. H. Starnes, Jr., *J. Org. Chem.*, **35**, 1974 (1970); (c) M. M. Sidky, M. R. Mahran, and W. M. Abdo, *J. Prakt. Chem.*, **316**, 377 (1974); (d) H-D. Becker and D. Sanchez, *Tetrahedron Lett.*, 3745 (1975).
(4) R. C. Paul, R. Parkash, S. S. Sandhu, and S. S. Sandhu, *J. Indian Chem. Soc.*, **44**, 319 (1967).
(5) (a) In ref 3d, it was reported that reductive dimerization of **1** by ketyl radicals gave **16**. (b) The compound **16** was prepared independently in a 96% yield by the hydrolysis of 1,2-bis(9-acetoxy-10-anthryl)ethane formed on reductive acetylation of **1** with zinc and acetic anhydride: mp 232 °C (lit.[3d] 245 °C); IR (KBr) 1665 cm^{-1} (ArCOAr C=O); NMR ($CDCl_3$) δ 1.48 (t, 4, CH_2), 4.10 (m, 2, 10-, and 10-H), and 7.0–8.3 ppm (m, 16, aromatic H); mass spectrum 414 (M^+).
(6) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970, p. 120.
(7) H. Duerr, W. Schmidt, and R. Sergio, *Justus Liebigs Ann. Chem.*, 1132 (1974).
(8) P. L. Julian, W. Cole, and E. W. Meyer, *J. Am. Chem. Soc.*, **67**, 1724 (1945).

Octopus Molecules in the Cyclotriveratrylene Series

John A. Hyatt

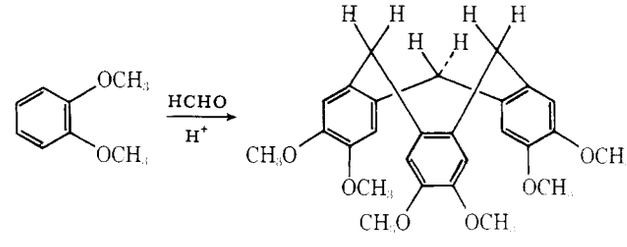
Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee 37662

Received October 3, 1977

Cyclotriveratrylene (**1**) was converted into a series of oligo(ethylene glycol) ether derivatives (**3a–f**). These many-armed polyethers (octopus molecules) are capable of adopting cavity-containing conformations and possess complexing properties typical of crown ethers. Analogous derivatives of macrocycle **9** do not show crown ether behavior; this is attributed to their lack of conformational rigidity. The length of polyether arms is of less importance than the stereochemistry and conformational rigidity of the framework to which they are attached.

The condensation product of veratrole and formaldehyde, originally described by Robinson[1] and formulated as a dimer, has been shown by Lindsey[2] and by Erdtman and co-workers[3] to possess the conformationally stable[4,5] cyclotriveratrylene structure **1**. Despite the novel crown structure and known clathrate-forming ability of **1**,[6] relatively little chemistry in the series has been reported.[7-9]

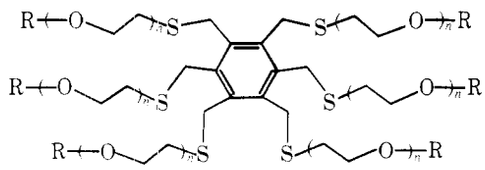
Recently, Vögtle and Weber[10] demonstrated that acyclic, many-armed polyether benzene derivatives of the structural type **2** (octopus molecules) act as complex-forming ligands capable of solubilizing alkali-earth salts in aprotic organic solvents. Since such behavior is of considerable utility,[11] we



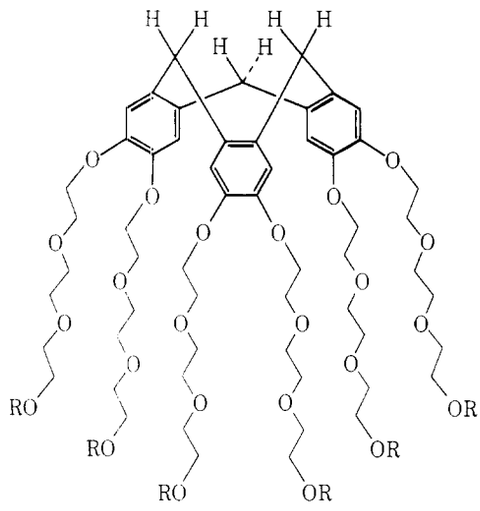
1

undertook the synthesis and study of analogous compounds in the cyclotriveratrylene series. We anticipated that the fixed

0022-3263/78/1943-1808$01.00/0



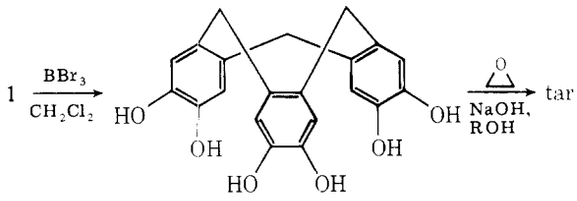
2, n = 1–4; R = alkyl



3e, R = ethyl

crown conformation of 1 would lend increased complex-forming ability to derivatives such as **3.**

Synthesis. Following Lindsey,[9] 1 was demethylated with boron tribromide to afford the air-sensitive hexahydroxy compound **4** in 73% yield. Initial attempts to react **4** with ethylene oxide in the presence of base afforded only intractable material; oxidation of **4** under these conditions occurs



4

rapidly enough to preclude clean reaction. Attention was then turned to attaching preformed oligo(ethylene oxy) ether chains to **4.** Commercially available mono-, di-, tri-, and tetraethylene glycol monoethers (**5a–f**) were converted to their respective tosylates (**6a–f**) using *p*-toluenesulfonyl chloride in pyridine. Slow addition of tosylates **6a–f** to a mixture of **4** and excess sodium hydride in dry dimethylformamide (DMF) under oxygen-free conditions, followed by a brief reflux and chromatographic workup, afforded octopus molecules **3a–f** in the indicated yields (Scheme I).

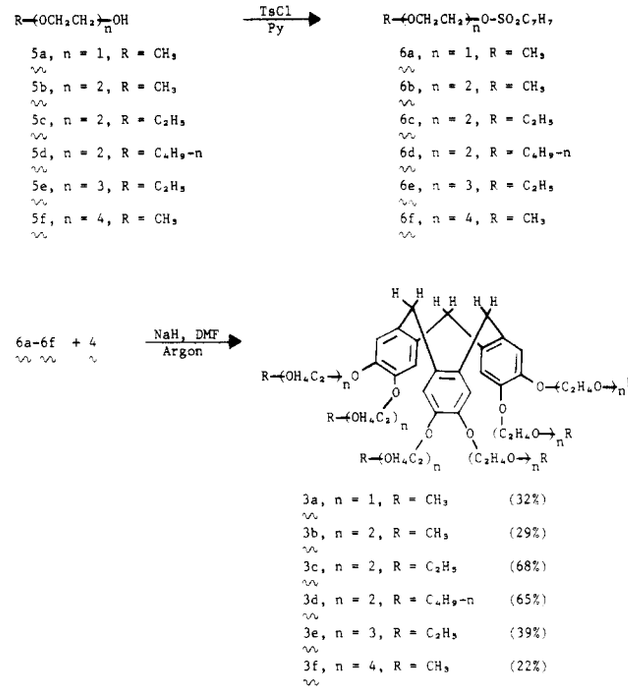
With the exception of **3a** (a crystalline solid), compounds **3** were viscous syrups which occluded solvents strongly and refused to give acceptable combustion analyses. However, high-pressure liquid chromatography showed **3a–f** to be at least 90% pure, and IR, ^{1}H NMR, and ^{13}C NMR spectra were in accord with the structures proposed. Furthermore, **3a** and **3b** were independently synthesized by the routes shown in Scheme II.

The rather circuitous route to **7a** was followed because ethylene glycol monobenzoate was much more easily isolated than either the monotosylate or monotetrahydropyranyl derivative. Compounds **3a** and **3b** produced via this sequence were identical to those prepared from **6a** and **6b.**

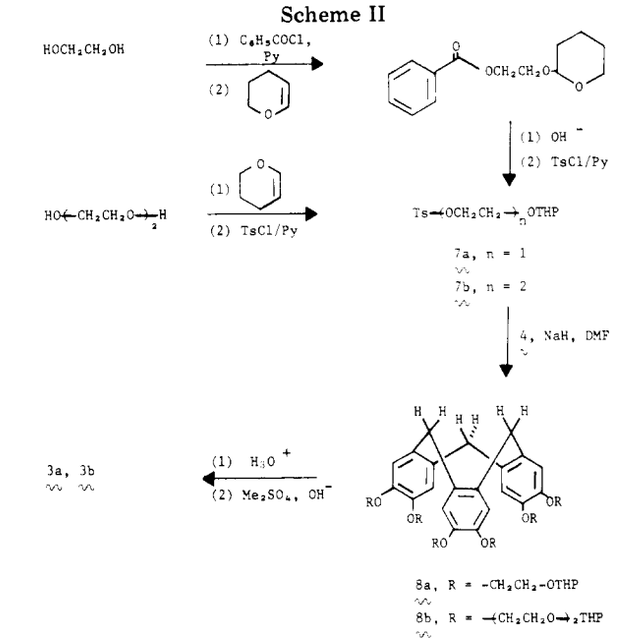
Results and Discussion

Compounds **3a–f** were examined for their ability to solvate

Scheme I



Scheme II



alkali metal salts in organic solvents; the methanol–toluene procedure of Hatay and Meth-Cohn[12] was followed. The results are shown in Table I. It will be noted that the short-armed octopus **3a** is inactive but that the solubilizing power of the longer-armed compounds **3b–f** is generally uniform and comparable to that of 18-crown-6. This contrasts with the octopus molecules **2** prepared by Vötle and Weber,[10] wherein the nature of the alkyl group R strongly influenced complexation behavior.

The importance of a framework of fixed conformation in the complexing ability of octopus molecules was also investigated. Macrocycle **9,** prepared from resorcinol and acetaldehyde,[3,13] is a mobile system which does not readily adopt a crown or bowl-shaped conformation.[14] Elaboration of **9** into octopus molecules **11a** and **11b** was carried out as shown in Scheme III.

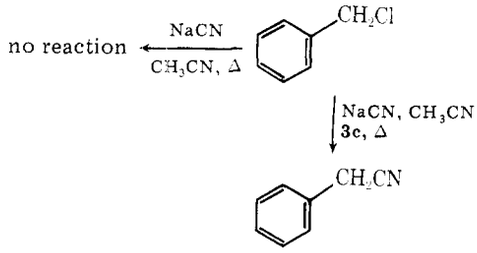
Table I. Complexation Behavior of Octopus Molecules[a,b]

Comp	NaBr	KBr	NH_4I	CsBr	BaI_2	$MgCl_2$
3a	−	−	−	−	−	−
3b	+	+	+	+	±	±
3c	+	+	+	+	±	±
3d	+	+	+	+	±	±
3e	+	+	+	+	±	±
3f	+	+	±	±	−	−
11a	−	±	±	−	−	−
11b	±	±	−	−	−	−
18-Crown-6	+	+	+	+	±	±

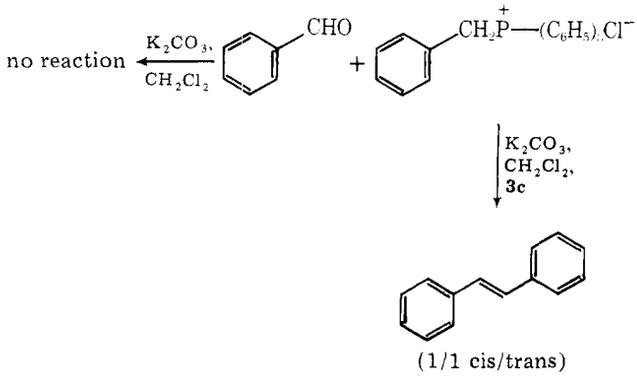
[a] Procedure of ref 12. [b] + indicates strong, rapid complexation. ± indicates weak, slow complexation. − indicates no observed complexation.

As delineated in Table I, compounds **11a** and **11b** have very little complexing or solubilizing ability. Examination of models of **11a** and **11b** demonstrates that a cavity-containing, octopus conformation of the type imposed by the rigid framework in **3a–f** cannot readily be attained in **11a** and **11b.** Therefore, conformational stability and ease of cavity formation, rather than arm length, are crucial factors for complex formation in these octopus molecules.

Although ion-selective complexation was not observed in the series **3a–f,** the utility of such compounds as catalysts was confirmed. Thus, **3c** was capable of transporting such reagents as NaCN and K_2CO_3 into polar, aprotic solvents. Benzyl chloride failed to react with NaCN in CH_3CN at reflux until 5 to 10 mol % **3c** was added; quantitative conversion to phenylacetonitrile then occurred rapidly.



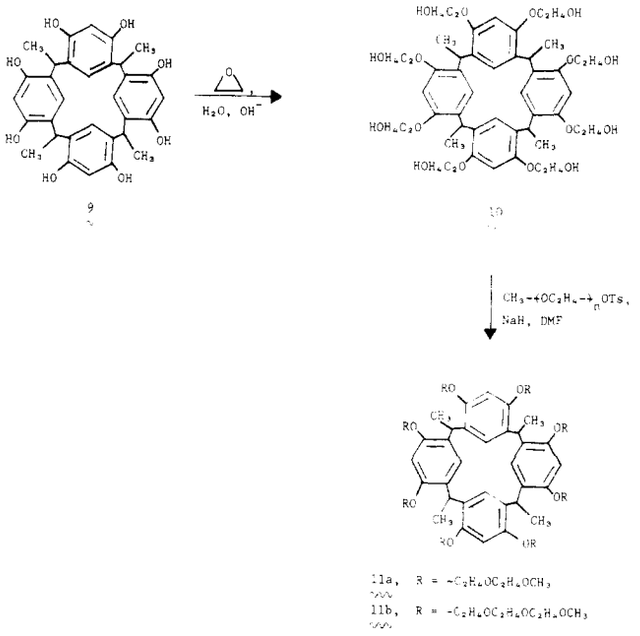
Similarly, benzaldehyde and benzyltriphenylphosphonium chloride failed to react with K_2CO_3 in dichloromethane until 10 mol % of **3c** was added; rapid conversion to 1/1 *cis-/trans*-stilbene then occurred.



(1/1 cis/trans)

Polyether derivatives of cyclotriveratrylene have been prepared and shown to be complexing agents effective in transporting alkali metal salts into polar, aprotic, organic solution. Evidence was obtained which indicates that the length of the polyether arms is of less importance than the shape and conformational stability of the framework to which they are attached. The utility of cyclotriveratrylene octopus molecules as catalysts in organic synthesis was demonstrated.[15]

Scheme III



Experimental Section[16]

Hexaol 4. A solution of 50 g of cyclotriveratryiene (1)[17] in 1500 mL of dry, distilled dichloromethane was stirred under argon during the addition (1.5 h, external cooling) of 200 g of boron tribromide. The reaction mixture was stirred at reflux overnight, cooled, and quenched by slow addition of 500 mL of water (external cooling). The resulting emulsion was filtered under argon (24-cm Buchner funnel) and the crude, wet solid was recrystallized from aqueous EtOH (Norit). Yield, 29.8 g (73.2%) of **4,** whose properties were as previously reported.[9]

Tosylates 6a–f. Tosylates were prepared by reaction of the corresponding alcohols **5a–f** with 1.1 equiv of *p*-TsCl in dry pyridine at 20 °C for 8 h, drowning in ice water, Et_2O extraction, and removal of solvent under vacuum. Compounds **6a–f** were all tan syrups which were used without further purification; purity was judged >95% by NMR in each case.

Octopus Molecules 3a–f. The preparation of **3e** is typical of all members of the series. A solution of 7.32 g (0.02 mol) of hexaol **4** in 100 mL of dry dimethylformamide was treated with 53.3 g (0.16 mol) of triethylene glycol monoethyl ether *p*-toluenesulfonate **6e** and stirred during argon purging for 4 h. Sodium hydride, 3.36 g (0.14 mol), was added to the reaction mixture over 1 h, and the mixture was stirred at 90 °C for 4 h. The mixture was let stand overnight, the dimethylformamide was distilled off in vacuo, the semisolid residue was diluted with 100 mL of methylene chloride and filtered, and the filtrate was stripped of methylene chloride in vacuo. The residual crude product was purified by chromatography on silica gel to afford 11.0 g of **3e** as a light yellow syrup (39% yield): IR (neat) 3.52, 6.62, 7.94, 9.0 (br), 10.5, 13.30 μm; NMR ($CDCl_3$) δ 6.91 (s, 6 H), 4.78 (d, J = 16, 3 H), 4.4–3.5 (m, 87 H), 1.20 (t, J = 7, 18 H).

Ethylene Glycol Monotetrahydropyranyl Ether Tosylate (7a). A solution of 62 g (1.0 mol) of ethylene glycol in 400 mL of pyridine was stirred at 10 °C and 1.0 mol of benzoyl chloride was added dropwise. After 3.0 h at 25 °C, the mixture was poured into 1 L of H_2O, the solid (80 g of dibenzoate) was filtered, and the filtrate was extracted with $CHCl_3$. The organic phase was dried, stripped, and distilled to give 40.2 g of ethylene glycol monobenzoate, bp 105 °C (0.5 mm). Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.03; H, 6.14.

Monobenzoate (100 g) as prepared previously was treated with 0.25 g of *p*-toluenesulfonic acid and 51.0 g (1.0 equiv) of dihydropyran was added with stirring over 0.5 h. After the initial exotherm subsided, infrared analysis disclosed absence of all OH absorption. The total crude product (150 g, 0.6 mol) was added to a solution of 26 g (0.65 mol) of NaOH in 350 mL of H_2O, and the mixture was stirred at reflux for 1.0 h. The resulting homogenous solution was cooled, extracted with $CHCl_3$, dried, and stripped to afford 64.7 g (76%) ethylene glycol monotetrahydropyranyl ether as a light yellow oil. This crude product was immediately tosylated in pyridine as described for **6a–f** to give **7a** in 72% yield as a light yellow syrup that was used immediately in the preparation of **8a.**

Cyclotriveratrylene Derivative 8a. A solution of 7.32 g (0.02 mol) of **4** in 100 mL of dry dimethylformamide was purged with argon for

4 h, treated with 6.72 g (0.14 mol) of 50% NaH–oil dispersion, and stirred 1 h further under argon. An argon-purged solution of 48 g (0.16 mol) of **7a** in 25 mL of dimethylformamide was added dropwise over 1 h; the mix was heated at 80 to 100 °C for 2 h (foams), cooled, and worked up as was **3e** to give 19.4 g (85%) of **8a** as a yellow syrup. The cyclotriveratrylene derivative was used for deblocking and methylation to afford **3a** without further characterization.

Deblocking of 8a and Preparation of 3a. A solution of 17.5 g of **8a** in 150 mL of MeOH was treated (with stirring at 25 °C) with 15 mL of 10% aqueous HCl. Solid product began to crystallize after 20 min; after 8 h, the mix was cooled and filtered to give 5.96 g (61.3%) of **8a** (R = CH_2CH_2OH), mp 233 to 236 °C. An analytical sample was recrystallized from CH_3OH, and had mp 237 to 239 °C: IR (KBr) 2.95, 6.21, 6.62, 7.95, 8.77, 9.25 (br), 10.47, 11.05, and 13.41 μm; NMR (Me_2SO-d_6) δ 7.18 (s, 6 H), 4.72 (m, 12 H), 4.1–3.5 (m, 24 H); ^{13}C NMR (Me_2SO-d_6) 147.06, 132.56, 116.28, 72.89, 59.63, 35.08. Anal. Calcd for **8a** (R = CH_2CH_2OH)·CH_3OH: C, 61.62; H, 6.99. Found: C, 61.86; H, 6.79.

A sample of the crystalline alcohol thus obtained was methylated with excess dimethyl sulfate in DMF; chromatographic workup afforded **3a** as a white solid: mp 86 to 88 °C; IR (KBr) 6.21, 6.61, 7.92, 8.90, 9.15, 9.68, and 13.38 μm; NMR ($CDCl_3$) δ 6.84 (s, 6 H), 4.65 (d, J = 16, 3 H), 4.12 (m, 12 H), 3.70 (m, 12 H), 3.61 (d, J = 16, 3 H), 3.42, (s, 18 H). Anal. Calcd for $C_{39}H_{54}O_{12}$: C, 65.5; H, 7.62. Found: C, 65.6; H, 7.43.

Compound **3a** prepared from **4** and **6a** was identical in all respects to material prepared as described here. Compounds **7b, 8b,** and **3b** were also prepared by a sequence analogous to the above.

Macrocycle 9. The macrocycle was prepared according to Niederl and Vogel.[13] It was noted that the yield of **9** was reduced and gummy by-products were formed if the rate or mode of acetaldehyde addition was changed from that reported.[13]

Octahydroxy Compound 10. A solution of 20 g of compound **9** and 5 g of NaOH in 800 mL of H_2O was heated with 25 g of ethylene oxide in an autoclave at 100 °C for 8 h. The cooled reaction mix was filtered and the crude product was recrystallized from EtOH–hexane to give 7.5 g of **10,** mp 310 to 320 °C dec. Compound **10** was characterized as the octaacetate: mp 40 to 49 °C (Et_2O–hexane); IR (KBr) 5.73, 6.65, 7.27, 8.01 (br), 8.37, 9.48 μm; NMR ($CDCl_3$) δ 7.6–6.3 (br m, 8 H), 4.7 (q, J = 7, 4 H), 4.30 (br s, 32 H), 2.16 (s, 24 H), 1.42 (d, J = 7, 12 H). Anal. Calcd for $C_{64}H_{80}O_{24}$: C, 62.32; H, 6.53. Found: C, 61.89; H, 6.68.

Octopus Molecules 11a and 11b. The preparation of **11a** is illustrative: A solution of 0.89 g (1×10^{-3} mol) of ethylene oxide adduct **10** in 5 mL of dry DMF was stirred at 25 °C under argon and treated with 0.3 g (ca. 12 equiv) of sodium hydride. A solution of 2.3 g (10 equiv) of 2-methoxyethyl tosylate in 5 mL of DMF was added over 10 min, and the mix was stirred for 2.0 h. An additional 0.10 g of NaH was added, and after 2.0 h of further stirring, the reaction mixture was poured into 250 mL of water and extracted with ether (2 × 75 mL). The dried (Na_2SO_4) extract was evaporated to leave a yellow syrup containing **11a** and excess tosylate. The mixture was separated by preparative thin-layer chromatography (TLC) and the product band was isolated to afford 1.10 g of **11a** as a clear syrup: IR (neat) 6.21, 6.33, 6.71, 7.77, 8.40, 9.10 (br), 11.8 μm; NMR ($CDCl_3$) δ 6.58 (br, 8 H), 3.5–4.8 (br m, 68 H), 3.58 (s, 24 H), 1.47 (d, J = 7, 12 H). Compound **11a** retained solvent, and combustion analysis was not obtained.

Preparation of Phenylacetonitrile from Benzyl Chloride Using 3c as Catalyst. A mixture of 0.635 g (0.005 mol) of benzyl chloride, 0.50 g of sodium cyanide (0.010 mol), 0.53 g (0.0005 mol) of **3c,** and 15 mL of acetonitrile was stirred at reflux for 3.0 h, at which time vapor-phase chromatographic analysis of the reaction mixture showed complete consumption of benzyl chloride and formation of phenylacetonitrile as the sole product. The reaction mixture was poured into water and extracted with petroleum ether to afford phenylacetonitrile and recovered catalyst **3c** (82% yield).

A control experiment in which the complexing agent **3c** was omitted gave less than 5% conversion to phenylacetonitrile in 3.0 h.

Use of Compound 3c to Catalyze a Wittig Reaction. A reaction mixture composed of 0.26 g (0.0003 mol) of compound **3c,** 0.40 g (0.003 mol) benzyltriphenylphosphonium chloride, 1.2 g (0.003 mol) of benzaldehyde, 0.33 g (0.003 mol) of potassium carbonate, and 15 mL of dichloromethane was stirred at reflux for 2 h. Analysis of the mixture at this point disclosed consumption of the benzaldehyde and benzyltriphenylphosphonium chloride and formation of 1,2-diphenylethylene (1/1 mixture of cis and trans) in about 90% yield.

Registry No.—**1,** 1180-60-5; **3a,** 65338-93-4; **3b,** 63239-73-6; **3c,** 63283-49-8; **3d,** 65338-94-5; **3e,** 63239-74-7; **4,** 1506-76-9; **5a,** 109-86-4; **5b,** 111-77-3; **5c,** 111-90-0; **5d,** 112-34-5; **5e,** 112-50-5; **5f,** 23783-42-8; **6a,** 17178-10-8; **6b,** 50586-80-6; **6c,** 54176-27-1; **6d,** 50964-16-4; **6e,** 62921-75-9; **6f,** 62921-76-0; **7a,** 65338-95-6; **8a** (R = CH_2CH_2OTHP), 65338-96-7; **8a** free hexaol, 65338-97-8; **9,** 65338-98-9; **10,** 65378-51-0; **10** octaacetate, 65338-99-0; **11a,** 65339-00-6; **11b,** 65339-01-7; ethylene glycol monobenzoate, 94-33-7; ethylene glycol monotetrahydropyranyl ether, 2162-31-4; dimethyl sulfate, 77-78-1; 2-methoxyethyl tosylate, 17178-10-8; 18-crown-6, 17455-13-9.

References and Notes

(1) G. M. Robinson, *J. Chem. Soc.*, **107,** 267 (1915).
(2) A. S. Lindsey, *Chem. Ind. (London)* 823 (1963).
(3) H. Erdtman, F. Haglid, and R. Ryhage, *Acta Chem. Scand.*, **18,** 1249 (1964).
(4) R. C. Cookson, B. Halton, and I. Stevens, *J. Chem. Soc.*, **8,** 767 (1968).
(5) A. Luttringhous and K. Peters, *Angew. Chem., Int. Ed. Engl.*, **5,** 593 (1966).
(6) V. Gaglioti, A. Liquori, N. Galo, E. Giglio, and M. Scrocco, *J. Inorg. Nucl. Chem.*, **8,** 572 (1958).
(7) J. Manville and G. Troghton, *J. Org. Chem.*, **38,** 4278 (1973).
(8) T. Sato, T. Akima, and K. Uno, *J. Chem. Soc., Perkin Trans. 1,* 891 (1973).
(9) A. S. Lindsey, *J. Chem. Soc.*, 1685 (1965).
(10) F. Vögtle and E. Weber, *Angew. Chem., Int. Ed. Engl.*, **13,** 814 (1974).
(11) C. Pedersen and H. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11,** 16 (1972).
(12) M. Hatay and O. Meth-Cohn, *Tetrahedron Lett.*, 469 (1976).
(13) J. Niederl and H. Vogel, *J. Am. Chem. Soc.*, **62,** 2512 (1940).
(14) B. Nilsson, *Acta Chem. Scand.*, **22,** 732 (1968).
(15) Portions of the work described here have been disclosed in U.S. Patent 4 018 832 (April 19, 1977, to Eastman Kodak Co.).
(16) Melting points are uncorrected. Infrared spectra were recorded using a Perkin-Elmer Model 137 instrument; ^1H NMR spectra were obtained with Varian EM-360 and JEOLCO MH-100 spectrometers, using Me_4Si internal standard. ^{13}C NMR spectra were obtained on a Brüker 90 instrument using Me_2SO-d_6 as internal standard. High pressure liquid chromatography utilized Corasil II columns on Waters equipment.
(17) Parrish Chemical Co.