ether and then the ethereal solution was poured onto a column of silica gel (50 times the amount of starting amine oxide). The ethereal solution of the product was then poured onto the column. Elution with diethyl ether (2 bed volumes) was followed by rotary evaporation of the solvent to give the carboxylic acid. The results are summarized in Table VI.

Registry No. 1 (R = Ph), 19069-56-8; 1 (R = p-CH_3Ph), 70415-62-2; 1 (R = p-CH_3OPh), 62557-46-4; 1 (R = p-$(CH_3)_3$CPh), 14377-42-5; 1 (R = p-NO_2Ph), 30727-41-4; 1 (R = $(CH_2)_{14}CH_3$), 70415-63-3; 2 (R = Ph), 70415-64-4; 2 (R = p-CH_3Ph), 70415-65-5; 2 (R = p-CH_3OPh), 70415-66-6; 2 (R = p-NO_2Ph), 70415-67-7; 2 (R = p-$(CH_3)_3$CPh), 70415-68-8; 2 (R = $(CH_2)_{14}CH_3$), 70415-69-9; 3 (R = Ph), 66310-15-4; 3 (R = p-CH_3Ph), 70415-70-2; 3 (R = p-NO_2Ph), 70415-71-3; 3 (R = p-CH_3OPh), 70415-72-4; 3 (R = p-$(CH_3)_3$CPh), 70415-73-5; 3 (R = $(CH_2)_{14}CH_3$), 70415-74-6; 4 (R = Ph), 50908-25-3; 4 (R = p-CH_3Ph), 70415-75-7; 4 (R = p-NO_2Ph), 50908-24-2; 4 (R = p-CH_3OPh), 70415-76-8; 4 (R = p-$(CH_3)_3$CPh), 70415-77-9; 4 (R = $(CH_2)_{14}CH_3$), 70415-78-0; 6 (R = p-NO_2Ph), 831-69-6; 6 (R = Ph), 769-78-8; 6 (R = p-CH_3Ph), 2653-44-3; 6 (R = p-CH_3OPh), 13351-86-5; 6 (R = p-$(CH_3)_3$CPh), 15484-80-7; 7 (R = $(CH_2)_{14}CH_3$), 70415-79-1; 7 (R = p-NO_2Ph), 70415-80-4; 7 (R = Ph), 70415-81-5; 7 (R = p-CH_3Ph), 70415-82-6; 7 (R = p-CH_3OPh), 70415-83-7; 7 (R = p-$(CH_3)_3$CPh), 70415-84-8; 2-pyridylcarbinol, 586-98-1; benzoyl chloride, 98-88-4; benzoic acid, 65-85-0; *p-tert*-butylbenzoic acid, 98-73-7; *p*-methylbenzoic acid, 99-94-5; *p*-methoxybenzoic acid, 100-09-4; *p*-nitrobenzoic acid, 62-23-7; palmitic acid, 57-10-3; 2-(*N*-piperidyl)ethanol, 3040-44-6; *p*-methylbenzoyl chloride, 874-60-2; *p*-methoxybenzoyl chloride, 100-07-2; *p-tert*-butylbenzoyl chloride, 1710-98-1; *p*-nitrobenzoyl chloride, 122-04-3; palmitoyl chloride, 112-67-4.

Synthesis and Solvolysis of β,β-Divinyl-β-phenethyl Tosylate[1,2]

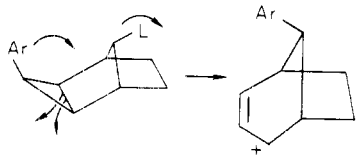
James W. Wilt* and Rein Niinemae[3]

Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626

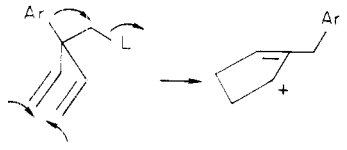
Received January 3, 1979

To seek aryl migration coupled with electrocyclic ring closure during solvolysis, we prepared and solvolyzed the title tosylate in aqueous dioxane and in acetic acid. The products were completely rearranged, both by vinyl (major) and phenyl (minor) migration. No cyclization via the sought electrocyclic closure was detected. The rate of acetolysis of the title tosylate was comparable to that of neophyl tosylate, indicating a balance of the opposing factors of inductive retardation and anchimeric acceleration centered in the vinyl groups.

In principle, the known process of aryl migration coupled with electrocyclic ring *opening*[1] found in eq 1 should have a converse process, viz., that of aryl migration coupled with electrocyclic ring *closure* as in eq 2. The two processes



(1)



(2)

can be viewed, as the aryl group migrates, in terms of a disrotatory cyclopropyl cation ring opening (eq 1) and a conrotatory pentadienyl cation ring closure (eq 2)—reactions with considerable literature precedent.[4] As an initial investigation of this latter possibility, the synthesis and solvolytic rearrangement of β,β-divinyl-β-phenethyl tosylate (**9**) has been studied. Although the desired result of eq 2 was *not* observed, certain synthetic and solvolytic items of interest were obtained, as well as a hindsight rationalization for the absence of the closure process.

Scheme I

$$PhCH_2CN \xrightarrow{1} PhCM_2G\ (1) \xrightarrow{2} 2 \xrightarrow{3} 3 \xrightarrow{4} 4 \xrightarrow{5} 5 \xrightarrow{6} 6 \xrightarrow{7} 7 \xrightarrow{8} 8 \xrightarrow{9} 9$$

	M	G	conditions (yield, %)
1	$CH_2CH_2OCH{=}CH_2$	CN	1. $ClCH_2CH_2$-$OCH{=}CH_2$, NaH, Me_2SO (80)
2	CH_2CH_2OH	CN	2. dilute HCl (75)
3	CH_2CH_2OTs	CN	3. TsCl, pyridine (72)
4	$CH{=}CH_2$	CN	4. KO-*t*-Bu, Me_2SO (85)
5	$CH{=}CH_2$	CONH-*t*-Bu	5. *t*-BuOH, HOAc, H_2SO_4 (40)
6	$CH{=}CH_2$	$CONH_2$	6. $BF_3 \cdot Et_2O$, $Cl_2C{=}CCl_2$ (91)
7	$CH{=}CH_2$	COOH	7. *i*-AmONO, HCl (87)
8	$CH{=}CH_2$	CH_2OH	8. $LiAlH_4$, Et_2O (60)
9	$CH{=}CH_2$	CH_2OTs	9. TsCl, pyridine (70)

Results and Discussion

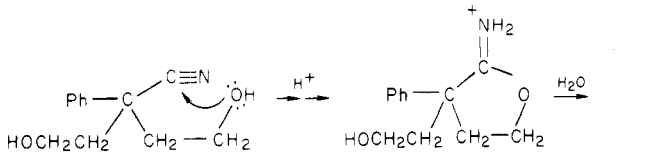
After a number of unsuccessful attempts with other reagents, dialkylation of phenylacetonitrile was accomplished, using vinyl β-chloroethyl ether. The bis vinyl ether **1** so obtained was then eventually transformed to the desired tosylate **9** as shown in Scheme I.

A number of misadventures attended Scheme I, as might be expected for such hindered substances. Conversion of **1** to diol **2** was sensitive to the residence time with the dilute acid used in the hydrolysis. Longer contact times led to removal of **2** through the formation of lactone **10**,

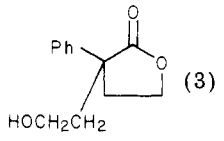
(1) Electrocyclic Effects in Solvolysis. 2. Part 1: J. W. Wilt, T. P. Malloy, P. K. Mookerjee, and D. R. Sullivan, *J. Org. Chem.*, **39**, 1327 (1974).
(2) Taken in part from the dissertation of R.N., Loyola University of Chicago, 1977.
(3) University Fellow, 1975–1976.
(4) The disrotatory cyclopropyl cation opening has many examples and is discussed in a number of texts: e.g. T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", Harper and Row, New York, N.Y., 1976, pp 647–50. The conrotatory pentadienyl cation closure is less referenced. A few recent studies are Y. Gaoni, *Tetrahedron Lett.*, 371 (1977), N. W. K. Chiu and T. S. Sorensen, *Can. J. Chem.*, **51**, 2776 (1973), and C. W. Shoppee and B. J. A. Cooke, *J. Chem. Soc., Perkin Trans. 1*, 1026 (1973).

0022-3263/79/1944-2533$01.00/0

probably via internal participation[5] as shown in eq 3.

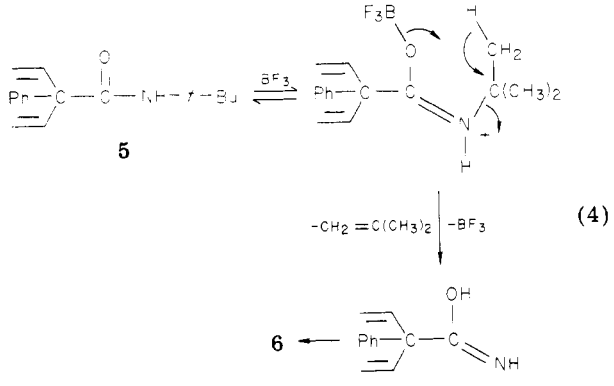


2



10 (3)

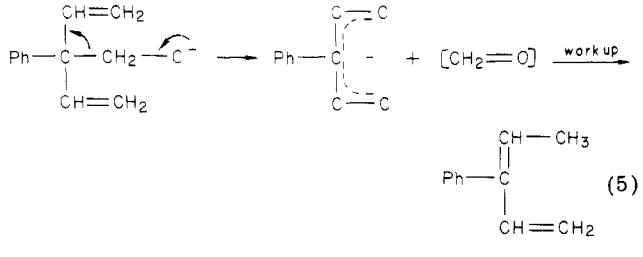
Lactone **10** could be converted to a sodium salt of the opened acid upon treatment with base, but acidification invariably led back to **10**, making it a useless intermediate in the sequence. Formation of the divinyl nitrile **4** by pyrolysis of the diacetate or bis(*S*-methyl xanthate) of diol **2** was moderately successful, but the purification steps involved made these approaches to **4** less attractive than the route via tosylate **3**. Due to its hindered position, the nitrile function in **4** was very resistant to hydrolysis. Only the Ritter reaction[6] was found to convert the nitrile to an acid derivative, albeit in only modest yield. Subsequent transformation of the *N-tert*-butylamide **5** so formed was itself quite difficult.[7] Apparently the conversion of sp(CN) to sp^2(C=O) carbon (**4** → **5**), which involves a trigonal intermediate, could be forced, but not the conversion **5** → **7** wherein a tetrahedral intermediate is involved. Rather a dealkylative fragmentation process using BF_3 was employed, presumably as in eq 4, to avoid the tetrahedral



5 (4)

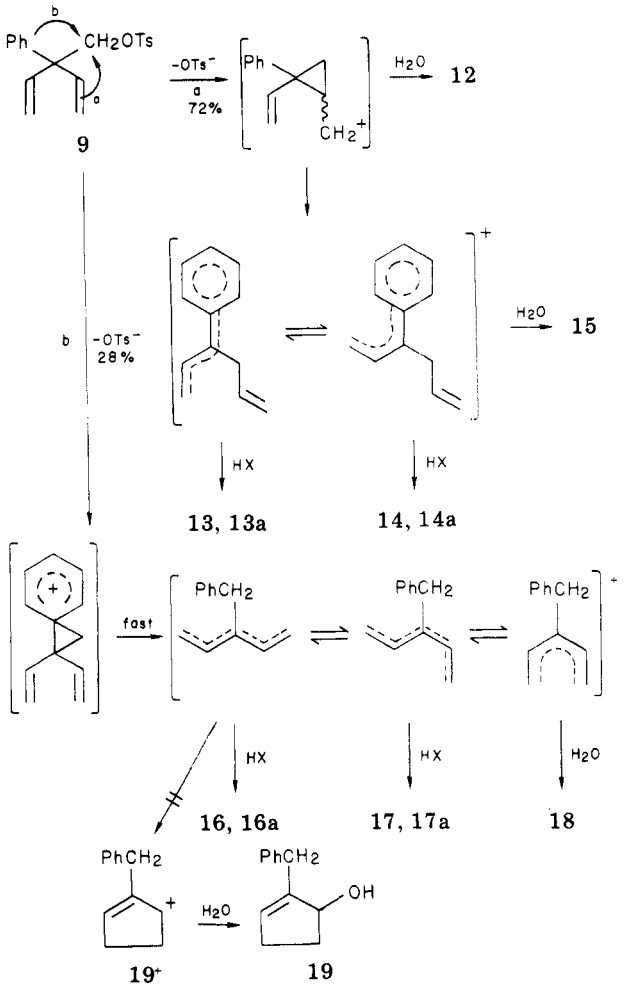
6

intermediate of normal amide hydrolysis and to set up amide **6** for hydrolysis via diazotization with isoamyl nitrite and dry hydrogen chloride. Lastly, reduction of acid **7** with lithium aluminum hydride afforded a lower yield of carbinol **8** than expected. The lower yield was caused by another fragmentation, one related to a reverse aldol condensation,[8a] as shown in eq 5.



(5)

Scheme II



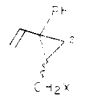
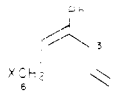
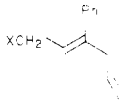
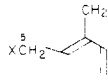
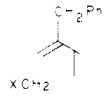
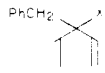
Both (*E*)- and (*Z*)-3-phenyl-1,3-pentadiene (γ-phenylpiperylene, **11**) were isolated from the reaction and confirmed by comparsion with samples prepared by the literature method.[8b] The formaldehyde undoubtedly was further reduced to methanol under the reaction conditions but this was not determined.

Tosylate **9** was solvolyzed under two sets of conditions: acetic acid buffered with sodium acetate, and dioxane–water (80:20 (v/v)) buffered with 2,6-lutidine. The former solvolysis produced a complex mixture containing hydrocarbons (10%), polymeric material (20%), and acetate esters (70%). Only the last substances were investigated. Because the composition of the acetate fraction was thermally sensitive, analysis by NMR spectroscopy was performed in conjunction with authentic mixtures.[9] Solvolysis in dioxane–water led to a similar set of products which were grouped by dry-column chromatography. The alcohol fraction again amounted to 70 ± 5%. The products formed and the proposed pathway for their formation are given in Table I and Scheme II, respectively. As indicated there, *no electrocyclic closure to a benzylcyclopentenol or its acetate was observed.* 2-Benzyl-2-cyclopentenol (**19**)[10] was synthesized independently and was observed to

(5) F. Bergel, A. L. Morrison, and H. Rinderknecht, *J. Chem. Soc.*, 267 (1944); R. M. Anker and A. H. Cook, *ibid.*, 806 (1948).
(6) L. I. Krimen and D. J. Cota, *Org. React.*, **17**, 213 (1969).
(7) Cf. N. Sparber, D. Papa, and E. Schwenk, *J. Am. Chem. Soc.*, **70**, 3091 (1948).

(8) (a) This uncommon example is testimony for the stability (and therefore good leaving ability) of the highly delocalized 3-phenylpentadienyl anion. (b) K. Alder, J. Haydin, K. Heimbach, K. Neufang, G. Hansen, and W. Gerhard, *Justus Liebigs Ann. Chem.*, **586**, 110 (1954).
(9) This analysis used synthesized samples for authentic chemical shifts (see Experimental Section) and relied on methylene resonances. The vinyl proton region was too complex for reliable assignment.

Table I. Solvolysis Product Data

product	X, no.	compn,[a] %	$^1H_1$ chem shift data[b] group	δ (alcohol)	δ (acetate)
		Vinyl-Shifted Products			
	OH, 12	12	2-CH_2	0.6 br m	
	c		Cp-CH_2	3.98 d[d]	*e*
	OH, 13	20	6-CH_2	4.28 d	4.67 d
	OAc, 13a	58	3-CH_2	3.28 d	3.30 d
	OH, 14	5	6-CH_2	4.05 d	4.45 d
	OAc, 14a	14	3-CH_2	3.12 d	3.12 d
	OH, 15	35	4-CH_2	2.62 d	
	c				
		Phenyl-Shifted Products			
	OH, 16	12	5-CH_2	4.32 d	4.70 d
	OAc, 16a	17	Ph-CH_2	3.63 s	3.67 s
	OH, 17	8	5-CH_2	4.32 d	4.70 d
	OAc, 17a	11	Ph-CH_2	3.57 s	3.55 s
	OH, 18	8	Ph-CH_2	2.85 s	
	c				

[a] For hydrolysis in aqueous dioxane at 85 °C; for acetolysis at 118 °C. Values are precise to ±2% and were determined by NMR spectral analysis. Because the olefinic products were labile to conditions, the percentage of each isomer at times varied. The values given represent the average reaction mixture. Ranges of ±10% sometimes were observed. [b] For all the products other resonances were as follows: Ph H's, δ 7.0-7.5 (m); vinyl H's, δ 4.9-7.0 (complex m). These regions were too complex for secure diagnostic use. The alcohol products showed HO at δ 2.33-2.45 (broad m, varied with concentration). The acetate products showed a number of CH_3COO singlets in the region δ 1.92-2.07 (s). Alcohol **12** exhibited the cyclopropyl ring H's at δ 0.3-0.85 (complex m). [c] Product not observed in acetolysis. [d] J = 6-7 Hz in all doublets. [e] This acetate (**12a**) was formed in the acetylation of the alcohol products (δ CH_3COO 4.35, d), presumably because the reaction temperature was lower.[11]

be stable to reaction conditions (dioxane–water, 88 °C, 24 h, *p*-toluenesulfonic acid and 2,6-lutidine present). Therefore the absence of **19** was not caused by its instability in the reaction or to the workup procedures. Rather in both solvents vinyl-group migration was the principal process observed (72%), with phenyl migration accounting for the balance of the product.[11] The detection of **12** is especially interesting in that its formation indicates the mode of participation by the vinyl group. No product of retained structure was detected. Clearly k_Δ processes predominate over k_s processes in this system in these solvents. Moreover, the vinyl and phenyl group migrations were statistically approximately equal in these k_Δ processes.[12a]

Table II. Acetolysis Rate Constants and Activation Parameters

compd	T,[a] °C	10^5k,[b] s^{-1}	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu
9	100	41.4 ± 0.7		
	80	5.48 ± 0.04		
	56	0.376 ± 0.002		
	(25)[c]	(6.02×10^{-8})	25.4 ± 0.2	−6.54 ± 0.6
neophyl tosylate	(25)[c,d]	(3.09×10^{-8})	25.8	−6.3

[a] ±0.3 °C. [b] Determined by computer fit. [c] Extrapolated from data at other temperatures. [d] Taken from the data of S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, 78, 2763 (1956), and S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, 74, 1113 (1952).

The kinetics of acetolysis were followed titrimetrically and these data may be found in Table II.

From the comparison given in Table II, tosylate **9** was comparable in rate to neophyl tosylate, a result that must reflect a combination of effects. Although the immense accelerative effect of a homoallylic double bond in 7-norbornenyl substrates is well-known in solvolysis, the situation is less dramatic in other cases. In fact, π participation by homoallylic double bonds in acyclic systems varies with both substrate and conditions.[12b] The situation with respect to phenyl π participation is similar. Within the bounds of the work done in this study (keeping in mind

(10) A. I. Chirko, A. F. Matishev, and A. N. Karnitskaya, *Zh. Org. Khim.*, 3, 28 (1967), prepared alcohol **19** by air oxidation of 1-benzylcyclopentene. Our sample was prepared by reduction of the corresponding ketone. Its structure was confirmed by its mode of formation and spectra (see Experimental Section).

(11) The higher temperature used for acetolysis, together with the lability of tertiary and cyclopropylcarbinyl acetates in the acidic medium, accounts for the absence of acetates corresponding to **12**, **15**, and **18**. Cf. J. H. Babler and D. O. Olsen, *Tetrahedron Lett.*, 351 (1974). Admittedly, as pointed out by a referee, the acidic medium was buffered in the present case, unlike that of Babler and Olsen. However, uncatalyzed (or non-proton-catalyzed) hydrolyses of esters are known. Cf. A. G. Davies and J. Kenyon, *Q. Rev., Chem. Soc.*, 9, 203 (1955). Such processes become more facile as the stability of the carbon cation so formed increases, and the entries of **12**, **15**, and **18** would so qualify.

(12) (a) Of special interest is the conclusion that phenyl and vinyl groups have comparable migrating abilities, reached indirectly by comparison of separate cases by R. S. Bly and R. T. Swindell, *J. Org. Chem.*, **30**, 10 (1965), and (b) B. Capon, *Q. Rev. Chem. Soc.*, **18**, 93 (1964).

that the objective was the detection of electrocyclic closure and not a measurement of competitive anchimeric abilities), the inductive retardation and anchimeric acceleration observed for the phenyl and vinyl groups in the solvolysis of **9** must be in approximate balance, relative to the case for neophyl tosylate.[12a] The competitive ability of both groups to migrate in **9** undoubtedly reflects the comparable stability of the product-forming ion manifolds in each case.

Lastly, the failure to observe electrocyclic closure in this investigation may be rationalized. First, vinyl-group migration was more extensive than was originally expected. The ion manifold thus produced cannot so cyclize, thereby reducing the opportunity for success. Second, with regard to the potentially productive phenyl-migrated ion it would appear that insufficient alkylation was present in the vinyl groups, causing the *secondary*[13] cyclopentenyl cation **19**$^+$ to be insufficiently stabilized relative to the pentadienyl cation manifold precursor. This in turn allowed solvent capture to the exclusion of closure and afforded acyclic products only. Future work will therefore search for the closure in highly alkylated bis vinyl analogues of **9**.[14]

Experimental Section

Melting points were determined on a calibrated Fisher–Johns block. Boiling points are uncorrected. Gas chromatography was performed on Aerograph Model 920 or A 90-P instruments with helium carrier gas. Infrared spectra were determined on a Perkin-Elmer Model 700A spectrophotometer.[15] Proton NMR spectra were taken in deuteriochloroform (unless otherwise noted) on a Varian A-60A spectrometer. Microanalyses were performed by Micro-Tech Laboratories.

α,α-Bis(β-vinyloxyethyl)phenylacetonitrile (1). This compound was prepared by using a literature procedure[16] with only minor modifications: 80%; bp 125–135 °C (0.1 mm); NMR (CCl_4) δ 7.63 s (PhH), 6.46 dd, 4.16 dd, 3.88 dd (CH=CH_2, ABX, J_{AX} = 7, J_{BX} = 14, J_{AB} = 2 Hz), 3.70 t (CH_2CH_2O, J = 8 Hz), 2.38 t (CH_2CH_2O, J = 8 Hz); ν (neat) 2260 cm^{-1} (CN). Runs yielding ca. 100 g are easily achieved.

α,α-Bis(β-hydroxyethyl)phenylacetonitrile (2). Hydrolysis of the vinyl ether **1** was accomplished as reported.[16,17] The crystalline diol (75%) was used without purification in the next step except for a small sample which was recrystallized from benzene and methanol: mp 95–97 °C; NMR (Me_2SO-d_6) δ 7.50 s (PhH), 3.33 m, 2.21 t (CH_2CH_2O); ν (neat) 3300 (OH), 2260 cm^{-1} (CN); lit.[16] mp 96–98 °C.

α,α-Bis(β-tosyloxyethyl)phenylacetonitrile (3). Reaction of diol **2** with *p*-toluenesulfonyl chloride and pyridine in the usual fashion[18] afforded tosylate **3**: 72%; mp 134–135 °C (chloroform–methanol).

Anal. Calcd for $C_{26}H_{27}O_6NS_2$: C, 60.80; H, 5.30. Found: C, 60.55; H, 5.32.

α,α-Divinylphenylacetonitrile (4). Potassium *tert*-butoxide was prepared from the metal (8.85 g, 0.23 g-atom) and dry *tert*-butyl alcohol (80 mL) by refluxing the materials for 2 h. The solution was cooled to 15 °C and dimethyl sulfoxide (200 mL, recently distilled and dried over calcium hydride) was added. A slurry of tosylate **3** (58 g, 0.113 mol) in further dry dimethyl sulfoxide (200 mL) was added over 30 min, maintaining the temperature at 20 °C or below, with stirring. After 45 min of additional stirring, the white slurry was poured into water (1 L) and extracted with ether (three 150-mL portions). The combined extracts were dried (Na_2SO_4) and evaporated. Distillation afforded the product: 15 g; 85%; bp 80–85 °C (1.0 mm); NMR δ 7.55 s (ArH), 6.18 dd, 5.70 dd, 5.46 dd (CH=CH_2, ABX, J_{AB} = 2, J_{AX} = 10, J_{BX} = 17 Hz); ν (neat) 2250 (CN), 1625, 1600, 985, 925 cm^{-1} (CH=CH_2).

Anal. Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.55. Found: C, 85.25; H, 6.63.

Olefinic nitrile **4** was also formed (~10% yield) by passage of the diacetate of **2** over glass helices at 450 °C. The products were entrained in a nitrogen stream under a partial vacuum. The product mixture was complex, however, and not easily separable by GLPC. A somewhat better yield (20%) of **4** was obtained by the use of the bis(*S*-methyl xanthate) ester of **2**. Thermal elimination at 250 °C formed **4**, but purification from sulfur-containing byproducts made the route unattractive.[2]

***N-tert*-Butyl-α,α-divinylphenylacetamide (5).** Nitrile **4** (35 g, 0.21 mol) was dissolved in dry *tert*-butyl alcohol (100 g, 1.34 mol) and glacial acetic acid (350 g). This solution was stirred at 5 °C as concentrated sulfuric acid (35 g, 0.35 mol) was added dropwise over 4 h. After the addition the mixture was stirred at room temperature for 2 days. The reaction material was poured into ice and water (1.5 L) and extracted with a mixture of ether (10%) in benzene (three 400-mL portions). The combined extracts were washed with sodium carbonate (10% solution) until neutral and then dried (Na_2SO_4). After evaporation of the solvent, distillation yielded forecuts of polyisobutylene and recovered nitrile **4** (ca. 40–50% recovery), followed by the desired amide **5** (21 g; 40%, bp 85–100 °C (0.1 mm)), which solidified on standing. A portion was recrystallized twice from hexane: mp 51–52 °C; NMR δ 7.35 s (PhH), 6.48 dd, 5.38 dd, 5.00 dd (CH=CH_2, ABX, J_{AX} = 11, J_{BX} = 17.5, J_{AB} = 1.5 Hz), 5.53 broad (NH), 1.31 s (*t*-Bu); ν (melt) 3440 (NH), 1680 cm^{-1} (C=O).

Anal. Calcd for $C_{16}H_{21}ON$: C, 78.97; H, 8.70. Found: C, 78.96; H, 8.74.

α,α-Divinylphenylacetamide (6). Amide **5** (30 g, 0.12 mol), tetrachloroethylene (500 mL), and boron trifluoride etherate (60 mL) were stirred while under reflux for 20–24 h. Ice (200 g) was added to the cooled material which was then stirred for 2 h. The organic layer was separated, washed with water (200 mL) and sodium bicarbonate (5% solution) until neutral, and then dried (Na_2SO_4). The solvent was evaporated and the solid residue was crystallized from ether–hexane: 21 g; 91%; mp 60–61 °C (after two further recrystallizations); NMR δ 7.50 s (PhH), 6.60 dd, 5.41 dd, 5.11 dd (CH=CH_2, ABX, J_{AX} = 11, J_{BX} = 18, J_{AB} = 1.5 Hz), 5.96 broad (NH_2); ν (melt) 3500–2900, 1600 ($CONH_2$), 1600, 939 cm^{-1} (CH=CH_2).

Anal. Calcd for $C_{12}H_{13}ON$: C, 76.98; H, 7.00. Found: C, 77.30; H, 7.00.

Amide **5** was completely resistant to normal acid or base hydrolysis.

α,α-Divinylphenylacetic Acid (7). A solution of amide **6** (21 g, 0.11 mol) in dioxane (300 mL) was chilled in an ice bath and saturated with hydrogen chloride gas. Dropwise addition of isoamyl nitrite (50 mL, 0.36 mol) to the cold (10 °C), stirred solution was then performed over 2 h. The solution was allowed to come to room temperature and stirred for an additional 2 h, after which time it was heated under reflux for 3 h. The dioxane was evaporated and the residue was taken up into ether (200 mL). The ether solution was extracted with sodium carbonate solution (10%, three 75-mL portions), and the alkaline extracts were then acidified with hydrochloric acid (10%). The precipitated material was extracted into ether (two 100-mL portions) and the combined extracts were dried (Na_2SO_4) and evaporated. The residue was chromatographed over Florisil (1 in. × 6 in. column), using 30% ether in hexane (600 mL) as the eluant. Evaporation produced crystalline acid (18 g, 87%), a portion of which was purified by crystallization thrice from hexane: mp 67.5–68 °C; NMR δ 12.4 s (COOH), 7.53 s (PhH), 6.63 dd, 5.56 dd, 5.10 dd (CH=CH_2,

(13) Increased methylation of pentadienyl cations leads to dramatic increases in cyclization; cf. R. Bladek and T. S. Sorensen, *Can. J. Chem.*, **50**, 2806 (1972). A significant effect appears to be due to methyl stabilization of the nonplanar "u" (*Z,Z*) intermediate ion which is the precursor to cyclization.

(14) Diazotization of β,β-divinyl-β-phenethylamine [from **4** and $LiAlH_4$: 76%; bp 60–62 °C (0.25 mm); NMR ($CDCl_3$) δ 7.43 s (PhH), 6.26 dd, 5.35 dd, 5.05 dd (CH=CH_2, ABX, J_{AX} = 11, J_{BX} = 18, J_{AB} = 2 Hz), 3.10 s (CH_2NH_2), 0.73 s (CH_2NH_2); ν (neat) 3375 cm^{-1} (NH_2). Anal. Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73. Found: C, 83.19; H, 9.05] at 0 °C in acetic acid followed by 24 h at 25 °C gave an extremely complex mixture that resisted adequate characterization, although cyclization appeared to be absent. Use of such higher energy ions for cyclization thus seems ineffectual also. See ref 2 for details.

(15) Only portions of spectra are reported. For complete spectra, see ref 2.

(16) F. Bergel, A. L. Morrison, and H. Rinderknecht, *J. Chem. Soc.*, 265 (1944). Cf. F. Bergel, N. Hindley, A. L. Morrison, and H. Rinderknecht, U.S. Patent 2 418 289, 1947.

(17) Hydrolysis times greater than 10 min (0.2-mol scale) led to mixtures of diol **2** and lactone **10**[5] (viscous oil, no ν_{CN}, ν_{CO} 1704 cm^{-1}; lit.[5] bp 172 °C (0.1 mm)).

(18) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

ABX, J_{AX} = 11, J_{BX} = 18, J_{AB} = 0.5 Hz); ν (melt) 3300–2400, 1701 cm^{-1} (COOH).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.70; H, 6.51.

Attempts to hydrolyze nitrile **4** to either acid **7** or amide **6** by the following reactions gave only recovered starting material: refluxing concentrated hydrochloric acid; sodium ethoxide in refluxing ethanol; and potassium hydroxide in refluxing ethylene glycol.

β,β-Divinyl-β-phenethyl Alcohol (8). Reduction of acid **7** (17 g, 0.09 mol) with lithium aluminum hydride (5.0 g, 0.135 mol) in dry ether in the usual fashion (25 °C, 1 h) led to a forecut mixture of (*E*)- and (*Z*)-γ-phenylpiperylene (bp 40–45 °C (1.5 mm)), separable by GLPC (140 °C, OV-1 column) into the *Z* isomer (NMR δ 1.6 d, *J* = 7 Hz (CH_3)) and the *E* isomer (NMR δ 1.93 d, *J* = 7 Hz (CH_3)),[15] confirmed by comparison with authentic material (lit.[8b] bp 72–73 °C (12 mm)), and alcohol **8**: 9.4 g; 60%; bp 94–95 °C (1.5 mm); NMR δ 7.48 s (PhH), 6.78 dd, 5.40 dd, 5.16 dd (CH=CH, ABX, J_{AX} = 11, J_{BX} = 18, J_{AB} = 2 Hz), 3.95 s (CH_2OH), 2.18 s (CH_2OH); ν (neat) 3400 (OH). A spinning-band 40-plate distillation column was used to separate these products efficiently.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.62; H, 8.33.

The acetate of **8** was made from the alcohol and acetic anhydride (reflux for 12 h). Both alcohol **8** and its acetate were adjudged absent from the solvolyses on the basis of their CH_2O resonances, δ 4.41 for the latter.

β,β-Divinyl-β-phenethyl Tosylate (9). Reaction of alcohol **8** (5.2 g, 0.03 mol) with recrystallized *p*-toluenesulfonyl chloride (8.0 g, 0.042 mol) in dry pyridine (20 mL) at 25 °C for 48 h led, after the normal processing, to tosylate **9** (7 g, 70%), which was crystallized thrice from hexane to afford the solvolysis reactant: mp 53–54 °C; NMR δ 7.49 q (ArH, A_2B_2, *J* = 8 Hz), 7.25 s (PhH), 6.05 dd, 5.28 dd, 4.98 dd (CH=CH_2, ABX, J_{AX} = 11, J_{BX} = 17, J_{AB} = 2 Hz), 4.33 s (CH_2OTs), 2.41 s ($ArCH_3$); ν (melt) 1355, 1170 cm^{-1} ($-SO_2-$).

Anal. Calcd for $C_{19}H_{20}O_3S$: C, 69.48; H, 6.14. Found: C, 69.31; H, 6.15.

α,α-Divinyl-β-phenethyl Alcohol (18). Vinyllithium (Alfa Inorganics, 45 mL of a 2.2 M solution in tetrahydrofuran) was stirred while being treated dropwise under nitrogen with a solution of ethyl phenylacetate (8.21 g, 0.05 mol) in freshly distilled, dry tetrahydrofuran. The 45-min addition was followed by 30 min of further stirring. An aqueous solution of ammonium chloride (10%, 30 mL) was added slowly, followed by water (250 mL). The layers were separated and the aqueous layer was extracted with ether (two 10-mL portions). The organic phase and the ether extracts were combined, dried (Na_2SO_4), and evaporated. The oily residue was chromatographed on alumina (activity 1, 150 g), eluting first with hexane (300 mL) to remove mineral oil (from the vinyllithium sample) and then with ethyl acetate (200 mL) to obtain the alcohol. Removal of the ethyl acetate followed by distillation through a 40-plate column yielded alcohol **18**: 4.1 g; 47%; bp 50–51 °C (0.07 mm); NMR δ 7.36 s (PhH), 6.13 dd, 5.25 dd, 5.13 dd (CH=CH_2, ABX, J_{AX} = 11, J_{BX} = 18, J_{AB} = 2 Hz), 2.90 s (CH_2Ph), 1.70 s (OH); ν (neat) 3560, 3460 cm^{-1} (OH).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.60; H, 8.17.

Use of vinylmagnesium bromide in the above process led to a poorer yield of **18** which was contaminated with a ketone, presumably 1-phenyl-5-hexen-2-one (NMR δ 3.67 s ($PhCH_2CO$), 2.43 t ($COCH_2CH_2$)) formed by conjugate addition to benzyl vinyl ketone (the intermediate first formed from the ester).

2-Benzyl-2-cyclopenten-1-ol (19). 2-Benzalcyclopentanone was prepared as reported.[19] Its isomerization to 2-benzyl-2-cyclopentenone was achieved as described[20] in 43% yield. Reduction to alcohol **19** was accomplished with lithium aluminum hydride, following the procedure reported for reduction of the benzal isomer:[21] 74%; distilled in a Kugelrohr apparatus at 105 °C (0.35 mm); NMR δ 7.23 s (ArH), 5.43 broad s (=CH), 4.58 m (CHOH), 3.43 s ($ArCH_2$), 2.65–1.57 m (OH, 4,5-CH_2's); ν (neat) 3350 broad (OH), 1607 (C=C), 1050 cm^{-1} (CO); lit.[10] bp 91–92 °C (0.2 mm). This alcohol was recovered in essentially quantitative yield upon treatment under the exact hydrolysis conditions and workup used for **9** (see below). No spectral evidence for isomerization was found. The benzyl resonance at δ 3.43 was not observed in the NMR spectrum of the hydrolysis product from **9**, indicating the absence of **19** in this solvolysis.

Acetolysis of Tosylate (9). Tosylate **9** (1.0 g, 3.04 mmol) and sodium carbonate (0.193 g, 3.65 mmol of potential sodium acetate) were dissolved in purified acetic acid containing 1% (v/v) acetic anhydride (121 mL). The mixture was heated at reflux under nitrogen for 24 h. The cooled solution was poured into ice water (1 L) and extracted with methylene chloride (three 100-mL portions). The combined extracts were washed with aqueous saturated sodium bicarbonate until the washes were basic, and then they were dried (Na_2SO_4) and evaporated. The residual oil was distilled at 0.15 mm in a Hickman microstill (bath temperature 60–80 °C) to separate the volatile products from nonvolatile polymeric material. The distillate was chromatographed on a dry column of Florisil, using 99:1 hexane–ether as the eluant. This procedure removed hydrocarbon product. Elution with 50:50 hexane–ether was then performed. The oil so obtained was again distilled as above to afford the solvolysis acetates as a colorless oil: 250 mg; 39% yield.

Anal. Calcd for $C_{14}H_{16}O_2$ (mixture): C, 77.75; H, 7.45. Found: C, 77.67; H, 7.64.

Investigation of the crude product subsequently, using spectral properties established from authentic samples, indicated ~70% ester, 10% hydrocarbon, and 20% polymer product in the acetolysis. Attempted separation of the acetate esters by GLPC at 200 °C (Reoplex column, $^1/_4$ in. × 6 ft) led to extensive isomerization and decomposition. Catalytic hydrogenation (Pd/C, 25 °C, 15 min) converted the acetates into saturated material. The NMR spectrum of the saturated product was consonant with that expected for a mixture 3-phenyl-1-hexyl acetate and 3-benzyl-1-pentyl acetate.

The only fruitful approach adopted was to analyze the distilled acetate fraction by NMR, using Schoolery's values[23] expected for the various possibilities together with probable coupling constants. By this method the data in Table I were garnered. The phenyl-shifted acetates **16a** and **17a** were easily observed by comparison with those formed from alcohol **18** upon standing in acetic acid containing a trace of sulfuric acid.

Hydrolysis of Tosylate 9. Into purified[24] dioxane (240 mL) and distilled water (60 mL) were added tosylate **9** (2.5 g, 7.61 mmol) and 2,6-lutidine (0.823 g, 7.68 mmol). The mixture was flushed with nitrogen and maintained at 85 °C under nitrogen for 24 h. The solvent was removed to a volume of 150 mL, keeping the temperature below 50 °C. Water (200 mL) was added and the mixture was extracted with ether (three 100-mL portions). The combined extracts were washed with dilute hydrochloric acid (5%, 100 mL), water (100 mL), and saturated aqueous sodium bicarbonate (150 mL). The material was dried (Na_2SO_4) and evaporated. The crude product was chromatographed on Florisil (200 g) deactivated with water (10 g) and ethyl acetate (5 g), using the dry-column technique.[25] Elution with hexane–ethyl acetate (95:5, 260 mL) afforded the viscous alcohol products (900 mg, 68%).

The analysis of the product was again by NMR spectroscopy as with the acetates. Confirmatory evidence for the products was obtained by acetylation (100 mg of alcohol mixture, 150 mg of acetic anhydride, 2 mL of benzene, 24 h) to mixtures of acetates which were then compared to those from acetolysis of **9**. Aside from the absence of acetates of alcohols **12**, **15**, and **18** (cyclopropylcarbinyl and tertiary alcohols), the acetate and alcohol mixtures conformed in structure although compositions varied.[11]

(19) A. P. Phillips and J. Mentha, *J. Am. Chem. Soc.*, **78**, 140 (1956).
(20) M. Elliott, N. F. Janes, and M. C. Payne, *J. Chem. Soc. C*, 2548 (1971).
(21) H. O. House and R. L. Wasson, *J. Am. Chem. Soc.*, **78**, 4394 (1956).
(22) D. J. Cram and F. L. Harris, Jr., *J. Am. Chem. Soc.*, **89**, 4642 (1967).
(23) For a convenient list, see A. J. Gordon and R. A. Ford, "The Chemist's Companion", Wiley, New York, 1972, p 257.
(24) L. F. Fieser, "Experiments in Organic Chemistry", 3rd ed., D. C. Heath, Boston, Mass., 1957, p 285.
(25) J. M. Boha, M. M. Jouillie, F. A. Kaplan, and B. Loev, *J. Chem. Educ.*, **50**, 367 (1973); B. Loev and M. M. Goodman, *Chem. Ind. (London)*, 2026 (1967).

The presence of **18** was confirmed through authentic comparison; those of **12** and **15** are based upon spectral assignment.

Kinetic Study on Tosylate 9. Purified[22] acetic acid containing acetic anhydride (1% (v/v)) was the solvent. The reactions were performed on a 0.03-M scale in the presence of sodium acetate (0.04 M). The well-known titrimetric procedure was followed, using crystal violet (0.03% solution in acetic acid) as indicator and standardized *p*-toluenesulfonic acid as the titrant. The kinetic data were processed by computer for the values in Table II.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. **1**, 70179-05-4; **2**, 10469-27-9; **3**, 70179-04-3; **4**, 70179-03-2; **5**, 70179-02-1; **6**, 70179-01-0; **7**, 70179-00-9; **8**, 70178-99-3; **8** acetate, 70178-98-2; **9**, 70178-97-1; **12**, 70178-96-0; **13** (X = OH), 70178-95-9; **13** (X = OAc), 70178-94-8; **14** (X = OH), 70178-93-7; **14** (X = OAc), 70178-85-7; **15**, 53847-13-5; **16** (X = OH), 70178-86-8; **16** (X = OAc), 70178-87-9; **17** (X = OH), 70178-88-0; **17** (X = OAc), 70178-89-1; **18**, 38553-10-5; **19**, 13694-30-9; *tert*-butyl alcohol, 75-65-0; (*E*)-γ-phenylpiperylene, 70178-90-4; (*Z*)-γ-phenylpiperylene, 64035-02-5; 2-benzalcyclopentanone, 5679-13-0; 2-benzyl-2-cyclopentenone, 22354-39-8; 3-phenyl-1-hexyl acetate, 70178-91-5; 3-benzyl-1-pentyl acetate, 70178-92-6.

Host–Guest Complexation. 19. Cyclic, Bicyclic, and Tricyclic Polyether Systems[1,2]

Roger C. Helgeson, Thomas L. Tarnowski, and Donald J. Cram*

Department of Chemistry, University of California at Los Angeles, Los Angeles, California 90024

Received January 18, 1979

Eighteen new macrocyclic polyethers are described, many of which are multistranded. The free energies of complexation in $CDCl_3$ at 25 °C of these hosts with Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+ picrates are reported. In the following line structures, the letters stand for the following units: E is CH_2CH_2; M is CH_2; D is 1,1′-dinaphthyl substituted in the 2,2′-positions by OCH_3, OH, or $(OE)_nO$ bridges and in the 3,3′-positions by $M(OE)_nOM$ or $(OE)_nO$ bridges or CH_3 groups; T is 1,1′-ditetralyl substituted in the 2,2′-positions by $(OE)_nO$ bridges and in the 3,3′-positions by H, $M(OE)_nOM$, or $M(SE)_nSM$ bridges. The substituents (or bridges) attached to the 2,2′-positions of the units designated as D or T are written on the right, whereas those attached to the 3,3′-positions are written on the left, the exception being when two D or T units are involved. When bridges connect the 2- and 3-positions to one another, the bridges are written on both sides. The hosts containing a single bridge connecting the 3,3′-positions of D are as follows: $E(OEOM)_2D(OCH_3)_2$, **8**; $O(EOEOM)_2D(OCH_3)_2$, **9**; $E(OEOEOM)_2D(OCH_3)_2$, **10**; $E(OEOM)_2D(OH)_2$, **11**; $O(EOEOM)_2D(OH)_2$, **12**; $E(OEOEOM)_2D(OH)_2$, **13**. Hosts containing two bridges connecting the 2- to the 2′- and 3- to the 3′-positions are $O(EOEOM)_2D(OEOEO)_2E$, **16**, and $E(OEOEOM)_2D(OEOEO)_2E$, **17**. An example of a host with two bridges connecting two D units through their 2,2′-positions and a bridge connecting the 3,3′-positions of one D unit is $O(EOEOM)_2D(OEOEO)_2D$, (*S,S*)-**19**. For comparison, host $(CH_3)_2D(OEOEO)_2E$ (**35**), whose bridge connects the 2,2′-positions, was included. The $-\Delta G°_{av}$ values (kcal/mol) for each host binding the six ions decreased in the following order: $O(EOEOM)_2D(OEOEO)_2E$ (8.7), $Nap(OEOEO)_2E$ (8.7), $(CH_3)_2D(OEOEO)_2E$ (8.5), $E(OEOEO)_2D(OEOEO)_2E$ (8.2), $O(EOEO)_2MDM(OEOE)_2O$ (8.2), $BrNap(OEOEO)_2E$ (7.9), $E(OEOM)_2D(OCH_3)_2$ (7.8), $O(EOEOM)_2D(OCH_3)_2$ (7.4), (*R,S*)-$T(MOEOM)_2(OEOEO)_2T$ (7.1), $E(OEOEOM)_2D(OCH_3)_2$ (6.8), (*R,R*)(*S,S*)-$T(MOEOM)_2(OEOEO)_2T$ (6.7), $O(EOEOM)_2D(OH)_2$ (6.6), $E(OEOEOM)_2D(OH)_2$ (6.4), $Br_2Nap(OEOEO)_2E$ (5.8), $E(OEOM)_2D(OH)_2$ (5.5), (*R,R*)(*S,S*)-$(CH_3O)_2D(MOM)_2D(OCH_3)_2$ (4.9), (*R,R*)-$T(MSESM)_2(OEOEO)_2T$ (≥4.6). A similar order was followed for maximum selectivity in binding the six ions, as measured by $-\Delta(\Delta G°)_{max}$ (kcal/mol). The values ranged from a high of 5.3 kcal/mol for $O(EOEOM)_2D(OEOEO)_2E$ to a low of 0.5 kcal/mol for (*R,R*)(*S,S*)-$(CH_3O)_2D(MOM)_2D(OCH_3)_2$. The four-stranded host with the most enclosed cavity, (*R,R*)(*S,S*)-$T(MOEOM)_2(OEOEO)_2T$, gave the relatively high $-\Delta(\Delta G°)_{max}$ of 4.3 kcal/mol for its relatively low $-\Delta G°_{av}$ of 6.7 kcal/mol. This host gave the very high $-\Delta G°$ difference of 3.7 kcal/mol for K^+ and Cs^+. The highly rigid host with seven well-organized oxygen binding sites, $O(EOEOM)_2D(OEOEO)_2E$, gave the highest $-\Delta G°$ value of 11.1 kcal/mol for K^+. The two hosts with "jaws"-type organization of 10 to 12 oxygen binding sites, $E(OEOEO)_2D(OEOEO)_2E$ and $O(EOEO)_2MDM(OEOE)_2O$, gave the highest $-\Delta G°$ values (kcal/mol) observed for Cs^+ of 9.3 and 9.2, respectively. Their complexes with the larger ions probably possess a sandwich-type structure. Hosts containing two D units with bridges connecting the 3- to 3- and 3′- to 3′-positions are $(CH_3O)_2D(MOM)_2D(OCH_3)_2$, (*S,S*)-**20** and (*R,R*)(*S,S*)-**20**, and $(HO)_2D(MSM)_2D(OH)_2$, (*R,R*)(*S,S*)-**22**. Stereoisomeric hosts containing two T units with bridges connecting their 2- to 2- and 2′- to 2′-positions are $T(OEOEO)_2T$, (*R,S*)-**23** and (*R,R*)(*S,S*)-**23**. Stereoisomeric hosts containing two T units with two $(OE)_2O$ bridges connecting their 2- to 2- and 2′- to 2′-positions and two other kinds of bridges connecting their 3- to 3- and 3′- to 3′-positions are $T(MOEOM)_2(OEOEO)_2T$, (*R,R*)-**25**, (*R,R*)(*S,S*)-**25**, and (*R,S*)-**25**, and $T(MSESM)_2(OEOEO)_2T$, (*R,R*)-**26**. Two hosts with bridges connecting the 2- to the 3- and 2′- to 3′-positions of a D unit are $E(OEOEO)_2D(OEOEO)_2E$, **27**, and $O(EOEO)_2MDM(OEOE)_2O$ (M's at 3,3′-positions), **34**. Hosts based on 2,3-naphtho-18-crown-6 (**30**), $Nap(OEOEO)_2E$, with Br in their 1- or 1- and 4-positions are $BrNap(OEOEO)_2E$, **31**, and $Br_2Nap(OEOEO)_2E$, **32**.

The literature is rich in descriptions of macrocyclic ligand systems synthesized to complex alkaline metal ions.[3] The cavities of most of these hosts are defined by a monocycle whose chain is conformationally flexible enough so that the binding sites can be nearly coplanar or their chains can coil in a variety of ways to adapt to the propensities of potential metal ion guests. A relatively small

(1) The authors thank the Division of Basic Sciences of the Department of Energy for a contract (AT(04-3)34, P.A. 218), which supported this research.

(2) Two small parts of this paper appeared as parts of previous Communications: (a) K. E. Koenig, R. C. Helgeson, and D. J. Cram, *J. Am. Chem. Soc.*, **98**, 4018–20 (1976); (b) T. L. Tarnowski and D. J. Cram, *J. Chem. Soc., Chem. Commun.*, 661–3 (1976).

(3) J. S. Bradshaw in "Synthetic Multidentate Macrocyclic Compounds", R. M. Izatt and J. J. Christensen, Eds., Academic Press, New York, 1978, Chapter 2.

0022-3263/79/1944-2538$01.00/0