for samples prepared from [1-^{18}O]1-PP or directly from [1-^{18}O]1-OH.

The results of our experiments with [1-^{18}O]1-PP using 2-PP and 2-fluoroisopentenyl-PP (3-PP)[26] as prenyl acceptors are summarized in Table I. The progress of each reaction was followed by the acid lability method,[27] and each reaction was run until the prenyl acceptor was consumed.[28] The 1′-4 condensation between 1-PP and 2-PP was not accompanied by scrambling of ^{18}O from a bridging to a nonbridging position when the incubation was carried out at the pH optimum of the enzyme (7.0). It is, however, necessary to show that this result is not simply an artifact resulting from insufficient quantities of 1-PP escaping from the active site before catalysis, once 2-PP has added to the enzyme. When the concentrations for 1-PP and 2-PP presented in Table I along with the known individual rate constants for the reaction[29] were used, it was possible to calculate by numerical integration[30] of the kinetic expression for the reaction[29] that 37% of the 1-PP which remained at the end of the reaction at pH 7 had been released from the ternary complex. We conservatively estimate the accuracy of the GC/MS analyses at ±1% and conclude that as little as 8% of exchange of ^{18}O into a nonbridging position in 1-PP would have been detected. An experiment with [1-^{18}O]1-PP and 2-PP was also conducted at pH 4.75,[31] where the initial velocity is only 1% of the value at pH 7.0, in an unsuccessful effort to detect scrambling by optimizing release of 1-PP from the ternary complex. Finally, 3-PP was employed as a prenyl acceptor. The fluorine at C(2) in 3-PP deactivates the adjacent double bond to electrophilic attack[26,32] and should enhance the possibility for bridge to nonbridge scrambling. Again, no exchange was detected in recovered 1-PP.

Our experiments with [1-^{18}O]1-PP clearly establish that the geranyl cation–PP_i ion pair does not react via path c (Scheme I). The question of whether path a competes favorably with b depends on the relative nucleophilicities of PP_i and the double bond in 2-PP. Although data are not available for these two specific moieties, negatively charged nucleophiles are usually considerably more reactive than their neutral counterparts.[33] Also, in an extensive series of studies, Goering[34] found that *p*-nitrobenzoate competes effectively with water for allylic cations in intimate ion pairs. One would expect that carbon–carbon double bonds are considerably less nucleophilic than any of these oxygen-containing species. We therefore submit that ion pair return does occur during the enzymatic reaction but is not detected because of topological constraints which restrict movement of the two partners.

A highly structured ion pair would have specific advantages with respect to the 1′–4 condensation reaction. A symmetrically solvated geranyl cation is a charge-delocalized species with significantly higher charge at C(3) than at C(1).[35] However, the distribution of charge in the allylic moiety will be altered substantially in a structure where the geranyl cation is sandwiched between 2-PP and PP_i, with a negatively charged oxygen near C(1).[36] The resulting increase in charge at C(1) and concommitant decrease at C(3) will enhance the reactivity of the primary center relative to C(3). This phenomenon has important implications with regard to reactivity and regiocontrol in electrophilic reactions. In the case of farnesylpyrophosphate synthetase, the desired selectivity is best accomplished in an enzyme bound ion pair complex whose topology is similar to that of the covalent substrates. Other enzymes, such as bornyl synthetase and farnesyl-PP:nerolidylpyrophosphate isomerase, may rely on an enzyme-mediated relocation of PP_i to regulate regiochemistry.[37]

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(37) It is easy to envision numerous variations of this concept, including regiocontrol by ion pair repulsion and situations where the counterion is an integral part of the enzyme. In the latter case, it is important to recognize that putative intermediates formed by internal return must regenerate the electrophilic species at a rate not significantly lower than the catalytic rate, or the enzyme will be irreversibly inhibited.

Synthesis and Complexing Properties of Chiral Macrocycles Containing Enforced Cavities[1]

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Synthetic organic compounds containing enforced cavities large enough to embrace molecules or ions larger than H^+, Li^+, or Mg^{2+} are virtually unknown. Crowns or cryptands in the uncomplexed state fill their own potential cavities with inward-turning CH_2 groups when their rings are large enough to accommodate such conformations.[2] Crowns whose rings are too small to accommodate inward-turned CH_2 groups possess cavities too small to embrace guests larger than the smallest ions.[2] In space-filling molecular models (CPK), compounds such as [1.2.1.2]paracyclophane[3a] or its analogues[3b-d] possess conformations in which their potential cavities can be filled with halves of aryl groups. Even the bicyclophane 1,3,5-C_6H_3(1,4-CH=CHC_6H_4CH=CH)$_3C_6H_3$-1,3,5 in molecular models possesses a cavity-free conformation. Models of the cyclic oligomers [2,6-$CH_2C_6H_3$(OH)CH_2]$_n$ with n = 4 to 8 (the calixarenes)[4] in some conformations contain substantial cavities which disappear in others. Kekulene[5] contains a disk-shaped cavity of about 3.4-Å depth whose existence is enforced by the rigidity of the fused aryl groups. The spherands contain enforced cavities, but in those reported to date, the cavities are large enough to capsularly complex ions only as small as Li^+ or Na^+.[6,7] Thus no synthetic organic compounds have been reported that contain enforced cavities the sizes of those in the cyclodextrins[8] or proteases[9] that contain lipophilic pockets. We report here stereochemically directed syntheses of such com-

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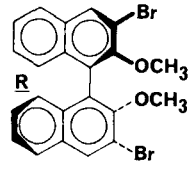
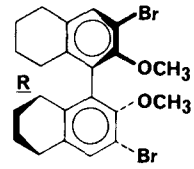
pounds and a survey of the binding properties of two of them.

A THF solution of optically pure (*R*)-**1**[10] was lithiated at −80 °C with *sec*-butyllithium. The solution was added under high



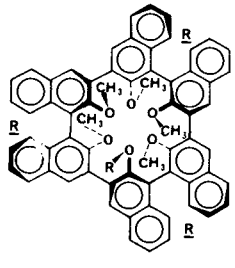
(*R*)-1



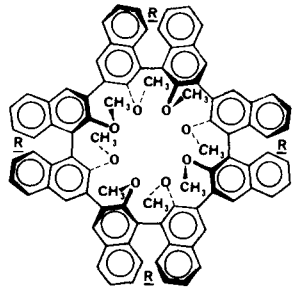
(*R*)-2

dilution conditions to a refluxing benzene solution of $Fe(AcAc)_3$.[6] Spherands **3**,[11] **5**,[11] and **6**[11] were isolated after chromatographic separation on silica gel in 2.6, 7, and 1.6% yields, respectively.[12] Lithiospherium bromide (**4**·LiBr) was probably initially formed but was monodemethylated and decomplexed during isolation to give **3**. Treatment of **3** with KOH and $(CH_3)_2SO_4$ gave **4**[11,12] (51%) and sodiospherium complex **4**·$NaSO_4CH_3$[11,12] (45%), the sodium having been scavenged from impure KOH. Molecular model examination reveals that coupling of monomeric diradicals derived from (*R*)-**1** provide *convergent* diradical oligomers that can cyclize, whereas coupling of diradicals derived from both (*R*)-**1** and (*S*)-**1** gives *divergent* diradical oligomers that can lead only to noncyclic products. Thus syntheses of **2**, **4**, and **5** were stereodirected. Dibromide (*R*)-**2**[11,12] was prepared from (*R*)-2,2′-dihydroxy-1,1′-bitetralyl of maximum rotation[13] by a method similar to that used to prepare (*R*)-**1**.[10] When subjected to the cyclization reaction, (*R*)-**2** gave **7**[11,12] (5.1%).

Treatment of spheranol **3** with LiOH and $(CH_3)_2SO_4$ gave complex **4**·$LiSO_4CH_3$[11,12] (65%) and with NaOH and $(CH_3)_2SO_4$ gave **4**·$NaSO_4CH_3$[11,12] (82%). Solutions of each of these complexes in $CHCl_3$ were shaken with aqueous LiCl and NaCl solutions, respectively. Complexes **4**·LiCl[11,12] and **4**·NaCl[11,12] formed by anion exchange were isolated from the corresponding organic layers. When a solution of **4**·$LiSO_4CH_3$ in $CDCl_3$ was shaken for 84 h with D_2O, the ^1H NMR spectrum of the $CDCl_3$ layer showed the presence of $ArOCH_3$ singlets for **4**·$LiSO_4CH_3$[12] (39%) and **4**[12] itself (61%). Thus decomplexation by extraction is slow



3, R = H
4, R = CH_3



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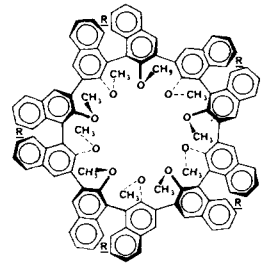
on the human time scale, and equilibration between complexed and uncomplexed **4** is slow on the ^1H NMR time scale. When a solution of **4**·$NaSO_4CH_3$ was heated at reflux in 2:1 (v/v) H_2O–CH_3OH, decomplexation occurred to produce **4**, the reaction being driven by the separation of the insoluble free spherand from the medium. Molecular models of **4** suggest its cavity is greater in size than that of the similar spherand composed of six metalinked *p*-methylanisyl units [$(p\text{-}CH_3C_6H_2OCH_3)_6$ or **8**] whose crystal structure shows the hole to be 1.62 Å in diameter.[7] The naphthyl–naphthyl dihedral angles in **4** are sterically inhibited from attaining the low value of 52° observed in **8**.[7] The lowest value observed in nine crystal structures of crowns or their complexes containing the 2,2′-dioxa-1,1′-binaphthyl unit is 68°.[14] The filled-cavity diameter of complex **8**·$NaSO_4CH_3$ is 1.76 Å, and the phenyl–phenyl dihedral angle is 60°.[7] These facts suggest that **4** might bind Na^+ ion better than Li^+ ion. Obviously **4** is unable to complex K^+.

The free energies of complexation ($-\Delta G°$, kcal mol^{-1}) by spherand **5** of picrate salts in $CDCl_3$ saturated with D_2O at ~25 °C were determined by the picrate extraction procedure.[15] The values obtained were as follows: Li^+, 5.4; Na^+, 6.1; K^+, 5.4; Rb^+, 6.6; Cs^+, 8.2; NH_4^+, 6.3; $CH_3NH_3^+$, 6.0; $(CH_3)_3CNH_3^+$, 3.4 kcal mol^{-1}. Thus **5** is a cesium ion selective ionophore. The association constant for **5**·CsPic is 17 times that for **5**·RbPic, ~110 times that for **5**·KPic, and 36 times that for **5**·NaPic.

In qualitative extraction experiments, **5** in $CHCl_3$ was shaken with aqueous solutions of potential guest picrate salts. In parallel experiments, 2-methoxynaphthalene was used as standard. The differences in intensities of the yellow picrate color in $CDCl_3$ solutions of **5** and 2-methoxynaphthalene (1–6 molar ratios) were used to measure qualitatively any enhanced complexing ability of **5** associated with collection and organization of the eight potentially binding oxygens. Picrates of $^+H_3NOH\cdot H_2O$ and $^+H_3NNH_3^+$ were strongly bound; salts of $^+H_3N(CH_2)_2CH(CO_2H)NH_3^+$, 1,3-$^+H_3NC_6H_4NH_3^+$ and 1,3,5-$HO_2CC_6H_3(NH_3^+)_2$ were moderately bound, those of UO_2^{2+} and $C_6H_5NH_3^+$ were weakly bound, and those of $(CH_3)_4N^+$, $C(NH_2)_3^+$, and $^+H_3NCH_2CH_2NH_3^+$ were essentially unbound. Changes in chemical shifts of the CH_3O singlets, the aromatic protons of **5**, and picrate ion were easily detectable in the 200-MHz spectrum of the complexes as compared to those of uncomplexed guest and host. Qualitative extractions of CsPic solutions in D_2O with host **7** in $CDCl_3$ indicated this spherand also to be a good binder of Cs^+. A similar experiment with the larger host **6** showed it to be a poor binder of Cs^+ and the other alkali metal ions.



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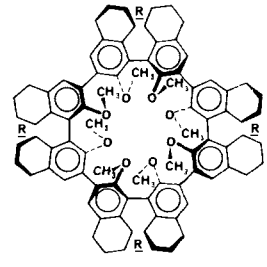

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The rigidity of the 1,1′-binaphthyl and 1,1′-bitetralyl units that compose spherands **4**–**7** makes their molecular models (CPK) particularly useful for making correlations and predictions. In models, **4** has no conformational degrees of freedom aside from small rotations about the naphthyl–naphthyl bonds. Spheres of about 1.5–2.0 Å insert and fill its cavity, which is lined with 24 unshared electrons associated with the 6 octahedrally arranged oxygens. Spherand **5** contains eight oxygens arranged to occupy the apexes of a square antiprism. In models, each of the eight attached methyl groups has two possible conformations. In one of these, the oxygen's unshared electrons face toward the cavity and the attached methyl group faces away from it. In the other, the methyl faces toward the cavity and the unshared electrons

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(12) All cycles melted with decomposition: **3**, 340–360; **4**, 370–400; **5**, >400; **6**, 340–350; **7**, 343–346 °C. Salt complexes melted with decomposition at >350 °C after decomposing in the solid state starting at: **4**·$NaSO_4CH_3$, 170; **4**·$LiSO_4CH_3$, 100; **4**·LiCl, 90; **4**·NaCl, 130 °C. Singlets, $ArOCH_3$, in the 200-MHz spectra in $CDCl_3$ appeared at δ 2.98 (3 H), 2.90 (3 H), 2.87 (3 H), 2.635 (6 H) for **3**; 2.74 for **4**; 3.01 for **5**; 3.25 for **6**; 3.01 for **7**; 3.01 for **4**·$LiSO_4CH_3$; 3.05 for **4**·LiCl; 2.92 for **4**·$NaSO_4CH_3$; 2.945 for **4**·NaCl. Optical rotations in $CHCl_3$, $[\alpha]^{25}_{546}$: **3**, −786 (*c* 0.5); **4**, −563 (*c* 0.14); **5**, −178 (*c* 0.5); **6**, −87.4 (*c* 0.23); **7**, −77 (*c* 0.8); **4**·$LiSO_4CH_3$, −710 (*c* 0.36); **4**·$NaSO_4CH_3$, −600 (*c* 0.5). Dibromide (*R*)-**2**: mp 143–144 °C; δ 3.57 (OCH_3, 6 H); $[\alpha]^{25}_{546}$ −26.5° (*c* 0.6, $CHCl_3$).

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face away from it. With all electrons facing inward, inserted spheres of diameters that range from about 3.4 to about 5.2 Å fill the cavity, depending on the aryl–aryl dihedral angles. The diameter of Cs^+ is about 3.4 Å. A molecular model of chair cyclohexane can be inserted into the cavity. Host **5** crystallizes with 1 mol of cyclohexane to give **5**·C_6H_{12}.[11] With all methyl groups turned inward, the cavity shrinks to a cylinder of about 2.7–3.0-Å diameter and a length of about 7.7 Å. This cylinder is lined with methyl hydrogens and neatly accommodates a model of diacetylene. Thus, depending on which and how many methyl groups or electron pairs are turned inward, the cavity can assume a variety of shapes, sizes, and distributions on its surface of hydrophilic or lipophilic sites. The 10 oxygens in molecular models of spherand **6** possess an arrangement complementary to that of the 10 hydrogens of ferrocene. With all methyl groups turned outward, a model of ferrocene beautifully fills the minimum sized cavity, with each hydrogen of the guest touching an oxygen of the host. The dimensions of the cavity of this conformation range from about 6 × 8 Å to about 7.2 × 8.4 Å. With all of the methyl groups turned inward, the cylindrical cavity is about 4.8 Å in diameter and about 7.2 Å in length. A model of chair cyclohexane nicely fills this cavity.

A comparison of these spherands with the cyclodextrins is instructive. Both sets of hosts are cyclic oligomers composed of rigid, chiral support units arranged in the form of a torus whose diameter increases with the number of monomer units. Both sets of hosts contain attached functional groups which possess some degrees of conformational freedom, but which cannot fill the cavity of the torus in any of their conformations. Thus the host *cavities are enforced*. The cavity sizes of the spherands can be designed to be smaller than that of the smallest cyclodextrin or comparable to those of α-, β-, or γ-cyclodextrin. The spherands reported thus far are highly lipophilic on the outside and somewhat hydrophilic on the inside. The cyclodextrins are very hydrophilic on their rims but lipophilic on the remainder of their inner and outer surfaces. Since the spherands are totally synthetic, they are more subject to structural design than the cyclodextrins.

On the Structure of $C_4H_4^+$ Produced in the Unimolecular Fragmentation of $C_6H_6^+$ and $C_5H_5N^+$

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The $C_4H_4^+$ ion is one of the major primary fragment ions produced in the unimolecular decomposition of excited $C_6H_6^+$ isomers:

$$C_6H_6^+ \rightarrow C_4H_4^+ + C_2H_2 \quad (1)$$

Appearance potential measurements indicate that at *threshold*, the $C_4H_4^+$ ion originating from C_6H_6, as well as from pyridine, may have the methylenecyclopropene structure.[1-4] Furthermore, $C_6H_6^+$ ions from all precursors dissociate, when their total energy (heat of formation plus excitation energy) is in the range 15–15.6 eV, to give $C_3H_3^+$ and $C_4H_4^+$ in a ratio which does not depend on the structure of the precursor. This implies the existence of a common structure for the $C_6H_6^+$ ions of this energy and also common structures for the $C_3H_3^+$ and $C_4H_4^+$ fragments. At total internal energies above 15.6 eV, there is a sudden increase of the $C_4H_4^+/C_3H_3^+$ branching ratio, in apparent contradiction to RRKM calculations which predict a monotonic decrease of this ratio with increasing energy, assuming a cyclic structure for both $C_3H_3^+$ and $C_4H_4^+$ throughout the energy range. As pointed out by Baer et al., this result suggests the accessibility of a different, probably linear, $C_4H_4^+$ isomer.

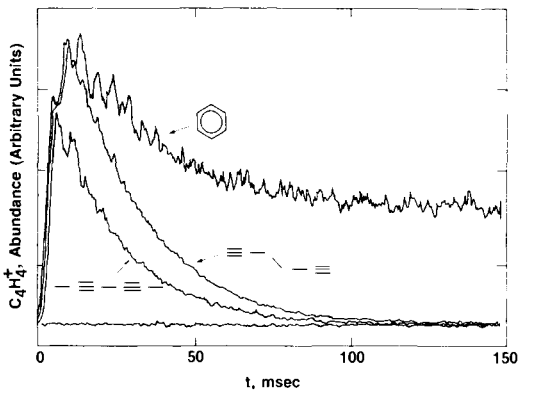

Figure 1. Abundance of $C_4H_4^+$ ions in benzene, 1,5-hexadiyne, and 2,4-hexadiyne as a function of time. Nominal electron energy, 30 eV; pressure, 1.4 × 10^{-6} torr. In benzene, no further decay of the $C_4H_4^+$ abundance was observed from 150 to 400 ms.

In this work, we present proof that, indeed, at least two distinct $C_4H_4^+$ structures are produced in the fragmentation of $C_6H_6^+$ and $C_5H_5N^+$. The relative abundances of these two isomeric ions are dependent on the internal energy of the parent ion.

A pulsed ion cyclotron resonance spectrometer (ICR) was utilized in this work. The technique for determining the abundance and identities of the various structurally distinct ion populations based on their kinetic properties has been described before.[5,6] A similar procedure has been used by Gross et al.[7]

Figure 1 shows decay tracings of $C_4H_4^+$ isomers produced in a 3-ms pulse of 30-eV electrons. The time-dependent behavior of $C_4H_4^+$ ions in benzene indicates that there are at least two different $C_4H_4^+$ isomers present in benzene, one which reacts with benzene and one which does not. The $C_4H_4^+$ population which shows a fast decay as a function of time (Figure 1) reacts mainly by charge transfer to benzene:

$$C_4H_4^+ + C_6H_6(B) \rightarrow C_4H_4 + C_6H_6^+ \quad (2)$$

About 10% of these ions undergo condensation reactions to give $C_{10}H_8^+$ and $C_9H_7^+$ products. These two reaction channels have been reported before,[8-10] and the branching ratio found in this study is in good agreement with that obtained in a tandem ion cyclotron resonance study of ionic reactions in benzene.[10]

The total decay rate constant of the reactive $C_4H_4^+$ population is $(6 \pm 1)10^{-10}$ cm^3/(molecule s), independent of electron energy (15–30 eV) and benzene pressure (3×10^{-7}–5×10^{-6} torr). The upper limit of the corresponding rate constant for loss of the unreactive $C_4H_4^+$ ions in benzene is 5×10^{-13} cm^3/(molecule s). The $C_4H_4^+$ fragment ions formed in 1,5-hexadiyne, 2,4-hexadiyne, and pyridine decay by reaction with the parent compounds with rate constants of 7.9, 12.9, and 22 × 10^{-10} cm^3/(molecule s), respectively. However, when the total pressure of these precursor compounds is kept low enough (5×10^{-8} torr) that reaction of $C_4H_4^+$ with the precursor compound is unimportant on the time scale (150–300 ms) of the experiments, the rate of reaction with various added reagents (benzene-d_6, NO, c-C_6H_{12}, n-C_5H_{12}, etc.) can be determined (precursor–additive = 1:10–1:50). Results

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