tion processes than the previous work might be obtainable as shown in Figures 1 and 2. The molecular energy of each state depicted in Figures 1 and 2 is slightly lower than that of end-on bonding in the previous work.

By taking the reference models as the structure 1 in Figures 1 and 2, we carried out the same computational procedures as described in the previous paper[1-4]. In the model of end-on bonding being the electrons in N_2 inclined to Fe(II) of Fe-substrate, it is possible to form a bond between electron sufficient nitrogen atom and electron defficient Fe(II) atom of Fe-substrate. Only based on the end-on bonding, various schemes and processes were considered and discussed in the preceeding work[1]. In the case of side-on bonding, the situation is quite different, because of difficulties to get the induced dipole due to the symmetric electrostatic fields. However, we can get the reasonable reduction process as in Figures 1 and 2 even though N_2 molecule was approaching in the direction perpendicular to that used in the previous work.

Under the condition of intermediate water structure made by Fe-substrate and water molecules, the role of intermediate water might be very important in reduction process[1,5-6]. The intermediate water structure makes structural changes as shown in Figures 1 and 2.

In fact, it is believed that the effective site of nitrogenase was constituted with the composition of $MoFe_{6-8}S_{8-9}$, and 4Fe-4S clusters were considered as the main active component of Fe-protein[7-10]. Being the active site quite large and symmetric as mentioned above, we can imagine that N_2 molecule captured at the active site might not be affected by its orientation.

As a result, the model of side-on bonding could also show the reasonable reduction process same as in the model of end-on bonding, and we can conclude that the reduction processes in nitrogen fixation are not affected by the orientation of N_2 molecule.

Acknowledgement. This research was financianlly supported by a grant from the Basic Science Institute Program, Ministry of Education of Korea, 1992.

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Facile Synthesis and Functionalizations of a Tetrakis(bromomethyl)cavitand

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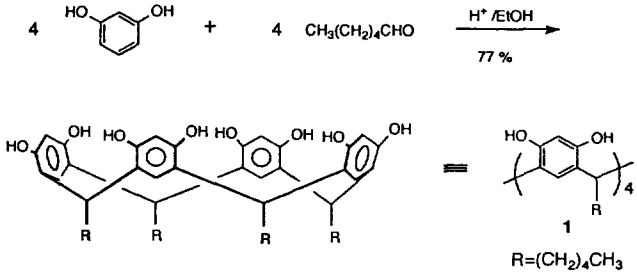
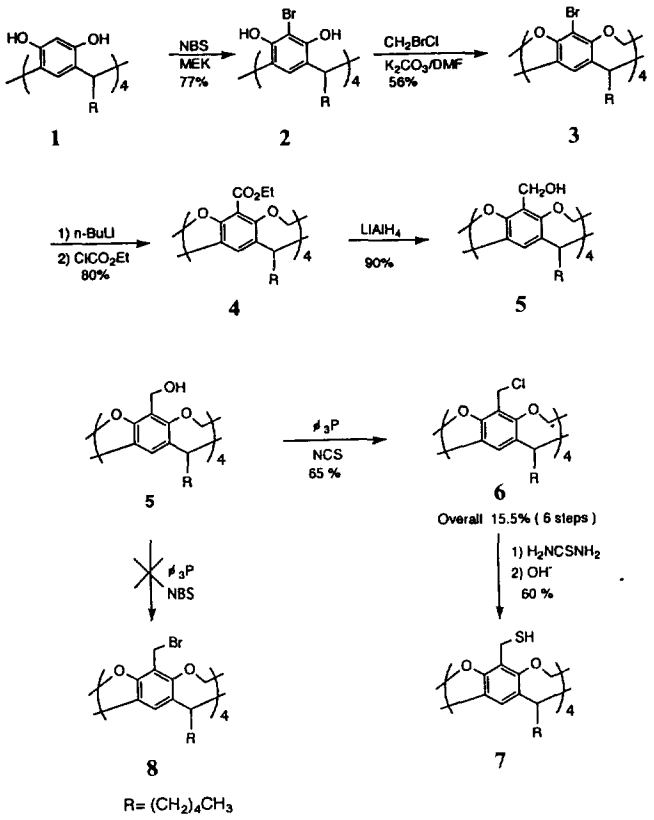
The recognition study on a molecular level is the fundamental scientific object to understand the beginning of biological system. The interactions interested in molecular recognition are hydrogen-bonding force, hydrophobic, charge-charge, charge-dipole, and dipole-diople interactions. These interactions are usually less than 10% of covalent forces and so very delicate to the structural and electronic complementarity between receptor (host) and substrate (guest).[1] Several of these interactions function cooperatively to maximize the recognition efficiency enough to sustain and evolve the biological systems.

Many artificial organic receptors have been developed as models for the study of various biological phenomena. Crown ethers[2], cryptands[3], spherands[4], cyclophanes[5], calixarenes[6], cavitands[7], carcerands[8], hemicarcerands[9], molecular clefts[10], molecular tweezers[11], and cyclodextrins[12] are among them. Cavitands are the compounds which have a defined cavity for substrate binding. They are being used as various hosts as well as important intermediates for carcerands and hemicarcerands, but only a few functionalized cavitands are reported.[7,8] In this paper we report the facile synthesis and multifunctionalization of tetrakis(bromomethyl)cavitand **8A**.

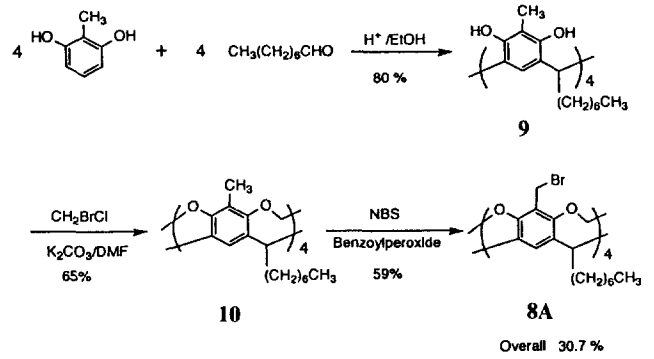
The acid-catalyzed condensations of resorcinols and aldehydes by the four fold oligomeric cyclization reaction (Scheme 1) give various conformationally stable octols (cyclotetramers) in high yields.[13] The easy syntheses and functionalizations of the bowl-shaped octols could provide potential sources of molecular vessels for the preparation of polyfunctional host systems whose convergent heteroatoms can act



Scheme 1.



Scheme 2.

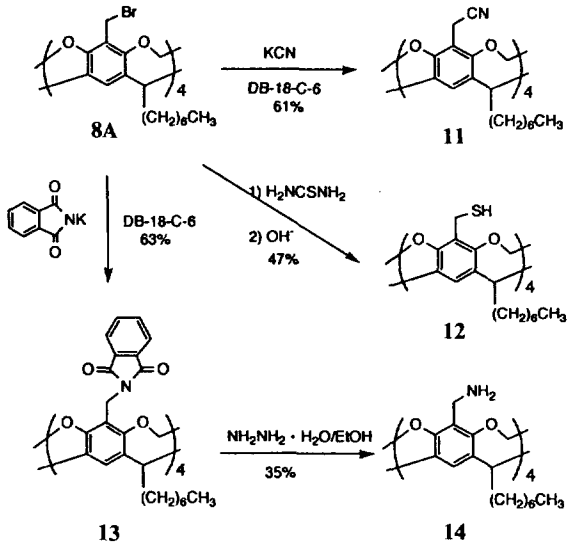


Scheme 3.

cooperatively to bind and catalyze their guests.

Scheme 2 shows the reported procedures for the functionalization of octol **1**.[8a] Tetrabromocavitand **3** can be transformed into various intermediates *via* transmetallation and quench with electrophiles. Tetrakis(hydroxymethyl)cavitand **5** was further functionalized to give compounds **6** and **7** which are semifinal compounds for carcerands and hemicarcerands. The electrophilic cavitand **6** was obtained in overall 15.5% yield by the six-step reaction from resorcinol. But it was difficult to prepare more reactive cavitand **8** from compound **5** using NBS and triphenylphosphine.

The preparation of tetrakis(bromomethyl)cavitand **8A** was accomplished in overall 30.7% yield by the three-step reaction shown on Scheme 3. The acid catalyzed condensation between 2-methylresorcinol and octylaldehyde in ethanol gives tetramethyloctol **9** in 80% yield. The conformationally



Scheme 4.

mobile tetramethyloctol **9** was rigidified by bridging hydroxyl groups using $CH_2BrCl/K_2CO_3/DMF$ to give tetramethylcavitand **10** (65%). Tetramethylcavitand **10** was brominated with 4.5 equivalents NBS/benzoylperoxide in CCl_4 to give tetrakis (bromomethyl)cavitand **8A** in 59% yield.[14]

The representative functionalizations of cavitand **8A** were shown on Scheme 4. The treatment with KCN/DB-18-C-6 in CH_3CN gives tetrakis(cyanomethyl)cavitand **11** in 61% yield.[15] The treatment with thiourea followed by basic hydrolysis gives tetrakis(thiomethyl)cavitand **12** in 47% yield. Also, the treatment with potassium phthalimide/DB-18-C-6 in toluene gives compound **13** in 63% yield. Compound **13** was treated with NH_2NH_2/H_2O in EtOH to give tetrakis (aminomethyl)cavitand **14** in 35% yield.

The development of various electrophilic and nucleophilic cavitands are important for the preparation of functioning organic hosts. Those intermediates **8A**, **11**, **12**, **14** are being further functionalized.

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14. mp. 170-175℃ ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.85 (t, 12H, CH_3), 1.31 (m, 40H, $CH_2(CH_2)_5CH_3$), 2.20 (m, 8H, CH_2 α to methine), 4.42 (s, 8H CH_2Br), 4.57 (d, 4H, inner OCH_2), 4.79 (t, 4H, methine), 6.04 (d, 4H outer OCH_2), 7.13 (s, 4H, Ar*H*).
15. mp. 243-246℃ ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.85(t, 12H, CH_3), 1.32 (m, 40H, $CH_2(CH_2)_5CH_3$), 2.20 (m, 8H, CH_2 α to methine), 3.54 (s, 8H, CH_2CN), 4.47 (d, 4H, inner OCH_2), 4.79 (t, 4H, methine), 6.03 (d, 4H, outer OCH_2), 7.17 (s, 4H, Ar*H*).; Mass(EI) m/e (relative intensity) 1084. 5 (100, M^+).

Reaction of Dimethyl L-Tartrate 2,3-Cyclic Sulfate with Dimethyl Sulfide and with Pyridine

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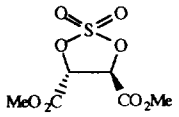
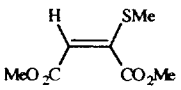
Synthesis of the cyclic sulfate and its reaction with nucleopiles have been known for a long time,[1] especially in the field of carbohydrate chemistry.[2] Recent works by Sharpless *et al.* have provided an easier access to cyclic sulfates and have shown their usefulness in organic synthesis.[3] We have also employed the cyclic sulfates for the efficient synthesis of Ara-U.[4] We further investigated the reaction of cyclic sulfates with certain nucleophiles and have found that the reactions of dimethyl L-tartrate 2,3-cyclic sulfate(**1**) with dimethyl sulfide and with pyridine give unusual products. Herein we report the preliminary results.

Reaction of cyclic sulfate **1** with dimethyl sulfide in xylene at 80-85℃ for 3 days afforded an equal amount of dimethyl 2-(methylthio)maleate(**2**)[5] and dimethyl 2-(methylthio)fumarate(**3**)[6] in 40% yeild. Prolonged reaction time, higher reaction temperature, or reactions in different solvents did not improve the yield. Reaction of **1** with ethyl phenyl sulfide also afforded **2** and **3** though in low yield, but the reaction using *t*-butyl methyl sulfide did not proceed. The assignment of E- and Z-isomers, **2** and **3** was made on the basis of NOE experiments. Upon irradiation of the vinyl proton, NOE was observed on methyl protons of methylthio group in E-isomer, **2** but not in Z-isomer, **3**. Although the reaction mechanism is not clear, the first step might be the sulfate ring opening by dimethyl sulfide.[7]



1



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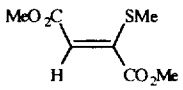
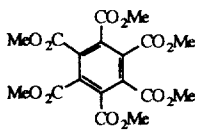


3

Since the product mixture was quite acidic, the effect of base on this reaction was examined. The reaction of cyclic sulfate **1** with dimethyl sulfide in the presence of pyridine afforded unexpected hexamethyl mellitate **4**. However, it was found that dimethyl sulfide did not actually participate in the formation of **4**. Heating of cyclic sulfate **1** in refluxing THF in the presence of one or two equivalents of pyridine for 10 hr afforded **4** in 49% yield. Higher reaction temperature and different amount of pyridine did not improve the yield of **4**. Although N,N-dimethylaminopyridine was as effective as pyridine for the formation of **4**, the reaction did not occur with other bases such as triethylamine, DBU, potassium carbonate, and potassium *t*-butoxide.

At room temperature, on the other hand, the reaction of **1** with pyridine in THF gave pyridinium salt **5** in 82% yield. Salt **5** was very hygroscopic and could not be completely purified, while N,N-dimethylaminopyridinium salt **6** was stable solid and fully characterized by NMR.[8] Heating of salt **5** or **6** in various solvents gave only very small amount of mellitate **4** even in the prolonged reaction time. We examined the possibility of involvement of dimethyl acetylenedicarboxylate(DMAD) as an intermediate although trimerization of DMAD to mellitate **4** is known to require special conditions.[9] Attempts to detect or trap DMAD during reaction employing various methods were not fruitful.



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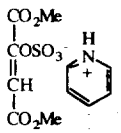
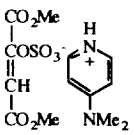


5



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