The mechanisms postulated in eq 2 and 3 invoke the intermediacy of both metal–hydrogen and metal–carbon σ bonds. Since the reduction of CCl_4 to $CHCl_3$ is a reaction characteristic of transition-metal hydrides,[10] we have added an excess of CCl_4 to the Mo–THF matrix at −196 °C. This reaction yields 0.15 mmol of $CHCl_3$ when 1.79 mmol of Mo is vaporized. Direct evidence for the intermediacy of carbon–molybdenum σ bonds in these reactions has not been obtained. Hydrolysis with D_2O cannot show deuterium incorporation in the hydrogenation products as water inhibits the hydrogenation. A search for deuterium incorporation in THF recovered after addition of D_2O to the Mo–THF matrix is hampered by the fact that a large excess of THF is employed. Skell, Williams-Smith, and McGlinchey[11] were able to overcome this problem in the reaction of metal atoms with propene by removing the excess propene before hydrolysis. However, in the present case, the Mo–THF complex appears to decompose at a lower temperature than is convenient for removal of THF. In any case, the search for molybdenum carbon σ bonds using hydrolysis techniques may not be conclusive, since the metal alkyl **2** may represent only a small component of the equilibrium in eq 2.

The mechanism in eq 3 involves a series of equilibria in which ligands are added to and removed from the molybdenum. If this is the case, addition of a ligand which forms strong bonds to molybdenum(0) should displace the equilibria in such a way as to produce a stable molybdenum complex. Accordingly, we have added carbon monoxide to the matrix after cocondensing Mo and THF. Upon warming the matrix to 25 °C, $Mo(CO)_6$ is isolated in 8.5% yield based on vaporized Mo. Although eq 3 depicts intermediates which are monomeric in molybdenum, we cannot be sure that this is the case. The fact that $Mo(CO)_6$ can be isolated may implicate a monomeric molybdenum species.

Although there is ample evidence for the formation of hydrides in metal atom reactions,[2,3,12] this is the first report of the utilization of such hydrides to effect hydrogenation of olefins. Klabunde, Davis, Hattori, and Tanaka[13] have condensed Ni atoms with various solvents to obtain substances which are effective hydrogenation catalysts upon addition of H_2. Klabunde and Murdock[14] have observed that alkyl halides can be partially reduced by a Ni–THF slurry with THF serving as the source of hydrogen. We are currently extending our investigations to other ethers in order to develop a system in which catalytic transfer of hydrogen from ether to olefins will occur.

Acknowledgment. The technical assistance of Mr. Eugene Nelson is gratefully acknowledged. This work was supported by an Auburn University Energy Research Grant-in-Aid.

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[11] Skell, P. S.; Williams-Smith, D. L.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 3337.

[12] A referee has pointed out that Sobota et al. (Sobota, P.; Pluzinski, T.; Jezowska-Trzebratowska, B., *J. Organomet. Chem.* **1980**, *185*, 69) have observed the formation of hydrogen and hydrocarbons upon hydrolysis of the products of the reaction of $MoOCl_3$ with Mg in THF.

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Regiospecific A,C- and A,D-Disulfonate Capping of β-Cyclodextrin

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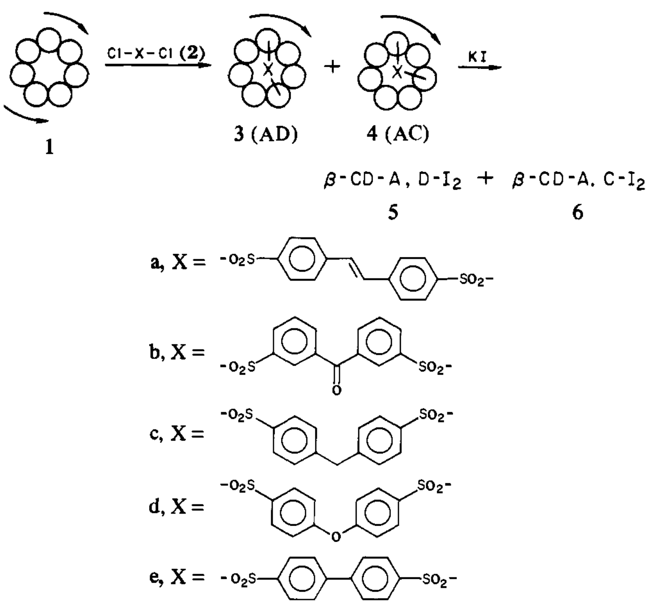
Cyclodextrins exhibit unique and significant characteristics to provide hydrophobic recognition sites in aqueous solution, which are often conveniently and successfully utilized as (part of) enzyme models.[1] However, preparation of more refined and sophisticated enzyme models requires the introduction of efficient catalytic sites onto the recognition sites, mostly consisting of two or more cooperating functional groups in appropriate spacial arrangements, as found in the enzyme catalysis, for instance in the so-called charge-relay system, Asp[102] ... His[57] ... Ser[195] of chymotrypsin.

Scheme I[a]



[a] Arrow indicates molecular asymmetry.

Table I. Positional Isomer Distribution of the Capping

capping reagent 2	capped β-cyclodextrin	
	3 (AD)	4 (AC)
a	nearly exclusive	very small
b	small	nearly exclusive
c	nonselective	
d		

This type of bifunctionalization was investigated by us, leading to the successful preparation of transannularly bifunctionalized β-cyclodextrins[2] through rigid capping[3] with 1,1′-methylenebis(benzene-4-sulfonyl chloride) (**2c**). Starting from our capped cyclodextrin as well as Breslow's,[4,5] beautiful enzyme models of bifunctional catalysis with hydrophobic recognition were provided.[4-6]

This transannular capping with **2c** is not regiospecific but gives isomers AC, substituted at A,C rings, and AD[4] (see Scheme I). Now we wish to report that regiospecific disulfonate capping was first achieved with *trans*-stilbene-4,4′-disulfonyl chloride (**2a**) for A,D and benzophenone-3,3′-disulfonyl chloride (**2b**) for A,C positions, respectively.

Thus, 2 g of β-cyclodextrin dissolved in 50 mL of pyridine was treated with 0.68 g of **2b** at 60 °C. After 1 h, crude capped cyclodextrin **4b** was obtained by the usual workup and purified by repeated flush column chromatography to give pure **4b** in 40% yield. Spectra: NMR (Me_2SO-d_6) δ 3.3 (42 H), 4.73 (C_1–H, 7 H), 4.30, 5.53 (C_2, C_3, C_6–OH, 19 H), 7.70, 7.87 (aromatic,

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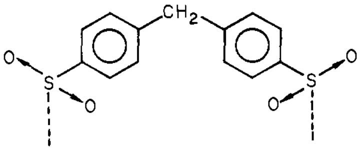
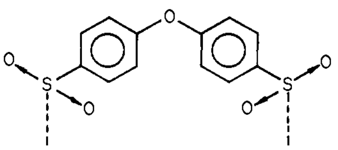
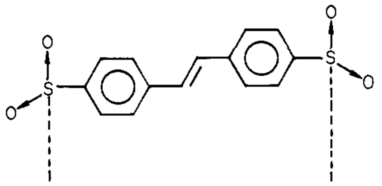
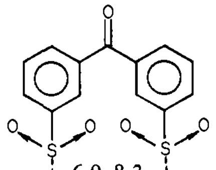
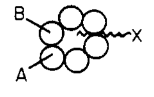
Table II. Estimated Distance (nm) between Two Reacting Sites of Some Capping Reagents

			
9.0–11.0 (9.7)[5]	8.6–11.4 (10.2)[5]	ca. 13.5	6.0, 8.3 9.8
near perpendicular, near coplanar conformation	do	planar	*Z*-oid, near perpendicular, *E*-oid

8 H); IR (KBr) 1650, 1180 cm^{-1}. A similar procedure gave **3a** in 20% yield.

These capped cyclodextrins were readily converted to the corresponding diiodo derivatives (AC and/or AD) by treatment with KI in DMF at 80–90 °C for 2 h;[7] these were further converted to dideoxy derivatives by treatment with $NaBH_4$. Spectral characteristics of the capped cyclodextrins and corresponding diiodo and dideoxy derivatives were satisfactory, but no appreciable difference has been observed between AC and AD isomers. Most characteristic is the ^{13}C NMR spectrum where the AC and AD isomers exhibit practically identical absorptions: 102.03 (C_1), 81.39 (C_4), strong peak centered at 72.11 (C_2, C_3, C_5), 59.87 (C_6 adjacent to hydroxyl), and 9.50 (C_6 adjacent to iodine) for the AC isomer and 101.91 (C_1), 81.39 (C_4), strong peak centered at 72.11 (C_2, C_3, C_5), 59.87 (C_6 adjacent to hydroxyl), and 9.50 (C_6 adjacent to iodine) for the AD isomer. The possibility of an AB isomer is easily excluded on the basis of ^{13}C NMR chemical shifts of the present capped cyclodextrins listed above which are slightly but appreciably different from that of the AB isomer expected from the α-A,B,X isomer, **7**.[8]

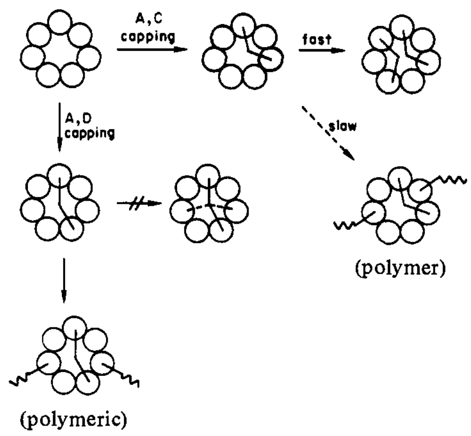


7

The A,C capping with **2b** was strongly supported by our results of formation of the doubly capped β-cyclodextrin with **2b**[9] in good yield (ca. 35% based on cyclodextrin used, which is very close to the yield of single A,C capping of 40%), since any double capping is not possible from a A,D capping reagent (Table I). Actually A,D capping reagent **2a**[10] leads to polymeric material almost exclusively, and double cap was obtained in less than 2.5% yield under the conditions of **2b** capping (Scheme II).

The presence of AC and AD isomers was first proved by Breslow[4] for C in Scheme I, the observed isomer ratio being dependent on the nature of the capping reagent (**2c** and **2d**). This structural dependence of regioselectivity, not remarkable for such similar capping reagents as **2c** and **2d**, is dramatically shown in the present examples. Judging from the CPK molecular model, the major determining factor of the present regiospecific AC and AD capping is concluded to be the "looper's walk" mechanism of the capping reaction, i.e., the first functionalization determines the site of the second functionalization at the "best fit" position, considering the distance between two reacting sites (see Table II), strain in a transition state, direction of approach of an entering group, etc. This mechanism seems to be generally applicable to regiospecific multifunctionalization of large molecules to afford models of enzymes or other biologically important molecules.

Scheme II



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(7) Polymeric materials, the (hydrolyzed) capping reagent, and monosulfonate–monosulfonic acid were removed through flash column chromatography, and the resultant crude capped cyclodextrin was converted to the corresponding diiodo derivative according to the procedure described.[6]

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(9) Double cap was obtained as a sharp round spot on TLC (silica gel, *n*-PrOH/H_2O/AcOEt/25% NH_3 = 5:3:2:1, R_f double cap 0.64, single cap 0.54, β-CD 0.18, polymeric 0; CH_3CN/H_2O = 5:1, R_f double cap 0.6, single cap 0.2, β-CD 0), and the ^1H NMR intensity of the corresponding pure tetradeoxy derivative ($NaBH_4$ reduction of the tetraiodide) was satisfactory. Impure compound was contaminated with benzophenone-3,3′-disulfonic acid ascertained by ^1H NMR of the cap, which was successfully eliminated by repeated reprecipitation with tetrachloroethylene. Electronic and IR spectra were also satisfactory. Details will be described in a forthcoming article.

(10) Structure of the A,D cap was ascertained by its photochemistry. Two well-separated peaks, P_1 and P_2, were observed for the *cis*-stilbene-4,4′-disulfonyl cap, where P_2 was identical with the cis cap, derived from the present *trans*-stilbene-4,4′-disulfonyl cap by irradiation in every respect. Since neither P_1 nor P_2 was an AB isomer, the present stilbene cap is concluded to have the AD structure.

Facile Degradation by Superoxide Ion of Carbon Tetrachloride, Chloroform, Methylene Chloride, and *p,p′*-DDT in Aprotic Media

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Although there is ample evidence that superoxide ion ($O_2^-\cdot$) is an effective nucleophile in aprotic sovlents,[1] studies have been limited to alkyl halides[2-5] and esters.[6-8] Kinetic studies confirm

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