pounds. Results are summarized in Table IV.

Photodecomposition of *tert*-Butyl Hypoiodite. A solution of the reagent (0.2 M) prepared from the reaction of *tert*-butyl hypochlorite and mercuric iodide was irradiated with a 200-W tungsten lamp for 52 h. The products were separated by preparative GLPC (10 ft × $^1/_4$ in. 10% SE-30, 60/80 Chromosorb W) and the compounds analyzed by NMR. The results are shown in Table V. The product yields were determined by using bromocyclohexane as an added external standard.

Photoinitiated Reactions with Hydrocarbons. Preparative reactions were run in Freon 113 solutions 1.0–1.2 M in *tert*-butyl hypoiodite and 3.8–4.2 M in hydrocarbon and photolyzed at 47 °C for 8 h. The products were characterized by comparison of their IR and NMR spectra and GLPC retention times with those of authentic samples. GLPC analysis was carried out on a 10 ft × $^1/_4$ in. SE 30 on Chromosorb PAW glass column using Freon 112 as an internal standard. Results are summarized in Table VI.

Competitive Reactions of Alkyl Iodides and Cyclohexane. The competitive reactions were run in Freon 113 solutions 0.133 M in *tert*-butyl hypoiodite and 0.270 M in substrate. The ratio of alkyl iodide to cyclohexane was determined by GLPC (25 ft × $^1/_8$ in. Ucon Polar column using Freon 112 as an internal standard) before and after photoinitiated reaction at 40 °C for 15 min. The relative reactivities of alkyl iodides and cyclohexane were thereby determined (see Table VII).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for their generous support of this work.

Registry No. 4, 91083-56-6; **5**, 91083-61-3; **6**, 91083-57-7; **7**, 91083-62-4; **8**, 91083-63-5; **9**, 917-97-5; **10**, 91083-58-8; **11**, 91083-59-9; *t*-C_4H_9OCl, 507-40-4; I_2, 7553-56-2; AgI, 7783-96-2; HgI_2, 7774-29-0; $C_6H_{11}Cl$, 542-18-7; $C_6H_{11}I$, 626-62-0; *trans*-$C_6H_{10}Cl_2$-1,2, 822-86-6; *trans*-$C_6H_{10}ClI$-1,2, 33427-17-7; *t*-C_4H_9OH, 75-65-0; potassium *tert*-butoxide, 865-47-4; cyclohexane, 110-82-7; acetone, 67-64-1; iodomethane, 74-88-4; 1-iodo-2-methylpropanol, 91083-60-2; isobutylene oxide, 558-30-5; 1-iodo-2-propanone, 3019-04-3; neopentane, 463-82-1; *n*-butane, 106-97-8; isobutane, 75-28-5; toluene, 108-88-3; neopentyl iodide, 15501-33-4; 2-iodobutane, 513-48-4; 1-iodobutane, 542-69-8; isobutyl iodide, 513-38-2; *tert*-butyl iodide, 558-17-8; benzyl iodide, 620-05-3.

Characterization of Regiospecific A,C- and A,D-Disulfonate Capping of β-Cyclodextrin. Capping as an Efficient Production Technique†

Iwao Tabushi,* Kazuo Yamamura, and Tatsuya Nabeshima

Contribution from the Department of Synthetic Chemistry, Kyoto University, Sakyo-ku Kyoto 606, Japan. *Received January 3, 1984*

Abstract: The fundamental aspects underlying the regioselective capping reaction of β-cyclodextrin (hereafter abbreviated as β-CD) were studied, using a series of rigid, aromatic disulfonyl chlorides $ClSO_2XSO_2Cl$ (**2**) (**2a–f**, X = 1,1′-methylene-bis(benzene)-4,4′-, 1,1′-oxybis(benzene)-4,4′-, benzophenone-3,3′-, *N*-methylcarbazole-3,6-, biphenyl-4,4′-, and *trans*-stilbene-4,4′-disulfonyl chloride, respectively). A new and convenient method of analysis of regiochemistry has been developed in which the product mixture of each capping was directly converted to the corresponding regioisomeric bis(sulfides), A,B-, A,C-, and A,D-β-CD(SPh-*t*-Bu)$_2$, by treatment with NaSPh-*t*-Bu, and the regioisomer ratio was determined by HPLC. The observed "overall" regiochemistry for all of the capping reagents, except *trans*-stilbene (**2f**), was insensitive to concentration, thus capping seems very attractive as a versatile method, since a high-dilution technique is not necessary and, therefore, cap preparation in large quantities is feasible. On the basis of the concentration-insensitive regiochemistry, *intramolecular capping* (looper's walk) was shown to be much more effective than intermolecular oligomerization. Highly regioselective capping was found in benzophenone-3,3′-disulfonyl chloride (**2c**), which gave mostly A,C regioisomer, while *trans*-stilbene-4,4′- (**2f**) and biphenyl-4,4′-sulfonyl chloride (**2e**) led to almost regiospecific A,D capping.

In cyclodextrin chemistry, considerable attention has been focused on developing techniques to modify primary[1] or secondary hydroxyl group(s).[2] Since 1976, when the first rigid cap (diphenylmethane-capped β-CD, **3a**) was reported by the authors,[3] disulfonate rigid capping has been successfully utilized to difunctionalize cyclodextrin's primary rim[4] for the preparation of sophisticated inclusion hosts[3,4,5a] or enzyme models.[4b,c,5b,c] This concept is also applied to host–guest energy transfer.[6]

The first transannular capping using diphenylmethane-4,4′-disulfonyl chloride **2a** was not regiospecific, but instead gave regioisomers A,C and A,D[4a] (see Scheme I). This unique type of regiochemistry on CD is of considerable interest and, therefore, was investigated further by the authors.[7] Nearly exclusive selection of A,C- and A,D-disulfonate capping was achieved by using benzophenone-3,3′-disulfonyl chloride **2c** and *trans*-stilbene-4,4′-disulfonyl chloride **2f**, respectively. Therefore, the dramatic structural dependence in regioselectivity presents an interesting problem, that is, how the second transannular functionalization can be achieved at the best-fit position (*looper*'s *walk*). The

Table I. Preparation of Capped β-Cyclodextrin Purified after Discarding Less Soluble Materials

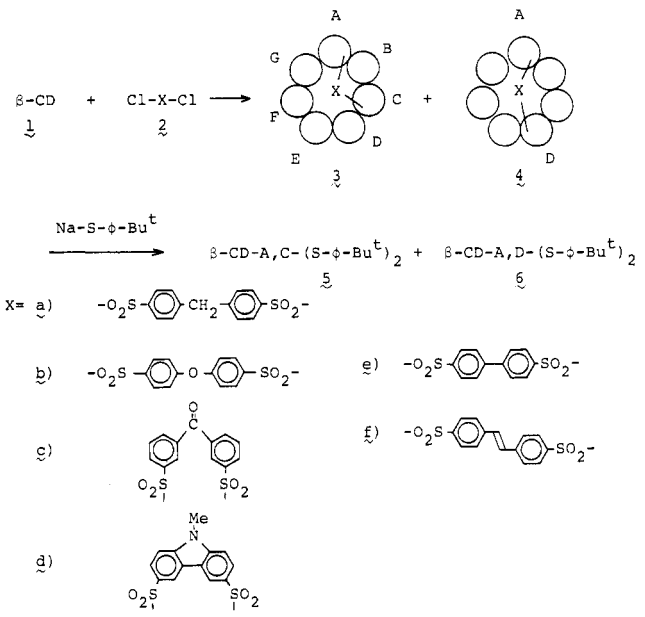
capping reagent, M	β-CD, M	°C	h	yield, %	ref
2a, 6.0×10^{-2}	5.0×10^{-2}	50	2.5	35	4a
2c, 3.6×10^{-2}	3.5×10^{-2}	60	1	40	7a
2f, 1.8×10^{-2}	1.8×10^{-2}	60	1	20	7a,b

† Sample of A,C- or A,D-β-CD(SPh-*t*-Bu)$_2$ for a HPLC standard will be given on request.

(1) (a) Cramer, F.; Mackensen, G.; Sensse, K. *Chem. Ber.* **1969**, *102*, 494. (b) Emert, J.; Breslow, R. *J. Am. Chem. Soc.* **1975**, *97*, 670. (c) Tabushi, I.; Shimokawa, K.; Shimidzu, N.; Shirakata, H.; Fujita, K. *Ibid.* **1976**, *98*, 7855. (d) Tabushi, I.; Shimidzu, N.; Sugimoto, T.; Yamamura, K. *Ibid.* **1977**, *99*, 7100. (e) Boger, J.; Brenner, P. G.; Knowles, J. R. *Ibid.* **1979**, *101*, 7630. (f) Breslow, R.; Bovy, P.; Hersh, C. L. *Ibid.* **1980**, *102*, 2115. (g) For reviews, see: Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66. Bender, M. L.; Komiyama, M. "Cyclodextrin Chemistry"; Springer-Verlag, New York, 1978. Szejtli, J. "Cyclodextrins and Their Inclusion Complexes"; Akademiai Kiado: Budapest, 1982. Croft, A. P.; Bartsch, R. A. *Tetrahedron* **1983**, *39*, 1417.

0002-7863/84/1506-5267$01.50/0

Scheme I



fundamental aspects underlying looper's walk deserve to be investigated in detail. Principal contaminants (tri- or monosubstituted derivatives) observed in the final product may arise from oligomeric materials and monosulfonate–monosulfonic acid. The oligomeric materials and monosulfonate–monosulfonic acids may also cause a decrease in regioselection. Therefore, detailed characterization of products and an understanding of the capping mechanism are necessary to determine the inherent regioselection, as well as optimizing the capping conditions.

Now the authors wish to report details of regiospecific capping of β-cyclodextrin using a series of aromatic disulfonyl chlorides, $ClSO_2X'SO_2Cl$ (**2a–f**), in dry pyridine (Scheme I), as a versatile preparation method.

Results and Discussion

The capping reaction illustrated in Scheme I was successfully carried out by treating meticulously dried β-CD (see Experimental Section) with 0.8–1.2 equiv of a capping reagent (**2a–f**) in "extremely" dry pyridine. Crude capped CD's were separated from viscous oligomeric precipitates by decantation and were purified through chromatography. Yields of capped CD's are given in Table I, together with the reaction conditions.

A,C-, A,D-Regioisomer Separation on HPLC. A Convenient Procedure for Regioisomer Determination. Skeletal structure and

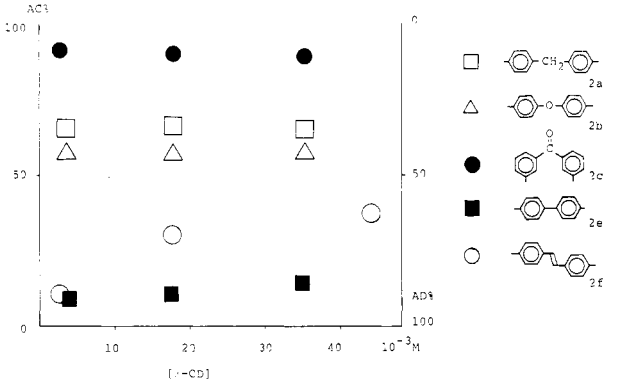
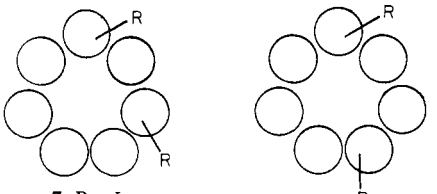


Figure 1. Concentration dependence of A,C/A,D ratio (25 °C); 0.85 equiv of capping reagent was used.

functionality of caps and their derivatives were made spectroscopically[7a] and chemically.[7b,c] A crude mixture of the regioisomers was converted to corresponding bis(*p-tert*-butylbenzenesulfenyl) derivatives **5** and **6** (Scheme I) by treatment with NaSPh-*t*-Bu in DMF at 80 °C for 12 h. For further structure determination, conversion to diiodo (**7** and **8**) and dideoxy-β-



7, R = I
9, R = H

8, R = I
10, R = H

cyclodextrin (**9** and **10**) was also carried out.[7a-c] Both bis(sulfides) **5** and **6** showed satisfactory IR, NMR spectra, and elemental analyses (see Experimental Section). However, spectroscopic distinction between these was very small and not enough to determine the regiochemistry, bringing about a similar situation as that encountered in ^1H NMR and ^{13}C NMR spectra of dideoxy or diiodo derivatives.[7] Fortunately, however, the bis(sulfides) **5** and **6** were separable on HPLC through a carbohydrate column (μ-Bondapak, Waters Associates), and each separated isomer was identified with the corresponding authentic compound of known regiochemistry.[7a-c] The observed retention time was 13.0 min for A,D isomer **6** and 15.2 min for A,C isomer **5**, respectively. Each isomer was easily distinguishable from the A,B isomer (11.6 min) (CH_3CN–H_2O = 3.5:1, v/v, 2.0 mL/min, 900 psi). The sensitivity of peak detection (UV, 254 nm) and peak separation was quite satisfactory for quantitative analyses, providing a very useful method of investigation of cyclodextrin regiochemistry.

Intramolecular Transannular Capping (Looper's Walk) and Intermolecular Difunctionalized β-Cyclodextrin. Clearly, each cap must be derived from the first functionalization product, monosulfonate–monosulfonyl chloride **11**, through an efficient transannular sulfonylation. Intermolecular functionalization also leads to various difunctionalized products **12**. Therefore, formation of **12** is the primary source of the impurities in the capping reaction,[8] and deserves further discussion.

In order to estimate the contribution of the **12** formation to the overall product distribution, a crude cap mixture containing **3**, **4**, and **12** was converted directly to a mixture of corresponding sulfides by treatment with NaSPh-*t*-Bu, without any preceded purification. Then the amounts of **5** and **6** were determined quantitatively by HPLC as described above. Figure 1 and Table II show the result of the A,C/A,D ratio determined for cap preparations under varied reagent concentration ((2.6×10^{-3})–(4.4×10^{-2}) M) and varied reaction temperature (25–60 °C).

(2) (a) Breslow, R.; Overman, L. E. *J. Am. Chem. Soc.* **1970**, *92*, 1075. (b) Ueno, A.; Breslow, R. *Tetrahedron Lett.* **1982**, *23*, 3451. (c) Breslow, R.; Czarnik, A. W. *J. Am. Chem. Soc.* **1983**, *105*, 1390.

(3) Tabushi, I.; Shimokawa, K.; Shimidzu, N.; Shirakata, H.; Fujita, K. *J. Am. Chem. Soc.* **1976**, *98*, 7855.

(4) (a) Tabushi, I.; Shimokawa, K.; Fujita, K. *Tetrahedron Lett.* **1977**, *18*, 1527. (b) Tabushi, I.; Kuroda, Y.; Mochidzuki, A. *J. Am. Chem. Soc.* **1980**, *102*, 1152. (c) Breslow, R.; Bovy, P.; Hersh, K. L. *Ibid.* **1980**, *102*, 2115. (d) Tabushi, I.; Nabeshima, T.; Kitaguchi, H.; Yamamura, K. *Ibid.* **1982**, *104*, 2017.

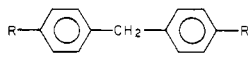
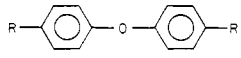
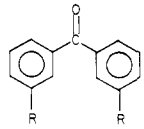
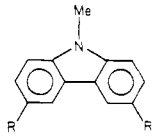
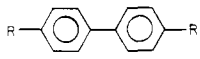
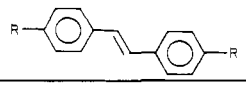
(5) (a) Tabushi, I.; Kuroda, Y.; Shimokawa, K. *J. Am. Chem. Soc.* **1979**, *101*, 1614. (b) Breslow, R.; Doherty, J.; Guillot, G.; Lipsey, C. *Ibid.* **1978**, *100*, 3227. (c) Breslow, R.; Hammond, M.; Lauer, M. *Ibid.* **1980**, *102*, 421.

(6) Tabushi, I.; Fujita, K.; Yuan, L. C. *Tetrahedron Lett.* **1977**, *18*, 2503.

(7) (a) Tabushi, I.; Kuroda, Y.; Yokota, K.; Yuan, L. C. *J. Am. Chem. Soc.* **1981**, *103*, 711. (b) Tabushi, I.; Yuan, L. C. *Ibid.* **1981**, *103*, 3574. (c) Tabushi, I.; Yuan, L. C.; Shimokawa, K.; Yokota, K.; Midzutani, T.; Kuroda, Y. *Tetrahedron Lett.* **1981**, *22*, 2273. (d) According to the preliminary experiments, difference in ^{13}C NMR chemical shifts of two methyl carbons in 2,6-per(*tert*-butyldimethylsilyl)-A,B-dideoxycyclodextrin was small but appreciable ($\Delta\delta$ = 0.17), clearly distinguishable from the A,D isomer. The observed magnitude of the substituent effect of remote methyl group to methyl carbon in the A,B-dideoxycyclodextrin is reasonable judging from the effect in 6′-chloro-6′-deoxymaltose and 6,6′-dichloro-6,6′-dideoxymaltose (0.1–0.2 ppm): Colson, P.; Slessor, K. N.; Jennings, H. J.; Smith, I. C. P. *Can. J. Chem.* **1975**, *53*, 1030. The detailed description on the preparation and the characterization of A,B-disubstituted β-CD will appear in an article under preparation.

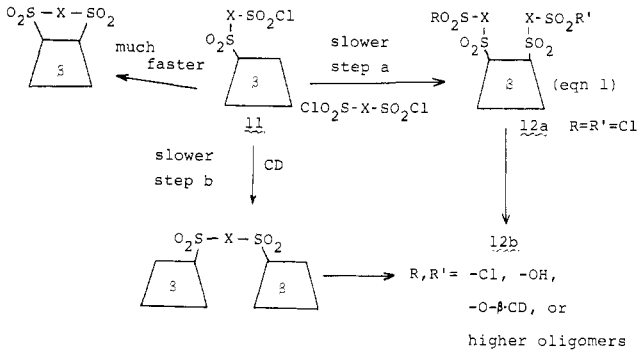
(8) Insoluble materials without any sulfonate group were also formed in small amounts.

Table II. A,C/A,D Regioisomer Distribution in the Crude Cap Mixture of β-Cyclodextrin at 25 °C

capping reagent[d]	concn, 10^{-3} M	[β-CD], 10^{-3} M	time, h	total yield of disubstituted β-CD,[a] %	A,C:A,D[b]	
	15.0	17.6	4	40	56 ± 3	34 ± 3
	15.0	17.6	7	39	51 ± 3	38 ± 3
	15.0	17.6	5	53	75 ± 2	8 ± 2[c]
	15.0	17.6	4	41	61 ± 15	35 ± 15
	15.0	17.6	7	54	10 ± 2	84 ± 2
	2.2	2.6	7	30	11 ± 3	81 ± 3
	15.0	17.6	7	33	24 ± 3	57 ± 3
	37.4	44.0	7	33	30 ± 3	50 ± 3

[a] Analytical yield. Esculin was used as an internal standard in the HPLC analysis. [b] The sum of A,B, A,C, and A,D isomers is 100. [c] A,C/A,D ratios at 60 °C were 94 ± 2/6 ± 2, 93 ± 2/7 ± 2, 92 ± 2/8 ± 2 ([β-CD]10^3, M) = 17.6, 5.9, 3.2, respectively); 0.85 equiv of the capping reagent was used. Temperature dependence of the regioisomer distribution will be reported in detail in a forthcoming article. [d] R = SO_2Cl.

For all the capping reagents used in this study except *trans*-stilbenedisulfonyl chloride, the observed "overall" regiochemistry was insensitive to concentration (Figure 1). This insensitivity indicates that either (i) telomerization gives almost the same regioisomer distribution as capping or (ii) telomerization has a minimal effect on the overall product distribution. Mechanism i is quite unlikely, considering the fact that the overall regiochemistry (A,C/A,D) observed for a series of capping reagents of a common local structure, ClO_2S–C_6H_4–Y, must be spread over an extremely wide range (nearly zero to infinity), too wide in fact to expect from the simple substituent effect in step a and other related steps, eq 1. Therefore, mechanism ii is probably operating.



The intramolecular looper's walk is more favorable than intermolecular condensation.[9]

This fortuitous situation makes capping very attractive as a versatile preparative method, since a high-dilution technique *is no longer necessary*. Thus, benzophenone **2c** was concluded to be an excellent A,C selective capping reagent under *less dilute* conditions, where the overall A,C/A,D ratio observed was 90/10 (Table II). Mechanism ii provides a reasonable basis for the successful preparation of the A,C-benzophenone cap (40% preparative yield, with 1.0 equiv of reagent) and the A,C:A′,C′-benzophenone double cap (35% preparative yield, with 2.6 equiv of the reagent) in a relatively condensed solution. Therefore, direct treatment of a crude product mixture with an appropriate nucleophile is an attractive procedure, preparing A,C-regiospecific difunctionalized cyclodextrins in some cases, where mono- and/or polysubstituted cyclodextrins are easily separated.

Table III. A,C/A,D Regioisomer Distribution for **2e** and **2f** Capping of β-Cyclodextrin[a]

capping reagent	method A[b]		method B[c]	
	A,C	A,D	A,C	A,D
2f	12	88	0	100
2e	11	89	0	100

[a] Analytical product distribution; analyzed as **5**(A,C)/**6**(A,D) by HPLC. [b] Capping reaction was carried out at 25 °C; complete evaporation of pyridine from a crude reaction mixture. [c] At 60 °C; decantation of reaction mixture from viscous oligomeric substances followed by pyridine evaporation.

Highly regioselective A,D capping was successfully made by reaction with 4,4′-biphenyldisulfonyl chloride and 4,4′-*trans*-stilbenedisulfonyl chloride, both of which have a looper's walk that is too long to bridge A,C positions. In both cases, simple decantation of insoluble materials and the precipitation of β-CD through the addition of the supernatant to CH_3CN–H_2O (5.5:1, v/v) afforded satisfactorily pure A,D regioisomers, providing a versatile preparative method.

As shown in Figure 1, the A,C/A,D ratio for the *trans*-stilbene changed significantly from 37/63 at [**2f**] = 4.4×10^{-2} M to 12/88 at [**2f**] = 2.6×10^{-3} M (Table II), showing a considerable concentration dependence only in this particular example.[10] The observed efficiency of looper's walk is primarily controlled by the rapid rate of transannular condensation, details of which will be reported in a forthcoming article.

Conclusions

A new and convenient procedure has been developed for the analysis of regiochemistry at the primary rim of β-cyclodextrin. Concentration-insensitive regiochemistry, thus clarified, reveals that capping of β-cyclodextrin with rigid disulfonyl chlorides is a versatile method of preparing difunctionalized CD derivatives under low-dilution conditions. Satisfactory A,D regioselection was achieved by the use of a *trans*-stilbene as well as a biphenyl capping reagent, whereby satisfactorily pure A,D regioisomers were easily obtained. For the preparation of regiospecific A,C-difunctionalized cyclodextrins, benzophenone cap was shown to be most satisfactory.

(9) Detailed kinetic analysis will appear in a following article.

(10) Kinetic reasoning will be given in a forthcoming article.

Experimental Section

Instruments and Apparatus. ^1H NMR spectra were recorded on a JEOL PMX-60, Varian H-100, or JEOL JMN-GX 400 spectrometer. ^{13}C NMR spectra were recorded on a JEOL JMN-GX 400 spectrometer. The chemical shifts are given in δ values from Me_4Si. IR spectra were obtained using a Hitachi Model 215 spectrophotometer. Electronic absorption spectra were measured with a Union Giken high-sensitivity spectrophotometer SM 401. Mass spectral data were provided by the Analytical Laboratory, Department of Synthetic Chemistry, Kyoto University, and elemental analyses were performed by the Microanalytical Laboratory of Kyoto University.

Thin-layer chromatography (TLC) was carried out on 0.25-mm E. Merck precoated silica gel plates (60F-254). Spot detection was carried out by UV light and/or staining with 0.45% anisaldehyde in MeOH–AcOH–H_2SO_4 (860:90:45, v/v).[11] For column chromatography, E. Merck silica gel-60 (70–230 mesh) was used. Melting points were obtained by using a Yanagimoto micro melting point apparatus and were corrected by using benzoic acid as a standard. High-performance liquid chromatography (HPLC) was performed analytically on a Waters Model 6000 instrument with a carbohydrate analysis column (3.9 mm × 30 cm, Waters p/n 84038).

Materials. Commercially available β-cyclodextrin (Ando Kasei Industry) with further purification was used and was dried in vacuo (<0.1 mmHg) at 80–90 °C over 12 h by using a liquid N_2 trap. Pyridine was purified by refluxing over KOH for 12 h and then over anhydrous BaO for at least 12 h and finally distilled just before use.[12] Dimethylformamide was kept standing over CaH_2 overnight and then was distilled under reduced pressure before use.[13] *p-tert*-Butylthiophenol was purchased from Tokyo Kasei Co., Ltd. 1,1′-Methylenebis(benzene)-4,4′-disulfonyl chloride (**2a**),[14] 1,1′-oxybis(benzene)-4,4′-disulfonyl chloride (**2b**),[15] and benzophenone-3,3′-disulfonyl chloride (**2c**)[16] were prepared according to the procedures reported previously. **2a**: mp 124–125 °C (lit. 124 °C);[14] ν_{max}(KBr) 1582, 1403, 1375 (SO_2Cl), 1310, 1291, 1187, 1172 (SO_2Cl), 1079, 1015, 875, 815, 741, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.23 (s, 2 H), 7.45 (A of A_2B_2, J = 8.4 Hz, 4 H), 8.02 (B of A_2B_2, J = 8.4 Hz, 4 H). **2b** (67% yield): mp 132–133 °C (lit. 128–129 °C);[15] IR (KBr) 1567, 1480, 1370 (SO_2Cl), 1240, 1185, 1162 (SO_2Cl), 1080, 865, 835, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.34 (A of A_2B_2, J = 8.6 Hz, 4 H), 8.19 (B of A_2B_2, J = 8.6 Hz, 4 H). **2c** (48% yield): mp 139–141 °C (lit. 139.5–141 °C);[16] IR (KBr) 1660, 1360 (SO_2Cl), 1160 (SO_2Cl), 990, 740 cm^{-1}.

N-Methylcarbazole[17] and biphenyl[18] were sulfonylated according to the reported procedures for the preparation of *N*-methylcarbazole-3,6-disulfonic acid and biphenyl-4,4′-disulfonic acid. *trans*-Stilbene-4,4′-disulfonic acid sodium salt was prepared from *p*-sulfocinnamic acid.[19]

N-Methylcarbazole-3,6-disulfonyl Chloride (2d). Sodium *N*-methylcarbazole-3,6-disulfonate (7 g, 18 mmol) was mixed with 15 g (73 mmol) of PCl_5 then shaken vigorously until it became viscous. After heating at 90 °C for 3 h, phosphorous oxychloride was distilled off in vacuo, and the residual solid was poured into 100 g of ice, giving the precipitates of disulfonyl chloride **2d** in 83% yield; mp > 170 °C dec; IR (KBr) 1620, 1580, 1470, 1370 (SO_2Cl), 1350, 1300, 1240, 1220, 1170 (SO_2Cl), 1140, 1110, 1060, 990, 800, 680 cm^{-1}; ^1H NMR ($CDCl_3$–Me_2SO-d_6) δ 3.93 (s, 3 H, NMe), 7.55 (d, J = 9 Hz, 2 H), 7.9 (d of d, J = 9, 2 Hz, 2 H), 8.5 (d, J = 2 Hz, 2 H); ^{13}C NMR ($CDCl_3$–Me_2SO-d_6) 38.28 (NMe), 117.76 (C-1), 127.12 (C-4), 130.27 (C-4a), 133.19 (C-2), 146.00 (C-1a), 150.78 (C-3). Mass spectrum, parent peak appeared at m/e 377 (relative intensity, 100) with isotope peaks 381 (17), 379 (73), 378 (17). Anal. Calcd for $C_{13}H_9Cl_2NO_4S_2$: C, 41.28; H, 2.40; N, 3.70; S, 16.95. Found: C, 41.48; H, 2.25; N, 3.66; S, 16.72.

Biphenyl-4,4′-disulfonyl Chloride (2e). The dipotassium salt (140 g, 0.395 mol) of biphenyl-4,4′-disulfonic acid was dried before use at 100 °C for 12 h in vacuo (0.1 torr). Then it was treated with 350 g (1.68 mol) of PCl_5 for 5 h at 100 °C. After the resultant phosphorous oxychloride was distilled off in vacuo, the residue was poured into 500 g of ice. The resultant solid collected by filtration was recrystallized from $CHCl_3$, yield of the disulfonyl chloride, 73 g (0.21 mol, 58%): mp 209–212 °C; IR (KBr) 1590, 1480, 1370 (SO_2Cl), 1270, 1190, 1170 (SO_2Cl), 1080, 1000, 810, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.94 (A of A_2B_2, J = 8.6 Hz, 4 H), 8.26 (B of A_2B_2, J = 8.6 Hz, 4 H). Anal. Calcd for $C_{12}H_8Cl_2O_4S_2$: C, 41.04; H, 2.30. Found: C, 41.25; H, 2.23.

***trans*-Stilbene-4,4′-disulfonyl Chloride (2f).** Disodium *trans*-stilbene-4,4′-disulfonate (2.0 g, 5.21 mmol) was mixed with 3.3 g (15.8 mmol) of phosphorous pentachloride to give a slurry mixture, which was then heated at 90 °C for 2 h. The resultant phosphorous oxychloride was distilled off in vacuo, and the residue was poured into 15 mL of ice water. The precipitates were collected by filtration to yield the disulfonyl chloride almost quantitatively, which was purified by recrystallization from $CHCl_3$. All procedures described above were carried out in the dark: mp 204 °C dec; IR (KBr) 1580, 1375 (SO_2Cl), 1330, 1170 (SO_2Cl), 1080, 968, 952, 832, 648 cm^{-1}; ^1H NMR ($CDCl_3$–Me_2SO-d_6, 1:1) δ 7.38 (s, 2 H), 7.71 (A of A_2B_2, J = 8.6 Hz, 4 H), 7.90 (B of A_2B_2, J = 8.6 Hz, 4 H); UV ($CHCl_3$) λ_{max} 320, 330 (sh), 350.4 nm. Anal. Calcd for $C_{14}H_{10}Cl_2O_4S_2$: C, 44.57; H, 2.67; S, 17.00. Found: C, 44.28; H, 2.77; S, 16.75.

Biphenyl-4,4′-disulfonyl-A,D-Capped β-Cyclodextrin (4e). Reprecipitation Purification. To a solution of dry β-CD (75 g, 0.066 mol) in 2 L of dry pyridine at 50 °C, 20 g (0.051 mol) of biphenyl-4,4′-disulfonyl chloride (**2e**) was added in four portions during 1 h, while being stirred with a magnetic bar. After 3 h at 50 °C, pyridine was removed by distillation in vacuo below 40 °C producing 90 g of a waxy residue. A 20-g portion of the waxy residue was dissolved in 40 mL of H_2O, and the resulting solution was added dropwise into vigorously stirred CH_3CN–H_2O (5.5:1, v/v) to precipitate oligomeric products and unreacted β-CD. Sufficiently pure capped β-CD **4e** (2.8 g, 17.5%) was obtained from the filtrate after suction filtration of the white precipitates. The cap (**4e**) was detected on TLC by the anisaldehyde procedure, but no detectable amount of recovered β-CD (R_f 0.12) was present. Cap **4e**, thus prepared, was pure enough to use without further purification procedures. **4e**: R_f 0.45 (*n*-PrOH–AcOEt-H_2O–NH_3(aq), 5:3:1), by UV and anisaldehyde detection; mp 164 °C dec; ν_{max}(KBr) 3400, 2900, 1610, 1360 (ν_{SO_2}), 1170 (ν_{SO_2}), 1160, 1080, 1040, 1020, 970, 900, 820, 710 cm^{-1}; ^1H NMR (Me_2SO-d_6) 7.7–8.3 (8 H, Ar H), 4.9 (br s, 7 H, C_1-H), 3.0-4.7 (54 H, other H).

***trans*-Stilbene-4,4′-disulfonyl-A,D-Capped β-Cyclodextrin (4f). Chromatographic Purification.** To a solution of dry β-cyclodextrin (2.0 g, 1.76 mmol) in 100 mL of dry, pure pyridine at 60 °C 0.68 g (1.79 mmol) of *trans*-stilbene-4,4′-disulfonyl chloride was added, with stirring. After 2 h, a viscous wax separated and was removed by decantation at room temperature. The pale brown solid was obtained by evaporation of the solution in vacuo (bath temperature was kept below 50 °C). Wako C-200 column chromatography (CH_3CN–H_2O, 5:1), followed by repeated flash column chromatography, afforded pure **4f** in 20% yield: TLC, R_f 0.51 (*n*-PrOH–AcOEt-H_2O–NH_3(aq), 5:2:3:1); ^1H NMR (Me_2SO-d_6) δ centered at 3.3 (42 H), 4.90 (7 H, C_1-H), 4.4, 5.7 (19 H, C_2, C_3, C_6-OH), 7.63 (2 H, olefinic), 7.90 (8 H, Ar); IR (KBr) 1358, 1175, 970 cm^{-1}; electronic spectrum (20% aqueous DMF) 315.0 (ϵ = 12725), 326.4 (1347), 342.4 (8175) nm. Anal. Calcd for $C_{56}H_{78}O_{39}S_2 \cdot 7H_2O$: C, 42.97; H, 5.92; S, 4.10. Found: C, 42.83; H, 5.50; S, 4.16.

(11) "Handbook of Chromatography"; Zweig, G., Sherma, J., Eds.; CRC Press: Cranwood Parkway, **1972**; Vol. 1, p 127.
(12) Riddick, J. A.; Bunger, W. B. In "Techniques of Chemistry: Organic Solvent"; Weissberger, A., Ed.; Wiley-Interscience: New York, 1070; Vol. 2, p 826.
(13) Riddick, J. A.; Bunger, W. B., ref 12, p 839.
(14) Losa, N. L., *Sb. Mater. Nauch.—Tekh. Konf. Ukr. Saoch. Politekh. Inst., Vlth* **1966**, 202; *Chem. Abstr.* **1968**, *68*, 114350*y*.
(15) Suter, C. M. *J. Am. Chem. Soc.* **1931**, *53*, 1112.
(16) Work, J. L.; Herweh, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *6*, 2022.
(17) Dykhanov, N. N.; Shevchenko, Z. N. *Med. Prom. SSSR* **1959**, *13*, 35; *Chem. Abstr.* **1960**, *54*, 1413*f*.
(18) Feldmann, J. *Helv. Chim. Acta* **1931**, *14*, 751.
(19) Es,van T.; Backeberg, O. G.; Morrison, I. *J. S. Afr. Chem. Inst.* **1964**, *17*, 95; *Chem. Abstr.* **1965**, *62*, 11721*b*.
(20) Analytical yield at 25 °C was given, since the yield was higher at 25° than at 60°, and the isomer distribution was practically the same. Reaction condition for these analytical experiments were the optimal ones where oligomerization or hydrolysis of products was minimal.