mixture was cooled, the solid material was eluted with benzene (50 mL). The yield was determined by GLC (Silicon OV 17, 3 m × 3 mm, 180 °C) using *n*-pentadecane as an internal standard.

***n*-Butyl Acetate.** A mixture of *n*-butyl bromide (1.37 g, 10 mmol) and KOAc–XAD-2 reagent (wet) made from KOAc (3.93 g, 40 mmol) and XAD-2 resin (8.0 g) was vigorously shaken for several minutes and then heated at 65 °C for 24 h. After the same treatment as benzyl cyanide, the yield was determined by GLC (PEG-20M, 3 m × 3 mm, 80 °C) using toluene as an internal standard.

***n*-Octyl Iodide.** A mixture of *n*-octyl bromide (1.93 g, 10 mmol) and KI–XAD-2 reagent (wet) made from KI (6.64 g, 40 mmol) and XAD-2 resin (8.0 g) was vigorously shaken for several minutes and then heated at 65 °C for 24 h. After the same treatment as *n*-butyl acetate, the yield was determined by GLC (silicon OV 17, 3 m × 3 mm, 180 °C) using *n*-pentadecane as an internal standard.

The Influence of Water in the Reaction of KCN and Benzyl Chloride (Molar Ratio, H_2O/KCN = 0.2). Water (0.14 g, 8 mmol) was added to the KCN–XAD-2 reagent (dry) made from KCN (2.60 g, 40 mmol) and XAD-2 resin (8.0 g). This mixture had been vigorously shaken for several minutes at 65 °C before benzyl chloride (1.26 g, 10 mmol) was added. The mixture was vigorously shaken for several minutes and heated at 65 °C for 24 h. The same treatment was made as benzyl cyanide described above.

Acknowledgment. I thank Nihon Tokushu Kagaku Kogyo Co., Ltd., for permission to publish this article.

Registry No. $PhCH_2Cl$, 100-44-7; *n*-C_4H_9Br, 109-65-9; *n*-$C_8H_{17}Br$, 111-83-1; $PhCH_2Br$, 100-39-0; *n*-C_4H_9I, 542-69-8; *n*-$C_8H_{17}I$, 629-27-6; $PhCH_2CN$, 140-29-4; *n*-C_4H_8OAc, 123-86-4; *n*-C_4H_9CN, 110-59-8; *n*-$C_8H_{17}CN$, 2243-27-8; $PhCH_2OAc$, 140-11-4; *n*-$C_8H_{17}OAc$, 112-14-1; KCN, 151-50-8; KOAc, 127-08-2; KI, 7681-11-0; H_2O, 7732-18-5; XAD-2, 9060-05-3; XAD-4, 37380-42-0; XAD-7, 37380-43-1.

Boron Trifluoride Catalyzed Addition of Disulfides to Alkenes

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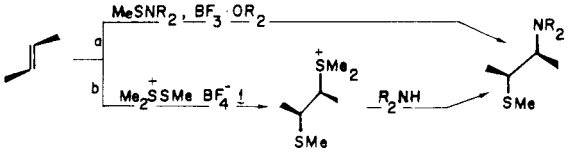
Addition of sulfenyl compounds RSX to carbon–carbon multiple bonds is well documented for reagents such as sulfenyl halides and thiosulfonium salts in which the X atom or group is electron-attracting (X = Cl, $^+SR_2$).[1,2] Less polar reagents such as disulfides RSSR and sulfenamides $RSNR_2$ normally do not add to alkenes. However, we reported recently that addition of sulfenamides to alkenes can be achieved under the catalytic influence of boron trifluoride etherate (eq 1a) —thereby providing a



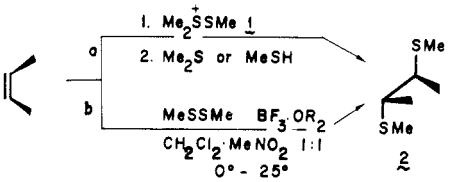
(1)

reasonable alternative to azasulfenylation of alkenes by addition of methylthiodimethylsulfonium salts 1 followed by displacement with amines (eq 1b).[3,4] We now report that a similar BF_3-catalyzed addition of disulfides to alkenes is a very convenient way to prepare 1,2-dithioalkanes.

There are scattered reports in the literature relating to the electrophilic addition of dialkyl disulfides to alkene double bonds in the presence of iodine[5–7] or hydrogen fluoride.[8,9] The most explicit of these is a description of iodine-catalyzed addition of dimethyl disulfide for the determination of double bond position in linear alkenes.[5] There is, however, little information in the literature, as far as we know, that describes the yields, stereochemistry, and scope of catalyzed disulfide addition. The results that we now report hopefully will serve as useful information on the synthetic utility of disulfide addition under electrophilic conditions.

Results and Discussion

The reaction conditions are remarkably simple and, in most cases, involve addition of a catalytic amount of boron trifluoride etherate ($BF_3{\cdot}OMe_2$ or $BF_3{\cdot}OEt_2$) to a mixture of the disulfide and alkene in a solvent mixture of dichloromethane and nitromethane maintained at 0 °C to ambient temperature. Generally, the alkene was in excess of the disulfide. Methyl disulfide reacted with *cis*-2-butene to give a *single* adduct in high yield (>90%), which was identified as racemic *threo*-2,3-bis(methylthio)butane (**2**) (eq 2b). *trans*-2-Butene gave a single, but different, adduct identified as *meso*-2,3-bis(methylthio)butane **3** in 96% yield (eq 3b). The products were identified by comparison with authentic samples and were, in fact, found to be indistinguishable from the adducts of a stepwise sequence of addition of 1 to *cis*- or *trans*-2-butene followed by reaction of the adduct thus formed with methyl sulfide or methanethiol (eq 2a or 3a).[3,11] These results illustrate that sulfenylation with dimethyl disulfide is a stereospecific reaction which leads to the product of *anti* addition.



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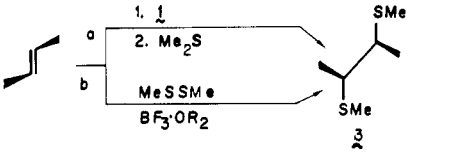

(3)

The scope of the reaction can be seen from the results summarized in Table I. Dimethyl, diethyl, and diphenyl disulfides gave excellent yields of adducts in high stereospecificity with both *cis*- and *trans*-2-butene. Yields were moderate to low for diisopropyl disulfide, although ste-

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(2) Helmkamp, G. K.; Olsen, B. A.; Pettit, D. J. *J. Org. Chem.* **1965**, *30*, 676. Helmkamp, G. K.; Olsen, B. A.; Koskinen, J. R. *Ibid.* **1965**, *30*, 1623.
(3) Caserio, M. C.; Kim, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3231.
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(5) Francis, G. W.; Veland, K. *J. Chromatogr.* **1981**, *219*, 379.
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(7) Holmberg, B. *Ark. Kemi, Mineral. Geol.* **1939**, *13*, 1.
(8) Radical, electrochemical, and photochemical additions of disulfides to alkenes have also been reported. See also: Meyerson, S.; Fields, E. K. *Chem. Abstr.* **1981**, *94*, 174510.
(9) McCaulay, D. A.; Lien, A. P. U.S. Pat. 2519586; *Chem. Abstr.* **1950**, *44*, 10728.
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0022-3263/85/1950-4390$01.50/0

Table I. Addition of Disulfides to Alkenes and Alkadienes

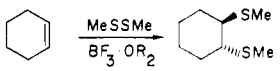
RSSR + alkene (2 equiv) $\xrightarrow[CH_2Cl_2,\ MeNO_2]{BF_3OMe_2}$ adduct(s)

disulfide, R	alkene	product(s) (yield, %)	bp (mm) or mp, °C
Me	*cis*-2-butene	(±)-2,3-bis(methylthio)butane [**2**] (91)	71–73 (6)
Me	*trans*-2-butene	*meso*-2,3-bis(methylthio)butane [**3**] (96)	71–73 (6)
Et	*cis*-2-butene	(±)-2,3-bis(ethylthio)butane (92)	41–2 (0.1)
Et	*trans*-2-butene	*meso*-2,3-bis(ethylthio)butane (90)	53–4 (0.2)
i-Pr	*cis*-2-butene	(±)-2,3-bis[(1-methylethyl)thio]butane (76)	54–55 (0.1)
i-Pr	*trans*-2-butene	*meso*-2,3-bis[(1-methylethyl)thio]butane (20)	54–55 (0.1)
t-Bu	*cis*-2-butene	no adduct	
t-Bu	*trans*-2-butene	no adduct	
Ph	*cis*-2-butene	(±)-2,3-bis(phenylthio)butane [**12**] (98)	62–64
Me	propene	1,2-bis(methylthio)propane (8)	52–54 (6)[h]
Me	3-methyl-1-butene	1,2-bis(methylthio)-3-methylbutane (5)	104–106 (6)
Me	phenylacetylene	[1,2-bis(methylthio)ethenyl]benzene[cis:trans = 3:1] (<10)	125–127 (1)
Me	*cis*-ClCH=CHCl	no adduct	
Me	*trans*-ClCH=CHCl	no adduct	
Me	*trans*-$ClCH_2CH$=$CHCH_2Cl$	no adduct	
Me	$ClCH_2C{\equiv}CCH_2Cl$	no adduct	
Me	cyclohexene	*trans*-1,2-bis(methylthio)cyclohexane [**8**] (81)	73 (0.3)
Me	1,5-cyclooctadiene	*trans*-5,6-bis(methylthio)cyclooctene [**4**] (18)	92–93 (0.2)
Me	1,3-butadiene	*trans*-1,4-bis(methylthio)-2-butene [**6**] (52)	41–42 (0.2)
Ph	1,3-butadiene	*trans*-1,4-bis(phenylthio)-2-butene [**7**] (25)	64–66
Me	cyclopentadiene	*trans*-3,4-bis(methylthio)cyclopentene [**11a**] (45) *trans*-3,5-bis(methylthio)cyclopentene [**11b**] (18) *cis*-3,5-bis(methylthio)cyclopentene [**11c**] (37)	
Me, Ph[a]	*cis*-2-butene	2-(methylthio)-3-phenylthiobutane [**10**] (58), **2** (29), **12** (12)	98–100 (0.2)[c]
Me, Ph[b]	*cis*-2-butene	**10** (61), **2** (26), **12** (13),	
Me, Ph[a,d]		MeSSMe (22), PhSSPh (22), PhSSMe (56),	
Me, Ph[b,d]		MeSSMe (25), PhSSPh (25), PhSSMe (50),	
1,2-dithiane	*cis*-2-butene	polymer[e] (67–88)	
1,2-dithiane	*trans*-2-butene	polymer[f] (60)	
1,2-dithiane	cyclopentadiene	polymer[g] (>90)	
cis-3,5-dimethylthiolane	1,3-butadiene	polymer (68)	

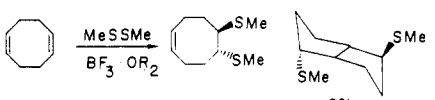
[a] Unsymmetrical disulfide MeSSPh. [b] 1:1 mixture of MeSSMe and PhSSPh. [c] Bp of major product **10**; small amounts of MeSSMe and PhSSPh were detected. [d] After 30 min at 0–5 °C. [e] 65% of product insoluble in ethanol; 35% soluble in ethanol. [f] 90% of product insoluble in ethanol; 10% soluble. [g] Insoluble in ethanol. [h] Reference 14b.

reospecificity was maintained. An attempt to react di-*tert*-butyl disulfide with *cis*-2-butene failed to give an adduct under the mild reaction conditions employed.

Table I also indicates the influence of alkene structure on the reaction. Cyclohexene with dimethyl disulfide gave *trans*-1,2-bis(methylthio)cyclohexane (**8**) in high yield (>80%, eq 4), whereas propene and 3-methyl-1-butene produced adducts in unexpectedly low yield. 1,5-Cyclooctadiene gave a monoadduct **4** (18%, eq 5) with no trace of the bicyclic adduct **5** anticipated from a transannular ring closure similar to that reported for the reaction of 1,5-cyclooctadiene with iodine.[12]

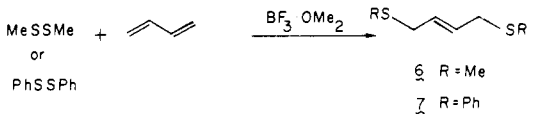


81% (4)



18% (**4**) 0% (**5**) (5)

Disulfide addition to 1,3-dienes proceeded smoothly in the presence of boron trifluoride etherate although the yields reported in Table I are not necessarily optimum. Cyclopentadiene and MeSSMe gave a mixture of three adducts corresponding to 1,2-addition (**11a**, trans adduct) and cis and trans adducts of 1,4-addition (**11b** and **11c**). The adducts were separated by GLPC and characterized spectroscopically (see supplementary material for NMR assignments). In contrast, 1,3-butadiene gave only 1,4-trans adducts **6** and **7** with MeSSMe and PhSSPh, respectively (eq 6). The structures of **6** and **7** were determined by comparison with samples prepared by alternate routes, specifically from reaction of 1,4-dichloro-*trans*-2-butene with sodium thiomethoxide and thiophenoxide.



6 R = Me
7 R = Ph (6)

Extension of the reaction to chloro-substituted alkenes proved to be disappointing. No evidence of addition of MeSSMe to either *cis*- or *trans*-1,2-dichloroethene, or even 1,4-dichloro-2-butene or 1,4-dichloro-2-butyne, was found. It may be noted that related attempts at sulfenylation of chloroalkenes were unsuccessful.[13] A simple alkyne, phenylacetylene, gave a complex mixture of products with MeSSMe and BF_3-OEt_2 from which two monoadducts were isolated in low yield (<10%); these were identified as *cis*- and *trans*[1,2-bis(methylthio)ethenyl]benzene with the cis isomer favored by 3:1.[14a] However, the ratio changed with time, indicating the onset of rearrangement under the reaction conditions.

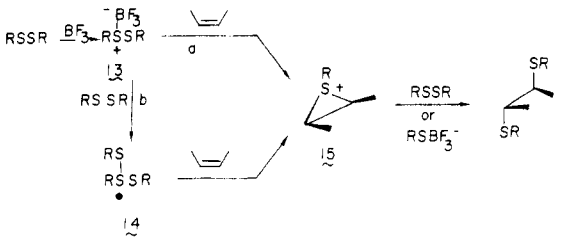
Reaction of the cyclic disulfide 1,2-dithiane with *cis*- and *trans*-2-butene under the same conditions described for acyclic disulfides gave complex mixtures of products that

(12) Uemura, S.; Fukuzawa, S.; Toshimitsu, A.; Okamo, M. *J. Org. Chem.* **1983**, *48*, 270.

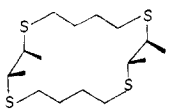
(13) Hester, N. E.; Helmkamp, G. H. *J. Org. Chem.* **1973**, *38*, 461.

(14) (a) Russell, G. A.; Ochrymowycz, L. A. *J. Org. Chem.* **1970**, *35*, 764. (b) Sharp, D. W. A.; Miguel, H. T. *Isr. J. Chem.* **1978**, *17*, 144.

Scheme I

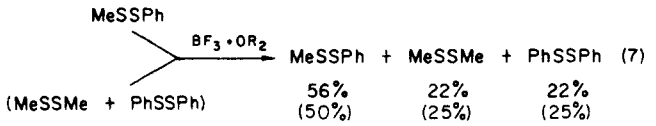


we have been unable to fully characterize. It is clear, however, that the products are not simple 1:1 adducts but are polymeric in character. Furthermore, the products from *cis*-2-butene are not identical with those from *trans*-2-butene, which suggests that stereospecificity is preserved even in the formation of polymeric adducts. At least three products were formed in the ratio 65:30:5 from *cis*-2-butene, and an ethanol-soluble fraction produced a solid of mp 134–138 °C comprising the minor components (35%). Spectral analysis of this material (see supplementary material) indicates a composition $C_{16}H_{32}S_4$ consistent with an adduct consisting of two units of each monomer. A possible structure is the macrocyclic polythioether 2,3,10,11-tetramethyl-1,4,9,12-tetrathiacyclohexadecane (**9**),[15] but the assignment is tentative.



9

Disulfide Interchange. The reactions described thus far have involved addition of symmetrical disulfides. Addition of the unsymmetrical disulfide methyl phenyl disulfide to *cis*-2-butene in the presence of BF_3 etherate gave excellent conversion to a mixture of three adducts corresponding to the mixed dithioether **10** (58%) and the symmetrical dithioethers **2** (29%) and **12** (12%) (Table I). A mixture of the same composition was produced from the BF_3-catalyzed reaction of *cis*-2-butene with a 1:1 mixture of the two symmetrical disulfides MeSSMe and PhSSPh. This result indicates that disulfide interchange precedes addition. In fact, when methyl phenyl disulfide (or a 1:1 mixture of MeSSMe and PhSSPh) was treated with the BF_3 catalyst in the *absence* of alkene, an equilibrium mixture of disulfides in the ratio 56:22:22 (or 50:25:25) was obtained within 30 min at room temperature (eq 7).[10] The

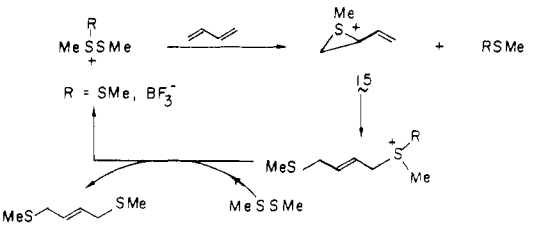


MeSSPh	$BF_3 \cdot OR_2$	MeSSPh +	MeSSMe +	PhSSPh (7)
(MeSSMe + PhSSPh)		56% (50%)	22% (25%)	22% (25%)

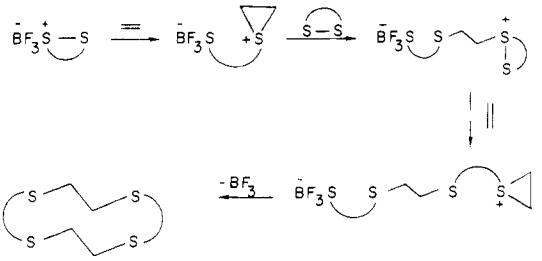
equilibrium distribution of disulfides is not greatly different from the distribution of adducts obtained, implying that the reactivities of the three disulfides toward *cis*-2-butene are not very different.

Mechanism. The stereospecificity and reactivity observed in the sulfenylation of alkenes with disulfides is strikingly similar to that observed previously in sulfenylation with thiosulfonium ions 1.[2-4,11] Both reactions are

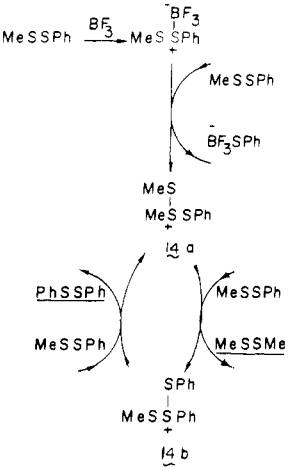
Scheme II



Scheme III



Scheme IV



a source of "$^+SCH_3$", although it is unlikely that the free ion is actually formed. It is reasonable to expect BF_3 to coordinate with the disulfide to form a thiosulfonium-like species **13** that can deliver +SR to the alkene double bond either directly (Scheme I, path a) or indirectly by way of dithiosulfonium ions **14** (Scheme I, path b). Either way, an episulfonium ion intermediate **15** is almost certainly formed which is trapped by the disulfide nucleophile to produce a neutral adduct of anti (trans) addition. In the case of addition to conjugated dienes, formation of 1,4-adducts can be understood as the result of S_N2' attack at the allylic double bond of an episulfonium intermediate **15** (Scheme II). Polymeric adducts from 1,2-dithiane can also be rationalized as the sequential attack of disulfide and alkene monomers, the former on an episulfonium ion and the latter on a thiosulfonium ion (Scheme III).

The observed BF_3-catalyzed disulfide interchange is also analogous to interchange catalyzed by thiosulfonium ions 1[10] and no doubt also proceeds by way of dithiosulfonium ion intermediates **14**, as proposed in Scheme IV.

Experimental Section

General Procedure for Adduct Formation. Methyl disulfide (1.88 g, 20 mmol) and 20 mL each of dichloromethane and nitromethane were placed in a flask equipped with a dry-ice condenser, thermometer, and gas inlet. After the mixture was cooled to −5 °C, *cis*-2-butene (2.24 g, 40 mmol) was added through the gas inlet. The inlet was replaced with a rubber septum through which was added boron trifluoride dimethyl etherate (0.2 mL).

(15) The unsubstituted ring analogue 1,4,9,12-tetrathiacyclohexadecane has been described. See: (a) Bradshaw, J. S.; Hui, J. Y.; Chan, Y.; Haymore, B. L.; Izatt, R. M.; Christensen, J. J. *J. Heterocycl. Chem.* **1974**, *11*, 45. (b) Travis, K.; Busch, D. H. *J. Chem. Soc., Chem. Commun.* **1970**, 1041. (c) Ochrymowycz, C.-P. Mak; Michna, J. D. *J. Org. Chem.* **1974**, *39*, 2079. (d) Musker, W. K.; Walford, T. L.; Roush, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 6416.

The mixture was stirred at 0 °C for 30 min and then allowed to warm to room temperature. After washing the mixture with 10 mL of saturated sodium bicarbonate solution, the organic layer was separated, dried and distilled to give *threo*-2,3-bis(methylthio)butane as a colorless liquid [2.69 g, 90%, bp 70–73 °C (6 mm)].[11] A rubber septum was used in place of the gas inlet tube for less volatile alkenes.

***trans*-1,4-Bis(methylthio)- and -Bis(phenylthio)-2-butene.** To a solution of sodium methoxide in methanol (1 M, 200 mL, 0 °C) was added methanethiol (9.6 g, 0.2 mol) or benzenethiol (22 g, 0.2 mol). The temperature was raised briefly to 25 °C and then cooled again to 0 °C. *trans*-1,4-Dichloro-2-butene (12.5 g, 0.1 mol) was added slowly to the stirred solution such that the temperature remained below 10 °C. Thereafter, the mixture was refluxed for 1 h, cooled, and poured into 1 L of ice–water. After extraction with ether (100 mL × 3), the ether extract was dried and distilled to give a colorless oil of *trans*-1,4-bis(methylthio)-2-butene [12.4 g, 85%, bp 41–42 °C (0.15 mm), (lit.[15] bp 115 °C (19 mm))]: NMR ($CDCl_3$) δ 2.01 (s, SCH_3, 3 H), 3.05 (m, CH_2, 2 H), 5.45 (m, CH=, 1 H). With benzenethiol, a crystalline solid of *trans*-1,4-bis(phenylthio)-2-butene was obtained [mp 64–66 °C (lit.[16] mp 76–77 °C), 20 g, 74%); NMR ($CDCl_3$) δ 3.43 (m, CH_2, 2 H), 5.56 (m, CH=, 1 H), 7.20 (m, Ph, 5 H).

Methyl Phenyl Disulfide. Methyl disulfide (9.4 g, 0.1 mol) was converted to methanesulfenyl chloride by adding 7.1 g of chlorine at −40 °C. The product, as a clear reddish orange solution, was added to a cold (0 °C) solution of benzenethiol (26 g, 0.236 mol) in 200 mL of dry methanol with 20 g of powdered calcium carbonate. The mixture was stirred for an additional 2 h at room temperature. Ice–water (500 mL) was added, and when gas evolution ceased, the mixture was extracted with ether (100 mL × 3), and the ether extracts were washed with 10% NaOH and then water (100 mL × 2), dried, and fractionally distilled to give 19.6 g of the product free of symmetrical disulfides [63%, 60–61 °C (0.2 mm)]: NMR ($CDCl_3$) δ 2.44 (s, SCH_3, 3 H), 7.15–7.55 (m, Ph, 5 H).

Addition of Methyl Phenyl Disulfide to *cis*-2-Butene. To a cold solution of 10 mL each of dichloromethane and nitromethane were added *cis*-2-butene (1.1 g, 20 mmol) and boron trifluoride dimethyl etherate (0.1 mL) as described previously. The mixture was cooled to −10 °C, and methyl phenyl disulfide (1.56 g, 10 mmol) in 5 mL of 1:1 solvent mixture was added slowly with stirring. The products were obtained as described previously and the composition determined by GLPC and NMR. Tabulated NMR data are available as supplementary material.

Acknowledgment. This work was supported in part by Grant GM27319 awarded by the Institute for General Medical Sciences, DHEW.

Supplementary Material Available: Table II, containing NMR assignments for all adducts (1 page). Ordering information is given on any current masthead page.

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Unsymmetrically Disubstituted β-Cyclodextrins. 6A,6X-Dideoxy-6A-azido-6X-[(mesitylsulfonyl)oxy] Derivatives

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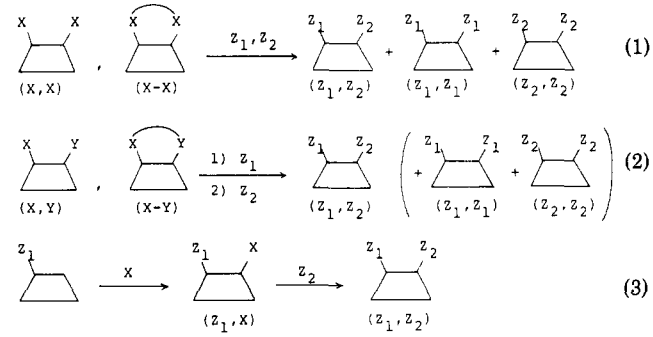
In the past decade, construction of artificial enzymes (or receptors) by chemical modification of cyclodextrins has been extensively studied. While monosubstitution of primary hydroxyl groups of cyclodextrins allowed simple designing of enzymes (or receptors),[1] transannular disulfonation (disulfonate capping) developed a new and quite interesting aspect of synthesis of symmetrically and specifically (6A,6C or 6A,6D) bifunctionalized enzyme (or receptor) mimics.[1,2] Recently, we also developed convenient preparation and effective separation of 6A,6B-, 6A,6C-, and 6A,6D-disulfonates of α- and β-cyclodextrins.[3,4] However, more sophisticated artificial enzmes (or receptors) should possess two different functional groups at desirable positions. Strategy of preparation of these artificial enzymes (or receptors) may be divided into three types as shown in Scheme I, where X and Y are activated primary hydroxyls such as sulfonates and Z_1 and Z_2 are functional groups. Since the product composition of the type (1) reaction is statistical, particular association between Z_1 and Z_2 (neither between Z_1 and Z_1 nor between Z_2 and Z_2) should be necessary for the formation of (Z_1,Z_2) in a composition more than 50% (statistical value). The type (2) reaction utilizing an unsymmetrically capped cyclodextrin (X–Y) has been reported by Tabushi.[5] This elegant and ingenious method permitted predominant production of (Z_1,Z_2), although information was not given with respect to the relative positions of Z_1 and Z_2.

Scheme I



We describe here a novel type (3) method which will permit isolation of pure (Z_1,Z_2) with respect to the relative positions of the substituents, 6A,6B-, 6A,6C-, or 6A,6D-isomers. The regioisomeric mixture of 6A,6X-dideoxy-6A-azido-6X-[(mesitylsulfonyl)oxy]-β-cyclodextrins was prepared by the reaction of 6-deoxy-6-azido-β-cyclodextrin[6] with mesitylenesulfonyl chloride in pyridine. After evaporation of pyridine, the crude mixture was applied on a reversed-phase column. After elution of water, a gradient elution of water–aqueous MeOH gave the recovered starting material (28.7%) and products 1 (11.2%), 2 (9.6%), and 3 (8.6%) (Figure 1). The products (1–3) were clearly separable from each other by reversed-phase HPLC (Figure 2A). The IR spectra of 1, 2, and 3 showed the absorptions of the azido (2100 cm^{-1}) and the sulfonate (1190, 1173, 760, and 648 cm^{-1}) in addition to the ab-

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