hydrogen bonding, "circular hydrogen bonding".[16a] Thus, calix[4]arenes have very low pK_a value and acidic character,[16b] and used as stabilizers for various organic polymers.[17] Solvents affected on the photopolymerization of MMA (Table 3).

Polymer formation decreased in the order THF>methanol>benzene. Solvent polarity does not account for the tendency of the polymer formation because the solvent polarity follows the order methanol>THF>benzene. The order of the solvent polarity corresponds to the order of polymer molecular weights. While the radical polymerization in methanol does not generally produce the high molecular weight of polymer, the high molecular weight of the polymer in our study was obtained as shown in Table 3. We do not have the rationalization for this at the present moment.

In conclusion, the percent conversion of the photopolymerization of MMA were found to depend upon structure of photoinitiators and solvents, but apparently not to be affected by calixarene.

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A Practical and Large Scale Synthesis of Phenyl Vinyl Sulfone from Benzenethiol and 2-Chloroethanol

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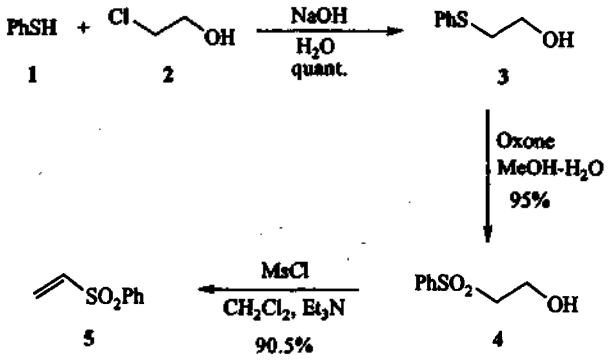
Vinyl sulfones, and in particular phenyl vinyl sulfone, have now become generally accepted as useful intermediates in organic synthesis.[1] The synthetic utility[2~3] of phenyl vinyl sulfone derives from their ability to serve not only as excellent Michael acceptors toward such reagents as enolate anions and organometallics but also as moderately reactive dienophiles in Diels-Alder reactions.

In connection with our research project, we required a large quantity of phenyl vinyl sulfone as an intermediate. Although phenyl vinyl sulfone is commercially available, it is very expensive. Literature[4] survey shows that applicable strategy for the preparation of phenyl vinyl sulfone involves the dehydrohalogenation of β-haloethyl phenyl sulfone which can be obtained by oxidation of the corresponding sulfide. Whereas β-haloethyl phenyl sulfide can be prepared by alkylation of benzenthiol with 1,2-dihaloethane, this reaction gives 1,2-bis(phenylthio)ethane as a byproduct.[5] The purpose of this paper is to describe a practical, versatile, high-yield synthesis of phenyl vinyl sulfone.

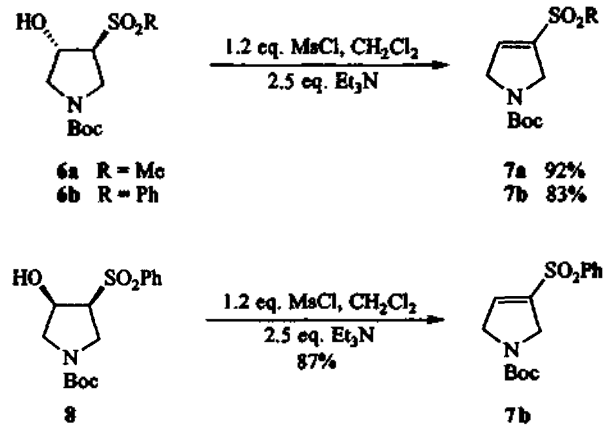
The preparation of phenyl vinyl sulfone began with the condensation of benzenethiol **1** with 2-chloroethanol **2** in the presence of sodium hydroxide. The alkylation of benzenethiol **1** with 2-chloroethanol **2** or 2-bromoethanol gave phenyl 2-hydroxyethyl sulfide **3** quantitatively with high purity. The previous published method for obtaining phenyl 2-haloethyl sulfide from 1,2-dihaloethane proceeded in low yield and afforded 1,2-bis(phenylthio)ethane as a side product. This pro-

blem could be overcome by making recourse to inverse addition[2] or by using a large molar excess of 1,2-dihaloethane as solvent and secondary reaction suppressant.[4] And the previous synthesis of phenyl 2-chloroethyl sulfide from benzenethiol was devised to avoid the formation of 1,2-bis(phenylthio)ethane by 1,2-dichloroethane but required two steps: reaction with thiophenol and 2-chloroethanol and chlorination.[6]



Step II of scheme was accomplished by oxidation with hydrogen peroxide in acetic acid[6] or by oxone® in methanol-water.[7] This step was achieved quantitatively and the reaction using oxone® proceeded in better purity (only one spot in TLC) than with hydrogen peroxide. The solubility of sulfone **4** in water was probably responsible for the incomplete isolation.

Just as we considered, 2-phenylsulfonylethanol **4** was successfully converted into the desired phenyl vinyl sulfone **5** by mesylation using methanesulfonyl chloride in the presence of excess triethylamine. The generation of double bond was derived from the mesylation of β-hydroxy sulfone and *in situ* β-elimination reaction by excess triethylamine.[8] Thus, this method affords a complementary route to phenyl vinyl sulfone. This process should be readily adapted to the synthesis of various vinyl sulfones from appropriate thiols and β-halo alcohols.



In order to gain support for the synthesis of vinyl sulfones from β-hydroxy sulfones, *trans*-4-hydroxy-3-methylsulfonylpyrrolidine **6a** and *trans*-4-hydroxy-3-phenylsulfonylpyrrolidine **6b** were allowed to react with methanesulfonyl chloride in the presence of excess triethylamine. This reaction resulted in the formation of 3-methylsulfonyl-3-pyrroline **7a** and 3-phenylsulfonyl-3-pyrroline **7b** in good yield. Also, the reaction of *cis*-pyrrolidine compound **8** with MsCl under excess triethylamine gave N-Boc-3-phenylsulfonyl-3-pyrroline **7a** in 87% yield.

In summary, phenyl vinyl sulfone was synthesized from the strategy of mesylation of β-hydroxy sulfone followed by *in situ* elimination reaction. The demonstrated process is carried out by very simple workup and useful in a practical and large scale synthesis.

Experimental Section

Benzenethiol, 2-chloroethanol, oxone®, methanesulfonyl chloride, and triethylamine were commercially available materials . Organic solvents were used without drying. ^{1}H NMR spectra were conducted on Brucker FT-80 (80 MHz) spectrometers with tetramethylsilane (TMS) as an internal standard. Melting points were determined with a Gallenkamp melting point apparatus without calibration.

Phenyl 2-hydroxyethyl sulfide (3). In a 2-L, round-bottomed flask fitted with an addition funnel was placed NaOH (180 g, 4.5 mol) dissolved in 800 mL of water. Benzenethiol **1** (206 mL, 2 mol) was added with stirring. After 30 min, 2-chloroethanol **2** (141 mL, 2.1 mol) was slowly added at 0 ℃ and stirred at room temperature for 10 h. The reaction mixture was extracted with chloroform (1 L×2). The chloroform layer was washed with saturated NH_4Cl solution (500 mL), dried ($MgSO_4$), and concentrated under reduced pressure to afford a quantitative recovery of pure phenyl 2-hydroxyethyl sulfide **3** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.41 (br, 1H), 3.08 (t, J=5.65 Hz, 2H), 3.65-3.80 (m, 2H), 7.16-7.46 (m, 5H).

Phenyl 2-hydroxyethyl sulfone (4). In a 5-L, three-necked, round-bottomed flask fitted with mechanical stirrer, thermometer, and addition funnel was placed phenyl 2-hydroxyethyl sulfide **3** (305 g, 1.98 mol) dissolved in 600 mL of methanol and 1200 mL of water. Oxone® (1476 g, 2.4 mol) was carefully added at −10 ℃ slowly to maintain internal temperature below 40 ℃. After being stirred at room temperature for 2 h, the solid formed was filtered and the filterate was extracted with chloroform (2 L×3). The extract was washed with brine (1 L), dried ($MgSO_4$), and concentrated under reduced pressure to give 350.4 g (95%) of phenyl 2-hydroxyethyl sulfone **4** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.81 (br, 1H), 3.33 (t, J=5.83 Hz, 2H), 3.97 (t, J=5.79 Hz, 2H), 7.66-7.42 (m, 3H), 7.85-7.97 (m, 2H).

Phenyl vinyl sulfone (5). In a 5-L, three-necked, round-bottomed flask fitted with mechanical stirrer, thermometer, and addition funnel was placed phenyl 2-hydroxyethyl sulfone **4** (350 g, 1.89 mol) dissolved in 2 L of dichloromethane and cooled to −30 ℃. Methanesulfonyl chloride (257 g, 2.24 mol) was added and then triethylamine (655 mL, 4.7 mol) was slowly added at −30 ℃. The resulting mixture was stirred at room temperature for 2 h and treated with 1 L of dichloromethane and 1 L of water. The organic layer was separated, washed with saturated sodium bicarbonate solution (1 L), dried ($MgSO_4$) in the presence of 30 g of active carbon and 30 g of silica gel (230-400 mesh), and filtered. The filterate was concentrated to give a quantitative recovery of phenyl vinyl sulfone **5** as a solid. Although this material was sufficiently pure for our purposes, recrystallization from diethyl ether (300 mL) and *n*-hexane (900 mL)

afforded 286 g (90.5%), mp 66-68 ℃ (lit.[4] mp 66-67.5 ℃). The ^{1}H NMR spectrum was identical to those reported.[2]

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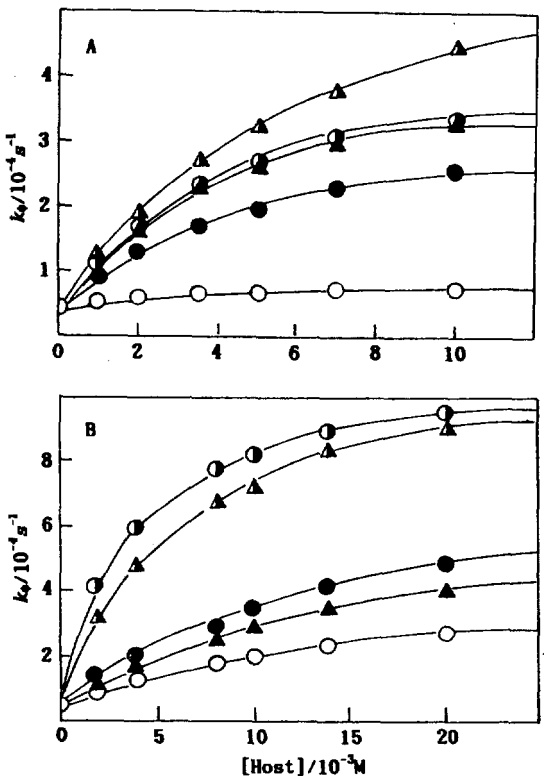

Figure 1. Variation of the pseudo-first-order rate constants for the deacylation reactions of *p*- (A) and *m*-carboxyphenyl acetate (B) as function of the concentration of hosts in the presence or absence of zinc ion: ○, β-CD; ▲, β-CDen; ●, β-CDdien; △, β-CDen/Zn^{2+}(4 : 1); ◑, β-CDdien/Zn^{2+}(4 : 3).

Deacylation Reaction of Carboxyl-Substituted Phenyl Acetate in the Presence of β-Cyclodextrin and Mono-(6-alkylamino)-β-Cyclodextrins : Effects of Carboxyl Group and Zinc Ion

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Cyclodextrins (CDs) have attracted great interest as enzyme mimics due to their ability to form inclusion complexes with a variety of substrates and to exhibit catalytic effects on various types of reactions.[1] The cleavage of phenyl esters in aqueous base is the most widely investigated of such CD-catalyzed reactions, and it is generally believed that the reactions take place from an ester-CD complexes in which the aryl group of the ester is included in the cavity of the CD.[2-6] We have been interested in the catalytic effects of β-CD and functionalized β-CDs on the cleavage of various aryl esters.[4-6] We now report the kinetic studies of the deacylation reactions of *p*- and *m*-carboxyphenyl acetates in β-CD (1), mono-6-deoxy-6-[N-(2-aminoethyl)]amino-β-CD (β-CDen, 2), and mono-6-deoxy-6-[N-(2-aminoethyl)-2-aminoethyl]-amino-β-CD (β-CDdien, 3) media. Carboxyphenyl acetates have a net charge on carboxyl group and can interact with the amine-derivatized β-CDs, electrostatically. In addition, the carboxyl group of the substrates and amine groups of β-CDen and β-CDdien could be binding sites for metal ions. The effects of the position of carboxyl group on phenyl ring and zinc ion on the stability and reactivity of the complexes between carboxyphenyl acetates and β-CDs are investigated.

β-CDen and β-CDdien were available from a previous study.[5,6] Carboxyphenyl acetates were prepared by a literature procedure.[2a] Deacylation reactions of carboxyphenyl acetates were initiated by adding 20 μL of 0.01 M solution of *p*-carboxyphenyl acetate in acetonitrile or 20 μL of 0.02 M solution of *m*-carboxyphenyl acetate in acetonitrile to 2.00 mL of the host solutions (0-20 mM) in 0.05 M pH 9.60 borate buffer (I=0.2 M) containing a desired amount of zinc ion in a cuvette pre-equilibrated at 25 ℃. The concentrations of zinc ion were adjusted such that [Zn^{2+}]/[host] ratio is 0.25 for β-CDen-containing media or 0.75 for β-CDdien-containing media. Reactions were followed spectrophotometrically by monitoring the formation of *p*-hydroxybenzoic acid at 279 nm or *m*-hydroxybenzoic acid at 289 nm. The reactions obeyed pseudo-first-order kinetics with respect to the esters, regardless of the presence of the hosts and zinc ion. The pseudo first-order rate constants (k_ψ) were determined in the presence of various concentrations of the hosts.

Figure 1 shows variation of k_ψ for the deacylation reactions