The various fluorinated sulfinate salts can be transformed to their corresponding sulfonate derivatives: chlorination gives the sulfonyl halides and oxidation by hydrogen peroxide leads to the sulfonic acids.[18] The use of sodium dithionite or sodium hydroxymethanesulfinate allows now the preparation of trifluoromethanesulfonic acid on a large scale.

Experimental Section

Fluorine magnetic resonance spectra were obtained on a Varian EM360L spectrometer (56.4 MHz) and were recorded in ppm (^{19}F) downfield from trichlorofluoromethane (solvents: water, acetone, ethyl acetate); bromotrifluoromethane and sulfur dioxide were purchased from Setic Labo, inorganic bases from Prolabo, sodium dithionite from Fluka, Rongalite from Aldrich, and Decroline from BASF. DMF from Aldrich was distilled in vacuo before use.

For experiments that needed a pressure until 6 bars, a Parr low-pressure hydrogenation apparatus was used. The hydrogen tank was removed, and the bromotrifluoromethane bottle was directly fitted with the manometer. The 250-mL glass bottle was tested for 8 bars and placed in a steel jacket. For experiments up to 20 bars, a Mula 1-L glass reactor, with a double fence, was used. In this case, the mixture was mechanically stirred. This reactor was kept in confinement in a secure polycarbonate box. In both cases, the reaction temperature was controlled by a thermostated water circulation.

Preparation of Sodium Trifluoromethanesulfonate from Sodium Dithionite. A 150-mL portion of water and 32.6 g (0.23 mol) of disodium phosphate was charged as a solution into a 400-mL reactor, followed by 48.3 g (0.24 mol) of 86.5% sodium dithionite and 100 g of dimethylformamide.

After closing the reactor, a vacuum (10 Torr) was created. Trifluorobromomethane was introduced at a pressure of 13 bars. The contents were stirred and heated to 65 °C, and additional CF_3Br was introduced when the pressure dropped to 12 bars.

The total duration of the trial was 70 min. After cooling and degassing, the upper phase was decanted and distilled to dryness. The solid was washed with methylene chloride and extracted with ethyl acetate. After evaporation of the solvent, crude 64% sodium trifluoromethanesulfinate was collected with a yield of 41.7 g (69% based on sodium dithionite).

A 8-g (0.035-mol) portion of crude sodium trifluoromethanesulfinate was dissolved in 25 mL of 35% hydrogen peroxide. Nuclear magnetic resonance measurements (^{19}F) showed that the conversion was complete within 5 h and that a single signal at δ_F −78 ppm remained. Two pieces of pumice were added, and the mixture was brought to reflux to decompose the hydrogen peroxide excess, giving 2.3 L of oxygen. The water was evaporated and the solid was extracted with acetone to give, after evaporation, 7.2 g (0.032 mol) of a crude 77% sodium trifluoromethanesulfonate as a colorless solid.

A mixture of 3 g of sodium trifluoromethanesulfonate and 3 g of 95% sulfuric acid was heated to 140 °C at 0.8 Torr to yield 2.25 g trifluoromethanesulfonic acid monohydrate (mp 45 °C) (lit.[17] mp 45 °C). This material was neutralized with 12.6 mL of IN sodium hydroxide. After the solid was isolated and dried at 80 °C (0.5 Torr), 2.3 g (0.0132 mol) of sodium trifluoromethanesulfonate was obtained as a colorless solid (yield from trifluoromethanesulfinate: 96%); mp 251 °C (lit.[19] mp 248 °C), δ_F = −78 ppm.

Preparation of Trifluoromethanesulfonyl Chloride from Sodium Hydroxymethanesulfinate. A mixture of 50 mL of dimethylformamide, 15.4 g (0.1 mol) of sodium hydroxymethanesulfinate, and 10 g (0.052 mol) of sodium bisulfite was charged in a thick-glass flask. The mixture was placed under 5 Torr, and the temperature was maintained at 20 °C. The flask was stirred at a bromotrifluoromethane pressure ranging from 3 to 5 bars for 3 h or until the gas absorption ceased. The flask was opened. After filtration, the dimethylformamide was distilled under vacuum. The resulting solid was washed with dichloromethane and extracted with ethyl acetate. After evaporation, the solid was dissolved in water. The pH was adjusted to 7. After filtration, the solution was stirred under a chlorine pressure of 3 bars during 2 h with the temperature maintained between 0 and 10 °C. The lower layer was distilled to give 4.7 g (0.028 mol) of trifluoromethanesulfonyl chloride:[19] yield 28%; bp 29–32 °C; δ_F ($CFCl_3$ ext) = −74 ppm.

Preparation of Trifluoromethanesulfonyl Chloride from Zinc Hydroxymethanesulfinate. A mixture of 50 mL of dimethylformamide and 12.7 g (0.05 mol) of zinc hydroxymethanesulfinate was placed in a thick-glass flask. The flask was placed under 5 Torr and heated to 65 °C. The mixture was stirred at a bromotrifluoromethane pressure ranging from 3 to 5 bars for 3 h or until the absorption of gas ceased. The flask was then opened. After filtration, the dimethylformamide was distilled under vacuum; 100 mL of water were added, followed by sufficient sodium hydroxide pellets to get a slightly basic pH. The unsoluble zinc salts were filtered off. The water was evaporated in vacuo. The residual solid was washed with dichloromethane and extracted with ethyl acetate. After evaporation, 100 mL of water was added. The solution was stirred under a chlorine pressure of 3 bars during 2 h, the temperature being maintained between 0 and 10 °C. The lower layer was separated and distilled to give 5.9 g (0.035 mol) of trifluoromethanesulfonyl chloride, yield 35%.

Preparation of Chlorodifluoromethanesulfonyl Chloride from Zinc Hydroxymethanesulfinate. A mixture of 50 mL of DMF and 12.7 g (0.05 mol) of zinc hydroxymethanesulfinate was placed in a thick-glass flask. A vacuum was created in the flask, and then the mixture was stirred for 15 hours at a bromochlorodifluoromethane pressure of 1.2 bars. The flask was opened, the solids were removed by filtration, and 1 g (0.01 mol) of trifluoroethanol was added. The yield of chlorodifluoromethanesulfinate (δ_F = −69 ppm/$CFCl_3$) was determined by ^{19}F nuclear magnetic resonance relative to trifluoroethanol (δ_F = −76 ppm). Yield: 20%. Water (30 mL) was added. The dimethylformamide was extracted with dichloromethane. After filtering, 2 L of chlorine was passed through the aqueous solution, and 3.2 g (0.018 mol) of chlorodifluoromethanesulfonyl chloride[14] (δ_F = −58 ppm) was obtained, bp 84 °C.[20] The yield relative to zinc hydroxymethanesulfinate was 18%.

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Resolution of Secondary Alcohols Using Lipase in Diisopropyl Ether

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Since Klibanov et al.[1] discovered enzymatic activity in anhydrous organic solvents, it has become a major field of research. Not only can one now carry out reactions like esterification, transesterification, etc., which otherwise would have been impossible to conduct in the presence of water but also the need to immobilize the enzymes by using tedious procedures is avoided. Enzymes can be separated by filtration and reused.

Lipases are one class of such enzymes that are presently being explored for their stereo- and regioselective esterification and transesterification reactions. They have been successfully used to resolve a host of alcohols[2–5] and for

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Table I. Lipase-Catalyzed Transesterification of Acetate Derivatives of Mandelate Esters 1 and 2, Mandelonitrile 3, 2-Chloro-1-phenylethanol 4, and Pantolactone 5[a]

substr (±), OAc	ROH	time, days	convn, %	recovered OAc[b] $[\alpha]^{25}_D$	recovered OAc[b] isomer (ee,[c] %)	product OH[b] $[\alpha]^{25}_D$	product OH[b] isomer (ee,[c] %)	E[d]
1	MeOH	23	25	+46.2 (2.6, C_6H_6)	S (29)[e]	−210 (0.6, CS_2)	R (98)[f]	136.3
2	*n*-BuOH	7	45	+74.78 (6, EtOH)	S (82)[g]	−80.71 (7, EtOH)	R (92)[g]	54.4
3	*n*-BuOH	2	38	+11.03 (15, C_6H_6)	S[h]	+33.5 (7, C_6H_6)	R (77)[i]	12.2
3	*n*-BuOH	3	54	+21.46 (4, C_6H_6)	S[h]	+19.4 (5, C_6H_6)	R (44)[i]	4.2
3[j]	*n*-BuOH	4	40	−9.18 (3, C_6H_6)	R[h]	−29.32 (3, C_6H_6)	S (67)[i]	7.8
4	*n*-BuOH	19	42	−14.37 (3.2, cyclohexane)	R (19)[k]	+10.32 (1.9, hexane)	S (22)[l]	1.8
4	*n*-OctOH	14	40	−11.81 (3.6, cyclohexane)	R (16)[k]	+11.32 (2.4, hexane)	S (24)[l]	1.9
4[j]	*n*-BuOH	20	23	−19.81 (5.4, cyclohexane)	R (27)[k]	+26.9 (3, hexane)	S (56)[l]	4.2
5	*n*-BuOH	14	34	+5.06 (10, EtOH)	S (36)[m]	−35.5 (2.3, H_2O)	R(70)[n]	8.0

[a] All reactions, unless otherwise mentioned, were performed in diisopropyl ether (45 mL) at 30 °C with 15 mmol of substrate, 60 mmol of ROH (nucleophile), and 3 g of yeast lipase. [b] Isolated in 70–90% yields by column chromatography separation on silica gel using dichloromethane as the solvent. [c] Attempts to determine ee using $Eu(dcm)_3$ as chiral shift reagent were not successful. Hence, the ee values were determined on the basis of the comparison of the observed rotation with either literature-reported values or the value of a chemically synthesized optically pure authentic sample. [d] See ref 10. [e] Literature[11] value for R isomer $[\alpha]^{18}_D = -160$ (C_6H_6). [f] Literature[11] value $[\alpha]^{18}_D = -214$ (CS_2). [g] In comparison with authentic samples prepared from (*S*)-(+)-mandelic acid (Aldrich), OAc, $[\alpha]^{25}_D = +91.37$ (9.2, EtOH); OH $[\alpha]^{25}_D = +87.94$ (6.4, EtOH). [h] To our knowledge, optically active **3** has never been prepared before. [i] Literature[12] value $[\alpha]^{25}_D = +43.75$ (5, C_6H_6). [j] Using 6 g of PPL instead of YL. [k] Literature[13] value $[\alpha]^{25}_D = -73.6$ (2.9, cyclohexane). [l] Literature[13] value $[\alpha]^{25}_D = -47.8$ (2.8, hexane). [m] Literature[14] value $[\alpha]^{25}_D = +14.0$. [n] Literature[15] value $[\alpha]^{25}_D = -50.7$ (2.05, H_2O).

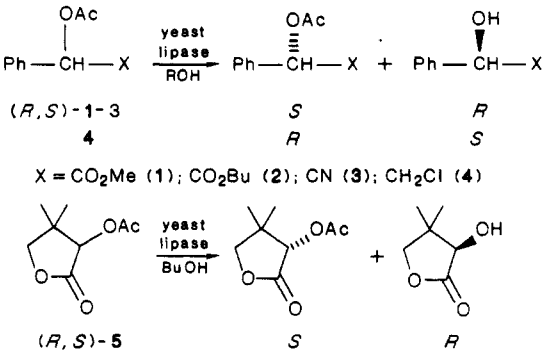
regioselective esterification of diols[6a] and, more recently, sugars.[6b]

Although lipase-catalyzed esterification is effective for primary alcohols,[5,6a] secondary alcohols require the use of "activated esters" to achieve reaction.[2,4] Unfortunately, this "activated-ester strategy" holds only for simple secondary alcohols. More sterically hindered secondary alcohols do not react with these activated esters, thus rendering resolution by lipase catalysis impractical.[2] In order to overcome this drawback, we report here a new approach to solve this problem through lipase-catalyzed transesterification.

Owing to the reversible nature of esterification and transesterification in enzyme-catalyzed kinetic resolution, it is often essential to design the substrates in such a way that the products formed would not take part in the reverse reaction. Successful utilization of trihaloalkyl[2,4] and enol[7] esters in the lipase-catalyzed transesterification is based on this principle. The leaving group in these cases is either an unreactive or an unstable alcohol, thus making the reaction irreversible. Following the same line of thought, we decided to subject the *O*-acetyl esters of sterically hindered secondary alcohols to lipase-catalyzed transesterification with primary alcohols as nucleophiles. The secondary alcohol thus liberated after the reaction, being more sterically hindered,[2,8] would be unreactive toward reversal.[9]

We have been able to apply this strategy successfully to the partial resolution of mandelic acid esters **1** and **2**, mandelonitrile **3**, 2-chloro-1-phenylethanol **4**, and pantolactone **5**. Substrates **1**–**3** and **5** were chosen because of

Scheme I



previous unsuccessful attempts to resolve them.[2] Substrate **4** was selected because it can serve as a useful starting material for preparation of chiral intermediates. Of the two lipases—porcine pancreatic lipase (PPL) and *Candida cylindracea* (yeast lipase (YL), Sigma)—tried, we found the latter to be more suitable for our studies. Except in cases of **3** and **4**, the conversions using the porcine lipase were too slow to be of practical utility (Scheme I). We found diisopropyl ether to be a better solvent for our studies compared to hexane, heptane, or chloroform. Substrate solubilities in hexane and heptane were poor while reactions in chloroform were too sluggish.

When methyl and butyl *O*-acetylmandelates (**1** and **2**, respectively) were subjected to lipase-catalyzed transesterification in diisopropyl ether using methanol and 1-butanol as nucleophiles, respectively, only the *R* isomers were selectively cleaved to give free mandelates with >90% optical purity. The conversion of **1** with methanol was extremely slow (25% in 23 days) compared to that of **2** (45% in 7 days) where 1-butanol was used as a nucleophile. This may be explained by competing deactivation of the enzyme by methanol. Attempts to resolve *O*-acetylmandelic acid by using butanol resulted in a mixture of *O*-acetyl and deacylated acids and their butyl esters. On the other hand, conversion of *O*-acetylmandelonitrile (**3**) was much faster (38% in 2 days and 40% in 4 days with yeast and porcine lipases, respectively). The enhanced rate may be attributed to the presence of the electron-withdrawing cyano group. While yeast lipase selectively catalyzed the cleavage of the *R* enantiomer of **3**, the opposite selectivity was observed with the porcine lipase. It should be noted that mandelonitrile and its acetate of opposite

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configuration have the same signs of rotation (Table I).

While yeast lipase catalyzed the selective cleavage of *R* isomers in most cases, including the case of pantolactone **5**, the selectivity observed in the case of 2-chloro-1-phenylethanol **4** was opposite albeit rather low (E = 1.8).[10] Changing the nucleophile from 1-butanol to 1-octanol had a marginal effect on the stereoselectivity (E = 1.9). However, porcine lipase, which also cleaved the *S* isomer, showed improved selectivity (E = 4.2).

In summary, the feasibility of kinetic resolution of secondary alcohols by using lipase in an organic solvent has been demonstrated. Further research is needed to reduce the reaction time and to improve the enantioselectivity. Work in this direction is in progress.

Experimental Section

GLC analyses were carried out by using an HP 101 capillary column (methyl silicone) (25 m × 0.2 μm thickness). Optical rotations were measured on a JASCO DIP-140 digital polarimeter. Porcine pancreatic and *Candida cylindracea* lipases were purchased from Sigma Chemical Company and were used "straight from the bottle". All organic solvents used in this work were of analytical grade, and prior to use they were dried overnight over 3A molecular sieves.

All racemic alcohols and (*S*)-(+)-mandelic acid used in this work were obtained commercially. Racemic alcohols were converted to their *O*-acetyl esters by following the standard procedure using acetic anhydride and triethylamine. Mandelic acid was first converted to its methyl or butyl ester before acetylation. All the compounds were purified by silica gel column chromatography using dichloromethane as the solvent and were characterized by their IR and ^{1}H NMR spectra. The ee values were determined on the basis of comparison of the observed rotations either with literature-reported values or with the value of a chemically synthesized optically pure authentic sample as detailed in the footnotes to Table I.

(*RS*)-Butyl *O*-Acetylmandelate[16] (2). A solution of butyl mandelate (6.24 g, 0.03 mol), acetic anhydride (15 mL), and triethylamine (15 mL) was stirred at room temperature for 24 h. Cold water (100 mL) was added, and stirring was continued for 1 h. Chloroform extraction (2 × 50 mL) followed by drying and removal of solvent yielded crude **2**, which was further purified on a silica gel column to give 6.82 g (91%) of pure **2**: IR (neat) ν (cm^{-1}) 1750; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.41 (m, 5 H, aromatic), 5.93 (s, 1 H, CHO), 4.14 (t, 2 H, J = 6.3 Hz, OCH_2), 2.20 (s, 3 H, $COCH_3$), 1.40 (m, 4 H, CH_2), 0.86 (t, 3 H, J = 6.1 Hz, CH_3). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.20; H, 7.20. Found: C, 67.09; H, 7.26.

(*S*)-(+)-Butyl *O*-acetylmandelate was also similarly prepared from *S*-(+)-butyl mandelate, which in turn was prepared from (*S*)-(+)-mandelic acid (Aldrich).

General Procedure for Yeast Lipase Catalyzed Transesterification. To a magnetically stirred solution of 15 mmol of substrate (**1**–**5**) in 45 mL of diisopropyl ether was added 60 mmol of ROH (nucleophile) and 3 g of yeast lipase. Periodically 1-μL aliquots of the liquid phase were withdrawn and analyzed by gas chromatography. After attaining a certain degree of conversion (see Table I), the reactions were stopped by filtration. Removal of the solvent on a rotary evaporator followed by column chromatography using dichloromethane as solvent afforded optically active alcohol and unreacted *O*-acetate (70–90% yield).

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Registry No. (*RS*)-**1**, 86561-27-5; (*S*)-**1**, 79416-45-8; (*R*)-**1** (OH product), 20698-91-3; (*RS*)-**2**, 119718-86-4; (*S*)-**2**, 85805-89-6; (*R*)-**2** (OH product), 119656-72-3; (*RS*)-**3**, 119718-87-5; (*S*)-**3**, 119718-88-6; (*R*)-**3**, 119718-89-7; (*S*)-**3** (OH product), 28549-12-4; (*R*)-**3** (OH product), 10020-96-9; (*RS*)-**4**, 79465-05-7; (*R*)-**4**, 33942-01-7; (*S*)-**4** (OH product), 70111-05-6; (*RS*)-**5**, 28227-35-2; (*S*)-**5**, 28387-34-0; (*R*)-**5** (OH product), 599-04-2; MeOH, 67-56-1; *n*-BuOH, 71-36-3; *n*-OctOH, 111-87-5; lipase, 9001-62-1; diisopropyl ether, 108-20-3; (±)-butyl mandelate, 119718-90-0; (*S*)-(+)-butyl mandelate, 74879-33-7; (*S*)-(+)-mandelic acid, 17199-29-0.

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Synthesis of Sulfur–Oxygen-Transposed Dihydro-1,4-oxathiin Derivative by Unusual Rearrangement of β-Hydroxy-1,3-oxathiolanes

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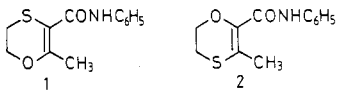
5,6-Dihydro-2-methyl-1,4-oxathiin-3-carboxanilide (**1**) or carboxin is a well-known systemic fungicide used for seed treatment.[1,2] The fungicidal activity of the isomer of **1** with O and S transposed was of interest, and we now describe the synthesis of this isomeric compound **2**. Our



synthesis of **2** required as a key intermediate β-hydroxy-1,3-oxathiolane derivative **5** as shown in Scheme I. Treatment of α-chloroacetoacetanilide[3] with potassium acetate in refluxing acetone gave α-acetoxyacetoacetanilide **3**.[6] Reaction of **3** with 2-mercaptoethanol produced β-acetoxy-1,3-oxathiolane **4**[6] as a mixture of diastereomers, which was hydrolyzed to the β-hydroxy-1,3-oxathiolanes **5**.[6] Acid-catalyzed dehydration of diastereomers **5** gave a high yield of the desired dihydro-1,4-oxathiin **2** (90%) and carboxin **1** (10%). Compound **2** was a colorless crystalline solid and identified by elemental analysis, IR and NMR spectroscopy, and mass spectrometry. Further proof for this structure was provided by independent synthesis involving the reaction of 3-bromo-2-oxo-*N*-

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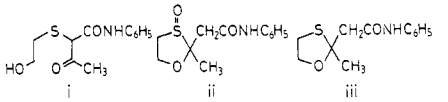

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