Clearly, mechanisms that involve oxidation by O_2 or peroxides can be ruled out for Rh(111)-p(2×2)-O.

Mechanisms involving OH insertion into the C=C bond of alkenes have also been proposed for some Rh complexes.[11] We have no evidence for the presence of adsorbed OH on the Rh(111)-p(2×2)-O surface during alkene reaction. Chemisorbed OH would produce gaseous water below 250 K,[15,16] yet no water is formed below 350 K during sytrene reaction (Figure 1). Furthermore, no OH is detected in X-ray photoelectron spectra.

The oxidation of styrene to acetophenone by oxygen adsorbed on Rh(111)-p(2×2)-O is an unprecedented reaction for both homogeneous and heterogeneous systems. This study demonstrates that the acidity of C–H bonds does not control selectivity or kinetics for this oxidation reaction. Future work will be directed toward investigation of the mechanism of this unusual process.

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Immobilized Cellulase (CBH I) as a Chiral Stationary Phase for Direct Resolution of Enantiomers

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The growing need for analytical as well as preparative methods for separation of enantiomers in the life sciences has led to an extensive search for such methods. To the best of our knowledge, no one has reported that the easily available cellulases could be used as chiral selectors.

About 5 × 10^{14} kg of cellulose is converted in nature each year.[1] The most important actors in this process are fungi and bacteria, which produce the enzymes, cellulases, which catalyze the cleavage of the glycosidic bonds in the cellulose, i.e., the degradation of cellulose in nature. Fungi are efficient producers of cellulases, and as much as 20 g of different cellulases, e.g., cellobiohydrolases and endoglucanases, per liter can be isolated from the culture filtrate of the fungus *Trichoderma reesei*.[2] Cellobiohydrolase I, CBH I, is the quantitatively dominating cellulase formed by the fungi *T. reesei*,[2] *Phanerochaete chrysosporium*,[3] and *Penicillium pinophilum*,[4] and there are good reasons to believe that it is widespread among fungi that can attack crystalline cellulose. CBH I is an acidic glycoprotein with a M_W in the range 60 000–70 000 and the isoelectrical point pH 3.5–3.6, and in the case of the *Trichoderma*, both protein[5] and gene[6] are well characterized. The CBH I enzyme, like all *Trichoderma* cellulases, has a common structural organization with a short terminal binding domain (36 amino acids) connected to the main part of the protein, the core, with a flexible arm.[2] The three-dimensional structure of the binding domain has been determined by 2-D NMR.[7] The interconnecting region is rich in serine, threonine, and proline residues and is highly glycosylated. The core is catalytically active and can easily be separated from the binding domain by limited proteolysis. The core can be crystallized, and in the case of CBH II, the three-dimensional structure has been solved.[8]

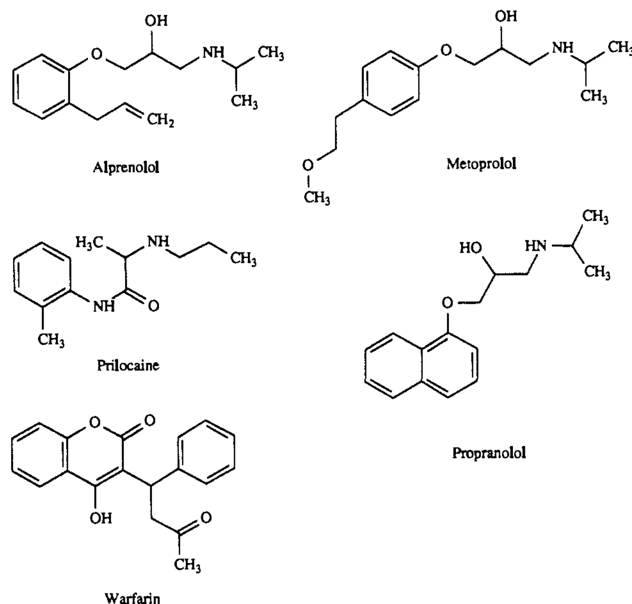

Figure 1. Structures of the solutes.

Table I. Chromatographic Resolution of Racemic Drugs on Cellulase–Silica CPS[a]

compd	pH 4.7 k'_1	pH 4.7 α	pH 4.7 R_s	pH 6.8[b] k'_1	pH 6.8[b] α	pH 6.8[b] R_s
alprenolol	0.16	5.1	4.8	2.8	8.3	4.9
metoprolol	0.10	1.7	0.7	0.81	2.6	3.9
prilocaine	<0.01			0.13	2.1	1.2
propranolol	0.46	2.6	4.6	6.2	4.7	4.3
warfarin[c]	3.9	1.3	1.2	0.75	1.0	

[a] Conditions are shown in Figure 2. [b] Eluent: sodium-phosphate buffer pH 6.8, $I = 0.01$, containing 0.5% 2-propanol. (+)-Norefedrin (pH 4.7) or buffer solution without 2-propanol (pH 6.8) was used as a marker for t_0, $k' = (t_R - t_0)/t_0$, $\alpha = k'_2/k'_1$, $N = 16(t_r/t_w)^2$, $R_s = (N^{1/2}k'_2(\alpha - 1))/(4(1 + k'_2)\alpha)$, where t_0 is the retention time of a nonretarded solute, k'_1 the capacity factor of the first eluted enantiomer, k'_2 the capacity factor of the last eluted enantiomer, α the selectivity factor, N the number of theoretical plates, R_s the resolution, and t_w the bandwidth at base line. [c] UV detection at 306 nm.

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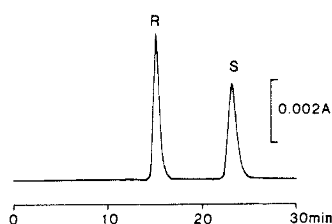

Figure 2. Chromatographic resolution of propranolol. Column 250 × 5 (i.d.) mm; eluent, sodium-acetate buffer pH 4.7, $I = 0.01$, containing 0.5% 2-propanol; (*RS*)-propranolol was dissolved in the eluent; 20 μL of the solution (6×10^{-5} mol/L) was injected; flow rate 0.3 mL/min, temperature 22 °C; UV detection at 254 nm. The elution order was established by injecting the pure enantiomers.

Hermansson has successfully used the plasma protein α_1-acid glycoprotein (AGP or orosomucoid) as a chiral stationary phase (CSP) for liquid chromatographic separations of enantiomers.[9] It has been suggested that the carbohydrate domain of AGP, about 45% of the molecular weight, is involved in the chiral recognition.[10] Proteins without carbohydrates, e.g., bovine serum albumin,[11,12] and carbohydrates without proteins, e.g., cellulose,[13,14] have also been utilized as CSPs.

In this study we report briefly the preparation and use of a CSP based on one cellulase, CBH I. Salts and pigments were removed from the crude culture filtrate of *T. reesei QM 9414* by gel chromatography. Ion-exchange chromatography was used for all remaining purification steps.[15] The homogeneity was tested by SDS-PAGE and IEF-PAGE.[15] The cellulase (CBH I) was covalently bonded to aldehyde silica (particle size 10 μm) according to the following method. The aldehyde silica, obtained by oxidation of diol silica by periodic acid, and sodium cyanoborohydride were added to a phosphate buffer solution (pH 7) of CBH I. The Schiff's base obtained was reduced by sodium cyanoborohydride to get a stable covalent bond between the cellulase and the silica derivative. The CSP was washed on a sintered-glass filter with the buffer solution. Finally, the material was packed into a steel column (250 × 5 mm i.d.) by using a descending slurry-packing technique.

Examples of direct resolution of racemic drugs (Figure 1) are given in Table I. Alprenolol, metoprolol, propanolol (Figure 2) (β-adrenergic blockers), prilocaine (local anesthetic), and warfarin (anticoagulant) were all well resolved with high stereoselectivity on this cellulase-based CSP using aqueous mobile phases. A surprisingly high stereoselectivity was obtained for alprenolol ($\alpha = 8.3$).

The cellulase-silica material seems to be a promising contribution to the pool of CSPs. The fact that the cellulases are available in huge quantities indicates their potential as chiral selectors in preparative as well as analytical applications.

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Registry No. Alprenolol, 13655-52-2; Metopralol, 37350-58-6; prilocaine, 721-50-6; propanolol, 525-66-6; warfarin, 81-81-2.

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(Thioallyl)iron Tricarbonyl Complex by the Reaction of Allene Episulfides with Diiron Nonacarbonyl

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Tautomerism of allene episulfide and cyclopropanethione via a thioallyl intermediate[1,2] is of great interest since these entities are the sulfur analogues of the well-studied allene oxide-cyclopropanone-oxyallyl[3] and methylenecyclopropane-trimethylide systems[4] (Scheme I). According to the kinetic[2f-i] and MCSCF calculation studies,[2e,g] thioallyl is a biradical with partial ionic character similar to trimethylenemethane[3c] rather than oxyallyl.[4c-e] Recently, we proposed the thioallyl cation to account for the acid-catalyzed isomerization of allene episulfide.[5] Meanwhile thioallyl biradical would be expected to be easily complexed with metals such as (trimethylenemethane)iron tricarbonyl.[6a,b] We now report the formation of the new type of (η^4-thioallyl)tricarbonyliron complex obtained from the reaction of allene episulfide with diiron nonacarbonyl.

Tetramethylallene episulfide (**1a**)[2a] was treated with 1.2 equiv of diiron nonacarbonyl in benzene at 60 °C for 10 min. After the solvent was removed at reduced pressure, the residue was separated by preparative HPLC, and subsequent recrystallization from hexane gave rise to two iron carbonyl derivatives, **2a** ($Me_4C_3SFe(CO)_3$, 16%) and **3** ($Me_4C_3Fe_2(CO)_6$, 11.5%), and 1-isopropenyl-2-methyl-1-propenyl) disulfide **4** (6.5%) (see Scheme II). In contrast, a reaction with aryl- and *tert*-butyl substituted allene episulfide **1b** provided single iron carbonyl complex **2b** ($^tBuPh_2C_3HSFe(CO)_3$, 29%) along with diaryl-*tert*-butylallene **5b** (25%) (Scheme III). The molecular formulas and group assignments shown in parentheses are based on mass, ^1H and ^{13}C NMR, and IR spectral analysis.[7] Compounds **2a** and **2b** were

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