In summary, we have clearly demonstrated that two kinds of reducing systems ($NaBH_4/Me_3SiCl$ or $NaBH_4/BF_3 \cdot OEt_2$) in combination with the new, chiral, polymer-supported *N*-sulfonamide **1** are effective in the reduction of prochiral ketones. The best *ee* values are obtained when the reduction is carried out in refluxing THF. The chiral polymer can be recovered easily and reused. The two reducing systems described should offer advantages over other reducing systems and thus find new applications.

Experimental Section

All reactions were carried out under nitrogen. THF was dried over sodium and freshly distilled before use. (*S*)-Diphenylprolinol was prepared according to a literature procedure.[12] Cross-linked polystyrene resin (2%, 200–400 mesh) was obtained from Merck Company. The purity of all the reagents were checked by NMR spectroscopy.

Preparation of ***1***: Polymeric sulfonyl chloride (0.214 g, 1 mmol) was added to a solution of (*S*)-diphenylprolinol (1.016 g, 4 mmol) in CH_2Cl_2 (30 mL) and Et_3N (0.104 g, 1 mmol) at room temperature. The resulting mixture was stirred for four days. The polymer was then filtered off and washed successively with methanol, water, methanol/water (1:1), and methanol. After drying in vacuo at 50 °C for 5 h, the desired polymer (0.451 g) was obtained in approximately 96% yield.

General procedure for the asymmetric reduction of prochiral ketones using ***1*** *and* $NaBH_4/Me_3SiCl$: Me_3SiCl (0.132 mg, 1.2 mmol) was added to a suspension of $NaBH_4$ (45 mg, 1.2 mmol) in THF (10 mL). The suspension was heated at reflux and stirred for 1 h. Polymer-supported catalyst **1** (98 mg, 0.25 mmol) was added, and the reaction mixture was heated at reflux for a further 0.5 h. A solution of acetophenone (120 mg, 1 mmol) in THF (10 mL) was added at a rate of 3 mL h^{-1} with a syringe pump. After the addition was complete, the mixture was treated with water and filtered. The polymer-supported catalyst was washed several times with EtOAc and water. The resulting aqueous solution was extracted with EtOAc (3 × 10 mL) and dried with $MgSO_4$. The solution was evaporated and purified by silica-gel chromatography to give the pure product (120 mg, 0.98 mmol, 98%). $[\alpha]_D^{20} = +52.6$ ($c = 2.23$, $CHCl_3$). The optical yield was determined to be 95.7% by using chiralcel OJ column chromatography.

General procedure for the asymmetric reduction of prochiral ketones using polymer-supported catalyst ***1*** *and* $NaBH_4/BF_3 \cdot OEt_2$: $BF_3 \cdot OEt_2$ (0.254 mg, 1.8 mmol) was added to a suspension of $NaBH_4$ (46 mg, 1.2 mmol) in THF (10 mL). The suspension was heated at reflux for 0.5 h. Polymer-supported catalyst **1** (59 mg, 0.15 mmol) was added, and the reaction mixture was heated at reflux for a further 0.5 h. A solution of acetophenone (120 mg, 1 mmol) in THF (10 mL) was then added at a rate of 3 mL h^{-1} with a syringe pump. After the addition was complete, the mixture was treated with water and filtered. The polymer-supported catalyst was washed several times with EtOAc and water. The resulting aqueous solution was extracted with EtOAc (3 × 10 mL) and dried with $MgSO_4$. The solution was evaporated and purified by silica-gel chromatography to give the pure product (120 mg, 0.98 mmol, 98%). $[\alpha]_D^{20} = +52.4$ ($c = 1.01$, $CHCl_3$). The optical yield was determined to be 95.1% by using chiralcel OJ column chromatography.

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An Asymmetric Enzyme-Catalyzed Retro-Claisen Reaction for the Desymmetrization of Cyclic β-Diketones**

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The desymmetrization of prochiral compounds is of increasing importance in asymmetric synthesis because, in principle, quantitative yields with absolute optical purity may be obtained.[1] Enzyme-catalyzed approaches to desymmetrization have, for the most part, involved the application of carbon–heteroatom hydrolases such as lipases and esterases.[2] Reactions involving C–C bond cleavage are much rarer, although the group of Taschner was successful in applying an enzyme-catalyzed Baeyer–Villiger reaction to the desymmetrization of a variety of prochiral ketones.[3] The desymmetrization of prochiral β-diketones by a retro-Claisen reaction has been reported using chiral bases, although diastereomeric and enantiomeric excesses were generally

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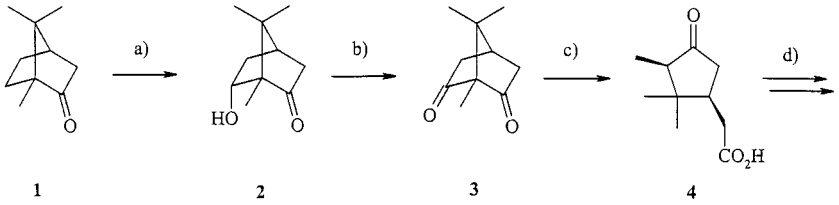
poor and stoichiometric amounts of reagent were required.[4] The class of enzymes required for hydrolysis of β-diketones, β-diketone hydrolases, (EC 3.7.1.X)[5] have rarely been studied and only three have been purified to homogeneity. Of these, fumarylacetoacetate hydrolase from beef liver[6] and acetopyruvate hydrolase from *Pseudomonas putida*[7] have limited substrate ranges, in that they have been shown only to accept 3,5-diketo acids as substrates. No chiral transformations by these enzymes have been reported. We now report an enzymatic process for the desymmetrization of bicyclic prochiral β-diketones by employing a novel carbon–carbon bond hydrolase which we have named 6-oxocamphor hydrolase (6-OCH).

The starting point for this work involved the microbial degradation of (1*R*)-(+)-camphor (**1**) by *Corynebacterium* T1 (now deposited as *Rhodococcus* sp. NCIMB 9784), which was first described by the research group of Gunsalus (Scheme 1).[8] One of the intermediates in the pathway is the symmetrical diketone **3** which undergoes cleavage in a retro-Claisen reaction to yield the keto acid **4**. The acid **4** was reported by the research group of Gunsalus to have a negative



Scheme 1. Metabolism of (1*R*)-(+)-camphor (**1**) by *Rhodococcus* sp. NCIMB 9784: a) cytochrome P450camr, b) alcohol dehydrogenase, c) 6-oxocamphor hydrolase, d) further metabolism.

optical rotation, and thus the degradation pathway can be envisaged to proceed from optically pure camphor through an achiral symmetrical intermediate **3** to another optically active metabolite **4** through a desymmetrization step. We decided to isolate the enzyme activity responsible for the conversion of **3** into **4** and define its substrate specificity with respect to other prochiral β-diketones.

The enzyme 6-oxocamphor hydrolase was isolated from *Rhodococcus* sp. NCIMB 9784 cultures grown on (1*R*)-(+)-camphor as the sole carbon source, which yielded approximately 40 units L^{-1} of pure enzyme. The enzyme has now been purified to homogeneity, characterized biochemically, and the gene encoding the relevant protein cloned and sequenced. These data will be published elsewhere.

First the stereoselectivity of enzymatic hydrolysis of the natural substrate diketone **3** needed to be established. Diketone **3** was obtained by pyridinium chlorochromate oxidation[9] of 6-*endo*-hydroxycamphor (**2**) obtained from extractions of the fermentation mother liquor. The pure enzyme was used to hydrolyze the symmetrical diketone **3** to the keto acid **4**, which was recrystallized from chloroform and its crystal structure determined by X-ray analysis (Figure 1). Refinement of the flack parameter suggested that the C2 carbon center was of the *R* configuration and the C4 center of the *S* configuration, although the standard deviation was rather high.[10] However, statistical analysis of the 200 most

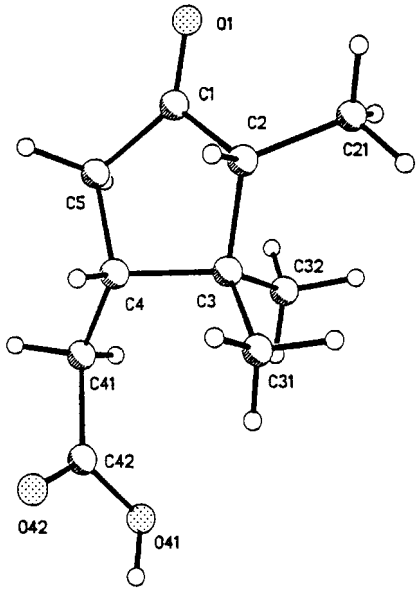
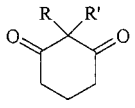


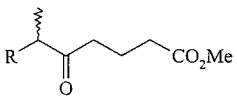
Figure 1. Crystal structure of (2*R*,4*S*)-campholinic acid (**4**) derived from enzymatic hydrolysis of 6-oxocamphor (**3**) by 6-oxocamphor hydrolase.

enantioselective reflections supported this assignment of absolute configuration. The enantiomeric excess of **4** was determined to be greater than 95% by chiral-shift NMR analysis of the methyl ester. Use of 10 mole% of [Eu(hfc)$_3$] allowed successful discrimination in the signals of one of the geminal methyl groups at C3 of the racemate. NMR spectroscopy also indicated the presence of the (2*S*,4*S*) diastereomer of **4** in a ratio of 1:6 to the predominant (2*R*,4*S*) product **4**. It should be noted that chemical hydrolysis of **3** with aqueous hydrochloric acid yielded the same mixture of *cis* and *trans* isomers as a racemate. Thus, whilst the C4 configuration is clearly determined by enzymatic specificity, it is likely that the C2 configuration is under thermodynamic control.

The substrate range of the enzyme was explored with a variety of β-diketones, including **5**–**9**; thin layer chromatography was applied to detect the evolution of product. None of



5 R = H, R' = Me
6 R = R' = Me
7 R = Me, R' = Et
8 R = Me, R' = Pr
9 R = Me, R' = Bu



10 R = Pr
11 R = Bu

the acyclic diketones (pentane-2,5-dione and 3,3-dimethylpentane-2,5-dione) nor the simple monocyclic diketones (cyclohexane-1,3-dione, 5,5-dimethylcyclohexane-1,3-dione, 2-acetylcyclopentanone, 2-acetylcyclohexanone, and 2-methylcyclohexane-1,3-dione (**5**)) that were tested were substrates. On the other hand, other α,α-disubstituted cyclohexane diones, such as 2-methyl-2-ethylcyclohexane-1,3-dione (**7**),

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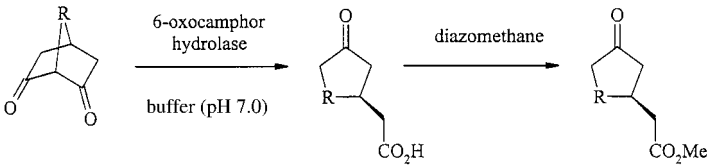
2-methyl-2-propylcyclohexane-1,3-dione (**8**), and 2-methyl-2-*n*-butylcyclohexane-1,3-dione (**9**), resulted in hydrolysis by the enzyme.

Preparative scale transformations (with amounts of 0.5 mmol) of diones **8** and **9** led to keto acid products **10** and **11**, which were racemic. Thus, it may be that stereodifferentiation by the enzyme is poor in these cases, or that the inherent enantioselectivity of the process is masked by a subsequent nonenantioselective and perhaps nonenzymatic step.

The observed requirement for α,α-disubstituted β-diketones may be due to steric effects important for enzyme binding or activation due to a requirement for nonenolizable β-diketones. To probe these ideas further, the demethyl analogues of **3**, the diones **12** and **15**[11] were prepared. Compounds such as **12** are well known to be nonenolizable due to ring strain (Bredt's rule). The synthesis of **12** was achieved by tetrapropylammonium perruthenate (TPAP) oxidation[12] of 6-*endo*-hydroxynorbornanone, which was itself synthesized using the method of Werstiuk and Kadai.[13]

When subjected to the same reaction conditions as employed for the enzymatic hydrolysis of **3**, diketones **12** and **15** were transformed into keto acids **13** and **16** (Scheme 2). The



12 R = CH_2 **13** R = CH_2 **14** R = CH_2
15 R = CH_2CH_2 **16** R = CH_2CH_2 **17** R = CH_2CH_2

Scheme 2. Hydrolysis of bicyclic ketones **12** and **15** by 6-oxocamphor hydrolase from *Rhodococcus* sp. NCIMB 9784.

methyl ester **14** was prepared (by treatment with diazomethane) and analysis of the product with chiral GC indicated an *ee* value of 84%. The absolute configuration of **14** was established as *S* by comparison of its sign of optical rotation with the literature value.[14] It should be noted that **12** was hydrolyzed completely to **13** in buffer over a period of two hours, and thus the measured optical purity of **14** may have been lowered by background chemical hydrolysis of the diketone substrate.

The larger ethylene bridge in **15** made this compound more stable and, thus, background hydrolysis was negligible. After complete hydrolysis to keto acid **16**, the methyl ester **17** of the product was prepared (overall yield for two steps: 91%) and was assigned the *S* configuration by comparison of the sign of the optical rotation obtained with the literature value.[15] The *ee* value was determined by comparative ^{13}C NMR spectroscopy of the acetals formed from the racemate and the enzymatic product with (2*R*,3*S*)-butane-2,3-diol, and it was found to be 94%.

We have described the application of a novel enzymatic activity for the desymmetrization of three prochiral bicyclic β-diketones **3**, **12**, and **15**. The initial results with unsubstituted bicyclic diketones **12** and **15** are highly encouraging; good stereoselectivities and access to useful chiral intermediates are obtained. For example, chiral cyclopentanones of type **13** are potential intermediates in the synthesis of natural products such as the jasmonic acids.[16] Current studies are directed toward extending the substrate range of the enzyme and incorporating the chiral cycloalkanone products into asymmetric synthesis.

Experimental Section

Spectral data for norbornane-2,6-dione (**12**): IR (Nujol): $\tilde{\nu}_{max} = 1751\ cm^{-1}$, $1774\ cm^{-1}$; ^1H NMR (250 MHz; $CDCl_3$): $\delta = 2.08$ (m, 1H), 2.17 (m, 1H), 2.24 (m, 2H), 2.39 (m, 1H), 2.48 (m, 1H), 3.20 (m, 2H); ^{13}C NMR (63 MHz; $CDCl_3$): $\delta = 32.9$ (CH), 38.1 (CH_2), 43.3 (CH_2), 69.0 (CH), 206.2 (C=O); HR-MS: *m*/*z* calcd: 124.05243; found: 124.05242.

Purification of 6-oxocamphor hydrolase: The enzyme used for biotransformations (6-oxocamphor hydrolase, 6-OCH) was purified from a 10-L fermentation of *Rhodococcus* sp. NCIMB 9784 grown on (1*R*)-(+)-camphor as the sole carbon source. Wet cell paste (40 g) from the fermentation was disrupted using a Type KDL Dynomill, and, after removal of cell debris by centrifugation, a 40–80% ammonium sulfate cut of the cell supernatant was obtained. Sequential chromatography of the sample over Phenyl Sepharose, Fast Flow Q Sepharose, and Phenyl Superose on fast phase liquid chromatography (FPLC) resulted in 5% yield of pure 6-OCH that was homogeneous as judged by sodium dodecylsulfate polyacrylamide gel electrophoresis (SDS-PAGE). During chromatography, fractions containing 6-OCH were identified by spectrophotometric assay based on the decrease in absorbance at 294 nm of the native substrate, 6-oxocamphor (**3**). Using this assay, the specific activity of the pure protein was determined to be 357 U per mg of protein (where 1 U is 1 μmol of substrate converted per minute).

Preparative scale enzymatic hydrolysis of diketones **3**, **12**, and **15**: 6-oxocamphor hydrolase (100 U) was added to a stirred solution of diketone **3**, **12**, or **15** (0.5 mmol) in 100 mM potassium phosphate buffer (pH 7.0, 50 mL) at room temperature. Thin layer chromatography analysis suggested completion of the reaction after 10 min (for **3**), 2 h (for **12**), and 24 h (for **15**). The mixture was acidified to pH 3.0 with dilute HCl and then extracted into ethyl acetate. After drying over $MgSO_4$, the solvent was removed and the crude carboxylic acid converted into its methyl ester using diazomethane. Isolated yields of the methyl ester of **4** and of **14** and **17** were 86%, 25%, and 91% respectively. Spectroscopic data for **14**[13] and **17**[15] were in agreement with the literature.

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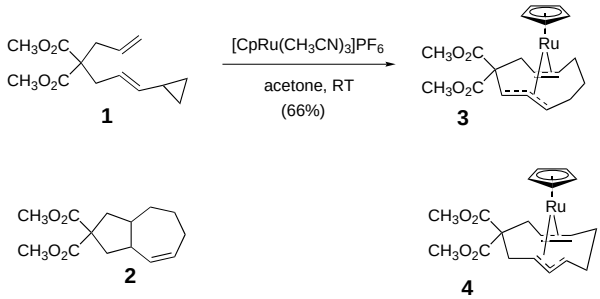
Synthesis of the First (1-3:6,7-η-Cyclodecadienyl)ruthenium Complex by the Intramolecular Reaction of an Alkene and a Vinylcyclopropane**

Barry M. Trost* and F. Dean Toste

The development of cyclization methods constitutes a continuing challenge because of the ubiquitous occurrence of cyclic structures, especially among bioactive targets. Improving synthetic efficiency by expanding the cycloaddition type protocols, especially to rings that cannot be formed by Diels–Alder type methods, and facilitating formation of unusual ring sizes, notable medium and large rings, then represent two significant objectives. Transition metal catalysis plays a major role towards meeting these objectives. In developing cyclization strategies[1] centered around $[CpRu(CH_3CN)_3]PF_6$[2] as a catalyst, we have discovered an unprecedented reaction that led to the formation of a novel organometallic complex in which a medium-sized carbocycle was effectively created—a result that stands in sharp contrast to the Rh chemistry.

We have recently reported that $[CpRu(CH_3CN)_3]PF_6$[2] catalyzes the intramolecular [5+2] cycloaddition of alkynes and vinylcyclopropanes.[3] To establish the scope and limitations as well as compare the Ru catalyst to the highly successful Rh system developed by the Wender group,[4] we investigated the extension of the ruthenium-catalyzed reaction to alkenes and vinylcyclopropanes. Reaction of diene **1** with 10% $[CpRu(CH_3CN)_3]PF_6$ in acetone did not produce any of the desired [5+2] adduct **2**, but produced a small amount of an unknown ruthenium complex along with recovered diene. By carrying out the reaction of **1** with 0.5 equivalents of $[CpRu(CH_3CN)_3]PF_6$, we were able to isolate an air-stable ruthenium complex in 66% yield [Eq. (1)].[5]



(1)

Analysis of the ^1H NMR spectrum of the complex indicated that the product possessed a cyclopentadienyl moiety and a second ligand derived from **1**. Notably, the spectrum showed that the methoxycarbonyl groups were no longer equivalent and that the ligand derived from **1** had one proton less than the starting diene. Based on the ^1H and ^{13}C NMR data and the structure of the substrate **1**, we tentatively assigned the structure of the unknown complex as the (1-3:7,8-η-cyclodecadienyl)ruthenium complex **4**. However, since we could not find previous examples of η^5-cyclodecadienyl[6] complexes, it was difficult to confirm the structure. Gratifyingly, we were able to grow crystals of the complex suitable for X-ray structure analysis.[7] X-ray analysis concretely established the structure as the (1-3:6,7-η-cyclodecadienyl)ruthenium complex **3** (Figure 1).

Complex **3** has a distorted octahedral structure with the two η^2-olefin carbon atoms and the terminal carbon atoms of the η^3-allyl moiety occupying one plane. The η^2-olefin is situated *endo* and the cyclopentadienyl ligand *exo* with respect to the η^3-allyl group. Similar geometry is found in (arene)ruthenium-(1-3:5,6-η-cyclooctadienyl) complexes.[6a,e] Despite the presence of a quaternary carbon atom adjacent to C1,[8] the η^3-allyl moiety and η^2-olefin in complex **3** are essentially symmetrically bound to the ruthenium center. This symmetry is also similar to that of the neutral complex [Ru(1-3:6,7-η-cod)(η^5-pyrrole)],[6a] but differs from that of the cationic complex $[Ru(1\text{-}3\text{:}5,6\text{-}\eta\text{-cod})(cot)]^+$ which shows a difference of 0.25 Å in the ruthenium–allyl terminal carbon bond lengths (cod = 1,5-cyclooctadienyl; cot = cyclooctatriene).[6b] The sp^3-carbon atoms adjacent to the π-allyl group are placed *exo* to the allyl plane, with the quaternary carbon atom C(10) having a greater displacement. The deviation from planarity is only slightly less than observed in the [Ru(1-3:5,6-η-cod)] complexes. However, the olefin in complex **3** is essentially planar

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