free H^- is produced at low conversions of D^-, nor does $HCr(CO)_3^-$ undergo H/D exchange with the ND_3 which is present in the flow reactor. Thus, we conclude that ring attachment must occur at some point in the course of an ion–molecule collision. Moreover, from the fact that the observed $HCr(CO)_3^-/DCr(CO)_3^-$ product ratio is near the statistical value of 6:1, we can conclude that complete H/D scrambling occurs within the collision complex prior to expulsion of benzene. Our view of the mechanism is outlined in Scheme I. Initial ring addition by D^- produces a vibrationally and rotationally excited cyclohexadienyl anion complex which can undergo rapid hydrogen shifts in either a thermally allowed sigmatropic manner[13] or with mediation by the $Cr(CO)_3$ fragment. This latter possibility seems unlikely, however, since we have found that $HCr(CO)_3^-$ does *not* undergo H/D exchange in the presence of C_6D_6, although an adduct readily forms by termolecular association. This implies that a barrier exists for hydride migration from chromium to the arene ligand and, by inference, that once the metal–hydrogen bond is formed expulsion of benzene follows. Thus, H/D scrambling proceeds entirely within the benzene moiety prior to a slower chromium–hydride bond formation step which is accompanied by loss of neutral benzene.

Preliminary studies of the reactions of $HCr(CO)_3^-$ with a variety of small molecules have exposed a striking and enhanced reactivity relative to other transition-metal negative ions which have been examined previously.[14-17] For example, $HCr(CO)_3^-$ undergoes facile oxidative insertion/reductive elimination reactions with a variety of n-donor Brønsted acids (eq 2), as well as H/D exchange

$$HCr(CO)_3^- + HX \xrightarrow[HX = NH_3,\ H_2O,\ ROH]{} XCr(CO)_3^- + H_2 \quad (2)$$

in the presence of D_2.[16,17] While **2** does not appear to react with alkanes or cyclopropane, it does react readily with alkenes, cycloalkenes, and alkynes in a manner reminiscient of atomic metal cations.[18-21] For instance, propylene and many other olefins possessing allylic CH bonds give insertion/elimination products which we formulate as 16-electron π-allyl complexes (eq 3).

$$CH_2{=}CH{-}CH_3 + \underset{\mathbf{2}}{HCr(CO)_3^-} \longrightarrow HC\begin{matrix}CH_2\\ \diagup\\ \diagdown\\ CH_2\end{matrix}{-}Cr(CO)_3^- + H_2 \quad (3)$$

Cyclic and acylic conjugated dienes react exclusively by simple adduct formation; in this case coordinatively saturated (18-electron) complexes are initially produced, so elimination of H_2 is apparently disfavored. Interestingly, acetylene also reacts with **2** by insertion/H_2 elimination, whereas ethylene produces only an adduct. A complete accounting of the rich chemistry of $HCr(CO)_3^-$ will be reported in a future publication.

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Enantioselective Lactonization of Sodium 4-Hydroxypimelate under Abiological Conditions[1]

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Enantiotopic group differentiation by biochemical methods has been shown to be a prevailing method of choice for asymmetric syntheses.[2] On the other hand, only a few abiological methods, useful for providing enantiomerically rich compounds, exist to date,[3] although considerable attention[4] has been paid since Marckwald[5] reported decarboxylation of geminal dicarboxylic acid with brucine in low enantioselectivity. Here we describe a simple and preparative method for enantiotopic group differentiation between two carboxylate groups by protonation.

Sodium 4-hydroxypimelate (**1**) has been chosen as a starting dicarboxylate because monoprotonation allows rapid cyclization in the reaction medium to afford a stable γ-lactone. Careful neutralization[6] of the ethanolic solution of **1** with (1*S*)-(+)-10-camphorsulfonic acid (*S*-CSA) monohydrate as a chiral proton source gave rise to the expected lactone **2** in nearly quantitative yield.[7] Results are summarized in Table I. The degree of

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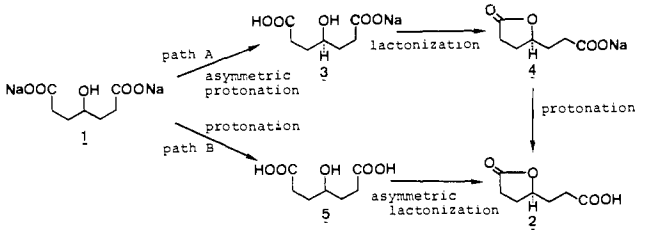

asymmetric induction strongly depends upon the concentration of the substrate **1**. As the concentration of the substrate was lowered a higher degree of enantiomeric excess (ee) was obtained. Using a 2–5 mmol solution is advisable because enantiomerically pure (−)-lactone **2** can be obtained from one recrystallization. Absolute stereochemistry of (−)-butyrolactone **2** was proved to be *S* by an X-ray crystallographic analysis of the (*S*)-(−)-α-methylbenzylamine salt as shown in Figure 1.

The successful asymmetric lactonization of hydroxy dicarboxylate **1** might be attributed to the formation of a chiral species **3** (path A) through the enantioselective monoprotonation of the carboxylate with the hydronium ion captured by the sulfonate group in *S*-CSA as shown in Figure 1. Lactonization of **3** under the reaction conditions affords carboxylate **4** which is then converted into lactonic acid **2**. Treatment of the ethanolic solution of disodium salt **1** with 1 equiv of *S*-CSA followed by the addition of another equivalent of 0.5% hydrogen chloride in ethanol afforded (*S*)-**2** with 94% ee in quantitative yield.[8] On the other hand, the reverse process where **1** was treated with 1 equiv of 0.5% hydrogen chloride in ethanol and then with another equivalent of *S*-CSA yielded racemic butyrolactone **2**. Although these results cannot provide conclusive evidence, we prefer path *A* over the alternative path B which involves achiral diprotonated species **5**.

Asymmetric lactonization is remarkably affected by the concentration of water in the medium. As seen in Table II, less than 0.5% of water did not have a significant effect on the percent ee of the product, while 15% of water completely eliminates enantioselectivity. These results suggest that the acidic proton of the sulfonic acid moiety in *S*-CSA is fixed by the intramolecular hydrogen bonding with the carbonyl group even in the ethanolic solution, when the water content in the medium is small.

The optically active lactonic acid **2** provides a versatile chiral building block for the synthesis of biologically active natural products such as pheromones[9] and antifungal metabolities.[10] It is worth noting that both (*S*)-(−)-alcohol **6**, $[\alpha]^{21}_D$ −11.4° (*c* 0.36, EtOH), and its enantiomer, $[\alpha]^{21}_D$ + 11.5° (*c* 0.33, EtOH), were

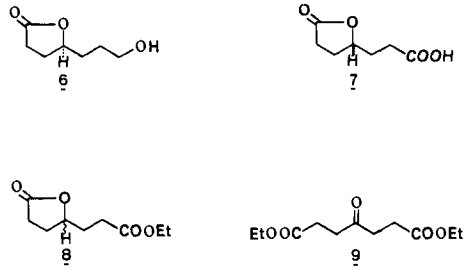

Table I. Asymmetric Lactonization[a] of Dicarboxylate **1**

dicarboxylate **1** concentration, Mmol	(*S*)-(−)-lactonic acid **2**	
	$[\alpha]^{25}_D$ (H_2O)[b]	% ee[c]
1.8	−20.9°	79
3.5	−22.3°	84
3.5	−24.9°	94[d]
4.5	−21.8°	80
6.5	−18.6°	70
7.2	−15.4°	58
9.1	−12.3°	46
10.0	−9.7°	37
10.6	−3.6°	14
11.8	−0.1°	0
12.7	±0	0

[a] All reactions were run with a 100-mL scale at −78 °C and yields are more than 95%. [b] *c* 0.66. [c] Calculated on the basis of the maximum rotation of the pure *S*-(−) isomer, $[\alpha]^{25}_D$(max) −26.5° (H_2O), obtained by the optical resolution through the (*S*)-(−)-α-methylbenzylamine salt. [d] After addition of 1 equiv of *S*-CSA, the reaction mixture was stirred for 30 min; then another equivalent of 0.5% hydrogen chloride in ethanol was added.

Table II. Effect of Water in Ethanol on the % ee of **2**

water, %	$[\alpha]^{21}_D$(H_2O)	% ee	yield, %
0	−22.4°	84.5	47[a]
0.5	−22.4°	84.5	94
2.0	−14.6°	55.1	92
5.0	−12.1°	45.0	94
10.0	−10.3°	38.9	95
15.0	0	0	94[b]

[a] Lactonic ester **8**, $[\alpha]^{21}_D$ −4.0° (c 0.21 MeOH), was obtained in 37% yield. [b] Frozen under the reaction conditions at −78 °C.

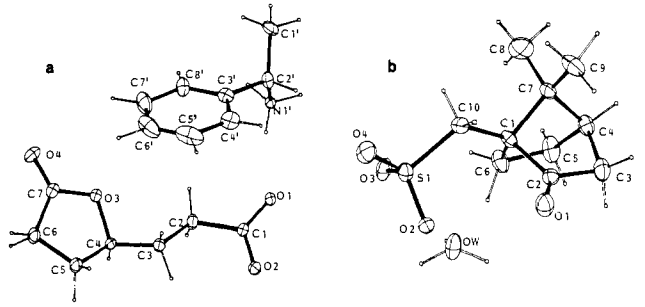

Figure 1. Perspective views of (a) (*S*)-(−)-α-methylbenzylamine salt of (*S*)-(−)-**2** and (b) (1*S*)-(+)-10-camphorsulfonic acid monohydrate showing the atom numbering schemes.

obtained from the single (*S*)-lactonic acid **2** by the reduction with borane–dimethyl sulfide complex and with $LiAlH_4$, respectively. The Jones oxidation of the latter furnished (*R*)-(+)-lactonic acid **7** with a slight loss of optical activity ($[\alpha]^{21}_D$ +21.6°).

Another interesting aspect of this enantioselective protonation is revealed by considering the structure of the starting material for dicarboxylate **1**. The most easily accessible starting compound is the racemic form of lactonic acid **2** or racemic ester **8**, because basic hydrolysis of them yields **1** without difficulty. Ester **8** was obtained by the reduction of the corresponding ketone **9**[11] with $NaBH_4$ in ethanol. Acid hydrolysis of racemic **8** afforded the racemic lactonic acid of **2** in good yield. Thus, the overall process from the racemic form of **2** to (*S*)-(−)-**2** described herein constitutes enantioconvergent transformation of a racemic mixture into a single enantiomer. Generally, reported methods[12-15] of

(8) The results that the *S*-CSA followed by HCl gives a higher ee than *S*-CSA alone can be explained as follows: As the lactonization step is slower than monoprotonation on carboxylate, some amount of achiral diprotonated species **5** will be produced after the half-neutralized point when addition of proton source is relatively fast. In the former case, time lag of 30 min between addition of *S*-CSA and that of HCl may eliminate the possibility of formation of **5**.

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enantiomeric enrichment involve the destruction of the sp^3-hybridized asymmetric carbon atom, thereby creating the sp^2-hybridized carbon followed by regeneration of the original sp^3-hybridized carbon atom under the asymmetric environment. For instance, proton abstraction from the asymmetric carbon atom followed by enantioselective protonation has been reported for α-amino acid derivatives[12] and α-substituted carbonyl compounds.[13] Enamine formation followed by hydrolysis with chiral acids has been used for the enantiomeric enrichment of α-substituted carbonyl compounds.[14,15] All of those reported methods involve the enantioface differentiation by protonation. The present method provides the first example of the enantiomeric enrichment in which the sp^3-hybridized carbon is not destroyed throughout the overall process.

The method for the asymmetric lactonization described here can be applied to other hydroxy dicarboxylates and dihydroxy monocarboxylates possessing σ-symmetry. Further studies along these lines are currently under way.

Supplementary Material Available: Tables of crystal data, bond lengths, bond angles, atomic coordinates, and thermal parameters for the (*S*)-(−)-α-methylbenzylamine salt of (*S*)-(−)-**2** and (1*S*)-(+)-10-camphorsulfonic acid monohydrate (5 pages). Ordering information is given on any current masthead page.

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Resonance Raman Scattering from Horseradish Peroxidase Compound I

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Horseradish peroxidase (HRP) catalyzes the oxidation of various substrates in the presence of hydrogen peroxide by forming sequential intermediates, compounds I and II (HRP-I and HRP-II).[1] The active site of resting HRP contains ferric protoheme, which is ligated in one axial position by histidine nitrogen. HRP-I is formed by the reaction of hydrogen peroxide with the resting enzyme and is two oxidation equivalents above the native ferric state. While one oxidation equivalent is thought to be located on the metal center as a low-spin (S = 1) oxyferryl structure ($Fe^{IV}O$),[2] the other equivalent most likely resides on the porphyrin ring as a π cation radical.[3] The second intermediate, HRP-II, is a single oxidation equivalent above the ferric state and retains the low-spin oxyferryl center.

Though resonance Raman (RR) techniques have been applied to the ferrous and ferric enzyme[4] and to HRP-II,[5-10] Raman data for HRP-I have been difficult to obtain owing to the reactivity and photolability of the first intermediate.[11] Cryogenic techniques may be insufficient to stabilize HRP-I to laser irradiation and past attempts to obtain RR measurements of HRP-I[9] resulted in photoreduction to a mixture of HRP-II, ferric, and ferrous species.[12] Thus a reliable RR spectrum of HRP-I has not yet

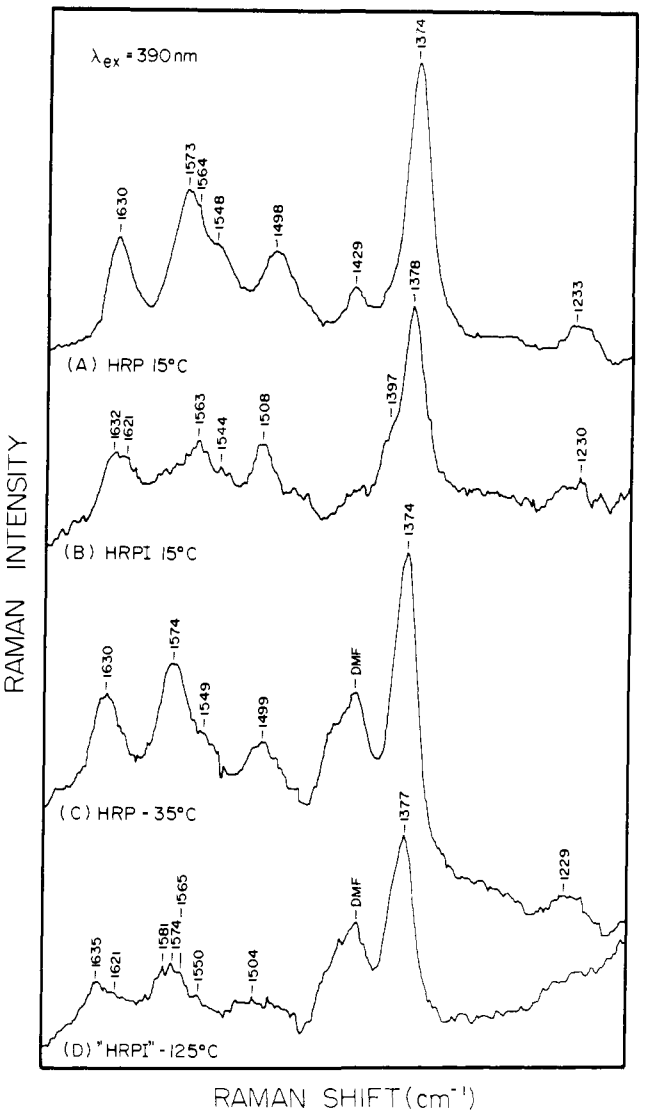

Figure 1. RR spectra of native HRP and HRPI, pH 7.2, excited at 390 nm (10-ns pulses, 10 Hz): (A) native HRP, 0.1 mM, 50 mM phosphate, 15 °C, 90° scattering, 10–15 mW, 25-min acquisition time; (B) HRPI, 0.05 mM, 50 mM phosphate, 15 °C, 90° scattering, 10–15 mW, sum of eight 5-min runs; (C) native HRP, 0.6 mM, 66% DMF, 34% 50 mM phosphate, −35 °C, spinning EPR tube, backscattering, 20 mW, 12 min; (D) HRPI, 0.6 mM, generated at −40 °C in 66% DMF, 34% 50 mM phosphate by the reaction of resting HRP with a slight excess of H_2O_2; spectra were recorded at −125 °C by backscattering from a spinning EPR tube with vertical translation of the sample in the laser beam; 15 mW, 6 min.

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