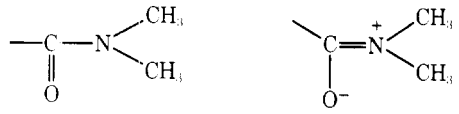
bution of the canonical structure B. However, in the ^1H NMR spectrum of **6**, only a singlet due to the *N*-methyl protons was observed, which indicates that the tetrathiafulvalene component of **6** has strong electron-donating properties.



A B

The ^1H NMR spectrum of **7** also showed a singlet due to *N*-methyl protons. The olefin protons of **7** appeared as two singlets at δ 6.34 and 6.61, which can be assigned to the olefin protons on the unsubstituted ring and the dimethylcarbamide-substituted ring, respectively, based on the correspondence of the chemical shifts noted above with those of TTF (δ 6.33) and **6** (δ 6.63). This is the first example of the synthesis of monosubstituted TTF from a tetrasubstituted one.[8]

The decarboxylation of acid derivatives, which are facilely derived from **2**,[5,6] gave parent TTF in better yields. Tetraacid **3** was heated with copper chromite in HMPA at 150 °C for 3 h, and the reaction mixture was treated with water. The benzene extracts, upon evaporation, gave a 57% yield of tetrathiafulvalene. This synthetic method is more available than the other method because of easy manipulation and no byproducts. Without copper chromite, **3** was recovered quantitatively. Diacid **4** also afforded parent TTF in 69% yield under similar reaction conditions. Copper(II) sulfate or copper powder in quinoline was also useful for decarboxylation of acid derivatives.

Experimental Section

Melting points were determined using a Büchi melting point apparatus in sealed tubes and are uncorrected. The infrared spectra were determined on a Hitachi grating IR spectrophotometer, Model 215, the mass spectra were determined on a Hitachi RMU-6C or RMS-4 mass spectrometer, and the ^1H NMR spectra were recorded on a Varian HA-100 spectrometer. Elemental analyses were carried out at the Elemental Analytical Center of Kyoto University.

$\Delta^{2,2'}$-Bis[4,5-bis(carbomethoxy)-1,3-dithiolidene] (**2**), $\Delta^{2,2'}$-bis(4,5-dicarboxy-1,3-dithiolidene) (**3**), and $\Delta^{2,2'}$-bis[4(5)-carboxy-1,3-dithiolidene] (**4**) were prepared as described in our previous paper.[6d]

Reaction of 2 with Lithium Bromide. A mixture of 436 mg of **2**, 3.0 g of lithium bromide monohydrate, and 10 mL of hexamethylphosphoramide was heated gradually to 80 °C. Gas evolution and a considerable lightening of color occurred. When gas evolution ceased, the mixture was cooled and treated with deaerated water to give a red solid. After filtration, the solid was subjected to column chromatography on silica. The first yellow fraction upon evaporation gave 22 mg of **1**: yield 11%; mp 117–119 °C (lit.[3] 119–119.5 °C); ^1H NMR ($CDCl_3$) δ 6.33 (s, =CH); MS *m/e* 204 (M^+).

The second red fraction gave bis(carbomethoxy)tetrathiafulvalene (**5**, 166 mg): yield 53%; mp 226–228 °C dec[9] (lit.[3] 244–245 °C); ^1H NMR ($CDCl_3$) δ 3.85 (s, 6 H, OCH_3) and 7.30 (s, 2 H, =CH); IR (KBr) 1708 (C=O), 1548 (C=C), 1440 and 1255 (C–O) cm^{-1}; MS *m/e* 320 (M^+). Anal. Calcd for $C_{10}H_8O_4S_4$: C, 37.48; H, 2.52; O, 19.97. Found: C, 37.45; H, 2.64; O, 20.09.

After gas evolution ceased, the temperature was raised to 150–160 °C for 10 min. The cooled mixture was diluted with water and extracted with benzene. The orange organic extract was washed, dried over Na_2SO_4, and after concentration subjected to chromatography on silica, eluting with methylene chloride. The first yellow fraction gave 27 mg of orange-yellow crystals of **1**, yield 13%.

The second yellow fraction gave 51 mg of tetrathiafulvalene-*N*,*N*-dimethylcarbamide (**7**): yield 18.5%; mp 162.5–163.5 °C; IR (KBr) 3050 (C=CH), 1603 (C=O), 1580, 1540, and 1395 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.09 (s, 6 H, $N-CH_3$), 6.34 (s, 2 H, HC=CH), and 6.61 (s, 1 H, HC=CC=O); MS *m/e* 275 (M^+). Anal. Calcd for $C_9H_9NOS_4$: C, 39.25; H, 3.29; N, 5.09; S, 46.57. Found: C, 39.46; H, 3.02; N, 5.06; S, 46.44.

The third orange-red fraction afforded 77 mg of tetrathiafulvalenebis(*N*,*N*-dimethyl)carbamide (**6**) as orange crystals after recrystallization from methylene chloride–ether: yield 22.3%; mp 231–232 °C; IR (KBr) 3090, 1602 (C=O), 1550 (C=C), and 1400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.10 (s, 12 H, $N-CH_3$) and 6.63 (s, 2 H, HC=C-C=O); MS *m/e* 346 (M^+). Anal. Calcd for $C_{12}H_{14}N_2O_2S_4$: C, 41.59; H, 4.07; N, 8.08; S, 37.01. Found: C, 41.58; H, 3.80; N, 8.05, S, 37.00.

Decarboxylation of 3 with Copper Chromite. A mixture of 760 mg of **3**, 300 mg of copper chromite, and 15 mL of HMPA was heated at 150–160 °C for 3 h. The cooled mixture was diluted with water and extracted with benzene. The yellow organic extract was washed, dried over Na_2SO_4, and evaporated to afford orange-yellow crystals, which were recrystallized from hot hexane to give orange needles of **1** (231 mg): yield 57%; mp 118.5–119.2 °C. No byproducts were observed.

Decarboxylation of 4 with Copper Chromite. A mixture of 146 mg of **4**, 150 mg of copper chromite, and 7 mL of HMPA was treated as above to afford 70 mg of **1**, yield 69%.

Decarboxylation of 3 with Copper(II) Sulfate. A mixture of 130 mg of **3**, 300 mg of copper(II) sulfate pentahydrate, and 4 mL of quinoline was heated at 100–200 °C for 0.5–1 h. Workup afforded 35 mg of **1**, yield 50%.

Decarboxylation of 3 with Copper Powder. Using 150 mg of copper powder instead of the 300 mg of $CuSO_4 \cdot 5H_2O$ in the above case, **1** was obtained in 40% yield.

Registry No.—**1**, 31366-25-3; **2**, 26314-39-6; **3**, 59269-79-3; **4**, 69440-12-6; **5**, 69440-11-5; **6**, 69440-13-7; **7**, 69439-76-5.

References and Notes

(1) (a) J. P. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973); (b) L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973); (c) *Science*, **180**, 1041 (1973).

(2) (a) H. Prinzbach, H. Berger, and A. Lüttringhaus, *Angew. Chem., Int. Ed. Engl.*, **4**, 435 (1965); (b) K. M. Pazdro, *Rocz. Chem.*, **43**, 1089 (1969); (c) F. Wudl, G. M. Smith, and E. J. Hufnagel, *Chem. Commun.*, 1453 (1970); (d) J. P. Ferraris, T. O. Poehler, A. N. Bloch, and D. O. Cowan, *Tetrahedron Lett.*, 2553 (1973).

(3) L. R. Melby, H. D. Harzler, and W. A. Sheppard, *J. Org. Chem.*, **39**, 2456 (1974).

(4) F. Wudl and M. L. Kaplan, *J. Org. Chem.*, **39**, 3608 (1974).

(5) C. U. Pittman, Jr., M. Narita, and Y. F. Liang, *J. Org. Chem.*, **41**, 2855 (1976).

(6) (a) Z. Yoshida, T. Kawase, and S. Yoneda, *Tetrahedron Lett.*, 235 (1975); (b) *ibid.*, 331 (1975); (c) S. Yoneda, T. Kawase, M. Inaba, and Z. Yoshida, *J. Org. Chem.*, **43**, 595 (1978); (d) S. Yoneda, T. Kawase, and Z. Yoshida, *ibid.*, **43**, 1980 (1978); (e) Z. Yoshida, S. Yoneda, T. Kawase, and M. Inaba, *Tetrahedron Lett.*, 1285 (1978).

(7) A similar procedure for removing carbomethoxy substituents was used in the preparation of tetraselenafulvalene: M. V. Lakshmikantham and M. P. Cava, *J. Org. Chem.*, **41**, 882 (1976).

(8) Another synthesis of monosubstituted TTF's has been reported: D. C. Green, *J. Chem. Soc., Chem. Commun.*, 161 (1977).

(9) The large difference in melting point from the literature value is probably due to a variation in the "cis/trans" isomer ratio.

1,2-Bis(diphenylphosphino)-1-phenylethane: A Chiral Ditertiary Phosphine Derived from Mandelic Acid Used as a Ligand in Asymmetric Homogeneous Hydrogenation Catalysts

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During the last few years rhodium(I) complexes of chiral phosphines have been shown to be effective catalysts for the asymmetric hydrogenation of prochiral olefins.[1,2,3] The optical yields in such reactions have been shown to be particularly high when chiral ditertiary phosphines are used which form rigid five-membered chelate rings. Examples of such chiral ditertiary phosphines include the ligand (−)-(*o*-$CH_3OC_6H_4$)-(C_6H_5)$PCH_2CH_2P(C_6H_5)(C_6H_4OCH_3$-*o*) of Knowles et al.[4] and the ligands (−)-(2*S*,3*S*)-$(C_6H_5)_2PCH(CH_3)CH(CH_3)P(C_6H_5)_2$ ("(*S*,*S*)-chiraphos")[5] and $(C_6H_5)_2PCH(CH_3)CH_2P(C_6H_5)_2$ ("*R*-prophos")[6] of Fryzuk and Bosnich.

An attractive synthetic objective is the development of methods for the synthesis of chiral ditertiary phosphines forming rigid five-membered chelate rings using as raw ma-

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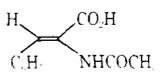
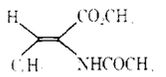
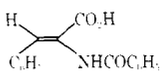
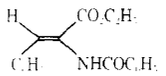
Table I. Optical Yields for the Hydrogenation of α-Acylaminocinnamic Acid Derivatives Using Rhodium Complexes Containing (*S*)-(+)-$(C_6H_5)_2PCH(C_6H_5)$-$CH_2P(C_6H_5)_2$

precursor	registry no.	hydrogenation optical yield,%[b] method A[a] (cationic complex)	method B[a] (in situ method)
	55065-02-6	78[c]	82
	60676-51-9	85[d]	76
	26348-47-0	84[e]	76
	26348-46-9	86[f]	88

[a] For a detailed description of the reaction conditions see the Experimental Section. [b] In all cases the (*R*)-(−) enantiomers were formed in excess. [c] Registry no.: 10172-89-1. [d] Registry no.: 21156-62-7. [e] Registry no.: 37002-52-1. [f] Registry no.: 64896-35-1.

terials inexpensive optically active natural products. This paper describes the synthesis of both enantiomers of the chiral ditertiary phosphine $(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2$ from the corresponding enantiomers of the readily available mandelic acid. Rhodium(I) complexes of this new ligand were found to give good optical yields in the asymmetric carbon–carbon double bond hydrogenation of prochiral olefin precursors to phenylalanine.

Experimental Section

Preparation of $(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2$ from Mandelic Acid. (a) Phenyl-1,2-ethanediol. The mandelic acid was reduced with $LiAlH_4$ in diethyl ether by a modification of the procedure of Jensen and Kiskis.[7] In a typical experiment 25 g (0.16 mol) of L-(+)-mandelic acid [$[\alpha]_D$ +154° (*c* 2.8, H_2O)] dissolved in 250 mL of diethyl ether was added dropwise to a suspension of 13.4 g (0.35 mol) of $LiAlH_4$ in 500 mL of diethyl ether at a rate sufficient to maintain a rapid reflux. After the addition was complete (~1.5 h) the reaction mixture was boiled under reflux for 25 min, cooled, and treated with 35 mL of ethyl acetate to destroy excess $LiAlH_4$. The resulting mixture was hydrolyzed by the successive addition of 13.4 mL of water, 13.4 mL of 15% aqueous sodium hydroxide, and 40.2 mL of water. The precipitate was filtered and washed with diethyl ether. The diethyl ether solution was dried over magnesium sulfate and then concentrated at 25 mm. The residue was crystallized from a mixture of diethyl ether and 35–60 °C petroleum ether to give 14.4 g (65% yield) of (*S*)-(+)-$C_6H_5CHOHCH_2OH$: $[\alpha]^{13}_D$ +39.3° (*c* 3.13, ethanol); mp 66–67 °C; proton NMR in $CDCl_3$ δ 7.23 (s, 5 H, C_6H_5), 4.7 (br, 3 H, CH + OH), 3.5 (br, 2 H, CH_2).

A completely analogous procedure was used to convert D-(−)-mandelic acid into (*R*)-(−)-$C_6H_5CHOHCH_2OH$, $[\alpha]^8_D$ −39.6° (*c* 2.44, ethanol).

(b) Phenyl-1,2-ethanediol Bis(*p*-toluenesulfonate). In a typical experiment a solution of 6.9 g (0.05 mol) of (*S*)-(+)-1-phenyl-1,2-ethanediol in 41 mL of purified pyridine was treated at 0 °C with 23.0 g (0.12 mol) of *p*-toluenesulfonyl chloride. The mixture was stirred at 0 °C for 3 h and then kept at −10 °C for 16 h. It was then poured into 300 mL of ice water with vigorous stirring. The resulting fine suspension was poured into a mixture of 35 mL of concentrated hydrochloric acid and excess crushed ice. The resulting white crystalline precipitate was filtered, washed thoroughly with water and petroleum ether, and then crystallized from diethyl ether to give 16.6 g (75% yield) of (*S*)-(+)-1-phenyl-1,2-ethanediol bis(*p*-toluenesulfonate): $[\alpha]^8_D$ +67.4° (*c* 1.50, $CHCl_3$); proton NMR in $CDCl_3$ δ 7.67 (dd, J_1 = 9, J_2 = 2 Hz, 4 H, *p*-C_6H_4), 7.24 (dd, 4 H, *p*-C_6H_4), 7.22 (5 H, C_6H_5), 5.60 (t, *J* = 6 Hz, 1 H, CH), 4.21 (d, *J* = 6 Hz, 2 H, CH_2), 2.44 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3). Anal. Calcd for $C_{22}H_{22}O_6S_2$: C, 59.2; H, 5.0; S, 14.4. Found: C, 57.9; H, 5.1; S, 14.0.

A completely analogous procedure was used to convert (*R*)-(−)-1-phenyl-1,2-ethanediol into the corresponding bis(*p*-toluenesulfonate), $[\alpha]^8_D$ −66.8° (*c* 4.09, $CHCl_3$). Anal. Found: C, 57.9; H, 5.1; S, 13.9.

(c) 1,2-Bis(diphenylphosphino)-1-phenylethane. In a typical experiment a solution of 7.2 mL (8.8 g, 0.04 mol) of $(C_6H_5)_2PCl$ in 150 mL of dioxane was boiled under reflux for 7 h with 3.8 g (0.166 mol) of sodium metal in a nitrogen atmosphere with strong mechanical stirring. The resulting yellow-orange reaction mixture was treated with 100 mL of anhydrous tetrahydrofuran and then decanted from the unreacted sodium. A solution of 6.6 g (0.0147 mol) of (*S*)-(+)-1-phenyl-1,2-ethanediol *p*-toluenesulfonate ($[\alpha]^8_D$ +67.4°) in 50 mL of dry tetrahydrofuran was added dropwise over 30 min. At the end of this addition the reaction mixture had become a light yellow, almost as a titration. After stirring for an additional 30 min, the reaction mixture was filtered through glass wool. Solvents were removed from the filtrate under reduced pressure to give an oil. Treatment of this oil with degassed absolute ethanol gave a white solid which was crystallized from ethanol to give 2.8 g (40% yield) of white crystalline (*R*)-(−)-$(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2$; mp 155–158 °C; $[\alpha]^{27}_D$ −9.6° (*c* 0.71, CH_2Cl_2); proton NMR in $CDCl_3$ δ 7.0–7.4 (complex m, 25 H, C_6H_5), 3.3 (m, 1 H, CH), and 2.5 (m, 2 H, CH_2); carbon-13 NMR spectrum in CH_2Cl_2 δ 142.1–127.5 (complex phenyl multiplet), 42.5 (t, *J* = 15 Hz, aliphatic CH), and 33.9 (dd, J_1 = 21, J_2 = 16 Hz, aliphatic CH_2); phosphorus-31 NMR in $CDCl_3$ δ −2.3 (d, *J* = 15 Hz, $(C_6H_5)_2PCH(C_6H_5)$ resonance) and 22.2 (d, *J* = 15 Hz, $(C_6H_5)_2PCH_2$ resonance). Anal. Calcd for $C_{32}H_{28}P_2$: C, 81.0; H, 5.9; P, 13.1. Found: C, 81.3; H, 5.8; P, 13.2.

A completely analogous procedure was used to convert (*R*)-(−)-1-phenyl-1,2-ethanediol bis(*p*-toluenesulfonate)($[\alpha]^8_D$ −66.8°) into (*S*)-(+)-$(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2$ in 38% yield: mp 155–158 °C; $[\alpha]^{20}_D$ +10.1° (*c* 0.99, CH_2Cl_2). Anal. Found: C, 81.1; H, 5.9; P, 13.1.

Preparation of [(*S*)-(+)-$(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2$-$Rh(nor\text{-}C_7H_8)][ClO_4]$. A mixture of 0.0575 g (0.125 mmol) of $[(nor\text{-}C_7H_8)RhCl]_2$[8] and 0.1185 g (0.25 mmol) of (*S*)-(+)-$(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2$ ($[\alpha]^{20}_D$ +10.1°) in 40 mL of methanol was stirred under argon for 40 min. A solution of 0.4 g of sodium perchlorate in 40 mL of water was added. The resulting yellow-orange precipitate was filtered and washed with water. After crystallization from a mixture of methanol and water by slow evaporation of the methanol 0.17 g (90% yield) of [(*S*)-(+)-$(C_6H_5)_2PCH(C_6H_5)$-$CH_2P(C_6H_5)_2Rh(nor\text{-}C_7H_8)][ClO_4]$ was obtained. Anal. Calcd for $C_{39}H_{36}ClO_4P_2Rh$: C, 60.9; H, 4.7; Cl, 4.6; P, 8.1; Rh, 13.4. Found: C, 60.3; H, 4.7; Cl, 4.6; P, 8.1; Rh, 13.5.

Catalytic Reactions (Table I). The prochiral olefin was weighed and added to the hydrogenation vessel which was purged several times and filled with prepurified hydrogen. The catalyst solution was transferred by syringe to the hydrogenation vessel. The hydrogenation was then carried out under the indicated conditions (see below). After the reaction was complete, the solvent was removed at ~25 °C (35 mm). The product was separated from the catalyst by one of the following two methods. In the case of esters, the product was either chromatographed on a silica gel column and eluted with hexane/ethyl acetate or preferably passed in methanol solution through a column of 200–400 mesh Dowex 50W-X2 ion exchange resin in the H^+ form. In the case of acids, the product was dissolved in 10% aqueous sodium hydroxide and filtered and the filtrate was treated with 10% aqueous hydrochloric acid followed by extraction with diethyl ether. The resulting ether or methanol solutions of the products were concentrated in vacuum to give the product. The resulting products were either clear or only faintly yellow, indicating essentially complete removal of the catalyst. The identity and chemical yield of these products were determined by proton NMR spectroscopy at 80 MHz on a Telsa Model BS 487C spectrometer. The optical rotations of the products were measured in methanol solutions on a Schmidt-Haensch LM visual polarimeter with approximately 0.01° precision. The optical yields were calculated using reported[4,5] values for the optical rotations of the pure hydrogenation products. All optical yields listed in Table I were obtained from experiments where the chemical yields, as shown by proton NMR spectra, were greater than 95%.

Two general methods were used for the hydrogenation experiments summarized in Table I.

Method A (Cationic Complex). The preformed complex $[(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2Rh(nor\text{-}C_7H_8)][ClO_4]$ obtained from one of the pure ditertiary phosphine enantiomers was used as the catalyst in methanol solution. The hydrogenations were conducted in conventional apparatus at 30 °C and 1 atm of hydrogen. Under such conditions the olefins listed in Table I were hydrogenated at rates corresponding to 8–40 mL of hydrogen absorbed per hour.

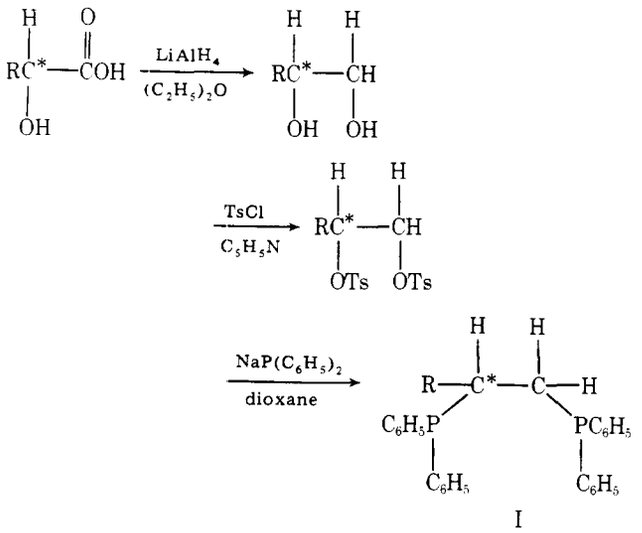


Figure 1. General scheme for converting chiral α-hydroxycarboxylic acids to chiral ditertiary phosphines (Ts = *p*-toluenesulfonyl).

Method B (In Situ Method). In these experiments the catalyst was generated in situ from $[(nor\text{-}C_7H_8)RhCl]_2$ and the ditertiary phosphine $(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2$ using a phosphorus/rhodium mole ratio of 2.2:1 and a substrate/catalyst ratio of 100:1. The hydrogenations were conducted at 70 bars of hydrogen pressure in 20-mL stainless steel autoclaves at room temperature overnight. A catalyst for a typical in situ experiment was prepared from 5.75 mg of $[(nor\text{-}C_7H_8)RhCl]_2$ and 13.04 mg of $(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2$ under argon in a mixture of 4.5 mL of benzene and 4.5 mL of methanol

Results and Discussion

The procedure for converting mandelic acid to the ditertiary phosphine $(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2$ (Figure 1, R = C_6H_5) corresponds entirely to the procedure previously used by Fryzuk and Bosnich[6] for the conversion of (*S*)-(+)-lactic acid to (*R*)-(+)-$(C_6H_5)_2PCH(CH_3)CH_2P(C_6H_5)_2$ (Figure 1, R = CH_3) and apparently represents a general procedure for the conversion of α-hydroxycarboxylic acids to chelating ditertiary phosphines containing $PCHRCH_2P$ structural units and an asymmetric carbon atom. The ready commercial availability of both enantiomers of mandelic acid makes readily available both enantiomers of the chiral ditertiary phosphine $(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2$ (I, R = C_6H_5) in contrast to the synthesis of $(C_6H_5)_2PCH(CH_3)CH_2P(C_6H_5)_2$ (I, R = CH_3) from lactic acid,[6] where only one of the enantiomers is readily available.

The ligand $(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2$ (I, R = C_6H_5) is more readily isolated in the pure state than its methyl analogue I (R = CH_3), apparently because of its higher melting point. The analyses and NMR spectra (proton, carbon-13, and phosphorus-31) of $(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2$ agree with the proposed structure I (R = C_6H_5). The phosphorus-31[9] and carbon-13[10] NMR assignments indicated in the Experimental Section are made by analogy with the NMR spectra of related compounds described in the cited references.

The catalytic activities of rhodium(I) complexes of both enantiomers of $(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2$(I, R = C_6H_5) were evaluated for the asymmetric hydrogenation of α-amidocinnamic acid precursors of phenylalanine. The results for the (*S*)-(+) enantiomer of I (R = C_6H_5) are given in Table I; in all cases the *R* configuration of the product was found. Two general types of reaction conditions were used: (1) use of the preformed cationic complex of the type [(diene)Rh(diphos)]$^+$, which was isolated as the perchlorate salt;[11] (2) use of a catalyst prepared in situ from the diene complex $[(nor\text{-}C_7H_8)RhCl]_2$ and the free ditertiary phosphine in a P/Rh mole ratio of 2.2:1.[12] The in situ catalysts were appreciably less reactive and required elevated hydrogen pressures for complete hydrogenation within a reasonable period of time. The optical yields from hydrogenation of a given substrate under both types of reaction conditions, however, were very similar (Table I) and also were similar or slightly lower (~80% vs. ~90%) than corresponding optical yields found by Fryzuk and Bosnich[6] for the related chiral ditertiary phosphine $(C_6H_5)_2PCH(CH_3)CH_2P(C_6H_5)_2$ (I, R = CH_3). As expected, rhodium(I) complexes of the (*R*)-(−) enantiomer of $(C_6H_5)_2PCH(C_6H_5)CH_2P(C_6H_5)_2$ (I, R = C_6H_5) gave the same optical yields of the *S* configuration of the product within experimental error as those reported in Table I for the (*S*)-(+) enantiomer of I (R = C_6H_5).

Several less successful attempts were made to use the chiral phosphine I (R = C_6H_5) in rhodium(I) catalysts for the asymmetric hydrogenations of the other substrates. Thus the in situ (method B) hydrogenation of citraconic acid dimethyl ester at 50 °C (70 bars) gave chemical yields of the hydrogenation product in the range 77–90%, but the optical yields were only 2–3%.

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Registry No.—(*S*)-(+)-phenyl-1,2-ethanediylbis(diphenylphosphino)norbornadienerhodium perchlorate, 69401-65-6; (*S*)-(+)-phenyl-1,2-ethanediylbis(diphenylphosphine), 69381-90-4; (*R*)-(−)-phenyl-1,2-ethanediylbis(diphenylphosphine), 69381-91-5; (*S*)-(+)-1-phenyl-1,2-ethanediol bis(*p*-toluenesulfonate), 69381-92-6; (*R*)-(−)-1-phenyl-1,2-ethanediol bis(*p*-toluenesulfonate), 69381-93-7; (*R*)-(−)-phenyl-1,2-ethanediol, 16355-00-3; (*S*)-(+)-phenyl-1,2-ethanediol, 25779-13-9; D-(−)-mandelic acid, 611-71-2; L-(+)-mandelic acid, 17199-29-0; chlorodiphenylphosphine, 1079-66-9; bis[(2,3,5,6-η)-bicyclo[2.2.1]hepta-2,5-diene]di-μ-chlorodirhodium, 12257-42-0.

References and Notes

(1) L. Markó and B. Heil, *Catal. Rev.*, **8**, 269 (1973).
(2) J. D. Morrison, W. F. Masler, and S. Hathaway in "Catalysis in Organic Syntheses, 1976", P. N. Rylander and H. Greenfield, Eds., Academic Press, New York, 1976.
(3) J. D. Morrison, W. F. Masler, and M. K. Neuberg, *Adv. Catal.*, **25**, 81 (1976).
(4) W. S. Knowles, M. J. Sabacky, B. D. Vineyard, and D. J. Weinkauff, *J. Am. Chem. Soc.*, **97**, 2567 (1975); B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachmann, and D. J. Weinkauff, *J. Am. Chem. Soc.*, **99**, 5946 (1977).
(5) M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, **99**, 6262 (1977).
(6) M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, **100**, 5491 (1978).
(7) F. R. Jensen and R. C. Kiskis, *J. Am. Chem. Soc.*, **97**, 5825 (1975).
(8) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).
(9) R. B. King and P. N. Kapoor, *J. Am. Chem. Soc.*, **93**, 4158 (1971).
(10) R. B. King and J. C. Cloyd, Jr., *J. Chem. Soc., Perkin Trans. 2*, 938 (1975).
(11) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, **98**, 2134 (1976).
(12) J. A. Osborn, F. J. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, 1711 (1966).

Reaction of Enol Silyl Ethers with Silver Acetate–Iodine. Synthesis of α-Iodo Carbonyl Compounds

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The reaction of enol acetates with thallium(I) acetate–iodine[1] and the oxidation of alkenes with silver chromate–

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