was stirred (300–600 rpm) at ambient temperature for 4 h, and then water and methylene chloride were added. The organic layer was separated, washed with water, dried, and concentrated. Without purification, the crude product was dissolved in THF (15 mL). Water (0.50 mL) and 2% Na–Hg (6.5 g, 5.7 mmol of Na°) were added, and the mixture was stirred rapidly. After 1 h, more water (0.25 mL) and 2% Na–Hg (3.3 g, 2.9 mmol of Na°) were added, and stirring was continued for 1 h. Methylene chloride (15 mL) and anhydrous sodium sulfate were added, and after 10 min the mixture was filtered and concentrated. The crude product was purified by Kugelrohr distillation. In all cases the β-cyanohydrin was obtained in >90% purity (VPC), but traces of low-boiling impurities were present.

3-Hydroxyheptanenitrile (6a). The product (95% pure by VPC) was obtained in 69% yield as an oil, bp 65–75 °C (0.02 torr). The analytical sample was further purified by preparative VPC: IR (film) 3450 (OH), 2260 cm^{-1} (CN); NMR δ 3.6–4.1 (m, 1 H), 3.04 (br s, 1 H, exchanges with D_2O), 2.52 (d, 2 H, J = 5.5 Hz), 0.7–1.8 (m, 9 H).

3-Hydroxy-3-(4-methyl-3-cyclohexenyl)butanenitrile (6b). Prepared in 44% yield by the general procedure. The product (90% pure by VPC, several volatile constituents were present in low yield) was obtained as an oil, bp 80–95 °C (0.02 torr). The analytical sample was purified by preparative VPC (SE-30 column, 170 °C): IR (film) 3460 (OH), 2260 cm^{-1} (CN); NMR δ 5.35 (br s, 1 H), 2.72 (s, 1 H, exchanges with D_2O), 2.53 (s, 2 H; at 250 MNz[10] appears as two overlapping AB quartets), 1.1–2.1 (m, 13 H).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56. Found: C, 73.49; H, 9.61.

Starting with purified cycloadduct, an 87% yield of β-cyanohydrin **6b** was obtained.

***(exo,exo)*-3-Hydroxybicyclo[2.2.1]heptane-2-carbonitrile (6c).** The product was obtained in 88% yield as an oil (>95% pure by VPC) which refused to crystallize, bp 90–100 °C (0.025 torr) [lit.[1e] bp 110 °C (0.001 torr)]. The spectra were identical with those published.

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Registry No. 1, 57359-33-8; 2, 70367-23-6; 3, 66074-00-8; 4, 70367-24-7; 5a, 70367-25-8; 5b, 79466-78-7; 5c, 79466-79-8; 5d, 70367-31-6; 6a, 70102-87-3; 6b, 79466-80-1; 6c, 79466-81-2; (phenylsulfonyl)nitromethane, 21272-85-5; 1-hexene, 592-41-6; *d*-limonene, 5989-27-5; 1-methylcyclohexene, 591-49-1; 2,3-dimethyl-2-butene, 563-79-1; norbornylene, 498-66-8.

(10) We thank Dr. George Furst (University of Pennsylvania, Department of Chemistry) for obtaining these spectra.

Use of Heterogeneous Asymmetric Hydrogenation for the Preparation of a Chiral Phosphinite and Its Application as a Ligand in Homogeneous Asymmetric Hydrogenation

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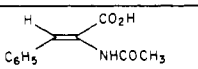
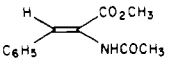
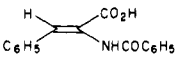
The success of homogeneous asymmetric hydrogenation of prochiral olefins with rhodium complexes as catalysts depends mainly on the structure of the chiral ligand, a phosphine, or a phosphinite. Three different methods have been used up until now for the preparation of such compounds: resolvation of a racemic mixture,[1] use of a chiral natural product as the starting compound,[2] and asymmetric homogeneous hydrogenation.[3] We report now on a fourth procedure, the use of asymmetric heterogeneous hydrogenation.

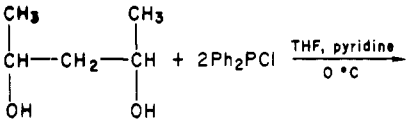
(1) W. S. Knowles and M. J. Sabacky, *Chem. Commun.*, 1445 (1968).

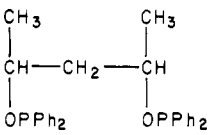
Table I. Hydrogenation of Prochiral Olefins with Rhodium Complex Catalysts Containing BDPOP[a]

olefin	Et_3N/Rh molar ratio	optical yield, % (*S,S*)-(+)-BDPOP[b]	optical yield, % (*R,R*)-(−)-BDPOP[d]
	0	53	63
	0.5	58	65
	1.0		54
	3.0		54
	3.0		48[c]
	8.0		10
	0	48	
	2.0		53
	0	78	

[a] Reaction conditions: substrate/[(nor-C_7H_8)RhCl]$_2$/BDPOP ratio of 100:1:2.2, solvent benzene/methanol (1/1), 1 bar of H_2, 25 °C. [b] The absolute configuration is *S* in all cases. [c] Catalyst [(nor-C_7H_8)Rh(BDPOP)]$^+$-ClO_4^-, substrate/Rh ratio of 100:1, solvent methanol. [d] The absolute configuration is *R* in all cases.

By use of the method of Izumi and co-workers[4] (−)-(2*R*,4*R*)- and (+)-(2*S*,4*S*)-2,4-pentanediol were prepared by hydrogenating acetylacetone in the presence of a Raney nickel catalyst modified with an aqueous solution of tartaric acid (the *R,R* or *S,S* enantiomer, respectively) and NaBr. The pentanediol enantiomers (optical purities above 97%) were transformed with Ph_2PCl to the two corresponding enantiomers of 2,4-bis[(diphenylphosphinyl)oxy]pentane (BDPOP).





BDPOP

Both chiral phosphinites were tested as ligands in the homogeneous catalytic hydrogenation of (acylamino)-cinnamic acid derivatives with (phosphine)rhodium complexes as catalysts. The results are compiled in Table I.

The optical yields achieved correlate well with that obtained with the only other diphosphinite containing an OC_3O bridge between the two phosphorous atoms.[5] Et_3N had no significant effect at low N/Rh ratios on the enantioselectivity, but large amounts of Et_3N were disadvantageous.

In addition the (*R,R*)-pentanediol was transformed in the usual way over the ditosylate into (−)-(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane.

This chiral ditertiary phosphine, however, proved to be an oily substance, and we could not obtain it in a sufficiently pure state necessary for complete characterization. With this oil as a ligand, 37–44% optical yields were

(2) T. P. Dang and H. B. Kagan, *Chem. Commun.*, 481 (1971).
(3) M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, 100, 5491 (1978).
(4) K. Ito, T. Harada, A. Tai, and Y. Izumi, *Chem. Lett.*, 1049 (1979).
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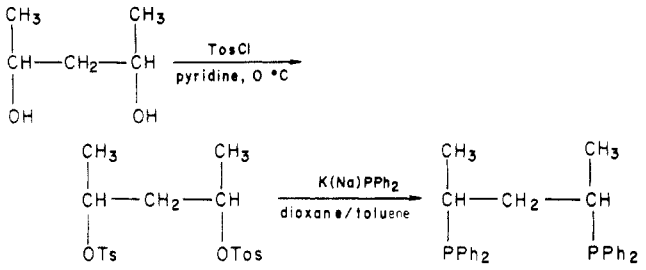

achieved with (benzoylamino)cinnamic acid as a substrate. Although this result is rather modest as compared to those reported for many other ditertiary phosphines,[6] it is significantly better than the only other value (12%) published[7] until now for a 1,3-diphosphine.

Experimental Section

(+)-(2*S*,4*S*)-2,4-Pentanediol. Raney nickel alloy (3.9 g) was added in small portions to a solution of 9 g NaOH in 40 mL water, and the suspension kept at 100 °C for 1 h. After the alkaline solution was decanted, the catalyst was washed 15 times with 40 mL of water. The so-obtained Raney Ni was treated at 100 °C for 1 h with a solution of 2 g of (*S,S*)-tartaric acid and 20 g of NaBr in 178 mL of water which had been adjusted to pH 3.2 with 1 M NaOH. The modifying solution was decanted and the procedure repeated two times. Finally, the catalyst was washed with 40 mL of water, 50 mL of methanol, and twice with 50 mL of THF.

The modified Raney Ni was weighed into a 100-mL autoclave with 22 mL of THF, 10.3 mL (0.1 mol) of acetylacetone, and 0.2 mL of acetic acid, and the autoclave was flushed several times with hydrogen and pressured to 100 bar. Hydrogenation was carried out at 100 °C with repeated repressuring from 80 to 100 bar (8–10 h). After H_2 consumption ceased, the pressure was blown off, the product and the catalyst were separated by filtration, and the solvent was evaporated in vacuo. The ratio of the diol diastereomers was determined by GLC (3% neopentyl glycol succinate on Chromosorb W-HP, 150 °C). The diastereomeric mixture was separated by recrystallizing it first at −50 °C and then at −5 °C from ether: Yield of the *S,S* enantiomer 4.7 g (0.044 mol, 44%); $[\alpha]^{20}_D$ +53.5° (*c* 1.89, EtOH); optical purity 99.6%.[4]

The (−)-(2*R*,4*R*)-2,4-pentanediol was prepared in the same way only by using (*R,R*)-tartaric acid for the modification of the catalyst: $[\alpha]^{20}_D$ −52.2° (*c* 2.56, EtOH); optical purity 97.2%; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.12 (d, $J_{H,H}$ = 6 Hz, CH_3), 1.46 (t, $J_{H,H}$ = 6 Hz, CH_2), 4.15 (sextet, $J_{H,H}$ = 6 Hz, CH), ^{13}C NMR ($CDCl_3$, 20 MHz) δ 23.4 (s, CH_3), 46.2 (s, CH_2), 64.9 (s, CH).

(+)-(2*S*,4*S*)-2,4-Bis[(diphenylphosphinyl)oxy]pentane (BDPOP). In a flask equipped with a magnetic stirrer, a thermometer, and a dropping funnel and flushed with Ar were dissolved 1.1 g (10.6 mmol) of (2*S*,4*S*)-pentanediol in 40 mL of absolute THF and 1.71 mL (21.2 mmol) of pyridine. The solution was cooled to 0 °C, and a solution of 3.80 mL (21.2 mmol) of Ph_2PCl in 25 mL of absolute THF was added slowly with stirring. Following the addition, the reaction mixture was left to warm to room temperature and stirred overnight. The pyridine hydrochloride was filtered off under Ar, the filtrate evaporated to dryness, and the residue dissolved in 20 mL of ether. When this solution was cooled to −5 °C, the product separated in the form of white crystals: yield 4.05 g (8.6 mmol, 81%); $[\alpha]^{20}_D$ +51.8° (*c* 2.18 $CHCl_3$); mp 86–89 °C.

The (−)-(2*R*,4*R*) enantiomer was prepared in the same way by starting from the (2*R*,4*R*)-diol: $[\alpha]^{20}_D$ −53.2 (*c* 3.48, $CHCl_3$); mp 86–89 °C; ^{1}H NMR ($CDCl_3$, 80 MHz) 1.15 (d, $J_{H,H}$ = 6 Hz, CH_3), 1.80 (t, $J_{H,H}$ = 6 Hz, CH_2), 4.15 (sextet, $J_{H,H}$ = 6 Hz, CH, J_{POCH} not detectable), 7.15 (m, C_6H_5); ^{13}C NMR ($CDCl_3$, 20 MHz) 22.1 (d, J_{POCC} = 4.6 Hz, CH_3), 47.6 (t, J_{POCC} = 1.6 Hz, CH_2), 73.7 (d, J_{POC} = 21.6 Hz, CH); ^{31}P NMR ($CDCl_3$, 32.1 MHz) + 106.1 ppm (chemical schift is given downfield from external 85% phosphoric acid); mass spectrum (75 eV), *m/e* (relative intensity) 472 (M^+, 10), 386 ($[(C_6H_5)_2POP(C_6H_5)_2]^+$, 10), 287 ($[M - P(C_6H_5)_2]^+$, 67), 271 ($[M - OP(C_6H_5)_2]^+$, 48), 262 ($[(C_6H_5)_3P]^+$, 93), 203 ($[(C_6H_5)_2POH_2]^+$, 95), 202 ($[(C_6H_5)_2POH]^+$, 43), 201 ($[(C_6H_5)_2PO]^+$, 100), 185 ($[(C_6H_5)_2P]^+$, 40), 183 ($[C_{12}H_8P]^+$, 36).

Asymmetric Hydrogenations. To a reaction vessel were added under hydrogen 11.6 mg (0.025 mmol) of $[(nor\text{-}C_7H_8)RhCl]_2$ and 26.0 mg (0.055 mmol) of BDPOP dissolved in a mixture of 5 mL of benzene and 2.5 mL of methanol. Et_3N (if used) was introduced into the hydrogenation flask by means of a syringe. After 40 min of prehydrogenation, 2.5 mmol prochiral olefin dissolved in 2.5 mL methanol was added to the solution. The reaction was followed by measuring H_2 absorption; 50% conversion was reached within 30–90 min. After H_2 uptake was complete (2–6 h) the reaction mixture was evaporated to dryness, and the following two procedures were used to isolate the hydrogenation product.

Method A. For *N*-acetylphenylalanine and *N*-benzoylphenylalanine the residue was dissolved in 20 mL of 10% aqueous sodium hydroxide and filtered, the filtrate acidified with 10% aqueous hydrochloric acid, and the product extracted with diethyl ether.

Method B. For *N*-acetylphenylalanine methyl ester the product was isolated by column chromatography on silica gel with ethyl acetate–hexane as the eluant.

The resulting ether or ethyl acetate–hexane solutions were evaporated in vacuo to give the product. The identities and chemical yields of these products were determined by proton NMR spectroscopy. The optical rotations of the products were measured on a Schmidt-Haensch LM visual polarimeter with approximately 0.01° precision. The optical yields were calculated by using reported[8,9] values for the optical rotations of the pure hydrogenation products.

Acknowledgment. We acknowledge the support of the Ministry of Education and the help of Dr. G. Szalontai at the Research Institute for Heavy Industries with the NMR spectra.

Registry No. I, 79499-46-0; II, 79499-47-1; (−)-(2*R*,4*R*)-2,4-pentanediol, 42075-32-1; (+)-(2*S*,4*S*)-2,4-pentanediol, 72345-23-4; 2-(acetylamino)-3-phenyl-2-propenoic acid, 5469-45-4; methyl 2-(acetylamino)-3-phenyl-2-propenoate, 52386-78-4; 2-(benzoylamino)-3-phenyl-2-propenoic acid, 1155-48-2; *N*-acetyl-L-phenylalanine, 2018-61-3; *N*-acetyl-D-phenylalanine, 10172-89-1; *N*-acetyl-L-phenylalanine methyl ester, 3618-96-0; *N*-acetyl-D-phenylalanine methyl ester, 21156-62-7; *N*-benzoyl-L-phenylalanine, 2566-22-5.

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Synthesis and Diels–Alder Reactions of 1-Acylated 1,3-Cyclopentadienes[1]

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Acylcyclopentadienes are of potential interest for Diels–Alder reactions and as novel ligands for sandwich compounds and η-cyclopentadienyl compounds in general.[2] Hitherto only acetylcyclopentadiene (3) and formylcyclo-

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(2) Hart, W. P.; Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 1196.

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