may, however, exist at equilibrium to the extent of 5%,[12] it is reasonable to suppose that the same nearness of approach of a methyl group (or its hydrogen atoms) and a hydrogen atom (measured in the Dreiding model of axial methylcyclohexane) can be tolerated in the camphene system between C(9) and syn-H-7 provided that there is enough strain elsewhere to hold the nonbonded atoms in place.

Where the nearness of approach is *less* than in axial methylcyclohexane there is going to be considerable repulsion. The resultant strain can best be relieved by a twisting of the *gem*-dimethyl system about the C(2)-C(3) bond in a direction which increases the C(10)/endo-H-5 distance while decreasing the C(9)/exo-H-7 distance until a satisfactory balance of nonbonded interactions and resultant strains is achieved. Such twisting should result in an increase in the torsion angle for C(9) (α) and a corresponding decrease in the corresponding angle for C(10) (β). And as a consequence the σ orbital for C(3)-C(9) becomes more nearly parallel to the p orbital for C(2), thus allowing better orbital overlap in approaching the transition state for rearrangement while at the same time bringing the C(3)-C(10) σ orbital less nearly parallel to the p orbital of C(2), thus disfavoring effective orbital overlap in approaching the transition state for C(10)/C(2) migration. Furthermore, as noted above, this twisting positions C(10) closer to its final position, which should favor the overall rearrangement process.

Until now the only support for the effects of unequal nonbonded interactions in favoring exo at the expense of endo alkyl migration has been the rate studies involving three homocamphenes in which exo-methyl migration is enhanced by an endo ethyl group, and exo-ethyl migration is slower than exo-methyl migration.[6] But with the present x-ray diffraction data which clearly demonstrate an increase in the torsion angle α and a concomitant decrease in the torsion angle β, there is strong support for the postulated twisting. Thus it is possible to offer this crystallographic finding as entirely consistent with the kinetic data on the three homocamphenes and as the source of the strong preference for exo-methyl migration over endo-methyl migration[5] in the racemization of camphene via the Nametkin rearrangement.

Supplementary Material Available: List of structure factors for (−)-camphene-8-carboxylic acid (16 pages). Ordering information is given on any current masthead page.

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Transition Metal Catalyzed Asymmetric Organic Syntheses via Polymer-Attached Optically Active Phosphine Ligands. Synthesis of *R* Amino Acids and Hydratropic Acid by Hydrogenation[1]

Naotake Takaishi, Hirosuke Imai, Christopher A. Bertelo, and J. K. Stille*[2]

Contribution from the Department of Chemistry, University of Iowa, Iowa City, Iowa 52242.

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Abstract: The reaction of (−)-1,4-ditosylthreitol (**2**) with 4-vinylbenzaldehyde afforded 2-*p*-styryl-4,5-bis(tosyloxymethyl)-1,3-dioxolane (**3**), which was copolymerized (radical) with hydroxyethyl methacrylate to incorporate 8 mol % **3** in the cross-linked copolymer **4.** Treatment of **4** with enough sodium diphenylphosphide to react with all the hydroxyl functions plus the tosylate groups gave a hydrophilic polymer (**5**) (after neutralization) bearing the optically active 4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane ligand. Exchange of rhodium(I) onto **5** with $[(C_2H_4)_2RhCl]_2$ gave the polymer-attached catalyst **6**, that would swell in alcohol and other polar solvents. Hydrogenation of α-*N*-acylaminoacrylic acids in ethanol with this catalyst gave the amino acid derivatives having the same optical yields and absolute configuration as could be obtained with the homogeneous analogue. The catalyst could be removed by filtration and reused with no loss of optical purity in the hydrogenated product.

Introduction

Of the methods of synthesis of optically active organic compounds, the generation of an optically active product from a prochiral reactant by use of an optically active catalyst or enzyme has several advantages, the most important of which is that either an available, naturally occurring catalyst or enzyme is utilized, or resolution is achieved with the catalyst instead of with the product. When resolution is carried out with the catalyst, only small quantities of resolved material are necessary; product resolution often results in loss of one enantiomer and possibly the resolving agent.[3]

Homogeneously catalyzed reactions generally take place at lower temperatures and pressures and are more selective. Because of this, homogeneously catalyzed reactions have

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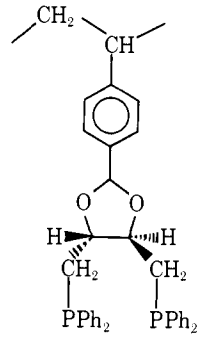
proven to be valuable in asymmetric synthesis from prochiral reactants through the utilization of optically active ligands on the transition metal. Amino acids, including D-Dopa, for example, can be synthesized in high optical yields by the asymmetric hydrogenation of the prochiral α-*N*-acylaminoacrylic acids with an optically active Wilkinson catalyst.[4-9] In these syntheses, neither the rhodium nor the optically active phosphine are readily recovered, however.

One practical limit to performing homogeneously catalyzed reactions in the liquid phase is the difficulty of separating the product from the catalyst or removing the product continuously. To overcome this difficulty, homogeneous catalysts have been attached to a variety of supports including cross-linked polymers.[10] In this way the catalyst acquires the property of insolubility and may retain the same reactivity exhibited in solution. Most of the synthetic polymer supports for catalysts containing polymer-attached phosphine ligands coordinated to a transition metal are cross-linked polystyrenes. In some cases, in more polar solvents, higher rates,[11-14] greater selectivity for nonpolar hydrocarbons (vs. polar ones),[13,15,16] and greater stereoselectivity[15,17,18] have been reported.

Only a few asymmetric polymer-attached ligands have been synthesized, however, so that the full potential of these polymeric catalysts has not been realized. Polystyrenes containing optically active phosphine ligand sites have been synthesized,[19-21] but the results, aimed at effecting asymmetric syntheses, have been disappointing. A DIOP-type ligand, [2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane], attached to cross-linked polystyrene (**1**) reacts with soluble rhodium(I) complexes to give asymmetric hydrogenation[19] or hydroformylation[21] catalysts. The hydroformylation of styrene gave predominantly 2-phenylpro-



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panal in only 2% enantiomeric excess. This is surprising, considering the optical yields which have been achieved with the homogeneous DIOP catalysts. Hydrogenation of α-substituted styrenes with the polymer-bound Wilkinson-type catalyst gave lower optical yields (1.5%) than the homogeneous counterpart (15%),[19] while the hydrosilation of acetophenone gave comparable optical yields (58%).[19]

Although the cross-linked polystyrene catalyst swells in nonpolar solvents—accounting for the success in the hydrosilation reactions of ketones—it collapses in polar solvents, preventing penetration of the substrate. Acylaminoacrylic acids are hydrogenated to amino acid derivatives in high enantiomeric excess in the presence of a homogeneous rhodium catalyst containing the DIOP ligand. This same catalyst bound to the cross-linked polystyrene bead will not hydrogenate the acylaminoacrylic acid in a nonpolar solvent, since the substrates are not soluble.[19] In polar solutions of the substrates, the beads collapse, preventing entry of the acylaminoacrylic acid to the catalyst site. We have now been able to surmount this problem by preparing a Rh(I)-DIOP catalyst attached to a cross-linked polymer that swells in polar solvents.

Results and Discussion

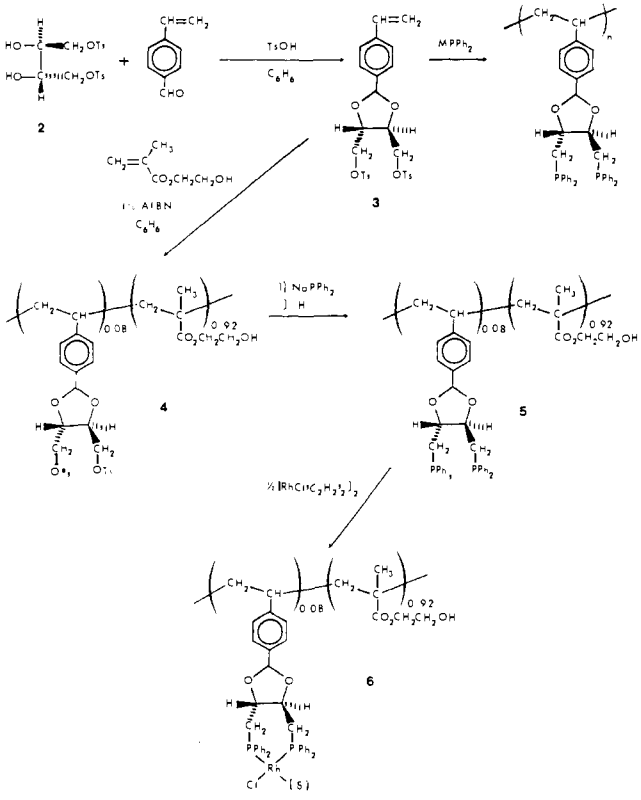
A number of optically active phosphines effect various asymmetric syntheses when catalytic amounts of metal complexes of the phosphine are employed in a reaction with prochiral substrates. The asymmetric synthesis of amino acids by the hydrogenation of acylaminoacrylic acids with optically active rhodium catalysts can be carried out with >95% enantiomeric excess.[4] As a result of these hydrogenation (and hydroformylation) studies a wide variety of optically active mono- and chelating phosphines have been synthesized.[22,23] Those phosphines that owe their asymmetry to phosphorus[4] generally give high optical yields of product from the hydrogenation of prochiral substrate, but they are difficult to synthesize and resolve. Those phosphines that are asymmetric as a consequence of an asymmetric carbon at a center adjacent to phosphorus[8] or one atom removed from phosphorus are more readily synthesized, usually from readily available optically active starting materials. For these reasons, and because the Wilkinson-type homogeneous catalyst containing DIOP gave high optical yields in hydrogenations of prochiral acylaminoacrylic acids, we chose to attach DIOP to the appropriate polymer support.

The most challenging problems in polymer-supported catalysis are encountered in the choice of the polymer matrix and the synthesis of the catalyst site in the matrix. The methods that have been reported[19-21] require the introduction of a reactive site on a cross-linked polystyrene bead followed by the reaction of an optically active phosphine-containing ligand at the site. Our approach, the synthesis of ligand-bearing monomer followed by its copolymerization with a second monomer, has several advantages. First, the optical purity of the ligand on the monomer can be assured. Second, with one monomer, its concentration in the polymer could be controlled, and polymers containing a wide range of ligand concentrations can be synthesized. Third, depending on the comonomer and thus the reactivity ratios of the two monomers, isolation of the ligand-bearing monomer can be assured. Fourth, the nature of the polymer backbone, polar or nonpolar, can be varied depending on the selection of the comonomer. Fifth, varying degrees of cross-linking may be introduced.

The reaction of (−)-1,4-ditosylthreitol (**2**)[19]—obtained from L-tartaric acid—with 4-vinylbenzaldehyde[24] in the presence of *p*-toluenesulfonic acid gave a 74% yield of a new styrene monomer, 2-*p*-styryl-4,5-bis(tosyloxymethyl)-1,3-dioxolane (**3**) (Scheme I). This monomer could be expected to polymerize by all three different propagation mechanisms, and undergo radical copolymerization, having *q* and *e* values close to those of styrene. The reaction of **3** with either lithium[19] or sodium diphenylphosphide,[25] however, resulted in anionic polymerization.

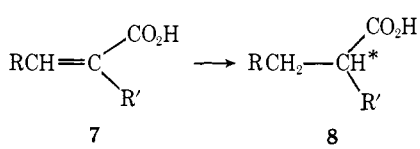
The radical polymerization of **3** with methyl methacrylate (MMA) to nearly 70% conversion gave a copolymer, the composition of which corresponded to the monomer feed, which was 85 mol % MMA. These results are consistent with a reactivity ratio for **3** in radical copolymerization reactions that is near that of styrene. The radical polymerization of **3** with hydroxyethyl methacrylate (HEMA) was effected with azobisisobutyronitrile (AIBN) at 70 °C using the reactivity ratios for styrene (r_1 = 0.44) and HEMA (r_2 = 0.65) and a charge of 8.3 and 75 mmol, respectively, to incorporate 8 mol % of the styryl monomer **3**. Since commercial hydroxyethyl methacrylate contains ethylene dimethacrylate, copolymer **4** was obtained (>90% conversion) as a cross-linked polymer that was insoluble in all solvents, but swelled in polar solvents. Sulfur analysis on **4** confirmed 8 mol % incorporation of the styryl monomer, and the ^{13}C NMR spectrum of polymer **4** swollen in Me_2SO-d_6 confirmed the incorporation of **3** (Table III). Conversion of the tosylated polymer (**4**) to the phosphi-

Scheme I



nated polymer (**5**) was accomplished by a method similar to that used for the preparation of DIOP.[25] The reaction of sodium diphenylphosphide with **4** in a THF-dioxane mixture afforded phosphinated polymer **5**, which contained (elemental analysis) 0.25 mequiv of diphosphine unit per gram, revealing that half the tosyl sites had been replaced with phosphine. Enough sodium diphenylphosphide was used to react with the hydroxyl functions in the HEMA portion plus the DIOP-tosylate groups. On workup, the unreacted tosyl groups were hydrolyzed. Assuming a statistical distribution of phosphine, a rhodium to phosphorus ratio of 1:4 then ensures that there is just enough rhodium to complex with sites containing bidentate phosphine, leaving sites containing one phosphine and one hydroxymethyl group void of rhodium. After the exchange, no rhodium was detected in solution. Polymer **6** swells in alcohol, and the swelled, gelatinous polymer can be easily filtered from ethanol and methanol.

The hydrogenation of various prochiral olefin substrates was carried out at 25 °C with 1-2.5 atm of hydrogen and catalyst **6**, using an olefin to rhodium ratio of 50. Within this pressure range, as observed in similar systems,[46] the optical yields did not vary. The results of asymmetric hydrogenation of olefins catalyzed by the polymer-attached catalyst (**6**) together with those obtained using the homogeneous Rh(I)-DIOP complex are shown in Table I. The high optical yields obtained with the polymer-attached catalyst **6** are quite comparable to those obtained with the homogeneous catalyst.[5,25] The same absolute configuration of the products is also observed, and in the hydrogenation of **7b**, a slightly better optical yield was observed than was obtained with the soluble Rh(I)-DIOP catalyst.



7 **8**

	R	R′
a	H	$NHCOCH_3$
b	C_6H_5	$NHCOCH_3$
c	H	C_6H_5

Table I. Asymmetric Hydrogenation of Olefins by Polymer-Attached Rh-DIOP Catalyst[a]

Substrate (g)	Catalyst (g)	Conditions: Temp, °C	Time, h	Optical yield,[b] %	Confign
7a (1.03)	**6** (2)	28	5	52-60	*R*
	Rh(I)-DIOP	25		73	*R*
7b (1.31)	**6** (1.6)	25	24	86	*R*
	Rh(I)-DIOP			81	*R*
7c (0.95)	**6** (1.6)	25	24	58-64	*S*
	Rh(I)-DIOP			63	*S*

[a] Conversion in each example was 100%, as measured by ^1H NMR. [b] Optical yields are calculated with respect to the following values of the optically pure compounds: *N*-acetyl-(*R*)-alanine, $[\alpha]_D$ +66.5° (*c* 2, H_2O);[26] *N*-acetyl-(*R*)-phenylalanine, $[\alpha]^{26}_D$ +46.0° (*c* 1, EtOH);[5a] (*S*)-hydratropic acid, $[\alpha]^{25}_D$ +76.3° (*c* 1.6, $CHCl_3$).[27] Some variation in optical yields was observed between batches; however, the optical yields varied <10% upon repetitive use of the catalyst when oxygen was strictly excluded.

Table II. Asymmetric Hydrogenation of **7a** with Recycled Catalyst **6**

Recycle (filtration atmosphere)	Reaction conditions[a]: Temp, °C	Time, h	Optical yield, %[b]
Original hydrogenation	22-25	5	52.5
Nitrogen	22-25	5	53.2
Air	24-29	24	47.4
Air	20-26	48	34.6

[a] 100% conversion, as determined by ^1H NMR, within the reaction time given. [b] See Table I, footnote *b*.

The fact that the optical yields obtained from catalyst **6** and the Rh(I)-DIOP catalyst were essentially the same is good evidence for only catalyst sites containing chelating bidentate phosphine ligands and the absence of a rhodium catalyst at a site containing one phosphine and one hydroxymethyl group.

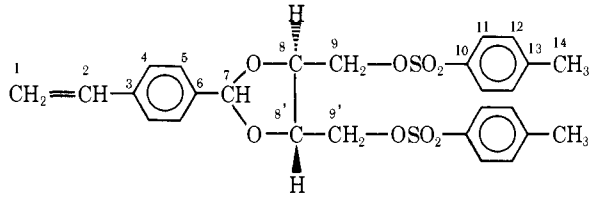
Although the polymer-attached catalyst (**6**) was less sensitive to oxygen than the homogeneous Rh(I)-DIOP catalyst, lower optical yields and slower rates were experienced after the catalyst had come in contact with air (Table II). The insoluble catalyst, **6**, could be reused many times by its filtration from the reaction solution, and this filtration generally was carried out under an inert atmosphere in order to preserve catalyst activity and the optical yield.

Experimental Section

Ir spectra were taken on a Beckman IR-20A instrument. ^1H NMR spectra were carried out on Varian A-60A and EM-360 spectrometers. ^{13}C NMR spectra were performed on a 90-MHz Bruker HX-90E Fourier transform NMR spectrometer. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter.

2-*p*-Styryl-4,5-bis(tosyloxymethyl)-1,3-dioxolane (3). Under a stream of nitrogen, a mixture of 3.5 g (26.5 mmol) of 4-vinylbenzaldehyde,[24] 10.92 g (25.4 mmol) of 1,4-ditosyl-L-threitol (**2**),[19] 150 mg of *p*-toluenesulfonic acid, 150 mL of benzene, and a small amount of

Table III. ^{13}C NMR Chemical Shifts of **3** and Copolymer **4**



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Monomer **3**		Copolymer **4**	
Carbon	Chemical shift, ppm (Me_4Si)		Chemical shift, ppm (Me_4Si)
1	104.4	HEMA(-CO_2-)	177.1-176.3
2	114.9	HEMA(-CCH_3)	17.9-15.7
3, 6, 7	139.0, 136.3, 135.6	OTs(*p*-CH_3Ph-)	20.9
4, 5	126.2, 126.8	(-SO_2C<)	145.1
8, 8′	75.4, 75.7		
9, 9′	68.3, 68.4		
10	145.4		
11	128.0		
12	130.1		
13	132.3		
14	21.7		

tert-butylcatechol was heated to the reflux temperature for 5 h under a phase-separating head. The solution was allowed to cool, and was neutralized with potassium carbonate. The mixture was filtered, and the filtrate was evaporated to afford 13.86 g of an oil residue. Crystallization of the residue from 100 mL of ethanol gave 10.16 g (73.6%) of 2-*p*-styryl-4,5-bis(tosyloxymethyl)-1,3-dioxolane (**3**). The crude product was recrystallized from benzene-Skelly B (1:1): mp 84-86 °C; ^1H NMR ($CDCl_3$) δ 7.9-7.1 (m, 12 H), 7.0-5.1 (m, 3 H, -CH=CH_2), 5.77 (s, 1 H, -CHO_2), 4.16 (s, 6 H, -CH_2CH-), 2.40 (s, 6 H CH_3); IR (Nujol) 1590, 1180, 1165, 1085, 1070, 955, 825, 805, 650, 555, 530 cm^{-1}; ^{13}C NMR ($CDCl_3$) given in Table III; $[\alpha]^{25}_D$ −30.94° (*c* 2.65, benzene). Anal. Calcd for $C_{27}H_{28}O_8S_2$: C, 59.54; H, 5.18; S, 11.78. Found: C, 60.75; H, 5.35; S, 11.73. Mass spectrum *m/e* (rel intensity) 174 (9.8), 154 (3.9), 134 (2.9), 118 (11.3), 105 (98.5), 94 (26.5), 78 (57.4), 77 (100), 51 (43.1), 44 (42.2).

Reaction of 2-*p*-Styryl-4,5-bis(tosyloxymethyl)-1,3-dioxolane (3) with Lithium Diphenylphosphide. Under a nitrogen atmosphere, a solution of 2.26 g (4.15 mmol) of **3** and a small amount of 4-*tert*-butylcatechol in 10 mL of tetrahydrofuran was added dropwise at 25 °C to a solution of lithium diphenylphosphide in 20 mL of tetrahydrofuran which had been prepared by the reaction of 3.67 g (16.6 mmol) of chlorodiphenylphosphine with 0.46 g (66.6 mmol) of lithium.[28] The reaction mixture was stirred at room temperature for 4 h. At the end of the reaction the color of the reaction mixture was light yellow. After a drop of methanol was added, the crude product was poured into 100 mL of chloroform. The mixture was filtered to remove chloroform-insoluble materials. The filtrate was evaporated to give 4.15 g of white powder. No vinyl protons could be seen in the ^1H NMR spectrum of the crude product. A reaction with sodium diphenylphosphide[29] produced similar results.

Copolymerization of 2-*p*-Styryl-4,5-bis(tosyloxymethyl)-1,3-dioxolane (3) with Methyl Methacrylate (MMA). A solution of 1.01 g (1.85 mmol) of 2-*p*-styryl-4,5-bis(tosyloxymethyl)-1,3-dioxolane (**3**), 1.02 g (10.16 mmol) of MMA, and 20 mg of AIBN in 10 mL of benzene was stirred at 40 °C under a nitrogen atmosphere for 43 h. The product was purified by two successive precipitations by the addition of the benzene solution to methanol. Filtration and drying under vacuum gave 1.39 g (68.8%) of copolymer. The component of the copolymer was determined by ^1H NMR and elemental analysis. IR (Nujol) 1720, 1590, 1180, 1165, 1140, 1085, 970, 800, 650, 530 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0-6.8 (m, 42 H, phenyl), 5.75 (m, 2.5 H, -CHO_2), 4.17 (m, 20 H, -OCH(CH_2O)CH (CH_2O)O), 4.00-2.65 (m, 52 H, -CO_2CH_3), 2.60-2.25 (m, 22 H, *p*-CH_3Ph), 2.20-0.30 (m, 90 H). Anal. Calcd for a polymer containing 84% of MMA: C, 59.76; H, 6.59. Found: C, 59.99; H, 6.00.

Copolymerization of 2-*p*-Styryl-4,5-bis(tosyloxylmethyl)-1,3-dioxolane (3) with 2-Hydroxymethyl Methacrylate (HEMA). A solution of 4.53 g (8.31 mmol) of 2-*p*-styryl-4,5-bis(tosyloxymethyl)-1,3-dioxolane (**3**), 9.73 g (74.78 mmol) of hydroxyethyl methacrylate, and 0.1 g of AIBN in 60 mL of benzene was stirred at 70 °C under a nitrogen atmosphere for 15 h. The polymer began to precipitate after stirring for 1 h. The precipitated polymer was filtered, washed twice with 100-mL portions of benzene, and dried under reduced pressure to give 7.34 g of white powder (**4**). The polymer was insoluble in all organic solvents. Anal. Calcd for a polymer containing 92 mol % of HEMA: C, 56.49; H, 7.06; S, 3.14. Found: C, 56.21; H, 7.13; S, 3.06. IR (Nujol) 3400 (OH), 1720 (-CH_2-), 1590 (phenyl), 1260, 1165, 1145, 1060, 1010, 960, 885, 800, 650, 530 cm^{-1}; ^{13}C NMR (swelled in Me_2SO-d_6), Table III.

Preparation of Phosphinated Polymer (5). Under a stream of nitrogen, 2.31 g of tosylated polymer (**4**) (2.27 mmol of tosylate and 13.03 mmol of hydroxyl) was added in one portion at room temperature to the sodium diphenylphosphide solution which was obtained by the reaction of 1.17 g (51 mmol) of sodium with 3.37 g (15.3 mmol) of chlorodiphenylphosphine in the mixture of 20 mL of dioxane and 15 mL of tetrahydrofuran.[29] The reaction mixture was stirred at room temperature for 7 h. The yellow color of sodium diphenylphosphide had not been discharged at the end of the reaction. A small amount of methanol was added to destroy the excess sodium diphenylphosphide. The reaction mixture was poured into 200 mL of acetone. After filtration, the polymer was washed twice with 100-mL portions of acetone followed by 50 mL of acetone-benzene mixture, 150 mL of water, 50 mL of acetone-Skelly B mixture, and 50 mL of Skelly B. After drying under reduced pressure for 1 day, 2.46 g of phosphinated polymer (**5**) was collected: IR (Nujol) 3400, 1710, 1550, 1250, 1145, 1060, 1010, 950, 870, 830, 730, 680 cm^{-1}. The polymer was used as a support for catalyst after grinding to a fine powder. Anal. Calcd for 8% diphosphine: P, 2.99; S, 0.0. Found: P, 1.55; S, <0.10, corresponding to 0.25 mequiv of diphosphine per gram.

Acrylic and Cinnamic Acids (7a-c). α-Acetamidoacrylic acid (**7a**) was purchased from Aldrich Chemical Co and used without further purification. α-Acetamidocinnamic acid (**7b**), mp 190-192 °C (lit.[30] 191-192 °C), and atropic acid (**7c**), mp 108-109 °C (lit.[31] 106-107 °C), were prepared by known methods.

Asymmetric Hydrogenation of Olefins by Polymer-Supported Rh(I)-DIOP Catalyst (6). A typical hydrogenation was carried out as follows. To a 500-mL pressure bottle equipped with a magnetic stirrer under a nitrogen atmosphere 25 mg (0.064 mmol) of $[RhCl(C_2H_4)]_2$,[32] 5 mL of benzene, 15 mL of ethanol, and 1.0 g (0.51 mequiv of P) of phosphinated polymer **5** were added. The mixture was stirred at room temperature for 48 h under a stream of nitrogen to give the light yellow polymer-supported Rh catalyst **6.** Following the addition of 6.4 mmol of substrate and 10 mL of ethanol under a nitrogen atmosphere, the reaction mixture was purged by filling and evacuating with hydrogen. The hydrogenation was carried out with 20 psig of hydrogen at ambient temperature. Results are summarized in Tables I and II.

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Transition Metal Catalyzed Asymmetric Organic Syntheses via Polymer-Attached Optically Active Phosphine Ligands. Synthesis of *R* Amino Acids by Hydrogenation with a Polymer Catalyst Containing Optically Active Alcohol Sites

T. Masuda and J. K. Stille*[1]

Contribution from the Department of Chemistry, University of Iowa, Iowa City, Iowa 52242. *Received June 13, 1977*

Abstract: The radical copolymerization of methyl vinyl ketone, 2-*p*-styryl-4,5-bis(tosyloxymethyl)-1,3-dioxolane (**4**), and *p*-divinylbenzene (2%) gave cross-linked resins (**5**) containing 9:1 and 14:1 ratios of methyl vinyl ketone to **4** in the polymer. Asymmetric reduction (hydrosilylation) of the ketone groups in **5** with catalysts (**3**) formed from the reaction of μ-dichlorotetraethylenedirhodium(I) and both (+)- and (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP) gave a polymer (**6**) bearing either *S* or *R* secondary alcohol groups, respectively. The reaction of **6** with sodium diphenylphosphide afforded a polymer (**7**) containing the (−)-2,3-*O*-benzal-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ligand and either *R* or *S* pendent alcohol functions. Exchange of Rh(I) onto the polymer-attached ligand provided a catalyst that hydrogenated α-acetamidoacrylic acid, α-acetamidocinnamic acids, and atropic acid in alcohol (solvent) to the corresponding *R* amino acids or hydratropic acid of the same absolute configuration and the same optical yield as can be obtained with the analogous homogeneous catalyst, DIOP-Rh(I). Hydrogenations of α-acetamidoacrylic acid in tetrahydrofuran, however, gave widely different optical yields of amino acid, depending on the configuration of the pendent alcohol group, suggesting that the alcohol plays a role in the transition state leading to the generation of the asymmetric center. The catalyst can be removed by filtration and reused with no loss of optical purity in the product on subsequent hydrogenations.

Introduction

In the previous paper,[2] we described the syntheses of a polar cross-linked polymer containing an optically active 4,5-bis-(diphenylphosphinomethyl)-1,3-dioxolane ligand, on which rhodium(I) was exchanged. This catalyst hydrogenated α-*N*-acylaminoacrylic acid to the corresponding amino acid derivatives having the same optical yields and absolute configurations as could be obtained with the homogeneous catalyst analogue, chloro[2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane]rhodium(I), Cl(DIOP)Rh(I). The advantage of the cross-linked polymer-attached catalyst over the homogeneous Cl(DIOP)Rh(I) catalyst is that it can be removed from the reaction by filtration and reused. A necessary requirement of such a catalyst for the hydrogenation of α-*N*-acylaminoacrylic acid, however, is that the polymer swells in the polar solvents required for dissolution of the substrates, thereby allowing access to the catalyst sites.

The ability of this polar polymer to swell in alcohol was achieved by the introduction of hydroxyethyl methacrylate units in the main chain. These units have the disadvantage, however, that they could be expected to undergo hydrolysis and alcoholysis on continued use. It was of interest, therefore, to introduce more stable, polar units into the polymer backbone of a DIOP-bearing polymer. Thus, the copolymerization of 2-*p*-styryl-4,5-bis(tosyloxymethyl)-1,3-dioxolane (**4**) with methyl vinyl ketone was of interest for a number of reasons. The polar character of the resulting copolymer could be expected to provide a suitable catalyst matrix for the hydrogenation of α-*N*-acylaminoacrylic acids. The ketone function could be reduced to a secondary alcohol, another suitably polar group, and under the appropriate conditions could be asymmetrically reduced to an alcohol of either configuration. Both ketone and secondary alcohol groups would be relatively stable under the reaction conditions.

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