$LiAlH_4$ Reductions. Allyl alcohol (5.0 mL) was hydroformylated in dry THF at 60 °C and 400 psi in the presence of $RhH(CO)(PPh_3)_3$ as described above. A portion (1.0 mL) of the resulting solution was analyzed by GLC, using *o*-xylene as an external standard, demonstrating the presence of the following known products: allyl alcohol (1.69 mmol), aldehyde **1** (2.09 mmol), and aldehyde **2** (1.22 mmol). An aliquot (1.0 mL) of the product solution was added to dry THF (10 mL) and $LiAlH_4$ was slowly added until no further reaction occurred and a small excess of $LiAlH_4$ was present. After the solution was refluxed for 3 h, cooled, and hydrolyzed with water, the organic layer was analyzed by GLC (*o*-xylene external standard). The products were 1,4-butanediol (2.08 mmol) and 2-methyl-1,3-propanediol (1.26 mmol), demonstrating that no increase in desired products could be achieved by reducing the unknown products.

Acknowledgment. This work was partially supported by the National Science Foundation, Grant DAR 7824875.

Registry No. **1**, 25714-71-0; **2**, 38433-80-6; allyl alcohol, 107-18-6; $RhH(CO)(PPh_3)_3$, 17185-29-4; $RhH(CO)(P(OPh)_3)_3$, 18346-73-1; $RhH(CO)(P(OC_6H_4Cl)_3)_3$, 22829-75-0; $RhH(CO)(P(n\text{-}Bu)_3)_3$, 22829-69-2; $RhH(CO)(PPh_3)(Ph_2PCH_2CH_2PPh_2)$, 64611-33-2; RhH(CO)(triphos), 73347-65-6; BDPF, 12150-46-8; Rh, 7440-16-6.

Supplementary Material Available: The dependence of selectivity on P/Rh using polymer-anchored catalysts; the dependence of selectivity on pressure for several systems not shown in Table III of this manuscript; and a summary of product distribution data not given in Table IV of this manuscript (3 pages). Ordering information is given on any current masthead page.

Isomerization of *N*-Allylamides and -imides to Aliphatic Enamides by Iron, Rhodium, and Ruthenium Complexes

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Received February 19, 1980

Substituted aliphatic *N*-propenylamides and -imides are readily synthesized from *N*-allylamides by double bond migration induced by rhodium or ruthenium hydrides. *N*-Propenylimides can be prepared from allylimides only in the presence of iron pentacarbonyl.

The available methods of synthesis of enamides are rather limited, allowing neither a wide variety of reactants nor reaction conditions. The most widely used method consists of the acylation of an imine with an acid chloride or an anhydride.[2]

In this paper, we report the catalytic isomerization of allylamide derivatives to a series of enamide derivatives. These compounds are potential precursors for catalytic asymmetric hydroformylation to afford amino acid intermediates, as described in the following paper.

Double-bond migration catalyzed by soluble transition-metal compounds has found few useful applications in organic synthesis. The Rh(I)-catalyzed isomerization of an allyl ether to the corresponding enol ether is used in a relatively new method for the selective removal of a protecting group from an alcohol.[3] This type of isomerization can also be effected by Fe(0)[4] complexes. The isomerization of 3-pentenonitrile to the thermodynamically unfavorable 4-isomer by a Ni(0) catalyst is an important step in the synthesis of adiponitrile from butadiene and HCN.[5]

After the work described in this paper had been completed, the enantioselective isomerization of prochiral allylamines to the corresponding optically active enamines was reported.[6] This process, effected by an optically active Co(I) catalyst, provides a new route to optically active aldehyde precursors. The iron(0)-catalyzed photoisomerization of unsubstituted *N*-allylamides[7] or the iron(0)-catalyzed thermal isomerization of *N*-allylimides affords the 2-propenyl enamides or enimides.[8]

Results and Discussion

The isomerization of *N*-allylamides to *N*-propenylamides is best effected by heating toluene or xylene solutions of the substrates with a catalytic amount (5×10^{-3} mol) of (triphenylphosphine)hydridorhodium or -ruthenium complexes. The reaction must be conducted under an inert atmosphere, and usually several hours are required for complete conversion (Table I). Unfortunately, a general catalyst could not be found, and it was necessary to match the transition-metal complex, temperature, and time with a particular substrate in order to reach optimum conditions.

The isomerization of *N*-allylacetamide (**1**) by $HRuCl(PPh_3)_3$ (**2**) or $HRh(PPh_3)_4$ (**3**) affords a cis–trans mixture of isomers (**1a,b**); the cis isomer predominates. The same isomeric composition is obtained by using a polymer-supported rhodium catalyst bearing DIOP as the phosphine ligand.[9] With the polymer-attached catalyst, the product is readily recovered simply by filtration of the catalyst and evaporation of the solvent. The catalyst may be reused for further isomerization, although a decrease in its activity was observed. A much more reactive catalyst toward substrates **1** and **5** bearing an NH group was the ruthenium hydride catalyst **2**. The isomerization of these substrates in the presence of **2** is almost completed (TLC) after 3 h in refluxing toluene. Much longer reaction times are required to achieve the same conversion with **3** (Table I). If traces of oxygen are present, the purple solutions of **2** in aromatic hydrocarbons turn green immediately, and the catalytic activity disappears. However, under an inert

(1) Present address: Research Department, Plantex-Ikapharm, Netania, Israel.
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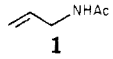
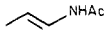
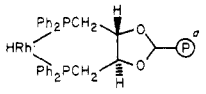
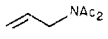
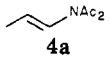
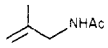
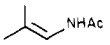
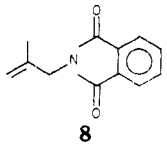
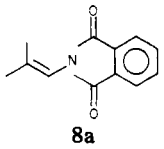
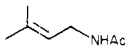
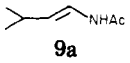
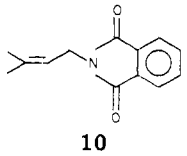
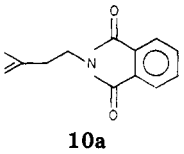
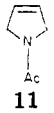
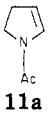
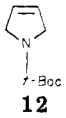
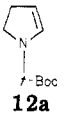
0022-3263/80/1945-2139$01.00/0

Table I. Synthesis of Enamides and Enimides

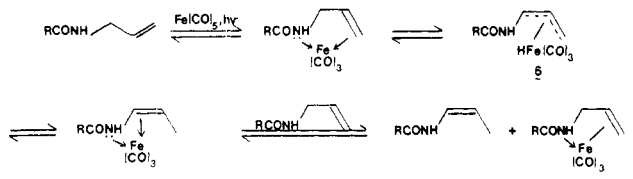
reactant	catalyst	solvent (temp, °C)	time, h	reactant/ catalyst	product	% conversion	cis/ trans
 1	$HRuCl(PPh_3)_3$ (2)	benzene (80)	40	200	 1a	80	
	2	toluene (110)	15	200	 1b	100	2
	$HRh(PPh_3)_4$ (3)	toluene (110)	24	200		80	2
		toluene (110)	24	200		80	2
 4	2	xylene (138)	48	200	 4a	trace	
	$Fe(CO)_5/Me_3NO$	benzene (80)	22	0.5		12	
 5	2	toluene (110)	22	124	 5a	95	
 8	2	toluene (110)	24	200	 8a	no reaction	
	3	xylene (138)	24	200		no reaction	
	$Fe(CO)_5$ (14)	xylene (138)	15	1		83	
 9	2	toluene (110)	24	100	 9a	traces	
	14					decomposition	
 10	14	xylene (138)	15	2	 10a	29[b]	
	$RhCl_3 \cdot 3H_2O$	ethanol (78)	15	12		29	
 11	$HRh(CO)(PPh_3)_3$	xylene (138)	44	100	 11a	92	
	2	xylene (138)	48	250		60	
	3	xylene (138)	22	200		90	
 12	14	xylene (138)	6	3.3	 12a	62	
 13	3	xylene (138)	48	250	 13a	88	

[a] A polymer-bound catalyst was used. See Experimental Section. [b] This figure indicates the composition of the reaction mixture at equilibrium.

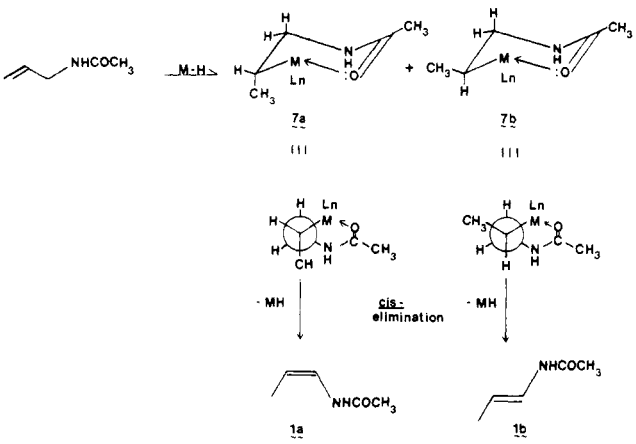
atmosphere no appreciable drop in the activity of 2 was observed. In particular, when the isomerization of 5 in the presence of 2 was completed, a fresh sample of the starting olefin was added, and heating was continued. The second batch of 5 was readily converted to 5a.

As mentioned above, the isomerization of 1 by either 2 or 3 affords as the major product the cis isomer 1a. We have established that this is a kinetically controlled product since no cis–trans thermal interconversion takes place under the reaction conditions. The observation that 1a predominates is in contrast to the Fe(0)-catalyzed photoisomerization of 1;[7] in this system the cis–trans ratio decreases with time, and eventually the major product observed is the trans isomer 1b. In order to account for the selectivity to the cis isomer 1a during the early stages of the reaction, two mechanisms, each involving coordination of the amide function to the metal, may be written (Scheme I).

Scheme I

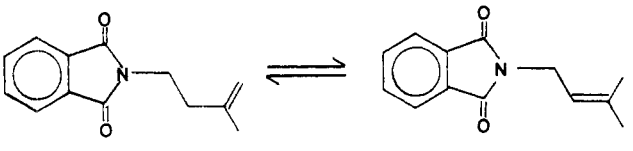


Scheme II



The hydrido-π-allyl intermediate **6** should lead exclusively to the cis olefin by hydride transfer to the terminal methylene group. Alternatively, addition of metal hydride across the terminal olefin may lead to the chelates **7a,b** (Scheme II) differing in the configuration of the methyl group α to the metal. The interaction of the methyl group with the ligands presumably is smaller in **7a** than in **7b**, thus accounting for the preponderence of **1a**. Surprisingly, the *N,N*-diacetyl derivative **4** and the imides **8** and **10** do not undergo double bond migration in the presence of **2** or **3**, even at elevated temperatures. Only $Fe(CO)_5$ (**14**) can induce isomerization in these systems.

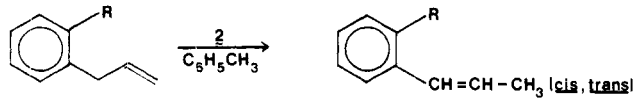
A facile isomerization of an imide is observed only in systems possessing a terminal vinyl group or endocyclic double bond. A trisubstituted double bond as in **10** can be isomerized only by using a stoichiometic amount of **14** at elevated temperatures. Under these conditions an equilibrium mixture of reactant and unexpected product (**10a**), where the double bond has migrated to the terminal



10a **10**

position of the aliphatic chain, is observed. That such an equilibrium exists was demonstrated by subjecting **10a** to the action of **14**. A ratio of **10** to **10a** of 30:70 was obtained.

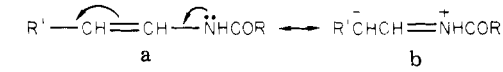
Substitution on nitrogen is essential for isomerization. Model studies conducted on substituted allylbenzene derivatives **15a–c** reveal that while **15a** and **15b** undergo smooth rearrangement to **16a,b**, the free amino derivative **15c** remains intact under the same conditions.



15a R = H
b R = $NHCOCH_3$
c R = NH_2

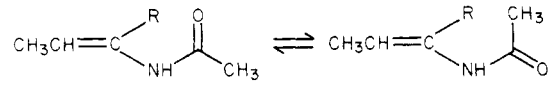
16a R = H
b R = $NHCOCH_3$
c R = NH_2

An important feature of the ^1H NMR spectra (Table II) of the enamides and enimides prepared in this study is the upfield shift of the β olefinic proton relative to the α-proton adjacent to nitrogen. This observation is in agreement with a contribution from the canonical form b. A similar trend

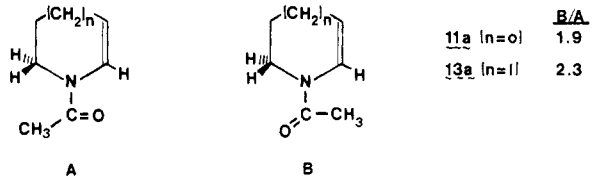


a b

is also observed in the ^{13}C NMR spectra (Table III). The NMR spectra were consistent with hindered rotation around the >NC(O)R bond at room temperature. The linear *N*-acetylpropenylamides gave rise to two forms in approximately equal concentrations:



However, in the cyclic eneamides **11a** and **13a** form B predominates.[10] Apparently the ground-state energy of form A is higher than form B due to steric repulsion between the methyl group and the methylene group α to nitrogen.



	B/A
11a (n=0)	1.9
13a (n=1)	2.3

A B

Experimental Section

A. Preparation of *N*-Allylamides. *N*-Allylacetamide (1). The procedure described by Sato[11] was followed. Allylamine (25 g, 0.43 mol) was added dropwise with stirring to acetic anhydride (75 g, 0.735 mol) at 0 °C. After the addition was completed (~1 h) the temperature was raised to ~100 °C for 1.5 h, and then the mixture was fractionally distilled. The product was collected at 87 °C (5 mmHg) [lit.[11] 100 °C (10 mmHg)] as a colorless oil: yield 40.7 g (94%); IR ($CHCl_3$) 3460 (NH free), 3340 (NH bonded), 1680 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.9 (s, CH_3CO), 3.72 (t, J = 6 Hz, CH_2—N), 5.75 (m, CH=), 4.88 (m, =CH), 5.1 (dq, J = 6.2 Hz, =CH), 6.2 (br s, NH).

***N*-Allylacetimide (4).** The procedure described above was followed.[11] When the addition was completed, the mixture was heated for 15 h. The product was distilled at 84 °C (5 mmHg) to give 27 g (36.3%) of the expected product: NMR ($CDCl_3$) δ 2.28 (s, CH_3CO), 4.2 (m, $>NCH_2$), 4.9 (dq, J = 8, 1.5 Hz, =CH), 5.15 (m, =CH), 5.75 (m, $=CHCH_2$).

***N*-(2-Methylallyl)acetamide (5).** This compound was prepared similarly from 2-methylallylamine (21.3 g, 0.3 mol) and acetic anhydride (52.3 g, 0.513 mol) in quantitative yield: bp 94–99 °C (1 mmHg); IR ($CHCl_3$) 3480 (NH free), 3370 (NH bonded), 1680 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.7 (s, CH_3CH=), 2.0 (s, CH_3CO), 3.7 (d, J = 6 Hz, $>NCH_2$), 4.76 (m, $=CH_2$), 6.23 (br s, NH).

***N*-(2-Methylallyl)phthalimide (8).** A mixture of 2-methylallylamine (10 g, 0.1 mol) and phthalic anhydride (10 g, 0.067 mol) in acetic acid (40 mL) was heated to reflux for 30 min. The solvent was removed in vacuo. The resulting solid was recrystallized from ethanol to yield 9.0 g (60%) of colorless crystals: mp 87–88 °C; NMR ($CDCl_3$) δ 1.72 (s, CH_3), 4.14 (s, $>NCH_2$), 4.78 (m, $=CH_2$), 7.65 (cm, 4 H, aromatics).

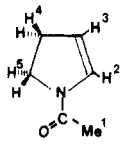
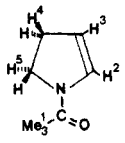
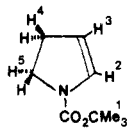
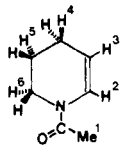
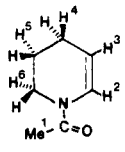
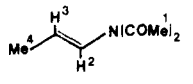
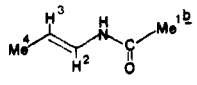
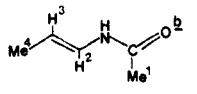
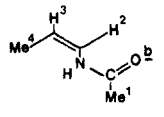
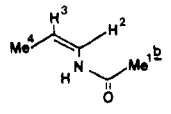
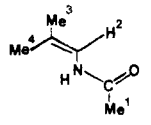
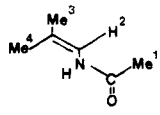
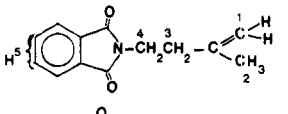
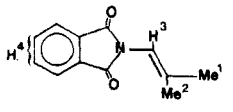
***N*-(3,3-Dimethylallyl)acetamide (9).** 3,3-Dimethylallylamine was prepared from dimethylallyl bromide as described.[12] The crude hydrochloride was not purified as in the original preparation

(10) Assignment of the two rotamers A and B is in accordance to the assignment of the methyl groups in DMF. See: Anet, F. A. L.; Bourn, A. J. R. *J. Am. Chem. Soc.* **1965**, *87*, 5350; Bovey, F. A. In "Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1969; pp 75–77.

(11) Sato, Seiichi *Nippon Kagaku Zasshi* **1969**, *90*, 404.

(12) Hebrard, P.; Olomucki, M. *Bull. Soc. Chim. Fr.* **1970**, 1938.

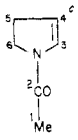
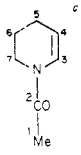
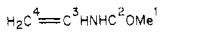
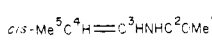
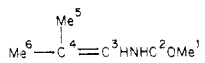
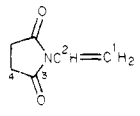
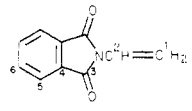
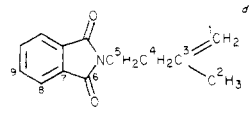
Table II. ^{1}H NMR Spectra of Isomeric Enamides

compd[a]	H^1	H^2	H^3	H^4	H^5	H^6
	2.1 (s)	6.38 (m)	5.15 (m)	2.8 (cm)	3.8 (t, J = 9 Hz)	
	2.0 (s)	6.82 (m)	5.15 (m)	2.8 (cm)	3.8 (t, J = 9 Hz)	
	1.49 (s)	6.46 (br m)	4.95 (m)	2.6 (m)	3.7 (t, J = 8 Hz)	
	2.1 (s)	6.46 (dt, J = 9, 2 Hz)	4.9 (m)	1.99 (cm)		3.6 (br t)
	2.1 (s)	7.08 (dt, J = 9, 2 Hz)	4.9 (m)	1.99 (cm)		3.6 (br t)
	1.98 (s)	6.64 (dt)	5.1 (dq, J = 14 Hz)	1.6 (dd, J = 6, 2 Hz)		
	1.91 (s)	6.76 (dq, J = 14.3 Hz)	5.13 (dq)	1.61 (dd, J = 6.72, 1.71 Hz)		
	1.91 (s)	6.65 (dq)	5.13 (dq)	1.61 (dq)		
	1.974 (s)	6.70 (dq, J = 9.52 Hz)	4.65 (dq)	1.6 (dd, J = 7.18 Hz)		
	1.974 (s)	6.6 (dq)	4.65 (dq)	1.6 (dd)		
	2.0 (s)	6.6 (m)	1.62 (s)	1.64 (s)		
	2.0 (s)	6.3 (m)	1.62 (s)	1.64 (s)		
	4.65 (cm)	1.8 (s)	2.28 (t, J = 7 Hz)	3.8 (t, J = 6.8, 7.3 Hz)	7.7 (cm)	
	1.68 (d, J = 2 Hz)	1.95 (d, J = 2 Hz)	5.8 (m)	7.7 (m)		

[a] All spectra were run at 60 MHz in $CDCl_3$, and all values are given in δ units relative to Me_4Si unless otherwise noted. [b] Spectra were run at 90 MHz in $(CD_3)_2CO$.

but instead was suspended in benzene, excess moist K_2CO_3 was added, and after the mixture was stirred for 30 min an excess of acetic anhydride was added. After 1 h the mixture was cooled to 25 °C and filtered, and the mother liquor was concentrated in vacuo. The residue was purified by column chromatography on silica gel. The product was eluted with 30% acetone–petroleum ether as a colorless oil: 17.3% yield; NMR ($CDCl_3$) δ 1.80 (m, $(CH_3)_2C=$), 1.97 (s, CH_3CO), 3.80 (t, J = 6 Hz, $>NCH_2$), 5.17 (tm,

Table III. ^{13}C NMR Spectra of Enamides

compd[a]	chemical shifts[b] [$J(^{13}C\ H)$, Hz, in parentheses]						
	C^1	C^2	C^3	C^4	C^5	C^6	C^7
	21.4 21.8	165.8	129.7 129.3	109.5 108.7	30.2 28.3	45.6 44.8	
	21.5 21.2	167.4 167.2	125.6 123.6	107.8 107.6	39.9	21.7	44.25
	22.87 (17.19)	168.32	128.56 (32.67)	95.51 (48.1)			
	22.91 (17.2)	168.18	121.75 (48.14)	105.85 (33.52)	11.06 (15.4)		
	22.75 (14.6)	167.81	115.8 (6.87)	117.85	22.5 (8.6)	16.57 (15.5)	
	105.8	123.9	175.2	27.7			
	103.9	123.5	165.8	131.2	123.2	134.0	
	112.5	22.0	141.8	36.3	36.4	167.9	131.8

[a] All chemical shifts are in δ units and were recorded in $CDCl_3$ at 90 MHz relative to Me_4Si unless otherwise noted. [b] Two different sets of ^{13}C chemical shifts were observed for each rotameric pair. [c] Spectra were run in C_6D_6. [d] C^8, δ 122.9; C^9, δ 133.6.

J(t) = 6 Hz, =CH), 5.60 (vbr, NH).

***N*-(3,3-Dimethylallyl)phthalimide (10).** A solution of 3-methyl-2-buten-1-ol (5.0 g, 58 mmol) in 20 mL of ether was cooled to 0 °C, 2.1 mL (22 mmol) of phosphorous tribromide was added over 0.5 h, and then the mixture was stirred at 25 °C overnight. The mixture was heated to reflux for 1 h and then poured on ice, and the aqueous phase was extracted with ether (4 × 30 mL). The combined extracts were dried ($MgSO_4$), and after removal of the solvent at 200 mmHg the colorless residue was characterized as 1-bromo-3-methyl-2-butene (6.7 g, 77.5%) by its NMR spectrum.

The above product was stirred with potassium phthalimide (8.93 g) in DMF (30 mL). An exothermic reaction was observed. Stirring was continued overnight, and after being heated to 60 °C for 1 h, the mixture was cooled to 25 °C and poured on ice. The aqueous layer was extracted with chloroform (3 × 30 mL), and the $CHCl_3$ extracts were washed with 0.2 N sodium hydroxide and water and dried ($MgSO_4$). The solvent was evaporated under reduced pressure, and the residue was recrystallized from methanol: mp 100–102 °C (lit.[13] mp 101–102 °C); NMR ($CDCl_3$) δ 1.67 (s, CH_3), 1.78 (s, CH_3), 4.2 (d, J = 8 Hz, $>NCH_2$), 5.2 (t, CH=), 7.72 (cm, 4 H, aromatics).

***N*-Acetyl-3-pyrroline (11).** This compound was prepared by the procedure described:[14] mp 60–62 °C (lit.[14] mp 56–61 °C); IR ($CHCl_3$) 1650, 1620 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.9 (s, CH_3CO), 4.08 (s, $>NCH_2$), 5.68 (m, CH=).

***N*-(*tert*-Butoxycarbonyl)-3-pyrroline (12).** A mixture of 3-pyrroline (5.0 g, 72.3 mmol), *tert*-butoxycarbonyl azide (10.4 g, 72.3 mmol), *p*-dioxane (20 mL), water (20 mL), and triethylamine (10 mL) was stirred at 50 °C for 15 h. The mixture was concentrated under reduced pressure to one-third of its original volume, and the residue was extracted with ether (4 × 30 mL). The combined extracts were dried ($MgSO_4$), the solvent was removed under reduced pressure, and the residue was distilled at 60–61 °C (65 μm). The product was obtained as a colorless oil: 10.5 g (63.25 mmol, 87.5%); NMR ($CDCl_3$) δ 1.49 (s, $(CH_3)_3C$), 4.15 (s, $>NCH_2$), 5.78 (br s, CH=).

***N*-Acetyl-1,2,3,6-tetrahydropyridine (13).** A mixture of 1,2,3,6-tetrahydropyridine (24 g, 0.29 mol), potassium carbonate (45 g), and benzene (80 mL) was vigorously stirred while acetic anhydride (36 g) in benzene (20 mL) was added. When the evolution of carbon dioxide subsided, the mixture was heated to 80 °C for 2 h. The mixture was diluted with benzene (80 mL) and filtered. The solid was washed with chloroform, and the combined filtrates were concentrated in vacuo. The residue was distilled at 87 °C (1 mmHg) to yield 27.4 g (75.5%) of product: IR (neat) 1650 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 2.0 (s, CH_3CO), 3.5 (dq, NCH_2CH=, J = 10, 6 Hz), 5.6 (m, CH=CH), 2.08 (m, CH_2CH_2CH=), 3.89 (m, NCH_2CH_2).

B. Preparation of Enamides. *N*-Propenylacetamide (1a,b). A solution of 1.0 g (10 mmol) of 1 in 5 mL of degassed benzene containing $HRuCl(PPh_3)_3 \cdot C_6H_6$ ($2 \cdot C_6H_6$;[15] 50 mg, 0.05 mmol) was stirred and heated to reflux under argon for 40 h. After the mixture cooled, the solvent was removed under reduced pressure, and the oily residue was distilled in a Kugelrohr apparatus at 110 °C (20 μm). The resulting colorless solid (919 mg) contained 71% of the isomerized olefin and 29% of unchanged 1.

The reaction was repeated with refluxing toluene as solvent and a substrate to catalyst ratio of 250. After 15 h, TLC analysis indicated complete conversion. The product was purified as above and recrystallized twice from ether/hexane to afford colorless

(13) Desrages, G.; Olomucki, E. M. *Bull. Soc. Chim. Fr.* **1969**, 3229.
(14) Oida, S.; Kumano, H.; Ohashi, Y.; Ohki, E. *Chem. Pharm. Bull.* **1970**, *18*, 2478.
(15) Hallman, P. S.; McGarvey, B. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3143.

needles of the cis isomer **1a**. Traces of the trans isomer were still present (NMR). For **1a**: mp 67–70 °C; IR ($CHCl_3$) 3460 (NH free), 3370 (NH bonded), 1690, 1670 (C=O) cm^{-1}. Anal. Calcd for C_5H_9NO: C, 60.52; H, 9.07; N, 14.13. Found: C, 60.08; H, 9.28; N, 14.23. The reaction mixture was completely separated on a medium-pressure liquid chromatograph (silica gel, 30% acetone–hexane, 40 psi, 100 × 2 cm glass column). Each isomer was sublimed at 40 °C (0.01 mmHg). The melting point of the cis isomer **1a** was 71 °C and that for **1b** was 73 °C.

Determination of the cis–trans ratio in the reaction mixture was readily carried out by means of NMR at 60 MHz in C_6D_6. Integration between 4.3 and 5.4 ppm yielded the exact isomeric composition. Compound **1** was isomerized by a 20% divinylbenzene cross-linked polystyrene-supported Rh catalyst containing the DIOP ligand.[9] Rhodium was exchanged onto the polymer (78 mg, 0.05 mequiv, of diphosphine) by heating a suspension of the polymer in 5 mL of degassed benzene containing **3**[16] (58 mg, 0.05 mmol) at 50 °C for 20 h. The yellow material was filtered under argon, continously extracted with benzene for 2 days, and then dried in vacuo. This catalyst was used to isomerize 1.0 g of **1** in 5 mL of boiling toluene under argon. In a controlled experiment, **1** (1.0 g) was isomerized by **3** (56 mg) in 5 mL of boiling toluene. The reactions were monitored by TLC. After 24 h both reaction mixtures were analyzed by NMR. In each case about 80% conversion was observed, and the cis–trans ratios (**1a**/**1b**) were approximately 2. Unlike the homogeneous system, in the heterogeneous system a colorless solution was obtained, and the catalyst was readily recovered by filtration. Although the polymer-supported catalyst darkened during the reaction, it could be used for another catalytic cycle. However, after 24 h only 50% conversion was obtained by using **1** again as the substrate.

***N*-Propenylacetimide (4a).** Isomerization of **4** (2.0 g, 14.2 mmol) with **2** (114 mg, 0.114 mmol) in boiling *m*-xylene for 48 h yielded only traces of **4a**. Compound **4** (1.0 g, 7 mmol) was stirred with anhydrous trimethylamine oxide (2.1 g, 28 mmol) in benzene (10 mL) at 0 °C, and iron pentacarbonyl (**14**) (1.92 mL, 14 mmol) was added. Gas evolution was observed, and the solution turned red. Heating the mixture to reflux under argon for 22 h induced some isomerization (TLC analysis, silica gel chromatoplate, 30% acetone–hexane as developer; R_f of **4** 0.45; R_f of **4a** 0.28). The product was obtained in 11.4% yield by chromatography on silica gel (20% acetone–hexane). NMR indicated that only the trans isomer was formed (J(vicinal) = 14 Hz).

***N*-(2-Methylpropenyl)acetamide (5a).** A solution of **5** (1.0 g, 8.85 mmol) and **2** (85.2 mg, 0.085 mmol) in toluene (5 mL) was heated to reflux under nitrogen. After 5 h most of the starting material disappeared (TLC analysis on silica gel chromatoplate, 1:2 benzene–ethylacetate; R_f of **5** 0.24; R_f of **5a** 0.35). Complete conversion was reached after 21.5 h. The resulting homogeneous red solution was still catalytically active since an aliquot (2.0 mL) from this solution added to a solution of **5** (1.0 g) in 2.5 mL of thoroughly degassed toluene brought about almost complete conversion to **5a** after 24 h at 110 °C.

The product was isolated by removal of the solvent in vacuo followed by distillation of the residue in a Kugelrohr apparatus (100 °C at 12 μm). A colorless solid was obtained in 95% yield. An analytical sample was prepared by chromatography on silica gel (30% acetone–hexane) followed by sublimation at 65 °C (0.01 mmHg): mp 44–45 °C (lit.[17] mp 48–50 °C); IR ($CHCl_3$) 3480 (NH free), 3360 (NH bonded), 1685 (C=O) cm^{-1}. Anal. Calcd for $C_6H_{11}NO$: C, 63.68; H, 9.79; N, 12.37. Found: C, 63.79; H, 10.06; N, 12.43.

***N*-(2-Methylpropenyl)phthalimide (8a).** Attempted isomerization of **8** with **3** in boiling *m*-xylene or **2** in boiling toluene for 22 h did not produce the desired product. Addition of equivalent amounts of acetamide had no effect.

When **8** (1.0 g, 4.98 mmol) and **14** (0.682 mL, 4.98 mmol) in *m*-xylene (10 mL) were heated to reflux under nitrogen for 21 h, a dark brown heterogeneous mixture was obtained. After the mixture cooled to room temperature, charcoal was added and the mixture filtered. The yellow filtrate was concentrated in vacuo, and the residue was recrystallized from hexane to afford off-white needles (83%). NMR analysis indicated that the isomeric purity was ~90%. An analytical sample was prepared by sublimation at 80 °C (20 μm) followed by recrystallization from hexane; mp 90–91 °C. Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.64; H, 5.47; N, 6.96. Found: C, 71.67; H, 5.56; N, 7.21.

Attempted Preparation of *N*-(3-Methyl-1-butenyl)acetamide (9a). A solution of **9** (750 mg, 5.9 mmol) in 5 mL of toluene was heated for 24 h in the presence of **2** (59 mg, 0.059 mmol) under nitrogen. NMR and TLC analysis indicated that no change took place. Heating **9** in boiling *m*-xylene in the presence of an equivalent amount of **14** caused complete decomposition.

***N*-(3-Methyl-3-butenyl)phthalimide (10a).** Compounds **10** 3.0 g, 15.7 mmol) and **14** (1 mL, 7.28 mmol) were heated to reflux in *m*-xylene (10 mL) under nitrogen for 15 h. NMR analysis indicated 29% conversion to **10a** and 70% of **10**. No change in this composition occurred with an extended period of heating or additional amounts of **14**. Removal of the solvent in vacuo yielded crystalline material, which was purified by five successive triturations with hexane (10 mL each). From 1.982 g of the crude mixture of **10** and **10a** this process yielded an oily residue (0.406 g) containing 84% of **10a**. Purification by recrystallization from hexane afforded a crystalline product, mp 54 °C (92–96% isomerically pure).

All attempts to achieve any isomerization with other catalysts [(triphenylphosphine)iron carbonyl, diiron carbonyl, tetrakis(triethyl phosphite)nickel/TFA, tetrakis(triphenylphosphine)rhodium hydride] did not afford isomerized product. However, heating **10** in ethanol in the presence of rhodium trichloride trihydrate yielded the same isomeric mixture as obtained with **14**.

Equilibration of 10a with 14. Isomer **10a** (0.5 g, 85% isomerically pure) was heated in toluene (12 mL) in the presence of **14** (0.5 mL) for 18 h under nitrogen. The reaction mixture was filtered, and the solvent was removed under reduced pressure to yield 0.4 g of semisolid. NMR analysis indicated that a mixture of **10** and **10a** (30:70) was obtained.

***N*-Acetyl-2-pyrroline (11a).** Compound **11** (1.0 g, 9.0 mmol) in degassed *m*-xylene (5 mL) and tris(triphenylphosphine)-hydridocarbonylrhodium (82.8 mg, 0.09 mmol) were heated to reflux under nitrogen for 44 h. After cooling to room temperature, the solution was mixed with hexane (20 mL) and filtered, and the filtrate was concentrated in vacuo. Distillation in a Kugelrohr apparatus at 130 °C (20 mmHg) afforded 818.5 mg (92%) of 90% isomerically pure product.

Compound **11** (2.0 g, 18 mmol) in *m*-xylene (10 mL) and **2** (72 mg, 0.072 mmol) were heated to reflux under nitrogen for 48 h. Purification on a silica gel column (ethyl acetate–hexane) followed by distillation in a Kugelrohr apparatus at 130 °C (15 mmHg) afforded 1.185 g, 59% of 90% isomerically pure product.

Compound **11** (1.89 g, 17 mmol) in *m*-xylene (10 mL) and **3** (98 mg, 0.085 mmol) were heated to reflux under argon for 22 h. The usual workup afforded 1.71 g (90.5%) of **11a** as a colorless oil, 93% isomerically pure. TLC analysis indicated traces of **11**: IR ($CHCl_3$) 1645, 1620 (C=O) cm^{-1}. Anal. Calcd for C_6H_9NO: C, 64.84; H, 8.16; N, 12.60. Found: C, 65.93; H, 8.64; N, 1.23. **11a** decomposes completely in chloroform after several days. It darkens on exposure to air for several days and is best stored at −20 °C under argon.

***N*-(*tert*-Butoxycarbonyl)-2-pyrroline (12a).** A mixture of **12** (4.0 g, 24 mmol) and **14** (1 mL, 7.28 mmol) in degassed *m*-xylene (10 mL) was heated to reflux under nitrogen for 6 h. After the mixture was cooled to room temperature and filtered, the resulting solution was passed through a silica gel column, eluting the product with 10% acetone–hexane. Distillation in a Kugelrohr apparatus at 80 °C (10 μm) afforded **12a** as a colorless oil (62% yield). The compound is air sensitive and should be stored under an inert atmosphere. Anal. Calcd for $C_9H_{15}NO_2$: C, 63.90; H, 8.87; N, 8.28. Found: C, 63.13; H, 9.02; N, 8.13.

***N*-Acetyl-1,2,3,4-tetrahydropyridine (13a).** Compound **13** (3.0 g, 24 mmol) was isomerized with **3** (138 mg, 0.12 mmol) in boiling *m*-xylene (10 mL) under nitrogen for 48 h. Fractionation of the mixture under reduced pressure afforded the product (2.65 g, 88% recovery) in >80% isomeric purity; bp 135 °C (10 mmHg). Further purification was achieved by chromatography on silica

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(17) Kurtz, P.; Disselnkotter, H. *Justus Liebigs Ann. Chem.* **1972**, *764*, 69.

gel, eluting the isomerically pure product with 20% acetone–hexane: yield 1.833 g (61%); IR (neat) 1670, 1645 (C=O) cm^{-1}. The compound should be handled as **12a**.

Isomerization of Substituted Allylbenzenes (15a–c). Isomerization on **15a–c** was effected in boiling toluene by using **2** as a catalyst and a substrate to catalyst ratio of 200.

Acknowledgment. The authors wish to thank Dr. A. Eisenstadt for isolating compound **10a** in pure form and for the establishment of the existence of the equilibrium **10** ⇌ **10a**. This research was supported by the National Science Foundation (Grant CHE 77-08349).

Registry No. **1**, 692-33-1; **1a**, 5202-79-9; **1b**, 5202-80-2; **2**, 22493-02-3; **3**, 18284-36-1; **4**, 14778-37-1; **4a**, 65693-80-3; **5**, 73286-67-6; **5a**, 5202-82-4; **8**, 6335-03-1; **8a**, 73286-68-7; **9**, 73286-69-8; **10**, 15936-45-5; **10a**, 20213-82-5; **11**, 21399-13-3; **11a**, 23105-58-0; **12**, 73286-70-1; **12a**, 73286-71-2; **13**, 18513-75-2; **13a**, 19615-27-1; **14**, 13463-40-6; **15a**, 300-57-2; **15b**, 68267-69-6; **15c**, 32704-22-6; **16a**, 637-50-3; **16b**, 73286-72-3; allylamine, 107-11-9; acetic anhydride, 108-24-7; 2-methylallylamine, 2878-14-0; phthalic anhydride, 85-44-9; 3,3-dimethylallylamine hydrochloride, 26728-58-5; 3-methyl-2-buten-1-ol, 556-82-1; 1-bromo-3-methyl-2-butene, 870-63-3; potassium phthalimide, 1074-82-4; 3-pyrroline, 109-96-6; *tert*-butoxycarbonyl azide, 1070-19-5; 1,2,3,6-tetrahydropyridine, 694-05-3; $RhCl_3 \cdot 3H_2O$, 13569-65-8; $HRh(CO)(PPh_3)_3$, 17185-29-4.

Asymmetric Hydroformylation and Hydrocarboxylation of Enamides. Synthesis of Alanine and Proline

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Received February 19, 1980

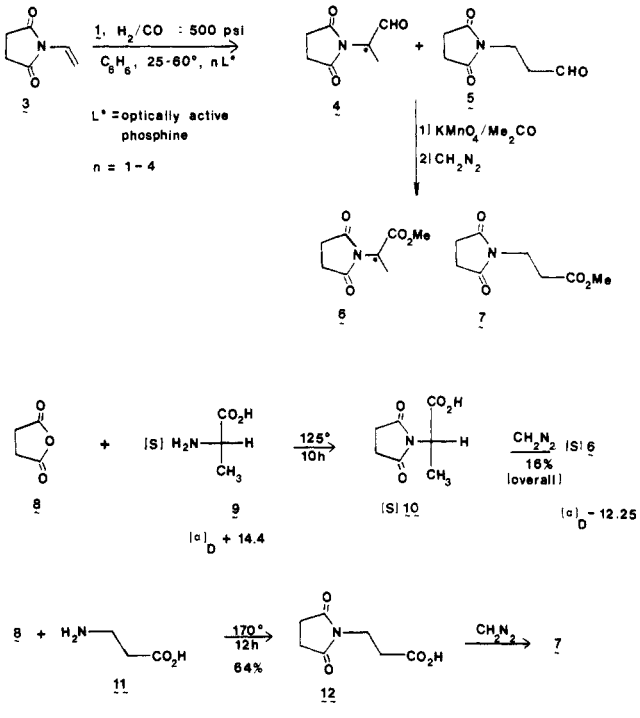
Carbonyltris(triphenylphosphine)hydridorhodium (1) catalyzed the hydroformylation of *N*-vinylimides in the presence of optically active 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP) or 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(5*H*-dibenzophospholyl)butane (DIPHOL) to afford optically active α-amido aldehydes. Linear disubstituted *N*-vinylimides or -amides reacted very sluggishly, while the cyclic *N*-acyl-2-pyrroline (**19**) was very reactive. In the unsubstituted *N*-vinylimides moderate (20–40% ee) asymmetric induction was observed. The optically active α-amido aldehydes were readily converted to the corresponding α-amino acids. Asymmetric hydrocarboxylation of the same substrates in the presence of bis(triphenylphosphine)palladium chloride (**2**) produced α-amido esters in low optical purity.

The rhodium-catalyzed asymmetric hydroformylation has been confined in the past mainly to simple olefins. Generally, low asymmetric induction (up to 27% ee) was observed with DIOP as the chiral phosphine[2] (Figure 1). Higher optical yields (~44% ee) and better selectivity to the branched aldehyde were claimed with DIPHOL as a ligand.[3] The palladium-catalyzed asymmetric hydrocarboxylation of simple olefins afforded high optical yields (up to 60% ee) of branched esters but at relatively high pressures.[4] However, when DIPHOL was used in place of DIOP and the pressure was lowered, the maximum asymmetric induction observed was ~47% ee.[5]

In the rhodium-catalyzed asymmetric hydrogenation of vinylamides, considerably higher optical yields were obtained than with simple olefins as substrates. Recently it was demonstrated[6] that prior coordination of the substrate through the amide group and the double bond takes place, creating a π complex in which the rigidity is responsible for the high stereoselectivities observed.

We had expected the same trend in stereoselectivity in going from simple olefins to vinylamides as substrates for hydroformylation or hydrocarboxylation, provided that a similar type of coordination also takes place in these systems. Limited information on the cobalt-[7a] and rhodium-catalyzed[7b] hydroformylations of vinylamides has been published, but no asymmetric hydroformylation or hydrocarboxylation of these substrates has been reported.

Scheme I



Results and Discussion

1. Hydroformylation. The hydroformylation of vinylamides or -imides generally was carried out under 500 psi of synthesis gas (H_2/CO ratio of 1:1), temperatures in

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