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Homogeneous and heterogeneous catalytic asymmetric reactions

IV *. Hydrogenation of the Ni complexes of cinnamic acid salts over MRNi catalyst

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Abstract

Substituted cinnamic acids containing a prochiral C=C bond, and their Li^{I}, K^{I}, Ni^{II} and Ca^{II} salts, were prepared and their surface complexes on Ni were studied over a Raney–Ni catalyst modified with tartaric acid. The hydrogenation product of sodium cinnamate is optically active. Of the alkali metal salts of (*E*)-α-phenylcinnamic acid, the hydrogenation of the Na salt gives the highest optical yield (17%). The solvent used significantly influences the selectivity. The published data for the chiral Rh complexes are listed for comparison with the results of the homogeneous and heterogeneous hydrogenations described.

The enantioselectivity in the presence of Raney–Ni is the result of a complex formed by the interaction of (*R*,*R*)-tartaric acid with the substrate.

Introduction

Numerous investigations have been performed to determine the correlation between the structure of the substrate and the optical selectivity of the catalyst. TA–NaBr–MRNi, a Raney–Ni catalyst modified with tartaric acid and sodium bromide, has proved to be a specific catalyst for the hydrogenation of ketones [1], β-ketoesters [2], β-diketones [3], β-ketoalcohols [4] and β-ketosulphones [5]. The prochiral substrates containing the C=N bond, however, show only moderate enantioselectivity [6–9], and efforts to achieve the enantioselective hydrogenation of the prochiral C=C bond on MRNi have met with little success [7,10,11].

* For part III see ref. 27.

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Table 1

Published data on chiral hydrogenation of the C=C bond on heterogeneous catalysts

Entry	Substrate	Catalyst	Optical yield (%)	Ref.
1	PhC(Me)=CHCOO$^-$ K$^+$	RNi-*d*-glucose	0.5	12
2	PhC(Me)=CHCOOH hydrocinchonine salt	Adams PtO_2	8–9	13
3	PhCH=C(Me)COOH	Pd–quinine salt/silicagel	3.21	14
4		Pd–quinidine salt/silicagel	1.66	14
5		Pd–cinchonine salt/silicagel	1.74	14
6		Pd–cinchonidine salt/silicagel	3.25	14
7		Pd–poly-L-leucine	1.18	15
8		Pd–poly-γ-benzyl-L-glutamic acid	4.15	16
9		Pd–poly-β-benzyl-L-aspartic acid	1.43	16
10		Pd–poly-L-valine	0.90	15
11	MeOOCC(Me) = CHCOOMe	RNi–D-tartaric acid	0	17
12	CH_2=C(Ph)COOMe	RNi–MeCH(OMe)COOH	0.03	18
13		RNi–MeCH(OMe)CH_2COOH	0.02	18
14		RNi–MeCH(OMe)$(CH_2)_2$COOH	0.09	18
15	CH_2=C(Ph)COOEt	RNi–L-alanine	0.44	18
16		RNi–L-glutamic acid	0.14	18
17		RNi–L-tartaric acid	0.01	18
18	PhCH=C(Ph)COOMe	RNi–L-tartaric acid	0	7

Since the monographs covering this field [10,11] do not discuss the enantioselective hydrogenation of the prochiral C=C bond, in Table 1 we have collected all the experimental observations relating to this topic (Table 1). In this context, Izumi and Tai [11] state that "there are two types of enantioface-differentiating heterogeneous catalysts: in one, the metal is deposited on a chiral support (silk–palladium type), and in the other the chiral modifier is adsorbed on the metal catalyst (MRNi type). Both types can hydrogenate C=O, C=N and C=C bonds".

A special chapter in the monograph by Klabunovskii and Vedenyapin [10] deals with the correlations between substrate structure and optical yield. Apart from the essential observations, however, they do not describe the anomalies associated with the enantioselective hydrogenation of substrates containing C=O and C=C bonds.

The latest monograph by Izumi [1] does go further, and makes the following note on the hydrogenation of the C=C bond: "The hydrogenation of C=C must take place at a distant place from the surface with weakly polarized hydrogen, because polarization of C=C is very weak. Thus, the hydrogenation activity of RNi for C=C is not affected by modification". The experimental results we reported previously [19] do not support this statement.

In our opinion, the failure of C=C compounds to display enantioselectivity is probably attributable to the absence of an appropriate binding site in the examined substrates, which do not form a complex with the catalyst or with the chiral group of the modifier. This was set as the starting-point. From published findings [19–25], we selected various salts of carboxylic acids containing a prochiral C=C bond as model compounds for a study of enantioselective hydrogenation.

Experimental

Materials

Ni–Al alloy (Fluka, Ni: Al = 1 : 1) was used to prepare the catalyst. Ethyl acetoacetate (EAA) (Reachim.) was dried over $MgSO_4$ (siccative) and distilled before use.

(2*R*,3*R*)-(+)-Tartaric acid (Aldrich), (2*S*,3*S*)-(−)-tartaric acid (Reanal) and α-methylcinnamic acid (Aldrich) were sufficiently pure, and were therefore not purified before reaction.

(*E*)- and (*Z*)-α-phenylcinnamic acid and (*E*)- and (*Z*)-α-phenyl-4-methoxycinnamic acid were synthesized by the method of Fieser [26]. β-Methylcinnamic acid was prepared by the method of Lipkin and Stewart [13]. For the comparison of the free acids with the esters, methyl (*E*)-α-phenylcinnamate, methyl α-methylcinnamate and methyl β-methylcinnamate were prepared from the corresponding acids with diazomethane in ether. The physical constants of the compounds are given in Table 2.

Synthesis of alkali metal salts of (E)-α-phenylcinnamic acid. The appropriate carboxylic acid was dissolved in 15% alkali metal hydroxide solution with heating. After dissolution, the solution was filtered and cooled. Some minutes later, the salt crystallized out. The crystals were filtered off and dried under vacuum at 150 °C. The yield was around 70%.

Synthesis of sodium (Z)-α-phenylcinnamate and sodium β-methylcinnamate. The appropriate carboxylic acid was dissolved in absolute diethyl ether (a nearly saturated solution was made) and was mixed with an equimolar quantity of 20% sodium ethylate in ethanol. The sodium salt crystallized out quickly. The product was filtered off, washed with diethyl ether and dried. The yield was around 40%.

Synthesis of nickel and calcium di((E)-α-phenylcinnamate). To a solution of sodium (*E*)-α-phenylcinnamate in water (a 2% solution), was added 0.6 mole solid $CaCl_2$ or $NiCl_2$. Upon gentle heating, the Ca^{II} or Ni^{II} salt crystallized out. The crystals were filtered off, washed with water and dried. The yield was around 40%.

The salts were characterized by CH analysis and identified from their IR and ^1H NMR spectra. Their physical constants are given in Table 3.

The solvents used were dried and distilled before use.

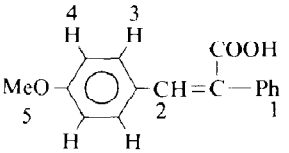
Table 2

Physical data for compounds previously prepared by published procedures

Compounds	Physical data (°C)	Ref.
(*E*)-α-Phenylcinnamic acid	mp: 172–173	26
(*Z*)-α-Phenylcinnamic acid	mp: 136–137	26
Methyl-(*E*)-α-phenylcinnamate	mp: 74.5–75.5	26
Methyl-α-methyl-cinnamate	mp: 38–39 bp: 137–138/16 mmHg	(Aldrich)
Methyl-β-methylcinnamate	mp: 28–29 bp: 127–128/10 mmHg	13
(*E*)-α-Phenyl-4-methoxycinnamic acid	mp: 192–194	26
(*Z*)-α-Phenyl-4-methoxycinnamic acid	mp: 125–127	26

Table 3

Various physical, analytical and spectroscopic data for the newly synthesized compounds



Compounds	Mp (°C)	Anal. (found (calcd.) (%))		IR [a] (cm^{-1})		^{1}H NMR [b] (ppm)				
		C	H	C(=O)$_2$ as	C(=O)$_2$ sym	5	4	3	2	1
Sodium (*E*)-α-phenylcinnamate	354–355	73.28(73.16)	4.66(4.50)	1600	1390	–	7.15		7.65	7.34
Potassium (*E*)-α-phenylcinnamate	300–307	68.65(68.67)	4.19(4.23)	1580	1380	–	7.05		7.55	7.30
Lithium (*E*)-α-phenylcinnamate	295–297	78.11(78.26)	4.68(4.82)	1590	1400	–	7.10		7.88	7.30
Calcium di-[(*E*)-α-phenylcinnamate]	320–325	73.96(74.05)	4.67(4.56)	1560	1410	–	7.07		7.98	7.24
Nickel di-[(*E*)-α-phenylcinnamate]	318–322	70.85(71.32)	4.71(4.71)	1600	1400	–	7.15		7.75	7.32
Sodium (*Z*)-α-phenylcinnamate	303–310	72.89(73.16)	4.81(4.50)	1552	1412	–	7.23		7.63	6.42
Sodium (*E*)-α-phenyl-4-methoxycinnamate	304–306	68.94(69.56)	4.40(7.74)	1560	1390	3.63	6.52	6.88	7.59	7.18
Sodium (*Z*)-α-phenyl-4-methoxycinnamate	294–296	68.70(69.56)	4.76(4.74)	1570	1414	3.72	6.77	7.23	6.35	7.57
Sodium β-methylcinnamate	321–324	65.13(65.21)	4.82(4.92)							

[a] IR spectra were recorded in KBr tablets on a Unicam SP 200 instrument. [b] NMR spectra were recorded in Me_2SO in the presence of Me_4Si as internal standard on a JEOL C-60HL instrument.

The hydrogen for the catalytic hydrogenation was purified by passage through a Pd thimble (Johnson-Matthey Metals, Model H(28)1, London).

The methods A and B that were used in the preparation of RNi, and the hydrogenation procedure are described in detail in part III of this series [27].

Isolation of the hydrogenation products of the cinnamic acid salts

The catalyst was removed from the solution and the solvent was evaporated off. The solid residue was dissolved in a mixture of 20 cm^3 ethyl acetate and 40 cm^3 0.5 *N* HCl. The ethyl acetate phase was washed with water and dried over Na_2SO_4 (siccative). After filtration, the ethyl acetate was evaporated off in vacuo.

Isolation of the hydrogenation products of the cinnamic acid esters and cinnamic acids

The products were isolated by the same method as that used for the hydrogenation products of the cinnamic acid salts, except that the reactant mixture was dissolved in pure ethyl acetate.

The purity of the compounds was determined by CH analysis, ^1H NMR and IR spectroscopy.

The optical activity of 2,3-diphenylpropionic acid was determined in a 10 g/100 cm^3 acetone solution, and those of the other compounds in the solvents listed in Table 4, in a sample cell of length 0.5 dm (Polamat A, Zeiss).

The specific rotation was calculated from the following equation:

$$[\alpha]_D^{20} = \frac{\alpha_D^{20}\ (\text{measured})}{c \times l} \times 100$$

c = concentration of sample, g/100 cm^3,
l = length of the sample cell, dm.

The optical yield was calculated from the equation given in reference [27]. The specific rotation of 2,3-diphenylpropionic acid was taken to be $[\alpha]_D^{20} = 133.7°$ [28].

Results and discussion

Enantioselective hydrogenation of compounds containing a prochiral C=C bond

The MRNi catalyst is effective mainly in the hydrogenation of compounds containing a prochiral C=O bond. However no enantioselectivity was found in the transformations of prochiral olefins [29]. This marked difference is probably attributable to the exclusive ability of the ketones to interact with the tartaric acid adsorbed on the surface. This interaction is very much favoured when an oxo, an ester, a sulphone or a hydroxy group is β to the C=O group.

The results obtained during the study of the hydrogenation of compounds (**I–II**) containing a prochiral C=C bond are listed and named in Table 4.

The rate of hydrogenation of the olefin-carboxylic acid esters (Table 4, compounds **2** and **3**) is greatly improved over that of MRNi. The hydrogenation of (**1**) was slow and the optical activity was negligible.

During the hydrogenation of α-phenylcinnamic acids (Table 4, compounds **4–6**), Ni^{II} ions appeared in the solution; the acids were corroding the catalyst. **5** and **6** were not hydrogenated whereas, **4** was hydrogenated with 90% conversion, but with low optical yield.

Table 4

Data for the chiral hydrogenation of compounds **1–11** on MRNi catalyst

Substrate	Product	$[\alpha]_D^{20}$ (°)	Configuration [a]	Optical yield	$r \times 10^4$ $\left(\frac{\text{mmol}H_2}{g_{Ni}\ s}\right)$	Catalyst (mg)
Methyl(*E*)-α-phenyl cinnamate	Methyl-2,3-diphenyl-propionate [b]	+0.58				
(1)	bp: 168 °C/8 mmHg [30]	(*c*: 11, MeOH)	–	–	6.64	600
Methyl-α-methyl-cinnamate(*E*):(*Z*) = 6:4	Methyl-3-phenyl-2-methyl-propionate [b]	0.00				
(2)	bp: 230 °C/22 mmHg [31]	(*c*: 11, MeOH)	–	0.00	66.66	300
Methyl-β-methylcinnamate (*E*):(*Z*) = 6:4	Methyl-3-phenylbutirate [b]	0.00				
(3)	bp: 120–122 °C/15 mmHg [32]	(*c*: 10, MeOH)	–	0.00	75.00	350
(*E*)-α-Phenylcinnamic acid	2,3-Diphenylpropionic acid	−0.28				
(4)	mp: 82–84 °C [28]	(*c*: 10, acetone)	(*R*)	0.21	4.98	333
(*Z*)-α-Phenylcinnamic acid	no reaction	–	–	–	–	400
(5)						
(*E*)-α-Phenyl-4-methoxy-cinnamic acid	no reaction	–	–	–	–	300
(6)						
Sodium (*E*)-α-phenyl cinnamate	2,3-Diphenylpropionic acid	−12.31				
(7)		(*c*: 10, acetone)	(*R*)	9.20	19.85	475
Sodium (*Z*)-α-phenyl cinnamate	2,3-Diphenylpropionic acid	−0.66				
(8)		(*c*: 10, acetone)	(*R*)	0.49	6.66	300
Sodium (*E*)-α-phenyl-4-methoxycinnamate	2-Phenyl-3-(4-methoxy phenyl)propionic acid [b]	−2.12				
(9)	mp: 119–120 °C [33]	(*c*: 14, EtOH)	–	–	29.33	385
Sodium (*Z*)-α-phenyl-4-methoxycinnamate	2-Phenyl-3-(4-methoxy phenyl)propionic	−0.19				
(10)	acid [b]	(*c*: 12, EtOH)	–	–	15.16	443
Sodium β-methyl-cinnamate (*E*):(*Z*) = 6:4	3-Phenylbutyric acid [c]	+0.54				
(11)	bp: 142 °C/1 mmHg mp: 37–38 °C [34]	(*c*: 12, benzene)	(*S*)	0.94	54.50	320

[a] Configuration of the main product. [b] The specific optical rotation ($[\alpha]_{D(max)}^{20}$) is unknown. [c] $[\alpha]_{D(max)}^{20} = 57.23°$ (c: 9, benzene [34]). Hydrogenation: 12.18 mmol of substrate in 15 cm^3 EtOH at 30 °C.

MRNi is not an adequate catalyst for the enantioselective hydrogenation of the esters and carboxylic acids studied.

The adsorbed tartaric acid does not influence the ratio of enantiomers formed from the esters, and the chemical reaction between the acids and the catalyst prevented their transformation.

It is well known [35] that basic salts (e.g. Na_2CO_3) enhance the activity of RNi catalysts. To understand the effects of the salts on the optical yield, we prepared the sodium salts of the carboxylic acids, and studied their hydrogenation over MRNi. The hydrogenation of the sodium salts of olefin-carboxylic acids (Table 4, **7–11**) gave optically active products.

This is of interest, since the structures of these compounds are very different from the structures of the ketones and so the mechanism of the enantioselective hydrogenation should also be very different. It was expected that further studies would elucidate this mechanism, and therefore a more thorough investigation of the enantioselective hydrogenation of sodium (*E*)-α-phenylcinnamate (which gave the highest optical yield) was decided on.

*Enantioselective hydrogenation of sodium, potassium and lithium and nickel salts of (*E*)-α-phenylcinnamic acid*

To start with, the role of the adsorbed tartaric acid was studied (Table 5, Entries 1–3). In this investigation, both the modified and unmodified tartaric acid forms were used in the hydrogenation of **7**. The configuration of the enantiomer formed in greater quantities was determined by the configuration of the tartaric acid, and the optically inactive product was formed over the unmodified catalyst.

In order to decide whether racemization occurs after the reaction, optically active sodium 2,3-diphenylpropionate was treated over unmodified RNi catalyst under similar conditions (Table 5, Entry 4). No racemization was observed.

The optical yield of **4** was improved if the Na salt was used in place of the acid, and therefore an investigation of the hydrogenation reactions of other (*E*)-α-phenylcinnamic acid salts was desirable. The characteristics of the reactions of these salts are listed in Table 6.

The hydrogenation of the sodium salt gave the highest optical yield. Other solvents, in addition to ethanol were used in the hydrogenation of the calcium and

Table 5

Data for the chiral hydrogenation of **7**

Entry	Modifier	Substrate	Product $[\alpha]_D^{20}$ (*c*: 10, acetone)	Configuration	Catalyst (mg)
1	(2*R*,3*R*)-Tartaric acid	**7**	−12.31	(*R*)	346
2	(2*S*,3*S*)-Tartaric acid	**7**	+12.50	(*S*)	360
3	–	**7**	0.00		380
4	–	Sodium 2,3-diphenyl-propionate	−12.31	(*R*)	400

Hydrogenation: 12.18 mmol of substrate in 15 cm^3 EtOH, at 30 °C.

Table 6

Data for the chiral hydrogenation of various salts of (*E*)-α-phenylcinnamic acid

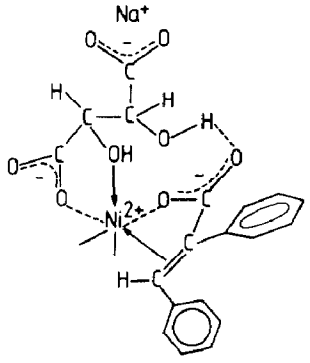
Entry	Substrate salt	Optical yield (%)	$r \times 10^4 \left(\frac{\text{mmol}H_2}{g_{Ni\ S}}\right)$	Catalyst (mg)	Solvent
1	Li^I	3.64	17.66	459	EtOH
2	K^I	5.40	12.75	474	EtOH
3	Na^I	9.00	20.80	453	EtOH
4	Ni^{II}	no reaction		433	EtOH
5	Ca^{II}	no reaction		400	EtOH
6	Ca^{II}	0.49	2.15	471	THF
7	Ni^{II}	0.56	2.45	345	THF
8	Na^I	0.35	10.33	460	THF
9	Na^I	2.56	33.66	616	0.1 cm^3 H_2O + 15 cm^3 EtOH
10	Na^I	0.47	23.50	643	H_2O

Hydrogenation: 12.18 mmol of the salt in 15 cm^3 solvent at 30 °C.

nickel salts. The reaction does proceed in tetrahydrofuran though both the optical yield and the reaction rate are low. Surprisingly, in this solvent, the hydrogenation of the sodium salt was slower and gave a lower optical yield than in pure ethanol. This led us to examine the influence of the polarity of the solvents (Entries 9 and 10).

Our results reveal that both the ionic character of the salt and the protic character of the solvent strongly affect the optical yield. The calcium(II) and nickel(II) salts are more covalent than ionic, while the alkali metal salts are more ionic. The protic character of the solvents determines the extent of dissociation of the salts.

Published data indicate that the carboxylic acids tend to form hydro complexes with alkali metal salts [36]. The differences in optical yield point to possible ionic



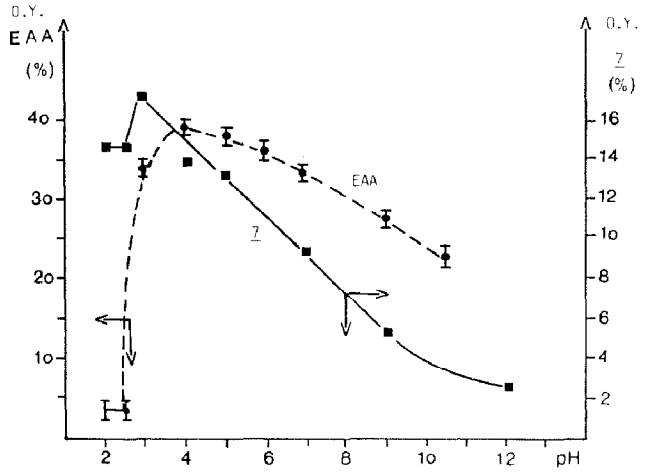


Fig. 1. Surface complex of (*R*,*R*)-tartaric acid and sodium (*E*)-α-phenylcinnamate (7) on RNi.

Fig. 2. Optical yield of the hydrogenation of sodium (*E*)-α-phenylcinnamate (7) and EAA on MRNi.

Table 7

Optical yield and rate of hydrogenation of sodium (*E*)-α-phenylcinnamate (7) on MRNi

Entry	pH	Optical yield (%)	$r \times 10^4$ $\left(\frac{\text{mmol}H_2}{g_{Ni}\ s}\right)$	Catalyst (mg)
1	2.0–2.6	14.56	37.93	300
2	3.0	17.22	44.76	361
3	4.0	14.19	24.65	430
4	5.0	13.30	19.61	533
5	7.0	9.21	14.68	424
6	9.0	5.21	7.98	481
7	12.0	2.61	6.66	493

Modification: method A (except Entry 1: method B) [27].

complex formation between the substrate and the adsorbed tartaric acid. Thus, the steric structure of the adsorbed tartaric acid directs the steric structure of the substrate transformation, and so the optically active product is formed (Fig. 1).

The chiral hydrogenation of methyl acetoacetate was similarly rationalized; it proceeds through an enolic form. The role of the C=C double bond in this chiral hydrogenation was confirmed by experiments in D_2 [37] and also by surface IR measurements (C=C = 1530 cm^{-1}) [38,39]. It was also revealed that the C=C bonds approach σ bonds as the reaction proceeds.

Effect of the pH of the modifying solution on the hydrogenation of sodium (E)-α-phenylcinnamate

In our earlier paper [26], we studied the effect of the pH of the modifying solution on the transformation of sodium (*E*)-α-phenylcinnamate. The results of these experiments are listed in Table 7. The optical yields and rates of the reactions are illustrated in Figs. 2 and 3. For the sake of comparison, the hydrogenation characteristics of EAA are also shown in the Figures [27].

The optical yield and rate of hydrogenation of sodium (*E*)-α-phenylcinnamate increase with decreased pH of the modifying solution.

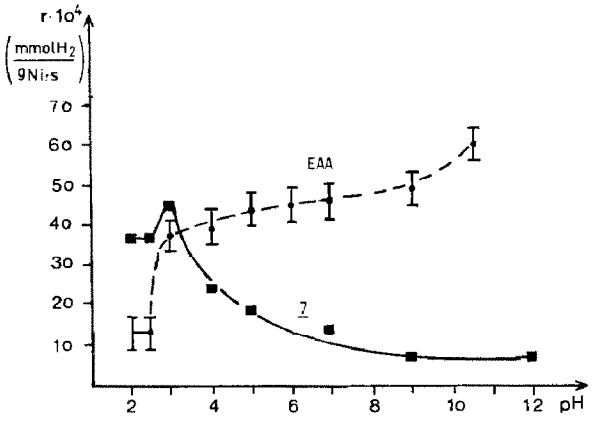


Fig. 3. Rate of hydrogenation of 7 and EAA on MRNi.

Table 8

Asymmetric, homogeneous hydrogenation of (*E*)-α-phenylcinnamic acid (**4**) with various rhodium(I)-phosphine catalyst to 2,3-diphenylpropionic acid

Catalyst	Yield (%)	Optical yield (%)	Configuration
Rh^{I}-(+)-NMDPP [a]	88.5	34.4	(*S*)
Rh^{I}-(−)-MDPP [b]	25	27.2	(*R*)
Rh^{I}-(+)-CAMPHOS [c]	80	11.8	(*S*)
Rh^{I}-(−)-DIOP [d]	89	14.9	(*R*)
$[Rh(COD)(ACMP)_2]^+ BF_4^-$ [e]	85	24.4	(*S*)

[a] NMDPP = neomenthyldiphenylphosphine. [b] MDPP = menthyldiphenylphosphine. [c] CAMPHOS = 1,2,3-trimethyl-1,3-bis(diphenylphosphinomethyl)cyclopentane. [d] DIOP = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane. [e] ACMP = *o*-anisylcyclohexylmethylphosphine.

Figure 2 shows that the optical yield increases with decreasing pH for both EAA and **7**, but at pH 4 the optical yield decreases again. There is a moderate decrease in the optical yield of **7** at pH 3.

The rate at which EAA is hydrogenated decreases moderately until pH = 3; at lower pH values the decrease is more pronounced. The rate at which **7** is hydrogenated changes in the opposite way: there is a moderate increase with decreasing pH to pH = 4; when the pH is further lowered, the increase is more dramatic.

The low optical yield and rate of hydrogenation of EAA at pH < 3 can be explained in terms of the unfavourable surface concentration of tartaric acid, the nickel(II) ions and the substrate. The change in optical yield with the pH of tartaric acid for **7** is similar to that of EAA down to pH = 4. The fact that there is no appreciable decrease in the optical yield of the hydrogenation of **7** over the catalyst treated at pH < 3, as in the hydrogenation of EAA, shows that the main factor determining the optical yield for the hydrogenation of EAA is not the decrease in surface coverage of tartaric acid, but the increase in coverage by Ni^{II} ions. The surface Ni^{II} coverage does not influence the optical yield in the hydrogenation of **7** because of its ability to form complexes. The optical yield probably reflects the degree of tartaric acid surface coverage. The contrasting trends in the changes in the hydrogenation rates of EAA and sodium (*E*)-phenylcinnamate (**7**) is probably also because of the difference in the complex-forming abilities of the two compounds.

From the previous results, it is quite clear that the industrial or even large-scale laboratory use of the enantioselective hydrogenation of the C=C double bond over heterogeneous catalysts requires much refinement. Even in the 1970's the results in organometallic chemistry permitted the preparation of Rh complexes in much better optical yields (Table 8).

The most significant purpose of the hydrogenation of the prochiral C=C double bond is to combine the advantages inherent to homogeneous and heterogeneous catalysts in order to increase the optical yield, so that this hydrogenation can be used as a synthetic method.

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