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Enantioselective hydrogenation of α,β-unsaturated acids. Substrate–modifier interaction over cinchonidine modified Pd/Al_2O_3

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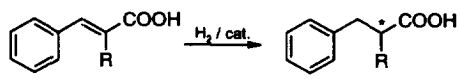
Abstract: X-Ray diffraction, IR measurements and catalytic hydrogenation of various substituted acrylic acids in apolar solvents, as well as molecular modelling provide new insight into the nature of the cinchonidine–substrate interaction and a general rule to predict the major enantiomer. © 1997 Elsevier Science Ltd

Introduction

One of the most frequently applied techniques for producing single enantiomers is the enantioselective hydrogenation of unsaturated compounds. Within this field the hydrogenation of dehydroamino acid derivatives and α,β-unsaturated carboxylic acids with chiral catalysts is extensively studied due to the pharmaceutical importance of amino acids and chiral carboxylic acids, such as *L*-DOPA, naproxen and ibuprofen.[1,2]

There is a wide variety of homogeneous chiral catalysts available for this purpose. In particular, chiral rhodium ($Rh^{0,I}$) and ruthenium complexes have been employed for dehydroamino acid hydrogenation and excellent enantiomeric excesses were achieved (ee>95%).[3–7] The catalytic potential of the application of ruthenium complexes increased enormously when rigid chiral ligands, such as BINAP, were used.[8,9] With Ru–BINAP complexes both α,β-and β,γ-unsaturated acids could be hydrogenated enantioselectively providing carboxylic acids in high ee.[10,11] Simple alkenoic acids (e.g. tiglic acid, angelic acid) were also hydrogenated with Ru–BINAP type catalysts affording higher than 90% ee.[12,13]

Due to the technical advantages of heterogeneous catalytic processes, the use of heterogeneous catalysts is a challenging subject. Unfortunately, there is no heterogeneous catalyst with synthetic potential available so far for the enantioselective reduction of C=C double bonds. The enantioselective hydrogenation of cinnamic acid derivatives has attracted most interest (Scheme 1).



Scheme 1. R=CH_3; C_6H_5.

Several papers have already been published reporting this type of hydrogenation reaction over Pd or Ni in the presence of a strongly adsorbing chiral modifier.[14–19] The most frequently applied modifiers are the cinchona alkaloids for Pd, and tartaric acid or amino acids for Raney Ni.

The heterogeneous enantioselective hydrogenation of aliphatic unsaturated acids has scarcely been investigated. Pt, Pd, Rh and Ru deposited onto β-cyclodextrin/epichlorohydrin copolymer afforded less than 10% ee.[20] The application of various alkaloids and amino acids as modifiers for the Pd catalysed hydrogenation of itaconic acid and its methyl ester was not successful.[21] A 1% Pd/SiO_2 catalyst modified with cinchonidine provided 27% ee to (*S*)-2-methyl pentanoic acid, from 2-methyl-2-pentenoic acid, which is the best result until now.[22] Note that these former studies could not provide any feasible explanation to the observed (low) enantioselectivity.

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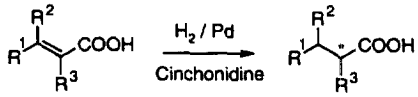
In our previous study we also chose the hydrogenation of 2-methyl-2-pentenoic acid as a model reaction and investigated the role of some important reaction parameters.[23] With the proper choice of reaction conditions (catalyst, solvent, H_2 pressure, modifier concentration) 52% ee of the *S* enantiomer was achieved. On the basis of this preliminary study and former physicochemical measurements, we assumed that in the enantioselective step the dimer of the unsaturated acid interacts with cinchonidine on the palladium surface. The aim of the present work was to provide experimental evidence for this assumption and extend the application range to other α,β-unsaturated alkenoic acids (Scheme 2).

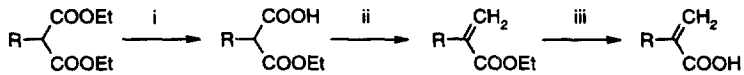


Scheme 2. R^1; R^2; R^3=H; methyl; ethyl; propyl; butyl.

Results and discussion

Synthesis of substrates

All of the propenoic acid derivatives were prepared by Knoevenagel condensation between alkyl malonic acid monoester and formaldehyde, according to Scheme 3.

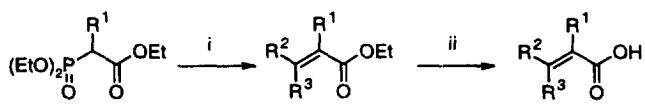


2

R	
a	C_2H_5
b	C_3H_7
c	C_4H_9

Scheme 3. (i) KOH, RT, 24 h, HCl; (ii) pyridine, piperidine, paraformaldehyde, reflux 130°C; (iii) KOH, HCl.

The Horner modification of the Wittig reaction, in which phosphonate esters are condensed with ketones or aldehydes, provided a convenient method for the preparation of compounds **3a–e**[24] (Scheme 4).



3

	R^1	R^2	R^3
a	CH_3	CH_3	CH_3
b	C_3H_7	CH_3	H
c	CH_3	C_2H_5	H
d	CH_3	CH_3	H
e	C_2H_5	C_3H_7	H

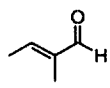
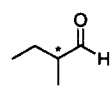
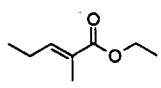
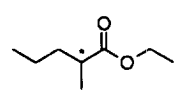
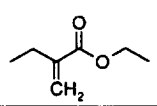
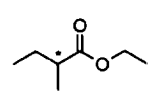
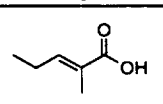
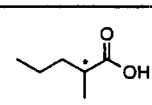
Scheme 4. (i) NaH in dimethoxyethane, ketone (or aldehyde), reflux; (ii) KOH, HCl.

The syntheses were followed by TLC and no significant side products were detected.

Nature of substrate–modifier interaction

In order to reveal the nature of the interaction between the chiral modifier and the α,β-unsaturated acid, attempts have been made to hydrogenate several alkenes possessing a functional group in the

Table 1. Enantioselective hydrogenation of α-functionalized olefins over Pd/Al_2O_3 modified with cinchonidine (standard reaction conditions)

Substrate	Product	ee, %[a]
		<2[b]
		0
		0
		52 *S*

a – ee was determined by GC analysis

b – chemical selectivity to the saturated aldehyde was >99 %; ee was determined after the saturated aldehyde had been oxidized to carboxylic acid ($KMnO_4$)

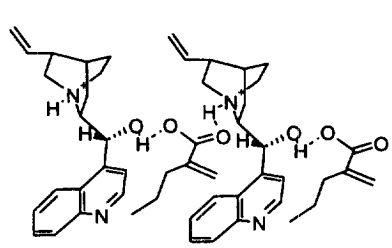


Figure 1. Hydrogen bonding in a cinchonidine salt.

α-position over the Pd/Al_2O_3–cinchonidine catalyst system. Some typical examples are collected in Table 1. Enantioselectivity was observed only in the presence of a carboxylic group, indicating an acid–base type interaction between the basic quinuclidine N of cinchonidine and the substrate.[22,23]

Note that the hydrogenation of isophorone over Pd/C and Pd/Al_2O_3 in the presence of cinchonidine provided also 0 and 2% ee, respectively.[21]

The types of possible association modes between cinchonidine and unsaturated acids have been investigated by XRD analysis of a **2b**:cinchonidine 1:1 salt. One fragment of the salt-chain is shown schematically in Figure 1. The chain-structure is stabilized by a hydrogen bond network. The acid molecules are connected to the quinuclidine nitrogen, as expected. Besides, H-bonding between the carboxylic group and the hydroxyl group of cinchonidine could also be observed. Carboxylic acid–cinchona alkaloid salts have already been investigated revealing the same type of H-bonding.[25–27]

A preliminary study of the hydrogenation of **3c** indicated that the cinchonidine–palladium system provides good ee only in apolar media. [23] It has been demonstrated that simple aliphatic acids form dimers in the gas phase or in apolar solvents.[28] Here we studied the structure of alkenoic acids and the acid–cinchonidine adduct in an apolar medium by IR spectroscopy (Figure 2).

The measurements were carried out in CCl_4. All the characteristic bands of carboxylic acid dimers could be found.[28–30] Note that in other apolar solvents (e.g. cyclohexane, hexane) the same bands of

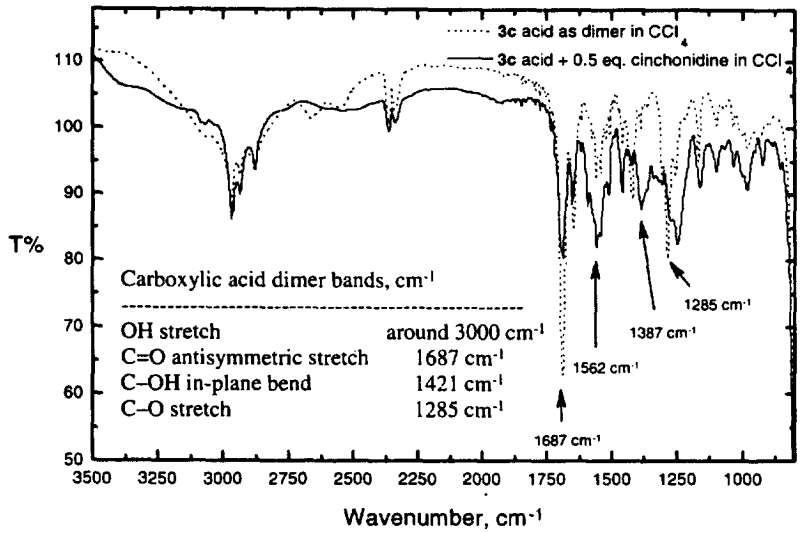


Figure 2

acid and cinchonidine–acid adduct could be found. In the hydrogen-bonded dimeric form, the OH stretching band centers around 3000 cm^{-1} and is superimposed on the CH stretch bands having a half intensity band width of roughly 600 cm^{-1}. The characteristic sharp band of the monomeric OH stretch at about 3500 cm^{-1} did not appear.

Addition of cinchonidine to the carboxylic acid solution resulted in an interaction similar to that observed in the acetic acid–triethyl amine reaction.[31] The nature of the cinchonidine–$(acid)_2$ species can be deduced from the observed spectrum of the half neutralized alkenoic acid in the presence of 0.5 equivalents cinchonidine. The dimer carbonyl band decreased to about half of its original intensity. Increasing the cinchonidine:acid ratio above 0.5 resulted in the partial or complete precipitation of the cinchonidine:acid 1:1 salt. Therefore, the new species contains a carboxyl group which is hydrogen bonded via only one bond to the other carboxylic group. The bands, appearing at 1562 cm^{-1} and 1387 cm^{-1} are clearly the asymmetric and symmetric COO− stretching bands, respectively.

These facts are in agreement with the structure shown in Figure 3 for the cinchonidine–$(acid)_2$ adduct in apolar solvent. A similar structure was suggested for the half neutralized acetic acid–triethyl amine species.[31] Note that the role of the OH group of cinchonidine is not yet clarified.

A molecular modelling study of **3c** revealed that the *trans* arrangement of acid dimers is more stable than the *cis* by approximately 8–10 kcal/mol (Figure 4).

Alkenoic acid–cinchonidine interaction during hydrogenation

The Pd-catalysed hydrogenation of reactant **3c** afforded 52% ee to the *S* enantiomer in the presence of cinchonidine.[23] Application of the diastereomer cinchonine resulted in the preferential formation of (*R*)-2-methylpentanoic acid. Other carboxylic acids including **3d–e** also provided the *S* enantiomer

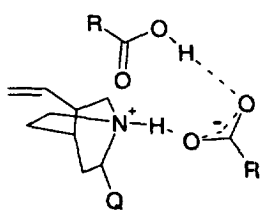


Figure 3. The half neutralized acid; Q=quinolyl moiety of cinchonidine.

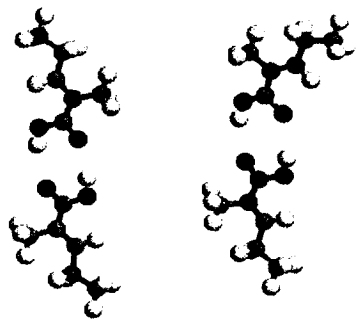


Figure 4. 2-Methyl-2-pentenoic acid dimers in *trans* and *cis* positions, calculated by HyperChem (H: white, O: black, C: gray).

in excess during hydrogenation over the Pd–cinchonidine catalyst. This is an indication that the adsorption of **3c–e** on Pd and their interaction with cinchonidine are similar. The adsorption geometries of α,β-unsaturated aldehydes and alcohols on Pd have already been extensively studied by molecular modelling.[32] An adsorption mode involving both the C=C and the C=O double bonds in a quasi planar geometry (η_4 or di-$\pi\eta_2$) was concluded from the calculations.

The adsorption mode of cinchonidine in the presence of hydrogen was studied by H/D exchange experiments.[33] The multiple nature of the exchange indicated that the quinoline rings adsorbed approximately parallel to platinum and ruthenium surface by multicenter π-bonding and the quinuclidine part was not in direct contact with the metal surface. Pd was found to be unique in its failure to catalyse measurable isotope exchange, therefore no useful information concerning the adsorption mode of cinchonidine on Pd could be obtained. In the following we presume that α,β-unsaturated acids as well as the quinoline moiety of cinchonidine adsorb parallel to the palladium surface.

Based on the above assumption and the fact that acids **3c–e** produce systematically the *S* enantiomer on hydrogenation, a likely adsorption arrangement of the cinchonidine–unsaturated acid adduct on the palladium surface and the hydrogenated product is illustrated in Figure 5. The proper geometry of the adsorbed adduct on the metal surface is stabilized by two-site adsorption of the quinoline ring and that of the unsaturated acids.

It is considered that the arrangement of the adsorbed unsaturated acid dimer should play an enantioselective role. If the addition of H (in two steps) occurs from the palladium side than the resulting molecule can be generally drawn as in Figure 5(B). Since in the hydrogenation product of acids **3c–e** the $-CH_2-R^2$ chain takes precedence over R^1 according to the sequence rule, the absolute configuration of the hydrogenated product is *S*. In order to confirm this adsorption arrangement, it was necessary to carry out control experiments.

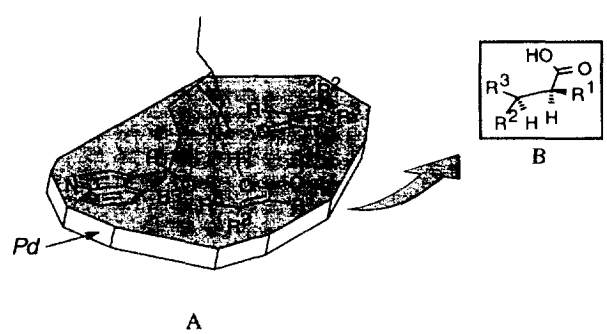


Figure 5. Proposed arrangement of the cinchonidine–unsaturated acid dimer adduct on an ideal flat (low index plane) Pd surface (A) and the hydrogenated product (B).

Table 2. Hydrogenation of some α,β-unsaturated acids over Pd/Al_2O_3–cinchonidine catalyst under standard reaction conditions

Entry	R^1	R^2	R^3	Code	ee, %	Configuration
1	CH_3	CH_3	H	**3d**	47	*S*
2	CH_3	C_2H_5	H	**3c**	52	*S*
3	C_2H_5	C_3H_7	H	**3e**	49	*S*
4	C_2H_5	H	H	**2a**	20	*R*
5	C_3H_7	H	H	**2b**	20	*R*
6	C_4H_9	H	H	**2c**	20	*R*
7	C_3H_7	CH_3	H	**3b**	53	*R*
8	CH_3	CH_3	CH_3	**3a**	25	*S*

Varying the substituents R^1, R^2 and R^3 the configuration of the chiral product should change unless the adsorption arrangement is different from the one shown in Figure 5(A). The result of the hydrogenation of several α,β-unsaturated aliphatic acids is collected in Table 2.

Depending on the length of the alkyl groups, the absolute configuration of the product changes. Reactants in which R^1 takes precedence over R^2 the major enantiomer is *S* (entry 1–3, 8) and where the carbon with R^2 and R^3 substituents is ranked higher than R^1 the major product is the *R* enantiomer (entry 4–7).

Conclusion

We propose a feasible structure for the modifier–substrate interaction, based on the following experimental observations and assumptions:

- in apolar solvents alkenoic acids are present as dimers;
- dimers are mainly in the *trans* arrangement and their structure is preserved upon adsorption;
- the quinuclidine-*N* of cinchonidine interacts with the dimer through an acid–base type interaction;
- the aromatic rings of cinchonidine and the C=C double bond–carboxylic group conjugation of the dimer adsorb parallel to a flat Pd surface;
- H is added from the bottom (from the Pd surface).

Varying the substituents R^1, R^2, R^3 the configuration of the chiral product changed, providing evidence for the suggested arrangement of the alkenoic acid–cinchonidine adduct adsorbed on palladium. On the basis of our model the configuration of the hydrogenation product is predictable.

Experimental

^1H and ^{13}C NMR spectra was recorded on a Bruker Advance DPX 300 operating at 300 MHz and 75 MHz, respectively, with chemical shifts related to TMS (δ=0). MeO^{t}Bu was used as the eluent for TLC.

Tiglic acid **3d** (Fluka) was used as received. 2-Methyl-2-pentenoic acid **3c** and 2-ethyl-2-hexanoic acid **3e** (Aldrich, 97%) were purified as follows: 0.2 mol DBU was added to a stirred solution of 0.2 mol acid and 0.24 mol ethyl bromide in toluene via a dropping funnel. The mixture was refluxed till TLC showed complete or almost complete conversion, and then poured into water. The carboxylic

acid ethyl ester was extracted twice with MeO^{t}Bu, dried over anhydrous $MgSO_4$ and distilled slowly to give the corresponding acid ethyl ester in very pure form (purity >99.8%, NMR). The ester was hydrolysed with NaOH in water/ethanol solution, acidified with HCl and recrystallized from hexane to give yellow crystals in 88–92% yield.

Syntheses of alkenoic acids

*2-Alkyl propenoic acids **2a–c**, general procedure*

The acids were prepared by the use of the Knoevenagel-condensation. KOH (1 mol) in ethanol was added via a dropping funnel to a stirred solution of 1 mol diethyl alkyl malonate in ethanol and the mixture was stirred at rt for 10 h. The alcohol was then removed under vacuum. The resulting half-ester was dissolved in water, and 1 eq cc. HCl was added dropwise to the solution under vigorous stirring. The alkyl malonic acid monoethyl ester was extracted with MeO^{t}Bu and dried over $MgSO_4$. After removing the solvent, 200 ml pyridine, 1 mol paraformaldehyde and 10 ml piperidine were added and refluxed at 130°C till CO_2 evolution was observed. The cooled transparent reaction mixture was poured into water and the unsaturated ester taken up in *n*-pentane. The organic phase was washed with HCl, water and $NaHCO_3$. Hydrochinone (1 g) was added to the collected organic phases and dried over $MgSO_4$. After filtration and solvent evaporation the ester was slowly distilled. A 90–92% yield of the corresponding 2-alkyl propenoic acid ethyl ester was obtained in very pure form in all cases. The ester was immediately hydrolysed at rt overnight in a dark bottle with 1.2 eq. KOH in ethanol. The carboxylic acid potassium salt was stored in a dark bottle and was acidified with HCl directly before use. ^{1}H-NMR **2c** ($CDCl_3$): 6.28 (s, CH_2), 5.63 (s, CH_2), 2.3 (t, CH_2) 1.39, 1.4 (n, n 2×CH_2) 0.92 (t, CH_3) ^{13}C-NMR **2c** ($CDCl_3$): 172.9 (COO), 140.38 (C), 126.79 (CH_2 olefin), 31.2 (CH_2), 30.5 (CH_2), 22.3 (CH_2), 13.8 (CH_3).

*2,3-Dimethyl-2-butenoic acid **3a***

The Horner modification of the Wittig reaction between triethyl α-phosphonopropionate and acetone provided a convenient route to the title compound.[34] Triethyl α-phosphonopropionate was gained with the Michaelis–Arbuzov reaction according to the general procedure as follows: 0.3 mol ethyl 2-bromopropionate was preheated to 140°C and 0.32 mol triethyl phosphite was added dropwise. The temperature was raised to 180°C and the reaction was refluxed overnight. The oily product was distilled to give triethyl α-phosphopropionate in 75% yield. 0.1 mol triethyl α-phosphonopropionate was added dropwise to a stirred solution of 0.11 mol NaH (55–60% dispersion in mineral oil) in 100 ml dry dimethoxyethane at 0°C. After stirring the mixture for 20 min, 0.1 mol acetone was added and refluxed till completion (TLC). The two phase mixture was cooled, diluted with water and extracted with MeO^{t}Bu. The combined organic phases were dried over $MgSO_4$. Vacuum distillation afforded 2,3,3-trimethyl acrylic acid ethyl ester in 92% yield. The ester was saponified with 1.1 eq. NaOH in water/ethanol solution at 110°C for 12 h. After cooling and removing ethanol, the solution was washed with MeO^{t}Bu, acidified with HCl and extracted with ether again. The organic phase was dried ($MgSO_4$), concentrated and the acid was recrystallized from pentane to give the pure title compound as colourless needles in 88% overall yield. ^{1}H-NMR ($CDCl_3$): 2.12 (s, CH_3), 1.89 (s, CH_3) 1.86 (s, CH_3). ^{13}C-NMR ($CDCl_3$): 174.9 (COO), 148.2 (C), 121.6 (C), 23.4 (CH_3), 23.3 (CH_3), 15.5 (CH_3).

*2-Propyl-2-butenoic acid **3b***

Triethyl α-phosphonopentanoate was prepared according to the general method.[35] Ethyl 2-bromovalerate (0.12 mol) was preheated to 160°C and 0.15 mol triethyl phosphite was added dropwise. The temperature was raised to 180°C and was kept at 180°C for about 2 h. Vacuum distillation afforded triethyl α-phosphonopentanoate in 65% yield. 37 mmol of the transparent oily product was used for further reaction. After reaction with NaH in dimethoxyethane, the mixture was cooled to 10°C and 37 mmol acetaldehyde was added. The mixture was allowed to warm up slowly, then heated to 60°C for 1 h to complete the reaction (TLC). The mixture was worked up as described above. Distillation gave

propyl butenoic acid ethyl ester in 90% yield. The ester was saponified with NaOH in water/ethanol mixture and recrystallised from hexane to give yellow crystals. ^{1}H-NMR analysis showed *cis:trans* ratio of 1:2.9. ^{1}H-NMR ($CDCl_3$): 7.03 (q, CH, *trans*), 6.16 (q, CH, *cis*), 2.23 (t, CH_2), 2.04 (d, CH_3, *cis*), 1.84 (d, CH_3, *trans*), 1.46 (n, CH_2), 0.91 (t, CH_3). ^{13}C-NMR ($CDCl_3$): 174 (COO), 140.2 (CH), 132.7 (C), 27.9 (CH_2) 22.1 (CH_2) 14.4 (CH_3), 13.8 (CH_3).

Enantioselective hydrogenation of α,β-unsaturated acids

5 wt% Pd/Al_2O_3 (Engelhard 40692) catalyst was used for the hydrogenation of alkenoic acid. The reactions were carried out in a 100 ml stainless steel autoclave equipped with magnetic mixing (1200 rpm). A 50 ml glass liner with teflon cap and stirrer was used to keep the system inert. The reaction was followed by a pressflow gas controller (Büchi). If not otherwise stated, the following standard conditions were used: 1 g reactant; 50 mg catalyst; 10 mg cinchonidine; 15 ml hexane; rt and 60 bar. After filtering off the catalyst, the acids were directly analysed by gas chromatography using a chiral column coated with CP-Cyclodextrin-β-2,3,6-M-19 (Chrompack). Absolute configurations were determined using authentic samples.

Acknowledgements

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