The enantioselective hydrogenation of 5,6-dihydro-2*H*-pyran-3-carboxylic acid over a cinchona alkaloid-modified palladium catalyst: asymmetric synthesis of a cockroach attractant

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A novel application of a cinchona-modified supported Pd catalyst is presented. The key step in the asymmetric synthesis of the cockroach attractant methyl (+)-tetrahydro-2*H*-pyran-3-carboxylate was the enantioselective hydrogenation of 5,6-dihydro-2*H*-pyran-3-carboxylic acid over 5% Pd/Al_2O_3 modified by cinchonidine, which afforded the saturated product in up to 89% optical purity.

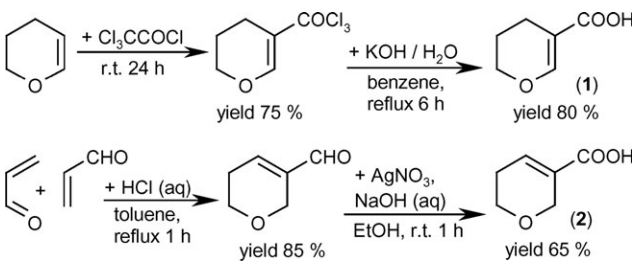
Chiral carboxylic acids are frequently-used intermediates in the production of optically-pure pharmaceuticals, agrochemicals, flavors and fragrances.[1] The enantioselective hydrogenation of prochiral α,β-unsaturated carboxylic acids is a convenient synthetic method for the preparation of optically pure acids that gained increased practical importance due to development of a large variety of efficient chiral metal complex catalysts.[2] Attractive alternatives to soluble metal complexes may be heterogeneous chiral catalysts that take advantage of the well known benefits of these catalytic systems. The simplest way of preparing chiral heterogeneous catalysts for the hydrogenation of prochiral unsaturated compounds is the modification of conventional metal catalysts by optically-pure substances, the so called modifiers.[3] The simplicity of these procedures and the availability of a large variety of modifiers, usually natural chiral compounds, was the driving force for the extensive studies, which led to the development of highly effective heterogeneous catalytic systems, such as tartaric acid-modified Ni and cinchona alkaloid-modified Pt catalysts.[3–5]

The most efficient modified catalysts for the enantioselective hydrogenation of prochiral α,β-unsaturated carboxylic acids are supported Pd catalysts in presence of cinchona alkaloids.[3,6–8] However, the reactions were found to be highly substrate sensitive. Aliphatic unsaturated acids in presence of a catalytic amount of cinchona alkaloids were hydrogenated in up to ~60% enantioselectivity,[9,10] while the hydrogenation of substrates bearing aromatic rings in α and β positions resulted in higher, up to 92%, enantiomeric excesses (ee).[11] The supported Pd-cinchona alkaloid catalytic system was also found to be efficient in the enantioselective partial hydrogenation of several 2-pyrone derivatives lacking acidic groups.[12] However, only moderate optical purities were obtained in the asymmetric hydrogenation of heteroaromatic furan carboxylic acids.[13]

Based on the high enantioselectivities obtained in the hydrogenation of oxygen-containing 2-pyrone derivatives and the promising results described in the hydrogenation of heteroaromatic furan carboxylic acids, we attempted to extend the scope of this catalytic system to the asymmetric preparation of a biologically-active cockroach attractant, methyl (+)-tetrahydro-2*H*-pyran-3-carboxylate. It is known that the enantiomers of tetrahydropyran-3-carboxylic acid methyl ester have different bioactivities, the (+)-enantiomer being a much more potent attractant than its optical antipode or a racemic mixture.[14] The enantioselective hydrogenation of either of the dihydro derivatives, 5,6-dihydro-4*H*-pyran-3-carboxylic acid (**1**) or 5,6-dihydro-2*H*-pyran-3-carboxylic acid (**2**), may be the key step to an easy preparation procedure of the target compound. Carboxylic acid **1** was prepared from 3,4-dihydro-2*H*-pyran according to a modified literature procedure in ~60% total yield,[15] while **2** was prepared by a two-step process, starting from acrolein in 55% total yield,[16] as presented in Scheme 1.

It was reasonable to expect that the above compounds would be saturated faster than the aromatic and semi-aromatic oxygen-containing heterocycles hydrogenated thus far using the Pd-cinchona alkaloid catalytic system. Thus, the transformation of the modifier during the reaction wouldn't alter the optical purity of the saturated product, as observed in the reaction of 2-pyrone and furan derivatives.[12,13] Surprisingly, under atmospheric H_2 pressure and using methanol as the solvent, **1** was not hydrogenated, even in the absence of any chiral modifier, and only **2** displayed the anticipated behaviour. This latter compound was completely transformed in 5 min, yielding exclusively saturated product **3**, as presented in Scheme 2.

The hydrogenation of **2**, even in presence of chiral modifier cinchonidine (CD), took only 25 min, as shown in Table 1,



Scheme 1 The preparation of **1** and **2**.

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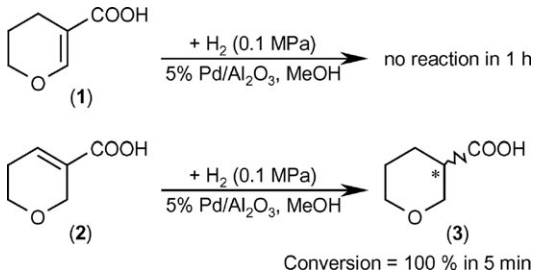


Scheme 2 Hydrogenation of dihydropyran-3-carboxylic acids. Reaction conditions: 50 mg Pd/Al_2O_3, 3 ml methanol, 0.78 mmol acid, 295 K.

entry 2. However, under these reaction conditions, the ee obtained was rather low; (+)-**3** being formed in excess, as determined by measuring the optical rotation of the isolated, crude, saturated acid after removing the modifier.

The addition of an achiral base additive to the reaction slurry may lead to a significant increase in the enantioselectivity during the hydrogenation of prochiral α,β-unsaturated carboxylic acids over cinchona-modified Pd catalysts.[7–11] The origin of the ee enhancement seems to be different for acids of different structures, expressively illustrated by the opposite effect of the amine on the initial rate of the hydrogenation of acids bearing either aromatic[7,11] or aliphatic[8–10] substituents. The addition of benzylamine (BA) to the reaction mixture resulted in a surprisingly high increase in the ee of the hydrogenation of **2**, and a decrease in the initial H_2 uptake rate (R_i) compared with the reaction in the absence of BA (Table 1, entries 2 and 3). It must be noted that the rate of production of both enantiomers decreased by the adding of BA. However, based on the ee and R_i values, one can approximate a more than threefold decrease in the racemic reaction, while the asymmetric hydrogenation was accelerated by a factor of 1.3. Thus, in the hydrogenation of **2**, the ee increase in the presence of BA was mainly due to a significant deceleration of the racemic hydrogenation.

The optical purity was further enhanced, up to 74%, by decreasing the reaction temperature (Table 1, entry 4). Changing the solvent from MeOH, even to another alcohol, resulted in lower ee values. In acetonitrile (AcCN), the enantioselectivity approached the value obtained in MeOH in presence of the BA additive (Table 1, entry 12). However, it is known that AcCN itself is hydrogenated to give amines over supported Pd catalysts and, opposite to the hydrogenation of 4-hydroxy-6-methyl-2-pyrone,[12] the presence of these products increased the enantioselectivity of the hydrogenation of **2**.

The ee was enhanced with increasing amounts of CD, as presented in Table 2, entries 1–3. However, even using the highest CD amount (10 mol%), the decrease in the amount of BA to 0.5 equiv. with respect to **2** diminished the ee and increased to more than double the R_i (Table 2, entry 4). Thus, the addition of one equiv. of BA is essential so as to obtain good enantiodifferentiation. Similar behavior concerning both the effect of the BA amount on the ee and the extent of the ee increase was observed in the hydrogenation of itaconic acid.[10] Accordingly, similar to itaconic acid, **2** is transformed in the liquid phase to a benzylammonium salt.[10b] The rate enhancement of the stereoselective reaction in presence of BA may be explained by the higher exchange rate of the adsorbed cinchonidinium salt of **3** and the dissolved benzylammonium salt of **2**, compared to the exchange of the free unsaturated acid or the cinchonidinium salt of **2** from solution. The drop in rate of the racemic hydrogenation might be due to the hindered adsorption or desorption of the benzylammonium salt of **2** or **3**, compared with the acids.

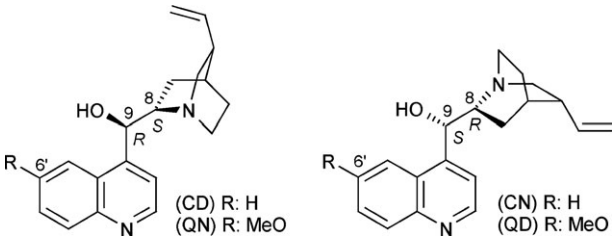
Similar to the hydrogenation of aliphatic α,β-unsaturated carboxylic acids,[6e,10] an increase in the H_2 pressure resulted in further ee enhancement (Table 2, entries 3, 5 and 6). The pressure dependence of the ee resembled the behavior observed in the hydrogenation of itaconic acid.[10] The ee reached a maxima at 5 MPa and then declined following further pressure increase (10 MPa). The high (89%) ee obtained under 5 MPa H_2 pressure, to the best of our knowledge, is the largest value reported to date in the enantioselective hydrogenation of an α,β-unsaturated carboxylic acid lacking aromatic substituents over a cinchona-modified Pd catalyst. The results obtained using three other natural cinchona alkaloids are presented in Table 2, entries 8–11. When using cinchonine (CN), which has the opposite configuration at the C^8 and C^9

Table 1 The enantioselective hydrogenation of **2** over a supported Pd catalyst modified by CD[a]

Entry	Solvent	Additive	Time/min	X (%)[b]	R_i/mmol h^{-1} g^{-1}[c]	ee (%)
1[d]	MeOH	—	5	100	668.6	—
2	MeOH	—	25	100	74.2	26
3	MeOH	BA	40	99	42.0	59
4[e]	MeOH	BA	90	100	10.7	74
5[e,f]	MeOH	BA	90	100	7.3	68
6	^{i}PrOH	BA	30	100	48.0	33
7	Toluene	BA	120	40	3.1	43
8	THF	BA	60	100	28.8	45
9	1,4-DO[g]	BA	30	100	58.3	43
10	DMF[g]	BA	80	95	18.8	39
11	H_2O	BA	70	100	20.3	30
12	AcCN	—	50	100	29.6	53
13	AcOH	—	40	100	39.7	34

[a] Reaction conditions: 50 mg 5% Pd/Al_2O_3, 3 ml solvent, 0.039 mmol CD, 0.78 mmol **2**, 0.78 mmol benzylamine (BA) (when used), p_{H_2} = 0.1 MPa, 1000 rpm stirring, 295 K. [b] X = conversion reached in the given time. [c] R_i = initial rate calculated from the initial H_2 uptake. [d] Racemic reaction in absence of chiral modifier. [e] Reaction temperature = 273 K. [f] Hydrogenation over 50 mg 5% Pd/TiO_2. [g] 1,4-Dioxane (1,4-DO) and DMF containing 2.5 vol% water.

Table 2 The effect of the reaction conditions and modifier structure on the enantioselective hydrogenation of **2** over cinchona-modified Pd/Al_2O_3[a]



Entry	Modifier (amount (mol%))[b]	p_{H_2}/MPa	Time/min	X (%)[c]	R_i/mmol h^{-1} g^{-1}[d]	ee (%)[e]
1	CD (1)	0.1	70	96	12.7	65
2	CD (5)	0.1	90	94	10.7	74
3	CD (10)	0.1	100	83	8.4	79
4[f]	CD (10)	0.1	70	100	19.0	42
5	CD (10)	1	60	100	19.2	82
6	CD (10)	5	60	95	n.d.	89
7	CD (10)	10	60	100	n.d.	70
8	CN (10)	0.1	120	100	7.8	32[g]
9	CN (10)	5	60	97	n.d.	56[g]
10	QN (10)	0.1	100	85	10.9	19
11	QD (10)	0.1	100	89	12.9	6[g]

[a] Reaction conditions: 50 mg catalyst, 3 ml MeOH, 0.78 mmol **2**, 0.78 mmol BA, stirring 1000 rpm, 273 K. [b] Modifier amount in relation to **2**. CD = cinchonidine, CN = cinchonine, QN = quinine and QD = quinidine. [c] X = conversion reached in the given time. [d] Initial rate calculated from the initial H_2 uptake. [e] Unless otherwise noted, (+)-**3** was formed in excess. [f] 0.39 mmol of BA was used. [g] (−)-**3** was formed in excess.

chiral centers compared to CD, (−)-**3** was formed in a lower ee under both 0.1 and 5 MPa H_2 pressure. The $C^{6\prime}$-methoxy substituent of both quinine (QN) and quinidine (QD) decreased even more the enantioselectivity of the hydrogenation, the latter giving the (−)-**3** enantiomer only in a very low ee. The results obtained using these cinchona alkaloids are in line with those obtained in the hydrogenation of aliphatic α,β-unsaturated carboxylic acids, such as *trans*-2-methyl-2-pentenoic acid and itaconic acid.[9,10]

In conclusion, we have reported the first enantioselective hydrogenation of a dihydropyran carboxylic acid over a cinchona alkaloid-modified, supported Pd catalyst. The use of CD as a chiral modifier and BA as an achiral additive afforded unexpectedly high enantioselectivities, up to 89%, unprecedented in the hydrogenation of aliphatic or cycloaliphatic unsaturated carboxylic acids in this heterogeneous catalytic system. The optical purity of the product approached the high values usually obtained in enantioselective hydrogenations of α,β-unsaturated carboxylic acids using chiral metal complexes,[2] though, to our knowledge, the asymmetric hydrogenation of **2** using a homogeneous catalyst has not yet been attempted. The reaction is applicable to the easy preparation of an optically enriched cockroach attractant, as shown in Scheme 3. We note that the optically pure enantiomers of **3** used in previously published bioactivity studies were prepared in low, only up to 15%, yields by resolution of the racemic mixture using an equivalent amount of QN.[14] The cyclic structure, the free carboxylic acid group and the position of the ring oxygen atom relative to the prochiral C=C group of the acid all have a crucial importance in determining the effect of the achiral amine additive, and consequently on the attained ee value. This is well illustrated by the lower ee obtained in the hydrogenation of furan and indene carboxylic acids,[13,17] and in the effect of amine additives on the hydrogenation of 4-hydroxy-2-pyrone derivatives.[12b] Furthermore, in the hydrogenation of aliphatic α-methyl-α,β-unsaturated carboxylic acids, the ee was increased much less as result of the addition of the same achiral amine, while ee enhancement to similar extent was obtained in the hydrogenation of itaconic acid.[10] Our present study shows that this effect is of kinetic origin. Detailed kinetic and spectroscopic studies to gain further insight into the origin of the enantiodifferentiation in this catalytic system will be the subject of a future investigation. This novel application of a cinchona-modified Pd catalyst open up new perspectives, broadening the scope of this chiral heterogeneous catalytic system.

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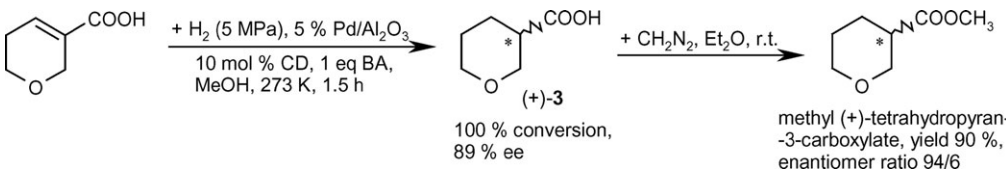

Scheme 3 The preparation of optically-enriched methyl (+)-tetrahydropyran-carboxylic acid by an enantioselective heterogeneous catalytic hydrogenation.

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Experimental

Cinchona alkaloids CD (≥ 98%), CN (≥ 98%), QN (≥ 98%), QD (≥ 98%) and BA (≥ 99.5%) are commercial products (Fluka), and were used as received. H_2 gas (99.999%) was purchased from Linde AG. The catalyst used in most of the studies was commercial 5% Pd/Al_2O_3 (Engelhard 40692), having a 0.19–0.21 Pd dispersion, 185–200 $m^2\ g^{-1}$ BET surface area and a 5.8 nm average Pd particle size.[6e,18] The 5% Pd/TiO_2 (TiO_2, Degussa P-25, 55 $m^2\ g^{-1}$ surface area) was prepared by deposition–precipitation according to a previously described procedure.[8] Commercial, high purity solvents and reagents (Aldrich and Fluka products) were used without purification.

All products were identified by GC-MS (Agilent Technologies 6890N GC-5973 MSD), and ^{1}H- and ^{13}C-NMR (Bruker AVANCE DRX-500 spectrometer) analysis. Their purity was checked by gas chromatography (HP-5890 II GC-FID).

Hydrogenations were carried out using a glass hydrogenation apparatus or a stainless steel autoclave equipped with a glass liner and an automatic pressure recorder. In a typical run, the catalyst was pre-treated by stirring (1000 rpm) in the given solvent for 0.5 h under H_2 at 297 K, followed by the addition of specified amounts of the modifier, BA (when used) and substrate. The reactor was flushed and filled with H_2 to the specified pressure, the temperature set to the chosen value and the reaction started by stirring the slurry. After H_2 uptake ceased, the catalyst was filtered, and the solution analyzed before and after work-up. The solvent was evaporated, the product was then washed with 10% aqueous HCl to remove the modifier and BA additive, and extracted with *tert*-butyl methyl ether. Repeat experiments gave conversions and ee values within ±2%.

The initial rates were calculated from the H_2 uptake up to 20 ± 2% conversion. The conversion and ee were determined by GC analysis using a Cyclosil-B (30 m × 0.2 mm, J&W Scientific Inc.) chiral capillary column. The ee was calculated using the formula:

$$\text{ee}\ (\%) = 100 \times |[(+)\textbf{-3}] - [(-)\textbf{-3}]|/([(+)\textbf{-3}] + [(-)\textbf{-3}]),$$

where [(+)-**3**] and [(−)-**3**] are the concentrations of the dextrorotatory and levorotatory enantiomers of the product, respectively. The sense of rotation of the excess enantiomer was determined by measuring the optical rotation (Polamat A polarimeter) of the crude product obtained after removal of the modifier and BA.

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