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# Synthesis of chiral amino acids and amines over solid catalysts

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**Abstract**

Diastereoselective heterogeneous catalytic hydrogenations producing chiral amino acids and amines are reviewed. The most important reactants are dehydroamino acids, dehydropeptides, dehydrodiketopiperazines, Schiff's bases, oximes, which possess prochiral groups of C=C and C=N bonds to be hydrogenated.

## 1. Introduction

The asymmetric catalytic hydrogenation over metal catalysts is a useful method for the preparation of various optically active amino acids and amines. These reactions involve the saturation of prochiral C=C and C=N bonds of compounds that contain a chiral moiety. In some hydrogenations, the chirality inducing group is removed after having fulfilled its task in the reduction step, while in the others it becomes the part of the product molecule. A good chiral auxiliary has high asymmetric induction effect and is recoverable. Since there are only a few examples for enantioselective heterogeneous catalysis in hydrogenation [1], this method will not be presented here. Asymmetric homogeneous hydrogenation, on the other hand, uses a "chiral reagent", a soluble transition metal complex catalyst containing chiral ligands. Optically active amino compounds can also be obtained, besides fermentation, with achiral synthetic methods followed by separation of the racemic product.

The aim of this review is to provide a survey of heterogeneous metal catalyst-mediated hydrogenations affording chiral amino acids or amines from Schiff's bases, dehydroamino acids or peptides, dehydrodiketopiperazines and oximes in diastereo-differentiating reactions.

## 2. Diastereoselective hydrogenation of C=C double bonds

For the hydrogenation of C=C double bonds under mild conditions, the catalysts most often used are supported palladium, platinum oxide and Raney nickel. At times rhodium and ruthenium on specific supports find application [2].

### 2.1. *N-acyl-α,β-dehydroamino acids*

Diastereoselective hydrogenation of dehydroamino acid derivatives containing an appended chiral auxiliary has provided a useful, preparative approach to make various optically active amino acids.

Heterogeneous catalytic hydrogenations of chiral *N*-acyl-α,β-dehydroamino acid esters and amides were carried out. The chiral alcohol used was (−)-

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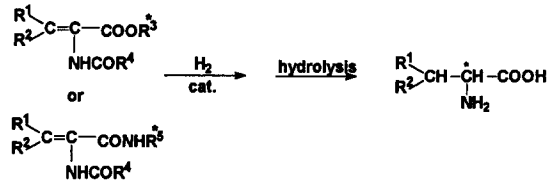


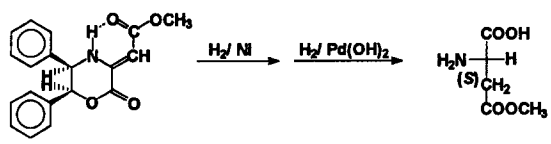
Scheme 1. Hydrogenation of chiral *N*-acyl-$\alpha,\beta$-dehydroamino acid esters and amides.

menthol [3–5], the chiral amines used were 2-phenylpropylamine [6], $\alpha$-methylbenzylamine [7,8], $\alpha$-ethylbenzylamine [8] and $\alpha$-(1-naphthyl)ethylamine [8]. The catalysts were Pd on carbon, Pd on alumina and Raney nickel. The hydrogenation product was hydrolyzed to give an optically active amino acid (Scheme 1). The optical purity of the resulting amino acids was poor (<40%). In some reactions, the inversion of the product configuration was observed [8].

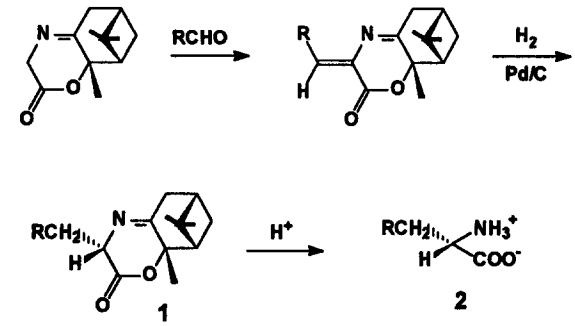
Catalytic hydrogenation and subsequent hydrogenolysis of a chiral dehydroamino acid prepared from dimethylacetylene dicarboxylate and *erythro*-2-amino-1,2-diphenylethanol afforded (*S*)-(+)-aspartic acid methyl ester in >98% ee and in high chemical yield (Scheme 2) [9]. On the other hand, a similar 1,4-oxazine derivative having only one phenyl group was hydrogenated and aspartic acid was obtained only in 12–17% ee [10]. Assuming hydrogen attack against the face of the C=C double bond away from the phenyl groups, two phenyl groups in the reactant molecule presumably provided much more steric shielding effect than one.

The trisubstituted olefinic bond of chiral cyclic $\alpha,\beta$-dehydroamino acid derivatives was hydrogenated over palladium on carbon with high asymmetric induction to give, after hydrolysis, the corresponding (*S*)-amino acids in high yield (Scheme 3) (Table 1) [11].

Chiral 2,3-dehydroamino acid derivatives were hydrogenated with complete stereoselectivity over



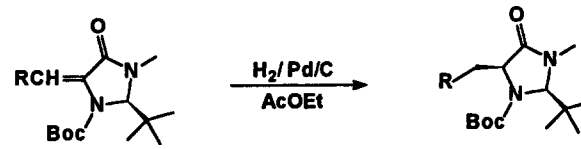
Scheme 2. Hydrogenation and subsequent hydrogenolysis of a chiral dehydroamino acid prepared from dimethylacetylene dicarboxylate and *erythro*-2-amino-1,2-diphenylethanol.



Scheme 3. Hydrogenation and hydrolysis of chiral cyclic $\alpha,\beta$-dehydroamino acid derivatives.

Table 1
Chemical and optical yields in the hydrogenation and hydrolysis of chiral cyclic $\alpha,\beta$-dehydroamino acid derivatives (Scheme 3)

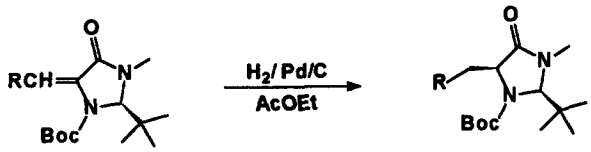
| R | Yield (%) (1) | de (%) | Yield (%) (2) | ee (%) |
|---|---|---|---|---|
| Methyl | 75 | >95 (*S*) | 93 | >95 (*S*) |
| Ethyl | 73 | >95 (*S*) | 92 | >95 (*S*) |
| Phenyl | 68 | >95 (*S*) | 93 | >95 (*S*) |
| 3,4-Dimethoxyphenyl | 63 | >95 (*S*) | 85 | >95 (*S*) |



Scheme 4. Hydrogenation of chiral 2,3-dehydroamino acid derivatives to unusual chiral amino acids.

Pd/C (Scheme 4) and then were converted to unusual chiral amino acids [12]. Presumably, the addition of the hydrogen molecule occurred from the face opposite to the *tert*-butyl group with complete selectivity.

Hydrogenation of unsaturated $\alpha$-amido-$\gamma$-lactones over rhodium on alumina afforded lyxo-1,4-lactones (Scheme 5) [13]. Hydrogenation of tetronic acid over Adams' platinum or Rh on carbon in ethyl acetate at ambient temperature under medium pressure resulted in the recovery of the starting material. The use of Rh on alumina catalyst gave the excess of the (*S*)-lyxo-1,4-lactone product (**3**). The yield of the (*S*)-lyxo-1,4-lactone increased (59% → 91%) and the reaction time decreased (96 h → 24 h) with increasing pressure (6.5

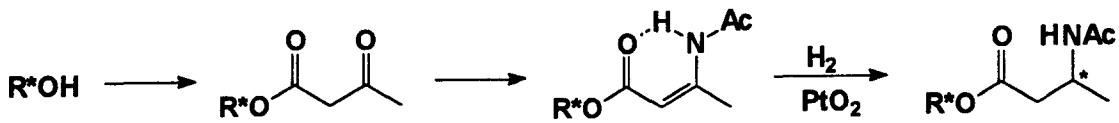



Scheme 5. Hydrogenation of tetronic acid.

bar → 120 bar). This complete stereoselectivity ((*S*)-lyxo-1,4-lactone obtained in 91% yield) could be due to the presence of the α-methyl group, which could completely block the hydrogen attack from the α-face of the C=C double bond. These lactones are versatile intermediates for amino sugars and *S*-configurated β-hydroxy-α-amino acids.

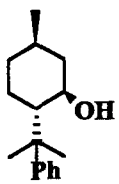
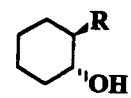
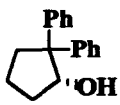
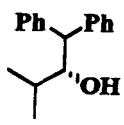
Catalytic hydrogenation of chiral β-acetamidocrotonic acid esters over platinum oxide gave β-acetamidobutyrates in optically active form (Scheme 6) [14]. Chiral alcohols (R*OH) (Table 2) were converted into acetoacetates and were sequentially treated with ammonia and acetic anhydride to provide the (*Z*)-β-acetamidocrotonates, except for the *trans*-2-(*p*-*tert*-butylphenyl) cyclohexanol derivative, which resulted in a separable mixture of (*E*)- and (*Z*)-acetamidocrotonates. β-Acetamidobutyrates were given by hydrogenation over $PtO_2$. An excellent diastereomeric excess was observed in the hydrogenation of the ester of *trans*-2-(4-biphenyl) cyclohexanol. Diastereoselectivity decreased substantially when *trans*-2-phenyl cyclohexanol or *trans*-2-(*p*-*tert*-butylphenyl) cyclohexanol was used, compared with de obtained with (−)-phenylmenthol, the chiral auxiliary, developed by Corey. 2,2-Diphenyl cyclopentanol proved to be a highly effective auxiliary, whereas the open chain version, 1,1-diphenyl-3-methyl-2-butanol gave slightly lower diastereomeric excess. Great decrease was observed in de in the hydrogenation of (*E*)-β-acetamidocrotonate when *trans*-2-(*p*-*tert*-butylphenyl) cyclohexanol was used, compared with the corresponding (*Z*)-isomer.

The results strongly supported that the aromatic part of these auxiliaries played a crucial role, probably in




Scheme 6. Hydrogenation of chiral β-acetamidocrotonic acid esters.

Table 2
Diastereomeric excesses in the hydrogenation of chiral β-acetamidocrotonic acid esters (Scheme 6)

| R*OH | de (%) | R*OH | de (%) |
|---|---|---|---|
|  | 95 |  R=Ph | 77 |
|  | 96 | R=*t*BuC$_6$H$_4$((*Z*)-enamido ester) | 80 |
|  | 86 | R=*t*BuC$_6$H$_4$((*E*)-enamido ester)<br>R=*p*-Ph-C$_6$H$_4$ | 6<br>95 |

shielding one of the π-faces in the corresponding enamido esters. The presence of a pseudoring, due to the intramolecular hydrogen bonding in (Z)-enamido esters, seemed to be important in order to obtain a good diastereoface-differentiation in this hydrogenation reaction.

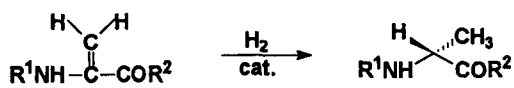
### 2.2. *Dehydrodi-, tri-, tetrapeptides*

*N*-Acetyldehydroalanyl amino acid methyl ester and *N*-formylaminoacyl-dehydroalanine methyl ester, in which amino acids used as the chiral moiety were valine, phenylalanine and phenylglycine, were hydrogenated with Pd/C using various solvents and at various temperatures. Systematic results were obtained; however, the optical purity of the resulting alanine was rather low (~30%) [15]. Optical purities of 40–50% were reported with (*S*)-proline *tert*-butyl ester as chiral moiety [15].

Harada and co-workers thoroughly studied the asymmetric catalytic hydrogenation of chiral dehydrotripeptides that contain a dehydroalanine and a proline residue, over palladium on carbon (Scheme 7) [16]. In all reactions, the absolute configuration of the resulting alanine was (*R*). The optical yield of the resulting alanine was up to 93%, and the chemical yield was in the range 86–97% (Table 3). The results showed that the amino acid in the C-terminal position had much larger contribution in determining the absolute sense and degree of asymmetric induction in producing the (*R*)-alanine moiety than the N-terminal amino acid; C-terminal (*S*)-proline derivatives gave (*R*)-alanine in every case, regardless of the absolute configuration of the N-terminal residue. The presence of proline *tert*-butyl amide as the C-terminal amino acid in the reactants appeared to be an important factor in performing an effective asymmetric induction by the heterogeneous hydrogenation.

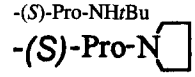
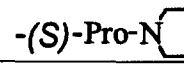
Asymmetric hydrogenation of dehydrodipeptides containing a proline amide residue was published by Schmidt et al. [17]. The catalysts used were Pd/C and $Pd/CaCO_3$. Asymmetric induction was generally high (Table 4). Proline methylamide and proline anilide as the C-terminal amino acid resulted in high diastereoselectivities as compared with the results of proline dimethylamide. Other chiral auxiliaries were not so efficient as the proline amides. It was found that the pressure, temperature and concentration had little effect, and the best solvent was toluene.

Asymmetric hydrogenation of dehydrotripeptides containing a dehydroalanine, a dehydrobutyrine and a C-terminal (*S*)-proline moiety was examined over



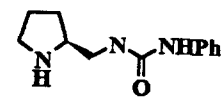
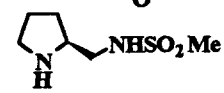
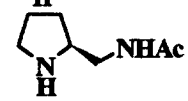

Scheme 7. Hydrogenation of chiral dehydrotripeptides.

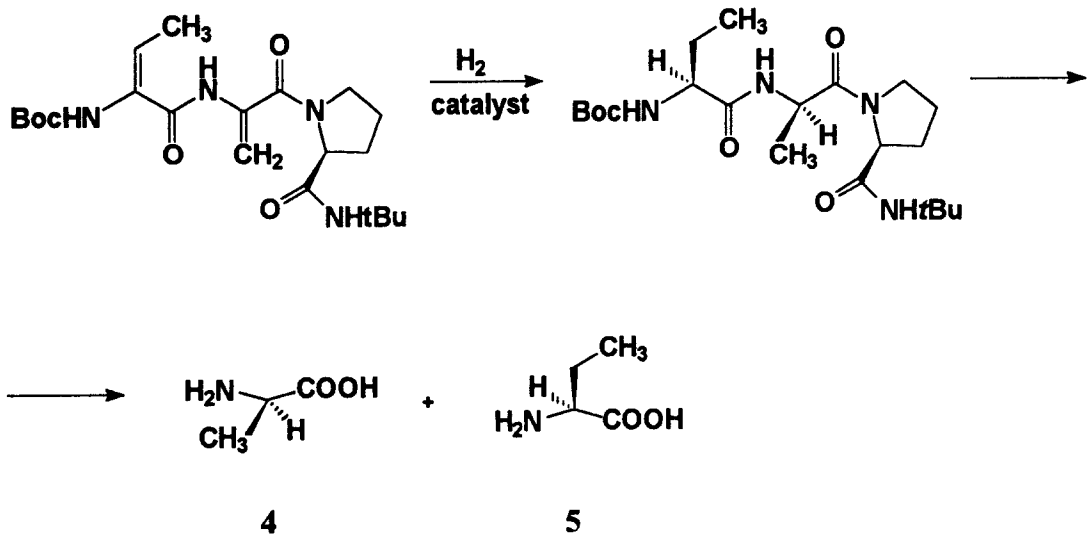
Table 3
Chemical and optical yields in the hydrogenation of chiral dehydrotripeptides (Scheme 7)

| $R^1$ | $R^2$ | Yield (%) | ee (%) |
|---|---|---|---|
| Boc[a]-Gly- | -(*S*)-Pro-NH*t*Bu | 96 | 84 |
| Boc-(*S*)-Val- | -(*S*)-Pro-NH*t*Bu | 97 | 87 |
| Boc-(*R*)-Val- | -(*S*)-Pro-NH*t*Bu | 97 | 81 |
| Boc-(*S*)-Ile- | -(*S*)-Pro-NH*t*Bu | 97 | 90 |
| Boc-(*R*)-Phe- | -(*S*)-Pro-NH*t*Bu | 92 | 89 |
| Boc-(*R*)-Pro- | -(*S*)-Pro-NH*t*Bu | 96 | 89 |
| Boc-(*R*)-Ser- | -(*S*)-Pro-NH*t*Bu | 86 | 82 |
| Boc-(*R*)-Ser(*t*Bu) | -(*S*)-Pro-NH*t*Bu | 96 | 93 |
| Boc-Gly- |  | 92 | 43 |
| Boc-(*S*)-Val- |  | 96 | 74 |

[a]Boc=*tert*-Butyloxycarbonyl.

Table 4
Diastereomeric ratio in the hydrogenation of dehydrodipeptides containing a proline amide residue (Scheme 7)

| $R^1$ | $R^2$ | *R,S* : *S,S* |
|---|---|---|
| PhCO; MeCO | (*S*)-Pro-NHMe | 90 : 10–95 : 5 |
| MeCO | (*S*)-Pro-NHPh | 95 : 5 |
| PhCO | (*S*)-Pro-$NMe_2$ | 71 : 29 |
| PhCO |  | 75 : 25 |
| PhCO |  | 77 : 23 |
| PhCO |  | 76 : 24 |
| PhCO |  | 76 : 24 |

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Scheme 8. Hydrogenation of dehydrotripeptides containing a dehydroalanine, a dehydrobutyrine and a C-terminal (*S*)-proline residue.

Table 5
Chemical and optical yields in the hydrogenation of dehydrotripeptides containing dehydroalanine and dehydrobutyrine and a C-terminal (*S*)-proline residue (Scheme 8)

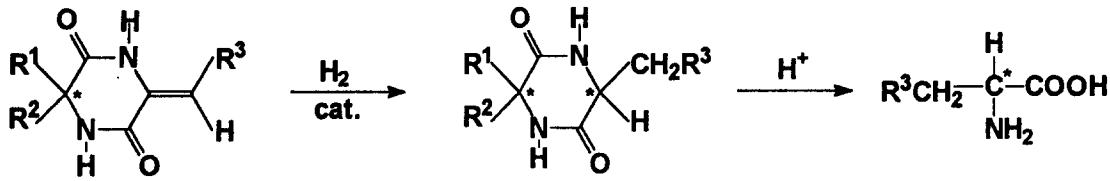
| Catalyst | Yield (%) (**4**) | ee (%) (**4**) | Yield (%) (**5**) | ee (%) (**5**) |
|---|---|---|---|---|
| W-1 Raney Nickel | 92 | 94 | 73 | 54 |
| 5% Pd/C | 97 | 91 | 84 | 22 |
| 5% $Pd(OH)_2/C$ | 95 | 95 | 98 | 25 |
| $PtO_2$ | 91 | 89 | 31 | 6 |

different catalysts in different solvents and at different temperatures (Scheme 8) [18]. The configuration of the resulting alanine and butyrine were (*R*) and (*S*), respectively. High optical yield of the internal alanine was reported, ranging from 89% to 94%, depending on the reaction conditions, while the butyrine residue was produced with much lower enantioselectivity, 54% in the best case (Table 5). A possible steric course of the catalytic hydrogenation of dehydrodi- and tripeptides that contain proline as the chiral moiety was proposed.

### 2.3. *Dehydrodiketopiperazines*

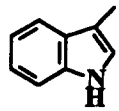
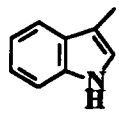
Many papers deal with the stereoselective hydrogenation of dehydrodiketopiperazines obtained from the condensation of cyclodipeptides with aldehydes. In earlier studies, optically active amino acids, such as (*S*)-phenylalanine and (*S*)-tyrosine, were produced by the asymmetric hydrogenation of dehydrodiketopiperazines containing (*S*)-isovaline [19,20] or (*S*)-(+)-α-amino-α-phenylpropionic acid as the chiral moiety [21]. The reactant was hydrogenated over a palladium catalyst, and the resulting product was then hydrolyzed. The observed optical purities of the products were low and could not be trusted to represent the actual chiral induction, since the final products were usually isolated by crystallization.

Izumiya and co-workers extensively studied the catalytic hydrogenation of dehydrodiketopiperazines containing dehydro-α-aminobutyric acid, dehydrovaline, dehydroleucine, dehydrophenylalanine, dehydro-2-amino-5-phenylpentanoic acid and dehydrotryptophan residues and generally obtained high levels of asymmetric induction (Scheme 9) (Table 6) [22–24]. In some reactions, excellent optical purities of the resulting amino acids (>99%) were reported. Lower




Scheme 9. Hydrogenation of dehydrodiketopiperazines.

Table 6
Chemical and optical yields in the hydrogenation of dehydrodiketopiperazines (Scheme 9) ($R^2$=H)

| $R^1$ | $R^3$ | Yield (%) | ee (%) |
|---|---|---|---|
| Me | Me | 48 | 99 |
| $AcNH(CH_2)_5$ | Me | 45 | 97 |
| Me | *i*Pr | 8 | 96 |
| Me | *i*Bu | 47 | 98 |
| *i*Pr | *i*Bu | 61 | >99 |
| *i*Bu | *i*Bu | 69 | 98 |
| $AcNH(CH_2)_5$ | *i*Bu | 22 | 95 |
| Me | Ph | 56 | 88 |
| *i*Pr | Ph | 63 | 94 |
| *i*Bu | Ph | 52 | 90 |
| $AcNH(CH_2)_5$ | Ph | 26 | 77 |
| Me | $PhCH_2CH_2$ | 55 | 98 |
| *i*Bu | $PhCH_2CH_2$ | 52 | 97 |
| Me |  | 49 | 71 |
| *i*Bu |  | 18 | 66 |

asymmetric induction could be achieved with dehydrophenylalanine and dehydrotryptophan. Solvent, temperature and catalyst effects on ee were found to be small. The wide range in chemical yields most likely reflects the experimental difficulties in the separation of the two amino acids.

Various optically active diketopiperazines containing dehydroalanine were prepared and catalytically hydrogenated (Table 7) [25]. The determination of the *R/S* ratio was carried out by converting the hydrolyzed products to (*S*)-leucyl derivatives by treating with [Cbz-(*S*)-Leu-ONSu], and the resulting (*S*)-Leu-(*S*)-Ala/(*S*)-Leu-(*R*)-Ala ratio was determined using an amino acid analyzer [26]. The results indicated that very effective asymmetric hydrogenation took place.

Table 7
Optical yields in the hydrogenation of diketopiperazines containing dehydroalanine (Dha)

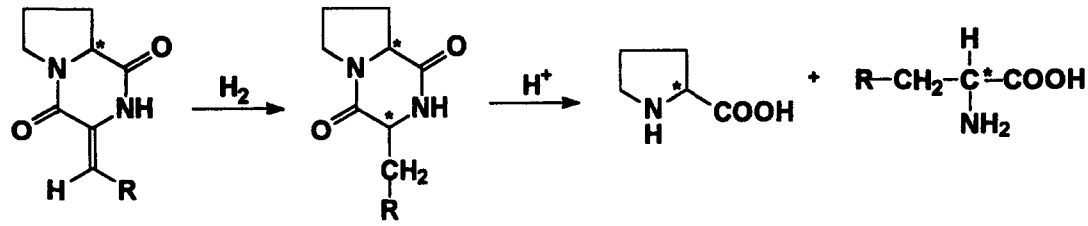
| Cyclic dehydrodipeptide | Chiral induction in the cyclic dipeptides (%) (*S*) |
|---|---|
| c((*S*)-Ala-Dha) | 94.6 |
| c((*S*)-Val-Dha) | 98.4 |
| c((*S*)-Leu-Dha) | 95.8 |
| c((*S*)-Phe-Dha) | 94.6 |
| c((*S*)-Lys(ε-Ac)-Dha) | 91.8 |
| c((*S*)-Leu-Z-Dhb[a]) | 95.6 |
| c((*S*)-Pro-Dha) | 84.8 |

[a]Dhb=Dehydrobutyrine.

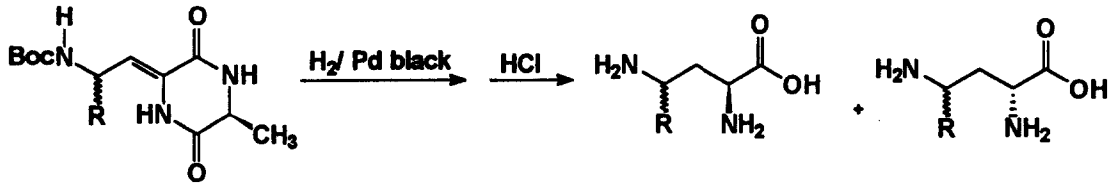
The isopropyl side chain of (*S*)-Val resulted in extremely high asymmetric induction, but even the small methyl group of (*S*)-Ala was highly efficient. Interestingly, the (*S*)-Pro residue caused lower asymmetric induction than other amino acids tested. The catalytic hydrogenation of *N-tert*-butoxycarbonyl-(*S*)-leucyl-dehydroalanine methyl ester gave only 2% chiral induction. Therefore, a rigid diketopiperazine ring seemed to be necessary for the effective asymmetric hydrogenation of dehydroamino acids.

Unusual aromatic amino acids, (*S*)-Tyr(Me) and (*S*)-Amp (Amp=2-amino-5-(*p*-methoxyphenyl)pentanoic acid), were synthesized by the hydrogenation of cyclo(dehydroTyr(Me)-(*S*)-Ala) and cyclo(dehydro-Amp-(*S*)-Ala) followed by hydrolysis and recrystallization. High chiral inductions in the hydrogenation of the cyclic dipeptides (95% and 97%, respectively) were observed [27].

Asymmetric hydrogenation of diketopiperazines containing (*S*)-proline as the chiral moiety was investigated [28,29], and optical purities up to 90% were reported (Scheme 10). While earlier studies emphasized the effectiveness of (*S*)-proline as a chiral moiety, later other amino acids proved to be more effective in asymmetric hydrogenations [52].



Scheme 10. Hydrogenation of diketopiperazines containing (*S*)-proline as the chiral moiety.



Scheme 11. Preparation of optically active unusual amino acids.

Optically active unusual amino acids, ornithine, 2,4-diaminopentanoic acid and 2,4-diamino-6-methylheptanoic acid were prepared by hydrogenation of 2-alkylidene-diketopiperazines (Scheme 11) (Table 8) [30]. The hydrogenated products were hydrolyzed and separated by chromatography. The degree of chiral induction was clearly influenced by the stereogenic center in the side chain.

Heterogeneous catalytic hydrogenation of dehydrodi-, tri- and tetrapeptides usually resulted in lower optical yields, as compared to the hydrogenation of dehydrodiketopiperazine derivatives.

## 3. Asymmetric hydrogenation of C=N double bonds

### 3.1. Synthesis of amino acids

The asymmetric heterogeneous catalytic hydrogenation of the carbon–nitrogen double bond affording optically active amino acids has been extensively studied. Some of the reactants used are oximes and hydrazones, but most of the reactions are carried out using Schiff's bases of α-keto acid derivatives. Enantiomeric excesses obtained by this approach are generally moderate or low.

Table 8
Chiral induction in the preparation of optically active unusual amino acids (Scheme 11)

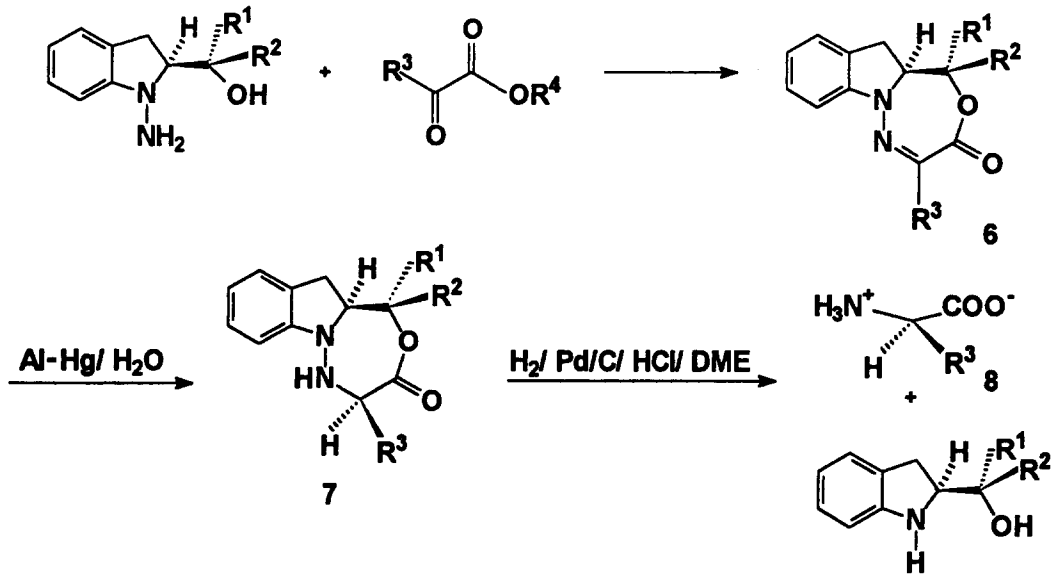
| R | Chiral induction (*S*/*R* ratio) |
|---|---|
| $CH_3$ (*S*) | 3:2 |
| $CH_3$ (*R*) | 5:1 |
| *i*Bu (*S*) | 19:1 |
| *i*Bu (*R*) | 3:2 |

Excellent optical and chemical yields were given by the hydrazino lacton method of Corey (Scheme 12) [31]. α-Keto esters were condensated with chiral *N*-aminoindolines affording the hydrazono lactones. Aluminum amalgam reduction proceeded with a very high degree of asymmetric induction (Table 9), followed by catalytic hydrogenation giving the amino acids and the chiral indolines, that could be recovered and regenerated with nitrosation and subsequent reduction to the *N*-amino reactants.

#### 3.1.1. Oximes and hydrazones of α-keto acid derivatives

Hydrogenation of oximes prepared from (−)-menthyl esters of pyruvic acid, α-ketobutyric acid and benzoylformic acid resulted in the corresponding amino acids with low optical purities ((*R*)-alanine (16–25%), (*R*)-α-aminobutyric acid (8–21%), (*R*)-phenylglycine (44–49%)) (Scheme 13) [32]. The catalyst used was palladium on carbon or palladium hydroxide on carbon.

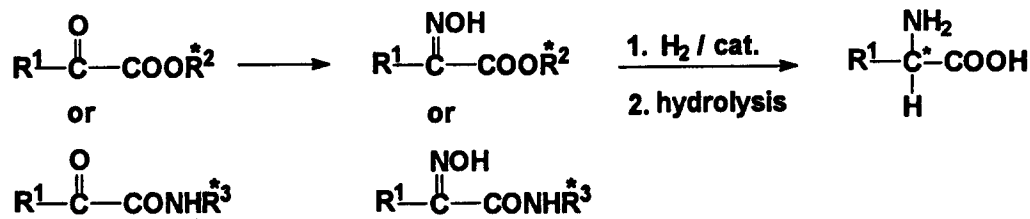
Catalytic hydrogenation of oximes of *N*-(*S*)- or *N*-(*R*)-α-methylbenzyl benzoylformamide and *N*-(*S*)- or




Scheme 12. The hydrazino lacton method of Corey in the preparation of amino acids.

Table 9
Chemical and optical yields in the hydrazino lacton method of Corey (Scheme 12)

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Yield 8 (%) (6) | Yield (%) (7) | Yield (%) (8) | ee (%) |
|---|---|---|---|---|---|---|---|
| H | Me | Me | *p*-Nitrophenyl | 70 | 95 | 78 | 96 |
| H | Me | Et | *p*-Nitrophenyl | 70.5 | 93 | 70 | 97 |
| H | Me | *i*Pr | Me | 65 | 79 | 53.5 | 97 |
| H | Me | *i*Bu | Me | 70 | 95 | 78 | 99 |
| Me | H | Me | *p*-Nitrophenyl | 62 | 97 | 90 | 92 |
| Me | H | Et | *p*-Nitrophenyl | 50 | 96 | 65 | 96 |



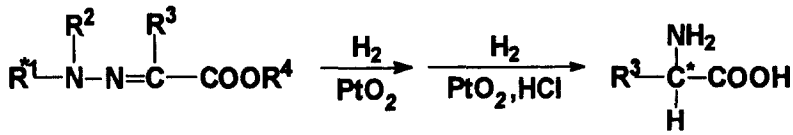

Scheme 13. Hydrogenation of oximes of α-keto acid esters or amides.

*N*-(*R*)-α-ethylbenzyl benzoylformamide afforded α-phenylglycine in low optical purity (5–10%) [33]. An inversion of the configuration was observed when the methyl group in the chiral moiety was replaced with an ethyl group.

The results on the hydrogenation of hydrazones prepared from α-keto acids are summarized in the papers of Akabori and Kiyooka (Scheme 14, Table 10) [6,34].

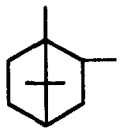
### 3.1.2. *Imines of α-keto acid derivatives*

Hydrogenation of the C=N bond of Schiff's base, prepared from an α-keto acid or its derivative and an optically active amine or amino acid, followed by



Scheme 14. Hydrogenation of hydrazones prepared from α-keto acids.

Table 10
Optical yields in the hydrogenation of hydrazones prepared from α-keto acids (Scheme 14)

| $R^{*1}$ | $R^2$ | $R^3$ | $R^4$ | ee (%) (S) |
|---|---|---|---|---|
| $C_6H_5CH_2CH(CH_3)CO$ | H | $CH_3$ | H | 8 |
| $C_6H_5CH_2CH(CH_3)CO$ | H | $C_6H_5CH_2$ | H | 4 |
|  (S) | $CH_3$ | $CH_3$ | $C_2H_5$ | 47 |
| (S)-1,2-Dimethylpropyl | $CH_3$ | $CH_3$ | $C_2H_5$ | 32 |

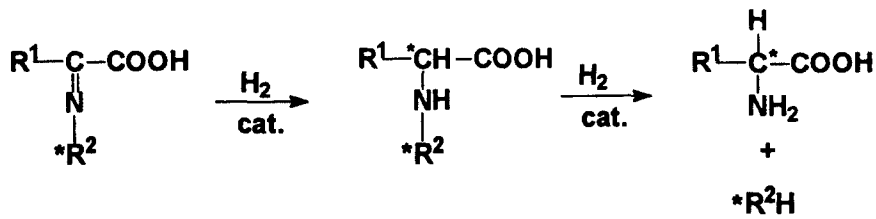
hydrogenolysis, results in an optically active amino acid (Scheme 15). This method is often called asymmetric transamination. Generally, palladium catalysts are used in both hydrogenation and hydrogenolysis processes. Asymmetric induction arises during the catalytic hydrogenation of the C=N double bond and the configuration produced changes only slightly or not at all during the hydrogenolysis. In the chiral amine, the N atom is most often linked to a benzylic position, and as a result the auxiliary can be removed by catalytic hydrogenation.

Optical purities and chemical yields achieved with α-methylbenzylamine as chiral auxiliary were low (12–18% ee and 20–80%, resp.) [35]. When (S)-amine was used, (S)-amino acid was obtained. It was found that the magnitude of asymmetric induction depended on the alkyl group of the α-keto acid as well as on the catalyst used.

The imine from benzoylformic acid and (S)-α-methylbenzylamine was hydrogenated over Raney nickel, $PtO_2$, 5% Pd/C (acidic and basic treatment) and 10% $Pd(OH)_2$/C catalysts [36]. (S)-Phenylglycine was obtained when (S)-amine was used. The optical purities were generally poor (1–7% ee), but 73% ee was reported with $Pd(OH)_2$/C catalyst. The proposed steric curse of the asymmetric hydrogenation was based on Prelog's rule [37].

Optically active alanine, α-aminobutyric acid, phenylglycine and glutamic acid were prepared by the hydrogenation of Schiff's bases of the corresponding α-keto acids and (S)-α-methylbenzylamine (Me(−)), (S)-α-ethylbenzylamine (Et(−)) and (R)-α-(1-naphthyl)ethylamine (Naph (+)) with modest to poor selectivities [38,39]. A considerable substituent effect on the extent of asymmetric induction was found: as the alkyl group increased, the optical purity of the resulting amino acid decreased (Table 11).

A study of Harada et al. [38] revealed that stereoselectivity decreased with increasing solvent polarity in the hydrogenolytic asymmetric transamination between α-keto acids and optically active benzylic amines. A similar solvent effect was found in the hydrogenation of the imine prepared from ethyl pyruvate and (R)-phenylglycine alkyl esters [40] or (R)-2-amino-2-phenylethanol [41]. The optical purity of the



Scheme 15. Hydrogenation of Schiff's base prepared from an α-keto acid or its derivative and an optically active amine or amino acid followed by hydrogenolysis.

Table 11
Optical yields in the hydrogenation of Schiff's bases prepared from the corresponding α-keto acids and optically active amines

| α-Keto acid (RCOCOOH) | Amine | Amino acid | Optical yield (%) |
|---|---|---|---|
| R=$CH_3$ | Me(−) | (*S*)-Alanine | 67 |
| | Et(−) | (*S*)-Alanine | 52 |
| | Naph(+) | (*R*)-Alanine | 83 |
| $C_2H_5$ | Me(−) | (*S*)-Butyrine | 44 |
| | Et(−) | (*S*)-Butyrine | 33 |
| $C_6H_5$ | Me(−) | (*S*)-Phenylglycine | 30 |
| | Et(−) | (*S*)-Phenylglycine | 24 |
| $CH_2C_6H_5$ | Me(−) | (*S*)-Phenylalanine | 14 |
| | Et(−) | (*S*)-Phenylalanine | 10 |
| $(CH_2)_2COOH$ | Me(−) | (*S*)-Glutamic acid | 12 |
| | Et(−) | (*S*)-Glutamic acid | 6 |

resulting alanine ranged between 10% and 62%. In the case of asymmetric synthesis of glutamic acid from α-ketoglutaric acid and (*S*)-α-methylbenzylamine, the use of polar solvent resulted in the inversion of the product configuration [38]. Whereas, in the hydrogenation of Schiff's base made of acetophenone and alanine ethyl ester, the asymmetric induction increased with increasing solvent polarity [42].

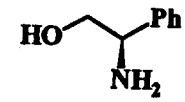
Baiker et al. investigated the effect of chiral modifiers in the Pt mediated hydrogenation of ethyl pyruvate. In contrast to what was reported in Refs. [38,39], they experienced the reductive amination of ethyl pyruvate with (*S*)-1-(1-naphthyl)ethylamine of 97% diastereoselectivity [43]. This could be due to the smaller substituent of the keto acid reactant and the Pt catalyst used.

Another study of the reductive amination of (*S,S*)-peptides with α-keto esters resulted in the (*S,S,S*) product in high de using Raney Ni. Ru, Pt and Rh, however, were ineffective. The product compounds are the ACE inhibitors enalapril and lysinopril [44].

Tungler et al. investigated the enantioselective hydrogenation of ethyl pyruvate in the presence of (*S*)-proline. The complete reductive alkylation of proline occurred with more than 60% de [45].

Temperature effect between −20°C and 65°C on the hydrogenation of Schiff's bases, prepared from ethyl pyruvate and several optically active amines, was studied [46,47]. At relatively low temperatures, when (*S*)-amine was used, (*S*)-alanine was obtained. The enantiomeric excess of (*S*)-alanine (80% at −20°C) decreased as the reaction temperature increased, and the configuration inverted to (*R*)-alanine at 50°C.

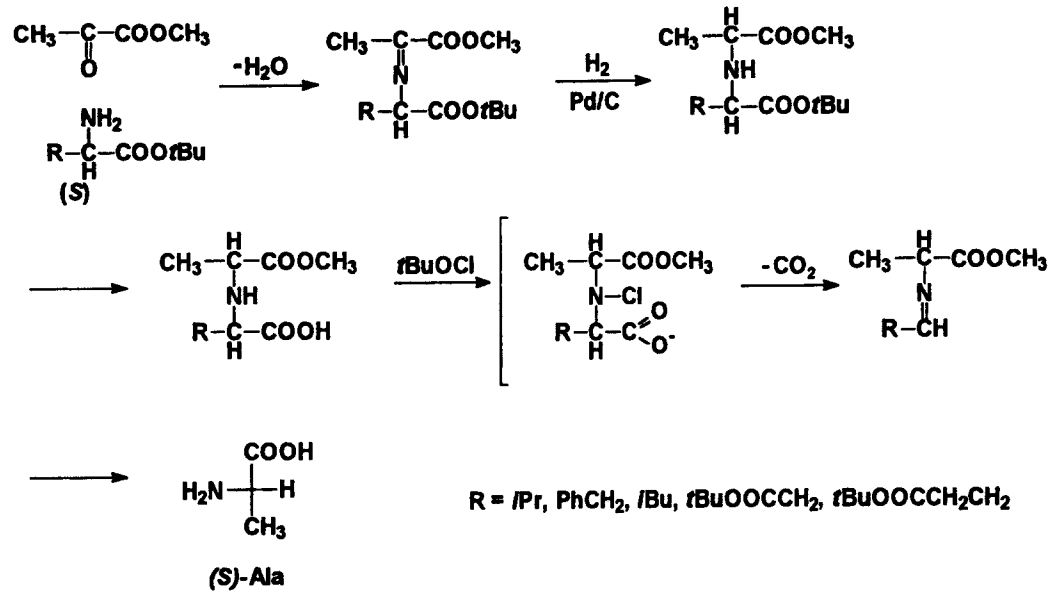
Table 12
Chemical and optical yields in the hydrogenation of Schiff's bases of phenylglycinol and α-keto acids

| α-Keto acid ($R^1COCOOH$) | Chiral amine | Yield (%) | ee (%) |
|---|---|---|---|
| $R^1=CH_3$ |  | 42 | 85 (*S*) |
| $C_2H_5$ | | 33 | 86 (*S*) |
| $PhCH_2$ | | 17 | 17 (*S*) |
| Ph | | 21 | 25 (*R*) |

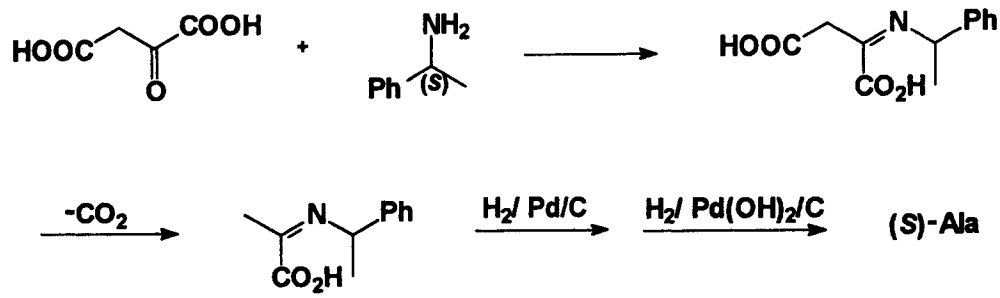
Similar inversion of the configuration was observed in the asymmetric transamination of ethyl pyruvate and (*R*)-α-phenylglycine ethyl ester [39,40].

Schiff's bases of phenylglycinol and α-keto acids were hydrogenated over Pd/C to the corresponding amino acids (Table 12) [48]. Phenylglycinol proved to be a more efficient chiral auxiliary than α-phenylethylamine.

The asymmetric transamination reaction between optically active amino acids and methyl pyruvate was investigated [49]. The resulting imine was hydrogenated and partially hydrolyzed, then oxidized with *tert*-butyl hypochlorite to form alanine (Scheme 16). The optical purity of alanine was moderate (50–70%). Similar transamination of ketones with optically active (*S*)-amino acids was carried out [50]. Optically active (*S*)-2-amino-3-phenylpropane and α-methylbenzylamine were obtained with optical purities of 20–87% and 30–69%, respectively.




Scheme 16. Hydrogenation of Schiff's bases prepared from α-keto acid esters and amino acid esters.



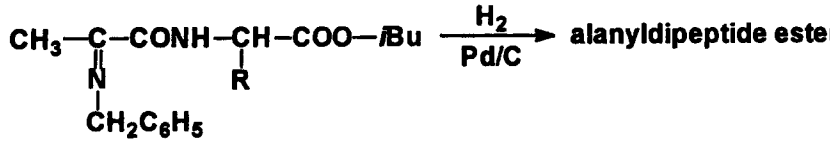

Scheme 17. Hydrogenolytic transamination reaction between a benzylic amine and oxalacetic acid.

Catalytic hydrogenation of Schiff's bases prepared from α-keto acid esters and amino acid esters was carried out [51]. Diastereomeric excesses were in the range 40–70%, a substituent and a temperature effect were observed.

It was found that decarboxylation of Schiff's base took place in the hydrogenolytic transamination reaction between a benzylic amine and oxalacetic acid [52], since alanine rather than aspartic acid was the product. Optical yields of 52–69% were reported (Scheme 17).

Moderate selectivities were given in the asymmetric catalytic hydrogenation of Schiff's base from α-ketoacyl amide derivatives [53].

Inversion of the configuration was observed in the synthesis of phenylglycine by the hydrogenation of oximes of the corresponding amides when (*S*)-α-methylbenzylamine was used, compared with the case when (*S*)-α-ethylbenzylamine was used [33]. In order to study this reversal of the configuration, Schiff's bases of pyruvylamino acid isobutyl esters were catalytically hydrogenated (Scheme 18) [54]. Similar inversion of the configuration was found; when (*S*)-alanine was the chiral moiety, the configuration of the resulting alanyl residue was predominantly (*R*). When the substituent in the asymmetric moiety was bulkier, the configuration of the product was inverted (Table 13). The steric

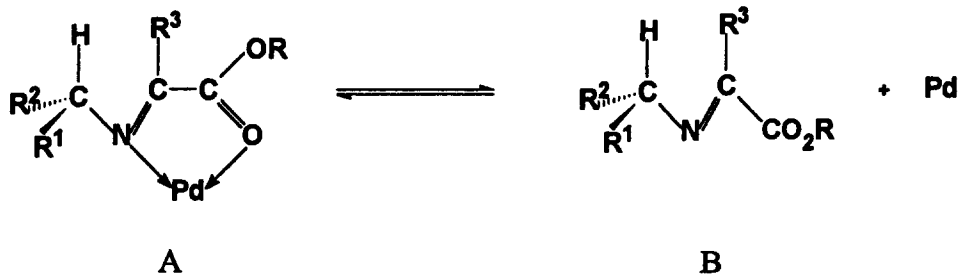



Scheme 18. Hydrogenation of Schiff's bases of pyruvylamino acid isobutyl esters.

Table 13
Results of the hydrogenation of Schiff's bases of pyruvylamino acid isobutyl esters (Scheme 18)

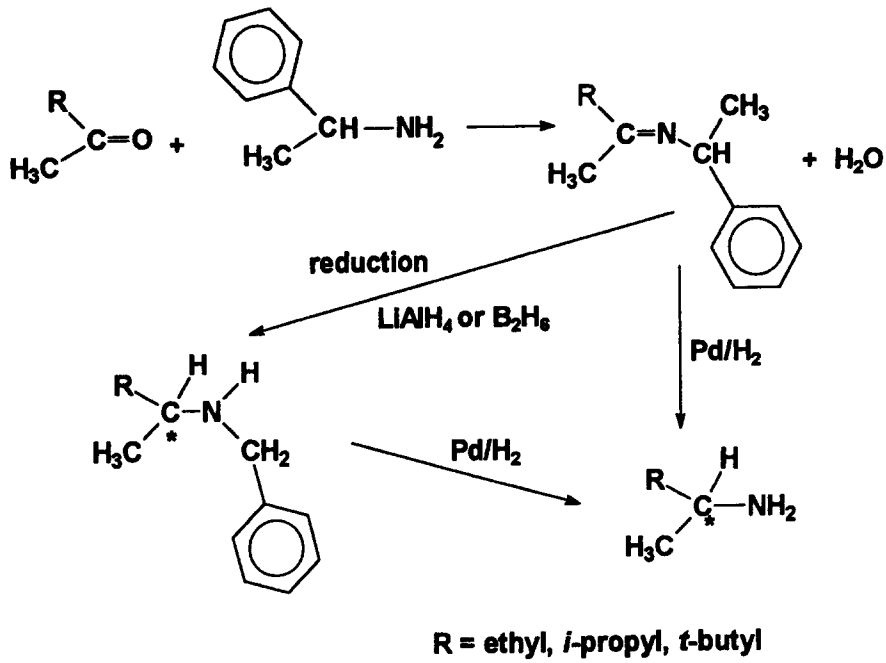
| R | Asymmetric moiety | Diastereomeric ratio | Configuration | OP[a] of alanine (%) |
|---|---|---|---|---|
| Me | (*S*)-Ala-*i*Bu | 82:18 | *R* | 64 |
| | (*S*)-Ala-Me | 76:24 | *R* | 52 |
| Et | (*S*)-α-$NH_2$-Bu-*i*Bu | 29:71 | *S* | 41 |
| *i*Pr | (*S*)-Val-*i*Bu | 34:66 | *S* | 32 |
| | (*R*)-Val-*i*Bu | 34:66 | *R* | 32 |
| | (*S*)-Val-Me | 42:58 | *S* | 17 |
| *i*Bu | (*S*)-Leu-*i*Bu | 32:68 | *S* | 39 |
| | (*S*)-Leu-Me | 41:59 | *S* | 18 |
| Benzyl | (*S*)-Phe-*i*Bu | 37:63 | *S* | 25 |
| $-CH_2COO$-*i*Bu | (*S*)-Asp-di-*i*Bu | 37:63 | *S* | 25 |
| $C_6H_5$ | (*R*)-Ph-gly-*i*Bu | 50:50 | rac. | 0 |

[a]Optical purity.




Scheme 19. The "chelation mechanism".

course of the heterogeneous catalytic hydrogenation of oximes and Schiff's bases, including the change of the configuration, was interpreted by the chelation mechanism developed by Harada et al. [55]. According to this theory, Schiff's base (or the oxime) forms a rigid five-membered cyclic ring involving a surface palladium atom as shown in Scheme 19. This reactant–catalyst complex is adsorbed on the catalyst surface from the less bulky side of the molecule, and the hydrogenation occurs. Although Schiff's base can take part in the reaction with two different structures (A and B), only the (Z) isomer can form the chelate complex. The optical yield of the product is determined by the ratio of the formation of the two structures, which are in equilibrium influenced by the reaction conditions. The existence of the chelate complex on the Pd surface was supported by some experimental data [55]. Baiker et al. suggested an alternative approach to the steric course of the Pd catalyzed hydrogenation of pyruvic acid oxime [56]. Their calculation showed that the six-membered chelate ring, involving the hydroxyl O atom of the oxime instead of the N atom, was more stable by 166 kJ/mol than the five-membered one.




Scheme 20. Asymmetric hydrogenation of Schiff's bases made of prochiral ketones and a chiral amine.

Table 14
Hydrogenation of Schiff's bases made of prochiral ketones and a chiral amine (Scheme 20)

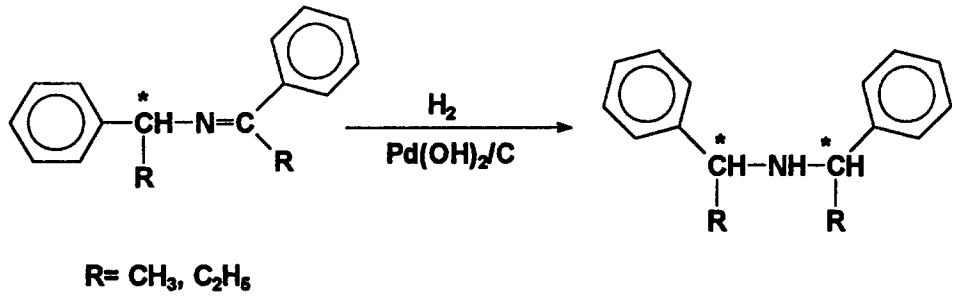
| R | Configuration of product amine | ee (%) with different reduction methods | | |
|---|---|---|---|---|
| | | $Pd(OH)_2/C$ | $LiAlH_4$ | $B_2H_6$ |
| Et | *S* | 28 | 10 | 20 |
| *i*Pr | *R* | 55 | 10 | 50 |
| *t*Bu | *R* | 56 | 5 | 60 |

### 3.2. *Diastereoselective hydrogenation of Schiff's bases to secondary amines*

In the following, the asymmetric hydrogenation of Schiff's bases made of a chiral amine and a prochiral ketone will be discussed.

French authors studied the asymmetric induction of different reduction methods of Schiff's bases: reduction with $LiAlH_4$ or with $B_2H_6$ and catalytic hydrogenation over Pd on carbon catalyst [57] (Scheme 20, Table 14). The use of $LiAlH_4$ gave poor optical yields. Moderate enantioselectivities, depending on the reactant structure, could be achieved with $B_2H_6$ or with Pd on carbon.

Harada and his co-workers investigated the effects of temperature, solvent, pressure, the amount of catalyst, and ratio of *syn* and *anti* isomers in the hydrogenation of imines made of aceto- and propiophenone and $\alpha$-methyl- and $\alpha$-ethylbenzylamine (Scheme 21, Table 15) [58]. Pressure exerted no significant effect on the stereochemical course of the reaction, neither did the *syn/anti* ratio of the imine. The latter was explained by the fact that the stereoisomers of the imine could easily be isomerized, especially on the surface of the palladium catalyst [42]. The catalyst's dispersion and its pre-treatment in hydrogen also influenced the asymmetric induction in the hydrogenation of Schiff's bases. The effect of solvent polarity




Scheme 21. Hydrogenation of imines made of aceto- and propiophenone and α-methyl- and α-ethylbenzylamine.

Table 15
The effect of reaction conditions on diastereomeric ratio in the hydrogenation of imines made of aceto- and propiophenone and α-methyl and α-ethyl benzylamine (Scheme 21)

| Reaction conditions | | Diastereomeric ratio | |
|---|---|---|---|
| | | $R=CH_3$ | $R=C_2H_5$ |
| Temperature | 50°C | 68:32 | 61:39 |
| | −20°C | 89:11 | 81:19 |
| Solvent | Methanol | | 81:19 |
| | Ethyl acetate | | 89:11 |
| Catalyst amount | 200 mg | 73:27 | |
| | 10 mg | 85:15 | |

on the diastereoisomeric ratio depended on whether the substituents, attached to the prochiral carbon atom in the reactant molecule, were more or less polar [42].

In the one-pot synthesis of a key-intermediate of opioid antagonist, hydrogenation proceeding with moderate diastereomeric excess could be combined with the separation of the diastereoisomers followed by hydrogenolytic cleavage of the aralkyl group, in this case the chiral auxiliary was a "self-immolative" one (Scheme 22) [59,60].

Similarly, the loss of the chiral auxiliary occurred in a reductive transamination reaction followed by an oxidative cleavage (Scheme 23). The chiral auxiliaries used were norephedrine enantiomers, the prochiral ketones were α-aryl ketones. Good chemical yields (80–90%) and moderate optical yields (50–67%) were obtained [61].

### 3.3. *Miscellaneous hydrogenations for the preparation of amino compounds*

In this part, some examples are presented which clearly demonstrate the versatility of the catalytic hydrogenation method in the preparation of different chiral amines (Scheme 24) [62].

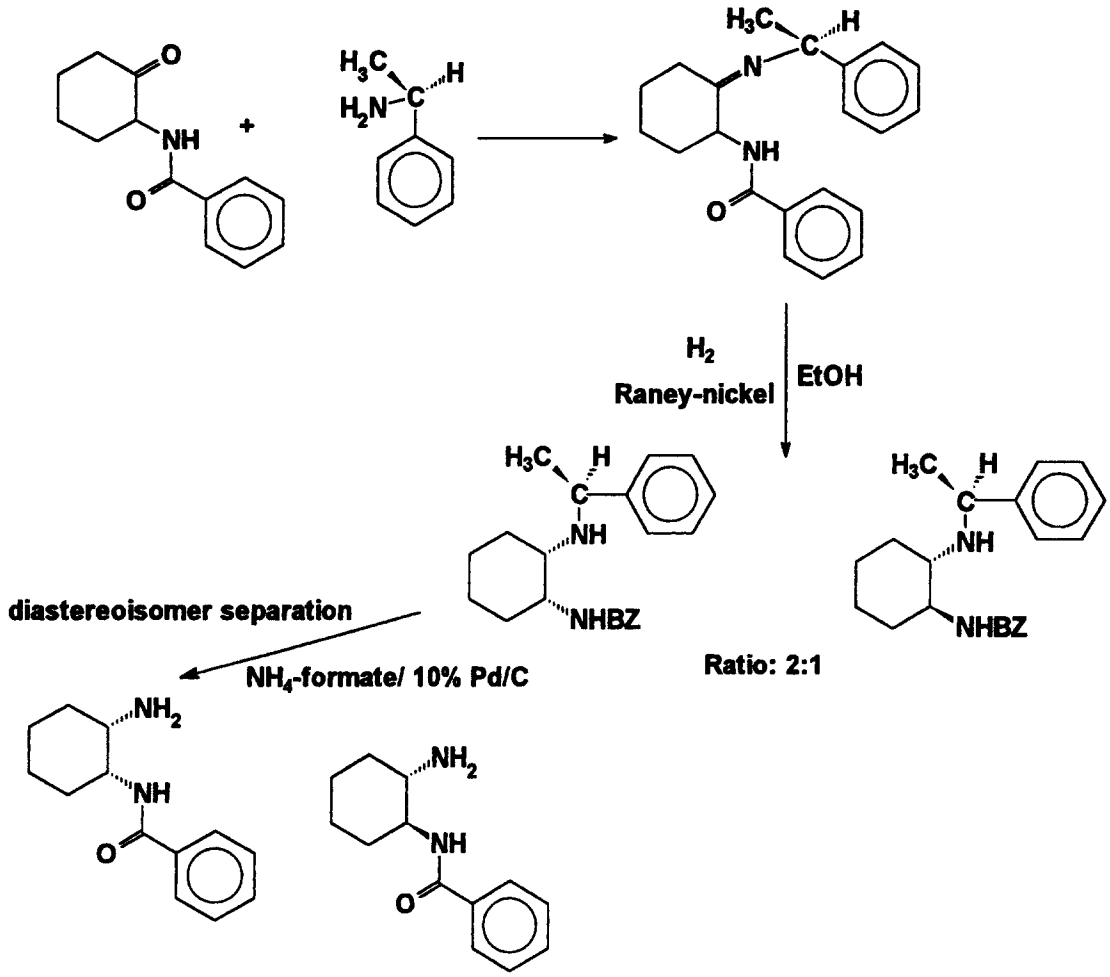
Hydrogenation of chiral nitriles on Rh/alumina resulted in secondary amines. In some cases, racemization through the intermediate imine occurred (Scheme 25) [63].

In the reduction of nitro and azido to amino groups, the configuration usually remained unchanged (Schemes 26 and 27, Table 16) [64,65].

High diastereoselectivity (>90%) was achieved in the palladium-mediated reductive amination of azido sugars (Scheme 28) [66].

Table 16
Chemical yields in the hydrogenation of chiral azido amines (Scheme 27)

| $R^1$ | $R^2$ | $R^3$ | Isolated yield (%) |
|---|---|---|---|
| H | Me | H | 97 |
| Ph | H | H | 98 |
| Me | H | Me | 96 |
| Me | Ph | Me | 98 |



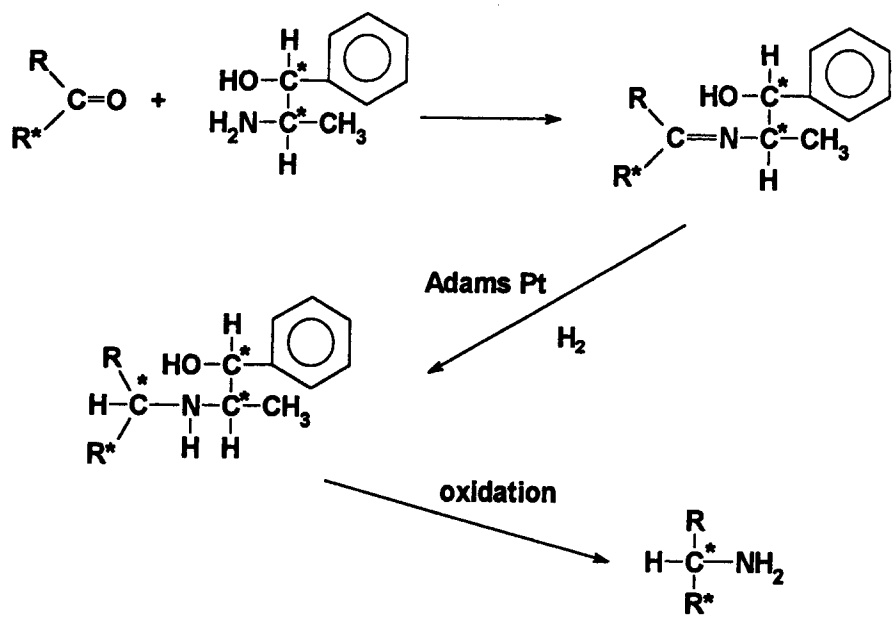

Scheme 22. Synthesis of a key-intermediate of an opioid antagonist.

## 4. Conclusions

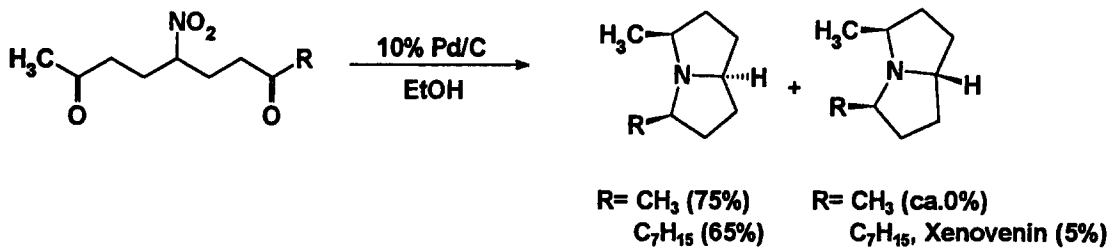
The asymmetric heterogeneous catalytic hydrogenation proved to be a useful method for the preparation of various chiral amino acids and amines. However, it can be applied as a synthetic tool mainly in the preparation of unusual amino acids; the chiral essential amino acids can be prepared more easily by fermentation. The asymmetric transaminations, even if the loss of the chiral auxiliary occurs, can result in valuable chiral amino compounds, which cannot be prepared by other means.

A review written for a catalytic journal has to place more emphasis on the choice of catalysts, reaction conditions or kinetics. In this case, however, the general experience including that of the authors', is that the stereoselectivity of hydrogenations producing optically active amino compounds is determined mainly by the structure and the substituents of the reactants. Another reason for the lack of discussion of the catalytic aspects is that most of the literature is coming from the synthetic organic chemistry community. The preparation of the reactants and the correct analysis of the products, including the determination of optical purity, in most cases, is a more complicated task than the hydrogenation itself.

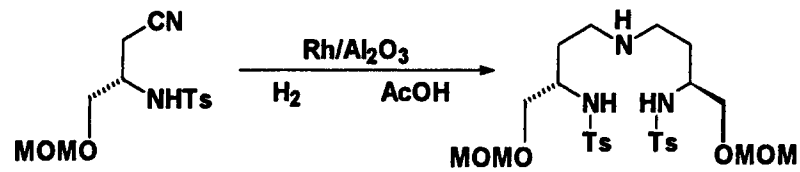
Summarizing the general features of diastereoselective heterogeneous catalytic hydrogenations:




Scheme 23. Reductive transamination reaction followed by oxidative cleavage, with norephedrine enantiomers as the chiral auxiliaries.

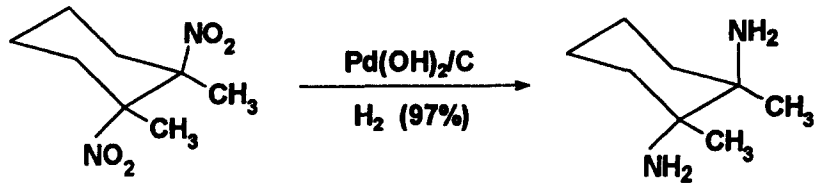



Scheme 24. Stereoselective hydrogenation of a nitro diketone.

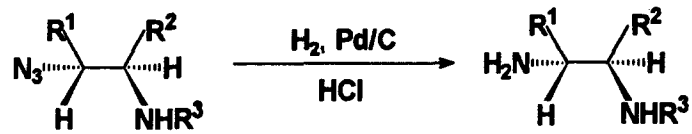



Scheme 25. Hydrogenation of chiral nitriles on Rh/alumina.

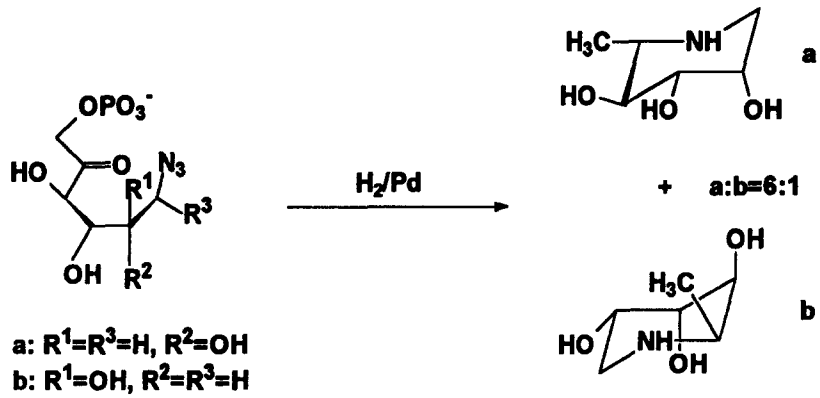
- The catalyst most often used is Pd on active carbon; if hydrogenolytic activity is needed for the cleavage of benzylic carbon–nitrogen bond, the catalyst is used in its unreduced form, as $Pd(OH)_2$ on carbon support.
- The extent of the asymmetric induction depends first of all on the structure of the reactant; the molecules containing a rigid ring give higher diastereoselectivities.
- The reaction conditions also influence diastereoselectivity; lower temperature and greater reactant : catalyst ratio increase asymmetric induction, in most cases, diastereoselectivity is higher in apolar solvents like toluene.




Scheme 26. Hydrogenation of vicinal dinitro compounds.




Scheme 27. Hydrogenation of chiral azido amines.




Scheme 28. Hydrogenation of azido sugars.

- As solid metal surfaces are involved in these reactions, it is hardly possible to predict the configuration of the product molecules according to Prelog's rule and Cram's rule, because they are more applicable in homogeneous catalytic reactions.

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