Ruthenium(II)-Chitosan, an Enantioselective Catalyst for the Transfer Hydrogenation of N-Heterocyclic Ketones

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The present study aimed at extending the applicability of a recently developed stereoselective catalytic system to the preparation of optically enriched N-heterocyclic alcohols. Chiral ruthenium catalyst formed in situ using the chitosan biopolymer as ligand, which provided good results in the transfer hydrogenation of heterobicyclic compounds, such as 4-chromanone and 4-thiochromanone, was used in reactions of various N-containing prochiral ketones. High enantioselectivities were reached in transfer hydrogenations of bicyclic compounds bearing nitrogen either in aromatic or cycloaliphatic moieties, provided that the amino group was protected or shielded by a nearby substituent. Results were rationalized by interactions of the nitrogen with the metal and/or ligand. N-containing bicyclic compounds having heteroatoms in both rings were also prepared and tested. The detrimental effect of the pyridyl moiety was compensated by the beneficial influence of the heteroatom in the cycloaliphatic ring, as indicated by high rates and good enantioselectivities obtained in reactions of these compounds. Preparation of several N-heterocyclic alcohols, in good yields and high optical purities was achieved using Ru(II)-chitosan complex.

Introduction

Synthesis of optically pure N-containing chiral compounds, such as amino acids and their derivatives, alkaloids and N-heterocyclic compounds, widely used in the pharmaceutical industry, is still a challenging task.[11] Enantioselective hydrogenations or transfer hydrogenations (ETH) of prochiral molecules are simple methods of introducing asymmetry in these chiral building blocks. A large variety of chiral catalysts have been developed to obtain optically enriched N-containing compounds by hydrogenation or ETH.[2,3] During the last few decades, decrease of the environmental impact of the applied processes became a basic requirement in the production of fine chemicals. Cheap, renewable, easily degradable chiral ligands of natural origin, applicable in aqueous systems, are the most promising for developing environmentally benign processes. Among the natural chiral compounds with possible applications in asymmetric catalysis, chitosan (CS) is a privileged biopolymer, owing to its versatility and large scale availability. It is easily obtained by deacetylation of chitin,[4,5] and is used in various industrial areas.[5,6] It was also tested in the development of stereoselective catalysts. Besides its application in organocatalysis,[7] CS served as ligand or support for obtaining catalytically active chiral metal complexes or metal nanoparticles.[8] Chitosan complexes were also tested as catalysts in ETH’s, however, these attempts gave moderate results with regard to the stereoselectivities, even using functionalized chitosan derivatives.[9]

Recently, we have reported that commercial, unfunctionalized CS used as ligand affords good, up to 86%, enantiomeric excess (ee) in the Ru(II)-catalyzed ETH of various acetonaphene derivatives in water-based solvent mixture.[10] Moreover, high, over 90% (up to 97%), ee’s were obtained in reactions of cyclic and heterocyclic ketones, such as 1-tetralone, 4-chromanone, 4-thiochromanone and their substituted derivatives. During the present work, our goal was to extend the applicability of this efficient stereoselective catalytic system on the ETH of N-containing heterocyclic prochiral ketones.

Results and Discussion

Transfer Hydrogenation of N-Heteroaromatic Ketones

Initially, we have attempted the ETH of the three acetylpyridine isomers 1 b, 1 c and 1 d, i.e. the N-containing analogues of acetonophene (1 a) (Scheme 1). The effect of the nitrogen position on the reaction was evaluated in comparison with results obtained with 1 a (Table 1).

The reaction conditions were selected based on our previous study, using several acetonaphene derivatives,[10] i.e. the ETH’s were carried out in aqueous solvent mixture, (H₂O/ iPrOH 4/1) with [Ru(p-cym)Cl₂]₂ (p-cym: para-cymene) as metal...
precursor and HCOONa as hydrogen donor (H-donor), at room temperature (rt, 23 ± 1 °C). However, under these conditions, conversions of acetylpyridines were low, even in five days (entries 2, 4, 6). To have better transformations, the amount of catalyst and the reaction temperature were increased (from 2.5 to 5 mol% Ru and from rt to 50 °C, respectively), and the reaction time prolonged to one week (entries 3, 5, 7). In accordance with our previous finding, which showed the detrimental effect of the ortho substituents on the ETH of acetonphene derivatives, only low conversion of 2-acetylpyridine 1d was reached even under these conditions and close to racemic mixture was obtained (entry 7). Although, the conversions of the other two compounds (1b, 1c) were fairly good, the obtained ee’s remained much lower as compared with the reaction of 1a (entries 3, 5).

Accordingly, the presence of nitrogen in the aromatic ring leads to low rates, probably due to strong attachment of the ketone to the metal, as may be expected based on the formation of various metal (including ruthenium) complexes with pyridyl-type ligands.[12]

Next, we continued our studies with N-heteroaromatic cyclic ketones, by investigating the transformations of 1f and 1g, containing five-membered N-heteroaromatic ring, condensed with a six-membered cyclic ketone moiety. Selected results are compared with the ones obtained in the reaction of the sulfur analogue (1e)[13] (Scheme 2). Contrary to the ETH of 6,7-dihydropbenz[b]thiophen-4(5H)-one (1e), the transfer hydrogenation of 1,5,6,7-tetrahydro-4H-indol-4-one (1f) did not take place under identical reaction conditions, even in one week. We attribute this to the strongly coordinating pyrrole moiety, which binds to Ru by deprotonation, similarly to what occurs in metal complexes of porphyrins and related pyrrole-ring containing ligands.[13] To avoid this deactivation we prepared a protected derivative of 1f. The N-ethoxycarbonyl derivative (1g), under identical conditions, was transformed in low yield. Moreover, the enantioselectivity obtained was also lower (ee 68 %) as compared with 1e. Increase of the reaction temperature to 50 °C resulted in better conversion, however, the ee of the hydrogenated product (2g), obtained only in 35 % selectivity, decreased to 47 %. The main product was the N-deprotected compound (1f).

Our investigations were continued by examining the ETH of compounds bearing pyridine ring condensed with a six-membered cyclic ketone moiety (1i–1k). The results were compared with those obtained in the ETH of the structurally related 1-tetralone (1h) (Table 2).[10] In the reaction of 1i much lower conversion was achieved as compared with 1h, under identical reaction conditions (compare entries 1, 2). Increase of the catalyst amount and extending the reaction time led to high conversion of 1i and higher ee, approaching the value

Table 1. Results obtained in the ETH of 1a and acetylpyridines 1b–1d using in situ formed Ru-CS catalyst.[24]

| Entry | Ketone | t [h] | T [°C] | Conv [%][24] | ee [%][24] |
|-------|--------|------|-------|--------------|------------|
| 1     | 1a     | 46   | rt    | >99          | 78         |
| 2     | 1b     | 120  | rt    | 9           | 54         |
| 3[b] | 1b     | 168  | 50    | 85          | 43         |
| 4     | 1c     | 120  | rt    | 27          | 44         |
| 5[b] | 1c     | 168  | 50    | 75          | 35         |
| 6     | 1d     | 168  | 50    | <1          | –          |
| 7[b] | 1d     | 50   | 31    | 10          | –          |

[b] Reaction conditions: 0.00625 mmol [Ru(p-cym)Cl]₂, 3 mg CS, 2.5 mmol ketone, 0.25 mmol HCOONa, 1 cm³ H₂O/iPrOH 4:1. [24] Conversion of the ketone determined by gas-chromatography (GC). [15] Enantiomeric excess determined by GC; the configuration of the excess enantiomers was assigned as S based on reactions catalysed by RuCl[(S,S)-N-Ts-dpen]([µ-cym])[15] N-Ts-dpen: N-(para-toluenesulfonyl)-1,2-diphenylethylendiamine. [14] Using 0.0125 mmol [Ru(p-cym)Cl]₂ and 5 mg CS.

Scheme 1. ETH of acetonphene (1a) and products (2b–2d) obtained in the ETH of acetylpyridines 1b–1d using Ru-CS catalyst.

Scheme 2. Results obtained in the ETH of five-membered N-heteroaromatic ring containing bicyclic ketones. Reaction conditions: 0.00625 mmol [Ru(p-cym)Cl]₂, 3 mg CS, 0.25 mmol ketone, 2.5 mmol HCOONa, 1 cm³ H₂O/iPrOH 4:1, rt, 168 h. [a] At 50 °C, Sel: selectivity; ee 61% (Sel: 35%), ee 47%[24]
obtained in the ETH of 1h (entry 3). Moreover, increasing the reaction temperature to 50 °C resulted in close to complete hydrogenation of this compound in 96 h without altering the enantioselectivity (entry 4). However, the ee value decreased by continuing the reaction under these conditions, which showed that racemization of 2i in the presence of the catalyst may occur.

The ETH of the compound substituted with methyl groups (1j) was hindered by these substituents, consequently, much lower conversion and slightly decreased ee were reached as compared to 1i (compare entries 3, 5). Although, the conversion increased at elevated temperature (50 °C), beside the desired alcohol, a side-product also formed, in equal amount with 2j, by partial hydrogenation of the aromatic moiety. Under these conditions the ee decreased significantly. Based on the above, it is reasonable to assume that the steric effect of the two methyl groups affects the interaction of the molecule with the catalyst, directing the approach of 1j to the metal in a manner, which allows the easier partial hydrogenation of the heteroaromatic ring. The isoquinoline derivative 1k was transformed selectively to the alcohol 2k in 74% at 50 °C, though in lower ee as compared with 1i (entry 7).

**Transfer Hydrogenation of Bicyclic Ketones Containing Nitrogen in Aliphatic Ring**

The promising results obtained in the ETH of the above bicyclic ketones, motivated us to examine reactions of N-analogues of 4-chromanone (1l)\(^{[19]}\) having the nitrogen in the cycloaliphatic moiety (1m–1q). Selected results are shown in Table 3.

The ETH of 2,3-dihydroquinolin-4(1H)-one (1m) proceeded with good conversion, using a higher amount of catalyst and longer reaction time as compared with 1i. The alcohol 2m was obtained with low selectivity, both at rt and 50 °C (entries 2, 3), whereas, a mixture of quinoline, 1,2,3,4-tetrahydroquinoline and 1,2-dihydroquinoline also resulted (selectivities at 50 °C, determined by GC: 10%, 8%, 58%, respectively). The formation of these side-products may be explained by a hydrogenolysis or dehydration – dehydrogenation – disproportionation sequence, which may occur as a result of the strong attachment of the nitrogen to the metal. The ee's were also low, 72% and 58%, respectively. In contrast, the reaction of the N-tert-butylcaronyl (Boc) protected compound (1n), was close to complete in four days using the same amount of catalyst and the alcohol 2n was obtained in high ee (95%), as the sole product (entry 4). Similar result was obtained at 50 °C in less than two days (entry 5). Interestingly, the compound substituted with bromine on the aromatic moiety, near the amine group (in position 8) (1o), was also transformed fairly selectively to alcohol 2o, in high extent and good ee (88%, entry 6). The predominant by-product was 8-bromoquinoline. Increasing the temperature allowed close to similar conversion in three days, while the ee did not change, whereas, decreasing the catalyst amount led to lower conversion in five days (entries 7, 8). Analogous behavior was observed with the N-acetyl derivative 1p, however, slightly lower ee was reached (entries 9, 10). The ETH of the corresponding N-Boc derivative 1q was slower under identical conditions (entry 11). The enantioselectivity reached in this reaction was almost as high as in the reaction of 1n, i.e. the N-Boc protected compound lacking Br substituent.

The above data showed that N-containing cyclic ketones are transformed slower as compared to the corresponding oxygen containing compound. However, the ee's in many reactions approached the value reached in the ETH of 1l, the best results were obtained using N-Boc protected derivatives. The stronger coordination of the amino group to the metal may explain these observations. The deactivation could be prevented either by protecting the amino group or by the presence of a bulky substituent (i.e. Br) in its proximity, which may hinder the coordination of the amine to the metal cation. Thus, with properly substituted derivatives, such as 1n, 1o and 1q, high conversions and high enantioselectivities may be reached. We note that compounds 1n and even 1o were transformed faster than the N-heteroaromatic ketones (1i or 1k), indicating that

| Entry | Substrate | X   | Y   | R    | Conv [%]\(^{[18]}\) | ee [%]\(^{[18]}\) |
|-------|-----------|-----|-----|------|---------------------|-----------------|
| 1\(^{[18]}\), 2\(^{[20]}\) | 1h | CH  | CH  | H    | 70                  | 61              | 93              |
| 3     | 1i        | N   | CH  | H    | 168                | 18              | 82              |
| 4     | 1i        | N   | CH  | H    | 168                | 95              | 91              |
| 4     | 1j        | N   | CH  | CH$_2$| 168               | 99 (> 99)        | 91, 77          |
| 5     | 1j        | N   | CH  | CH$_2$| 168               | 30              | 85              |
| 6     | 1j        | N   | CH  | CH$_2$| 168               | 95 (50)\(^{[20]}\)    | 43              |
| 7     | 1k        | CH  | N   | H    | 168                | 74              | 79              |

\(^{[18]}\) Reaction conditions: 0.0125 mmol [Ru(p-cym)Cl$_2$)$_2$, 5 mg CS, 0.25 mmol ketone, 2.5 mmol HCOONa, 1 cm$^3$ H$_2$O/PrOH 4/1. \(^{[20]}\) Conversion and ee determined by GC; the configurations were assigned based on GC analysis, literature data\(^{[18]}\) and results of reactions catalysed by RuCl(55)-N-Ts-dpen\([p-cym]\)\(^{[18]}\) 0.00625 mmol [Ru(p-cym)Cl$_2$], 3 mg CS. \(^{[20]}\) Selectivity of the 2j product.
the coordination of the aromatic nitrogen is indeed responsible for the poor results obtained with the latter substrates.

Encouraged by these results, we continued to explore the scope of this catalytic system, by attempting the ETH of ketones having pyridyl ring condensed with a heterocyclic moiety. For this purpose, we have prepared two bicyclic compounds, i.e. 2H-thiopyran-2,3-b:pyridine-4(3H)-one (1a) and 1-methyl-2,3-dihydro-1,8-naphthyridin-4(1H)-one (1t). Although, these compounds afford valuable heterocyclic chiral alcohols, their trans-dihydro-1,8-naphthyridin-4(1H)-one (1h)bispyridine-4(3H)2-thiopyran[2,3-i]thiochromanone (1o).

High conversions were obtained even with low catalyst amount (2.5 mol %, similarly as in the ETH of these compounds are summarized in Table 3 (entries 1–18), and are compared with the reaction of 4-thiacoamide ozonolysis (1r, entry 12). High conversions were obtained even with low catalyst amount (2.5 mol %, similarly as in that of 1r) in the transformation of both compounds following two days reactions. Interestingly, at rt the two nitrogen containing compound (1t) was transformed faster than 1s, which bears a nitrogen and a sulfur in rings (compare entries 13, 14 with 16, 17, respectively). By increasing the catalyst amount, complete transformations were achieved in one day (entries 15, 18). The obtained ee’s were also high, though slightly decreased as compared with that obtained in the reaction of 1r. Higher value was reached in the ETH of 1s, which may be attributed to the presence of the sulfur in the aliphatic ring and the interaction of this with the catalyst, as previously suggested.

It is accepted that the ETH of prochiral ketones catalyzed by Noyori-type ruthenium half-sandwich complexes occurs through a concerted process, via an outer-sphere type metal-ligand bifunctional mechanism (Figure 1). Our results showed that the ETH of the pyridyl ring-containing ketones is slower as compared to the reactions of the corresponding carbocyclic analogs. Moreover, the ETH of pyrrole ring-containing bicyclic ketones does not proceed, unless the NH group is functionalized. These observations may be interpreted by coordination of the nitrogen to the metal cation, which leads to deactivation of the catalyst. Suggested interactions of the catalyst with 7,8-dihydroquinolino[5,6-b]pyridine (11) and with the chiral ligand as well (Figure 1 (a, b, c)). We also note that the steric effect of the six-membered cycloaliphatic ring still assured good ee’s in these reactions.

The effect of the nitrogen in the cycloaliphatic ring of hydroquinoline derivatives was also detrimental, as shown by results obtained in the ETH of 2,3-dihydroquinolin-4(1H)-one (1m). However, protecting the NH group afforded high ee’s, comparable with that reached in the reaction of 4-chromanone, although, the steric constraints of the protecting group (Boc) slightly decreased the rate of the reaction (Figure 1 (b, c)). The high ee’s obtained in the ETH of these compounds confirmed the suggested beneficial effect of the heteroatom in the cycloaliphatic ring, attributed to an additional interaction with the catalyst, which favors the approach of a specific enantiomeric
Interestingly, a substituent in the proximity of the nitrogen, such as Br in 8-bromo-2,3-dihydroquinolin-4(1H)-one (1o), may also exert a proper steric hindrance and prevent deactivation (Figure 1 (b), iii). Delightfully, in the ETH of bicyclic compounds bearing heteroatoms in both rings (1s and 1t), the detrimental effect of the pyridyl moiety could be compensated by the beneficial influence of the heteroatom in the cycloaliphatic ring. Therefore, these compounds were transformed with high rates, affording the products in high ee's.

Finally, we have explored the synthetic potential of the examined catalytic system for preparing chiral N-heterocyclic alcohols at larger scale. For this purpose we selected ketones, which were transformed selectively to the corresponding alcohols and afforded high enantioselectivities. The ETH's of these compounds were carried out at 1 mmol scale (four-fold as compared to the previous reactions), by increasing proportionally the catalyst, H-donor and solvent amount. Yields of the isolated products obtained in the ETH of the selected six heterocyclic ketones are shown in Figure 2. In these reactions, the conversions and ee's were similar with those achieved at lower scale and the products were obtained in good isolated yields.

Conclusions

Recently, we have investigated the ETH of prochiral ketones using ruthenium complex formed with chitosan.[10] Besides good ee values reached in reactions of acetophenone derivatives, high enantioselectivities were obtained in the ETH of bicyclic compounds, especially in those of heterobicyclic ketones, such as 4-chromanone or 4-thiochromanone. Motivated by the practical importance of N-heterocyclic optically pure building blocks,[18] we aimed at extending the scope of this catalytic system on the ETH of N-containing prochiral ketones.

The ETH of compounds bearing nitrogen in aromatic ring were sluggish, however, in reactions of bicyclic ketones good ee's were obtained. High enantioselectivities were also reached in reactions of bicyclic compounds bearing nitrogen in the cycloaliphatic moiety, in case the amino group was protected or shielded by a nearby substituent. Results were rationalized of the molecule to the catalytic active site (Figure 1 (b), iv).[10] The concerted outer-sphere mechanism of the transfer hydrogenation catalysed by half-sandwich Ru complexes[17] and schematic illustration of the suggested interactions during ETH of N-containing heterocyclic ketones using Ru-chitosan complex: (a) and (b).

Figure 1. The concerted outer-sphere mechanism of the transfer hydrogenation catalysed by half-sandwich Ru complexes[17] and schematic illustration of the suggested interactions during ETH of N-containing heterocyclic ketones using Ru-chitosan complex: (a) and (b).

Figure 2. N-heterocyclic alcohols prepared at one mmol scale by ETH using Ru-CS catalyst.
based on possible interactions of the nitrogen with the metal and/or ligand. N-containing bicyclic compounds having heterocatoms in both aromatic and cycloaliphatic rings were also prepared and tested. The detrimental effect of the pyridyl moiety was compensated by the beneficial influence of the heteroatom in the cycloaliphatic ring, as indicated by the high rates and good enantioselectivities obtained in the transfer hydrogenations of these compounds.

Finally, our results showed that certain N-heterocyclic ketones might be transformed conveniently, in aqueous solvent mixture, to optically enriched alcohols, in good yields using in situ formed Ru-chitosan complex. These valuable chiral building blocks were prepared using an asymmetric catalytic procedure, which applies a biodegradable and biocompatible, abundant, readily available ligand of natural origin, as chirality source.

Experimental Section

Materials and Methods

High molecular weight chitosan (CS, Mw: 310,000–375,000 Da, >75% deacetylation degree, η 800–2000 cP of 1 wt.% in 1% acetic acid), the Ru-precursor [Ru(p-cym)(Cl)]+, HCOONa and analytical grade solvents were used as received (Sigma-Aldrich). Ketones 1a, 1b, 1c, 1d, 1e, 1f, 1h, 1k, 1l, 1n, 1o and 1r were commercial products (Aldrich) and with the exception of 1k (purified by flash chromatography before use) were used as received, whereas compounds 1g, 1i, 1j, 1m, 1p, 1q, 1s and 1t were prepared according to literature procedures (see Supporting information).

Gas-chromatographic analysis of the reaction products were carried out using Agilent Techn. 6890N GC-5973 MSD (GC-MSD) equipped with 30 or 60 m long HP-1MS capillary column for mass spectroscopic identification of the products. For identification of the product alcohols, commercial samples (if available) and racemic products prepared by reduction using NaBH₄ were used. For quantitative analysis Agilent 7890A GC-FID (GC-FID) gas chromatograph equipped with chiral capillary column (Cyclosil-B, 30 m, J&W or HP-Chiral 20|) 30 m, J&W from Agilent) was used. 1H and 13C NMR spectra of the purified products were recorded on a Bruker Avance DRX 400 or Bruker Ascend 500 spectrometer using CDCl₃ solvent. Products were isolated by flash chromatography on silica gel 60, 25–40 µm, using hexane isoamyl ether/ethyl acetate (EtOAc) mixtures (as indicated in the Supporting information). The purity of the fractions was checked by thin-layer chromatography on Kieselgel-G (Merck Si 254 F) layers. A Perkin-Elmer 2400 CHNS-2400 Ser II instrument was used for elemental analysis. Optical rotations were measured using Perkin-Elmer 341 polarimeter.

Transfer Hydrogenation: General Procedure

Reactions were carried out in 4 cm³ closed glass vials. The slurries were stirred magnetically (800 rpm). If higher than rt was necessary the vials were immersed in a preheated oil bath. In a typical run the given amount of [Ru(p-cym)(Cl)]+, chitosan and 1 cm³ solvent were introduced into the vial and stirred at rt 1 h followed by addition of the required amount of HCOONa and further stirred 0.5 h. Finally, the prochiral ketone (0.25 mmol) was added to the mixture and stirred for the given time. Following reactions the products were extracted in 3 cm³ EtOAc, the aqueous phase was washed twice with 2 cm³ EtOAc, the unified organic phases were dried on sicc. MgSO₄ and analyzed by gas-chromatography using n-dodecane as internal standard (GC-MSD and GC-FID). Reactions at 1 mmol ketone scales were carried out similarly in 8 cm³ vials using proportionally increased amounts of metal, chitosan, solvent and H-donor. Following GC analysis of the crude products the solvent was removed by evaporation and the pure products were obtained by flash chromatography. These products were analyzed by GC-MSD, GC-FID, 1H and 13C NMR spectroscopy and their optical rotations were measured (see Supporting information).

Conversions (Conv), selectivities (Sel) and enantioselectivities (expressed as enantiomeric excess, ee) were calculated based on the relative concentrations determined from chromatograms (see the formulae in the Supporting information). The absolute configuration of the excess enantiomers were assigned based on the optical rotation sign of the isolated products and literature data, or based on chromatographic analysis and comparison with products obtained according to literature methods using RuCl2((S,S)-N-Ts-dpen)(p-cym) catalyst and HCOOH/Et,N 5/2 hydrogen donor.1·13

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Conflict of Interest

The authors declare no conflict of interest.

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