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Hydrogen transfer reduction of different ketones in ionic liquids

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Abstract Ionic liquids were tested as the reaction media for hydrogen transfer reduction of substituted acetophenones and some other ketones with the $[RuCl(TsDPEN)]_2$ complex as the catalyst. Reactions were going well and faster than in common solvents. Corresponding alcohols had high *ee*s in the case of aryl alkyl ketones, but just medium *ee*s were reached in the case of dialkyl or unsaturated ketones. An interesting phenomenon was observed, namely that rise of the reaction temperature did not have negative influence on the *ee* of the reaction product.

Keywords Ionic liquids; Hydrogen transfer reaction; Asymmetric catalysis.

Introduction

Asymmetric transfer hydrogenation of prochiral ketones and imines represents an effective method for the preparation of optically active alcohols or amines [1]. The most popular catalysts for asymmetric hydrogen transfer reaction are [Ru(arene)(diamine)] complexes with chiral ligands [2]. In particular, a ruthenium catalyst bearing a chiral ligand, such as mono *N*-tosylated diphenylethylenediamine (*TsDPEN*) has been well studied on a variety of substrates [3].

Attempts on improving handling and separation of the catalyst from the reaction product and also its recycling led to immobilization of catalytic system on a variety of supports, either inorganic or organic support [4]. *Noyori*'s ligand has been immobilized on a variety of supports like dendritic polymers [5], silicas [6], polystyrenes [7], either heterogenized or modified by bonding of hydrophilic function for biphase catalysis [8]. *Noyori*'s ligand can be modified by introduction of imidazolium tags either at the complexed arene [9], or at the tosyl group in order to immobilize the resulting catalyst [10].

As has been shown in many papers, ionic liquids are very interesting alternative ''green'' solvents to common organic ones [11], and were used in many catalytic processes [9, 12], but there are just few papers published using ionic liquids for hydrogen transfer reactions. *Dyson* and *Geldbach* [9] described a modification of the ruthenium complex by its immobilization to ionic liquid 1-butyl-2, 3-dimethylimidazolium hexafluorophosphate. This complex in combination with (1*S*,2*R*)-2-amino-1,2-diphenylethanol and (1*R*,2*R*)-*N*-tosyl-1,2-diphenylethylenediamine was then used in transfer hydrogenation of acetophenone. Reactions were carried out at 40°C for 24 h and better results were observed with an azeotropic mixture of $HCOOH/Et_3N$ than with $NaOPr^i$/propane-2-ol. They have proved that the ionic liquid containing the ruthenium complex can be used several times in the same reaction. Similar work has been published by *Kawasaki et al.* [10]. They described the synthesis of chiral *TsDPEN* immobilized on an imidazolium ionic liquid moiety and its use at hydrogen transfer reduction of aryl ketones. An excess of $HCOOH/Et_3N$ mixture was

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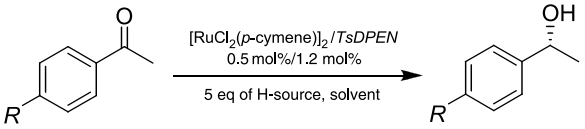
used as the solvent and reaction time, in dependence of the substrate, was 5–24 h. The yield of 1-phenylethanol as the product of transfer hydrogenation of acetophenone in the sixth recycle of the catalytic system was 75% with 90% *ee*.

Several ionic liquids have been tested very recently for hydrogen transfer reduction of acetophenone by *Joerger* [13]. They found that [*bmim*]PF_6 is the best solvent, but they have been working with 6 equivalents of a formic acid/triethylamine (5/2) mixture. The disadvantage of the reaction is a relatively long reaction time, which was at least 22 h.

The aim of this work was to test several ionic liquids for hydrogen transfer reaction of substituted acetophenones and to optimize the reaction conditions. The further aim of this work was to explore if the optimized reaction conditions can be applied also to a broad range of aryl alkyl ketones, but also to dialkyl and unsaturated ketones.

Results and discussion

Our work was initiated by a paper published by *Xiao et al*. [14] where acetophenone and its derivatives were reduced in water with HCOONa as a hydrogen donor, $[RuCl_2(p\text{-cymene})]_2$ as catalyst and *TsDPEN* as chiral ligand. At the beginning we tried to apply these reaction conditions to the reaction in ionic liquid (Scheme 1).



Scheme 1

The result, we achieved at reduction of 4-methoxyacetophenone, at the condition described by *Xiao et al*. [14], are comparable with the published ones (Table 1, entry 1).

Exchange of the water for ethylmethylimidazolium ethylsulfate ionic liquid was a failure because the reaction practically did not proceed. Unsuccessful were also reactions with azeotrope mixtures HCOOH/Et_3N and *i-Pr*ONa/*i-Pr*OH. We assumed that this failure could be caused by the insolubility of sodium formate in ionic liquids and therefore we decided to dissolve it in a minimum amount of water and add this solution to the ionic liquid containing a pre-formed catalyst. From Table 1 entry 5 it is possible to see that the reaction went well and with high enantioselectivity. Products were isolated in reasonable yields with 87% *ee*. Next experiments were carried out with acetophenone, which should be more reactive. The reactions went more rapidly and 1.5 h

Table 1 Search of reaction conditions of asymmetric hydrogen transfer reduction of 4-substitued acetophenones

Entry	*R*	Solvent	H-source	Time/h	Yield/%	*ee*/%
1	O*Me*	water	HCOONa	2	90	91
2	O*Me*	[*emim*]*Et*OSO_3	HCOONa	24	5	–
3	O*Me*	[*emim*]*Et*OSO_3	HCOOH/Et_3N	24	0	–
4	O*Me*	[*emim*]*Et*OSO_3	*iPrO*Na/i*Pr*OH	24	0	–
5	O*Me*	[*emim*]*Et*OSO_3	HCOONa/H_2O	24	50[a]	87
6	H	[*emim*]*Et*OSO_3	HCOONa/H_2O	1.5	80	90
7	H	[*emim*]*Et*OSO_3	HCOONa/H_2O	4	61[b]	91
8	H	[*emim*]*Et*OSO_3	HCOONa/H_2O	1.5	86[d]	90
9	H	[*bbim*]BF_4	HCOONa/H_2O	1.5	85	91
10	Br	[*emim*]*Et*OSO_3	HCOONa/H_2O	1.5	96	90
11	Br	[*emim*]*Et*OSO_3	HCOONa/H_2O	3	90[b]	83
12	Br	[*emim*]*Et*OSO_3	HCOONa/H_2O	3	96[c]	84
13	Br	ECOENG500	HCOONa/H_2O	1.5	94	88

The reactions were carried out in 2 cm^3 of the solvent that contains 1 eq. of the substrate, 5 eq. of the H-source, 0.5 mol% catalyst and 1.2 mol% of *TsDPEN* at 50°C for 2–24 h

[a] Complex [RuCl(*p*-cymene)*TsDPEN*)] was formed in CH_2Cl_2, reaction carried out at 50°C for 7 h and solution of 5 mmol of HCOONa in 0.4 cm^3 of water were added

[b] 1st recyclation

[c] Two phase – ionic liquid/toluene experiment

[d] Reaction carried out at 90°C

reaction time was enough for high conversion of the starting material (entry 6). The same reaction medium containing the catalyst can be used also in repeated experiment. Yield of the product was considerably lower, but stereoselectivity was not affected (entry 7). We decided to check if higher temperature would affect the yields as well as *ee* of the products. Rising the reaction temperature to 90°C gave similar yields of the product and stereoselectivity was not changed (entry 8).

In the case where ionic liquid was [*bbim*]BF_4, which is not miscible with water, the reaction was carried out in a biphasic system (entry 9). The reaction medium, that consist of ionic liquid [*bbim*]BF_4 and water in ratio 2/1 affords similar results as in [*emim*]*Et*OSO_3.

The next reactions were performed with 4-bromoacetophenone (entries 10–13). Reactions went smoothly with yields higher than 90% and *ee* higher than 80%. After the first recyclation the product was isolated in high yield with practically the same *ee* (entry 11), just the reaction time had to be prolonged. Entry 12 represents a biphasic medium, where toluene was added to the ionic liquid [*emim*]*Et*OSO_3. Reaction was completed after 3 h and the product was isolated in high yield with 84% *ee*. Recyclation was not successful in this case, because the catalytic complex was dissolved in toluene and was removed by product extraction and by work-up process. At the reduction of 4-bromoacetophenone was tested also another ionic liquid, namely ECOENG500. This is Peg-5 cocomonium methyl sulfate whose structure is depicted in Fig. 1 together with the structures of other ionic liquids that were used as reaction media in hydrogen transfer reactions.

From entry 13 it can be seen, that the course of the reaction is similar to those in [*emim*]*Et*OSO_3. This ionic liquid is miscible with water, but not with diethyl ether and the product can be easily extracted

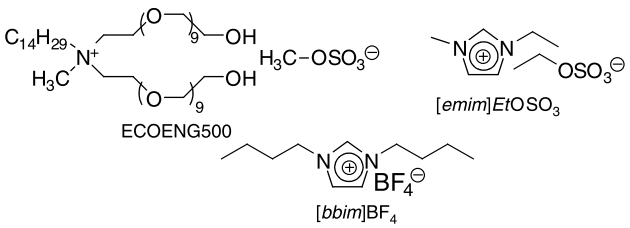
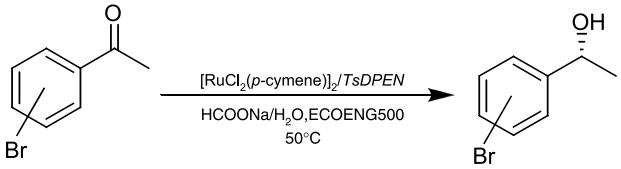


Fig. 1 Structure of ionic liquids used in hydrogen transfer reactions



Scheme 2

Table 2 Asymmetric hydrogen transfer reduction of bromoacetophenones with [Ru]-*TsDPEN*/HCOONa in ECOENG500/H_2O

Entry	Br position	*T*/°C	Time/h	Yield/%	*ee*/%
1	4	50	1.5	94	88
2	4	50	2	93[a]	89
3	4	50	18	78[b]	90
4	4	25	3	90	97
5	4	50	1.5	87[c]	82
6	4	50	1.5	89[d]	91
7	4	90	0.6	93	88
8	2	50	1.5	98	78
9	2	90	0.8	94	88
10	3	50	1.5	99	84

The reactions were carried out in 1 cm^3 of ECOENG500, 0.5 cm^3 H_2O that contains 1 eq. of the substrate, 5 eq. of HCOONa, 0.5 mol% of the catalyst and 1.2 mol% of *TsDPEN* at 50°C. Reaction procedure is described in experimental

[a] Results from the first recyclation

[b] Results from the second recyclation

[c] Reaction in toluene

[d] 0.2 mol% of the catalyst was used

from it at the end of the reaction. ECOENG500 seems to be an even better solvent than [*emim*]-*Et*OSO_3. For that reason we decided to test it more carefully at the hydrogen transfer reductions of different bromoacetophenones (Scheme 2). Results are given in Table 2.

This reaction medium can be used several times. The first recyclation was finished after 2 h with good yield of the product with the same *ee* (entry 2). The second recyclation gave the product in 78% after 18 h with the similar *ee* (entry 3). In order to compare the influence of the temperature on the yield and *ee* of the product, reactions were performed also at room temperature and at 90°C. Decrease of the temperature does not have negative influence on the yield, but longer reaction time was necessary and, as we expected, reaction was going with higher *ee* (entry 4). The reaction at 90°C was completed after 40 min with the a similar yield, and only a small decrease of the *ee* of the product was observed

(entry 7). For the comparison was also carried out the reaction in toluene (entry 5). In this solvent the reaction proceeds a bit worse than in ionic liquid ECOENG500 and without a possibility of recyclation of the catalytic system. The reaction proceeds well also with a lower amount of the catalyst. Decrease of the catalyst from 0.5 to 0.2 mol% had just a slight influence on the yield and *ee* of the product (entry 6).

To survey both electron and steric effects of bromine position on aromatic ring we performed transfer hydrogenation with both *ortho* and *meta* regioisomers. The yields of the corresponding alcohols were comparable to that of the *para* isomer (entries 8 and 10). In the case of the *ortho* derivative a lower *ee* of the product was observed, that is probably caused by the steric effect of bromine in position 2. Increase of the temperature to 90°C caused acceleration of the reaction, slight yield, and a small increase of *ee* of the product has been observed (entry 9).

The interesting fact that rising the reaction temperature does not have a negative influence on the enantioselectivity of the reactions in ionic liquids (Table 1, entry 8 and Table 2, entries 7, 9) was observed by us also previously [15]. This phenomenon would deserve a special attention and will be studied in our laboratory.

Reaction conditions found for asymmetric transfer-hydrogenation of acetophenone in ECOENG500 were applied for broad range of aryl alkyl ketones as well as for dialkyl and unsaturated ketones, whose structures are shown on Fig. 2. The reaction course of the reduction was followed by TLC and reaction was stopped when no starting material was observed in reaction mixture. Results of the reactions are given in Table 3.

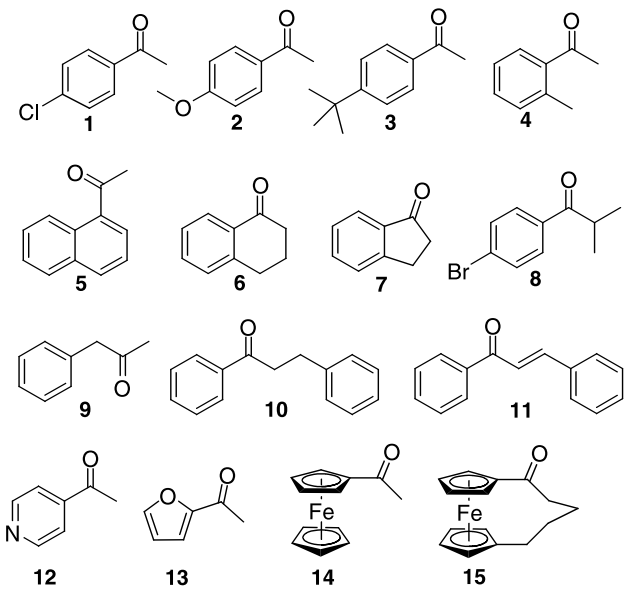


Fig. 2 Ketones used in hydrogen transfer reaction in ECOENG500

Table 3 Results from asymmetric hydrogen transfer reduction of various ketones

Entry	Ketone	Time/h	Yield/%	*ee*/%
1	**1**	1.5	99	92
2	**1**	1.5	98[a]	91
3	**2**	2	73	89
4	**3**	2.5	96	91
5	**4**	20	44	81
6	**4**	2.5	70[b]	96
7	**5**	4	94	92
8	**6**	2	90	52
9	**7**	3	84	88
10	**8**	20	53	45
11	**9**	1.5	97	31
12	**10**	5	90	80
13	**11**	1.5	83	34
14	**12**	1	65	82
15	**13**	1.5	58	88
16	**14**	24	0	–
17	**15**	24	0	–

[a] The first recyclation
[b] Reaction carried out at 90°C

A similar result was observed with an 4-bromoacetophenone as with a 4-chloroacetophenone and also the first recyclation was successful and the product was isolated in good yield with high *ee* (entry 2). The reaction rate of acetophenones with electronodonating group, as are 4-methoxy and 4-*t*-butoxy group was slower, but the reaction products, that are 4-methoxyphenylethanol and 4-tercbutylphenylethanol were isolated in good yields and with high *ee* (entries 3 and 4). The 2-methylacetophenone was less reactive. Reaction was not completed even after 20 h and the product in 44% yield and 2-methylacetophenone was recovered by chromatography (entry 5). Rising the temperature to 90°C resulted in a good yield of 2-methylphenylethanol and as in the case of 2-bromoacetophenone, also in the reaction of 2-methylacetophenone increase of the temperature did not have a negative influence on the *ee* of the product (entry 6). The lower reactivity of *ortho*-metylated acetophenone can be caused by steric hindrance of methyl (bromine) group in this position. Steric and

also electronic effects are displayed also in the reaction of 1-(4-bromophenyl)-2-methylpropan-1-one. The isopropyl group on the carbonyl function caused its low reactivity (entry 10). Reaction at 50°C gives product in the reasonable yield, but with low *ee*. Reactions with 1-acetylnaphthalene, 4-acetylpyridine and 2-acetylfuran went smoothly and with high enantioselectivity (entries 7, 13, and 14). The lower chemical yields at reactions with 4-acetylpyridine and 2-acetylfuran can be caused by higher solubility of the reaction products in ECOENG500, and therefore their worse extraction from the reaction mixture.

Good results were achieved also with tetralin-1-one (entry 8) and indan-1-one (entry 9). Phenylacetone gave in asymmetric transfer hydrogenation a very good yield of the corresponding alcohol, but with low *ee* (entry 11). Longer reaction time was needed in the case of 1,3-diphenylpropan-1-one, but after 5 h the corresponding alcohol was isolated in 90% yield with 80% *ee* (entry 12).

It has been described that in the hydrogen transfer reduction of α,β-unsaturated carbonyl derivates, a competition between vinyl and carbonyl group reduction is expected [16]. In general, the reduction proceeds preferentially at the carbonyl group producing the corresponding unsaturated alcohol. This is the case when aminoprolinate complexes of Ru and Rh are used as catalyst precursors, although the alcohols are obtained with modest enantioselectivity [17]. It has been recently demonstrated, that with ruthenium amido complexes, the chemoselectivity can be completely reversed form C=O to C=C reduction, if the polarization of the C=C double bond is enhanced by the presence of an additional electron-withdrawing substituent [16].

We observed a similar reaction course in the hydrogen transfer reduction of chalcone (entry 13). After 1.5 h at 50°C 1,3-diphenylpropan-1-ol was isolated as the main product in 83% yield with 33.5% *ee* (entry 13) and 17% of 1,3-diphenylpropan-1-one. It means, that the reduction proceeds first on the C=C bond yielding the 1,3-diphenylpropan-1-one and after that follows the reduction of the C=O bond.

No reaction was observed in the reaction of acetylferrocene and [5]ferrocenophane-1-one (entries 17 and 18), which can be caused by the strong electronodonating effect of the ferrocenyl group.

Experimental

The starting ketones were purchased from *Aldrich*, *Merck*, and Across companies and used as received. $[RuCl_2(p\text{-cymene})]_2$ catalyst and *TsDPEN* ligand was purchased from Lancaster Co. Ionic liquids were purchased from Solvent Innovation Co. and dried before use.

^{1}H NMR spectra were measured at 300 MHz Varian Mercury Plus instrument as the solution in $CDCl_3$ with *TMS* as the internal standart. Enantioselectivity of the reaction products were determined by HPLC chromatography using Chiracel OD-H (Daicel Chemical industries) column with *n*-hexane/*i*-propanol (9/1) as a mobile phase with a flow of 0.75 cm^3/min and detection by a UV detector at 254 nm. Optical rotatory index was measured at *Perkin-Elmer* 241 instrument.

General procedure for transfer-hydrogenation of acetophenones and other ketones

The catalyst was prepared by as follows: 3 mg (0.005 mmol) of $[RuCl_2(p\text{-cymene})]_2$ and 5 mg of *TsDPEN* (0.012 mmol) were dissolved in 1 cm^3 of dry CH_2Cl_2 and the solution was stirred under N_2 atmosphere at room temperature for 30 min. After removal of CH_2Cl_2 under reduce pressure, 1 cm^3 of degassed ionic liquid was added. The mixture was then stirred 10 min at 50°C under N_2 atmosphere, or until the catalyst was dissolved in the ionic liquid. The solution of the catalyst was cooled to room temperature and than 1 mmol of ketone and 203 mg of HCOONa (5 mmol) dissolved in 0.4 cm^3 of degassed water were added. The reaction mixture was then stirred at 50°C for a certain period of time. The reaction was followed by TLC and stopped after full conversion of the starting ketone. At the end of the reaction the mixture was cooled to room temperature, 5 cm^3 H_2O was added, and the solution was extracted with diethyl ether. Extracts were dried (Na_2SO_4), filtered, and the solvent was evaporated in a RVO. The residue was purified by column chromatography on silica gel using ethyl acetate/isohexane (1/4) as the eluent.

In the experiment with the recycled catalytic system, ionic liquid was thoroughly washed with diethyl ether and organic solvent was evaporated under reduced pressure. To this reaction medium was then added 1 mmol of ketone and 203 mg (3 mmol) of HCOONa dissolved in 0.4 cm^3 degassed H_2O. Work-up and purification at the end of the reaction was the same as described above. All of the products were characterized by ^{1}H NMR and their spectra were identical with those described in the references given below.

The following products were obtained:

1-phenylethanol (t_R (major) = 7.98 min, t_R (minor) = 7.04 min) ^{1}H NMR identical with that of Ref. [18]; 1-(4-bromophenyl)ethanol (t_R (major) = 9.72 min, t_R (minor) = 8.99 min) ^{1}H NMR identical with that of Ref. [19]; 1-(2-bromophenyl)ethanol (t_R (major) = 7.25 min, t_R (minor) = 6.49 min) ^{1}H NMR identical with that of Ref. [20]; 1-(3-bromophenyl)ethanol (t_R (major) = 8.19 min, t_R (minor) = 7.74 min) ^{1}H NMR identical with that of Ref. [21]; 1-(4-chlorophenyl)ethanol (t_R (major) = 9.51 min, t_R (minor) = 8.90 min) ^{1}H NMR identical with that of Ref. [22]; 1-(4-methoxyphenyl)ethanol (t_R (major) = 10.42 min, t_R (minor) = 9.40 min) ^{1}H NMR identical with that of Ref. [22]; 1-(4-

tert-butylphenyl)ethanol (t_R (major) = 6.66 min, t_R (minor) = 5.99 min) ^{1}H NMR identical with that of Ref. [22]; 1-(2-methylphenyl)ethanol (t_R (major) = 8.19 min, t_R (minor) = 7.45 min) ^{1}H NMR identical with that of Ref. [23]; 1-acetylnaphthalene (t_R (major) = 17.11 min, t_R (minor) = 16.47 min) ^{1}H NMR identical with that of Ref. [24]; 1,2,3,4-tetrahydronaphthalene-1-ol (t_R (major) = 7.87 min, t_R (minor) = 7.37 min) ^{1}H NMR identical with that of Ref. [25]; Indane-1-ol (t_R (major) = 8.30 min, t_R (minor) = 7.83 min) ^{1}H NMR identical with that of Ref. [25]; 1-(4-bromophenyl)-2′-methylpropanole (t_R (major) = 7.19 min, t_R (minor) = 6.38 min) ^{1}H NMR identical with that of Ref. [26]; 1-phenylpropan-2-ol (t_R (major) = 7.09 min, t_R (minor) = 7.43 min) ^{1}H NMR identical with that of Ref. [27]; 1,3-diphenylpropan-1-ol (t_R (major) = 16.46 min, t_R (minor) = 13.43 min) ^{1}H NMR identical with that of Ref. [28]; 1-(pyridin-4-yl)ethanol (t_R (major) = 15.53 min, t_R (minor) = 14.43 min) ^{1}H NMR identical with that of Ref. [29]; 1-(furan-2-yl)ethanol (t_R (major) = 7.40 min, t_R (minor) = 7.09 min) ^{1}H NMR identical with that of Ref. [30].

Acknowledgements

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