DOI: 10.1002/ejoc.201402884

Microwave-Enhanced Asymmetric Transfer Hydrogenation of *N*-(*tert*-Butylsulfinyl)imines

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Keywords: Asymmetric synthesis / Hydrogenation / Reduction / Asymmetric transfer hydrogenation / Amines / Sulfinylimines

Microwave irradiation has considerably enhanced the efficiency of the asymmetric transfer hydrogenation of *N*-(*tert*-butylsulfinyl)imines in isopropyl alcohol catalyzed by a ruthenium complex bearing the achiral ligand 2-amino-2-methylpropan-1-ol. In addition to shortening reaction times for the transfer hydrogenation processes to only 30 min, the amounts of ruthenium catalyst and isopropyl alcohol can be considerably reduced in comparison with our previous procedure assisted by conventional heating, which diminishes the environmental impact of this new protocol. This methodology can be applied to aromatic, heteroaromatic and aliphatic *N*-(*tert*-butylsulfinyl)ketimines, leading, after desulfinylation, to the expected primary amines in excellent yields and with enantiomeric excesses of up to 96 %.

Introduction

Asymmetric transfer hydrogenation (ATH) has proved to be a highly valuable method for the reduction of carbon–heteroatom double bonds, especially in ketones[1] and imines.[1b–1d,1f,2] There are several features that make this reduction methodology so convenient: 1) it requires very simple equipment, 2) it is safer than other widely used reduction methods because it avoids the use of hazardous chemicals such as highly flammable molecular hydrogen or metallic hydrides, 3) it can be performed in environmentally friendly solvents, for example, isopropyl alcohol, which also acts as the hydrogen source and 4) volatile reaction byproducts are formed, which facilitates the isolation of the reduction products in a pure form. These advantages have allowed the development of interesting industrial processes.[3] On the other hand, microwave irradiation has proven to be a very efficient technique for accelerating different kinds of reactions,[4] including ATH. Several examples of the use of microwaves to promote the ATH of ketones can be found in the literature.[5] However, the reports of microwave-assisted ATH of the C=N bond are scarce and, to the best of our knowledge, there are only three examples of the reduction of *N*-alkyl- or *N*-arylimines[5g,6] and only one of the reduction of a hydrazone,[7] but none of them are stereoselective processes.

In recent years, one of our main lines of research has been the synthesis of highly enantiomerically enriched amines by ATH of *N*-(*tert*-butylsulfinyl)ketimines.[8,9] The ATH process is catalysed by a ruthenium complex bearing the readily available and inexpensive achiral ligand 2-amino-2-methylpropan-1-ol with isopropyl alcohol used as the hydrogen source. The reduction of both aromatic and aliphatic sulfinylimines led, after desulfinylation, to the expected α-branched primary amines with excellent enantiomeric excesses. In the search for a procedure with a lower impact on the environment, and encouraged by our previous successful applications of microwaves in organic synthesis,[10] we have used microwave heating in an attempt to activate the reagents in our ATH protocol and we present the results of our investigation herein.

Results and Discussion

We chose imine **1a** as a model substrate and attempted its reduction by ATH utilizing the same amounts of reagents that we had used in our previous procedure promoted by conventional heating. The ruthenium catalyst was prepared by heating a mixture of $[RuCl_2(p\text{-cymene})]_2$, 2-amino-2-methylpropan-1-ol and 4 Å molecular sieves in isopropyl alcohol at reflux, according to our previously described procedure.[8c,8d,11] Fortunately, the ATH reaction proceeded very readily and was complete in only 30 min (Table 1, entry 1). This time is considerably shorter than that needed under conventional heating (2 h) and amine **2a** was obtained in 98% yield and with 95% *ee*, which is very similar

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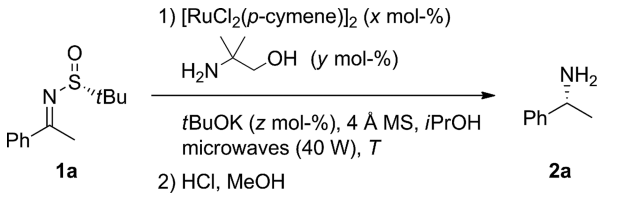
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201402884.

to the value we observed in the ATH performed under conventional heating (97% *ee*).[8c,8d] After this successful result, we decided to optimize the reaction conditions and the results are collected in Table 1.

Table 1. Optimization of the reaction conditions for the ATH reduction of imine **1a**.[a]



Entry	**1a**[b] [mmol]	*x* [mol-%]	*y* [mol-%]	*z* [mol-%]	*T* [°C]	Time[c] [min]	Yield of **2a**[d] [%]	*ee*[e] [%]
1	0.9	2.5	5	12.5	50	30	98	95
2	0.9	2.5	5	12.5	50	15	96	96
3	0.9	2.5	5	12.5	50	5	84[f]	96
4	0.9	2.5	5	12.5	50	1	74[f]	96
5	1.5	1.5	3	7.5	50	30	95	95
6	1.5	1.5	3	7.5	50	15	83[f]	95
7	1.8	1.25	2.5	6.25	50	60	95	94
8	1.8	1.25	2.5	6.25	50	30	91[f]	95
9	1.8	1.25	2.5	6.25	50	15	82[f]	94
10	1.8	1.25	2.5	6.25	60	30	78[f]	85

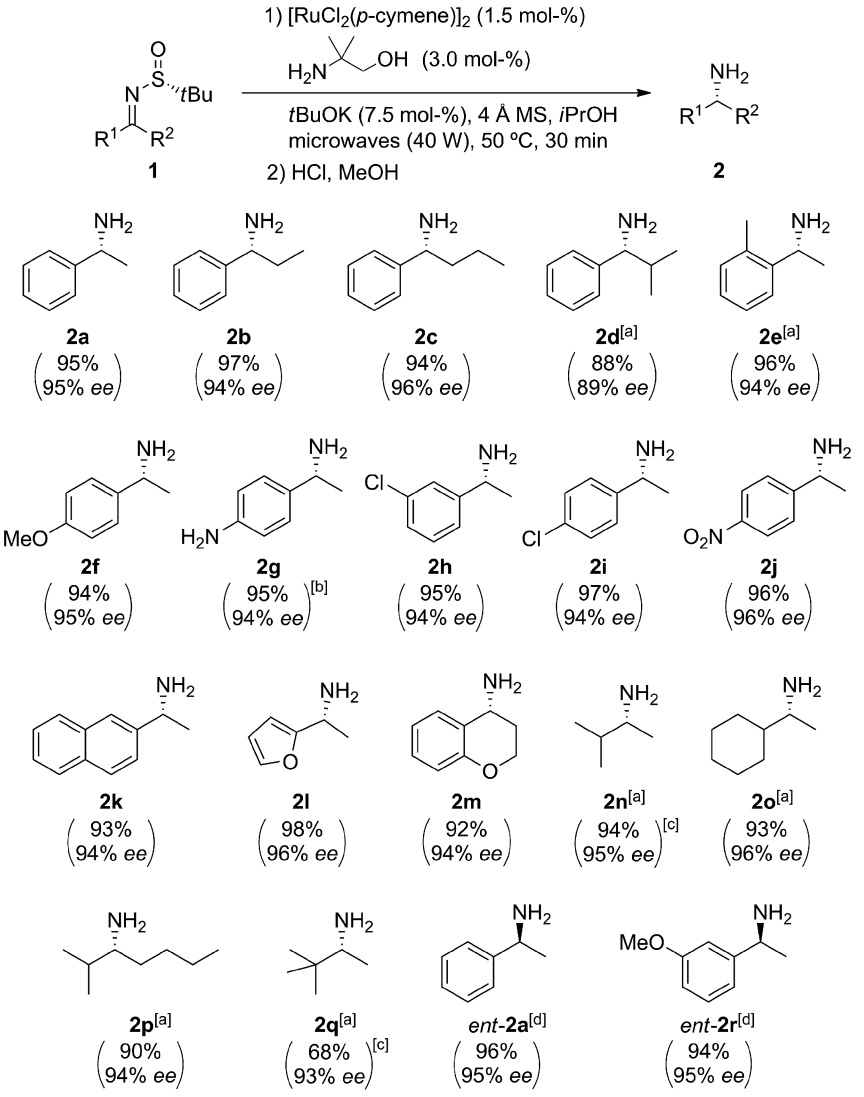
[a] The solution of imine **1a** in *i*PrOH was added to a solution of the ruthenium complex [prepared by heating a mixture of $[RuCl_2(p\text{-cymene})]_2$ (0.023 mmol), 2-amino-2-methylpropan-1-ol (0.045 mmol) and 4 Å molecular sieves (0.15 g) in *i*PrOH (1.25 mL) at reflux] at room temperature. Then, *t*BuOK (1.13 mL of a 0.1 M solution in *i*PrOH, 0.113 mmol) was added and the reaction was irradiated with microwaves (40 W) at the temperature and for the time indicated. [b] The amount of solvent used to prepare the solution of imine **1a** was adjusted to give a final volume of *i*PrOH (after the addition of all the reagents) of 6 mL. [c] Time for the microwave-promoted transfer hydrogenation reaction. [d] Yield of isolated amine **2a** after acid/base extraction based on the starting imine **1a**. The isolated compound **2a** was always ≥95% pure (300 MHz ^{1}H NMR). [e] Determined for the corresponding benzamide by HPLC using a ChiralCel OD-H column. The *R* enantiomer was the major one obtained in all cases. [f] Some unreacted imine **1a** was detected in the crude reaction mixture.

First, the irradiation time was reduced to 15, 5 and 1 min, maintaining the rest of the conditions the same. The result with an irradiation time of 15 min was practically the same as that obtained in 30 min (Table 1, entry 2). With irradiation times shorter than 15 min, the reactions did not reach completion and yields decreased as the time was reduced (cf. entries 2–4 in Table 1), but the *ee* was maintained. Next, we tried to reduce the catalyst loading by keeping the same amount of catalyst and base and increasing the amount of imine **1a**. Owing to limitations in the size of the reaction vessel used for the microwave-promoted ATH reaction, the final volume of isopropyl alcohol in the reaction mixture was kept to 6 mL in all cases, which implies that the concentration of substrate **1a** in the reaction mixture increased as its amount was increased. By using a common irradiation time of 30 min, the yield slightly decreased when the amount of imine was increased from 0.9 to 1.5 and 1.8 mmol, the reaction not going to completion in the final case (cf. entries 1, 5 and 8 in Table 1), but, interestingly, there was no diminution of the enantiomeric purity of amine **2a**. The same trend was observed when the reactions were irradiated for 15 min (cf. entries 2, 6 and 9 in Table 1). When using 1.8 mmol of the substrate, an irradiation time of 1 h was needed to obtain the product in 95% yield, but with an *ee* of 94%. An increase of the reaction temperature to 60 °C with an irradiation time of 30 min was deleterious for both the yield and the *ee* (cf. entries 8 and 10 in Table 1). Following this study, we chose to use the reaction conditions in entry 5 in further investigations.

We next investigated the substrate scope of the reaction. Replacing the methyl group in **1a** by other linear or branched aliphatic chains also led to very good results (**2b**–**d**, Scheme 1). The reduction of imines bearing different substituents on the phenyl group gave the expected amines in excellent yields and with *ee* values of up to 96%, irrespective of the electronic nature of the substituent or its position on the ring (**2e**–**j**, Scheme 1). Some highly optically enriched amines bearing other aromatic (**2k**) or heteroaromatic (**2l**) substituents and an amine having a heterocyclic bicyclic skeleton (**2m**) were also obtained in very high yields.

Remarkably, our microwave-promoted ATH procedure could also be applied to more challenging aliphatic imines and the expected aliphatic amines **2n**–**q** were isolated in good yields and with high enantioselectivities, including the highly sterically congested amine **2q**. It must be pointed out that, as was the case in our previous ATH of *N*-(*tert*-butylsulfinyl)imines by conventional heating, in the case of the reduction of sterically congested imines bearing aromatic substituents or aliphatic imines, the amounts of catalyst and base had to be doubled to achieve full conversion of the imines in 30 min (**2d**,**e**,**n**–**q**, Scheme 1). Finally, this new ATH protocol was equally efficient for the preparation of the *S*-configured amines *ent*-**2a** and *ent*-**2r** from the corresponding imines with the (*S*)-(*tert*-butylsulfinyl) chiral auxiliary. Thus, both enantiomers of an amine (e.g., **2a** and *ent*-**2a** in Scheme 1) can be prepared with the same enantiomeric purity by using the same catalyst by changing the absolute configuration of the sulfur atom in the sulfinyl moiety of the imine.

This new microwave-assisted ATH of *N*-(*tert*-butylsulfinyl)ketimines represents an interesting improvement on our previous procedure promoted by conventional heating for the following reasons: 1) the reaction times are much shorter, 2) the amount of catalyst has been reduced to almost half of that used in our previous procedure, 3) the reactions can be carried out at higher concentrations and, therefore, less solvent is needed. All of these features lower the reaction costs, the consumption of electric power and the amount of waste that is generated, thus minimizing the environmental impact of our microwave-promoted protocol. We assume that the rate enhancement observed in this new procedure in comparison with the conventionally heated process could be due to the fast dielectric heating that is generated by interaction of the microwave irradiation with the polar reaction medium (isopropyl alcohol).[12]



Scheme 1. Microwave-promoted ATH of *N*-(*tert*-butylsulfinyl)imines **1**: synthesis of α-branched primary amines **2**. The yield of the isolated product after acid/base extraction (based on the starting imine **1**) and enantiomeric excess (determined for the corresponding benzamide by HPLC using a ChiralCel OD-H column) are presented in parentheses. All isolated compounds **2** were ≥95% pure (300 MHz ^{1}H NMR). [a] $[RuCl_2(p\text{-cymene})]_2$ (3 mol-%), 2-amino-2-methylpropan-1-ol (6 mol-%) and *t*BuOK (15 mol-%) were used in this reaction. [b] In the precursor imine (**1g**) to this compound, R^1 = 4-BocNHC$_6$H$_4$. The Boc group was also removed during the desulfinylation step and diamine **2g** was isolated as its dihydrochloride. [c] The corresponding hydrochloride was isolated. [d] The (S_S)-imine *ent*-**1** was used in this reaction.

Conclusions

We have developed a very efficient procedure for the asymmetric transfer hydrogenation of *N*-(*tert*-butylsulfinyl)-imines promoted by microwave irradiation. Our methodology allows the reduction of a variety of aromatic, heteroaromatic and aliphatic ketimines in very short reaction times, leading, after desulfinylation, to the expected α-branched primary amines in excellent yields and with very high enantiomeric purities. Both enantiomers of an amine are readily accessible by using the same ruthenium catalyst by changing the absolute configuration of the sulfinyl group bonded to the nitrogen atom of the imine. This new protocol is more efficient and causes less impact on the environment than our previous ATH procedure assisted by conventional heating.

Experimental Section

General: Microwave reactions were performed with a CEM Discover Synthesis Unit (CEM Corp., Matthews, NC) with a continuous focused microwave power delivery system in a pressure glass vessel (10 mL) sealed with a septum under magnetic stirring. The temperature of the reaction mixture was monitored by using a calibrated infrared temperature control under the reaction vessel, and the pressure was controlled with a pressure sensor connected to the septum of the vessel. All glassware was dried in an oven at 100 °C and cooled to room temperature under argon before use. All reactions were carried out under argon. All the starting materials needed for the synthesis of imines **1** and *ent*-**1**, $[RuCl_2(p\text{-cymene})]_2$ and 2-amino-2-methylpropan-1-ol were commercially available and used as received. *t*BuOK was heated in a Kugelrohr distillation apparatus at 170–180 °C under vacuum for 4 h before use. Commercially available molecular sieves (4 Å) were dried in a

kugelrohr distillation apparatus at 120 °C under vacuum for 5 h before use. Commercially available anhydrous isopropyl alcohol was used as solvent in all the transfer hydrogenation reactions. Column chromatography was performed with silica gel 60 of 230–400 mesh. TLC was performed on pre-coated silica gel plates; detection was achieved by using UV_{254} light and staining with phosphomolybdic acid (solution of 1 g of phosphomolybdic acid in 24 mL of absolute ethanol). Unless otherwise stated, NMR samples were prepared by using $CDCl_3$ as solvent. TMS and $CDCl_3$ were used as internal references for ^1H and ^{13}C NMR spectroscopy, respectively. ^{13}C NMR assignments were made on the basis of DEPT experiments. FTIR spectra were recorded with a spectrophotometer equipped with an attenuated total reflectance (ATR) accessory. Mass spectra (EI) were obtained at 70 eV. Optical rotation measurements and HPLC analyses were performed at 20 °C.

General Procedure for the Synthesis of Imines 1 and *ent*-1: *N*-(*tert*-Butylsulfinyl)ketimines were prepared by condensation of the corresponding ketones with (*R*)-2-methylpropane-2-sulfinamide (for **1**) or (*S*)-2-methylpropane-2-sulfinamide (for *ent*-**1**) following our reported procedure.[10b] Imines **1a**,[13] **1b**,[13] **1c**,[14] **1d**,[15] **1e**,[8d] **1f**,[13] **1g** (R^1 = 4-$BocNHC_6H_4$),[8b] **1h**,[8b] **1i**,[16] **1j**,[15] **1k**,[17] **1l**,[18] **1m**,[19] **1n**,[8d] **1o**,[8b] **1p**,[8d] **1q**,[8d] *ent*-**1a**[15] and *ent*-**1r**[8b] were identified by comparison of their physical and spectroscopic data with those reported in the literature.

General Procedure for the Microwave-Promoted Asymmetric Transfer Hydrogenation of *N*-(*tert*-Butylsulfinyl)imines 1 and *ent*-1: A mixture of $[RuCl_2(p\text{-cymene})]_2$ (14 mg, 0.023 mmol), 2-amino-2-methylpropan-1-ol (4 mg, 0.045 mmol) molecular sieves (4 Å, 0.15 g) and anhydrous *i*PrOH (1.25 mL) under argon was heated at 90 °C (oil bath temperature) for 20 min. During this heating period, the initially orange reaction mixture turned dark red. The reaction mixture was then cooled to room temperature and a solution of the imine **1** or *ent*-**1** (1.5 mmol) in *i*PrOH (3.60 mL) and *t*BuOK (1.13 mL of a 0.1 M solution in *i*PrOH, 0.113 mmol) were successively added. Immediately, the reaction mixture was heated at 50 °C with microwave irradiation (40 W power) for 30 min. After completion of the reaction, the mixture was cooled to room temperature and passed through a small column of silica gel, eluting with ethyl acetate. The combined organic phases were evaporated to give a residue that was directly submitted to the desulfinylation step.

For the aromatic imines **1d**,**e** and the aliphatic imines **1n**–**q**, $[RuCl_2(p\text{-cymene})]_2$ (28 mg, 0.045 mmol), 2-amino-2-methylpropan-1-ol (8 mg, 0.090 mmol) and *t*BuOK (2.25 mL of a 0.1 M solution in *i*PrOH, 0.225 mmol) were used.

General Procedure for the Removal of the Sulfinyl Group: Isolation of Amines 2a–f, 2h–m, 2o–p and *ent*-2: The crude mixture of the transfer hydrogenation reaction was dissolved in a 2 M solution of HCl in methanol (7 mL; prepared by the dropwise addition of $SOCl_2$ to methanol at 0 °C) and stirred overnight at room temperature. Then the solvent was evaporated, a 2 M aqueous HCl solution (10 mL) was added and the mixture was extracted with ethyl acetate (3 × 10 mL). The organic layers were discarded and the aqueous layer was basified with a buffer solution of NH_3 (2 M)/NH_4Cl (2 M) (10 mL) and a 2 M aqueous NaOH solution to ensure pH > 11. The mixture was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic phases were dried (Na_2SO_4). After filtration and evaporation of the solvent, pure amines **2a**–**f**, **2h**–**m**, **2o**–**p** and *ent*-**2** were obtained with the *ee* values indicated in Scheme 1 and in the following yields: **2a** (173 mg, 95%), **2b** (197 mg, 97%), **2c** (210 mg, 94%), **2d** (197 mg, 88%), **2e** (195 mg, 96%), **2f** (213 mg, 94%), **2h** (222 mg, 95%), **2i** (226 mg, 97%), **2j** (239 mg, 96%), **2k** (239 mg, 93%), **2l** (163 mg, 98%), **2m** (206 mg, 92%), **2o** (177 mg, 93%), **2p** (174 mg, 90%), *ent*-**2a** (174 mg, 96%) and *ent*-**2r** (213 mg, 94%). Amines **2a**, *ent*-**2a** and **2b**, which are commercially available, were identified by comparison of their physical and spectroscopic data with those of authentic samples. Amines **2c**,[8b] **2d**,[20] **2e**,[8d] **2f**,[8b] **2h**,[8b] **2i**,[8b] **2j**,[8b] **2k**,[8b] **2l**,[8b] **2m**,[8b] **2o**,[8b] **2p**[8d] and *ent*-**2r**[8b] were identified by comparison of their physical and spectroscopic data with those reported in the literature.

Synthesis of Amines 2g·2HCl, 2n·HCl and 2q·HCl: A 2 M solution of HCl in Et_2O (10 mL, 20 mmol) was added to the crude residue of the asymmetric transfer hydrogenation of imine **1g** (R^1 = 4-$BocNHC_6H_4$), **1n** or **1q**, and the mixture was stirred overnight. After filtration, the solid was washed with Et_2O (3 × 10 mL) and dried to afford the corresponding hydrochlorides with the *ee* values indicated in Scheme 1 and in the following yields: **2g**·2HCl (298 mg, 95%), **2n**·HCl (174 mg, 94%) and **2q**·HCl (140 mg, 68%). Compounds **2g**·2HCl,[8b] **2n**·HCl[8d] and **2q**·HCl[8d] were identified by comparison of their physical and spectroscopic data with those previously reported by us.

Determination of the Enantiomeric Excesses of Amines 2 and *ent*-2: Amine **2** or *ent*-**2** (0.4 mmol) was dissolved in CH_2Cl_2 (5 mL) and cooled to 0 °C. A 2 M aqueous NaOH solution (5 mL) was added and the mixture was stirred for 5 min. Benzoyl chloride (93 μL, 0.8 mmol; for the benzoylation of diamine **2g**, 186 μL, 1.6 mmol were used) was added dropwise, the cold bath was removed and the reaction mixture was stirred at room temperature for 3 h. Then the layers were separated, the organic phase was washed with a 2 M aqueous NaOH solution (3 × 5 mL) and the aqueous layers were discarded. The organic phase was washed with brine (2 × 5 mL) and then dried (Na_2SO_4). After filtration and evaporation of the solvent, the expected benzamides were obtained, which were analysed by HPLC on a ChiralCel OD-H column using a 254 nm UV detector, 10% *i*PrOH in hexane as eluent and a flow rate of 0.5 mL/min. The major enantiomer had the lower retention time in all cases, except for amines *ent*-**2a** and *ent*-**2r**. The racemic amines were prepared by reaction of the corresponding ketones with a solution of NH_3 in EtOH following a literature procedure,[21] and were benzoylated as described above. The retention times of the two enantiomers of all the benzamides are collected in Table S1 in the Supporting Information.

Supporting Information (see footnote on the first page of this article): HPLC retention times of benzamides derived from amines **2** and *ent*-**2**, ^1H and ^{13}C NMR spectra for all imines **1** and *ent*-**1** and all amines **2** and *ent*-**2**.

Acknowledgments

This work was generously supported by the Spanish Ministerio de Ciencia e Innovación (MICINN) (grant numbers CONSOLIDER INGENIO 2010, CSD2007-00006, CTQ2007-65218 and CTQ2011-24151) and the Generalitat Valenciana (PROMETEO/2009/039 and FEDER). O. P. thanks the Spanish Ministerio de Educación for a predoctoral fellowship (grant number AP-2008-00989).

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Received: July 8, 2014
Published Online: September 18, 2014

