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Asymmetric Hydrogenation of Thiophenes and Benzothiophenes

Slawomir Urban,[†] Bernhard Beiring,[†] Nuria Ortega, Daniel Paul, and Frank Glorius*

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstrasse 40, 48149 Münster, Germany

Supporting Information

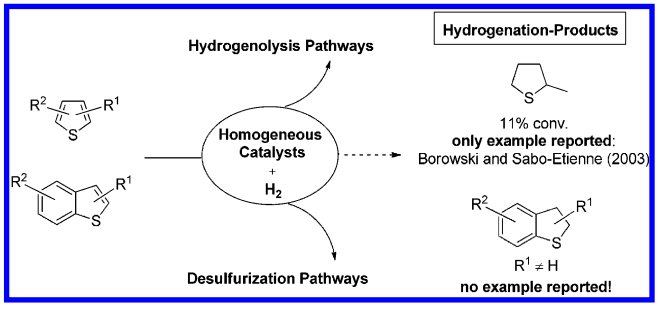
ABSTRACT: An efficient and highly asymmetric ruthenium-N-heterocyclic carbene-catalyzed hydrogenation of substituted thiophenes and benzothiophenes is described, providing a new strategy for the formation of valuable enantiomerically pure tetrahydrothiophenes and 2,3-dihydrobenzothiophenes.

The hydrogenation of (hetero)arenes provides a clean and straightforward method to obtain the corresponding saturated (hetero)cycles.[1] Recently, a lot of progress has been made in the *asymmetric* hydrogenation of (hetero)arenes, such as quinolines,[2] isoquinolines,[3] quinoxalines,[4] indoles,[5] pyrroles,[5j,k] (benzo)furans,[6] and naphthalenes.[7a] However, despite great effort in this field in recent years, many challenges remain and sulfur-containing arenes are particularly difficult substrates.

Extensive studies on the hydrogenation of unsubstituted thiophene and benzothiophene have been executed by many research groups in the past,[8] due to its importance in the hydrodesulfurization process (HDS). This effort led to the identification of several catalysts for the catalytic hydrogenation of unsubstituted benzothiophene, providing insight into possible binding modes and kinetics.[10] Thiophene, however, is still a challenge for homogeneous catalysts, probably due to its aromaticity and the strong coordination and poisoning ability of the reduced tetrahydrothiophene.[10d,f] Thus, only one example of catalytic thiophene hydrogenation has been reported, by the groups of Borowski and Sabo-Etienne in 2003.[10d] However, the hydrogenation becomes even more challenging for *substituted* thiophenes and benzothiophenes (Scheme 1).[8,9]

(Optically active) dihydro- and tetrahydrothiophene derivatives play an important role in organic, biological, and medicinal chemistry and are widely distributed.[11] Besides many approaches developed to obtain these important compounds, the formation of structurally diverse and enantiopure derivatives is particularly challenging. Unlike for many other chiral heterocyclic compounds, the asymmetric hydrogenation of the corresponding aromatic organosulfur compounds was, despite its attractiveness and due to the difficulties described above, so far not entertained as a possible synthetic pathway.[11a] Thus, the development of sulfur tolerant, highly reactive, and enantioselective catalyst systems would allow the use of readily available substituted aromatic organosulfur compounds as starting materials for the synthesis of valuable optically active dihydro- and tetrahydrothiophenes.

Scheme 1. Reactivity of Homogeneous Metal Complexes toward Substituted Thiophene Derivatives under H_2 Atmosphere



During the course of our investigation into the asymmetric hydrogenation of arenes, we found that the combination of ruthenium(II) and several monodentate NHCs (NHC = N-heterocyclic carbene)[12] led to the formation of selective hydrogenation catalysts for quinoxalines[7b] and benzofurans[6f,g] with very high levels of regio- and enantioselectivity. Herein we report the asymmetric homogeneous hydrogenation of substituted thiophenes and benzothiophenes using a Ru-NHC complex. The use of a chiral NHC-ligand enables a new route to biologically active dihydrobenzothiophenes and tetrahydrothiophenes of very high optical purity; both high levels of reactivity and selectivity are remarkable.

The requirements for a suitable homogeneous catalyst for the successful hydrogenation of substituted benzothiophenes and/or thiophenes seem to differ dramatically from the ones required for the hydrogenation of the corresponding unsubstituted compounds.[9] Indeed, none of the reported reactive benzothiophene hydrogenation catalysts showed reactivity toward substituted derivatives. Possible reasons for this are that substituents at C(2) or C(3) reduce the π-acceptor character of the olefin and also sterically hinder the η^2-(C,C)-coordination mode. In addition, electron-donating alkyl groups enhance the donor ability of the sulfur atom, thereby favoring S-coordination.[13] Usually organosulfur hydrogenation catalysts consist of phosphine, nitrogen, or Cp/Cp* type ligands. We assumed that carbene ligands, due to their strong ability to donate electron density to the metal center,[12f] might favor η^2-(C,C)-substrate–metal interactions through attractive π-back-donation. The electron-rich metal should thereby show only weak S-coordination. Furthermore, Ru(II)-complexes are expected to show rather low thiophilicity, which is an important requirement. This and the high reactivity of the previously developed Ru-NHC catalyst system in the reduction of heteroarenes[6f,g,7b] led us to test it in the hydrogenation of substituted aromatic organosulfur compounds. In our initial test

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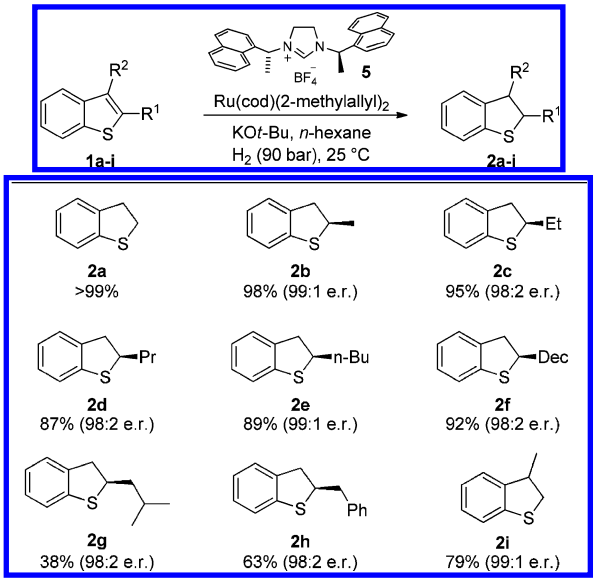
reactions we investigated the performance of the catalyst toward the hydrogenation of unsubstituted benzothiophene (**1a**) and thiophene (**3a**). Gratifyingly, using 1 mol % of catalyst prepared in situ from [Ru(cod)(2-methylallyl)$_2$] and SINpEt·HBF$_4$ (**5**), both substrates could be quantitatively reduced, even at room temperature (Tables 1 and 2).[14] No side reactions such as metal insertion into C−S bonds, hydrogenolysis, or hydrodesulfurization were observed.

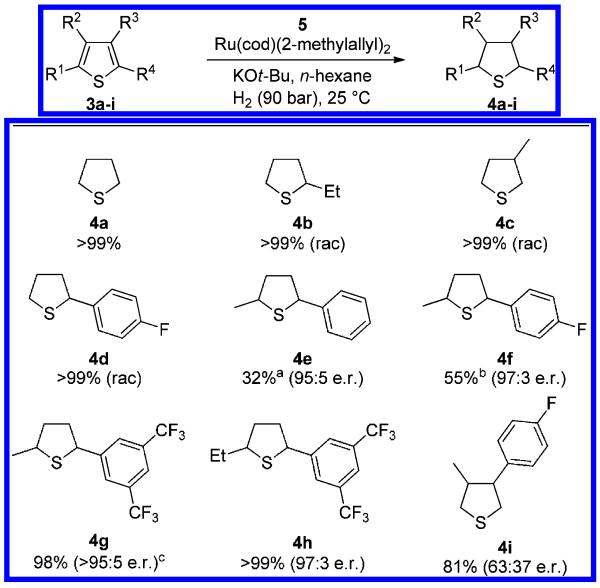
Table 1. Scope of the Asymmetric Hydrogenation of Benzothiophenes[a]



[a]General conditions: [Ru(cod)(2-methylallyl)$_2$] (0.015 mmol), KO*t*-Bu (0.045 mmol), and **5** (0.032 mmol) were stirred at 70 °C in hexane (1 mL) for 16 h, after which the mixture was added to benzothiophene (0.30 mmol) and hydrogenation was performed at shown conditions for 24 h. The yield was determined by GC or ^{1}H NMR using CH_2Br_2 as internal standard. E.r. (given in brackets) was determined by HPLC on a chiral stationary phase.

To find out if our catalyst system might also be applicable for substituted substrates, the hydrogenation of 2-methylbenzothiophene (**1b**) as a model substrate was investigated. Surprisingly, mild reaction conditions such as 10 bar of hydrogen at room temperature were sufficient to obtain 83% of the 2,3-dihydrobenzothiophene **2b** in 18 h, without any formation of side products. Remarkably, the product was obtained in an enantiomeric ratio (e.r.) of 99:1. The conversion could even be improved to 98% when the hydrogen pressure was raised to 90 bar (Table 1). The absolute configuration of 2-methyl-2,3-dihydrobenzothiophene (**2b**) was assigned as (*R*) by comparison of optical rotation data with the literature value.[15] Similarly, the isomer 3-methylbenzothiophene (**2i**) could also be smoothly reduced in a yield of 79% and 99:1 e.r. These results represent the first examples of a catalytic homogeneous hydrogenation of substituted benzothiophenes to the corresponding 2,3-dihydro derivatives. In addition, the high levels of enantioinduction of this transformation are unparalleled, rendering this method an efficient route to attractive optically active dihydrobenzothiophenes. The scope of this reaction was further examined. Several alkyl substituted benzothiophenes (**1b−f**) were reduced in good to high yields and excellent e.r.'s ranging from 99:1 to 98:2. Modest yields were obtained when using 2-isobutylbenzothiophene (**1g**) and

Table 2. Scope of the Asymmetric Hydrogenation of Thiophenes[a]



[a]General conditions: [Ru(cod)(2-methylallyl)$_2$] (0.015 mmol), KO*t*-Bu (0.045 mmol), and **5** (0.032 mmol) were stirred at 70 °C in hexane (1 mL) for 16 h, after which the mixture was added to thiophene (0.15 mmol), and hydrogenation was performed at shown conditions for 24 h. The yield was determined by GC or ^{1}H NMR using CH_2Br_2 as an internal standard. E.r. (given in brackets) was determined by HPLC on a chiral stationary phase. [b]Reaction time was 40 h; 70 bar H_2 were used. [c]Signals of enantiomeres are not baseline separated in the HPLC traces.

2-benzylbenzothiophene (**1h**) as substrates, but the high e.r.'s were maintained. Unfortunately, no conversion of arylated substrates was observed yet. Since the sign of the optical rotation values for all the 2-substituted benzothiophenes obtained in this study is the same (+), we assume that the obtained stereochemistry should be similar to the one obtained for (*R*)-2-methyl-2,3-dihydrobenzothiophene (**2b**) (see above).

Due to the unique performance of this complex in the hydrogenation of various substituted benzothiophenes, we wondered if the less reactive mono- and disubstituted thiophenes could undergo hydrogenation. Using our standard conditions, 2-alkylated and 2-arylated thiophenes such as 2-ethylthiophene (**3b**) and 2-(4-fluorophenyl)thiophene (**3d**), but also 3-methylthiophene (**3c**), could be reduced quantitatively (Table 2). Surprisingly, all of these monosubstituted products were obtained in racemic form only.

Remarkably, even when disubstituted thiophenes were tested, which have never been successfully applied in homogeneous hydrogenation reactions before, the catalyst still showed reactivity toward hydrogenation. Even though lower yields were obtained for the phenyl substituted substrate **3e**, moderate to excellent yields were obtained for thiophenes bearing electron-withdrawing substituents (**3f−h**). Intriguingly, in all cases, high enantio- (>95:5) and perfect diastereoselectivity (only cis-products) were obtained. Different regioisomers such as 3,4-disubstituted thiophene **3i** could also be reduced with the same catalyst system under the standard conditions, although the reaction proceeded with significantly lower enantioselectivity (63:37 e.r.). Before this work, 2-methylthiophene had been the only substituted (benzo)-thiophene that was successfully hydrogenated (in only 11%)

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by a homogeneous catalyst (Scheme 1).[10d] Thus, the high level of reactivity observed at room temperature with this Ru-NHC complex is really remarkable. Intriguingly, [Ru(cod)(2-methylallyl)$_2$], which is a powerful catalyst for several arene hydrogenations,[16] fails to show significant levels of activity in the hydrogenation of 2-methylbenzothiophene under our standard conditions (<5% conversion after 24 h), when the NHC SINpEt is left out. This is representative of the inability of most Ru species to catalyze this challenging transformation and shows the crucial role of the NHC ligands.

In summary we have developed the first asymmetric hydrogenation of substituted thiophenes and benzothiophenes. The efficient and enantioselective hydrogenation of S-containing heterocycles provides a new strategy for the formation of enantiomerically enriched tetrahydrothiophenes and 2,3-dihydrobenzothiophenes, compounds of great interest. These results lay the foundation to gain insight into the previously difficult hydrogenation of substituted thiophenes and benzothiophenes. The unique ability of the chiral Ru-NHC complex and the surprising discrepancy between the very high levels of enantioinduction in many cases and the formation of a racemic product for other classes of substrates will be the matter of further investigations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

glorius@uni-muenster.de

Author Contributions

†These authors contributed equally.

Notes

The authors declare no competing financial interest.

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(14) Hg(0) poisoning experiments performed in our previous work strongly indicate the homogeneous nature of this Ru-NHC catalyzed hydrogenation. For more details, see ref 7b.

(15) See Supporting Information.

(16) Unpublished results from our group.