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S-Benzyl isothiouronium chloride as a recoverable organocatalyst for the reduction of conjugated nitroalkenes with Hantzsch ester

Quynh Pham Bao Nguyen [a], Jae Nyoung Kim [b], Taek Hyeon Kim [a,*]

[a] School of Applied Chemical Engineering and Center for Functional Nano Fine Chemicals, Chonnam National University, Gwangju 500-757, Republic of Korea
[b] Department of Chemistry and Institute of Basic Science, Chonnam National University, Gwangju, 500-757, Republic of Korea

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ABSTRACT

The reduction of conjugated nitroalkenes into nitroalkanes with Hantzsch ester using *S*-benzyl isothiouronium chloride as a recoverable organocatalyst was successfully accomplished with high yield and excellent chemoselectivity.

1. Introduction

Nitroalkanes have great potential for organic synthesis because the nitro group is converted easily into the corresponding functionalities, such as carbonyl, nitrile oxide, and amino groups.[1] Several methods have been reported for the reduction of conjugated nitroalkenes to nitroalkanes. However, they have some limitations in controlling chemoselectivity.[2] For instance, lithium aluminum hydride provided a mixture of products containing saturated amines, nitroalkanes, oximes, and hydroxyl amines, whereas borohydride reduction furnished primarily the corresponding nitroalkane, which was often contaminated with the dimeric by-product formed by Michael addition of the nitronate intermediate to the starting nitroalkene.[2f]

Hantzsch esters have been explored as powerful biomimetic reductants because they overcome some limitations encountered with traditional reductive reagents, such as hydrogen gas/metal and metal hydrides.[3] The selective reduction of nitroalkenes into nitroalkanes using Hantzsch esters has done by the combination of effective catalysts, such as acetic acid,[2c] silica gel,[2d,g] and thiourea.[2h,5c] Recently, we reported *S*-benzyl isothiouronium chloride as a novel organocatalyst for the direct reductive amination of aldehydes using Hantzsch esters.[4] The combination of Hantzsch esters and *S*-benzyl isothiouronium chloride as an organocatalyst is herein introduced for the reduction of conjugated nitroalkenes into nitroalkanes resulting in high efficiency, chemoselectivity, and easy recovery of organocatalyst. Isothiouronium salts have been explored quite recently as a new class of hydrogen-bonding subunit for anion recognition.[5] Isothiouronium group as an anion-binding site has several advantages: (i) it enhances the NH acidity compared to the corresponding thiourea; (ii) the chemical modification is readily varied to prepare several types of functional molecular systems.[6f] Therefore we expect that some isothiouronium salts might work as an activator for the reduction of conjugated nitroalkenes (Scheme 1).

2. Results and discussion

Mechanically, the hydrogen bonding between the nitro group of the substrate and the isothiouronium moiety of organocatalyst may reduce the activation energy of the alkene (LUMO activation), leading to acceleration of the reaction (Scheme 1).[2h] With this mind, the reduction of nitrostyrene **1a** was first investigated. Pleasingly, this reaction gave the required product at 71% and 90% yields in dichloromethane and methanol, respectively (entries 3 and 4 in Table 1). To identify the hydrogen bonding between nitrostyrene and *S*-benzyl isothiouronium chloride catalyst, the ^{1}H NMR spectrometry method was used by monitoring the changes in the spectra of the catalyst in the presence of the excess reagent **1a** (10 equiv) in DMSO-d_6. It was obviously observed that the protons

* Corresponding author. E-mail addresses: thkim@chonnam.ac.kr, thkim@jnu.ac.kr (T.H. Kim).

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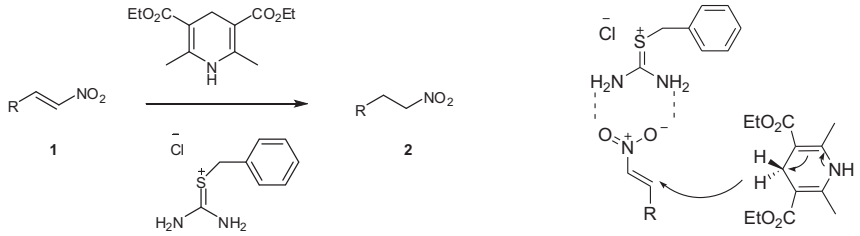
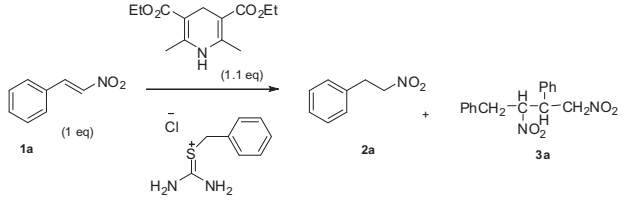


Scheme 1. Reduction of conjugated nitroalkenes using *S*-benzyl isothiouronium chloride catalyst.

Table 1
Optimization of the reduction of conjugated nitroalkenes



Entry	Equiv of catalyst	Solvent	Time (h)	Temperature (°C)	Yield of **2a** (%)
1	0	CH_2Cl_2	24	Reflux	0
2	0	MeOH	10	60	50
3	0.1	CH_2Cl_2	24	Reflux	71 (0)[a]
4	0.1	MeOH[b]	5	60	90 (41)[a]
5	0.1	MeOH	24	rt	55
6	0.05	MeOH	5	60	82

[a] Yields in the parentheses were obtained in the presence of the excess TBAA (1.5 equiv).
[b] The insoluble solvents of isothiouronium catalyst (heterogeneous solution), such as CH_2Cl_2, toluene, benzene, dioxane, and THF are less suitable than the soluble solvent MeOH (homogeneous solution).

of −NH and $-CH_2Ph$ moieties of the *S*-benzyl isothiouronium chloride catalyst were shifted from 9.37 to 9.44 ppm and from 4.55 to 4.57 ppm, respectively. In addition, the excess tetrabutylammonium acetate (TBAA) was added to the reaction mixture and their yields dramatically were reduced (entries 3 and 4 in Table 1), which can destroy the hydrogen bonding between the *S*-benzyl isothiouronium chloride and nitro group of the nitroalkene due to the higher coordination of the acetate anion with the isothiouronium ion.[6–8] From this control experiments the hydrogen bonding activation by isothiouronium ion would be a crucial factor in this reaction. Next the effect of solvents on the reduction was examined to optimize the reaction. The best solvent was MeOH dissolving the catalyst, while the insoluble solvents, such as CH_2Cl_2, toluene, benzene, dioxane, and THF were less suitable. This result was quite different from that of thiourea.[2h] One of the most considerable advantages of isothiouroniums over thioureas, as known in anion recognition field, is that they gave higher binding constants even in polar protic solvents, such as methanol or water, proving the strong hydrogen bonding of isothiouronium derivatives.[6] It is also worth noting that without the organocatalyst in the methanol (entry 2 in Table 1), there is generally loss of product due to the formation of the dimeric by-product **3a** derived from the Michael addition of the nitronate intermediate to the starting nitroalkene.[2a,h] Running the reaction at room temperature and loading low amount of catalyst gave reduced yields of **2a** (entries 5 and 6 in Table 1). In MeOH at 60 °C as a best conditions *S*-benzyl isothiouronium chloride provided 90% yields with only a trace of by-product **3a** (entry 4 in Table 1).

The various conjugated nitroalkenes (Table 2) were examined in MeOH at 60 °C. As expected, the present protocol provided the desired products in a various conjugated nitroalkenes **1**, such as aromatic (entries 1–10 and 15–16), aliphatic (entry 17), and heterocyclic (entries 11–13) nitroalkenes in high yields. The variations of the substituent in the aromatic ring made no effect on the outcome of this reaction. No reductions of the nitro (entry 7), nitrile (entry 8), and carbonyl (entries 9 and 10) moieties were observed and the free hydroxyl group (entry 4) was tolerated. The nitroalkene with the methyl group substituted at the β-position of the double bond also ran smoothly (entry 14). In the structures with two conjugated carbon–carbon double bonds, only the one adjacent to the nitro group was reduced selectively, while the other one remained intact even in an excess of the reducing reagent and catalyst as well as under extended reaction time (entries 15 and 16). In addition, the enone systems, such as cinnamaldehyde and 2-cyclohexen-1-one were not reduced at all under this reaction condition and recovered, showing only nitroalkenes were reduced chemoselectively.

Finally, the recycling of the catalyst was a remarkable feature of this protocol. As an organic salt, the *S*-benzyl isothiouronium chloride catalyst was readily precipitated out by adding the excess cooled dichloromethane. Therefore, commercially available *S*-benzyl isothiouronium chloride organocatalyst can be easily recovered and reused as many times as desired without loss of efficiency (Table 3).

3. Conclusion

In summary, *S*-benzyl isothiouronium chloride has been explored successfully as a new class of hydrogen bonding organocatalysts for the reduction of conjugated nitroalkenes. The isothiouronium catalyst acquired certain valuable characteristics, such as working even on polar protic solvents, and being recycled and reused. The asymmetric reduction of disubstituted or trisubstituted nitroalkenes using a novel chiral isothiouronium organocatalysts is under consideration.

4. Experimental section

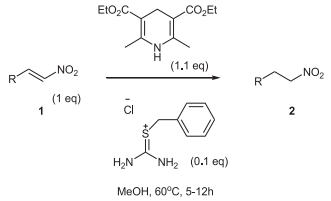
4.1. General

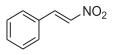
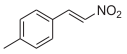
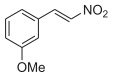
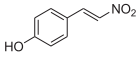
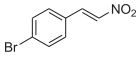
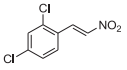
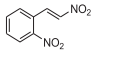
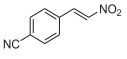
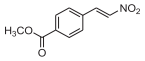
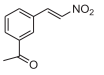
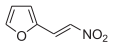
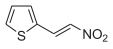
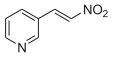
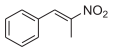
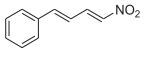
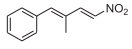
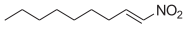
All reagents and solvents were obtained from commercial suppliers and were used without further purification. All air- and moisture-sensitive reactions were carried out under an argon atmosphere. The products were purified by using flash column chromatography. TLC was developed on Merck silica gel 60 F_{254} aluminum sheets. The ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, using $CDCl_3$ as solvent. HRMS were measured on a Micromass Q-TOF instrument (ES+ ion mode).

4.2. Typical procedure for the reduction of conjugated nitroalkenes

The mixture of nitroalkenes **1** (0.1 g, 0.67 mmol), Hantzsch ester (0.19 g, 0.74 mmol) and *S*-benzyl isothiouronium chloride (14 mg,

Table 2
Scope of conjugated nitroalkenes

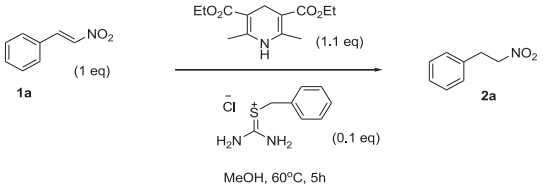


Entry	Nitroalkenes **1**	Product **2**	Yield (%)
1		**2a**	90
2		**2b**	97
3		**2c**	71
4		**2d**	96
5		**2e**	75
6		**2f**	80
7		**2g**	92
8		**2h**	95
9		**2i**	91
10		**2j**	82
11		**2k**	87
12		**2l**	82
13		**2m**	84
14		**2n**	90
15		**2o**[a]	65
16		**2p**[a]	68
17		**2q**	80

[a] Hantzsch ester (2.2 equiv), isothiouronium catalyst (0.2 equiv), 24 h.

0.067 mmol) in methanol (5 ml) was stirred at 60 °C for 5–12 h. After completion of the reaction, the crude product in methanol was concentrated and added into the excess cooled CH_2Cl_2. The *S*-benzyl isothiouronium chloride was readily precipitated out, and then filtered and washed many times with CH_2Cl_2 to be reused. The filtrate was evaporated and the residue was purified by flash column chromatography to give the required nitroalkanes products **2**. All nitroalkanes except **2j** and **2p** were characterized with the reported spectroscopic data.[2,5]

Table 3
Recovery of the catalyst



Recycle	Yield of recovered catalyst (%)	Yield of product **2a** (%)
First	93	90
Second	90	85
Third	94	88
Fourth	92	87

*4.2.1. Compound **2a** [6125-24-2].* Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.23 (t, *J*=7.35 Hz, 2H), 4.53 (t, *J*=7.35 Hz, 2H), 7.10–7.30 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=33.3, 76.2, 127.3, 128.5, 128.7, 135.6.

*4.2.2. Compound **2b** [72538-33-1].* Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.34 (s, 3H), 3.28 (t, *J*=7.35 Hz, 2H), 4.59 (t, *J*=7.35 Hz, 2H), 7.00–7.30 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.0, 33.0, 76.4, 128.4, 129.6, 132.5, 137.1.

*4.2.3. Compound **2c** [123312-23-2].* Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.29 (t, *J*=7.41 Hz, 2H), 3.80 (s, 3H), 4.61 (t, *J*=7.41 Hz, 2H), 6.78 (m, 3H), 7.25 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=33.4, 55.2, 76.1, 112.7, 114.4, 120.7, 130.0, 137.1, 160.0.

*4.2.4. Compound **2d** [37567-58-1].* Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.22 (t, *J*=7.23 Hz, 2H), 4.57 (t, *J*=7.23 Hz, 2H), 5.20 (br s, 1H), 6.76 (d, *J*=6.55 Hz, 2H), 7.04 (d, *J*=6.55 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=32.6, 76.6, 115.8, 127.6, 129.8, 154.8.

*4.2.5. Compound **2e** [137521-07-4].* Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.27 (t, *J*=7.20 Hz, 2H), 4.59 (t, *J*=7.20 Hz, 2H), 7.08 (d, *J*=6.63 Hz, 2H), 7.44 (d, *J*=6.63 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=32.8, 75.9, 121.5, 130.3, 132.1, 134.6.

*4.2.6. Compound **2f** [72538-34-2].* Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.40 (t, *J*=7.14 Hz, 2H), 4.63 (t, *J*=7.14 Hz, 2H), 7.20 (s, 2H), 7.40 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=30.8, 73.9, 127.6, 129.7, 131.9, 134.3, 134.6.

*4.2.7. Compound **2g** [155988-20-8].* Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.60 (t, *J*=6.84 Hz, 2H), 4.77 (t, *J*=6.84 Hz, 2H), 7.30–8.20 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=31.2, 75.2, 125.5, 128.9, 131.4, 132.8, 133.9.

*4.2.8. Compound **2h** [126158-10-9].* White solid; mp 80 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.37 (t, *J*=7.02 Hz, 2H), 4.65 (t, *J*=7.20 Hz, 2H), 7.34 (d, *J*=8.07 Hz, 2H), 7.62 (d, *J*=8.07 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=33.0, 75.2, 111.4, 118.3, 129.4, 132.6, 141.1.

*4.2.9. Compound **2i** [745059-98-7].* White solid; mp 60 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.36 (t, *J*=7.23 Hz, 2H), 3.90 (s, 3H), 4.64 (t, *J*=7.23 Hz, 2H), 7.28 (d, *J*=8.22 Hz, 2H), 8.00 (d, *J*=8.22 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=33.1, 52.0, 75.6, 128.5, 129.3, 130.1, 140.8, 166.6.

*4.2.10. Compound **2j**.* Colorless oil; IR (neat): ν_{max}=1681, 1547, 1267 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.60 (s, 3H), 3.38 (t, *J*=7.20 Hz, 2H), 4.65 (t, *J*=7.20 Hz, 2H), 7.20–7.90 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=26.6, 33.2, 75.9, 127.6, 128.2, 129.3, 133.2, 136.4,

137.9, 197.7; HRMS (ESI) calcd for $C_{10}H_{12}NO_3$ [M+H$^+$]: 194.0817, found: 194.0817.

4.2.11. Compound ***2k*** *[5462-90-8].* Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.36 (t, J=7.11 Hz, 2H), 4.64 (t, J=7.11 Hz, 2H), 6.13 (d, J=4.70 Hz, 1H), 6.30 (m, 1H), 7.34 (d, J=2.50 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=26.0, 73.3, 107.4, 110.5, 142.2, 149.3.

4.2.12. Compound ***2l*** *[30807-46-6].* Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.54 (t, J=7.08 Hz, 2H), 4.63 (t, J=7.08 Hz, 2H), 6.88 (d, J=5.40 Hz, 1H), 6.96 (m, 1H), 7.21 (d, J=5.40 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=27.5, 76.0, 124.9, 126.3, 127.3, 137.3.

4.2.13. Compound ***2m*** *[115149-33-2].* Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.38 (t, J=7.02 Hz, 2H), 4.68 (t, J=7.02 Hz, 2H), 7.37 (m, 1H), 7.68 (d, J=7.86 Hz, 1H), 8.56 (d, J=4.11 Hz, 1H), 8.62 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=30.5, 75.5, 123.7, 131.3, 136.1, 149.0, 149.9.

4.2.14. Compound ***2n*** *[17322-34-8].* Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.55 (d, J=7.50 Hz, 3H), 3.01 (q, J=7.50 Hz, 1H), 3.32 (q, J=7.50 Hz, 1H), 4.80 (m, 1H), 7.10–7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=18.8, 41.2, 84.4, 127.4, 128.8, 129.0, 135.5.

4.2.15. Compound ***2o*** *[76024-91-4].* Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.90 (m, 2H), 4.51 (t, J=7.00 Hz, 2H), 6.13 (m, 1H), 6.56 (d, J=13.29 Hz, 1H), 7.20–7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=30.7, 75.0, 122.9, 126.3, 127.8, 128.6, 134.0, 136.4.

4.2.16. Compound ***2p***. Colorless oil; IR (neat): ν_{max}=1547, 1377 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.90 (s, 3H), 2.87 (t, J=7.26 Hz, 2H), 4.58 (t, J=7.26 Hz, 2H), 6.36 (s, 1H), 7.20–7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=17.4, 38.1, 74.3, 126.7, 128.2, 128.8, 128.9, 132.3, 137.3; HRMS (ESI) calcd for $C_{11}H_{14}NO_2$ [M+H$^+$]: 192.1025, found: 192.1042.

4.2.17. Compound ***2q*** *[2216-21-9].* Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, J=7.08 Hz, 3H), 1.30 (m, 12H), 1.99 (m, 2H), 4.37 (t, J=7.08 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.0, 22.6, 26.2, 27.4, 28.8, 29.1, 29.2, 31.6, 75.7.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2012.05.104.

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