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Direct asymmetric aldol reaction co-catalyzed by L-proline and isothiouronium salts

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ABSTRACT

An efficient, simple, and highly selective protocol for the direct asymmetric aldol reaction between cyclohexanone and aromatic aldehydes using L-proline as a chiral catalyst is reported. Catalytic amounts of achiral isothiouronium iodide salt **1d** have been used for the first time as a co-catalyst for this reaction, which proved to be an excellent catalyst, producing good to excellent yields (up to 93%) with good stereoselectivities (up to 93:7 dr and 99% ee). These aldols are formed under solvent-free catalytic system, inside a standard laboratory refrigerator, and without stirring.

The aldol reaction is one of the most powerful strategies for the formation of carbon–carbon bonds in organic synthesis.[1] The stereoselectivity of this reaction has been a challenging and long-lasting task for synthetic chemists.[2] The finding of the first L-proline-catalyzed intermolecular aldol reaction in 2000 by List et al., attracted interest in organocatalyzed reactions.[3] Considering its ready availability and low price, it is obvious that L-proline would be first choice catalyst for preparing aldol adducts with high diastereo- and enantioselectivity. However, proline presents some major drawbacks, including poor performance in direct aldol reactions with aromatic aldehydes, limited solubility and reactivity in nonpolar organic solvents, and side reactions that make using high catalyst loadings necessary to reach satisfactory conversions. Therefore numerous proline-derived organocatalysts such as prolinamindes,[4] prolinethioamides,[5] sulfonamides,[6] chiral amines,[7] and organic salts[8] have been designed for direct aldol reactions. With this methodology, in order to achieve high yields and stereoselectivities, the use of a large excess of reagent, long reaction times, high catalyst loadings, and unfriendly solvents (DMF or DMSO) are also usually required. An alternative consists of including readily available additives to reactions containing proline. This late approach is clearly advantageous in eluding tedious chemical syntheses of organocatalysts and would ultimately allow the construction of libraries of catalyst protocols by simply changing the additive. In this sense, the addition of catalytic or substoichiometric amounts of water,[9] chiral diols,[10] thioureas,[11] and guanidinium salts[12] has been found to accelerate the reaction rate and increase the diastereo- and enantioselectivity of L-proline-catalyzed aldol reactions. So far developing more efficient and greener conditions for asymmetric aldol reactions has attracted a great deal of attention.

Isothiouroniums have been explored as prospective alternatives of thioureas in anion binding to enhance the acidity of the NH moieties and allow more hydrogen bonding.[13] Considering the investigated ability of isothiouroniums in binding carboxylic acids,[13e,i] we contemplated the possibility of using isothiouroniums as novel additives in the proline catalyzed aldol reaction. Herein, we report the results of high yields and enantioselectivities (91–99% ee) in the proline-catalyzed intermolecular direct aldol reaction between cyclohexanone and various aromatic aldehydes using isothiouronium salts. Recently, we reported *S*-benzyl isothiouronium chloride as a novel organocatalyst for the direct reductive amination of aldehydes and ketones[14] and for the reduction of conjugated nitroalkenes into nitroalkanes resulting in high efficiency, chemoselectivity, and easy recovery of organocatalyst using Hantzsch esters.[15] Therefore we expect that some isothiouronium salts might work in aldol reaction as an activator with L-proline.

The reaction between cyclohexanone and 4-nitrobenzaldehyde was selected as a standard model reaction for screening of the efficacies of designed organocatalysts. In the hunt for an inexpensive and green process, we decided to avoid the use of any organic solvent, apart from **2** (10-fold excess), which acts as both reagent and reaction media. Under these conditions, we postulate that the isothiouronium core of salts could form a network of H-bonding interactions with the carboxylate of proline, as well as with the

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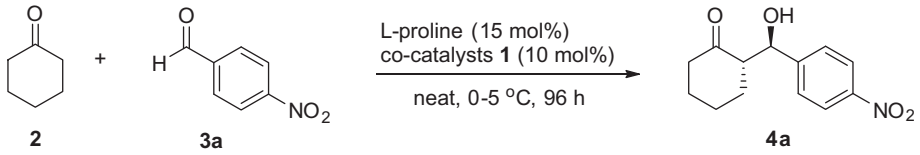
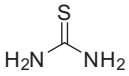
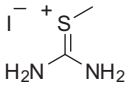
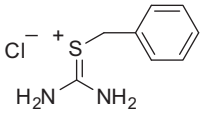
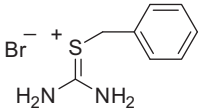
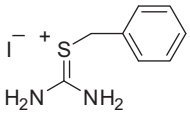
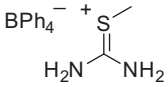
Table 1
Screening of isothiouronium co-catalysts **1** for the L-proline-catalyzed aldol reaction



2 **3a** **4a**

Entry	Co-catalyst	Yield[a] (%)	*anti*:*syn*[b]	ee[c] (%)
1	None	78	81:19	56
2		81	89:11	78
3	 **1a**	90	89:11	92
4	 **1b**	86	88:12	88
5	 **1c**	95	93:7	94
6	 **1d**	93	93:7	97
7	 **1e**[d]	90	92:8	97

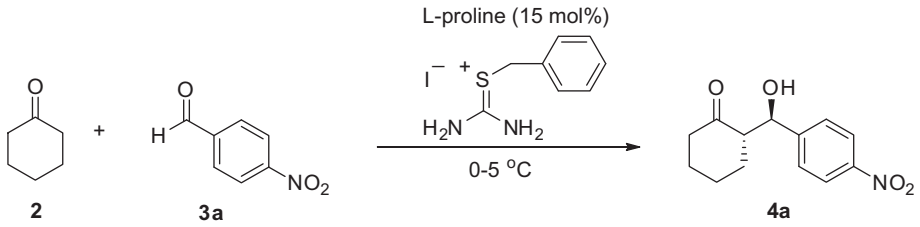
[d] **1e** was the mixture of **1a** and $NaBPh_4$.
[a] Isolated yields after column chromatography.
[b] *anti*/*syn* ratio was based on ^1H NMR spectroscopic analysis of the crude reaction mixture.
[c] The ee was determined by HPLC on chiral columns.

carbonyl moieties of cyclohexanone and the aromatic aldehyde, thus enhancing their electrophilicity. These interactions could control the reactivity and selectivity of proline in the aldol reaction. Also, the influence of the anion counterpart of salt **1** in the reaction might occur. The catalytic activities of prepared isothiouronium salts **1a–e** were evaluated under a suspension of 4-nitrobenzaldehyde **3a** (1 equiv) and L-proline (15 mol %) in cyclohexanone **2** (10 equiv) in solvent-free conditions for 96 h inside a refrigerator (0–5 °C) with no stirring (Table 1). All catalysts exhibited a high catalytic efficiency in the model reaction. A dependence of the catalytic activity on the counter anion was observed (Table 1, entries 4–6). Excellent stereoselectivities could be obtained in the presence of isothiouronium iodide **1d**, whereas high yield was obtained with isothiouronium bromide **1c**. The benzyl substituted catalyst **1d** was more efficient than the methyl catalyst **1a** (Table 1, entries 3 and 6), indicating that a more steric group has more efficient catalytic activity. Tetraphenyl borate salt **1e**, the simple mixture of iodide salt **1a** and $NaBPh_4$, afforded stereoselectively efficient aldol (Table 1, entry 7). In all cases, isothiouronium iodide **1d**, derived from thiourea emerged as the most promising catalyst both in yields and in stereoselectivities (Table 1, entry 6). Without co-catalyst as well as with thiourea as a co-catalyst, aldol **4a** was formed in 78% conversion (81:19 *anti*/*syn*, 56% ee) and 81% conversion (89:11 *anti*/*syn*, 78% ee), respectively, (Table 1, entries 1 and 2). Aldol reactions performed without co-catalyst showed lower conversion, as well as poorer diastereoisomeric ratios and enantiomeric excesses, thus demonstrating the positive effect of isothiouronium salt on the reaction course.

We next screened different parameters, such as the loading of the catalyst, temperature, time, solvents, additive (water), and stirring. A decrease in the catalyst loading to 5 mol % had slightly lower yield and lower enantioselectivity (Table 2, entry 1). When the reaction was performed at room temperature, a better enantioselectivity was not achieved and an obvious loss of the yield was observed (Table 2, entry 2), however for 96 h inside a refrigerator (0–5 °C), yield and enantioselectivity were clearly increased (Table 2, entries 4–7). The effect of the solvent was then considered. The reaction occurred in both polar and non-polar solvents, however neither proved to be better than the neat conditions (Table 2, entries 8 and 9). It has previously been assumed that water can help the catalyst turn-over by hydrolysis of the final product from the iminium intermediate,[9] but in this case the addition of water had detrimental effects both on yield and on enantioselectivity (Table 2, entries 10 and 11). This extensive screening showed that the optimized conditions were 10 mol % catalyst loading without the addition of any solvent for 96 h inside a refrigerator (0–5 °C) with no stirring.

With this optimized protocol established, we further explored the scope of the aldol reaction of cyclohexanone to the various aldehydes co-catalyzed by iodide salt **1d** and the results are

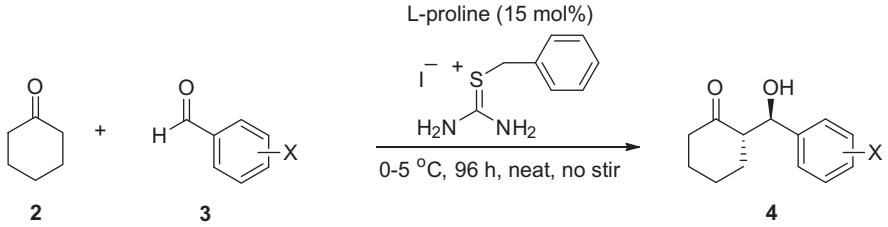
Table 2
Optimization of reaction conditions[a]



Entry	Time (h)	Yield[b] (%)	*anti*:*syn*[c]	ee[d] (%)
1[e]	96	80	90:10	94
2[f]	96	58	79:21	78
3[g]	24	88	88:12	87
4	24	85	91:9	96
5	48	85	92:8	96
6	72	92	90:10	95
7	96	93	93:7	97
8[h]	96	20	85:15	61
9[i]	96	53	76:24	89
10[j]	96	70	89:11	86
11[k]	96	48	84:16	72

[a] The mixture of cyclohexanone (10 equiv), 4-nitrobenzaldehyde (1 equiv), L-proline (0.15 equiv), and *S*-benzylisothiouronium iodide (0.1 equiv) was left to stand at 96 h inside a refrigerator (0–5 °C) with no stirring and no solvent.
[b] Isolated yields after column chromatography.
[c] *anti*/*syn* ratio was based on ^{1}H NMR spectroscopic analysis of the crude reaction mixture.
[d] The ee was determined by HPLC on chiral columns.
[e] Reaction carried out with 5 mol % of co-catalyst.
[f] Reaction carried out at room temperature.
[g] Reaction mixture was stirred.
[h] Hexane (3 mL) was employed with solvent.
[i] Acetonitrile (3 mL) was employed with solvent.
[j] H_2O (5 equiv) was added.
[k] H_2O (10 equiv) was added.

Table 3
Direct aldol reaction between various aldehydes and cyclohexanone with isothiouronium iodide **1d**



Entry	X	Product	Yield[a] (%)	*anti*:*syn*[b]	ee[c] (%)
1	2-Cl	**4b**	90	97:3	98
2	3-NO_2	**4c**	87	92:8	91
3	3-$COCH_3$	**4d**	81	93:7	97
4	2-OCH_3	**4e**	37	93:7	99
5	3-OH	**4f**	63	88:12	94
6	H	**4g**	47	89:11	92

[a] Isolated yields after column chromatography.
[b] *anti*/*syn* ratio was based on ^{1}H NMR spectroscopic analysis of the crude reaction mixture.
[c] The ee was determined by HPLC on chiral columns.

summarized in Table 3. In all cases the reactions occurred with high *anti* stereoselectivity. Electron-poor aldehydes such as 2-chlorobenzaldehyde, 3-nitrobenzaldehyde, and 3-acetylbenzaldehyde proceeded smoothly with cyclohexanone, producing high quantitative yields (81–90%) with high enantioselectivities (91–98% ee, Table 3, entries 1–3). Meanwhile electron-rich aromatic aldehydes such as 3-methoxybenzaldehyde and 3-hydroxybenzaldehyde produced the product in moderate yield (37–63%) although with high enantioselectivity (Table 3, entries 4 and 5). The reactions of aliphatic aldehydes have also been attempted but without success, probably due to the low reactivity of these acceptors.

The mechanism of the reaction using isothiouronium iodide **1d** is believed to be similar to that of the previously reported L-proline via an enamine intermediate.[11a,16] A network of H-bonding interactions between the carboxylate of L-proline, the corresponding isothiouronium salt, and the enamine in a Zimmerman–Traxler transition state (shown in Fig. 1) is established, which leads to the nucleophilic addition of *re*-enamine to the *re*-face of the carbonyl group. Therefore, the formation of a 1:1 complex between the isothiouronium salt **1d** and the L-proline would stabilize the chair like transition state that leads to the observed aldols.

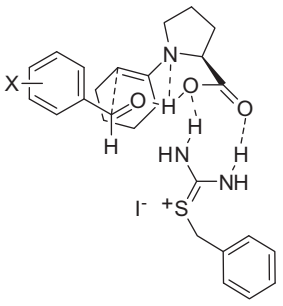


Figure 1. Proposed transition state model.

In summary, we have developed a simple, efficient, and highly stereoselective methodology for the direct aldol reaction of cyclohexanone with aromatic aldehydes using L-proline as a chiral catalyst. Catalytic amounts of isothiouronium iodide **1d** have been used for the first time as an achiral co-catalyst for this reaction, which proved to be excellent catalysts, producing good to excellent yields (up to 93%) with good stereoselectivities (up to 93:7 dr and 99% ee). This aldol protocol includes a solvent-free catalytic system inside a refrigerator without stirring.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.10.009.

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