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Asymmetric Michael addition of aldehydes to nitroolefins catalyzed by a pyrrolidine–pyrazole

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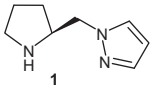
ABSTRACT

An effective protocol for the stereoselective Michael addition of aldehydes to nitroolefins using pyrrolidine–pyrazole as an organocatalyst is described. The catalytic cycle was found to be productive in terms of yield and selectivity, when performed under solvent-free reaction conditions and employing 15 mol % of catalyst and 10 mol % of benzoic acid at room temperature.

1. Introduction

Organocatalysis has emerged as a powerful synthetic tool for the stereoselective construction of chiral building blocks. Over the past few decades, asymmetric organocatalysis has witnessed a wide range of advances while various types of mechanistic perspectives have been introduced by different groups to establish the outcome of organocatalytic asymmetric transformations.[1] Due to these advances, asymmetric organocatalysis has been recognized as a competent and powerful new catalytic approach. A large number of small organic molecules with diverse structural features have been developed and employed as organocatalysts for various asymmetric transformations with various levels of success.[1,2] In particular, proline and proline derivatives have emerged as simple and useful elements in the organocatalyst toolbox. To reflect this, a large number of pyrrolidine based organocatalytic protocols are present in the literature.[2,3] Among the wide range of organic transformations, the exploration of asymmetric Michael reaction has been the focus of many research groups, as it results in the formation of functionalized products with multiple stereogenic centers in a single step.[3–5] In particular, γ-nitrocarbonyls, which result from the Michael additions of carbonyls to nitroolefins, are more prominent as they serve as versatile templates for the construction of various bioactive compounds.[5,6] Although many organocatalysts are known to be highly efficient for Michael additions of carbonyl compounds to nitroolefins, only some of them are effective for Michael reactions of aldehydes and nitroolefins.[7] Therefore, an investigation into alternative catalytic protocols for this transformation is highly desirable. In a continuation of our research interest on organocatalysis,[8] we recently reported that pyrrolidine–pyrazole **1** (Fig. 1) is an efficient catalyst for asymmetric Michael reactions of ketones and α,α-disubstituted aldehydes to nitroolefins via an enamine mechanism under additive mediated solvent-free reaction conditions.[8e,h] Inspired by these studies, we decided to investigate the catalytic performance of this pyrrolidine–pyrazole towards the Michael addition of aldehydes to nitroolefins. Since these substrates have a correlation to those reported earlier, a similar catalytic cycle could be expected to operate during the reaction course. The chiral pyrrolidine ring activates aldehydes towards enamine formation, while the pyrazole appendage serves as the stereoregulator.[9,10] With these objectives, the use of pyrrolidine–pyrazole **1** as an effective organocatalyst for the asymmetric Michael reaction of aldehydes to nitroolefins under solvent-free conditions at room temperature is reported.



1

Figure 1. Pyrrolidine–pyrazole.

2. Results and discussion

The catalytic performance of pyrrolidine–pyrazole **1** for asymmetric Michael additions of aldehydes to nitroolefins was evaluated by setting up a model reaction with propaldehyde **2a** as the donor substrate and nitrostyrene **3a** as the acceptor as shown in Scheme 1. Initially, solvent screening experiments were conducted by performing the model reaction simultaneously in various solvents using 20 mol % of the catalyst at room temperature and the results are summarized in Table 1. As evident from the survey,

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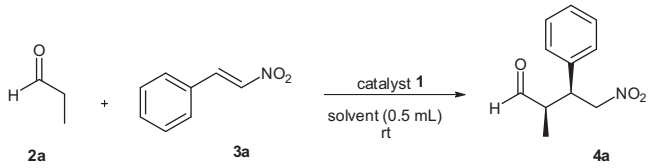


2a 3a 4a

Scheme 1. Michael addition of propaldehyde to nitrostyrene.

Table 1
Screening of solvents using **1**[a]

Entry	Solvent	Time (h)	Yield[b] (%)	(*syn*/*anti*)[c]	ee[d](%)
1	DMF	24	66	75:25	54
2	Toluene	36	74	8:2	65
3	Hexane	24	73	8:2	69
4	CH_3CN	36	77	82:18	61
5	CH_2Cl_2	24	79	85:15	75
6	Dioxan	36	69	8:2	60
7	$CHCl_3$	24	71	85:15	71
8	Neat	24	81	9:1	83
9	THF	24	76	88:12	74
10	EtOH	24	75	85:15	66
11	MeOH	24	72	85:15	69
12	H_2O	36	61	7:2	73

[a] Reaction conditions: propaldehyde (5 mmol), nitrostyrene (1 mmol), solvent (0.5 mL), catalyst (20 mol %).
[b] Isolated yields.
[c] Determined by ^{1}H NMR of crude product.
[d] Determined by chiral HPLC.

the Michael reaction proceeded well in all solvents irrespective of their polar/non-polar nature to afford the product γ-nitroaldehyde **4a** in good yield and stereoselectivity (Table 1, entries 1–12). However, solvent-free conditions were found to be more effective in terms of yield (81%), diastereoselectivity (*syn*/*anti* 9:1) and enantioselectivity (83% ee) among the conditions screened and was adopted for further studies. Encouraged by these initial results, we next conducted additive screening experiments with the aim of improving the catalytic activity. It has been well documented that the presence of an acid additive can enhance catalytic efficiency by acceleration of the enamine formation. In anticipation, we examined the effect of various acid additives under solvent-free conditions using 20 mol % of catalyst and 5 mol % of additive at room temperature and the results are summarized in Table 2. Benzoic acid turned out to be the most efficient additive in combination with catalyst **1** (Table 2, entries 1–6). The effect of loading was tested using 10 and 15 mol % of benzoic acid (Table 2, entries 7 and 8, respectively). As evident from Table 2, the use of 10 mol % of benzoic acid found to be the best value and subsequent experiments were carried out using 10 mol % of benzoic acid in combination with catalyst **1**.

Table 2
Screening of additives[a]

Entry	additive	(mol%)	Time (h)	Yield[b](%)	(*syn*/*anti*)[c]	ee[d](%)
1	TFA	5	24	86	9:1	85
2	CSA	5	24	71	7:3	70
3	pTSA	5	24	65	8:2	69
4	PhOH	5	24	76	85:15	78
5	HCOOH	5	24	79	8:2	80
6	PhCOOH	5	24	87	9:1	87
7	PhCOOH	10	20	94	93:7	92
8	PhCOOH	15	20	94	94:6	92

[a] Reaction conditions: propaldehyde (5 mmol), nitrostyrene (1 mmol), catalyst **1** (20 mol %), neat, rt.
[b] Isolated yields.
[c] Determined by ^{1}H NMR of crude product.
[d] Determined by chiral HPLC.

As part of our screening studies, we conducted experiments on catalyst loading and temperature conditions to establish the optimal reaction conditions. As shown in Table 3, the reaction performed at room temperature with 15:10 mol % catalyst/additive ratio under solvent-free conditions was found to be more operative and effective in overall terms (Table 3, entry 2), while reactions conducted under other conditions suffered either from long reaction times or a loss of yield with no considerable improvement in stereoselectivities (Table 3, entries 1, 3, 4 and 5).

Table 3
Effect of temperature and catalyst loading[a]

Entry	Catalyst (mol%)	Temp. (°C)	Time (h)	Yield[b] (%)	(*syn*/*anti*)[c]	ee[d] (%)
1	20	0	48	87	94:6	90
2	15	RT	20	93	93:7	91
3	15	0	48	83	91:9	87
4	10	RT	36	75	91:9	85
5	5	RT	48	62	9:1	81

[a] Reaction conditions: propaldehyde (5 mmol), nitrostyrene (1 mmol), PhCOOH (10 mol %).
[b] Isolated yields.
[c] Determined by ^{1}H NMR of crude product.
[d] Determined by chiral HPLC.

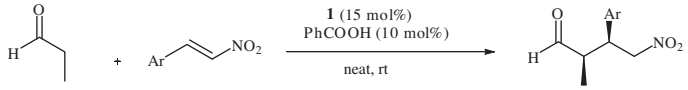
With the optimal reaction conditions in hand, we next studied the generality of this transformation using a series of aldehydes and nitroolefins in different combinations. As shown in Tables 4 and 5, all substrate combinations involving variations in nitroolefins **3b–j** reacted smoothly with propaldehyde **2a** (Table 4, entries 1–9) and other aldehydes **2b–f** (Table 5, entries 1–9) under the optimized reaction conditions and the corresponding Michael products **4b–j** and **4k–s** were obtained in good yields and with high levels of diastereoselectivities and enantioselectivities, regardless of the nature of the substitution pattern in the nitroolefins. However, reactions involving branched aldehydes (Table 5, entries 5 and 9) or nitroolefins with electron donating substituents (Table 4, entries 4 and 5) were found to be slightly inferior in overall productivity. Overall, the catalytic performance of pyrrolidine–pyrazole catalyst for the conjugate addition of aldehydes to nitroolefins was found to be effective and was in good agreement with those reported in the literature.[7]

The transition state[7,9,10] model, that was proposed[8h] for the asymmetric Michael reaction of α,α-disubstituted aldehydes to nitroolefins (Fig. 2) was used to rationalize the absolute stereochemical outcome of this transformation. The pyrrolidine ring of the catalyst activates the aldehyde towards enamine formation, while the pyrazole template serves as an efficient stereo-control element, by providing stereo-facial shielding and coordinating with the nitroolefin through the benzoic acid via H-bonding interaction. This results in a compact transition state, wherein the nucleophilic enamine attacks the nitroolefin from *Si* face and leads to the formation of the desired products with high diastereoselectivities and enantioselectivities.

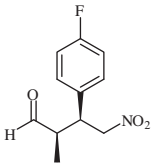
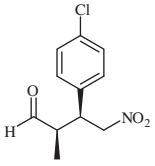
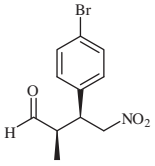
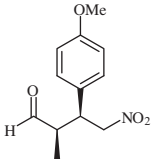
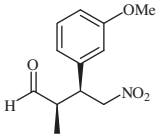
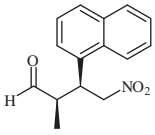
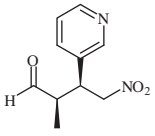
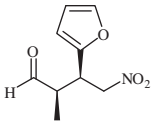
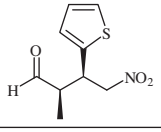
3. Conclusions

In conclusion, we have demonstrated the application of pyrrolidine–pyrazole **1** as an effective organocatalyst for enantioselective Michael additions of aldehydes to nitroolefins. The catalytic cycle was effective with 15 mol % of catalyst in combination with 10 mol % of benzoic acid. The resulting adducts were obtained in high yields and with high stereoselectivities under solvent-free reaction conditions at room temperature. Investigations into the catalytic activity of the pyrrolidine–pyrazole as an organocatalyst

Table 4
Enintioselective Michael addition of propaldehyde to nitroolefins[a]

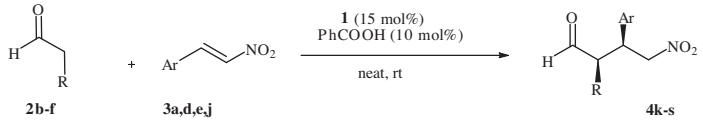


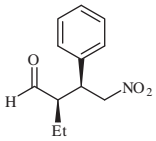
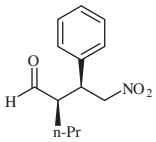
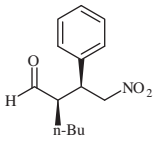
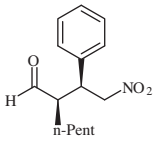
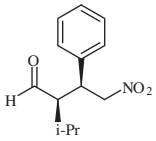
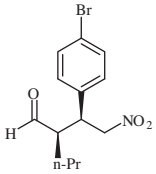
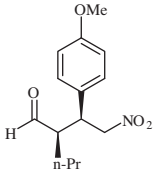
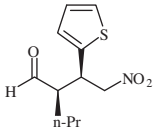
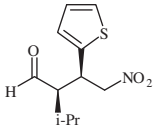
2a **3b-j** **4b-j**

Entry	Product		Time (h)	Yield[b] (%)	(*syn*/*anti*)[c]	ee[d] (%)
1		**4b**	20	89	91:9	91
2		**4c**	20	92	93:7	93
3		**4d**	20	90	91:9	94
4		**4e**	24	86	85:15	89
5		**4f**	24	84	88:12	86
6		**4g**	24	91	92:8	92
7		**4h**	24	90	90:10	90
8		**4i**	24	88	91:9	91
9		**4j**	24	90	90:10	90

[a] Reaction conditions: Propaldehyde (5 mmol), nitroolefin (1 mmol).
[b] Isolated yields.
[c] Determined by ^{1}H NMR of crude product.
[d] Determined by chiral HPLC.

Table 5
Enintioselective Michael addition of different aldehyde nitroolefins[a]



Entry	Product		Time (h)	Yield[b] (%)	(*syn*/*anti*)[c]	ee[d] (%)
1		**4k**	20	92	93:7	93
2		**4l**	20	94	95:5	95
3		**4m**	20	93	96:4	95
4		**4n**	20	90	92:8	92
5		**4o**	36	83	88:12	87
6		**4p**	20	94	96:4	96
7		**4q**	24	90	91:9	90
8		**4r**	24	91	92:8	91
9		**4s**	36	80	85:15	84

[a] Reaction conditions: aldehyde (5 mmol), nitroolefin (1 mmol).
[b] Isolated yields.
[c] Determined by ^{1}H NMR of crude product.
[d] Determined by chiral HPLC.

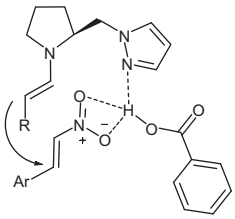


Figure 2. Proposed transition state.

for other transformations are currently in progress in our laboratory.

4. Experimental

4.1. General

All solvents and reagents were purified by standard techniques. Crude products were purified by column chromatography on silica gel of 60–120 mesh. IR spectra were recorded on a Perkin–Elmer 683 spectrometer. Optical rotations were obtained on a Jasco Dip 360 digital polarimeter. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Varian Gemini 200 and Brucker Avance 300. Chemical shifts are reported in parts per million with respect to internal TMS. Coupling constants (J) are quoted in Hz. Mass spectra were obtained on an Agilent Technologies LC/MSD Trap SL. Chiral HPLC analysis was carried out on chiral pak OD-H, IC or IA columns using a mixture of isopropanol and hexanes as the eluent.

4.1.1. General procedure for the Michael addition reaction

To a mixture of catalyst **1** (15 mol %), and aldehyde (5 mmol) was added PhCOOH (10 mol %) and stirred for 20 min at room temperature. Next, nitroolefin (1 mmol) was added to the resulting mixture and stirred for the appropriate time (Tables 4 and 5) at room temperature. After completion of the reaction (monitored by TLC), the mixture was purified by silica-gel column chromatography to afford the desired product. The relative and absolute configuration of the products were determined by comparison of ^{1}H NMR, ^{13}C NMR and specific rotation values with those reported in the literature.[7]

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