DOI: 10.1002/ejoc.201000945

Highly Enantioselective Michael Addition of Acetone to Nitro Olefins Catalyzed by Chiral Bifunctional Primary Amine-Thiophosphoramide Catalyst

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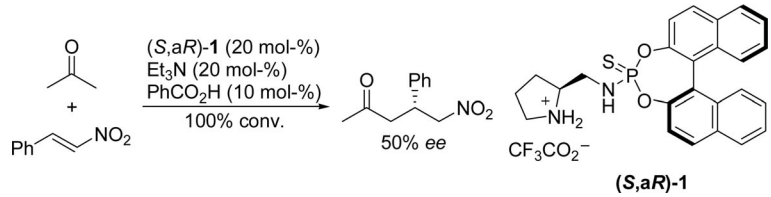
Keywords: Enantioselectivity / Michael addition / Nitro olefins / Chiral thiophosphoramide

A series of bifunctional primary amine-thiophosphoramides were synthesized, which proven to be effective organocatalysts for the asymmetric Michael reaction of acetone to both aryl and alkyl nitro olefins in the presence of phenol as a protic additive. The corresponding adducts were obtained in excellent chemical yields (up to >99%) with excellent enantioselectivities (up to 97% *ee*).

Introduction

Asymmetric Michael addition reactions of different carbon-centered nucleophiles to electron-deficient nitro olefins represent a direct and most appealing approach to synthetically valuable chiral nitro alkanes.[1] Among them, the Michael additions of ketones to nitro olefins represent a convenient access to γ-nitro ketones that are valuable building blocks in organic synthesis. Since the organocatalytic asymmetric Michael addition of ketones to *trans*-β-nitrostyrene was pioneered by Barbas[2] and List[3] independently, great effort has been devoted to the development of more selective and efficient catalytic systems for this synthetically useful transformation. Impressive progress that has been made recently in the development of bifunctional organic catalysts for the enantioselective addition of cyclic ketones, especially of cyclohexanone and its derivatives to nitro alkenes.[4] Acetone is still one of the most problematic substrates for the nitro-Michael addition. To the best of our knowledge, only limited cases have been reported with enantiomeric excesses of over 90% for the Michael product with an acetone substrate.[5] Most recently, we have developed (*S*,a*R*)-pyrrolidine thiophosphoramide **1** as an efficient organocatalyst for promoting the asymmetric Michael addition of cyclic ketones to nitro olefins.[6] It is believed that its high catalytic efficiency is attributable to its unique activation mode, arising from the thiophosphoramide moiety. This functionality serves as a hydrogen-bonding donor for the activation of nitro olefin substrates and formation of a well-controlled transition state. However, when acetone was employed as the substrate, the reaction is less enantioselective and only moderate stereocontrol was observed (Scheme 1). Inspired by the proven ability of the thiophosphoramide group in highly effective asymmetric conjugate addition reactions, we envisioned that the incorporation of this moiety into a chiral *trans*-cyclohexanediamine scaffold would result in a new bifunctional thiophosphoramide-primary amine organocatalyst **2**, which could be useful for effecting the Michael addition of challenging acetone to nitro olefins.



Scheme 1. (*S*,a*R*)-**1**-catalyzed asymmetric Michael addition of acetone to β-nitrostyrene.

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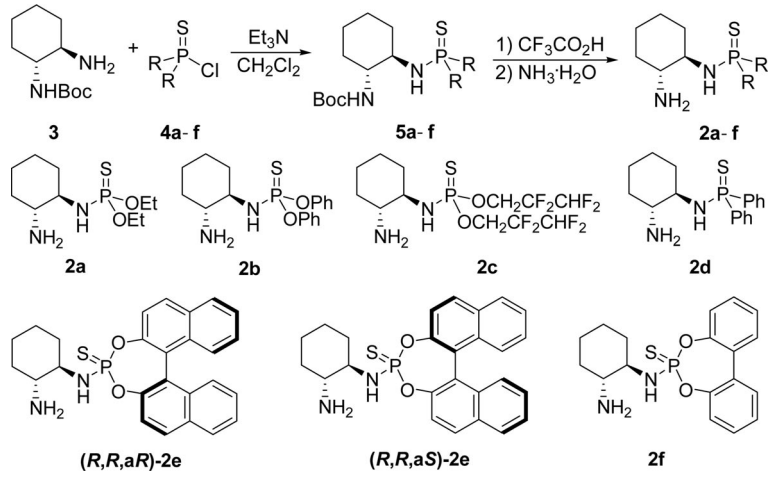
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201000945.

Results and Discussion

The newly designed primary amine-thiophosphoramides **2** were easily prepared as shown in Scheme 2. The condensation of *tert*-butyl (1*R*,2*R*)-2-aminocyclohexylcarbamate **3**

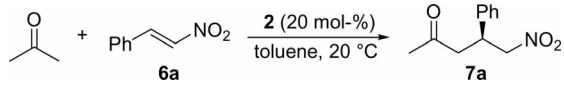


Scheme 2. Synthesis of catalysts.

and thiophosphoryl chlorides **4** gave the corresponding *N*-Boc-protected thiophosphoramides **5**. Deprotection of **5** with trifluoacetic acid affords the target catalysts **2**.

As shown in Table 1, the results of catalyst evaluation employing the reaction between β-nitrostyrene (**6a**) and acetone as the model indicate that the electronic nature of the substituents on the phosphorus atom of thiophosphoramides **2** have a prominent effect on both catalytic activity and stereoselectivity. When *O*,*O*-diethyl thiophosphoramide **2a** was employed as the catalyst, the reaction was completed after 69 h, the corresponding adduct was obtained with excellent yield (98%) in good enantioselectivity (72% *ee*), whereas catalyst **2c** with 2,2,3,3-tetrafluoropropyl proved to be much inefficient in terms of turnover frequency, a much longer reaction time (120 h) was needed for total conversion of the β-nitrostyrene **6a** (Table 1, entry 3 vs. entry 1). Catalyst **2b** with a phenoxy group and **2f** bearing a tropos biphenyl skeleton gave results that were comparable to that of catalyst **2a** (Table 1, entry 2 and 7). An improvement both on catalytic activity and stereoselectivtity was observed when a phenyl group was introduced (**2d**), which provided the corresponding adduct in quantitative yield with the highest *ee* value of 88% (Table 1, entry 4). In case of catalyst **2e** derived from axial chiral binaphthol, an obvious matching and mismatching effects was observed between the chiralities of the (*R*,*R*)-1,2-diaminocyclohexane and binaphthol. For example, the (*R*,*R*,a*R*)-**2e**-catalyzed reaction was complete within 96 h and afforded the Michael addition product in 84% yield with a enantioselectivity of 61% *ee*. Under the otherwise identical conditions, catalyst (*R*,*R*,a*S*)-**2e** demonstrated much lower catalytic activity. Although a little better stereocontrol was realized, the reaction became quite sluggish, and a dramatically decreased yield of <10% was attained at a prolonged reaction time (192 h) (Table 1, entry 6 vs. entry 5). This indicates that the (*R*)-configuration of binaphthol matched (*R*,*R*)-1,2-diaminocyclohexane to enhance the catalytic activity of the catalyst.

Table 1. Catalyst screening.[a]



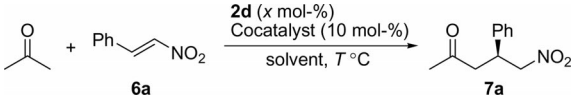
Entry	2	Time [h]	Yield [%][b]	*ee*[c]
1	**2a**	69	98	72
2	**2b**	96	95	69
3	**2c**	120	92	65
4	**2d**	50	92	88
5	(*R*,*R*,a*R*)-**2e**	96	84	61
6	(*R*,*R*,a*S*)- **2e**	192	<10[d]	68
7	**2f**	69	90	70

[a] All reactions were carried out using acetone (0.2 mL, 10 equiv.) and **6a** (44.7 mg, 0.3 mmol) in the presence of catalyst **2** (20 mol-%) in toluene (1.0 mL). [b] Yield of the isolated product after chromatography on silica gel. [c] Determined by chiral HPLC analysis. [d] Most of **6a** was recovered.

With the promising catalyst **2d** in hand, other factors, such as cocatalyst, solvent, catalyst loading, and reaction temperature, influencing the reaction were thoroughly investigated employing the reaction between β-nitrostyrene (**6a**) and acetone as the model. The results are listed in Table 2.

A survey of additives revealed that they play a certain role in governing reaction yields and enantioselectivity. To our delight, the addition of 10 mol-% of phenolic additive significantly accelerates the reaction as well as slightly improving the enantioselectivity relative to that with the catalyst in the absence of additive (Table 2, entries 2–7 vs. entry 1). With respect to enantioselectitivity, the readily available phenol gives the best result; the corresponding product is obtained in quantitative yield with 92% *ee* (Table 2, entry 2). The replacement of phenol with substituted phenols bearing either electron-withdrawing or electron-donating group or 1-naphthol leads to a slight loss of stereocontrol (Table 2, entries 3–7 vs. entry 2). It is worth noting that an obvious rate acceleration was also observed when using

Table 2. Optimization of reaction conditions.[a]



Entry	Cocatalyst [10 mol-%]	Solvent	Time [h]	Yield [%][b]	*ee* (%)[c]
1	–	toluene	132	90	89
2	PhOH	toluene	60	>99	92
3	2-$NO_2C_6H_4OH$	toluene	66	>99	91
4	4-$NO_2C_6H_4OH$	toluene	72	>99	90
5	2-MeC_6H_4OH	toluene	84	97	90
6	4-Me-2-*t*BuC_6H_3OH	toluene	84	>99	90
7	1-naphthol	toluene	60	>99	91
8	H_2O[d]	toluene	72	>99	89
9	*n*-$C_3H_7CO_2H$	toluene	120	75	92
10	$PhCO_2H$	toluene	120	85	92
11	PhOH	Et_2O	96	>99	88
12	PhOH	$CHCl_3$	96	95	83
13	PhOH	MeOH	120	20[e]	33
14	PhOH	acetone	96	98	77
15	PhOH	toluene	120	>99	91
16	PhOH	toluene	120	>99	93

[a] Reactioin conditions: solvent (1.0 mL); acetone (0.2 mL, 10 equiv.); **6a** (44.7 mg, 0.3 mmol); catalyst **2d** (20 mol-%) except for entry 15 (15 mol-%); T = 5 °C except for entry 16 (0 °C). [b] Yield of the isolated product after chromatography on silica gel. [c] Determined by chiral HPLC analysis. [d] 1 equiv. of water was added. [e] Most of **6a** was recovered.

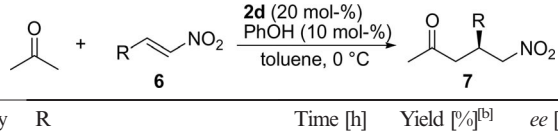
1 equiv. of water as an additive. This observation is consistent with the fact that water can increase the catalyst turnover, presumably due to facilitating the release of the primary catalyst from the imine.[7] Surprisingly, the use of more acidic carboxylic acids, such as benzoic acid and butanoic acid, as an additive was inefficient in this catalytic system. Although a slight improvement on enantioselectivity was observed, the addition of carboxylic acid resulted in reducing of the reactivity and a relatively poor yield (Table 2, entries 9, 10). Finally, phenol was selected as the additive for further investigation.

Solvent evaluation revealed that the solvent also has a significant effect on the rate and the enantioselectivity of the reaction. The reaction conducted best in a nonpoplar solvent like toluene, which provided the highest *ee* value (92%, see Table 2, entry 2). By contrast, the use of polar solvent, such as diethyl ether, $CHCl_3$, and acetone led, in general, to an obvious loss of stereocontrol with respect to toluene (Table 2, entry 2 vs. entries 11, 12, 14). Notably, when protic solvent, such as methanol, was employed as the solvent, a significant drop of both the reactivity and enantioselectivity was found (Table 2, Entries 13), probably because the protic solvent weaken or retard the formation of hydrogen bonds between *trans*-β-nitrostyrene and the thiophosphoramide moiety of catalyst **2d**. These results strongly demonstrate that hydrogen-bond formation has an important effect on both the reactivity and the enantioselectivity of the reaction.

In addition, reducing the catalyst loading to 15 mol-% led to a little loss of enantioselectivity with a prolonged reaction time (Table 2, entry 15). On the other hand, the stereoselectivity of the reaction was further slightly improved to 93% *ee* when variation the reaction temperature from 5 to 0 °C. Further lowering the reaction temperature resulted in a quite sluggish reaction.

With optimal catalyst (20 mol-% of **2d**) and reaction conditions established (phenol as an additive, in toluene, at 0 °C), a variety of nitro olefins were then evaluated as substrates and the results are summarized in Table 3.

Table 3. Substrate scope of **2d** catalyzed asymmetric Michael addition of acetone to nitro olefins.[a]



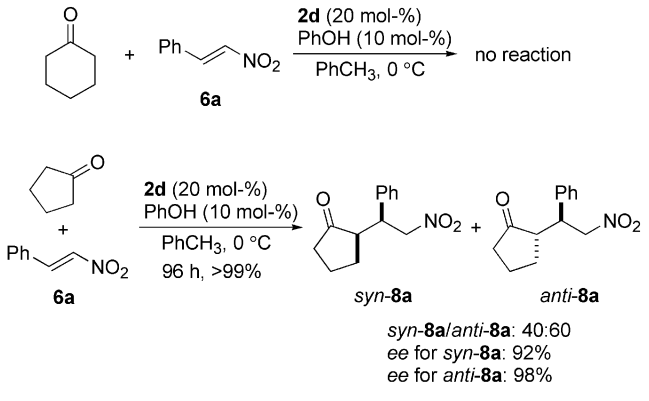
Entry	R	Time [h]	Yield [%][b]	*ee* [%][c]
1	Ph (**a**)	72	>99	93
2	Ph (**a**)[d]	72	90	90
3	2-$MeOC_6H_4$ (**b**)	120	82	96
4	3-$MeOC_6H_4$ (**c**)	96	95	94
5	4-$MeOC_6H_4$ (**d**)	120	80	93
6	4-MeC_6H_4 (**e**)	144	91	93
7	benzo[*d*][1,3]dioxol-5-yl (**f**)	108	93	94
8	2-ClC_6H_4 (**g**)	84	99	96
9	4-ClC_6H_4 (**h**)	69	95	93
10	2,4-$Cl_2C_6H_3$ (**i**)	96	98	97
11	2-BrC_6H_4 (**j**)	96	99	97
12	4-BrC_6H_4 (**k**)	120	96	94
13	2-$CF_3C_6H_4$ (**l**)	84	72	96
14	3-$CF_3C_6H_4$ (**m**)	42	99	95
15	2-$NO_2C_6H_4$ (**n**)	108	25[e]	97
16	4-$NO_2C_6H_4$ (**o**)	42	97	93
17	1-naphthyl (**p**)	168	90	97
18	2-furyl (**q**)	96	86	94
19	2-thienyl (**r**)	120	96	95
20	(*E*)-cinnamyl (**s**)[f]	72	85	93
21	phenylethyl (**t**)[f]	72	82	87
22	C_2H_5 (**u**)[g]	72	81	83

[a] All reactions were carried out using acetone (0.2 mL, 10 equiv.) and nitro olefin (0.3 mmol) in the presence of catalyst **2d** (20 mol-%) in toluene (1.0 mL). [b] Yield of the isolated product after chromatography on silica gel. [c] Determined by chiral HPLC analysis. [d] The reaction was performed in gram scale. [e] 70% of **6n** was recovered. [f] The reaction was performed at 20 °C. [g] The reaction was performed at 25 °C.

As shown in Table 3, the reaction has broad applicability with respect to the nitro olefins. The corresponding adducts were obtained in high enantioselectivity in all the cases examined. Generally, nitro olefins with electron-donating group on the benzene ring demonstrated slightly lower reactivity relative to unsubstituted or with an electron-withdrawing group substituted β-nitrostyrenes. At the same time, the nature of the substituents of the nitro olefin appears to have very little influence on the enantioselectivities of the reaction, which range from 93% to 97%. Surprisingly, in case of nitro-substituted substrates, the position of the nitro group plays an important role on the reaction. For example, the reaction of *para*-nitro-substituted nitro olefin **6o** ran smoothly to afford the addition product **7o** in excellent yield with high *ee* value within 42 h (Table 3, entry 16). Although an enhanced enantioselectivity was observed for *ortho*-nitro-substituted nitro alkene **6n**, the reaction became

quite sluggish, and the corresponding adduct **7n** was obtained with a significantly decrease in yield (Table 3, entry 15). This may be attributed to the competitive hydrogen-bonding interaction of the *ortho*-position nitro group with the thiophosphoramide moiety of the catalyst, which to some extent prohibits the activation of the electrophilic nitro olefin. Moreover, alkenyl-substituted nitro olefin **6s** can also be employed successfully, a same high level of enantioselectivity was observed as those found in the aryl-substituted ones. Perhaps more significant, nitro alkene bearing aliphatic substituent also proved to be viable electrophilic reacting partner in this catalytic system. For example, 3-phenylpropanal-derived nitro olefin **6t** worked well to give the desired product in good yield with a slightly loss of stereocontrol (Table 3, entry 21, 87% *ee*), the reaction of (*E*)-1-nitrobut-1-ene (**6u**) also ran smoothly to afford the corresponding adduct in satisfactory yield with good enantioselectivity (Tabe 3. entry 22, 83% *ee*), which clearly demonstrated the broad generality of this asymmetric Michael addition reaction. To demonstrate the potential of this method for preparative purposes, the reaction is also carried out in gram scale giving the isolated product with comparable *ee* value albeit with a slightly decrease in chemical yield (Table 3, entry 2).

The asymmetric addition of cyclic ketones to nitrostyrene **6a** using **2d** as a catalyst was also preliminarily investigated under the identical reaction conditions (Scheme 3). Unfortunately, this catalytic system is ineffective to cyclohexanone. The reaction is very sluggish even at room temperature, and failed to provide the corresponding adduct. However, the Michael addition of cyclopentanone to nitro olefin **6a** ran smoothly to give the desired product **8a** in quantitative yield with excellent enantioselectivity (92% *ee* for *syn*-**8a** and 98% *ee* for *anti*-**8a**, respectively) albeit with relatively low diastereoselectivity (*syn*/*anti*: 40/60). It is interesting that the observed *anti*-diastereoselectivity is just opposite to the result obtained for the secondary amine-thiophosphoramide catalyst (*S*,a*R*)-**1**.



Scheme 3. Reaction of cyclic ketones.

We envisioned that the acidic hydrogen of the thiophosphoramide can function as hydrogen-bonding donor in the reaction. To testify this hypothesis, an NMR study on the interaction between the thiophosphoramide catalyst and β-nitrostyrene was carried out. To avoiding interference of the hydrogen-bonding interaction between the amino and nitro group, the corresponding *N*-dimethylated compounds **9** was selected instead of catalyst **2d** for NMR investigation (see Supporting Information). In the ^{1}H NMR of a 1:1 (molar ratio) mixture of thiophosphoramide **9** and β-nitrostyrene (**6a**), the signal relative to the thiophosphoramide proton moved downfield from 4.45 to 4.46 ppm. At the same time, about 0.01 ppm downfield was also observed in the ^{31}P NMR spectra. This observation indicates that there may exist a weak hydrogen-bonding interaction between the nitro group and the thiophosphoramide moiety.

Based on the experimental results, a possible transition state for this reaction was proposed to account for the observed high enantioselectivity. As shown in Figure 1, thiophosphoramide **2d** functioned as a bifunctional catalyst. The primary amine will first react with a carbonyl compound to form an enamine with the aid of acidic co-catalyst. Subsequently, the acidic hydrogen will orientate the nitro group via hydrogen-bonding interaction so that the enamine will nucleophilic attack the nitro olefin from the *Si*-face to give the highly enantioselective product. This explanation is consistent with the experimental results.

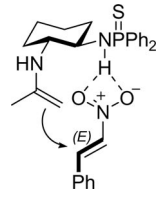


Figure 1. Possible transition state.

Conclusions

In conclusion, we have developed a novel chiral *trans*-cyclohexanediamine-based thiophosphoramdie primary amine catalyst **2d,** which worked well as a bifunctional organocatalyst to promote the asymmetric Michael reaction of acetone to both aryl and alkyl nitro olefins. The corresponding adducts were obtained in high yields (up to >99%) with excellent enantioselectivity (up to 97% *ee*). Moreover, this catalytic system can be applied to challenging cyclopentanone. Further efforts on the application of this catalyst to other valuable organic transformations are under active investigation.

Experimental Section

Thiophosphoramide 2d Catalyzed Asymmetric Michael Addition to Nitro olefins (General Procedure): A mixture the catalyst **2d** (19.8 mg, 0.06 mmol), phenol (2.8 mg, 0.03 mmol) and acetone (0.2 mL, 10 equiv.) in toluene (1.0 mL) was stirred at room temperature to form a clear solution. Then, to the resulting solution was added nitro olefin (0.3 mmol) at the required temperature. After the reaction is complete (monitored by TLC), the mixture was purified by column chromatography on silica gel (200–300 mesh, PE/EtOAc = 5:1) to afford the desired product. The enantiomeric

excess of the pure product was determined by chiral HPLC analysis.

Supporting Information (see also the footnote on the first page of this article): Experimental procedures, characterization of the prepared compounds and copies of NMR, IR, HRMS spectra as well as the chiral HPLC spectra of the Michael addition products.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (No. 20772058, 20972070), the National Basic Research Program of China (973 program 2010CB833301) and the Key laboratory of Elemento-Organic Chemistry for generous financial support of our programs.

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Received: July 5, 2010
Published Online: September 21, 2010

