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Highly enantioselective organocatalysis of the Michael addition of benzyloxyacetaldehyde to nitroolefins

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ABSTRACT

A novel category of di(*N*,*N*-dimethylbenzylamine)prolinol silyl ether catalyst, which when used in conjunction with an acidic co-catalyst, generates an ammonium salt supported organocatalyst. This catalytic system is shown to be very effective for the Michael reaction of benzyloxyacetaldehyde and various nitroolefins in isopropanol. Excellent enantioselectivities (up to 99%) and diastereoselectivities (*syn*/*anti* of 75:25) and short reaction times were obtained. The presence of the bulky OTMS group combined with the presence of two large *N*,*N*-dimethylbenzyl ammonium ion groups accounts for the effectiveness of this catalytic system.

1. Introduction

The catalyzed asymmetric Michael reaction of aldehydes with nitroolefins[1] is an especially important type reaction in organic synthesis. This type reaction is one of the most powerful tools for the formation of carbon–carbon bonds and can also afford synthetically useful γ-nitro carbonyl compounds with excellent diastereoselectivities both in Nature and in modern organic synthesis.[2] Oxyaldehydes are extremely important compounds in organic synthesis. The auto-aldol reaction of oxyaldehydes has been used for the synthesis of carbohydrates,[3] and benzyloxyacetaldehyde, which is used in the Mannich reaction for the synthesis of the side chain of Paclitaxel.[4]

The use of organocatalysts to catalyze asymmetric reactions has received much attention, and different types of organocatalysts have been developed over the past decade that result in high enantioselectivities for asymmetric transformations.[5] Organocatalysts are highly effective, relatively non-toxic, environmentally friendly, and require mild reaction conditions. As a result, they have become an integral component of asymmetric catalysis.[6] In 2008, List et al. and Hayashi et al. independently reported for the first time the asymmetric Michael addition in which a diarylprolinol silyl ether-based catalyst was used.[7] Subsequently, renewed interest has been generated in the use of secondary amines as organocatalysts.[8]

The development of ionic liquids as asymmetric organocatalysts is a growing area of research and many have been developed and applied to a wide range of organic transformations, in which asymmetric products are obtained with high stereoselectivities.[9] Recently, our research efforts have focused on the development of ionic liquid and ammonium salt supported organocatalysts that are effective for a wide range of reactions.[10] A major advantage of this category of organocatalysts is that they are highly soluble in polar protic solvents, such as water and alcohols, and are also very effective for the asymmetric Michael addition of aldehydes to nitroolefins in which high diastereo- and enantioselectivities are obtained.[11]

Herein, we report the results of further investigation of our catalytic system involving the reaction of benzyloxyacetaldehyde with various nitroalkenes. This type reaction is very important since recently an aldehyde, 3-pentyloxyacetaldehyde, was utilized in the synthesis of oseltamivir and a Michael addition was the key step.[12] Due to the importance of oseltamivir, which is also known as Tamiflu, to the pharmaceutical community, we were prompted to apply our organocatalytic system to study the key step in its synthesis. The catalysts and co-catalysts considered are shown in Figure 1; the Michael reaction that served as the model reaction to gain the optimized set of reaction conditions, catalyst, co-catalyst, catalyst loading, temperature, and solvent is shown in Figure 2, where R is the phenyl group.

For the optimization, separate reactions were carried out using catalyst **1** in methanol and isopropanol in which benzoic acid was used as a co-catalyst (entries 1 and 2 of Table 1), but the yields, diastereoselectivities, and enantioselectivities were only moderate, even though the reactions were completed within 2 h. The next solvents considered were water and brine (entries 3 and 4). Brine was considered since our research has shown it to be a very

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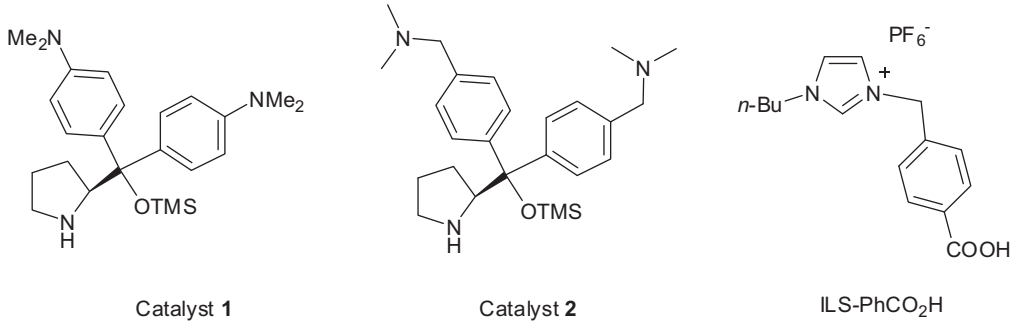

Figure 1. Catalysts and co-catalyst used for the optimization of the asymmetric Michael reaction of benzyloxyacetaldehyde and nitrostyrenes.

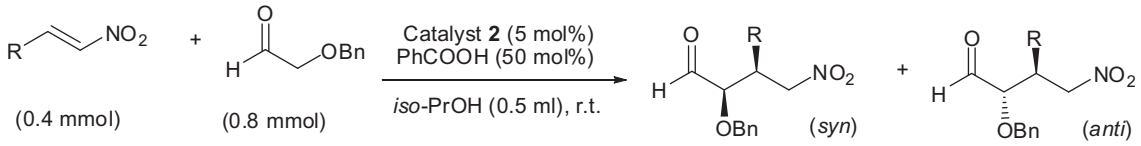

Figure 2. Reaction involving benzyloxyacetaldehyde and various substituted nitroolefins.

Table 1
Results for the optimization of catalysts, co-catalysts and reaction conditions for the asymmetric Michael reaction of benzyloxyacetaldehyde and nitrostyrene at 25 °C

Entry	Cat (mol%)	Solvent[a]	Time (h)	AcidX mol %	Yield (%)[b]	dr (*syn*/*anti*)[c]	%ee (*syn*/*anti*)[d]
1	**1** (5)	MeOH	2	$PhCO_2H$ 50 mol %	37	65/35	93/95
2	**1** (5)	*i*-PrOH	2	$PhCO_2H$ 50 mol %	41	70/30	92/90
3	**1** (5)	H_2O	5	$PhCO_2H$ 50 mol %	35	75/25	99/90
4	**1** (5)	Brine	3	$PhCO_2H$ 50 mol %	31	73/27	94/77
5	**1** (5)	MeOH/H_2O (1:1)	5	$PhCO_2H$ 50 mol %	39	69/31	95/91
6	**1** (5)	*i*-PrOH/H_2O (1:1)	3	$PhCO_2H$ 50 mol %	45	74/26	99/85
7	**1** (5)	*i*-PrOH/H_2O (1:1)	4	ILS-$PhCO_2H$ 50 mol %	43	74/26	99/88
8	**2** (5)	MeOH	6	$PhCO_2H$ 50 mol %	57	66/34	98/95
9	**2 (5)**	***i*-PrOH**	**7**	**$PhCO_2H$ 50 mol %**	**68**	**75/25**	**99/97**
10	**2** (5)	H_2O	5	$PhCO_2H$ 50 mol %	53	76/24	99/93
11	**2** (5)	Brine	5	$PhCO_2H$ 50 mol %	40	73/27	99/91
12[e]	**2** (5)	*i*-PrOH	53	$PhCO_2H$ 50 mol %	46	78/22	96/96
13	**2** (5)	*i*-PrOH	96	$PhCO_2H$ 30 mol %	48	70/30	99/95
14	**2** (3)	*i*-PrOH	120	$PhCO_2H$ 50 mol %	40	67/33	98/85

[a] Using 0.5 ml of solvent.
[b] Determined by ^{1}H NMR.
[c] Determined by ^{1}H NMR.
[d] Determined by chiral HPLC.
[e] Carried out at 4 °C.

effective solvent when used in conjunction with this type catalyst.[13] Water was also considered due to its unique solvation properties and its desirability as a solvent in general. As shown in Table 1, the yields, diastereoselectivities, and enantioselectivities were only moderate, and the reaction in water took a longer time to complete (5 h). The next set of solvents considered were aqueous mixtures of methanol and isopropanol (entries 5 and 6). It was observed that the reaction time in aqueous methanol was longer, compared to that in the isopropanol/water mixture. In an effort to improve the outcome of the reaction, another type of ionic liquid supported co-catalyst, which was developed in our lab, was considered (entry 7). This newly developed ionic liquid supported benzoic acid[14] however, showed similar results as those in which benzoic acid was used as co-catalyst.

Next, the reaction was screened using catalyst **2**. The reaction in methanol showed only a slight improvement in stereochemical

Table 2
Scope for the asymmetric Michael reaction involving benzyloxyacetaldehyde and various substituted nitroolefins

Entry	R	Time	Yield (%)	*syn*/*anti*	%ee
1	Ph	7	68	75/25	99/97
2	4-F-C_6H_4	24	70	80/20	92/89
3	2-F-C_6H_4	24	67	90/10	92/93
4	4-NO_2-C_6H_4	20	60	75/25	96/97
5	4-OMe-C_6H_4	18	79	76/26	98/92
6	4-Me-C_6H_4	18	79	79/21	95/96

outcome, compared to catalyst **1** (entry 8). In isopropanol however, catalyst **2** showed a dramatic improvement in the enantioselectivity under similar reaction conditions (entry 9), compared to catalyst **1**. Encouraged by these results for catalyst **2**, we next tested this catalytic system in aqueous media (entries 10 and 11), but there was not a significant improvement in these media, compared to that in isopropanol. Next, the effect of temperature was studied on the reaction (entries 12). It is obvious that at a lower temperature, there was no effect on the stereochemical outcome of the reaction and the yield was in fact reduced. Next, the concentration of the co-catalyst was changed and the results examined. It is obvious that a reduction in the concentration of the co-catalyst from 50 mol % did not improve the reaction outcome (entry 13). It appears that a high concentration of the acidic co-catalyst is needed in order to favor the formation of ammonium ions. Next, the amount of catalyst was decreased to 3 mol %, but it was observed that the reaction took a much longer time, 120 h, and there was no real improvement in the yield or diastereomeric ratio (entry 14).

These results show that the optimum set of reaction conditions are those shown in entry 9 and were used to study the reaction scope in which various substituted nitroolefins were considered, and the results are shown in Table 2.

The results in Table 2 indicate that the reactions proceeded efficiently affording the products in relatively high yields (67–79%), with excellent ee (up to 98:92) for both electron withdrawing and electron-donating substituted styrenes. The high enantioselectivities of catalyst **2** for the Michael additions can be explained by the formation of a polar transition state,[15] which would be favored in the polar medium of this reaction. Also, the presence of the bulky OTMS group, combined with two *N*,*N*-dimethylbenzyl ammonium ion groups, which exist in the acidic medium serves to make this catalyst effective.

2. Conclusion

In conclusion, a novel di(*N*,*N*-dimethylbenzylamine)prolinol silyl ether catalyst, which when used in conjunction with an acidic co-catalyst generates an ammonium salt organocatalyst. This catalytic system is shown to be very effective for the Michael reaction of benzyloxyacetaldehyde and various substituted nitroolefins. Excellent enantioselectivities (up to 99%) and diastereoselectivities (*syn*/*anti* of 75:25) were obtained. Further studies are being carried out on a broader scope of reaction substrates and other types of reaction and the results will be reported in due course.

3. Experimental

3.1. General procedure for the Michael addition reaction

The synthesis of catalysts **1** and **2**,[13] along with ILS-$PhCO_2H$[14] is described elsewhere. For the Michael reactions herein, benzyloxyacetaldehyde (0.8 mmol) was added to a solution of the catalyst (0.02 mmol, 5 mol %), nitroolefin (0.4 mmol) and benzoic acid (0.2 mmol, 50 mol %) in isopropanol (0.5 mL) at room temperature. The reaction mixture was stirred until complete conversion of the starting materials (monitored by TLC). The solvent was removed and the product was purified by flash column chromatography (silica gel, hexane/AcOEt) to afford the Michael adduct. Percentage yields and *syn*/*anti* ratios were determined by ^{1}H NMR spectroscopy. Racemates were synthesized using morpholine as a catalyst in order to identify enantiomers. Enantiomeric excess determinations were made based on comparisons with previously reported literature for determinations.[16] Similar chiral HPLC conditions were used for the separation of the enantiomers for each reaction and based on the retention times, NMR and IR data, the identity of each enantiomer was determined.

3.1.1. 2-(Benzyloxy)-4-nitro-3-phenylbutanal

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.51, 9.41 (d, J = 1.5 Hz, 1H), 7.21–7.39 (m, 10H), 4.85 (m, 1H), 4.77 (m, 1H), 4.65 (m, 1H), 4.52 (m, 1H), 4.09 (m, 1H), 3.99 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.7, 200.3, 136.6, 136.4, 135.3, 134.2, 128.5, 84.1, 82.6, 76.3, 76.2, 74.0, 73.5, 45.3, 44.8 ppm. HPLC (AD-H, ^{i}PrOH/*n*-hexane = 5:95, 1 mL/min, λ = 217 nm): t_R = 21.1 (*anti*-major), 18.4 (*syn*-minor), 18.0 (*anti*-minor), 14.8 (*syn*-major) min.

3.1.2. 2-(Benzyloxy)-3-(4-fluorophenyl)-4-nitrobutanal

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.54, 9.48 (d, J = 1.5 Hz, 1H), 7.11–7.49 (m, 9H), 4.80 (m, 1H), 4.77 (m, 1H), 4.60 (m, 1H), 4.42 (m, 1H), 4.19 (m 1H), 3.90 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.5, 200.3, 138.6, 136.4, 135.0, 134.4, 128.5, 80.1, 78.6, 76.3, 75.2, 74.2, 73.5, 45.0, 44.2 ppm. HPLC (AD-H, ^{i}PrOH/*n*-hexane = 5:95, 1 mL/min, λ = 217 nm): t_R = 26.5 (*anti*-major), 21.1 (*syn*-major), 19.3 (*anti*-minor), 16.0 (*syn*-minor) min.

3.1.3. 2-(Benzyloxy)-3-(2-fluorophenyl)-4-nitrobutanal

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.70, 9.51 (d, J = 1.5 Hz, 1H), 7.11–7.49 (m, 9H), 4.80 (m, 1H), 4.77 (m, 1H), 4.60 (m, 1H), 4.42 (m, 1H), 4.18 (m 1H), 4.10 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.6, 200.4, 137.6, 135.4, 134.3, 130.2, 128.7, 83.1, 82.8, 77.3, 76.5, 75.0, 73.4, 38.3, 37.8 ppm. HPLC (AD-H, ^{i}PrOH/*n*-hexane = 5:95, 1 mL/min, λ = 217 nm): t_R = 18.0 (*anti*-major), 17.5 (*syn*-major), 16.7 (*anti*-minor), 16.3 (*syn*-minor) min.

3.1.4. 2-(Benzyloxy)-3-(4-nitrophenyl)-4-nitrobutanal

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.52, 9.48 (d, J = 1.5 Hz, 1H), 7.11–7.49 (m, 9H), 4.80 (m, 1H), 4.77 (m, 1H), 4.60 (m, 1H), 4.42 (m, 1H), 4.19 (m 1H), 4.1 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.6, 201.3, 137.6, 136.5, 132.3, 130.2, 128.0, 83.1, 82.6, 77.5, 76.2, 74.3, 73.8, 45.7, 45.0, 44.8 ppm. HPLC (AD-H, ^{i}PrOH/*n*-hexane = 5:95, 1 mL/min, λ = 217 nm): t_R = 40.2 (*syn*-minor), 36.8 (*syn*-major), 31.7 (*anti*-minor), 30.1 (*anti*-major) min.

3.1.5. 2-(Benzyloxy)-3-(4-methoxyphenyl)-4-nitrobutanal

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.50, 9.9.41 (d, J = 1.5 Hz, 1H), 7.11–7.60 (m, 9H), 4.82 (m, 1H), 4.70 (m, 1H), 4.60 (m, 1H), 4.50 (m, 1H), 4.10 (m 1H), 3.86 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.2, 202.3, 135.6, 130.4, 129.3, 129.7, 128.0, 83.1, 82.2, 75.0, 74.2, 73.0, 72.5, 45.0, 44.5 ppm. HPLC (AD-H, ^{i}PrOH/*n*-

hexane = 5:95, 1 mL/min, λ = 217 nm): t_R = 19.6 (anti-major), 18.4 (syn-major), 17.7 (anti-minor), 16.5 (syn-minor) min.

3.1.6. 2-(Benzyloxy)-4-nitro-3-(*p*-tolyl)butanal

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.51, 9.46 (d, J = 1.5 Hz, 1H), 7.11–7.49 (m, 9H), 4.80 (m, 1H), 4.77 (m, 1H), 4.60 (m, 1H), 4.42 (m, 1H), 4.19 (m, 1H), 3.9 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.7, 200.2, 137.6, 137.42, 131.3, 130.2, 128.5, 84.1, 82.8, 82.3, 76.2, 74.0, 73.5, 45.3, 44.6 ppm. HPLC (AD-H, ^{i}PrOH/*n*-hexane = 5:95, 1 mL/min, λ = 217 nm): t_R = 19.0 (*syn*-major), 16.0 (*anti*-minor), 14.1 (*anti*-major), 13.1 (*syn*-minor) min.

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