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High acceleration of the direct aldol reaction cocatalyzed by BINAM-prolinamides and benzoic acid in aqueous media

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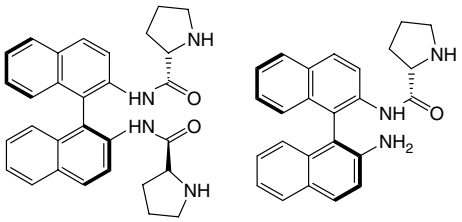
Abstract—The enantioselective direct aldol reaction, organocatalyzed by recoverable BINAM-prolinamide derivatives can be highly accelerated by a catalytic amount of a carboxylic acid without a detrimental of the obtained enantioselectivities. From the study of suitable acids and reaction conditions, benzoic acid in aqueous DMF or in water was shown to give the best results with high yields and enantioselectivities. Thus, the reaction between *p*-nitrobenzaldehyde and acetone catalyzed by (S_a)-BINAM-L-Pro and benzoic acid can be carried out at −20 °C in only 8.5 h to give the expected product with 86% ee. In the case of butan-2-one, the *iso*- and the *anti*-isomers are obtained in a 1:1 isomer ratio up to 99% ee. Cyclohexanone gives the *anti*-aldol in up to 99% dr and 97% ee in only 2 h. The opposite diastereoselectivity is obtained in the case of cyclopentanone with lower ee up to 65% for the *syn* and 85% for the *anti*-isomer.

1. Introduction

Enantioselective organocatalysis[1] is an old tool in organic synthesis, which has been used to carry out the decarboxylation of malonic acid.[2] Despite this fact, it has only been in the last decade when the use of this type of processes has become a fruitful research area. Organocatalysts have shown their synthetic usefulness in enantioselective C–C as well as heteroatom–C bond formation. In both types of transformations, proline[3] has shown its versatility as catalyst, its use being especially successful in the direct enantioselective aldol reaction.[4] Thus, proline is able to catalyze efficiently the coupling of two carbonyl components, ketone–aldehyde or aldehyde–aldehyde,[5,6] under mild reaction conditions to afford the expected products with high regio-, diastereo- and enantioselectivities. Although the use of proline as a catalyst has obvious advantages, it suffers from some problems, such as a lack of solubility in most organic solvents and difficult tuning of its reactivity through structural modifications. Therefore, several proline derivatives have been synthesized and used as catalysts.

Especially attractive is the use of prolinamides[7] or small peptides,[8] derived from proline as catalysts for the aldol reaction, since the robust and easily formed amide bond permitted structural modifications, therefore allowing the fine tuning of catalyst properties. Recently, it has been reported that the synthesis of BINAM-prolinamides (Fig. 1) and their use for the direct aldol condensation of aldehydes and alkyl ketones[9,10] and alkoxy ketones[11] gives the expected products with high regio-, diastereo- and enantioselectivities. We have shown that working in DMF as solvent, the BINAM-prolinamide **1a** gave the best performances and can be recovered after acidic work up (Fig. 1).[9,11] In general, these direct aldol reactions need relatively long reaction times in order to obtain good yields of the corresponding aldol.



1a, (S_a)-BINAM-L-Pro **1b**

Figure 1. BINAM-derived prolinamides.

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On the other hand, it has been established that Brönsted acids enhance the catalytic activity of pyrrolidine-based organocatalysts, favouring the first steps of the catalytic cycle.[12] Therefore, it can be expected that the use of such BINAM-prolinamide catalysts **1** in combination with acids would provide an acceleration of the reaction rate, facilitating the formation of the enamine, allowing a further optimization of the reaction conditions. We can also expect that this combination would protonate the catalyst to form the corresponding ammonium salt, thus enhancing the solubility of such catalysts in water and therefore allowing us to carry out the reaction in that solvent.

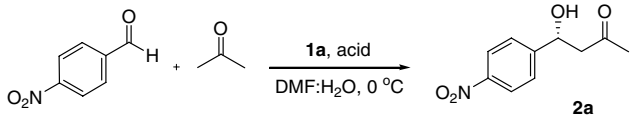
2. Results and discussion

At first, we investigated the influence of the amount and pK_a of the acid on the reaction between acetone and *p*-nitrobenzaldehyde in 1:1 DMF/H_2O at 0 °C catalyzed by (S_a)-BINAM-L-Pro **1a**[9] (Table 1). A large increase in the reaction rate was observed when 10 mol % of AcOH was added to the reaction mixture, to give product **2a** in a nearly quantitative yield in only 12 h in comparison with the 3 d required in the absence of acid with almost the same ee (Table 1, entries 1 and 2). When the amount of acetic acid was increased to 20 mol %, that is 1 equiv of acid per amine group on the catalyst, the reaction rate was increased further to 3 h without a detrimental effect on the enantioselectivity achieved (Table 1, entry 3). When the slightly more acidic benzoic acid was used, the reaction was over within 1 h, independent of the amount of acid used (Table 1, entries 4 and 5). In all these cases the yield was between 90% and 98% and the ee between 75% and 79%. As the pK_a of the used acid decreased, the reaction time increased (Table 1, entries 6–10), probably due to the protonation of the catalyst, which lowers its nucleophilicity.

Thus, chloroacetic acid gave the best yield and enantioselectivity but required 7.5 h to complete the reaction (Table 1, entry 8). The use of a stronger acid, such as methanesulfonic acid led to a total inactivation of the catalyst, with the starting material remaining unchanged after 4 d (Table 1, entry 11).

Thus, it seems that the acceleration of the reaction was most effective by the use of 20 mol % of benzoic acid, allowing us to further optimize the reaction conditions (Table 2). The influence of the presence of water as a co-solvent was then evaluated. The reaction in dry DMF, gave product **2a** in similar ee than in aqueous DMF but required longer reaction time and lower yield (Table 2, compare entries 1 and 2). The reaction in dioxane[10] was accelerated by the presence of acid but the ee achieved was lower than in DMF (Table 2, entry 3). Finally, the reaction was carried out in pure water, achieving the expected product **2a** with almost the same ee but in 20 h (Table 2, entry 4). The use of a mixture of DMF/H_2O allowed us to decrease the reaction temperature below 0 °C. Thus, the reaction was carried out at −20 and −40 °C and, as expected, the ee increased from 76% to 86% and 88%, respectively, although longer reaction times were required (Table 2, compare entry 1 with 5 and 6).

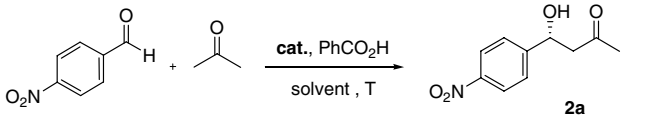
Table 1. Direct aldol reaction of 4-nitrobenzaldehyde with acetone catalyzed by **1a** and an acid[a]



Entry	Acid (mol %)	pK_a	t (h)	Yield[b] (%)	ee[c] (%)
1[d]	—	—	72	99	79
2	AcOH (10)	4.76	12	99	77
3	AcOH (20)	4.76	3	90	75
4	$PhCO_2H$ (10)	4.20	1.5	94	78
5	$PhCO_2H$ (20)	4.20	1	98	76
6	4-$MeOC_6H_4CO_2H$ (20)	4.47	2	90	77
7	4-$O_2NC_6H_4CO_2H$ (20)	3.44	5	93	83
8	$ClCH_2CO_2H$ (20)	2.87	7.5	95	83
9	Cl_2CHCO_2H (20)	1.29	21	86	84
10	F_3CCO_2H (20)	0.23	30	99	80
11	CH_3SO_3H (20)	−2.00	—[e]	—	—

[a] The reaction was carried out using 27.6 equiv of acetone per equivalent of aldehyde (0.25 mmol) in the presence of **1a** (10 mol %) and the indicated amount of acid in 0.5 mL of solvent.
[b] Isolated products after column chromatography.
[c] Determined by HPLC (Chiracel AS, hexane/isopropanol: 85/15), the absolute configuration for the major enantiomer being *R*.
[d] In the absence of acid.[9]
[e] The starting compounds were recovered after 4 d of reaction time.

Table 2. Optimization of reaction conditions of 4-nitrobenzaldehyde with acetone in the presence of benzoic acid[a]



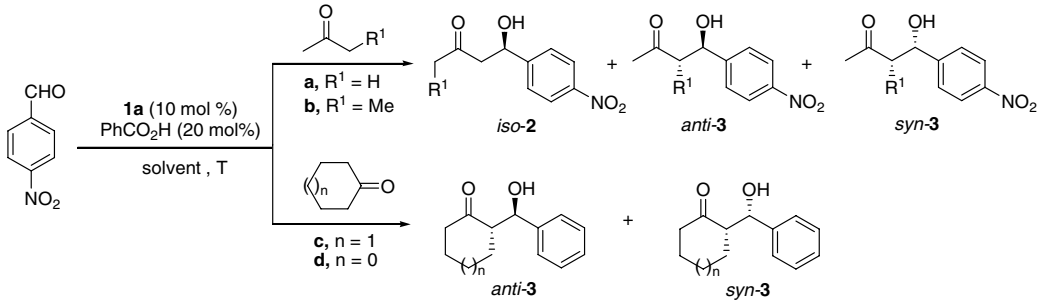
Entry	Cat.	Me_2CO (mmol)	Solvent	T (°C)	t (h)	Yield[b] (%)	ee[c] (%)
1	**1a**	27.6	DMF:H_2O[d]	0	1	98	76
2	**1a**	27.6	DMF	0	8.5	80	77
3	**1a**	27.6	Dioxane	0	3	95	65
4	**1a**	27.6	H_2O	0	20	99	75
5	**1a**	27.6	DMF:H_2O[d]	−20	8.5	94	86
6	**1a**	27.6	DMF:H_2O[d]	−40	36	92	88
7	**1a**	13.8	DMF:H_2O[d]	−20	7	98	81
8	**1a**	6	DMF:H_2O[d]	−20	18	90	83
9	**1a**[e]	6	DMF:H_2O[d]	−20	100	77	78
10	**1b**[f]	27.6	DMF:H_2O[d]	−20	48	95	75
11	**1b**[f]	27.6	H_2O	0	20	96	61
12	L-Pro[g]	27.6	DMF:H_2O[d]	25	54	60	38

[a] The reaction was carried out using the indicated equivalent of acetone per equivalent of aldehyde (0.25 mmol) in the presence of the catalyst (10 mol %) and benzoic acid (20 mol %) in 0.5 mL of solvent, otherwise stated.
[b] Isolated products after column chromatography.
[c] Determined by HPLC (Chiracel AS, hexane/isopropanol: 85/15).
[d] 1:1.
[e] 5 mol % of catalyst and 10 mol % of benzoic acid was used.
[f] 10 mol % of catalyst and 10 mol % of benzoic acid was used.
[g] 20 mol % of catalyst and 20 mol % of benzoic acid was used.

Thus, it seems that the best balance between ee and reaction time (86 ee, 8.5 h) could be obtained when carrying out the reaction at −20 °C (Table 2, entry 5). Under these reaction conditions, the amount of ketone and catalyst was evaluated. A decrease in the amount of acetone led to an increase of the reaction time with a slight decrease on the enantioselectivities achieved (Table 2, entries 5, 7 and 8). When the catalyst loading and the acid were decreased, the reaction time was even longer (4 d) thus achieving a 78% ee (Table 2, entry 9). The use of catalyst **1b**[9] with only one proline moiety in the presence of acid gave product **2a** in longer reaction times and with lower enantioselectivities than **1a** either in DMF/H_2O or in pure H_2O (Table 2, entries 10 and 11). Finally, when the reaction was carried using L-Pro as catalyst (20 mol %) in the presence of benzoic acid (20 mol %) in DMF/H_2O, the reaction did not take place either at −20 °C or at 0 °C. At 25 °C, product **2a** was achieved after 54 h in 60% yield and 38% ee (Table 2, entry 12).

The influence of the addition of benzoic acid on the aldol reaction of several ketones with *p*-nitrobenzaldehyde catalyzed by **1a** was studied in aqueous DMF and in H_2O and then compared with our previous studies in the absence of benzoic acid[9,10] (Table 3). When the reaction between 2-butanone and *p*-nitrobenzaldehyde, catalyzed by **1a** was performed in DMF in the absence[9] of benzoic acid at rt product, *iso*-**2b** was almost exclusively obtained (Table 3, entry 3). However, in the presence of $PhCO_2H$, a decrease in the reaction time from 264 to 31 h was observed and a 5/1 mixture of regioisomers *iso*-**2b** and *anti*-**3b** was obtained with lower regio- and enantioselectivities (Table 3, compare entries 3 and 4). The addition of water to DMF increased the enantioselectivity from 75% to 88% for the *iso*-**2b** and from 4% to 78% for the *anti*-**3b** but decreased the regioselectivity from 5/1 to 7/3 (Table 3, entry 4). Under the reaction conditions set up for acetone (Table 3, entries 1 and 2) either in DMF/H_2O at −20 °C or in pure water at 0 °C, a 1:1 mixture of *iso*-**2b** and *anti*-**3b** was obtained with high ee for both regioisomers, the reaction rate being higher in H_2O (Table 3, entries 6 and 7). Consequently, the aldol reaction with butan-2-one can be directed either to the *iso*-regioisomer in the absence of water and acid or to the 1/1 mixture of *iso* and *anti*-regioisomers in the presence of water. For cyclohexanone, the presence of $PhCO_2H$ increased the reaction rate from 72 to 2 h, even when working at −20 °C while the diastereoselectivity increased from 10/1 to 99/1 in favour of the *anti*-**3c** diastereomer (Table 3, compare entries 8 and 9). For the reaction in neat water, the dr was 19/1 (Table 3, entry 10). In all cases, the ee

Table 3. Reaction of 4-nitrobenzaldehyde with different ketones catalyzed by **1a** and benzoic acid[a]



Entry	R^1	Solvent	T (°C)	t (h)	Yield[b] (%)	Isomer ratio[c]		ee[d] (%)		
						Regioselectivity (**2**/**3**)	dr (*anti*/*syn*)	*iso*-**2**	*anti*-**3**	*syn*-**3**
1	H	DMF:H_2O[f]	−20	8.5	94	—	—	86	—	—
2	H	H_2O	0	20	99	—	—	75	—	—
3[e]	Me	DMF	25	264	96	>50:1	100:0	96	31	—
4	Me	DMF	25	31	70	5:1	100:0	75	4	—
5	Me	DMF:H_2O[f]	25	20	99	7:3	100:0	88	78	—
6	Me	DMF:H_2O[f]	−20	24	94	1:1	100:0	93	96	—
7	Me	H_2O	0	12	98	1:1	100:0	98	99	—
8[e]	$(CH_2)_5$	DMF:H_2O[f]	0	72	98	—	10:1	—	93	44
9	$(CH_2)_5$	DMF:H_2O[f]	−20	2	99	—	99:1	—	97	6
10	$(CH_2)_5$	H_2O	0	1.5	98	—	19:1	—	94	34
11[g]	$(CH_2)_4$	DMF:H_2O[f]	0	36	99	—	1:4	—	26	17
12	$(CH_2)_4$	DMF:H_2O[f]	−20	1.5	98	—	1:2	—	85	61
13	$(CH_2)_4$	H_2O	0	1	99	—	1:2	—	78	65

[a] The reaction was carried out using 26.4 equiv of ketone per equivalent of aldehyde (0.25 mmol) in the presence of **1a** (10 mol %) and benzoic acid (20 mol %) in 0.5 mL of solvent, otherwise stated.
[b] Of the isolated products after column chromatography.
[c] Determined by ^{1}H NMR.
[d] Determined by HPLC.
[e] In the absence of benzoic acid.[9]
[f] 1:1.
[g] In the absence of benzoic acid.

for the *anti*-**3c** diastereomer was kept between 93% and 97%. For the reaction of cyclopentanone with *p*-nitrobenzaldehyde the presence of $PhCO_2H$ again increased the reaction rate from 36 h at 0 °C to 1.5 h at −20 °C (Table 3, entries 11 and 12). Remarkably, the diastereoselectivity was reversed, with the product *syn*-**3d** being the major one in a 1/4 and 1/2 diastereomeric ratio. The presence of acid increased the ee from 17 to 61% for the *syn*-**3d** and from 26% to 85% for the *anti*-**3d** diastereomers. When this condensation was performed in neat water at 0 °C, the process took place in 1 h with similar regio- and enantioselectivities (Table 3, entry 13).

3. Conclusion

In conclusion, benzoic acid has shown to effectively increase the reaction rate as well the yield between *p*-nitrobenzaldehyde and several alkyl ketones catalyzed by (S_a)-BINAM-L-prolinamide **1a** in DMF/H_2O and in neat water. This is probably due to the acceleration of the formation of the enamine intermediate. In addition, the presence of benzoic acid incremented the enantio- and the diastereoselectivities. For 2-butanone, the presence of benzoic acid favoured the formation of the *anti*-isomer over the *iso*-regioisomer. For cycloalkanones, a noticeable increase of the reaction rate was also observed. In the case of cyclohexanone, the corresponding *anti*-isomer can be formed exclusively with higher ee. However, for cyclopentanone, the *syn*-isomer was the major diastereomer with or without benzoic acid, the ee being much higher in the presence of the acid. Additional studies about the use of BINAM-prolinamides and benzoic acid as organocatalysts are currently under investigation.

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