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Benzaldehyde Lyase-Catalyzed Direct Amidation of Aldehydes with Nitroso Compounds

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Dedicated to Prof. Dr. Ayhan Ulubelen on the occasion of her 80th birthday.

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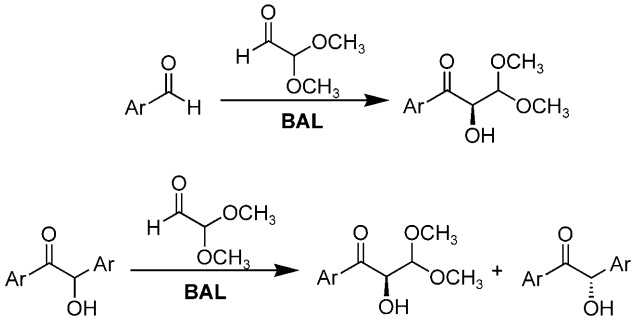
Abstract: Benzaldehyde lyase from the *Pseudomonas fluorescens* catalyzes the reaction of aromatic aldehydes with nitroso compounds and furnishes *N*-arylhydroxamic acids in high yields. Aromatic aldehydes and benzoins are converted into enamine-carbanion-like intermediates prior to their reaction with nitroso compounds. The kinetic resolution of *rac*-2-hydroxy-1,2-diphenylethanones furnished (*S*)-benzoins and arylhydroxamic acids with high enantioselectivities and conversions.

Keywords: amidation reaction; enzyme catalysis; hydroxamic acids; thiamine diphosphate-dependent enzyme

Introduction

Benzaldehyde lyase (BAL), a novel thiamine diphosphate (ThDP)-dependent enzyme from *Pseudomonas. fluorescens Biovar I*, is reported to perform the enantioselective formation of (*R*)- and (*S*)-benzoins and (*R*)-2-hydroxypropiophenone ((*R*)-2-HPP) derivatives *via* C–C bond cleavage and C–C bond formation. (*R*)-2-HPP derivatives are formed on a preparative scale by benzaldehyde lyase (BAL)-catalyzed C–C bond formation from aromatic aldehydes and acetaldehyde, methoxy- and dimethoxyacetaldehyde in a buffer/DMSO solution with remarkable ease in high chemical yields and optical purities (Scheme 1).[1]



Scheme 1. BAL-catalyzed C–C bond formation reactions.

Nitroso compounds exhibit high reactivity.[2] The polarization of the nitrogen-oxygen bond, resembling that of the carbon-oxygen bond in a carbonyl group, makes the nitroso group susceptible to the addition of nucleophiles. By exploiting the higher reactivity of the nitroso group compared to its carbonyl counterpart towards a nucleophilic attack, we suggest a possibility that involved the reaction of an enamine-carbanion intermediate with nitrosobenzene forming hydroxamic acid instead of acyloin. The chemistry and biochemistry of hydroxamic acids are well documented. They are strong metal ion chelators[3] and possess extensive pharmacological, toxicological, and pathological properties.[4] Some of them were examined in human clinical trials as drugs for the treatment of several diseases.[5]

Results and Discussions

N-Arylhydroxamic acids are also known to be proximate carcinogens[6] and demand simple synthetic protocols. Recently, many synthetic approaches to hydroxamic acids have appeared in the literature, mostly involving the acylation of hydroxylamines.[7] Other known synthetic pathways to *N*-arylhydroxamic acids involve the oxidation of arylacylamides[8] and hydroxamic acid production by the reaction of aro-

matic nitroso compounds with oxo acids in the presence of α-ketoglutarate dehydrogenase[9] or acidic media.[10] Uematsu et al.[11] reported the formation of *N*-hydroxy-*N*-arylacylamides from nitroso aromatic compounds, and 2-oxo acids that were investigated by means of a branched chain 2-oxo acid dehydrogenase complex (BCDHC) (a thiamine-dependent enzyme) in rat liver. The reaction of aromatic nitroso compounds with the chemical models of 'thiamine active aldehyde' was reported by Prabhakar et al.[12] and the N-heterocyclic carbene-catalyzed direct amidation of aldehydes with nitroso compounds was published recently by Seayad and Zhang et al.[13] They used nitrosobenzene as the electrophile in the reaction with the homoenolate equivalent to the enamine.

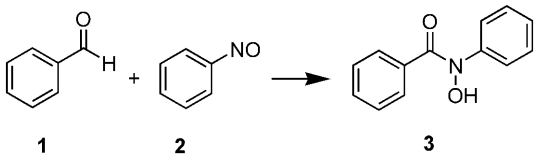
Here, we focus on the synthetic potential of BAL with regard to its ability to catalyze C–N bond formation with aromatic aldehydes and nitrosobenzene derivatives to obtain *N*-arylhydroxamic acids. No such reaction was observed before. This type of enzyme-catalyzed ligation reaction of aldehydes with nitrosobenzene derivatives may be a new and efficient way to obtain important *N*-arylhydroxamic acids.

Based on the preliminary information available to us from our previous work with BAL-mediated carboligation reactions,[1] we tried a series of aromatic aldehydes with nitrosobenzene for the formation of *N*-arylhydroxamic acids.

Under standard conditions, benzaldehyde (**1a**) was dissolved in potassium phosphate buffer containing $MgSO_4$, ThDP, 20 vol% DMSO and nitrosobenzene. By applying the typical procedure for BAL-catalyzed reactions, we had a solubility problem with nitrosobenzene. To overcome this problem, we tried two-phase systems with buffer and water immiscible solvents such as diisopropyl ether, dichloromethane. The best results were obtained with dichloromethane. The efficiency of BAL was first successfully tested in this two-phase system by following the classical benzoin formation. The experiments were performed by using benzaldehyde and nitrosobenzene in a 1:1.2 molar ratio in a two-phase system, which resulted in the following typical procedure:

Benzaldehyde (1 equiv.) (**1a**) and nitrosobenzene (1.2 equiv.) were dissolved in dicholoromethane and then MOPS (3-morpholinopropanesulfonic acid) buffer was added. After the addition of BAL (50 U), the reaction was started at 30 °C. The same amount of enzyme was added on a daily basis. The reaction was monitored by TLC and GC-MS. After 96 h, no further increase of the product concentration was observed and the purification of the crude products by column chromatography gave *N*-phenylhydroxamic acids in good yields (Scheme 2, Table 1).

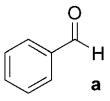
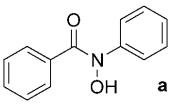
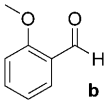
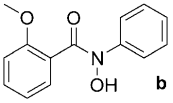
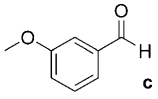
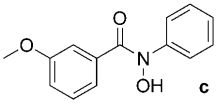
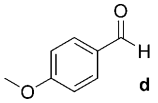
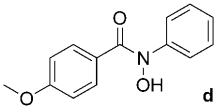
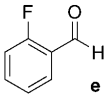
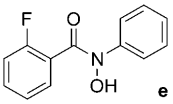
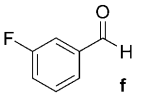
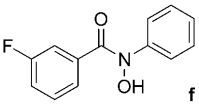
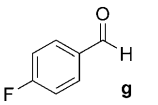
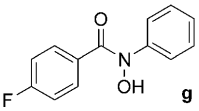
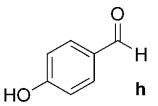
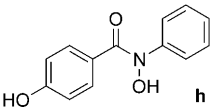
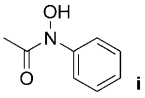
As a control, the reaction was carried out without enzyme and benzaldehyde remained unreacted in the reaction medium. This reaction was carried out with a wide range of aromatic aldehydes, and the corresponding N-arylhydroxamic acids were obtained in good yields, as summarized in Table 1.



1 2 3

Scheme 2. BAL-catalyzed direct amidation.

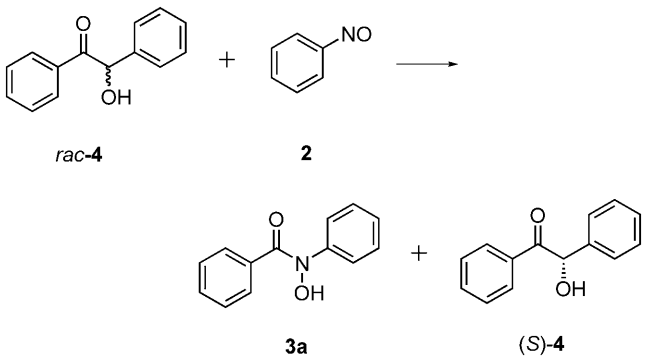
Table 1. BAL-catalyzed formation of *N*-arylhydroxamic acids according to Scheme 2.

Entry	Aldehyde **1**	Product **3**	Yield [%][a]
1	 **a**	 **a**	94[13]
2	 **b**	 **b**	65[15a]
3	 **c**	 **c**	88[15b]
4	 **d**	 **d**	72[13]
5	 **e**	 **e**	70[15b]
6	 **f**	 **f**	84[15c]
7	 **g**	 **g**	89[15b]
8	 **h**	 **h**	65
9	CH_3CHO **i**	 **i**	26[10]

[a] Isolated yields and the spectroscopic data of the compounds are in agreement with the published data.

Benzoin formation was detected only when benzaldehyde derivatives were used in excess amounts compared to nitrosobenzene (for example; benzaldehyde (1.5 or 2.0 mmol) and nitrosobenzene (1.0 mmol)).

The scope of the reaction was examined by varying the aldehyde. As shown in Table 1, a variety of aro-



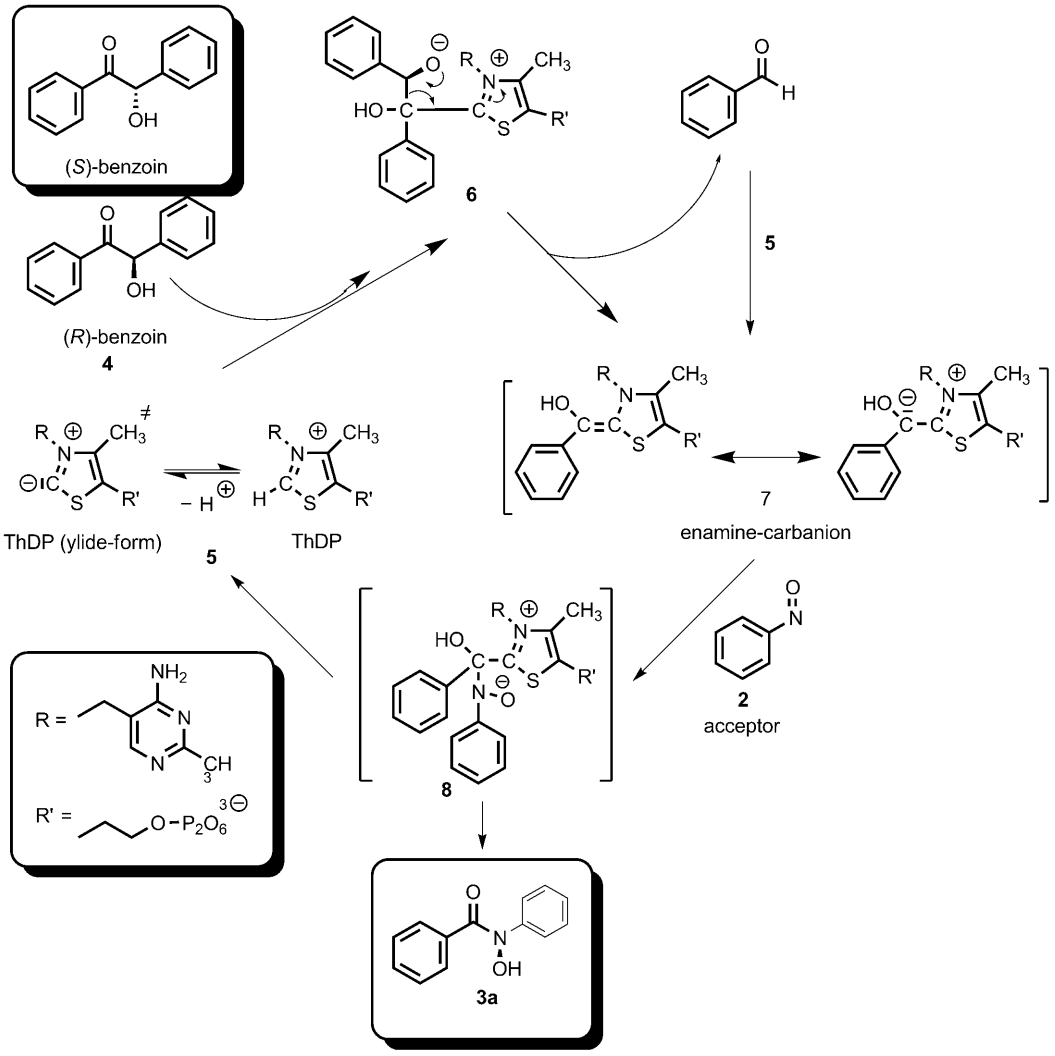
Scheme 3. BAL-catalyzed kinetic resolution of benzoin with nitrosobenzene.

matic aldehydes gave good to excellent yields (65–94%) of the corresponding *N*-arylhydroxamic acids. For BAL, aliphatic aldehydes are not good substrates to form acyl anions. BAL catalyzed the ligation of aliphatic aldehydes to afford 2-hydroxy ketones in a low conversion.[14] In the case of acetaldehyde, BAL enables the formation of a C–N bond with a low level of conversion.

Table 2. BAL-catalyzed kinetic resolution of benzoin derivatives with nitrosobenzene according to Scheme 3.

Entry	R	Conversion to **3** [%]	*ee* of **4** [%]
1	H	97	95
2	*m*-F	92	85
3	*m*-MeO	95	90
4	*p*-MeO	90	88

In our previous publications,[1] we showed that BAL is also able to accept (*R*)-benzoin as a substrate to catalyze the C–C bond cleavage followed by carboligation in the presence of acetaldehyde. Accordingly, (*R*)-benzoin was reacted with BAL in the presence of nitrosobenzene and the reaction was monitored by



Scheme 4. Mechanism of BAL-catalyzed direct amidation reaction with nitrosobenzene.

HPLC equipped with a chiral column. The addition of the corresponding nitrosobenzene derivative resulted in the formation of phenylhydroxamic acids in high yields. Repeating this reaction with *rac*-benzoin afforded **3a**, and (*S*)-benzoin in an almost optically pure form (95% *ee*) after the separation of the products by column chromatography (Scheme 3). To obtain full conversion of (*R*)-benzoin into phenylhydroxamic acid, nitrosobenzene has to be used in an excess amount (1.2 mmol to 1 mmol). Several derivatives of *rac*-2-hydroxy-1,2-diphenylethanone have been resolved with nitrosobenzene with high conversions (90–97%) and enantioselectivities (88–95%), which are given in Table 2.

The mechanism of the reaction is outlined in Scheme 4. BAL-catalyzed amidation of aldehydes occurs *via* the addition of the carbanion-enamine intermediate to aryl nitroso compounds. The carbanion-enamine can either be formed by the direct addition of benzaldehyde or by the previous cleavage of (*R*)-benzoin.

Thus, the first step of the catalytic cycle (Scheme 4) is the attack of the ylide form of ThDP **5** on the carbonyl carbon of (*R*)-benzoin to produce an adduct **6**. The enamine **7**, formed after the liberation of one molecule of benzaldehyde, is a common intermediate of all ThDP-dependent enzymes-catalyzed acyloin formation to obtain 2-hydroxy ketones. In the presence of an acceptor **2** (nitrosobenzene), the enamine intermediate **7**, is able to undergo a C–N bond formation reaction to afford **3a** *via* **8**. From these mechanistic considerations and assuming that the cleavage and formation of (*R*)-benzoin are in equilibrium, BAL should also catalyze C–C bond cleavage. Consequently, the BAL-catalyzed condensation of benzaldehyde with nitrosobenzene in an aqueous/organic two-phase system results in the formation of *N*-hydroxy-*N*-phenylbenzamide. This reaction for the first time demonstrates the potential of BAL for C–N bond formation in addition to C–C bond cleavage and C–C bond formation.

Conclusions

The method described herein represents the first enzyme-catalyzed highly selective synthesis of *N*-arylhydroxamic acids *via* C–N bond linkage. The reaction works in an organic-aqueous medium, overcomes the solubility problem with organic substrates, and may pave the way for large-scale preparations. A further improvement can be obtained with the use of an immobilized enzyme to utilize lower enzyme activities. The products are obtained in high yields starting from simple, easily available aromatic aldehydes, benzoins, and nitrosobenzene *via* C–N bond formation and C–C bond cleavage and followed by C–N bond formation reaction.

Experimental Section

General

NMR spectra were recorded with a Bruker-Spectrospin DPX-400, Ultra Shield high performance digital FT-NMR spectrometer using tetramethylsilane (TMS) as internal standard. Mass spectra were recorded with a Thermo Quest GC-MS equipped with a Phenomenex Zebron capillary GC column (60 m length, 0.25 mm ID, 0.25 μm film thickness). Mass spectra were recorded with an Agilent 7890 A GC system using Agilent 5975C VL MSD with a triple-axis detector with an HP-5 capillary GC column (30 m length, 0.32 mm ID, 0.25 μm film thickness). Flash column chromatography was performed by using Merck Silica Gel 60 (particle size: 40–63 μm, 230–400 mesh ASTM). Enantiomeric excess values were determined on an Agilent 1100 series HPLC device using Chiralpak chiral columns.

The *E. coli* BL21 (DE3) pLysS strain purchased from Invitrogen® was used as the host to produce the recombinant enzyme (BAL_{HIS}). Enzyme production was performed in a New Brunswick BioFlo110 Fermenter equipped with pH and temperature probes as well stirring rate controls. The purification of the hexa-histidine tagged enzyme was performed with an Ni^{2+}-NTA affinity column (Invitrogen®).

Preparation of Benzaldehyde Lyase

E. coli BL21 (DE3) pLysS carrying the pUC19-BAL_{HIS} plasmid was used for BAL (EC. 4.1.2.38) production. Cultures were maintained on LB agar plates. Cells from the freshly prepared plates were inoculated into the preculture in Luria broth (LB) where they were grown for 8 h at 37 °C, and then transferred to the production (LB) medium with an inoculation ratio of 1/10 (1.65 L) in a 2 L fermenter. BAL production was induced with 1 mM IPTG (isopropyl-β-D-thiogalacto-pyranoside) after 3 h at 37 °C. At 6 h after the induction, cells were harvested by centrifugation. Enzyme was either used in its crude form without purification (pelleted cells were transferred to a Petri dish and lyophilized for 36 h) or as a purified enzyme.

One unit (U) of BAL activity is defined as the amount of enzyme that catalyzes the cleavage of 1 μmol benzoin in potassium phosphate buffer (50 mM, pH 7) containing $MgSO_4$ (2.5 mmol L^{-1}), ThDP (0.15 mmol L^{-1}) and DMSO (20 vol%) per minute at 30 °C.

General Procedure for BAL-Catalyzed Synthesis of Hydroxamic Acids

The respective aldehyde (1 mmol) and nitrosobenzene (1.2 mmol, 128.4 mg) were dissolved in 10 mL dichloromethane (DCM) (20 vol%), and then to this solution 40 mL 50 mM MOPS (3-morpholinopropanesulfonic acid) buffer at pH 7 (containing 2.5 mmol L^{-1} $MgSO_4$ and 0.15 mmol L^{-1} ThDP) were added (80 vol%). The reaction was started by the addition of BAL (50 U) at 30 °C. BAL was added (50 U) on a daily basis. The reaction was monitored with TLC and

GC-MS and stopped after 96 h. The reaction mixture was extracted with chloroform (3×50 mL) and the combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The product was purified with flash column chromatography.

***N*-Hydroxy-4-methoxy-*N*-phenylbenzamide (3d):**[13] ^{1}H NMR (400 MHz, DMSO-d_6): δ=10.68 (s, 1H, OH), 7.67 (d, J=8.6 Hz, 2H, Ar-H), 7.53 (d, J=7.9 Hz, 2H, Ar-H), 7.38 (t, J=15.6 Hz, 2H, Ar-H), 7.19 (t, J=14.5 Hz, 1H, Ar-H), 6.97 (d, J=8.7 Hz, 2H, Ar-H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=167.4 (CO), 160.9, 142.5, 130.7, 128.4, 127.2, 125.4, 122.2, 113.1, 55.3; HR-MS: m/z=266.0789, calcd.for $C_{14}H_{13}NO_3Na$ ($M+Na^+$): 266.0793.

2-Fluoro-*N*-hydroxy-*N*-phenylbenzamide (3e):[15b] ^{1}H NMR (400 MHz, DMSO-d_6): δ=10.82 (s, 1H, OH), 7.80–7.58 (m, 2H, Ar-H), 7.57–7.45 (m, 2H, Ar-H), 7.44–7.34 (m, 2H, Ar-H), 7.33–7.18 (m, 3H, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=159.1 (CO), 157.9 (J=247.3 Hz), 141.1, 131.5 (J=7.9 Hz), 129.1, 128.6, 125.8, 124.8 (J=17.4 Hz), 124.2 (J=2.8 Hz), 121.2, 115.5 (J=21.3 Hz); HR-MS: m/z=254.0596, calcd. for $C_{13}H_{10}NO_2FNa$ ($M+Na^+$): 254.0593.

4-Fluoro-*N*-hydroxy-*N*-phenylbenzamide (3g);[15b] ^{1}H NMR (400 MHz, DMSO-d_6): δ=10.85 (s, 1H, OH), 7.78 (q, 2H, Ar-H), 7.62 (d, J=7.9 Hz, 2H, Ar-H), 7.45 (t, J=15.8 Hz, 2H, Ar-H), 7.35–7.24 (m, 3H, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=166.8 (CO), 162.9 (J=247.9 Hz), 141.9, 131.8, 131.1 (J=8.8 Hz), 128.5, 125.6, 122.1, 114.8 (J=21.6 Hz); HR-MS: m/z=254.0590, calcd. for $C_{13}H_{10}NO_2FNa$ ($M+Na^+$): 254.0593.

4-Hydroxy-*N*-hydroxy-*N*-phenylbenzamide (3h): ^{1}H NMR (400 MHz, DMSO-d_6): δ=10.59 (s, 1H, OH), 9.98 (s, 1H, OH), 7.58–7.55 (m, 2H, Ar-H), 7.52–7.48 (m, 2H, Ar-H), 7.39–7.34 (m, 2H, Ar-H), 7.20–7.15 (m, 1H, Ar-H), 6.79–6.74 (m, 2H, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=167.7 (CO), 159.5, 142.6, 130.9, 128.4, 125.5, 125.2, 122.2, 114.4; MS (EI): m/z=229 (M^+-O), 213, 121, 93, 77, 65.

Kinetic Resolution of *rac*-Benzoin with Nitrosobenzene

rac-Benzoin (1 mmol, 212.2 mg) and nitrosobenzene (1.2 mmol, 128.4 mg) were dissolved in 10 mL dichloromethane (DCM) (20 vol%), and then to this solution 40 mL buffer (containing 2.5 mmol L^{-1} $MgSO_4$ and 0.15 mmol L^{-1} ThDP) were added (80 vol%). The reaction was started with the addition of BAL (50 U) at 30 °C. BAL was added (50 U) on a daily basis. The reaction was concluded after 96 h. Two products [*N*-hydroxy-*N*-phenylbenzamide and (*S*)-benzoin] were separated *via* flash column chromatography. The *ee* value was determined by HPLC using Chiralpak OD column (254 nm, eluent: *n*-hexane/2-propanol=90:10, flow 1.0 mL min^{-1}, 20 °C): (*S*)-benzoin=13.0 min; (*R*)-benzoin=19.0 min.

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