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A copper(II)-catalyzed, sequential Michael–aldol reaction for the preparation of 1,2-dihydroquinolines

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ABSTRACT

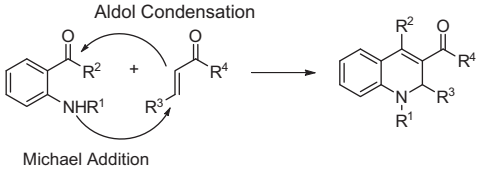
A copper(II)-catalyzed, sequential Michael addition-aldol condensation reaction of *N*-carboxybenzyl -protected aminobenzaldehyde with various α,β-unsaturated *N*-acyl pyrroles is described. Substrate scope was found to include both aryl and aliphatic *N*-acyl pyrroles as the Michael acceptors, and isolated product yields as high as 93% were observed. The use of acetonitrile as the reaction solvent proved to be crucial for catalysis, both to function as a labile ligand for copper, as well as an agent to minimize hydrolytic catalyst poisoning.

Introduction

1,2-Dihydroquinolines have received considerable attention due to their proven biological activity against a wide range of pharmaceutical targets.[1] These compounds also have utility as versatile synthons for a range of biologically active alkaloids.[2] In addition to medicinal applications, derivatives of these compounds can function as pesticides,[3] corrosion inhibitors,[4] fabric dyes,[5] and components in photographic and digital recording devices.[6] Due to the importance of this compound class, the development of inexpensive synthetic routes toward their preparation is of intrinsic value. To date, several methods for the construction of 1,2-dihydroquinoline rings have been reported,[7–9] some of which are enantioselective.[8a–c,9a,b,10] These methods are limited to specific substrate classes, however, and the lack of a general synthetic methodology leaves considerable room for further reaction development.

Of the possible routes for the preparation of 1,2-dihydroquinolines, one reaction holds particular promise for further elaboration: a sequential Michael addition-aldol condensation reaction for the preparation of 1,2-dihydroquinoline-3-carboxylic acid derivatives (Scheme 1).[8] In the envisioned reaction, the nitrogen atom of a 2-(aminophenyl)carbonyl compound attacks the β-position of an α,β-unsaturated carbonyl compound (Michael acceptor) to generate the corresponding enolate, which can then react intramolecularly to afford the corresponding aldol condensation product. Operationally simple, this strategy benefits from its modular design and the use of readily accessible starting materials. Previously reported Michael–aldol reactions have achieved these types of products via the use of strong magnesium bases,[8f] biphasic base catalysis,[8e] and iminium ion catalysis.[8a–d] In these examples, the selection of an appropriate amine protecting group for the 2-(aminophenyl)carbonyl compound is important, as insufficient substitution at R^1 can lead to unfavorable side reactions, a feature that has previously proven problematic.

Protecting the amine functionality as either a carbamate or sulfonamide is a simple strategy to eliminate these side reactions, and this tactic was successfully employed by Wang and Hamada.[8b,c] However, N-protection makes the amine considerably less nucleophilic, which results in the formidable synthetic challenge of sufficiently activating the Michael acceptor to enable amine conjugate addition. Herein, we report the use of copper(II) in acetonitrile as



Scheme 1. Sequential Michael–aldol reaction for the preparation of 1,2-dihydroquinoline-3-carboxylic acid derivatives.

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an effective catalyst for activating the Michael acceptor in such reactions.

Results and discussion

The N-protected, 2-(aminophenyl)carbonyl compounds **1a–c**[11] were selected for investigation with a variety of Michael acceptors (e.g., **2a–8a**; Scheme 2). As the initial conjugate addition sequence was anticipated to be the rate-limiting step of this reaction, our lead discovery investigations focused primarily on the use of metal sources known to catalyze Michael addition reactions,[12] particularly those involving the use of aza-nucleophiles.[13] Chiral phosphoric acid catalyst **10**[14] was included in our studies to investigate the possibility of Brønsted acid catalysis. Trifluoromethanesulfonic acid (TfOH) was also tested to rule out the possibility of triflate counterion catalysis when metal triflate salts were examined.

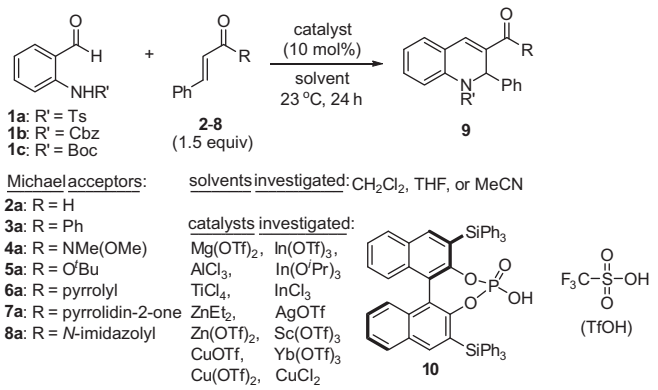
After extensive investigation, only three Michael acceptor/metal source combinations were found to generate appreciable conversion of starting material to **9** at room temperature (Table 1). Of these, only $Cu(OTf)_2$ in acetonitrile with the *N*-carboxybenzyl (*N*-Cbz)-protected **1b** and the α,β-unsaturated *N*-acyl pyrrole **6a** demonstrated significant catalyst turnover. The absence of reactivity with TfOH and CuOTf indicate that this reaction is copper(II) catalyzed. Interestingly, no reaction was observed with the phenyl ketone **3a**, although *N*-acyl pyrroles have been reported to display similar properties as phenyl ketones.[15] For example, in 2002, Wabnitz and Spencer reported the addition of benzyl carbamate to α,β-unsaturated ketones in the presence of $Cu(OTf)_2$ (10 mol %).[16] When these conditions were adapted to the reactions of **3a** or **6a** with benzyl carbamate, both Michael acceptors displayed comparable reactivity. This indicates that the different reactivity of **3a** and **6a** observed in the Michael–aldol reaction is due to preferences associated with the interaction between the Michael acceptors and **1b**.

The electron-donating character of the solvent was found to strongly correlate with reaction conversion (Table 2). For example, the best results (38% conversion to **9**) were observed when acetonitrile was used as the reaction solvent, whereas only 11% conversion was observed with nitromethane, a poor donor solvent with a similar dielectric constant to acetonitrile. However, solvent donicity is not the sole determining factor: tetrahydrofuran and diethyl ether were among the strongest donor solvents investigated, yet these solvents resulted in lower yields relative to acetonitrile.

The benefits of acetonitrile in the copper(II) catalysis of the Michael–aldol reaction appear to be twofold. First, acetonitrile is likely serving as an effective ligand for copper, conveying unique reactivity to the metal center. When alternative ligands, such as BINOL and bisoxazolines, were introduced in the place of acetonitrile, no conversion to product was observed. Second, the high polarity and hydrophilicity of acetonitrile may also play a role in sequestering water away from the copper complex coordination sphere. As 1 equiv of water is generated during the aldol condensation step of the Michael–aldol reaction, we investigated whether water could promote catalyst decomposition. When 1 equiv of water was added to the reaction mixture in acetonitrile, reaction conversion was reduced from 38% to 13%. Accordingly, we expected that reaction performance could be improved and catalyst decomposition circumvented by the addition of a suitable desiccant. Indeed, such an improvement was observed when 4 Å powdered sieves were added to the $In(O^iPr)_3$-catalyzed reaction of **6a** with **1b** (Table 1, entry 3). Unfortunately, the use of desiccants (4 Å sieves, K_2CO_3, Na_2SO_4, barium hydroxide, etc.) in the $Cu(OTf)_2$-catalyzed reaction in acetonitrile had the opposite effect—conversion to product was reduced by ca. 30%.

The ability of acetonitrile to ameliorate the effects of water and promote reactivity in copper(II)-catalyzed reactions has previously been observed in polymerization reactions of 2,6-dimethylphenol.[17,18] Reedijk and coworkers reported a spectacular increase in reaction rate and conversion when acetonitrile was employed as the reaction solvent. As with the Michael–aldol reaction, water is a co-product of this polymerization reaction, yet increasing the amount of water by just 3% in acetonitrile led to a 75% drop in catalyst activity.[17] The hydrophilicity of acetonitrile plays a noticeable role in minimizing catalyst decomposition in both reactions. Indeed, this 'acetonitrile effect' was not as efficient with other nitriles. Decreased catalyst performance was observed when propionitrile, a less hydrophilic nitrile, was employed as the reaction solvent (Table 2).

Further reaction optimization was achieved via heating (82 °C was optimal), coupled with a small increase in catalyst loading. In the reaction of **6a** with **1b** in the presence of $Cu(OTf)_2$ (15 mol %), the Michael–aldol product was isolated in 81% yields after 24 h; additional conversion (product yield 93%) was attained upon extending reaction time to 48 h. Interestingly, conventional heat proved to be more effective than microwave heating: when microwave heat was employed in the reaction of **6a** with **1b**, yields no higher than 57% could be attained. Despite this, broad substrate scope for the *N*-acyl pyrrole used as the Michael acceptor was observed, with both aromatic and aliphatic substrates being well-tolerated (Table 3). In addition, both electron-deficient and electron-rich aryl rings performed similarly (Table 3, entries 2–4). One of the attractive features of this methodology was the tolerance observed toward some Lewis basic substrates, enabling the preparation of furyl- and thienyl-substituted dihydroquinolines. However, one limitation that must be noted was observed when the 3-quinolinyl-substituted Michael acceptor **6h** was employed (Table 3, entry 8). Instead of the typical brown color of these reactions, a blue–green color was observed, and negligible conversion to **9** occurred. Presumably, in this case, the strong donor properties of the pyridyl ring have overridden the weak donor properties of acetonitrile as a ligand for copper(II), leading to a breakdown of the 'acetonitrile effect'.



Scheme 2. Lead discovery investigation of catalysts and Michael acceptors.

Conclusions

Copper(II) triflate combined with acetonitrile is a surprisingly robust catalyst system, allowing for reactions to proceed despite the generation of water as a reaction co-product. When applied to the sequential Michael–aldol reaction of *N*-carboxybenzyl (*N*-Cbz)-protected aminobenzaldehyde with α,β-unsaturated *N*-acyl pyrroles, the corresponding 1,2-dihydroquinoline-3-carboxylic acid derivatives were prepared in high yields. The *N*-acyl pyrrole moiety can be readily transformed into various functional groups,

Table 1
Lead discovery investigation—conditions resulting in the formation of **9**[a]

Entry	Amino aldehyde	Michael acceptor	Catalyst	Solvent	Conversion to **9**[b] (%)
1	**1b**	**2a**	$Cu(OTf)_2$	MeCN	12
2	**1b**	**6a**	$Cu(OTf)_2$	MeCN	38
3	**1b**	**6a**	$In(O^iPr)_3$	THF	13 (20)[c]

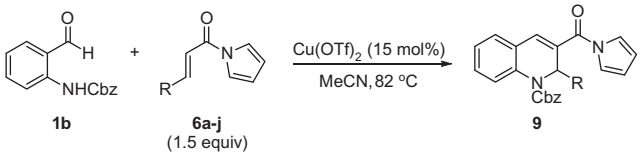
[a] Reactions were carried out with 0.66 mmol of **1b**, 1.0 mmol of **2a** or **6a** and catalyst (10 mol %) in 1.0 mL of solvent.
[b] Determined via GC relative to dodecane (0.2 equiv) as an internal standard and by ^1H NMR.
[c] Reaction run in the presence of 4 Å molecular sieves (80 mg).

Table 2
Effect of solvent on reaction performance[a]

Solvent	Dielectric constant[19] (ε; 20 °C)	Donor number[20] (kcal mol^{-1})	Conversion to **9**[b] (%)
MeCN	37.5	14.1	38
$MeNO_2$	35.9	2.7	11
Propionitrile	26.5	16.1	25
CH_2Cl_2	9.1	0.0	—
THF	7.6	20.0	26
Et_2O	4.3	19.2	17
Toluene	2.4	0.1	—

[a] Reactions were carried out with 0.66 mmol of **1b**, 1.0 mmol of **6a** and $Cu(OTf)_2$ (10 mol %) in 1.0 mL of solvent.
[b] Determined via GC relative to dodecane (0.2 equiv) as an internal standard and by ^1H NMR.

Table 3
Reaction scope[a]



1b **6a-j** (1.5 equiv) **9**

Entry	Michael acceptor	R	Yield of **9**[b] (%)	
			After 24 h	After 48 h
1	**6a**	Ph	81	93
2	**6b**	*p*-MeC_6H_4	80	90
3	**6c**	*p*-$OMeC_6H_4$	81	90
4	**6d**	*p*-FC_6H_4	80	92
5	**6e**	2-Naphthyl	73	82
6	**6f**	2-Furyl	80	92
7	**6g**	2-Thienyl	59	72
8	**6h**	3-Quinolinyl	—	—
9	**6i**	Butyl	60	72
10	**6j**	Isopropyl	67	73

[a] Reactions were carried out with 0.66 mmol of **1b**, 1.0 mmol of **6** and $Cu(OTf)_2$ (15 mol %) in 1.0 mL of MeCN.
[b] Isolated via flash chromatography on silica gel.

enabling the broader utility of these reaction products.[15,21] In addition, this methodology highlights the effectiveness of acetonitrile as both a weakly donating ligand to induce strong Lewis acidity of the metal as well as an additive for the minimization of catalyst decomposition under hydrolytic conditions.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.12.017.

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