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Catalyst-Free Three-Component Synthesis of Highly Functionalized 2,3-Dihydropyrroles

Dong Wang,^a Linna Li,^a Hairong Feng,^a Hua Sun,^a Fabrice Almeida-Veloso,^b Marine Charavin,^b Peng Yu,^a and Laurent Désaubry^{*a,b,c}

An efficient synthesis of fully substituted 2,3-dihydropyrroles has been achieved in one step through the three-component reaction of amines, aromatic aldehydes and α -ketoamides. This atom-economical and catalyst-free reaction is highly stereoselective and generates in a single step underexplored heterocycles. These compounds were examined in an enzymatic assay that led to the identification of potent α -glucosidase inhibitors, thereby demonstrating the utility of this novel methodology in medicinal chemistry.

Introduction

Dihydropyrroles are a common structural motif found in a number of naturally occurring alkaloids and biologically active substances.¹ In particular, 2,3-dihydropyrroles have been reported to be important precursors for the synthesis of a variety of natural products² and other complex molecules.³ Several elegant methods have been reported for the synthesis of these compounds but each of these is restricted to limited types of substrates, and consequently deliver 2,3-dihydropyrroles with a limited variety of substituents (Scheme 1).⁴ Herein, we report a highly efficient, one-step, stereoselective and green synthetic approach to 2,3-dihydropyrroles that display a novel pattern of substitutions using simple amines, aldehydes and easily accessible pyruvic amides as starting materials.

Three-component reactions are one-pot reactions that use three reagents to generate a single product containing most of the reagent atoms.⁵ Due to their atom-sparing and single-step nature, these reactions are extremely valuable in medicinal chemistry.⁶ The Doebner reaction is one of the oldest known three-component reactions. It generates substituted cinchoninic acids (or quinoline-4-carboxylic acids) from anilines, aldehydes and pyruvic acids (Scheme 2a).⁷ Since its discovery in 1887, only one article has been published

Cyclocarboamination of alkynes (P.A. Wender, 2009)

Intramolecular Pd^{II}-catalyzed annulation (T.-P. Loh, 2017)

Cascade metallo-ene/Suzuki coupling reaction (H. Liu, 2017)

Rh-catalyzed condensation (M. Murakami, 2013)

Cascade [2+2] cycloaddition/rearrangement (E. Vedejs, 1988)

Cascade Michael addition/annulation (A. Lattanzi, 2015)

Scheme 1. Selected processes for the synthesis of 2,3-dihydropyrroles.

^a Sino-French Joint Lab of Food Nutrition/Safety and Medicinal Chemistry, China International Science and Technology Cooperation Base of Food Nutrition/Safety and Medicinal Chemistry, College of Biotechnology, Tianjin University of Science and Technology, Tianjin 300457, China. E-mail: desaubry@unistra.fr

^b Laboratory of Therapeutic Innovation (UMR 7200), University of Strasbourg-CNRS, Faculty of Pharmacy, 67400 Illkirch, France

^c Laboratory of Biomolecules (UMR7203), Sorbonne University-CNRS, 4 place Jussieu, 75005 Paris, France

† Electronic Supplementary Information (ESI) available: Detailed experimental procedures, compound characterization, and NMR spectra. See DOI: 10.1039/x0xx00000x

describing this reaction with a pyruvic amide. While the latter

a) Classical Doebner reaction

b) Doebner reaction using an immobilized pyruvic amide

c) This work: five bonds formed in one step, green synthesis, simple SM

Scheme 2. a) A classical Doebner reaction, b) The sole published example of the Doebner reaction performed with a pyruvic amide⁸ and c) The unexpected formation of dihydropyrroles during an attempt to perform the Doebner reaction with a pyruvic amide in solution.

was immobilized on a Rink polystyrene resin (Scheme 2b)⁸ the same reaction in solution has never been described to our knowledge.

Results and discussion

Unexpected divergent pathway of the Doebner reaction using a pyruvic amide instead of pyruvic acid

When we attempted to perform the Doebner reaction in solution, we were surprised to find that a 2,3-dihydropyrrole **4** was formed, rather than the expected cinchoninic amide (Scheme 2c). It seems likely that this reaction has been attempted during the last 130 years but the products obtained were probably discarded because they were difficult to identify. Indeed, we had to resort to X-ray crystallography to establish the structure of the product unambiguously. Given the originality of this reaction and its potential utility in both organic and medicinal chemistry, we decided to explore the scope and limitations of this novel three-component reaction.

In our initial study, *p*-anisidine (**1a**), *p*-tolualdehyde (**2a**) and pyruvic amide **3a** were used to optimize the reaction conditions. We found that the solvent and the concentration significantly influenced the outcome of the reaction (entries 1 to 7, Table 1). Ethanol was shown to be superior to isopropanol or trifluoroethanol. The pyruvic amide was not completely consumed, so additional *p*-anisidine was added, but this resulted in a lower yield (entry 4). The product yield (22%, entry 8) was similar in complete darkness, indicating that light has no effect on the reaction. We then investigated whether various acids could increase yields (entries 9 to 16).

PTSA, TFA and L-proline had deleterious effects, but a much higher reaction yield was obtained with acetic acid (entry 13).

Table 1. Reaction optimization for the three-component reaction.^a

Entry	Additive	M	Solvent	Yield (%)
1	N.A.	0.05	EtOH	14
2	N.A.	0.02	EtOH	22
3	N.A.	0.01	EtOH	n/r ^[b]
4 ^[c]	N.A.	0.02	EtOH	13
5	N.A.	0.02	<i>n</i> -PrOH	n/r
6	N.A.	0.02	<i>i</i> -PrOH	n/r
7	N.A.	0.02	CF ₃ CH ₂ OH	n/r
8 ^[d]	N.A.	0.02	EtOH	22
9	TFA (0.4 ml)	0.02	EtOH	n/r
10	PTSA (25 mg)	0.02	EtOH	n/r
11	proline (12 mg)	0.02	EtOH	n/r
12	AcOH (0.2 ml)	0.02	EtOH	32
13	AcOH (0.4 ml)	0.02	EtOH	51
14	AcOH (0.6 ml)	0.02	EtOH	40
15 ^[e]	AcOH (0.6 ml)	0.02	N.A.	27
16 ^[f]	AcOH (0.4 ml)	0.02	EtOH	n/r

^a Unless otherwise noted, all reactions were conducted at 0.025 M (*p*-anisidine concentration) with *p*-anisidine (1.0 equiv), *p*-tolualdehyde (2.0 equiv), and pyruvic amide (40 mg, 2.0 equiv) under reflux conditions. ^b No reaction. ^c Reaction run with *p*-anisidine (2.0 equiv), *p*-tolualdehyde (2.0 equiv), and pyruvic amide (40 mg, 2.0 equiv) under reflux conditions. ^d reaction run in the dark. ^e Reaction run in neat conditions. ^f Reaction run under microwave conditions, temperature: 100°C.

Running the reaction under neat or microwave conditions resulted in a large yield loss (entries 15 and 16). We therefore concluded that the best ratio of *p*-anisidine, *p*-tolualdehyde and **3a** for this three-component reaction was 1:2:2, in ethanol (0.025 M) containing HOAc ($V_{\text{EtOH}} : V_{\text{AcOH}} = 12:1$) under reflux (51%, entry 13). It is worth noting that only product **4a** having the *cis* configuration (as confirmed by NOE NMR experiments, see the Supplementary Information for details) was produced in this transformation.

(12:1) under reflux conditions.^a The reaction was done without any acetic acid.

Scheme 3. Substrate scope for the three-component reaction. Unless otherwise noted, all reactions were conducted at 0.025 M concentration with **1** (1.0 equiv), **2** (2.0 equiv), and **3** (100 mg, 2.0 equiv) in EtOH-AcOH

Reaction scope and limitation

Using our optimized reaction conditions, we tested various amines (**1**), aldehydes (**2**) and pyruvic amides (**3**) (Scheme 3). Dihydropyrroles **4** were obtained with modest to good yields and with excellent diastereoselectivity (*cis* methyl and hydrogen) in all cases. Yields were highest for the chlorine-containing aromatic pyruvic amides **4a-c**, whereas lower yields were obtained for the electron-rich or poor aromatic pyruvic amides, **4d-g**. On the other hand, this reaction was not effective with aliphatic pyruvic amides as the adducts **4h** and **4i** were not observed. We then assessed the reactivity of various amines. The replacement of anisidine **1a** with 4-benzyloxy- or 4-phenyl aniline was slightly deleterious (**4j**: 37%, **4k**: 26 %), and the less nucleophilic 4-chloroaniline did not generate the expected adduct **4l**. 1-Naphthylamine did not produce the adduct **4m**, indicating a sensitivity of this three-component reaction to steric hindrance. We found that *n*-butylamine efficiently yielded the expected product **4n** (51%), demonstrating the suitability of aliphatic amines for this reaction. Benzylamine gave rise to **4o**, but with a yield of only 28%, confirming the sensitivity to steric hindrance of the amine. We were able to crystallize **4o** and to confirm its structure by X-ray crystallography (Supplementary Information, part 4). For the aldehyde component **2**, chloro- and methoxy-benzaldehydes generated adducts **4p-u** with yields between 30% and 40%. Surprisingly, furfural gave rise to **4v** with a yield of only 19%, and all attempts to use cyclohexane carboxaldehyde were unsuccessful, suggesting that aliphatic aldehydes are not suitable for the production of cognate dihydropyrroles.

We extended the scope of this reaction by performing the reaction displayed in Scheme 3 with the addition of chalcone **5a** to the reaction medium (Scheme 4). The expected products, **4b** and **6a**, were generated in a 1:1 ratio. These findings demonstrate that an enone resulting from aldol condensation between the pyruvic amide and the aldehyde is, indeed, an intermediate in the synthesis of dihydropyrroles **4**. We also

Scheme 4. Competitive Condensation in Presence of Chalcone **5a**.

Figure 1. X-Ray structure of **6a**.

Scheme 5. Attempted condensation reactions with homopyruvic and phenylpyruvic amides **3j-l**.

crystallized **6a** and determined its structure unambiguously by X-ray crystallography (Figure 1).

Condensation of the sterically more demanding homopyruvic amide **3j** and **3k** with the chalcones **5b** and **5c** generated dihydropyrroles **6b** and **6c** respectively, but phenylpyruvic amide **3l** did not take part in this reaction, probably due to steric hindrance or to the requirement for an enolisable ketoamide (Scheme 5).

In order to obtain some insight into the reaction mechanism, we next examined whether Mannich base **7** could be an intermediate in the course of this reaction (Scheme 6). Heating together *p*-tolualdehyde, ketoamide **3a** and Mannich base **7** did not deliver the adduct **6e** but instead gave **4a**, probably via an elimination of 4-anisidine, with concomitant formation of chalcone **5c** and 4-anisidine, which were then engaged in the three-component reaction. This observation strongly suggests that Mannich bases, such as **7**, are not involved in the construction of the 2,3-dihydropyrroles.

Scheme 6. Attempted condensation reactions with Mannich base **7** to generate adduct **6e**.

Based on our observations, we speculate that the formation of **4** involves imine **8** and enone **5** which react together to afford intermediate **9** (Scheme 7). Condensation with aldehyde **2** could lead to the 1,3-oxazine **11**. Dehydration of this latter intermediate would then generate the iminium **12** which, upon deprotonation, affords the azomethine ylide **13** stabilized by π -stacking between

the Ar¹ and Ar² moieties. This hypothesis would explain the requirement for an aromatic unit in the ketoamide **3** and the

Scheme 7. Putative mechanism for the formation of dihydropyrroles **4**.

observed stereochemistry of the adduct **4**. The intramolecular dipolar cycloaddition of azomethine ylides to form pyrrolidines has been widely studied.¹⁰ This approach has found utility in simplifying synthetic strategies to complex bioactive compounds. For this intramolecular process, the dipolarophile has been tethered to one of the carbon atoms or to the nitrogen atom of the azomethine ylide (respectively type I or type II, Scheme 8). To the best of our knowledge, no cycloaddition between a dipole and a dipolarophile directly connected together without any tether has been reported yet.

Scheme 8. Classification of intramolecular dipolar cycloaddition of azomethine ylides based on their connectivity.¹⁰

To validate the proposed mechanism we explored the possibility of directly condensing imine **8** with allylic alcohol **14a** to directly generate intermediate **10a** (Scheme 9). This first experiment did not deliver the expected adduct **16a**, probably due to the insufficient electrophilic character of the ester. However, we were pleased to observe that replacement of this function by a nitro group successfully afforded the adduct **16b**, in 19% yield, indicating that **10a** is a likely intermediate in the mechanism. Going one

Scheme 9. Attempted condensation reactions with allylic alcohols **14** and pivalic ester **15**.

step further, we examined the pivalic ester **15** as a 1,3-nucleophile,¹¹ which also delivered the adduct **16b**, revealing that **11a** is also a probable intermediate. Furthermore, the aldol product **5** was isolated as a byproduct in the reaction. Altogether, these observations strongly support the mechanism proposed in Scheme 7.

The drug-like character of our 2,3-dihydropyrrole library prompted us to examine whether it could be screened in biological assays to identify new drug candidates. As a proof-of-concept and based on our ongoing interest in the development of α -glucosidase inhibitors,¹² we determined whether 2,3-dihydropyrroles could inhibit this enzyme. Indeed, α -glucosidase inhibitors, such as acarbose, are widely used to treat type II diabetes, even though these agents display poor bioavailability and some adverse effects, such as bloating, intestinal spasm, abdominal pains and hepatic dysfunctions.¹³ Thus, there is currently an urgent need to develop novel antidiabetic α -glucosidase inhibitors. The synthesized 2,3-dihydropyrroles were screened for the inhibition of α -glucosidase at the dose of 5 μ M and two hits, **4a** and **4u** were found to inhibit this enzyme. Kinetic constants were then determined and compared to the standard inhibitor, acarbose.

Figure 2. Lineweaver-Burk plot of the inhibition of α -glucosidase by **4a** (A) and **4u** (B). Activities were determined with 4-nitrophenyl α -D-glucopyranoside (pNGP) as a substrate.

Dihydropyrroles **4a** and **4u** were shown to be non-competitive inhibitors with K_i 's of 2.4 and 3.5 μ M, respectively (Figure 2), which blocked α -glucosidase more efficiently than the standard competitive inhibitor acarbose (K_i of 320 μ M, Supplementary Figure S4). This observation, associated with the drug-like character of **4a**, suggest that these hits represent promising lead compounds for the development of novel antidiabetic agents.

Conclusions

In conclusion, we have discovered a useful reactivity of α -ketoamides towards imines, generated in situ from amines and aromatic aldehydes. Ketoamides have previously been used in diverse multicomponent reactions¹⁴ but their reactivity in the present fashion has never to our knowledge been described. Remarkably, highly substituted dihydropyrroles were prepared in a single step, using three varied starting materials that are commercially available or easily accessible. Furthermore, the reaction was highly stereoselective, atom economic, and eco-friendly. To confirm its green chemistry character, we calculated that the atom economy and atom efficiency of the synthesis of **4a** are respectively of 92.9 and 47.4%.¹³ The reaction had only moderate overall yield but it was nevertheless remarkably effective given that it generated five new bonds (~90% average yield per bond formation). Further mechanistic and synthetic studies on this new three-

component reaction are underway. With the discovery that **4a** and **4u** potentially inhibit α -glucosidase, we have illustrated that this methodology is likely to prove very useful for the generation of drugs harbouring a new scaffold.

Conflicts of interest

There are no conflicts to declare.

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