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Sustainable Pathways to Pyrroles through Iron-Catalyzed *N*-Heterocyclization from Unsaturated Diols and Primary Amines

Tao Yan and Katalin Barta^{*[a]}

Pyrroles are prominent scaffolds in pharmaceutically active compounds and play an important role in medicinal chemistry. Therefore, the development of new, atom-economic, and sustainable catalytic strategies to obtain these moieties is highly desired. Direct catalytic pathways that utilize readily available alcohol substrates have been recently established; however, these approaches rely on the use of noble metals such as ruthenium or iridium. Here, we report on the direct synthesis of pyrroles using a catalyst based on the earth-abundant and inexpensive iron. The method uses 2-butyne-1,4-diol or 2-butene-1,4-diol that can be directly coupled with anilines, benzyl amines, and aliphatic amines to obtain a variety of *N*-substituted pyrroles in moderate-to-excellent isolated yields.

Pyrroles are important building blocks in medicinal chemistry^[1] and many pharmaceutically active compounds contain these moieties. For example, aloracetam^[2] was previously used in studies for treating Alzheimer's disease, isamoltane^[3] was shown to exhibit anxiolytic effects on rodents, and elopiprazole^[4] is an antipsychotic drug (Figure 1).

Owing to the importance of pyrroles, many classical synthetic pathways such as the Hantzsch,^[5] Knorr,^[6] and Paal-Knorr^[7] synthesis (Scheme 1 A) as well as related multicomponent reac-

tions^[8] have already been established. These stoichiometric routes however, may suffer from poor substrate accessibility, harsh reaction conditions, and multi-step syntheses leading to the formation of waste and low atom economy.^[9] Thus, the development of new catalytic methods to create the pyrrole scaffold efficiently is subject of intensive research.^[10] Several elegant approaches were recently reported that rely on the catalytic dehydrogenation of easily accessible alcohol substrates (Scheme 1 A) that are broadly related to the borrowing hydrogen strategy.^[11] In 2013, Beller and co-workers reported a ruthenium-catalyzed three-component pyrrole synthesis where secondary alcohols, diols, and primary alcohols were coupled in analogy to the classical Hantzsch synthesis.^[12] Michlik and Kempe achieved the direct iridium-catalyzed coupling of alcohols and amino alcohols to obtain pyrroles.^[13] Milstein and co-workers described a method to obtain pyrroles from similar substrates using ruthenium catalysts.^[14] In 2011, Schley et al. described the formation of pyrroles from 1,4-diols and amines.^[15] During the course of these reactions, the alcohol substrates undergo dehydrogenation to the corresponding carbonyl compounds, which further react with the amine to form the desired pyrrole product; the hydrogen equivalents borrowed from the alcohol substrate are concomitantly liberated from the catalyst.^[12–15]

In the studies by the groups of Watanabe^[16] and Williams^[17] it was shown that pyrroles can also be directly obtained from amines and unsaturated diols such as 2-butyne-1,4-diol using an appropriate ruthenium catalyst. In this case it was proposed that the reaction likely proceeds through an internal hydrogen-transfer isomerization to the corresponding dicarbonyl compounds that subsequently undergo pyrrole formation with an amine reaction partner.

Our group has previously established the first iron-catalyzed formation of pyrrolidines^[18] from amines and 1,4-butane-diol using Knölker's homogeneous iron catalyst (Scheme 1 B).^[19,20] Based on our previous results^[18,21] and the reports by the groups of Watanabe and Williams, we envisioned the possibility of the iron-catalyzed direct pyrrole formation starting from primary amines and unsaturated diols. A reactivity similar to the ruthenium-based systems was expected since the iron complex is capable of alcohol dehydrogenation as well as double bond hydrogenation (Scheme 2; see also Schemes S1 and S2 in the Supporting Information).

We started our investigation using 2-butyne-1,4-diol (**2a**) and 4-(*N,N*-dimethylamino)-aniline (**1a**) to establish the iron-catalyzed methodology towards pyrroles (Table 1). Similar to our previous works,^[18,21] **Cat 1** was selected as the precatalyst

Figure 1. Bioactive compounds containing pyrrole moieties.

[a] T. Yan, Dr. K. Barta
Stratingh Institute for Chemistry
University of Groningen
Nijenborgh 4, 9747 AG Groningen (Netherlands)
E-mail: k.barta@rug.nl

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Scheme 1. (A) Classical synthetic and “modern”, catalytic pathways to access pyrroles. (B) Iron-catalyzed direct synthesis of pyrrolidines and pyrroles from amines and diols.

Scheme 2. Possible pathways for pyrrole formation based on Ref. [16]. TMS = trimethylsilyl.

whereas Me₃NO was used to generate the catalytically active iron complex (Scheme 2, see also the Supporting Information, Schemes S3 and S4).

A variety of solvents were screened, and the reaction temperature varied between 110–130 °C. The first attempts at

Table 1. Establishing ideal reaction conditions to obtain *N*-(4-dimethylamino-phenyl)-pyrrole (**3a**) from 4-(*N,N*-dimethylamino)-aniline (**1a**) and 1,4-diols (**2a**, **2b**).^[a]

Entry	2	Solvent	T [°C]	Conv. 1a [%] ^[a]	Select. 3a [%] ^[b]
1	2a	THF	110	67	65
2	2a	dioxane	110	70	68
3	2a	CH ₃ CN	110	68	67
4	2a	DMF	110	67	66
5	2a	CMPE	110	71	69
6	2a	toluene	110	73	71
7	2a	toluene	130	> 99	98 (83)
8	2a	toluene	120	> 99	95 (76)
9	2b	toluene	110	94	44
10	2b	CPME	110	90	25
11	2b	toluene	120	> 99	63 (59)

[a] General reaction conditions: General procedure (see Supporting Information, page S2), 0.5 mmol **1a**, 1 mmol **2**, 0.02 mmol **Cat 1**, 0.04 mmol Me₃NO, 2 mL solvent, 18 h, 110–130 °C. [b] Based on GC-FID (FID = flame ionization detector), isolated yields shown in parentheses.

110 °C in the solvents tetrahydrofuran (THF), dioxane, acetonitrile (CH₃CN), and dimethylformamide (DMF) resulted in very similar conversion values of up to 70% and moderate product selectivities (Table 1, entries 1–4). Conversion of **1a** and product selectivity slightly improved in cyclopentyl methyl ether (CPME) and toluene at 110 °C (Table 1, entries 5 and 6).

The results could be further improved to full conversion of **1a** and near perfect selectivity to **3a** at 130 °C in toluene and a very good 83% isolated yield of **3a** was achieved (Table 1, entry 7).

Similarly, full conversion but slightly lower **3a** yield (76%) was obtained when the reaction was conducted at 120 °C (Table 1, entry 8).

After having established that diol **2a** can be successfully used as the substrate to form **3a**, we explored the use of *cis*-2-butene-1,4-diol (**2b**) as the starting material. Catalytic runs conducted using **2b** in toluene and CPME at 110 °C resulted in 94% and 90% conversion but only 44 and 25% selectivity to **3a**, respectively (Table 1, entries 9 and 10). At 120 °C, full conversion of **1a** and a good isolated yield of **3a** (59%) was obtained (Table 1, entry 11) without significant over-reduction to pyrrolidines.^[16] Therefore, **2b** can be regarded as alternative reaction partner to **2a** despite the slightly lower product yields obtained.

With the optimized reaction conditions in hand, a variety of anilines were tested (Table 2). Electron-rich 4-methoxy-aniline (**1b**) reacted smoothly with 2-butyne-1,4-diol (**2a**), leading to 80% isolated yield of **3b** (Table 2, entry 1). When 4-methyl-aniline (**1c**) was used as substrate, much lower conversion and 36% isolated yield of **3c** was obtained. Similar behavior was observed in the reaction of electron-poor 4-fluoro-aniline (**1d**) with 2-butyne-1,4-diol (**2a**), which yielded 30% of **3d** at 33% substrate conversion. Interestingly, in both of these cases almost full conversion and much higher product selectivity were achieved when *cis*-2-butene-1,4-diol was employed as coupling partner instead of **1a**, providing 59% and 47% isolated yields of **3c** and **3d**, respectively (Table 2, entries 2 and 3). According to these results, **2b** was selected for further reactions with 4-chloro-aniline (**1e**), 4-bromo-aniline (**1f**), and 3,4-(methenedioxy)-aniline (**1g**). In all these cases excellent substrate conversions and very good product selectivity was observed and the desired products **3e**, **3f**, and **3g** were obtained in 45%, 44%, and 37% isolated yields respectively, (Table 2, entries 4–6). It was also shown that product selectivity and isolated yields could be improved in the coupling of **1e** with 4 equivalents of diol **2b**. *Ortho*-substituted anilines (**1h–1j**) could also be successfully used whereby electron-donating substituents gave better product yields (Table 2, entries 7–9).

After aniline derivatives were converted to *N*-phenyl-pyrroles successfully, primary aliphatic amines were explored under standard reaction conditions using 2-butyne-1,4-diol (**2a**) as reaction partner. Interestingly, a series of benzyl amines with varying electronic properties all afforded full substrate conversions, excellent product selectivity, and good isolated yields of the desired *N*-benzylpyrroles. The coupling of benzylamine (**5a**) with **2a** lead to the formation of *N*-benzylpyrrole (**6a**) with 61% isolated yield (Table 3, entry 1). Similarly, good results

Table 2. Direct synthesis of *N*-substituted pyrroles from anilines and 1,4-diols.^[a]

Entry	Amine (1)	Alcohol (2)	Product (3)	Conv. 1 ^[b] [%]	Select. 3 ^[b] [%]
1	1b 	2a	3b	92	90 (80)
2	1c 	2a 2b	3c	42 > 99	– (36) 90 (59)
3	1d 	2a 2b	3d	33 91	– (30) 75 (47)
4	1e 	2b 2b ^[c]	3e	85 98	63 (45) 72 (54)
5	1f 	2b	3f	94	61 (44)
6	1g 	2b	3g	> 99	68 (37)
7	1h 	2b	3h	77	42 (36)
8	1i 	2b	2i	90	52 (25)
9	1j 	2b	2j	56	36 (15)

[a] General reaction conditions: General procedure (see Supporting Information, page S2), 0.5 mmol **1a**, 1 mmol **2a**, 0.02 mmol **Cat 1**, 0.04 mmol Me₃NO, 2 mL toluene, 18 h, 130 °C unless otherwise specified; see also Table S2. [b] Based on GC-FID, isolated yields shown in parentheses. [c] The reaction was operated in a sealed 20 mL vial with 4 equiv. **2b** in 22 h.

were obtained with a variety of halogenated benzyl amines such as 4-chloro-benzylamine (**5b**), 4-fluoro-benzylamine (**5c**), 3-trifluoromethyl-benzylamine (**5d**), and 3-fluoro-4-chloro-benzylamine (**5e**), which afforded the corresponding *N*-(4-chlorobenzyl)-pyrrole (**6b**), *N*-(4-fluorobenzyl)-pyrrole (**6c**), *N*-(3-trifluoromethylbenzyl)-pyrrole (**6d**), and *N*-(3-fluoro-4-chlorobenzyl)-pyrrole (**6e**) products in 57%, 52%, 55% and 65% isolated yields, respectively (Table 3, entries 2–5). With electron-rich benzylamines **5f** and **5g**, the desired *N*-(4-methylbenzyl)-pyrrole (**5f**) and *N*-piperonyl-pyrrole (**5g**) were obtained in good

Table 3. Direct synthesis of *N*-substituted pyrroles from anilines and 1,4-diols.^[a]

$\text{Alkyl-NH}_2 \text{ (5)} + \text{HO-CH}_2\text{-CH=CH-CH}_2\text{-OH (2a)} \xrightarrow[\text{18 h, toluene, 130 }^\circ\text{C}]{\text{Cat 1 4 mol \%}, \text{Me}_3\text{NO 8 mol \%}} \text{Alkyl-N-pyrrole (6)}$				
Entry	Amine (5)	Product (6)	Select. 3 ^[b] [%]	
1	5a	6a	90 (61)	
2	5b	6b	85 (57)	
3	5c	6c	73 (52)	
4	5d	6d	88 (55)	
5	5e	6e	87 (65)	
6	5f	6f	87 (65)	
7	5g	6g	83 (55)	
8	5h	6h	92 (76)	
9	5i	6i	71 (43)	
10	5j	6j	– (41)	
11	5k	6k	86 (42)	
12	5l	6l	85 (33)	

[a] General reaction conditions: General procedure (see Supporting Information, page S2), 0.5 mmol **5**, 1 mmol **2a**, 0.02 mmol **Cat 1**, 0.04 mmol Me₃NO, 2 mL toluene, 18 h, 130 °C; see also Table S3; in all cases full conversion was obtained. [b] Based on GC-FID, isolated yields shown in parentheses.

isolated yields (65% and 55%; Table 3, entries 6 and 7). Interestingly, even 3-picolylamine (**5h**) reacted smoothly with 2-butyne-1,4-diol (**2a**), forming *N*-(3-picolyl)pyrrole in 76% isolated yield, although pyridine is a potential ligand that may coordinate to iron^[22] (Table 3, entry 8). Product *N*-furfuryl-pyrrole (**6i**), which was already proposed as food additive,^[23] was obtained in 43% yield from furfurylamine (**5i**) (Table 3, entry 9). For other aliphatic amines such as 2-phenylethylamine (**5g**) and dodecylamine (**5k**), the corresponding pyrrole products were obtained in 41% and 42% isolated yield (Table 3, entries 10 and 11). Cyclohexylamine (**5l**) reacted with **2a**, providing *N*-cyclohexylpyrrole (**6l**) in 33% yield (Table 3, entry 12).

To summarize the results in Tables 1, 2, and 3 discussed above, generally good-to-excellent substrate conversions were seen. Similarly, product selectivity was good to excellent based on GC-FID and GC-MS measurements, albeit the isolated product yields were lower. This may be an indication of side reactions involving species not detectable by these GC measure-

ments. Indeed, gel permeation chromatography (GPC) measurements of the crude product mixture confirmed the presence of oligomeric side products for a typical run with 2-butyne-1,4-diol and benzylamine (Supporting Information, Scheme S5) in the broad molecular weight (*M_w*) range of 300–5000 g mol^{−1}. In addition, when **2a** alone was subjected to standard catalytic conditions, full substrate conversion was observed alongside the formation of a black precipitate and no volatiles were detected by GC measurement (Supporting Information, Table S3, entry 3). Furthermore, GPC measurement confirmed the formation of oligomeric side products (Supporting Information, Scheme S6). Thus, the most likely source of such competing side reactions is the isomerization of substrate **2a** to the corresponding α,β-unsaturated aldehyde as shown in Scheme 2 and Schemes S1 and S2 in the Supporting Information.

Other reaction pathways such as the formation of secondary or tertiary amines that may be a result of over-alkylation and imine reduction were not observed, indicating the preference for intramolecular pyrrole formation. Also, the corresponding pyrrolidine analogues were only sparingly observed when **2b** was used as substrate. More mechanistic and spectroscopic insights are required to understand the sequence of reaction steps occurring. This will lead to improvement of product yields. Future research should also address a broader substrate scope, especially different substitution patterns on the pyrrole ring.

In conclusion, herein we describe the first iron-catalyzed direct method for the catalytic formation of pyrroles by coupling of unsaturated diols with primary amines. The work presented herein is aimed to be a proof-of-principle rather than a methodology study. Nonetheless, various derivatives of anilines and benzyl amines as well as other aliphatic primary amines were successfully used in the construction of pyrrole moieties, which are important scaffolds in medicinal chemistry. The desired product yields range from high to moderate and future studies will address further mechanistic details of this interesting transformation. The presented catalytic strategy is direct, straightforward, and allows the use of a wide range of amines. Notably, this new catalytic method relies on the use of an inexpensive and abundant homogeneous catalyst for the construction of scaffolds that are highly relevant in the pharmaceutical industry.

Experimental Section

Representative procedures—synthesis of 3a from 4-(*N,N*-dimethylamino)-aniline (1a) and 2-butyne-1,4-diol (2a). An oven-dried 20 mL Schlenk tube, equipped with stirring bar, was charged with 4-(*N,N*-dimethylamino)-aniline (0.5 mmol, 0.068 g), 2-butyne-1,4-diol (1 mmol, 0.086 g), iron complex **Cat 1** (4 mol %, 8 mg), and Me₃NO (8 mol %, 3 mg) under air. Then, the Schlenk tube was subsequently connected to an argon line and a vacuum–argon exchange was performed three times. Toluene (solvent, 2 mL) was charged under an argon stream. The Schlenk tube was capped, the mixture was rapidly stirred at room temperature for 1 min, and then placed into a preheated oil bath at 130 °C and stirred for 18 h. The reaction mixture was cooled to room temperature and

the crude mixture was filtered through Celite, eluted with ethyl acetate, and concentrated in vacuo. The residue was purified by flash column chromatography (SiO₂, Pentane/EtOAc 95:5 to 80:20) to provide the pure amine product **3a** (0.077 g, 83% isolated yield). For characterization see the Supporting Information, Pages S9 and S16.

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