

Methanol as a C1 Source for the Synthesis of 1,3-Polyheterocyclic Systems

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A very attractive approach toward 1,3-polyheterocyclic systems was provided exploiting the copper-catalyzed reaction of aminoalcohols and diaminoalkanes, in oxidative conditions and in the presence of methanol. The synthetic pathway showed

the involvement of methanol both as solvent and as a reagent, making the procedure particularly efficient and sustainable for the synthesis of five-, six-, and seven-membered polyheterocyclic rings.

Introduction

The research for sustainable processes devoted to the efficient heterocyclic synthesis continues to be an important goal of chemical investigations.^[1] In this context, methanol constitutes an interesting chemical subject able to perform in different roles: as source of raw material for chemicals, as energy carrier or as a convenient energy-storage material. In recent years, Olah recognized the wide applications of this small molecule, envisioning the so-called 'methanol economy'.^[2] In synthetic chemistry, methanol is often employed as solvent, but it can also act as proelectrophile in the presence of nucleophilic atoms. These features strongly intensified the development of new procedure involving methanol as reagent, also in formation of heterocycles. Recently, methanol has emerged as "green precursor" and "renewable" C1 source and has been considered to be a viable alternative compared to traditional reagents in different reactions typologies, in organic synthesis and drug discovery.^[3] In particular, methanol has been used as a C1 source in the C-methylation,^[4] N-methylation,^[5] C-methoxylation,^[6] N-formylation,^[7] and aminomethylation.^[8] To the best of our knowledge, the use of methanol as carbon source in heterocyclic synthesis was reported only on aromatic substrates such as quinazoline derivatives^[9] and benzimidazoles.^[10] In

particular, considering the copper-catalyzed reactions, *o*-carbonyl-substituted anilines were employed as substrates in the presence of ammonium acetate to provide quinazolines (Scheme 1, eq. 1)^[9a] and 1,2-diaminobenzenes were reacted in oxidative conditions in supercritical methanol over copper-doped porous metal oxide (Scheme 1, eq. 2)^[10c] to afford benzimidazoles through diamination processes. The literature reports the use of benzyl alcohols to obtain quinazolines and benzoxazoles using 2-aminobenzonitriles or *N*-arylamidines under copper catalysis^[9b,e] and 2-aminophenols under manganese heterogeneous catalyst, respectively.^[10a] Moreover, the use of paraformaldehyde as C1 source and β -amino alcohols in alkaline conditions has also been reported, affording 1,3-oxazolidines.^[11]

On the other hand, the ability to choose alternative synthetic pathways, instead of the well-established methods, is a significant task for both academic research and industrial production. It is, in fact, prerogative of the principles of the Green Chemistry the aim to avoid hazardous reagents and to minimize the waste generation through the use of inexpensive, nontoxic and readily available reagents and solvents. As well, among these principles, the catalysis plays an important role

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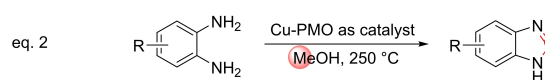
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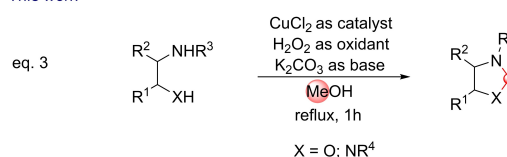
Ilangovan, *Org. Biomol. Chem.* **2019** ^[9a]



Barta, *Green Chem.* **2015** ^[10c]



This work



Scheme 1. Use of methanol and catalytic conditions for the synthesis of heterocycles: previous works and present work.

and the use of copper catalysts can be considered an added value, due to the low cost of the metal, the tolerance toward many reactive functional groups and the ease of processes, not requiring anaerobic and anhydrous conditions.^[12]

Devoting continuous interest in copper-catalyzed synthetic processes in oxidative conditions,^[13] our goal was to exploit the methanol as sustainable C1 building blocks to achieve 1,3-polyheterocyclic systems, under inexpensive catalytic conditions.

Starting from aminoalcohols and diaminoalkanes, the present work describes a novel copper-catalyzed aminoalkoxylation and diamination processes, as a very efficient procedure to access 1,3-polyheterocyclic systems (Scheme 1, eq. 3). The reaction of the 2- and 3-amino alcohols and 1,2-, 1,3-, 1,4- and 1,5-diaminoalkanes under copper catalysis in oxidative conditions, in methanol and in the presence of a base, affords 1,3-oxaza- and 1,3-diaza-heterorings of different size, from 5 to 7 members.

Results and Discussion

We used (*R*)-*N*-benzyl-2-amino-3-methylbutan-1-ol (**1a**) as model substrate to set up the best reaction conditions to obtain the cyclization process. A preliminary experiment performed with CuCl₂ as catalyst, H₂O₂ as the green oxidizing agent^[14] in methanol furnished the *N*-benzyl-oxazolidine **2a** in 48% yield (Table 1, entry 1). The addition of K₂CO₃ to the same reaction conditions afforded **2a** in 94% yield (Table 1, entry 2). H₂O₂ was proven to be the most effective oxidant compared with TBHP and PhI(OAc)₂, since they provided the expected product in 76 and 79% yields, respectively (Table 1, entries 3 and 4). Using 1,4-benzoquinone or activated MnO₂ resulted only in a complex

mixture of degradation products (Table 1, entries 5–6). Among other types of copper catalysts, CuBr₂ was unable to promote the reaction, while Cu(OTf)₂ led to the oxazolidine product **2a** in 82% yield (Table 1, entry 8). The Cu-catalyst is essential for the conversion of **1a**, in fact only starting material was observed in its absence (Table 1, entry 9). Finally, we sought hints on the feasibility of the oxazolidine nucleus with alcohols other than methanol, but the use of ethanol or propanol afforded unreacted starting material or a complex mixture of degradation products (Table 1, entries 10 and 11).

Having selected the best reaction conditions to convert the aminoalcohol **1a** in the *N*-benzyl-oxazolidine **2a** based on the activity of CuCl₂ catalyst, without the need for ligands, in the presence of H₂O₂ and K₂CO₃ with methanol in the double role of reagent and solvent, we examined the behaviour of differently substituted aminoalcohols (Scheme 2).

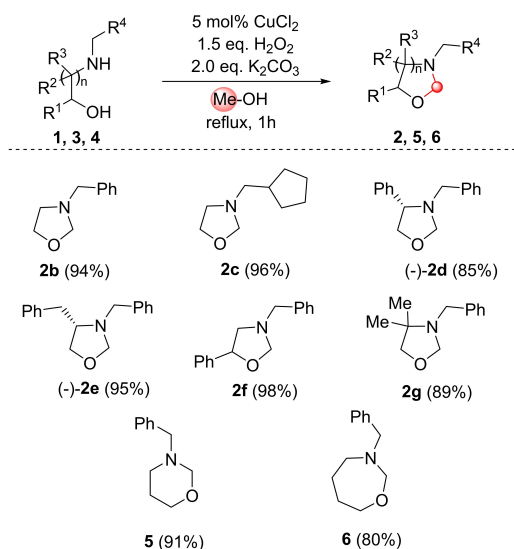
The study indicated that the success of this cyclization depended on the typology of the substituents. The nitrogen must be substituted with benzyl or alkyl groups. The presence of electron-withdrawing groups, such as tosyl or *t*-butoxycarbonyl, on the nitrogen atom as well as electron withdrawing substituent on the benzyl group (such as 3-nitrobenzyl) hampered the reaction. Carboxylic acids and primary amides didn't react as nucleophiles. In the case of chiral substrates **1a,d,e** the reaction occurs with retention of configuration. In the case of substrates **1b,d-f** affording the products reported in literature, the comparison with the reported methodologies, showed a more convenient procedure of the present strategy.^[15–17]

The reactions proceeded successfully also on substrate of different chain length, as *N*-benzyl-3-aminopropanol **3** and *N*-benzyl-4-amino-butanol **4** obtaining products **5**^[18] and **6** in very satisfactory yields.

Table 1. Amination/alkoxylation of (*R*)-*N*-benzyl-2-amino-3-methylbutan-1-ol **1a**.^[a]

entry	Catalyst ^[a]	Oxidant	Solvent	Product (% yield) ^[b]
1 ^[c]	CuCl ₂	H ₂ O ₂ ^[d]	MeOH	2a (48)
2	CuCl ₂	H ₂ O ₂ ^[d]	MeOH	2a (94)
3	CuCl ₂	TBHP	MeOH	2a (76)
4	CuCl ₂	PhI(OAc) ₂	MeOH	2a (79)
5	CuCl ₂	BQ	MeOH	Degradation products
6	CuCl ₂	MnO ₂	MeOH	Degradation products
7	CuBr ₂	H ₂ O ₂ ^[d]	MeOH	Degradation products
8	Cu(OTf) ₂	H ₂ O ₂ ^[d]	MeOH	2a (82)
9	–	H ₂ O ₂ ^[d]	MeOH	S.M.
10	CuCl ₂	H ₂ O ₂ ^[d]	EtOH	S.M. + degradation products
11	CuCl ₂	H ₂ O ₂ ^[d]	PrOH	S.M. + degradation products

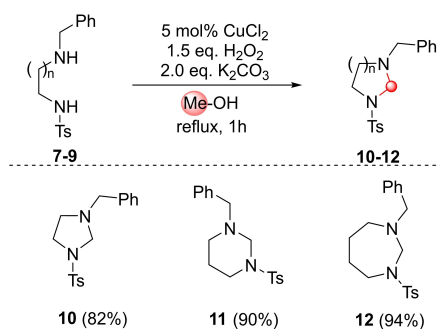
[a] Conditions: **1a** (1.0 mmol), copper catalyst (0.05 mmol), oxidant agent (1.5 mmol), K₂CO₃ (2.0 mmol), alcohol (0.1 M), reflux for 1 h in oil bath. [b] Isolated yield. [c] Reaction performed in the absence of K₂CO₃. [d] H₂O₂ (30% in water).



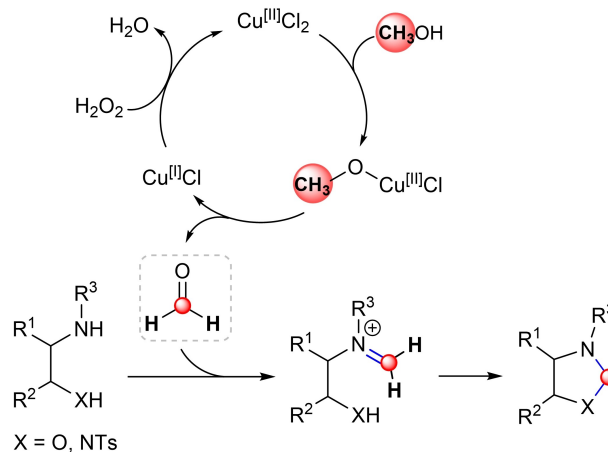
Scheme 2. Reaction performed with different aminoalcohols. Reaction conditions: substrate (1.0 mmol), CuCl₂ (0.05 mmol), H₂O₂ (1.5 mmol), K₂CO₃ (2.0 mmol), methanol (0.1 M), reflux for 1 h in oil bath.

To expand the substrate scope we tested the reaction on the *N*-benzyl-*N'*-tosyl-ethane-1,2-diamine **7**, which is structurally analogous to aminoalcohol, with the formation of 1-benzylimidazolidine in very good yields (Scheme 3). We subsequently examined the reaction on *N*-benzyl-*N'*-tosyl-propane-1,3-diamine **8** and *N*-benzyl-*N'*-tosyl-butane-1,4-diamine **9** obtaining *N*-benzyl-*N'*-tosylhexahydropyrimidine **11** and *N*-benzyl-*N'*-tosyl-1,3-diazepane **12** in almost quantitative yields.

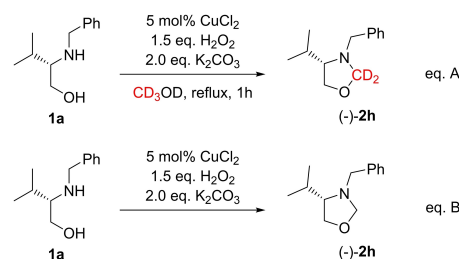
A plausible mechanism, depicted in Scheme 4. The key step is the oxidation of methanol to formaldehyde, which occurs through the formation of a Cu-methanolate complex and contemporary formation of a Cu(I) species.^[9a-e,19] The catalyst is reported to the original oxidation state by hydrogen peroxide. In the subsequent step, the formaldehyde provides the iminium ion intermediate able to undergo intramolecular nucleophilic attack with the formation of the cyclic product. Control experiments carried out upon addition of TEMPO rule out the intervention of a possible Cu(II)-hydroperoxo intermediate.^[20]



Scheme 3. Reaction performed with different diamines. Reaction conditions: substrate (1.0 mmol), CuCl₂ (0.05 mmol), H₂O₂ (1.5 mmol), K₂CO₃ (2.0 mmol), methanol (0.1 M), reflux for 1 h in oil bath.



Scheme 4. Proposed catalytic cycle.



Scheme 5. Reaction of **1a** with CD₃OD.

To confirm the supposed mechanism, the reaction on the substrate **1a** was performed using CD₃OD, which gave **2h** with complete deuteration at the 2-position of the *N*-benzyl-oxazolidine, preventing the observation of this methylene signal in the ¹H-NMR spectrum (Scheme 5, eq. A). The practical utility of this procedure was further demonstrated by performing a gram-scale reaction on substrate **1a**, which provided product **2a** in quantitative yield (Scheme 5, eq. B).

Conclusions

In summary, we have developed a simple, efficient and low-cost procedure for the synthesis of 1,3-polyheterocyclic systems, starting from the easily accessible aminoalcohols or diaminoalkanes, using CuCl₂ as catalyst, H₂O₂ as inexpensive oxidant agent, and methanol acting both as solvent and reagent, proceeding under mild conditions. Wide range of different heterocycles, especially 5-membered ones, could be accessed.

The use of methanol as starting material instead of the corresponding aldehyde and Cu(II)/H₂O₂ as green oxidant makes this procedure particularly attractive.

Experimental Section

General Information: Chemicals were purchased from Sigma Aldrich and FluoroChem and used without any further purification. IR spectra were measured with a Jasco FT/IR 5300 spectrometer.

Nuclear Magnetic Resonance Spectroscopy (NMR): ^1H NMR and ^{13}C NMR in open capillary tubes. NMR spectra were recorded with: AVANCE 400 Bruker spectrometer at 400 and 100 MHz, Varian Oxford 300 MHz spectrometer at 300 and 75 MHz and AVANCE 500 Bruker spectrometer at 500 and 125 MHz, respectively. Chemical shifts are given as δ values in ppm relative to residual solvent peaks (CHCl_3) as the internal reference, and the coupling constants J are reported in Hertz (Hz). ^{13}C NMR spectra are ^1H -decoupled and the determination of the multiplicities was achieved by the APT pulse sequence or by HSQC 2D NMR.

Melting points were determined by the capillary method with a Büchi B-540 apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 343 polarimeter at 20° C (concentration in g/100 mL). Elemental analyses were executed on Perkin-Elmer CHN Analyzer Series II 2400.

General procedure for the preparation of 1 a-g, 3, 4, 7-9: To a solution of aminoalcohol/diamine (10 mmol) in MeOH (0.1 M) was added the corresponding aldehyde (10 mmol). The reaction was stirred overnight at room temperature. The solution was then cooled to 0°C and then NaBH_4 (5 mmol) was added portionwise. The resulting solution was stirred at room temperature for 1 h. After the addition of water (30 mL), the solvent was removed under reduced pressure and the resulting phase was extracted with ethyl acetate (3 x 20 mL). The combined extracts were dried over Na_2SO_4 and concentrated in vacuo to give the desired product in quantitative yield. For the characterization, the product was purified by silica gel column chromatography.

General procedure for the preparation of compounds 2 a-h, 5, 6, 10-12: To a solution of the appropriate substrate (1 mmol) in MeOH (0.1 M) were added the CuCl_2 (5 mol%), the H_2O_2 (1.5 mmol) and the K_2CO_3 (2 mmol). The reaction was stirred at reflux for 1 h. The solvent was removed under reduced pressure, the resulting mixture was diluted with NH_4Cl saturated solution (20 mL) and extracted with ethyl acetate (2x20 mL). The combined extracts were dried over Na_2SO_4 , filtered and the solvent removed under reduced pressure. The residue was purified by silica gel FCC (see S.I.).

Gram-scale synthesis for the preparation of 2 a: To a solution of aminoalcohol 1 a (15 mmol) in methanol (0.1 M) was added H_2O_2 (30% aq.), K_2CO_3 (30 mmol) and CuCl_2 (5 mol%). The reaction was stirred at reflux for 1 h. The solvent was removed under reduced pressure, the resulting mixture was diluted with NH_4Cl (50 mL) and extracted with ethyl acetate (3x20 mL). The combined extracts were dried over Na_2SO_4 , filtered and the solvent removed under reduced pressure to give the desired product in quantitative yield without further purification.

Supporting Information

Additional references cited within the Supporting information [21–28].

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: copper-catalysis · hydrogen peroxide · methanol · oxidative conditions · 1,3-polyheterocycles

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