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PRELIMINARY EVALUATION OF A RECYCLABLE COPPER(I) IODIDE/[BMIM][BF_4] CATALYTIC SYSTEM FOR THE SYNTHESIS OF *N*-BENZYL 17-SPIRO-5'-OXAZOLIDIN-2'-ONES WITH THE ESTRANE SKELETON

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Three new steroidal oxazolidinones were synthesized starting from 17α-ethynylestradiol, benzylic amines and CO_2 using CuI as a catalyst. The ionic liquid solvent [BMIM][BF_4] made it possible to recycle the catalyst ionic liquid mixture with only a slight loss of catalytic activity.

Keywords: steroid, carbon dioxide, oxazolidinone, ionic liquid, catalysis

1. Introduction

Several applications of both steroidal drugs and relatively simple heterocyclic compounds are found in the pharmaceutical industry, so the incorporation of the two components into a single molecule might lead to hybrids with advantageous biological properties [1]-[3]. Among them, steroidal spiro-heterocycles exhibit a wide range of biological effects, including antifungal, antimicrobial, antimalarial and antiproliferative activities [4]. Some compounds inhibit 17β-hydroxysteroid dehydrogenases so they can be utilized in the treatment of hormone-dependent cancers [5]. The most well-known steroidal drug incorporating a spiro-heterocycle is spironolactone prescribed as a diuretic [6].

Estranes and androstanes with spiro-oxazolidinone moieties in position C3 or C17 exhibited anti-androgenic [7], 17β-hydroxysteroid dehydrogenase type 3 (17β-HSD3) inhibitory [5] and antiproliferative effects [8]. Synthetic routes towards these derivatives [4] follow the classical, multistep pathways developed for simpler derivatives often using toxic reagents, including the reactions of steroidal aminoalcohols with triphosgene [5,8,9] or diethyl carbonate [7], epoxides with carbamates [7], 17α-hydroxy-17-carboxylic acids with 1,3-dicyclohexylcarbodiimide [10], steroidal imidates with methyl chlorocarbonate [11] or 17-ethynyl-17-hydroxy steroids with alkyl isocyanates [12]. Some methods necessitate the application of strong bases like alkali alkoxides [7].

Recently, much attention has been paid to the development of synthetic methodologies towards the use of the abundant, low-cost and safe raw material CO_2 as a C1 building block for the construction of organic molecules [13]-[15]. These methods include several pathways towards 2-oxazolidinones starting from unsaturated (propargylic, allylic, allenic) amines [16], aziridines [17], amino alcohols [18] and propargylic alcohols together with primary amines [19]. A great variety of catalysts were tested for the latter reaction, including metal salts, -complexes or -nanoparticles (Ru [20], Cu [21]-[25], Ag [23,26-28] or Zn [29]) and organocatalysts [30]-[33]. These procedures usually require high pressure CO_2 (often exceeding 5 MPa). To the best of our knowledge, these methodologies have yet to be applied for the synthesis of steroidal oxazolidinones.

Based on our previous experience concerning the application of ionic liquids as solvents and/or catalysts for the conversion of steroidal substrates [34]-[37] and the fact that Cu(I) is known to be a highly suitable catalyst for the activation of the C≡C triple bond [38]-[40], the possibility of using a Cu(I)/[BMIM][BF_4] catalytic system was explored, previously only reported for simple molecules [21], to produce 17-spiro-5'-oxazolidin-2'-ones with the estrane skeleton from the

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readily available 17α-ethynylestradiol, a well-known synthetic hormone that exhibits estrogenic activity.

2. Experimental

2.1. General analytical methods

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in $CDCl_3$ by a Bruker Avance II spectrometer at 400.13 MHz and 100.62 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to $CHCl_3$ (7.26 ppm (^{1}H) and 77.00 ppm (^{13}C)). ESI-MS spectra were obtained using a Sciex 3200 Q TRAP MS/MS mass spectrometer (AB Sciex LLC, Marlborough, USA) in the positive electrospray ionization mode. All reactions were monitored by thin layer chromatography on Merck neutral aluminum oxide (TLC, UV254 nm) plates. TLC visualization was accomplished in an iodine chamber. Column chromatography was carried out on aluminum oxide (40-300 µm, 60A, neutral, Brockmann I, Thermo Scientific Chemicals). The copper leaching was evaluated by ICP-OES.

2.2. Materials

All reagents were purchased from Sigma-Aldrich. The copper complex with 3-(carboxymethyl)-1-methyl-1H-imidazol-3-ium ligands (**CuL_2**) was synthesized by a known method [41] and its spectroscopic properties corresponded well to data found in the literature. The steroid required for the synthesis was provided by the Chemical Works of Gedeon Richter Plc.

2.3. General procedures for the synthesis of steroidal oxazolidinones

In a typical experiment, the catalyst (0.010 mmol) was placed in a stainless-steel autoclave. The steroid (0.17 mmol), amine (0.17 or 0.34 mmol) and [BMIM][BF_4] were transferred into it. The autoclave was charged with carbon dioxide (0.5-4.0 MPa) and heated while stirred in an oil bath at 120 °C for 24 hours. After having been cooled to room temperature, the product was extracted with diethyl ether (5x3 ml) from the ionic liquid containing the catalyst that was reused after ether residues had been removed under vacuum. The reaction mixtures were analyzed by ^{1}H NMR measurements.

The products were purified by column chromatography (Al_2O_3, toluene/MeOH, 10:1).

2.4. Characterization of the products

(17S)-3'-benzyl-4'-methylene-2'-oxo-spiro[3-hydroxyestra-1,3,5(10)-trien-17,5'-oxazolidine] ***(3a)***

^{1}H-NMR ($CDCl_3$, 400.13 MHz) δ_H: 7.37-7.27 (5H, m, N-CH_2-*Ar*); 7.08 (1H, d, *J*=8.4 Hz, 1-H); 6.61 (1H, dd, *J*=2.6 Hz; 8.4 Hz, H-2); 6.55 (1H, d, *J*=2.6 Hz, 4-H); 4.85-4.93 (1H, brs, OH); 4.82 (1H, d, *J*=15.7 Hz, N-C$H_{2,a}$-Ar); 4.47 (1H, d, *J*=15.7 Hz, N-C$H_{2,b}$-Ar); 4.24 (1H, d, *J*=2.9 Hz, C=C$H_{2,a}$); 4.08 (1H, d, *J*=2.9 Hz, C=C$H_{2,b}$); 2.87-2.77 (2H, m, 6-H_2); 2.45-2.38 (1H, m, 11-$H_α$); 2.19-1.22 (12H, m, ring protons); 1.02 (3H, s, 18-H_3). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.62 MHz) δ_C: 156.5; 153.7; 149.7; 138.1; 135.5; 132.2; 128.8 (2C); 127.9; 127.6 (2C); 126.6; 115.4; 112.9; 94.9; 84.4; 48.4; 48.2; 45.5; 43.4; 39.0; 35.5; 31.3; 29.7; 27.5; 26.1; 23.1; 15.1.

ESI-MS: **[M+H]$^+$**: 431.00 m/z, Calculated molecular mass: 429.97 Da. R_f: 0.51 (Al_2O_3, toluene/MeOH, 10:1), white powder. Yield: 80%.

(17S)-3'-(4-methylbenzyl)-4'-methylene-2'-oxo-spiro[3-hydroxyestra- 1,3,5(10)-trien-17,5'-oxazolidine] ***(3b)***

^{1}H-NMR ($CDCl_3$, 400.13 MHz) δ_H: 7.24-7.16 (4H, m, N-CH_2-*Ar*); 7.09 (1H, d, *J*=8.6 Hz, 1-H); 6.69 (1H, dd, *J*=2.7 Hz; 8.6 Hz, H-2); 6.63 (1H, d, *J*=2.7 Hz, 4-H); 6.42-6.59 (1H, brs, OH); 4.82 (1H, d, *J*=15.8 Hz, N-C$H_{2,a}$-Ar); 4.47 (1H, d, *J*=15.8 Hz, N-C$H_{2,b}$-Ar); 4.32 (1H, d, *J*=2.9 Hz, C=C$H_{2,a}$); 4.15 (1H, d, *J*=2.9 Hz, C=C$H_{2,b}$); 2.78-2.86 (2H, m, 6-H_2); 2.37-2.48 (1H, 11-$H_α$); 2.39 (3H, s, 4'-Me); 2.24-1.29 (12H, m, ring protons); 1.03 (3H, s, 18-H_3). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.62 MHz) δ_C: 156.8; 154.1; 149.4; 137.8; 137.4; 132.2; 131.5; 129.4 (2C); 127.4 (2C); 126.3; 115.4; 113.0; 95.0; 84.8; 48.3; 48.0; 45.1; 43.3; 38.9; 35.4; 31.2; 29.5; 27.4; 26.0; 23.0; 21.2; 15.0.

ESI-MS: **[M+H]$^+$**: 445.40 m/z, Calculated molecular mass: 443.85 Da. R_f: 0.48 (Al_2O_3, toluene/MeOH, 10:1), white powder. Yield: 79%.

(17S)-4'-methylene-2'-oxo-3'-(4-trifluoromethylbenzyl)-spiro[3-hydroxyestra-1,3,5(10)-trien-17,5'-oxazolidine] ***(3c)***

^{1}H-NMR ($CDCl_3$, 400.13 MHz) δ_H: 7.62-7.66 (2H, m, H3', H5'); 7.39-7.45 (2H, m, H2', H6'); 7.08 (1H, d, *J*=8.3 Hz, H-1); 6.66 (1H, dd, *J*=3.0 Hz; 8.3 Hz, H-2); 6.60 (1H, d, *J*=3.0 Hz, 4-H); 6.08-6.26 (1H, brs, OH); 4.87 (1H, d, *J*=16.1 Hz, N-C$H_{2,a}$-Ar); 4.56 (1H, d, *J*=16.1 Hz, N-C$H_{2,b}$-Ar); 4.24 (1H, d, *J*=3.2 Hz, C=C$H_{2,a}$); 4.17 (1H, d, *J*=3.2 Hz, C=C$H_{2,b}$); 2.73-2.91 (2H, m, 6-H_2); 2.41-2.51 (1H, m, 11-$H_α$); 1.23-2.26 (12H, m, ring protons); 1.03 (3H, s, 18-CH_3). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.62 MHz) δ_C: 156.6; 154.0; 149.4; 139.4 (q, *J*=1.1 Hz); 137.8; 131.6; 130.2 (q, *J*=32.0 Hz); 127.7 (2C); 126.4; 125.8 (2C, q, *J*=3.7 Hz); 124.1 (q, *J*=272.1 Hz); 115.4; 113.0; 95.3; 84.8; 48.4; 48.2; 45.0; 43.3; 38.9; 35.5; 31.3; 29.6; 27.5; 26.0; 23.1; 15.0.

ESI-MS: **[M+H]$^+$**: 499.00 m/z, Calculated molecular mass: 498.00 Da. R_f: 0.54 (Al_2O_3, toluene/MeOH, 10:1), white powder. Yield: 67%.

3. Results and discussion

First, 17α-ethynylestradiol (**1**) reacted with benzylamine (**2a**) (*Figure 1*) in the presence of CuCl (*Table 1, entry 1*) and CuI (*Table 1, entry 2*) in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) at high pressure (4.0 MPa). The reaction mixture was

Table 1: Carboxylative cyclization of steroid **1** and benzylamine (**2a**) in the presence of different Cu catalysts[a]

Entry	Amine (**2**)	Catalyst	Pressure (MPa)	Yield of **3** (%)[b]
1	2a	CuCl	4.0	75
2	2a	CuI	4.0	>98
3	2a	CuI	2.0	93
4	2a	CuI	1.5	80
5	2a	CuI	1.0	71
6	2a	CuI	0.5	53
7	2a[c]	CuI	2.0	98
8	2a	$Cu(OAc)_2$	2.0	61
9	2a[c]	$Cu(OAc)_2$	2.0	85
10	2a[c]	$Cu(OAc)_2$	1.0	80
11	2a[c]	$Cu(OAc)_2$	0.5	41
12	2a	CuL_2[d]	2.0	68

[a]: Reaction conditions: 0.17 mmol **1**, 0.17 mmol **2a**, 0.010 mmol catalyst, 0.017 mmol base, 170 µl [BMIM][BF_4], 24 h, 393 K
[b]: determined by NMR based on the ratio of the integral areas of one of the exomethylene protons and that of aromatic protons H2 and H4
[c]: 0.34 mmol **2a**; [d]: L=3-(carboxymethyl)-1-methyl-1H-imidazol-3-ium tetrafluoroborate

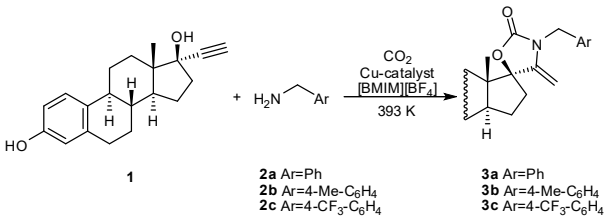
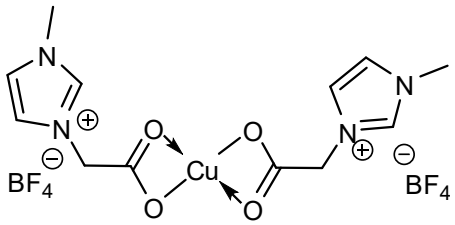


Figure 1: Reaction of 17α-ethynylestradiol (**1**) with benzylic amines and CO_2 in the presence of Cu catalysts in [BMIM][BF_4]



CuL_2 (**4**)

Figure 2: Structure of the CuL_2 catalyst (**4**)

extracted with diethyl ether then analyzed by TLC and, after the solvent had been removed, with ^{1}H NMR.

Interestingly, in contrast to the reaction of 1-ethynyl-1-cyclohexanol with cyclohexylamine reported [21], CuI was found to be a superior catalyst compared to CuCl, so further carboxylation reactions were carried out using the former one. The following experiments were performed under lower pressure to determine the mildest conditions appropriate for the synthesis of steroidal oxazolidinones. Although the yield of product **3a** decreased considerably when the pressure was reduced (*Table 1, entries 3-6*), a 53% yield could be achieved even at 0.5 MPa (*Table 1, entry 6*). In comparison, Gu et al. [21] found that the yield of the simple oxazolidinone product dropped from 92 to 9% when the CO_2 pressure was changed from 2.5 to 1.5 MPa, but these experiments were carried out at 373 K for 10h. A slightly better yield could be achieved when the amount of the amine reaction partner (**2a**) was doubled (*Table 1, entry 7*).

The possible use of Cu(II) catalyst precursors was also tested (*Table 1, entries 8-12*). Although $Cu(OAc)_2$ turned out to be a less effective catalyst than CuI (*Table 1, entry 8*), the addition of excess benzylamine (**2a**) improved the yield considerably (*Table 1, entries 9-10*). As an example, a yield of 80% could be achieved even under 1 MPa (*Table 1, entry 10*). However, the reaction under 0.5 MPa CO_2 only led to the product in a moderate yield (*Table 1, entry 11*). A Cu(II) complex with imidazolium carboxylate ligands (**CuL_2**, *Figure 2*) was also synthesized [41] and tested in the carboxylation of steroid **1** (*Table 1, entry 12*). In this case, however, the yield of **3a** was only slightly higher than under the same conditions with $Cu(OAc)_2$ (*Table 1, entry 8*).

In order to determine the optimal conditions for catalyst recycling, the copper content of the ethereal extracts of the reaction mixtures was determined by ICP-OES (*Table 2*).

The lowest leaching of copper to the organic phase could be detected in the CuI-catalyzed reaction (*Table 2, entry 1*). Although the increase in the amine/steroid ratio had a favorable effect on the yield of the oxazolidinone product (*Table 1, entries 7 and 9*), it led to a noticeable increase in the loss of the metal (*Table 1, entry 4*). The highest copper content was measured in the crude product obtained in the presence of $Cu(OAc)_2$.

Based on these findings together with the results of the catalytic experiments, the conditions corresponding to *entry 3, Table 1* were chosen to test catalyst recycling. After extraction of the product with diethyl ether and removal of the residue of the organic solvent under vacuum, fresh reagents were added to the ionic liquid/catalyst mixture and carboxylation/cyclization was repeated under the same conditions. The results (*Figure 3*) show a slight decrease in the activity of the catalyst in multiple consecutive experiments, but product **3a** formed with a yield of 80%, even in the 5th run. It should be mentioned that copper leaching also decreased steadily with a value of 1.9% in the 5th experiment.

The optimal conditions were used to convert steroid **1** into oxazolidinones **3b** and **3c** in 79% and 67% yields, respectively, using benzylic amines **2b** and **3b** as reaction partners.

4. Conclusions

Table 2: Copper content of the crude reaction mixtures obtained with different catalysts

Entry	Catalyst	Amine/steroid (**2a**/**1**) ratio	Cu-content (%)[b]
1	CuI	1	3.7
2	$Cu(OAc)_2$	1	12
3	CuL_2	1	5.4
4	CuI	2	9.5

[a]: Reaction conditions: 0.17 mmol **1**, 0.17 mmol or 0.34 mmol **2a**, 0.010 mmol catalyst, 170 µl [BMIM][BF_4], 2 MPa, 24 h, 393 K
[b]: determined by ICP-OES, % of the original Cu-loading

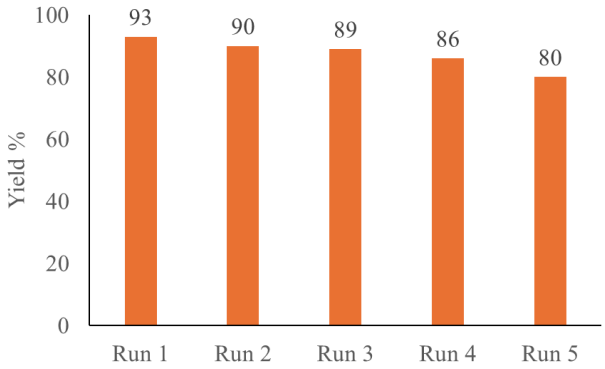


Figure 3: Catalyst recycling in the carboxylation/cyclization reaction of steroid **1** with benzylamine (**2a**). Reaction conditions: 0.17 mmol **1**, 0.17 mmol **2a**, 0.01 mmol CuI and 170 µl [BMIM][BF_4] (recycled); 2 MPa, 24 h, 393 K. Product yields were determined based on NMR measurements of the reaction mixtures

The mixture of CuI and [BMIM][BF_4] was proven to be an active and recyclable catalytic system in the synthesis of new steroidal oxazolidinone derivatives. CuI was found to be superior to CuCl, $Cu(OAc)_2$ and Cu carboxylate CuL_2 catalyst precursors in terms of activity and metal leaching. By the application of this methodology, three novel steroid derivatives were produced.

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