ChemPubSoc Europe
DOI: 10.1002/ejoc.201600476
EurJOC European Journal of Organic Chemistry
Full Paper

Iron Catalysis

Iron-Catalyzed Synthesis of Five-Membered Cyclic Carbonates from Vicinal Diols: Urea as Sustainable Carbonylation Agent

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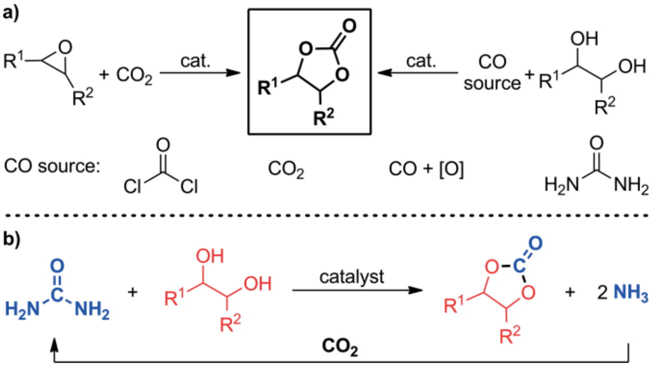
Abstract: A new iron-catalyzed synthesis of cyclic carbonates from the corresponding vicinal diols and urea is described. This straightforward transformation allows for the preparation of a variety of five-membered carbonates by employing an inexpensive and environmentally benign iron salt as the catalyst. The use of readily available feedstocks such as urea and polyols makes this a sustainable process. As ammonia is formed as the only stoichiometric byproduct, this process can also be characterized by its high atom economy.

Introduction

Cyclic carbonates are valuable synthetic targets because of their relevant properties and numerous applications.[1] They have been used as high boiling aprotic polar solvents, and because of their low toxicity and good biodegradability, they are capable of replacing traditional hazardous solvents.[2] In addition, they have served as components of electrolytes in Li-ion rechargeable batteries[3] and protecting groups in carbohydrate chemistry,[4] and they are found in several natural products and potential pharmaceuticals.[5] Of particular relevance is the use of such heterocyclic compounds as intermediates in the manufacturing of fine chemicals,[6] more specifically as monomers, for the preparation of polycarbonates, polyurethanes, and other polymeric material with applications in the field of plastics engineering.[7]

Within this class of compounds, five-membered derivatives are most significant according to the literature. Consequently, several catalytic methods have been published to date. Currently, the main route for their synthesis involves the reaction of epoxides with carbon dioxide, for which a large number of catalytic systems have been successfully developed (Scheme 1, a).[8] However, the synthesis of these starting epoxides is typically achieved by using olefins along with powerful oxidants and procedures that generate waste. Furthermore, epoxides can be toxic and difficult to handle. An alternative approach for the synthesis of cyclic carbonates has involved the use of 1,2-diols, which are generally bioavailable from renewable resources.[9] In this case, with the exception of CO_2,[10] carbonylation agents such as phosgene and carbon monoxide in combination with different oxidants have been used (Scheme 1, a).[11] Still, these latter reagents have significant drawbacks. Alternatively, a safe and easily accessible carbonate precursor is urea. This reagent allows for high atom efficiency as ammonia is the only stoichiometric waste that is formed. The possibility of the regeneration of the starting urea by treating such a byproduct with carbon dioxide would improve the sustainability of the process,[12] whereby urea becomes a potential feedstock for the indirect use of CO_2 (Scheme 1, b).



Scheme 1. Catalytic processes for the synthesis of cyclic carbonates from epoxides and diols. Urea is used as CO_2 equivalent.

These advantages led us to focus our research on the catalytic coupling of diols with urea. So far, there have been reports of different protocols that regularly use catalysts with the appropriate acidic and basic properties such as metal oxides, zinc, and magnesium chloride as well as other sophisticated heterogeneous systems.[13] However, many of these methods have disadvantages such as the need of a vacuum system to remove the generated ammonia to accelerate the process. In addition, these protocols often have a limited substrate scope. For these reasons, we became interested in a general study of the synthesis of cyclic organic carbonates and the development of new benign catalysts.

Because of the increasing interest in the implementation of green chemistry principles, iron-based catalysts have been widely employed in organic synthesis in recent years.[14] As iron is one of the most abundant metals, a variety of inexpensive and nontoxic derivatives are commercially available. Compared

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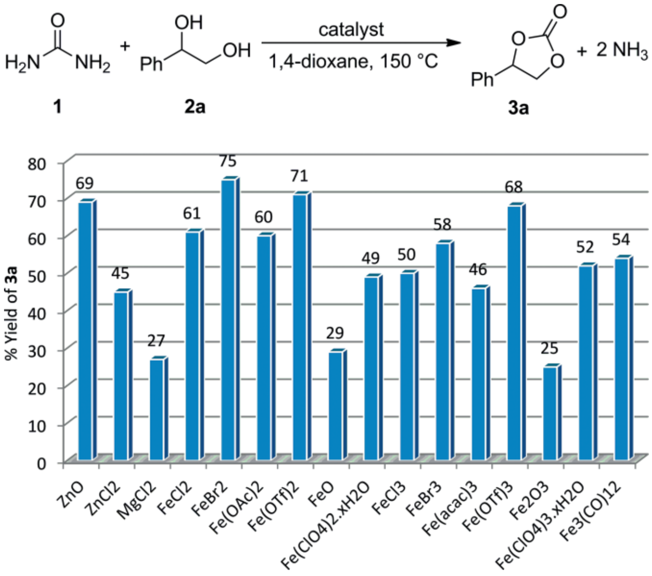
with noble metal complexes, their use in various transformations generally provides economic and ecological benefits. Additionally, Lewis acid catalyzed reactions with iron have been well-known for a long time.[15] For example, the corresponding electrophile of a nucleophilic substitution reaction is activated by metal coordination, which makes it more susceptible to the attack of an incoming nucleophile.[16] Applying this principle, we herein describe a new sustainable synthesis for cyclic carbonates from ureas and vicinal diols in the presence of an eco-friendly iron catalyst.

Results and Discussion

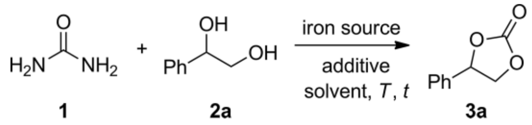
Our research began by selecting an effective catalyst for the model reaction of urea (**1**) with 1-phenylethane-1,2-diol (**2a**, Scheme 2). Initially, we compared the reported reactivities of catalysts that have been used in this transformation under a given set of reaction conditions (0.5 mmol of **1**, 0.5 mmol of **2a**, 1,4-dioxane, 150 °C, 18 h).[13m–13o] Employing the standard ZnO (0.02 mmol) as a catalyst provided the desired 4-phenyl-1,3-dioxolan-2-one (**3a**) in 69 % yield. The use of other zinc and magnesium salts, which are also known for carbonate synthesis, provided the same product but in lower yields (45 and 27 %, respectively).



Scheme 2. Variation of catalysts for the synthesis of 4-phenyl-1,3-dioxolan-2-one (**3a**) from urea (**1**) and 1-phenylethane-1,2-diol (**2a**). Reagents and conditions: catalyst (0.02 mmol), **1** (0.5 mmol), and **2a** (0.5 mmol) in 1,4-dioxane at 150 °C for 18 h (OTf = trifluoromethanesulfonate, acac = acetylacetone). Yields were determined by GC analysis using hexadecane as the internal standard.

Next, we studied this transformation by using various iron compounds. Here, we observed that classical inexpensive iron(II) salts provided the corresponding five-membered cyclic carbonate **3a** in good yields and obtained the best 75 % yield by using simple $FeBr_2$ (Scheme 2). Additionally, analogous iron(III) species and triiron(0) dodecarbonyl also showed some reactivity, although lower conversions were observed in all cases (25–68 % yield, Scheme 2). After investigating this first approach and establishing iron(II) bromide to be the most effective catalyst, we decided to explore other general factors to determine the optimal reaction conditions. Performing the same reaction in other solvents such as *tert*-amyl alcohol, toluene, and acetonitrile decreased the reactivity (37–70 % yield, Table 1, Entries 1–3), whereas studying different ratios of **1** and **2a** led to an excellent 91 % yield by using 1.5 equiv. of the corresponding diol (Table 1, Entries 4 and 5). We then examined the effect of changing the catalyst loading and temperature. In the presence of 0.01 mmol $FeBr_2$, the reaction afforded the desired product in a lower 71 % yield, whereas the use of higher amounts of iron did not significantly improve upon the earlier reactivity (92 % yield, Table 1, Entries 6 and 7). The temperature serves an important role in this transformation as **3a** was obtained in a moderate 61 % yield at 140 °C, and surprisingly no reactivity was observed at a lower temperature (Table 1, Entries 9 and 10). Next, we studied the potential effect of additives, but the use of an acid or base in substoichiometric amounts (5 mol-%) afforded the corresponding cyclic carbonate in lower yields (Table 1, Entries 11 and 12). Decreasing the reaction time led to a drop in the conversion (Table 1, Entry 13), and the experiment provided the cyclic carbonate in only 24 % yield in the absence of the catalyst (Table 1, Entry 14).

Table 1. Screening of reaction conditions for the iron-catalyzed synthesis of 4-phenyl-1,3-dioxolan-2-one (**3a**).[a]



Entry	Catalyst	Additive	Solvent	*T* [°C]	Yield [%][b]
1	$FeBr_2$	–	*tert*-amyl alcohol	150	55
2	$FeBr_2$	–	toluene	150	70
3	$FeBr_2$	–	MeCN	150	37
4[c]	$FeBr_2$	–	1,4-dioxane	150	58
5[d]	$FeBr_2$	–	1,4-dioxane	150	91
6[d,e]	$FeBr_2$	–	1,4-dioxane	150	71
7[d,f]	$FeBr_2$	–	1,4-dioxane	150	92
8[d]	$FeBr_2$	–	1,4-dioxane	160	89
9[d]	$FeBr_2$	–	1,4-dioxane	140	61
10[d]	$FeBr_2$	–	1,4-dioxane	130	–
11[d,g]	$FeBr_2$	K_2CO_3	1,4-dioxane	150	21
12[d,g]	$FeBr_2$	*p*TsOH	1,4-dioxane	150	65
13[d,h]	$FeBr_2$	–	1,4-dioxane	150	53
14[d]	–	–	1,4-dioxane	150	24

[a] Unless otherwise specified, all reactions were carried out with catalyst (0.02 mmol), urea (**1**, 0.5 mmol), and 1-phenylethane-1,2-diol (**2a**, 0.5 mmol) in a solvent (1 mL) at the indicated temperature for 18 h. [b] Yields determined by GC analysis using hexadecane as the internal standard. [c] Urea (0.75 mmol) was used. [d] Diol (0.75 mmol) was used. [e] Catalyst (0.01 mmol) was used. [f] Catalyst (0.03 mmol) was used. [g] An additive (0.025 mmol) was used (*p*TsOH = *para*-toluenesulfonic acid). [h] Reaction time was 5 h.

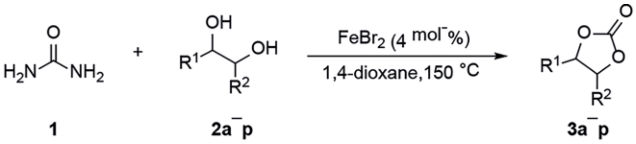
Remarkably, this process takes place selectively to avoid the formation of related side products, such as polycarbonates or urethanes, a common occurrence in such transformations. In addition, the atom economy of this process is another significant feature, as the substrates are converted into the product along with only two equivalents of ammonia as a byproduct. The ease of availability of the coupling partners as well as the safety and low price of the iron salt provides added value to this synthetic method.

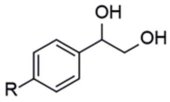
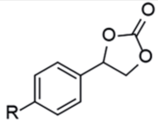
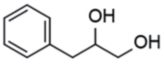
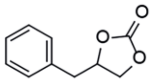
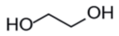
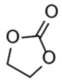
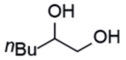
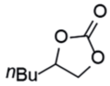
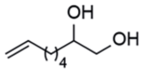
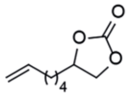
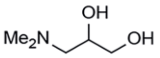
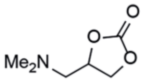
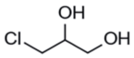
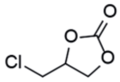
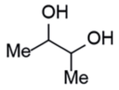
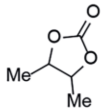
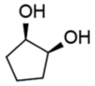
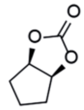
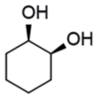
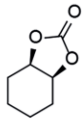
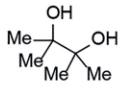
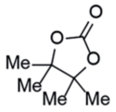
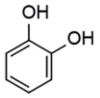
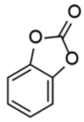
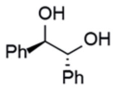
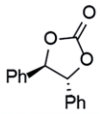
After the model reaction was studied, our next step involved investigating the reactivity of different vicinal diols to make this method more general. First, we applied the previously optimized conditions to the reaction of urea (**1**) with terminal diols. Such an approach would allow access to different 4-substituted cyclic carbonates. As shown in Table 2, we found that styrene diol derivatives that contain electron-withdrawing groups on the phenyl ring such as 1-(4-chlorophenyl)- and 1-(4-trifluoromethylphenyl)ethane-1,2-diol (**2b** and **2c**) provided the corresponding carbonates **3b** and **3c** in excellent yields (98 and 85 %, respectively, Table 2, Entries 2 and 3). Nevertheless, the same reaction with the electron-rich substrate **2d** afforded the product in only a low 23 % yield (Table 2, Entry 4), probably a result of undesired reactions caused by the electronic properties of the starting diol. However, benzyl derivative **2e** was effectively converted into the desired product **3e** in 92 % yield (Table 2, Entry 5). In contrast, this transformation also takes place with aliphatic diols. Thus, ethane-1,2-diol (**2f**) gave rise to ethylene carbonate (**3f**) in a moderate 65 % yield (Table 2, Entry 6), whereas the reaction of urea with hexane- and 7-octene-1,2-diol (**2g** and **2h**) under the previously determined conditions led to the desired heterocycles **3g** and **3h** in almost quantitative yields (92 and 97 %, respectively, Table 2, Entries 7 and 8). Notably, demanding substrates that contain heteroatoms such as derivatives **2i** and **2j** gave the desired carbonates, albeit in much lower yields (15 and 21 %, respectively, Table 2, Entries 9 and 10). The reactivity of **2i** may be related to the result from **2d**. Chlorohydrin derivative **2j** is susceptible to undergo multiple undesired reactions, which explains the low yield of its reaction .

To expand the scope of our protocol, we tested internal diols, which would afford the corresponding 4,5-disubstituted carbonates. Applying the optimal conditions (0.5 mmol of **1**, 0.75 mmol of **2k**, and 0.02 mmol of $FeBr_2$ in 1,4-dioxane at 150 °C), we obtained the 4,5-dimethyl-1,3-dioxolan-2-one (**3k**) in a good 86 % isolated yield (70:30 *dr*, Table 2, Entry 11). The reactions between urea and *cis*-1,2-cyclopentane- and *cis*-1,2-cyclohexanediol (**2l** and **2m**) provided carbonates **3l** and **3m** in 96 and 75 % yield, respectively (Table 2, Entries 12 and 13). Pinacol (**2n**), a vicinal diol with two tertiary alcohol moieties, even gave rise to the desired heterocycle **3n** in good yield (Table 2, Entry 14). However, the reaction with catechol (**2o**) showed no conversion, and only the unaltered starting material was recovered (Table 2, Entry 15). In this case, the formation of the carbonate did not occur because of the low nucleophilicity of aromatic alcohols, which are not capable of a nucleophilic attack on the iron-activated urea. Finally, (*R*,*R*)-hydrobenzoin (**2p**) afforded the five-membered heterocycle **3p** in 95 % yield, thus providing access to compounds substituted with two aromatic groups.

Encouraged by these results, we were interested in using diols from renewable feedstock for the synthesis of cyclic carbonates (Scheme 3). To this end, glycerol, a side product of the biodiesel industry, is especially interesting.[17] Because of the bulk production of this alcohol, its use as a platform chemi-

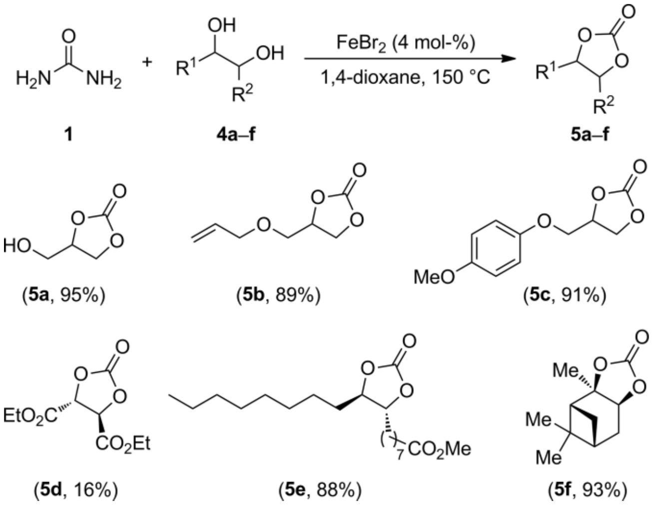
Table 2. Iron-catalyzed synthesis of substituted cyclic carbonates **3a**–**3p** from urea (**1**) and vicinal diols **2a**–**2p**.[a]



Entry	Diol		Product		Yield [%][b]
1	 R = H	2a	 R = H	3a	90
2	R = Cl	2b	R = Cl	3b	98
3	R = CF_3	2c	R = CF_3	3c	85
4	R = OMe	2d	R = OMe	3d	23
5		2e		3e	92
6		2f		3f	65[c]
7		2g		3g	92
8		2h		3h	97
9		2i		3i	15
10		2j		3j	21
11		2k		3k	86[d]
12		2l		3l	96
13		2m		3m	75
14		2n		3n	78
15		2o		3o	–[e]
16		2p		3p	95

[a] Unless otherwise specified, all reactions were carried out with $FeBr_2$ (0.02 mmol), urea (**1**, 0.5 mmol), and diol **2a**–**2p** (0.75 mmol) in 1,4-dioxane (1 mL) at 150 °C for 18 h. [b] Isolated yields are provided. [c] NMR yield with durene as the internal standard. [d] Carbonate **3k** was obtained as a mixture of diastereoisomers (70:30). [e] Only the remaining starting diol was observed.

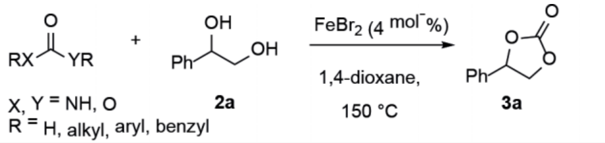
cal provides valuable opportunities for new products.[18] For example, the resulting cyclic carbonate is a biodegradable high boiling polar solvent with low toxicity and multiple applications.[19] Despite the apparent simplicity of carbonate production from glycerol and urea, this reaction could lead to the formation of side products such as urethanes, oxazolidinones, and cyclic carbonates with larger rings. Gratifyingly, the reaction of urea (**1**, 0.5 mmol) with glycerol (**4a**, 0.75 mmol) in the presence of iron(II) bromide as the catalyst selectively afforded glycerol carbonate (**5a**) in an excellent 95 % yield (Scheme 3). Additionally, this reaction was also tested with other valuable glycerol derivatives such as the corresponding 1-monoethers.[20] Hence, related experiments that employed 3-allyloxy- and 3-(4-methoxyphenoxy)-1,2-propanediol (**4b** and **4c**) as substrates gave rise to the formation of carbonates **5b** and **5c** in very good isolated yields (89 and 91 %, respectively, Scheme 3). Next, we applied this method to other bio-based diols such as the ethyl ester of (L)-(+)-tartaric acid.[21] Here, the ester moieties induce a lower nucleophilicity of the hydroxyl groups to provide the desired cyclic carbonate **5d** in only 16 % yield (Scheme 3). In contrast, we studied the reactivity of a long-chain internal diol that was derived from oleic acid, a monounsaturated omega-9 fatty acid that is present as triglycerides in biological systems.[22] Interestingly, the reaction of urea with such an (*R*,*R*)-diol under iron catalysis afforded the five-membered heterocycle **5e** in 88 % yield (Scheme 3). Finally, we expanded the scope of the reaction to an α-pinene-derived diol.[23] This substrate satisfactorily participated in the process to give tricyclic compound **5f** in excellent yield (93 %, Scheme 3). In general, the use of diols from renewable resources enables the selective synthesis of bio-based carbonates in high yields, which benefits this method by making it sustainable.

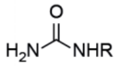
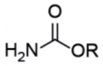
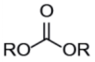


Scheme 3. Iron-catalyzed synthesis of cyclic carbonates **5** by using diols from renewable resources (i.e., **4a**–**4f**). Reagents and conditions: **1** (0.5 mmol), **4a**–**4f** (0.75 mmol), and FeBr$_2$ (0.02 mmol) in 1,4-dioxane at 150 °C for 18 h. Isolated yields are provided.

After studying the general applicability of this transformation, we compared the activity of urea with other convenient CO sources in the reaction with 1-phenylethane-1,2-diol (**2a**, Table 3). First, we extended this protocol to *N*-monosubstituted ureas **6**, the reaction of which would generate both ammonia and RNH$_2$ as byproducts. Thus, the iron-catalyzed reaction of **6a**–**6d** with vicinal diol **2a** in 1,4-dioxane at 150 °C provided the five-membered cyclic carbonate **3a** in all cases in low to moderate yields (26–53 % yield, Table 3, Entries 1–4). It seems that the generated primary amine in these cases may participate in undesired reactions, thereby decreasing the yield of the transformation. In fact, the least effective reaction involved derivative **6d** with highly nucleophilic benzylamine formed as a side product. To enhance the versatility of the system, we chose a urea analogue that contained a better leaving group such as the corresponding carbamates **7** (Table 3, Entries 5–8). Again, low yields were observed for the reaction of **2a** with methyl, *tert*-butyl, and benzyl carbamates. However, the synthesis of the desired product **3a** from the phenyl carbamate (**7c**) was achieved in a good 89 % yield because of the increased leaving group ability and low nucleophilicity of phenols (Table 3, Entry 7). Finally, another well-known alternative for the synthesis of the desired products includes the transesterification reaction of acyclic carbonates with 1,2-diols,[24] which is one of the simplest methods to be broadly applied in industrial processes for the manufacturing of biodiesel. The use of our previously optimized conditions for the reaction of **2a** and carbonates **8a**–**8d** led to low yields in most cases (Table 3, Entries 9–12). As for the case of the carbamates, the formation of the primary alcohol and the possibility of its involvement in side reactions decreases the effectiveness of the transformation, with the exception of diphenyl carbonate (**8c**), which afforded **3a** quantitatively.

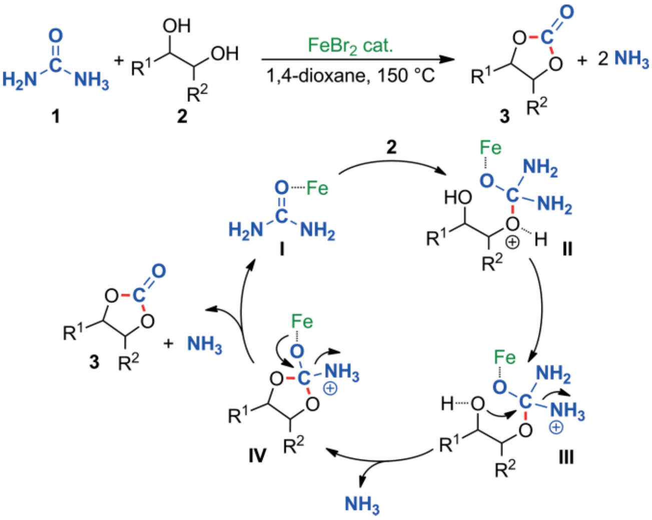
Table 3. Iron-catalyzed synthesis of 4-phenyl-1,3-dioxolan-2-one (**3a**) from the reactions of ureas, carbamates, and carbonates (i.e., **6**–**8**) with 1-phenylethane-1,2-diol (**2a**).[a]



Entry	Urea/carbamate/carbonate	R		Yield [%][b]
1	 $H_2NC(O)NHR$	Me	**6a**	50
2		Et	**6b**	51
3		Ph	**6c**	53
4		Bn	**6d**	26
5	 $H_2NC(O)OR$	Me	**7a**	29
6		*t*Bu	**7b**	26
7		Ph	**7c**	89
8		Bn	**7d**	58
9	 $ROC(O)OR$	Me	**8a**	55
10		Et	**8b**	35
11		Ph	**8c**	96
12		Bn	**8d**	56

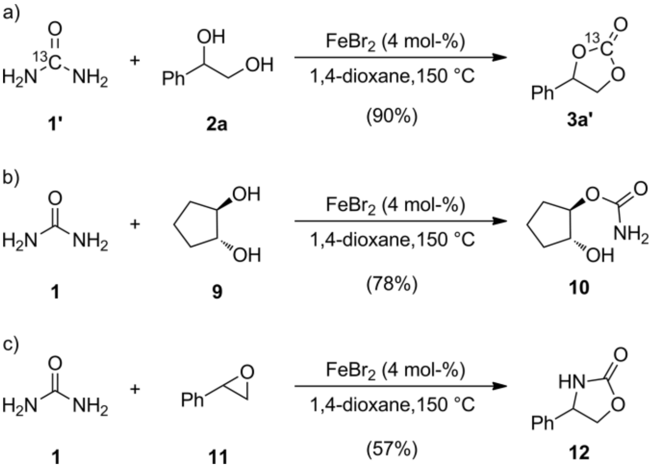
[a] Unless otherwise specified, all reactions were carried out with FeBr$_2$ (0.02 mmol), either a urea, carbamate, or carbonate derivative (i.e., **6**–**8**, 0.5 mmol), and diol **2a** (0.75 mmol) in 1,4-dioxane (1 mL) at 150 °C for 18 h. [b] Isolated yields are provided.

Once the scope and limitations of this protocol were analyzed, we proposed a reaction mechanism, as shown in Scheme 4.[25] In the first step, the carbonyl group of urea is activated by coordination to the metal through the oxygen atom. Here, the iron(II) bromide behaves as a Lewis acid to form intermediate **I**. Then, one hydroxy group of diol **2**, which is probably activated by hydrogen bonding, attacks the electrophilic carbonyl carbon of urea to generate intermediate **II**. Migration of a proton from the oxygen to the nitrogen atom provides species **III**, which undergoes an intramolecular substitution reaction with the oxygen atom of the other OH group to form five-membered ring **IV** and ammonia. Finally, the release of the catalyst gives carbonate **3** and the second molecule of NH_3 to complete the catalytic cycle. The high rate of the intramolecular cyclization of intermediate **III** is the reason of the high selectivity that is observed in this transformation. The formation of the heterocyclic structure appears to be more favorable than a nucleophilic substitution with a second diol molecule, a reaction that would lead to polycarbonates.



Scheme 4. Proposed reaction mechanism for the iron-catalyzed synthesis of cyclic carbonates from urea and vicinal diols.

On the basis of these results, additional experiments were performed. The use of ^{13}C-labeled urea (**1′**) confirms the origin of the carbonyl group in the cyclic carbonate (Scheme 5, a). Under the previously established reaction conditions, isotopically labeled **3a′** was obtained in 90 % yield, an identical result to that observed in the experiment with standard urea (Table 2, Entry 1). To isolate an intermediate carbamate, we carried out the iron(II) bromide catalyzed reaction of urea (**1**) with *trans*-cyclopentane-1,2-diol (**9**). In agreement with our mechanistic proposal, we obtained compound **10** in 78 % isolated yield (Scheme 5, b). Clearly, the *trans* configuration of the hydroxy groups prevents an internal nucleophilic substitution reaction from taking place, and less favorable intermolecular reactions do not take place to give any oligomeric or polymeric species. Lastly, this reaction was also studied with other coupling partners such as styrene oxide (**11**, Scheme 5, c), and its reaction with urea under the same conditions afforded oxazolidin-2-one **12** in a moderate 57 % yield as the only regioisomer. Besides urea, iron(II) bromide can also activate the epoxide to make it more electrophilic. Then, the regioselective ring-opening by attack of one amino group of urea to the more substituted carbon of **11** gives the intermediate *N*-(2-hydroxy-1-phenylethyl)urea, which subsequently undergoes an intramolecular substitution to provide heterocyclic compound **12**. This transformation confirms the ability of the iron salt to activate both coupling partners.



Scheme 5. Additional experiments: (a) Synthesis of isotopically labeled 4-phenyl-1,3-dioxolan-2-one from ^{13}C-urea; (b) Isolation of intermediate carbamate from *trans*-1,2-cyclopentanediol; (c) Reaction of urea with styrene oxide. Isolated yields are provided.

Conclusions

In summary, we have developed a general synthesis for five-membered cyclic carbonates from readily available urea and vicinal diols from renewable feedstocks. This versatile transformation allowed us to prepare a broad scope of carbonates in good yields by using a safe, inexpensive, ligand-free, and environmentally benign iron salt as the catalyst. The use of bioavailable diols allows for the valuable use of renewable resources in a straightforward manner.

Experimental Section

General Methods: Unless otherwise is stated, all reactions were conducted under argon with exclusion of moisture from reagents and glassware by using standard techniques for the manipulation of air-sensitive compounds. Reaction temperatures refer to external bath temperatures. TLC analysis was performed on silica gel 60 F_{254} (layer thickness: 0.2 mm), and components on the developed plates were visualized by observation under UV light and/or treating the plates with either phosphomolybdic acid solution or *p*-anisaldehyde reagent followed by heating. Column chromatography was performed on silica gel (230–400 mesh) with 30 % ethyl acetate/heptane as the eluent. The NMR spectroscopic data were recorded with a Bruker Avance 400 spectrometer. The residual solvent signal (for $CHCl_3$, $\delta = 7.26$ ppm) was used as the internal standard for ^{1}H NMR, and the solvent signal (for $CDCl_3$, $\delta = 77$ ppm) was used as the internal standard for ^{13}C NMR. All measurements were carried out at room temperature, unless otherwise stated, and analysis by DEPT was used to assign the types of carbon atoms. Mass spectrometry was, in general, recorded on a MAT 95XP or an HP 5973N mass selective detector. Gas chromatography was performed on an HP 6890N chromatograph with an HP5 column. Unless otherwise stated, commercial reagents were used as received without further purification.

General Procedure for the Iron-Catalyzed Synthesis of Cyclic Carbonates: In a glass pressure tube (25 mL) under argon, $FeBr_2$ (4.3 mg, 0.02 mmol), urea (30.1 mg, 0.5 mmol), and the diol (0.75 mmol) were dissolved in 1,4-dioxane (1 mL). The pressure tube was then closed, and the resulting mixture was stirred in an oil bath at 150 °C for 18 h. After cooling to room temperature, the crude mixture was directly purified by flash chromatography on silica gel, and after the combined fractions were concentrated and dried under high vacuum, the corresponding cyclic carbonates were afforded in the reported yields.

Acknowledgments

The authors thank the Federate State of Mecklenburg-Vorpommern, Germany and the Bundesministerium für Bildung und Forschung (BMBF), Germany for financial support. M. P.-L. thanks the European Union (EU), European Commission for a Marie Curie Intra-European Fellowship within the 7th Framework Programme (PIEF-GA-2012-328500). The Analytical Department of the Leibniz Institut für Katalyse (LIKAT) is thanked for technical support.

Keywords: Green chemistry · Carbonylation · Cyclization · Oxygen heterocycles · Iron · Diols

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Received: April 15, 2016

Iron Catalysis

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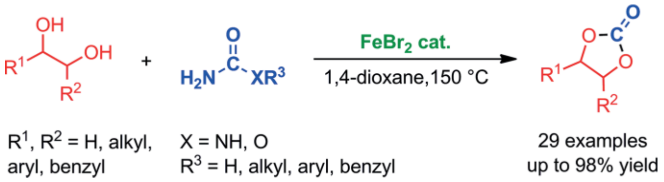
Iron-Catalyzed Synthesis of Five-Membered Cyclic Carbonates from Vicinal Diols: Urea as Sustainable Carbonylation Agent



A new catalytic approach for the synthesis of five-membered cyclic carbonates from the reaction of urea with vicinal diols has been developed. The use of an inexpensive nontoxic iron catalyst and readily available substrates in combination with the resulting high atom economy make this an operationally simple and sustainable process.

DOI: 10.1002/ejoc.201600476