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Catalysis

[4-(2-Hydroxyphenyl)imidazolium Salts as Organocatalysts for Cycloaddition of Isocyanates and Epoxides to Yield Oxazolidin-2-ones

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Novel salts based on 1,3-dibutyl-4-(2-hydroxyphenyl)-1*H*-imidazolium bromide or iodide have been developed as bifunctional organocatalysts for the cycloaddition reaction of epoxides and isocyanates to form 3,4- and 3,5-disubstituted oxazolidin-2-ones. The molecular structure of these compounds was determined spectroscopically and confirmed by X-ray diffraction analysis. Imidazolium compounds were screened as catalysts to produce a range of oxazolidinones. The influence of the substituents on the aromatic ring and the counterion of the catalysts on the catalytic activity have been studied, showing that 1,3-dibutyl-4-(5-fluro-2-hydroxyphenyl)-1*H*-imidazolium iodide (**4 d**) was the most active catalyst for this process in the absence of a cocatalyst.

Introduction

Oxazolidin-2-ones belong to a family of five-membered N,O-heterocycles carbamate derivative which have important medical applications as antibacterial agents,[1] for the treatment of atherosclerosis and hypercholesterolemia,[1c] as peroxisome proliferator-activated receptors agonists[1b] and as inhibitors of several enzymes as monoamine oxidase involved in mental and neurodegenerative disorders,[2] HIV-proteasa,[3] factor Xa involved in blood coagulation[4] and kallikrein-related peptidase 6 implicated in carcinogenesis and in Alzheimer's disease.[5] These compounds present important applications in organic synthesis as masked β-aminoalcohols,[6] as precursor of both formic acid and secondary alkyl(2-arylethyl)amines,[7] as chiral auxiliary[8] or as building blocks for the synthesis of oxazolidine-2-one based polymers.[9] These highlights reflect the importance of developing highly efficient synthetic methods to synthesize oxazolidin-2-one rings. One of the most important methodologies is the [3 + 2] cycloaddition reaction of epoxides to isocyanates to yield oxazolidine-2-one compounds with maximum atom-economy. Several compounds have been used as catalytic systems for this reaction including the combination of metal compounds,[10] lithium or tetraalkylammonium halides,[11] H-bond donor compounds in the presence of a quaternary ammonium salt,[12] tetraarylstibonium systems[13] or bifunctional catalysts which act as H-bond donors and contain halide anions in their structure that are among the most efficient organocatalysts.[14] In spite of the high efficiency of some metal-based catalyst, it is necessary to avoid the use of expensive, toxic and arduous synthesis of catalytic systems, which operate under harsh reactions conditions and require high catalyst loadings. For instance, enantio- and regioselective synthesis of 5-aryloxazolidin-2-ones was performed by cycloaddition of styrene oxide derivatives and sodium cyanate, biocatalyzed by halohydrin dehalogenase from Agrobacterium radiobacter.[15] On the other hand, organocatalysts are attractive alternatives that have solved some of these problems, but the number of organocatalysts which can catalyse this cycloaddition reaction is rather low.[11a,b,14] Therefore, it is necessary to develop a greater number of organiccatalysts that can perform the [3 + 2] cycloaddition of epoxides and isocyanates to afford oxazolidin-2-ones.

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We have previously shown that 4-(2-hydroxyphenyl)imidazolium halide salts act as excellent organocatalysts for de the cycloaddition of epoxides and CO_2 to obtain cyclic carbonates.[16] Based on these results and the current work on designing novel imidazolium-based organocatalysts, in this paper we report the synthesis of a new family of 4-(2-hydroxyphenyl)imidazolium halide salts and their use as efficient and versatile bifunctional catalysts for the cycloaddition reaction of epoxides and isocyanates to obtain oxazolidin-2-ones. The influence of the halide anion and the presence of electron withdrawing groups on the phenol ring on the catalytic activity has been investigated.

Results and Discussion

Synthesis and structural characterization of organocatalysts

A series of 4-(2-hydroxyphenyl)imidazolium halide compounds (**4a–f**) were obtained using a three-step process previously described (Scheme 1).[16a] The first step involves the synthesis of Schiff bases **2a–c** by condensation of salicylaldehyde derivatives (**1a–c**) and *n*-butylamine. The second step is a base assisted [3 + 2] cycloaddition reaction between the Schiff bases **2a–c** and tosylmethylisocyanide (TosMIC) to yield compounds **3a–c**. Finally, alkylation of pyridinic nitrogen atom of **3a–c** with *n*-butyl bromide or iodide at 100 °C afforded the corresponding imidazolium salts **4a–f**. Compounds **2–4** were characterized spectroscopically (See supporting information). The ^{1}H and ^{13}C {^{1}H} NMR spectra of compounds **4a–f** at room temperature showed two different sets of signals for the butyl protons, which indicated that the nitrogen atoms are different. The imidazole proton resonances from compounds **4a–f** are shifted to lower field (9.30–9.90 ppm and 7.20–8.00 ppm) with respect to those resonances in compounds **3a–c** (7.60 ppm and 6.90 ppm).

The molecular structures of compounds **3b**, **3c** and **4d** were determined by X-ray diffraction studies (See Supporting Information). The ORTEP drawings for complexes **3b**, **3c** and **4d** are depicted in Figure 1. Crystallographic data and selected bond distances and angles are collected in Tables S1 and S2 in Supporting Information. The solid-state structures are consistent with the NMR data.

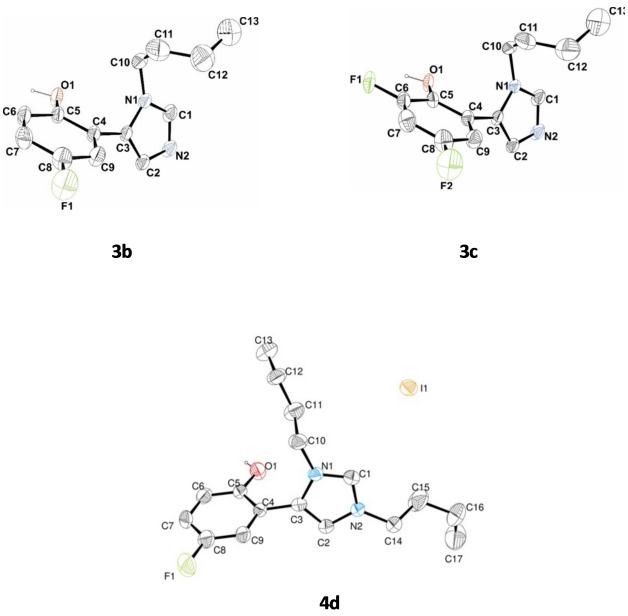
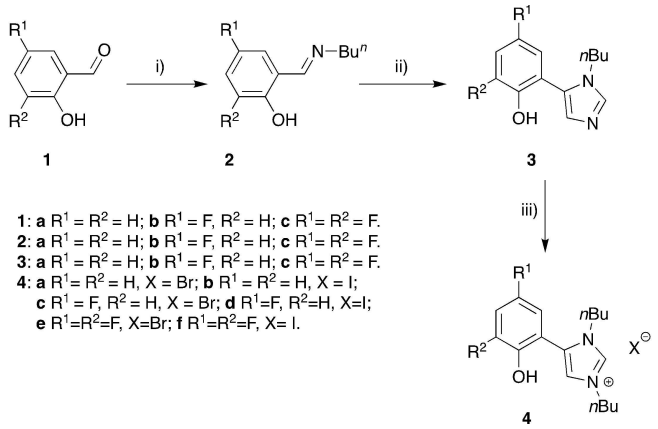


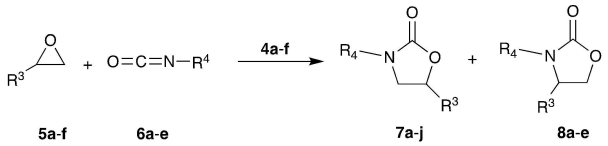
Figure 1. ORTEP drawing of compounds **3b**, **3c** and **4d**. Thermal ellipsoids are set at 30% probability and hydrogen atoms are omitted for clarity.



Scheme 1. Synthesis of compounds **4a–4f**. i) *n*-BuNH$_2$, CH_2Cl_2, rt, 14 h. ii) TosMIC + K_2CO_3, MeOH, reflux, 3 h. iii) *n*-BuBr or *n*-BuI, neat, 100 °C, 7 h.

Catalytic studies of oxazolidin-2-one synthesis

An initial catalyst screening was carried out to study the catalytic activity of imidazolium salts **4a–f** as catalysts for the reaction of styrene oxide (**5a**) and phenyl isocyanate (**6a**) as reference reaction (Scheme 2). For this reaction, two isomers can be isolated, the 3,4- and 3,5-disubstituted oxazolidin-2-ones. With the purpose of evaluating the catalytic activity of these salts, the reactions were carried out using 3 mol% of catalysts **4a–f** at 90 °C for 6 h in chlorobenzene as solvent. The reactions were monitored by ^{1}H NMR spectroscopy and the results are shown in Table 1. As can be seen in Table 1, compounds **4a–e** showed good catalytic activity for 3,5-diphenyloxazolidin-2-one (**7a**) and 3,4-diphenyloxazolidin-2-one (**8a**) formation under these reaction conditions (Table 1,



5: **a** R^3 = Ph; **b** R^3 = ClCH$_2$; **c** R^3 = CH$_3$; **d** R^3 = C_2H_5; **e** R^3 = nC_8H_{17}; **f** R^3 = $nC_{10}H_{21}$.
6: **a** R^4 = Ph; **b** R^4 = 4-MeC_6H_4; **c**: R^4 = 4-ClC_6H_4; **d** R^4 = 4-$NO_2C_6H_4$; **e** R^4 = 4-MeOC_6H_4.
7 and **8**: **a** R^3 = R^4 = Ph; **b** R^3 = Ph, R^4 = 4-MeC_6H_4; **c** R^3 = Ph, R^4 = 4-ClC_6H_4; **d** R^3 = Ph, R^4 = 4-$NO_2C_6H_4$; **e** R^3 = Ph, R^4 = 4-MeOC_6H_4; **f** R^3 = ClCH$_2$, R^4 = Ph; **g** R^3 = CH$_3$, R^4 = Ph; **h** R^3 = C_2H_5, R^4 = Ph; **i** R^3 = nC_8H_{17}, R^4 = Ph; **j** R^3 = $nC_{10}H_{21}$, R^4=Ph.

Scheme 2. Synthesis of oxazolidin-2-ones **7a–j** and **8a–e** using **4a–f** as catalyst.

Table 1. Reaction of styrene oxide (**5a**) with phenyl isocyanate (**6a**) using **4a–f** as catalyst.[a]

Entry	Catal. (R^1, R^2, X)	Conversion %[b] (**7a**:**8a**)	Yield %[c] **7a**	**8a**
1	**4a** (H, H, Br)	41 (1.3:1)	20	16
2	**4b** (H, H, I)	57 (1.3:1)	28	22
3	**4c** (F, H, Br)	50 (1.2:1)	25	21
4	**4d** (F, H, I)	70 (1.2:1)	35	30
5	**4e** (F, F, Br)	40 (6:1)	32	5
6	**4f** (F, F, I)	16 (1.2:1)	7	6

[a] Reaction conditions: 3 mol% of compounds **4a–f**, PhCl as solvent, 90 °C and 6 h. [b] Determined by ^{1}H NMR spectroscopy of the reaction crude. [c] Isolated yield.

entries 1–5). Iodide derivative **4b** displayed higher catalytic activity than bromide one (**4a**), obtaining conversions higher than 40% in both cases (Table 1, entries 1 and 2). The introduction of one fluorine atom in position 5 of the benzene ring (**4c** R^1 = F, R^2=H, X=Br and **4d** R^1=F, R^2=H, X=I) resulted in higher conversions (Table 1, compare entries 1 *versus* 3 and 2 *versus* 4), but the introduction of a second fluorine atom in the benzene ring (**4e** R^1=R^2=F, X=Br and **4f** R^1=R^2=F, X=I) resulted in a lower yield (Table 1 entries 5 and 6). This indicates that an increase in phenol acidity resulted in an increase of the catalytic activity to a limit point, above which, the catalytic activity decreases. On the other hand, the use of iodide derivative led to better results than bromide compounds (Table 1, compare entries 1 *versus* 2 and 3 *versus* 4), similarly to what was observed by Poater and D'Elia[12a] using ammonium halide as nucleophile. In all cases 3,5-diphenyloxazolidin-2-one (**7a**) was the main product of the reaction, however the selectivity was very low except for compound **4e** that was moderate (Table 1, entry 5). Based on the catalyst screening, compound **4d** was chosen as the optimal catalyst and it was used for the optimization of the reaction temperature, solvent, catalyst loading, and time.

With the purpose of finding the optimal reaction conditions, reactions were carried out in different solvents using 2 or 3 mol% of catalyst at 90 °C for 24 h. The results are listed in table 2. No conversion was observed when the reaction was carried out in neat conditions (Table 2, entry 1). However, when toluene, ethyl acetate, dimethyl sulfoxide or chlorobenzene were used as the reaction solvent, low to moderated conversions were obtained (Table 2, entries 2–5). As can be seen in Table 2, entry 5, chlorobenzene was shown to be the best solvent for this reaction.

Table 2. Influence of solvent on the reaction of styrene oxide (**5a**) and phenyl isocyanate (**6a**) using **4d** as catalyst.

Entry	% Catal.	T(°C)	t(h)	Solvent	Conv. %[a] (**7a**:**8a**)	Yield %[b] **7a**	**8a**
1	2	90	24	–	0	–	–
2	2	90	24	Toluene	40 (1.2:1)	20	17
3	2	90	24	EtOAc	20 (1.1:1)	7	6
4	2	90	24	DMSO	60 (1.3:1)	29	23
5	2	90	24	PhCl	71 (1.3:1)	39	29
6	2	90	48	PhCl	100 (1.1:1)	48	45
7	3	90	24	PhCl	100 (1.1:1)	49	45
8	2	100	24	PhCl	100 (1.1:1)	48	44
9	1	100	24	PhCl	70 (1.3:1)	39	28
10	3	90	14	PhCl	100 (1.1:1)	49	46

[a] Determined by ^{1}H NMR spectroscopy of the reaction crude. [b] Isolated

Then, the effect of the reaction time, temperature and catalyst loading on the synthesis of **7a** and **8a** was studied. Quantitative conversions were achieved by increasing either the reaction time (48 h, Table 2, entry 6), the reaction temperature (100 °C, Table 2, entry 8) or the catalyst loading to 3 mol% (Table 2, entry 7). However, increase of the catalytic activity resulted in a decrease of the selectivity. On the other hand, the decrease of the catalyst loading whilst keeping the temperature at 100 °C, led to a decrease in conversion (Table 2, entry 9). Therefore, the optimal conditions for this reaction were found to be 3 mol% of **4d** at 90 °C for 14 h in chlorobenzene (Table 2, entry 10).

Having determined the optimal catalyst and reaction conditions, the scope of the reaction was investigated. The study was carried out using a range of epoxides and isocyanates, under the optimal reaction conditions (3 mol% of **4d**, 90 °C in chlorobenzene). The results are shown in table 3. As can be seen in table 3, the use of aromatic epoxides afforded the corresponding 3,4- and 3,5-disubstituted oxazolidin-2-ones. Moderate yields were reached after 6 h of reaction (Table 3, entries 1–5). This allowed us to determine the influence of the nature of the isocyanate on thecatalytic activity, with phenyl isocyanate and 4-nitrophenyl isocyanate being the most reactive substrates (Table 3, entries 1 and 3). Longer reaction times resulted in high yields, 14 h for phenyl isocyanate (Table 3, entry 6) or 24 h for isocyanates **6b–e** (Table 3, entries 7–10). When aliphatic epoxides **5b–f** were used as substrates, moderate yields were obtained after 24 h of reaction showing that these substrates are less reactive than aromatic ones. Among them, epichlorohydrin and 1,2- epoxybutane were found to be the most reactive epoxide substrates

Table 3. Cycloaddition of epoxides and isocyanates catalysed by **4d**.[a]

Entry	Epoxide	Isocyanate	t(h)	Conv. %[b] (**7**:**8**)	Yield %[c] **7**	**8**
1	**5a**	**6a**	6	70 (1.2:1)	35	30
2	**5a**	**6c**	6	38 (1:1)	17	15
3	**5a**	**6d**	6	75 (1:1)	38	32
4	**5a**	**6e**	6	40 (1.4:1)	22	15
5	**5a**	**6b**	6	44 (1.1:1)	21	19
6	**5a**	**6a**	14	100 (1.1:1)	49	46
7	**5a**	**6b**	24	94 (1.2:1)	53	47
8	**5a**	**6c**	24	100 (1.4:1)	53	38
9	**5a**	**6d**	24	93 (1:1.4)	35	53
10	**5a**	**6e**	24	93 (1:1)	43	42
11	**5b**	**6a**	24	77 (1:0)	70	0
12	**5c**	**6a**	24	35 (1:0)	31	0
13	**5d**	**6a**	24	78 (1:0)	72	0
14	**5e**	**6a**	24	47 (1:0)	40	0
15	**5f**	**6a**	24	42 (1:0)	37	0

[a] Reaction conditions 3 mol% of **4d**, PhCl as solvent at 90 °C. [b] Determined by ^{1}H NMR spectroscopy of the reaction crude. [c] Isolated

(Table 3, entries 11 and 13). Except for propylene epoxide, as the alkyl chain lengthens, the yields become lower (Table 3, entries 13 to 15). For propylene oxide, the lower yield obtained (Table 3, entry 12) is probably due to the high volatility of this epoxide.

Regarding the selectivity for the synthesis of oxazolidine-2-ones, mixtures of **7a**–**e** and **8a**–**e** were obtained when styrene oxide was used as precursor (Table 3, entries 1–10). In these cases, selectivity is null or very low. However, it is higher than 99% when aliphatic epoxides were used with oxazolidine-2-ones **7f**–**j** being the only isolated compound.

Since epoxides were used as a racemic mixture, both *R* and *S* enantiomers of the oxazolidin-2-ones were obtained. Therefore, when the ^{1}H-NMR spectrum of oxazolidin-2-one **8a** was recorded in the presence of a chiral shift reagent such as (*S*)-(+)-(9-anthryl)-2,2,2-trifluoroethanol, the resonance of one of the diastereotopic H5 protons of the oxazolidinone ring was shifted to higher field and duplicated (Figures 2a and 2b). These two new signals observed were due to the two diastereomeric forms obtained from the corresponding enantiomers. However, when enantiomerically enriched styrene oxide (*R*)-**5a** was reacted with phenyl isocyanate **6a** and a ^{1}H-NMR spectrum of the reaction crude was recorded in the presence of the chiral shift reagent, no duplication of any **8a** signals was observed (Figure 2c) showing that there was no racemization of the products.

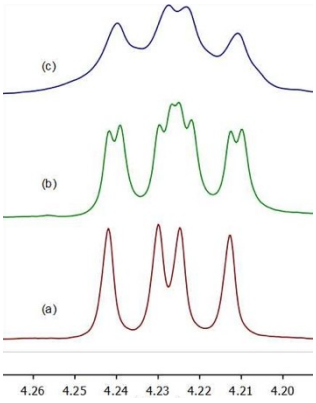


Figure 2. ^{1}H NMR experiment of 3,4-diphenyloxazolidin-2-one (**8a**). (a) (±)-**8a** without shift reagent. (b) (±)-**8a** with shift reagent. (c) (*R*)-**8a** with shift reagent.

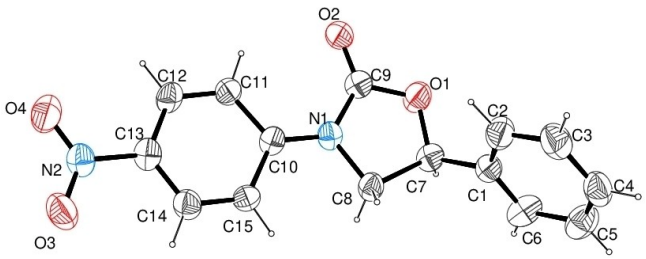
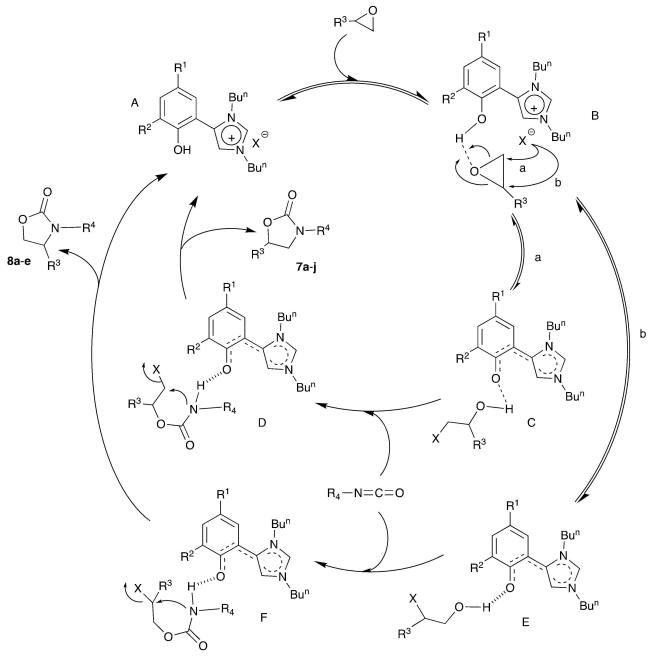


Figure 3. X-Ray structure of 3-(4-nitrophenyl)-4-phenyloxazolidin-2-one (**7d**). Thermal ellipsoids are set at 30% probability.

The molecular structure of 3-(4-nitrophenyl)-4-phenyloxazolidin-2-one (**7d**) was determined by an X-ray diffraction study. ORTEP diagram is shown in Figure 3 and crystallographic data and selected interatomic distances and angles are given in Tables S1 and S2 respectively. Both enantiomers *R* and *S* are present in the unit cell; only enantiomer *R* is shown in the Figure 3. The nitrophenyl group is on position 3 and the phenyl ring is on position 5 of the oxazolidine-2-one. The ring of the oxazolidin-2-one is almost planar and the nitrophenyl group and oxazolidin-2-one ring are almost coplanar, with a torsion angle around 1.79°. On the other hand, the torsion angle between the oxazoldin-2-one ring and the phenyl ring is 75.86°.

In a previous work,[16a] we showed that in the reaction between styrene oxide (**5a**) and 4-(2-hydroxyphenyl)-1,3-dibutylimidazolium iodide (**4b**) at 80 °C, a single halohydrin was formed by ring-opening of the epoxide through a S_N2 type reaction, due to the attack of the halide anion to the oxirane ring. That reaction was facilitated by hydrogen bonding between the hydrogen atom of the OH group and the oxygen atom of the epoxide. These experimental evidences led us to propose that halohydrins are also formed as intermediates in the reaction of epoxides and isocyanates with this kind of catalysts. However, in this reaction, oxazolidin-2-ones were obtained as a mixture of two regioisomers when aromatic epoxides were used due to the attack of the halide anion to both carbon atoms of the oxirane ring. This suggests that two regioisomer halohydrins were obtained as intermediates in a fast equilibrium.

Taking into account all these facts, a plausible mechanism for the oxazolidin-2-ones synthesis catalyzed by 5-(2-hydroxyphenyl)imidazolium salts is shown in Scheme 3. This mechanism is consistent with that previously proposed for oxazolidin-2-ones formation from epoxides and isocyanates catalyzed by hydroxyphenylphosphonium salts[14a] or triethylamine hydroiodide.[14c] In the first step, the epoxide is activated by the hydroxyl group of the phenol ring through a hydrogen bond which facilitates the ring-opening of the epoxide through a S_N2 type reaction by attack of iodide. The attack of halide anion to C3 of the epoxide (*pathway a*) affords halohydrin C which is coordinated to a neutral 5-(2-oxyphenyl)imidazolium that delocalize the negative charge through both six and five aromatic rings. Then, an isocyanate molecule is inserted into the O–H bond to form carbamate D. The intramolecular attack of nitrogen to C–X (X = Br, I) affords the five-membered ring and the corresponding 3,5-disubstituted oxazolidin-2-ones (**7a**–**j**) were formed with regeneration of the catalyst. Halohydrins E were obtained by attack of halide anion to C2 of the epoxide (*pathway b*) which affords the corresponding 3,4-disubstituted oxazolidin-2-ones (**8a**–**e**) after insertion of an isocyanate molecule. *Pathway b* is favored by electronic control and it is carried out through a transition state that develops a certain positive charge on the C2 that is stabilized when R^3 is an aromatic ring. As a result, there is a competition between the two mechanisms and a mixture of both oxazolidinones **7a**–**e** and **8a**–**e** was obtained. When R^3 is an aliphatic group the transition state of the attack to C2 is not stabilized enough and



Scheme 3. Proposed mechanism for the synthesis of 3,4- and 3,5-disubstituted oxazolidin-2-ones.

the reaction was driven only by steric control (pathway a) affording 3,5-disubstituted oxazolidin-2-ones (**7f–j**) as the only product.

The increase of catalytic activity by the introduction of a fluorine atom on the phenyl ring (Table 1, compare **4c** *versus* **4a** and **4d** *versus* **4b**) strongly suggests that the rate-determining step could be the ring-opening of the epoxide in presence of catalyst **4a–d**. The increase of acidity affords stronger epoxide activation via H-bonds and less energy is necessary to break the C–O bond. A further increase in catalyst acidity by placing two fluorine atoms in phenyl ring (**4e–f**) results in a decrease in catalytic activity, these results suggest that the rate-limiting step for these catalysts could be the intramolecular attack of nitrogen on the C–X bond to close the oxazolidin-2-one ring. Similar change of mechanism has been described by Poater and D'Elia for the synthesis of cyclic carbonates.[17] The H····O bonds of intermediates D and F are weaker and the nitrogen atoms are less nucleophilic, therefore more energy is necessary to close the ring affording lower yields under the same reaction conditions. Probably due to this lower reactivity, higher quantities of byproducts from the isocyanate such as urea and isocyanurate trimer were obtained, decreasing yields of oxazolidine-2-ones, similarly to as observed by Poater and D'Elia in related processes.[12a]

Conclusion

In conclusion, easily obtained 1,3-dibutyl-4-(2-hydroxyphenyl)imidazolium halides and their phenyl fluorinated derived are efficient catalysts for the synthesis of oxazolidin-2-ones, by [3 + 2] cycloaddition of epoxides and isocyanates. Iodide derivatives were shown to be more efficient organocatalysts than bromide ones, and the catalytic activity displayed by these compounds was increased by the introduction of a fluorine atom in the position 5 of the phenol ring versus non fluorinated catalyst, due to the increased acidity of the hydroxyl group. On the other hand, the addition of two fluorine atoms in positions 3 and 5 of the phenyl were shown to be detrimental and lower catalytic activity was obtained due to the increase of acidity of them. Furthermore, a complete selectivity in favour of 3,4-disubstituted oxazolidin-2-ones was observed when aliphatic epoxides were used.

Supporting Information Summary

The supporting information contains synthetic and analytical details for compounds **2–8** and crystallographic data for compounds **3b**, **3c**, **4d**, and **7b**.

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Conflict of Interest

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: Epoxides · Imidazolium salts · Organocatalysts · Oxazolidin-2-ones

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