Ruthenium Porphyrin-Catalyzed Synthesis of Oxazolidin-2-ones by Cycloaddition of CO_2 to Aziridines

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Abstract: The reaction between *N*-substituted-2-arylaziridines and CO_2 is efficiently promoted by ruthenium(VI) imido porphyrin complexes and yields a mixture of 5-aryl (**A**) and 4-aryl (**B**) substituted oxazolidin-2-ones with a regioisomeric **A**/**B** ratio up to 99:1. Several oxazolidin-2-one molecules were synthesized at 100°C and 0.6 MPa of carbon dioxide by using the low catalytic loading of 1% mol. The formation of a deactivated compound, deriving from the ruthenium catalyst, suggested a possible catalytic role of nitrogen imido atoms.

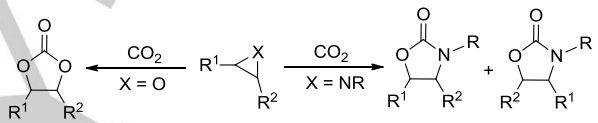
Introduction

Over the last decades, aziridines have been extensively studied as starting materials due to the high energy of the strained ring which permits the transformation of aziridines into a large variety of fine chemicals by ring-opening reactions.[1] Among all the organic transformations involving aziridines, the insertion of CO_2 into the three-membered ring is responsible for the synthesis of oxazolidin-2-ones, which are the pharmaceutically active moieties of several antibacterial and antimicrobial compounds,[2] such as Linezolid,[3] Tedizolid[4] and Radezolid.[5] In addition, oxazolidin-2-ones are widely used as chiral auxiliaries in various asymmetric synthetic reactions.[6]

The reaction of aziridines with CO_2 displays interesting features in terms of eco-sustainability because the catalytic valorization of the greenhouse CO_2 gas, as a renewable C1 building block,[7] is coupled with the 100% atom-efficiency of the ring-insertion process. The CO_2 cycloaddition into aziridines can be efficiently promoted by several homogeneous and heterogeneous species,[8] which are fundamental in ensuring good reaction performances by applying eco-friendly experimental conditions, such as low catalytic loadings, low reaction temperatures and low CO_2 pressures.

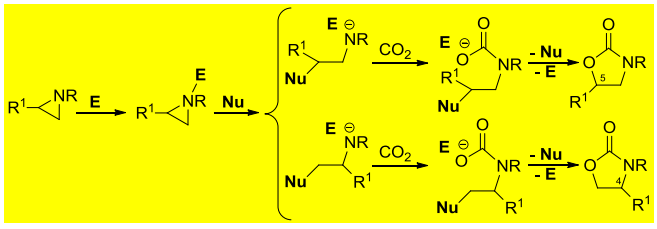
The synthesis of oxazolidin-2-ones from aziridines and CO_2 can also be performed in the absence of any catalytic species.[9] However, in these cases the required use of aziridine as the reaction solvent[10] restricts the reaction scope when the aziridine is not a liquid compound or its synthesis consists in time-consuming and/or expensive procedures.

It is important to remember that, while the analogous reaction of CO_2 with an achiral epoxide yields the corresponding cyclic carbonate as a single isomer, the CO_2 cycloaddition to an aziridine molecule can produce two different regioisomers. When $R^1 \neq R^2$, the ring opening reaction can take place on two inequivalent carbon atoms of the aziridine therefore, two regioisomers can be formed in a ratio which strongly depends on the nature of the promoter (Scheme 1).



Scheme 1. The coupling reaction between carbon dioxide and either epoxides or aziridines, which yields cyclic carbonates or oxazolidin-2-ones, respectively.

To date, the cycloaddition of CO_2 to aziridines has been less studied than the equivalent reaction to epoxides[11] and even if it is generally recognized that the presence of both an electrophilic (**E**) and nucleophilic (**Nu**) species is required for the productive insertion of CO_2 into an aziridine ring, the reaction mechanism is still under debate.[12] Analogously to the mechanism of the CO_2 cycloaddition to epoxides,[11c,11d] the coordination of an electrophilic species to the aziridine nitrogen atom could promote the ring opening reaction by the nucleophilic agent. The so-formed intermediate can therefore react with CO_2, yielding the desired oxazolidin-2-one. As reported in Scheme 1, oxazolidin-2-ones can be formed in two regioisomers and when 2-substituted aziridines are employed as starting materials, 5-substitued oxazolidin-2-ones[8h,8i] are usually formed as the prevalent regioisomer, due to the preferred nucleophilic attack on the most substituted aziridine carbon atom (Scheme 2).



Scheme 2. The proposed mechanism for the formation of oxazolidin-2-ones.

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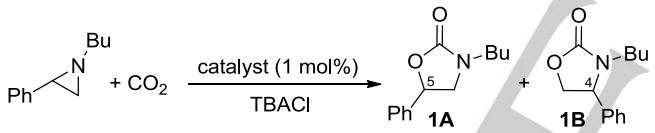
The present communication deals with the catalytic activity of metal porphyrins in mediating the reaction of *N*-substituted-2-arylaziridines with CO_2 forming 5-aryl- (**A**) and 4-aryl-oxazolidin-2-ones (**B**) with the large excess of the less-hindered 5-substituted regioisomer **A** over the 4-substituted one **B**. Despite the efficiency of metal porphyrin complexes in promoting the CO_2 cycloaddition to epoxide,[11b] the use of these catalysts for the synthesis of oxazolidin-2-ones has been very limited.[8b,8g,13]

Results and Discussion

In view of the reactivity of zinc porphyrin complexes to promote the CO_2 insertion into epoxides,[11b,13] the model reaction between 1-butyl-2-phenyl aziridine and carbon dioxide was first performed in the presence of Zn(TPP) but the formation of the desired compounds was not observed. Thus, the model reaction was run in the presence of less electrophilic metal species, such as iron and ruthenium porphyrin complexes. Obtained results are reported in Table 1. Considering the well-known catalytic role of ammonium salts[14] and their general use as co-catalysts in metal porphyrin-promoted reactions of CO_2 with epoxides,[11b,15] tetrabutyl ammonium chloride (TBACl) was initially tested alone in the model reaction and then employed in a catalyst/TBACl/aziridine ratio of 1:10:100. All the reactions were performed in a steel autoclave for 6 h at 100°C and 3 MPa of CO_2 by using benzene as the reaction solvent.

Table 1. Metal porphyrin-catalyzed cycloaddition of CO_2 to 1-butyl-2-phenylaziridine.[a]



entry	catalyst	Yield %[b]	**1A**/**1B** ratio[b]
1	-	20	88/12
2	Fe(F_{20}TPP)Cl	40	95/5
3	Fe(F_{20}TPP)OMe	30	92/8
4	Ru(TPP)CO	13	86/14
5	Ru(TPP)py_2	12	95/5
6	$[Ru(TPP)(OCH_3)]_2O$	35	91/9
7	Ru(TPP)$(NAr)_2$[c]	79	88/12
8	Ru(TPP)$(NAr')_2$[d]	62	90/10
9	Ru(F_{20}TPP)$(NAr)_2$[c]	34	85/15
10	Ru(TMP)$(NAr)_2$[c]	41	88/12
11	Ru(OEP)$(NAr)_2$[c]	65	90/10

[a] Reaction conditions: catalyst/TBACl/aziridine = 1:10:100 in benzene. Reactions were performed in a steel autoclave for 6 h at 100°C and 3 MPa of CO_2. [b] Determined by ^{1}H NMR spectroscopy using 2,4-dinitrotoluene as the internal standard. [c] Ar = 3,5$(CF_3)_2C_6H_3$. [d] Ar' = 4(*t*Bu)C_6H_4.

The reaction performed in the presence of the sole TBACl (Table 1, entry 1) formed oxazolidinones in 20% yield and **1A**/**1B** ratio of 88:12. As reported in Table 1, iron(III) porphyrin derivatives were less catalytically active than ruthenium catalysts and, even if the reaction occurred with good regioselectivities, moderate yields were achieved in the presence of Fe(F_{20}TPP)X species (F_{20}TPP = dianion of *meso*-tetrakis-(pentafluorophenyl) porphyrin; X = Cl[16] or OMe[17]) (Table 1, entries 2 and 3).

Low catalytic efficiencies were also observed in the presence of Ru(TPP)CO[18] and Ru(TPP)$(py)_2$[19] (TPP = dianion of *meso*-tetrakis-(phenyl) porphyrin) (Table 1, entries 4 and 5), while a slight enhancement of reaction yields was achieved by using $[Ru(TPP)OCH_3)]_2O$[20] (Table 1, entry 6).

When Ru(TPP)CO or Ru(TPP)$(py)_2$ (Table 1, entries 4 and 5) were used as the catalyst, the ^{1}H NMR spectrum of the crude revealed an aziridine conversion of 40% and 27%, respectively and the presence of several unidentified side-products. We suggest that even if Ru (II) porphyrin complexes were poorly active in promoting the oxazolidin-2-one synthesis, they can catalyze side-reactions which were responsible for the partial aziridine conversion.

Higher reaction yields were achieved by performing the reaction in the presence of *bis*-imido ruthenium porphyrin catalysts (Table 1, entries 7-11) which always promoted the formation of the 5-regioisomer **1A** as the major product.

Bis-imido complexes Ru(F_{20}TPP)$(NAr)_2$ (Ar = 3,5$(CF_3)_2C_6H_3$), Ru(TMP)$(NAr)_2$ (TMP = dianion of *meso*-tetrakis-(mesityl) porphyrin) and Ru(OEP)$(NAr)_2$ (OEP = dianion of octaethyl porphyrin) were synthesized by using the methodology already reported by us for preparing Ru(TPP)$(NAr)_2$.[21] On the other hand, Ru(TPP)$(NAr')_2$ (Ar' = 4(*t*Bu)C_6H_4) was prepared by using our reported procedure in which Ar'N_3 efficiently reacts with the electron-poor ruthenium(IV) $[Ru(TPP)OCH_3)]_2O$ complex.[20]

Collected data indicated that the catalytic activity of *bis*-imido ruthenium(VI) porphyrins was independent from the electronic nature of the *N*-imido ligand. Similar results, in terms of yields and regioselectivities, were obtained by using both Ru(TPP)$(NAr)_2$ (Ar = 3,5$(CF_3)_2C_6H_3$) and Ru(TPP)$(NAr')_2$ (Ar' = 4(*t*Bu)C_6H_4) catalysts, which show an electron-deficient and electron-rich axial imido ligand, respectively (Table 1, entries 7 and 8). The catalytic effect of the electronic and steric nature of the porphyrin ring was also investigated by comparing the catalytic efficiency of Ru(F_{20}TPP)$(NAr)_2$, Ru(TMP)$(NAr)_2$ and Ru(OEP)$(NAr)_2$ porphyrin catalysts. Catalytic results of the reactions performed in the presence of Ru(F_{20}TPP)$(NAr)_2$ and Ru(TMP)$(NAr)_2$ (Table 1, entries 9 and 10) indicated that both electron-deficient and sterically-hindered ligands have a negative effect on the activity of the ruthenium catalyst. On the other hand, the low-hindered *bis*-imido Ru(OEP)$(NAr)_2$ complex, which shows hydrogen atoms on *meso*-positions of the porphyrin ring, promoted the oxazolidin-2-one synthesis with 65% yield and **A**/**B** ratio of 90:10 (Table 1 entry 11).

Considering that the best combination of yield and regioselectivity was obtained in the presence of Ru(TPP)$(NAr)_2$ (Table 1, entry 6), this latter complex was employed for optimizing experimental conditions of the model reaction. The effect of the tetrabutyl ammonium salt's anion, temperature, solvent polarity and CO_2 pressure on the catalytic efficiency was investigated and the obtained results are displayed in Table 2.

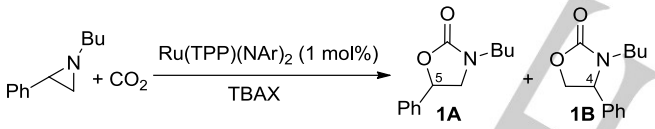
The catalytic influence of the nature of the anion of the tetrabutyl ammonium salt was examined by employing tetrabutyl ammonium iodide (TBAI), tetrabutyl ammonium bromide (TBAB),

TBACl and tetrabutyl ammonium fluoride (TBAF) as co-catalysts in the model reaction at 100°C and using benzene as the reaction solvent. When the reaction was performed in the presence of either TBAI or TBAF the product was not formed. It should be noted that TBAF was employed as a THF solution (1.0 M) due to its instability in the solid state[22] thus, considering the reactivity of $Ru(TPP)(NAr)_2$ in coordinating solvents,[21] THF was probably responsible for the catalyst deactivation.

Considering that similar results were obtained by using either TBAB or TBACl (Table 2, entries 1 and 2), the latter salt was employed for optimizing the other reaction conditions.

In view of the lack of the catalytic effectiveness at 50°C (Table 2, entry 3), the effect of the solvent polarity was studied by performing reactions at 100°C. Even if the addition of 10% of DMF to the benzene solution was responsible for the formation of regioisomer **A** as the only reaction product (**A**/**B** ratio=99:1) (Table 2, entry 4), the moderate reaction productivity did not justify a general use of this reaction medium. In view of the low productivity of the reaction performed in dichloroethane (Table 2, entry 5), the optimization of the CO_2 pressure was executed in benzene at 100°C. Similar results were obtained by using either 3 or 0.6 MPa of carbon dioxide (Table 2, entries 5 and 6) whilst the decrease of CO_2 pressure to 0.1 MPa was responsible for a large decrease of the catalytic performance; oxazolidin-2-ones were obtained in 35% yield and **A**/**B** ratio of 94:6 (Table 2, entry 7). The model reaction was also performed in a pressure tube where the good **A**/**B** ratio of 93:7 was obtained in the very low yield of 13%.

Table 2. Optimization of experimental conditions of the model reaction of 1-butyl-2-phenylaziridine with CO_2[a]

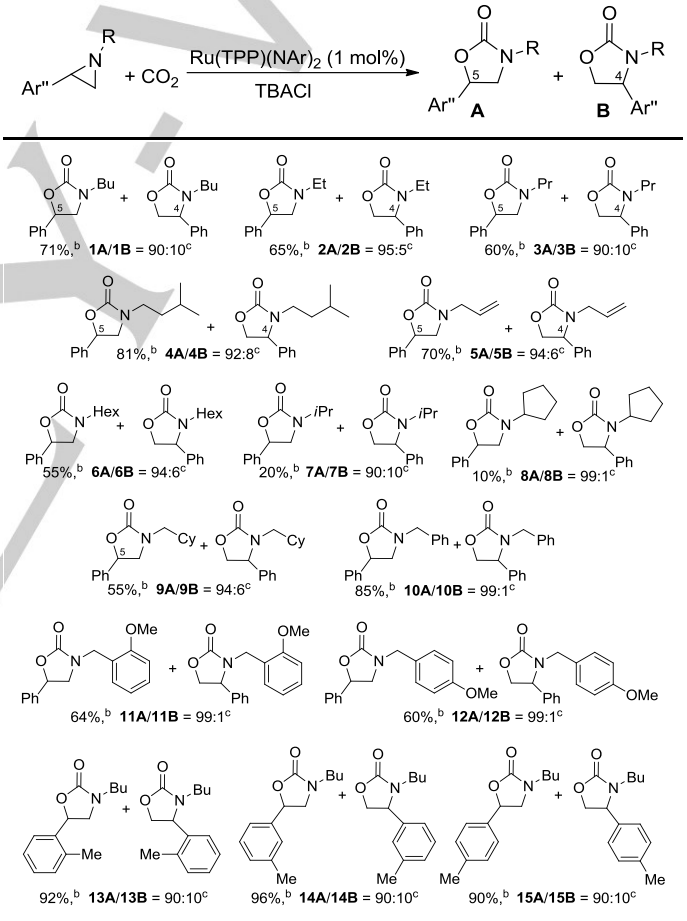


entry	T (°C)	P_{CO_2} (MPa)	solvent	X⁻	yield %[b]	1A/1B ratio[b]
1	100	3	C_6H_6	Br	68%	85/15
2	100	3	C_6H_6	Cl	79%	88/12
3	50	3	C_6H_6	Cl	-	-
4	100	3	C_6H_6/DMF(10%)	Cl	45%	99/1
5	100	3	$C_2H_4Cl_2$	Cl	22%	90/10
6	100	0.6	C_6H_6	Cl	70%	90/10
7	100	0.1	C_6H_6	Cl	35%	94/6

[a] Reaction conditions: $Ru(TPP)(NAr)_2$/TBAX/aziridine = 1:10:100 (Ar = $3,5(CF_3)_2C_6H_3$). Reactions were performed in a steel autoclave for 6 h. [b] Determined by ^1H NMR spectroscopy using 2,4-dinitrotoluene as the internal standard.

Then, the scope of the reaction was studied in the presence of $Ru(TPP)(NAr)_2$ 1% mol, TBACl 10% mol at 100°C, 0.6 MPa of CO_2 and using benzene as the reaction solvent. *N*-substituted-oxazolidin-2-ones were obtained with moderate to good isolated yields and **A**/**B** ratio up to 99:1 (Table 3). Collected data revealed a general decrease of reaction yields when the steric hindrance around the aziridine nitrogen atom was increased. When isopropyl (Table 3, compounds **7A**/**7B**) or cyclopentyl (Table 3, compounds **8A**/**8B**) groups were bonded to *N*-aziridine atom, the reaction productivity was low. Better results were achieved if less-hindered cyclohexylmethyl (Table 3, compounds **9A**/**9B**) or benzyl (Table 3, compounds **10A**/**10B**) substituents were linked to the nitrogen atom of the aziridine ring, also when a methoxy group was present on the benzylic moiety (Table 3, compounds **11A**/**11B** and **12A**/**12B**). It should be noted that in the latter reactions, the 5-regioisomer was obtained as the sole reaction product (**A**/**B** = 99:1). Considering that the catalytic performance decreased when a steric hindrance was present either on the nitrogen aziridine atom or the tetrapyrrolic core, an unfavorable interaction between these two moieties during the catalytic reaction can be envisaged.

Table 3. Synthesis of oxazolidin-2-ones from *N*-substituted-2-arylaziridine and CO_2.[a]



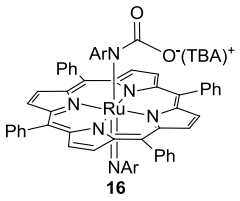
[a] Reaction conditions: $Ru(TPP)(NAr)_2$/TBACl/aziridine = 1:10:100 (Ar = $3,5(CF_3)_2C_6H_3$). Reactions were performed in a steel autoclave for 6 h at 100°C and 0.6 MPa of CO_2. [b] Isolated yields. [c] Determined by ^1H NMR spectroscopy using 2,4-dinitrotoluene as the internal standard.

The replacement of C_6H_5 with the more electron-rich $(Me)C_6H_4$ group on the C_2 position of the starting aziridine had a beneficial effect. Similar yields and regioselectivities of the synthesis of **13A**/**13B**, **14A**/**14B** and **15A**/**15B** compounds (Table 3) were observed independently from the position of the methyl group on

the phenyl substituent, pointing out that the steric hindrance of C_2 aziridine carbon atom does not influence the catalytic performance.

In order to study the catalyst robustness, the CO_2 cycloaddition to 1-butyl-2-phenylaziridine, forming **1A**/**1B** oxazolidin-2-one mixture, was performed for three consecutive times in the presence of 1% mol of Ru(TPP)$(NAr)_2$. Each reaction was run for 6 hours at 100°C and, after checking that the aziridine conversion was >95%, a same amount of 1-butyl-2-phenylaziridine was added before recharging the autoclave with 0.6 MPa of CO_2. At the end of the three runs, the ^{1}H NMR analysis of the reaction mixture revealed the formation of corresponding oxazolidin-2-ones in 70% yield (with respect to the total amount of added aziridine) and **1A**/**1B** ratio of 90:10, indicating that Ru(TPP)$(NAr)_2$ maintains its catalytic activity for at least three consecutive catalytic reactions (see SI for the experimental procedure).

The model catalytic reaction was then performed on a larger scale in order to identify the nature of ruthenium species after the complete transformation of aziridine into corresponding oxazolidin-2-one. The ESI-MS spectroscopic analysis of the crude revealed the formation of Ru(TPP)(NAr)(ArNCOO$^-$NBu$_4^+$) complex (**16**).



16

Figure 1. Molecular structure of complex **16**.

Thus, the reaction of Ru(TPP)$(NAr)_2$ with TBACl was repeated in the absence of aziridine at 100 °C and under 0.6 MPa of CO_2. The formation of compound **16** was again observed by ESI-MS analysis of the crude, the ^{1}H NMR analysis in CD_3OD revealed the presence of a paramagnetic compound and IR (ATR) spectroscopy showed the C=O stretching at 1604 cm^{-1}. The formation of complex **16**, which was catalytically inactive, suggested that CO_2 interacts with the nitrogen imido atom, which shows a very high electron density due to the presence of ruthenium, as indicated by our previous DFT study.[23] These preliminary experiments, as well as the isolation of complex **16**, were not sufficient to figure out a catalytic mechanism of this reaction, which will be deeply investigated by using both kinetic and DFT approaches.

Conclusion

In conclusion, we report the catalytic activity of ruthenium *bis*-imido porphyrin complexes in promoting the regioselective cycloaddition of CO_2 to aziridines. The procedure was effective for the synthesis of *N*-substituted oxazolidin-2-ones in yields up to 96% and regioselectivities up to 99:1. The formation of a deactivated ruthenium compound suggested the occurrence of a mechanism where the nitrogen imido atom of the ruthenium catalyst can play a role in activating CO_2 towards the cycloaddition to the aziridine ring.

Experimental Section

Synthesis of porphyrin complexes and aziridines, general catalytic procedures as well as NMR spectra, IR, UV/Vis, ESI-MS spectroscopic data of all compounds reported in the manuscript can be found in the Supporting Information.

Keywords: Carbon dioxide fixation • Cycloaddition • Homogeneous catalysis • Porphyrinoids • Ruthenium.

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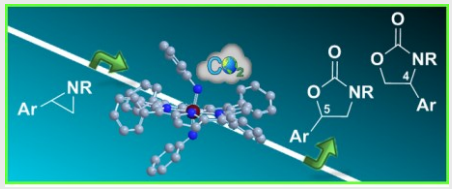

The catalytic activity of ruthenium(IV) *bis*-imido porphyrins in promoting the insertion of CO_2 into aziridines, forming oxazolidin-2-ones, is here reported.

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Ruthenium Porphyrin-Catalyzed Synthesis of Oxazolidin-2-ones by Cycloaddition of CO_2 to Aziridines