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**To be cited as:** *ChemCatChem* 10.1002/cctc.201800063

**Link to VoR:** http://dx.doi.org/10.1002/cctc.201800063

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FULL PAPER

# Boosting the catalytic performance of organic salts for the fast and selective synthesis of α-alkylidene cyclic carbonates from $CO_2$ and propargylic alcohols.

Bruno Grignard[a], Charlène Gabriela Ngassamtounzoua[a], Sandro Gennen[a], Bernard Gilbert[c], Raphaël Méreau[b], Christine Jerome[a], Thierry Tassaing[b], Christophe Detrembleur[a]*

**Abstract:** The synthesis of α-alkylidene cyclic carbonates (αCCs) by carboxylative coupling of $CO_2$ with propargylic alcohols is receiving increasing interest but requires the use of catalysts that are most often added in large quantity and/or are lacking of selectivity. Herein, we describe that the fine-tuning of the structure of organocatalysts of the ammonium-type enables to identify the important structural parameters that dictate their catalytic performance. Tetrabutylammonium oxalate revealed to be one of the most attractive organocatalysts with a remarkable fast, complete and selective production of αCCs at low catalyst loading (2.5 mol%) under solvent free-conditions. This study clearly opens new avenues for the facile and selective synthesis of libraries of αCCs from $CO_2$ and propargylic alcohol by using simple organocatalysts.

## Introduction

The chemical conversion of $CO_2$ into five-membered cyclic carbonates (5CCs) represents one of the most efficient ways to valorize this waste in useful organic synthons. Beside the extensively studied epoxide/$CO_2$ coupling reaction,[1-10] the synthesis of α-alkylidene cyclic 5-membered carbonates (αCCs) by carboxylative coupling of $CO_2$ with propargylic alcohols is gaining recent strong interest. αCCs differ in their structure from conventional 5-membered cyclic carbonates by the presence of an exocyclic olefinic group that facilitates the ring-opening of the cyclic carbonate by various nucleophiles such as amines and alcohols while selectively forming one regioisomer.[11] The thermodynamic driving force for the αCCs ring-opening relies on the formation of an enol species that rapidly rearranges into a more stable β-keto tautomer.[12,13] The exceptional reactivity of αCCs compared to 5CCs was recently exploited to access to novel classes of regioregular hydroxyl- or oxo-functional polyurethanes and/or polycarbonates under mild experimental conditions.[11] αCCs are synthesized by coupling of $CO_2$ with propargylic alcohols. The first reported metal catalysts (Ru, Co, Pd, Ag, …)[14-17] only showed acceptable activity and selectivity at high $CO_2$ pressure and high temperature under moisture-free conditions. Metal-free systems derived from (organic) bases such as phosphines, guanidine, $K_2CO_3$, N-heterocyclic carbenes (NHC) and olefins (NHO), or ionic liquids were also developed for this reaction. Their catalytic activity generally arose from their capability to activate the substrate or $CO_2$ through acid-base reaction or by forming stable zwitterionic guanidine, NHC or NHO–$CO_2$ adducts.[18-22] However, most of these catalysts were efficient at temperature between 60 to 100 °C and pressure up to 25 to 100 bar. Moreover, long reaction times at high catalyst loading were required for reaching a high propargylic alcohol conversion. In 2016, Wang et al. reported series of novel reusable ionic liquids (ILs) derived from 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) that were able to promote the synthesis of αCCs at 60 °C and 25 bar.[23] Even at ILs loading of 200 mol% compared to propargylic alcohols, the coupling reaction remained slow as attested by yields of 68 – 89 % after 24 h. This moderate activity might be related to the low basicity of ILs. Indeed, Wang et al. correlated the catalytic activity of phosphonium-based ILs with the basicity of their counter-anion. Anions such as imidazolides with a pKa value close to 7.4 represented the best compromise in terms of reaction yield and selectivity.[24] This trend was further confirmed by our groups for (super)bases promoted $CO_2$/alkynols coupling reactions. Organic bases of high pKa values showed outstanding catalytic activity but at the expense of the selectivity.[25] Very recently, Liu et al. developed series of novel phosphonium-based organocatalysts by introducing the concept of multiple-site activation of $CO_2$ via the use of anions derived from carboxylic acid and/or hydroxyl multifunctional pyridines. With a loading of 10 mol%, these catalysts showed good activity at 1bar and 30 °C, with yields between 33 and 91 % after 20h.[26] The scarce examples of the organocatalyzed coupling reactions promoted at low $CO_2$ pressure (1 bar) were performed with a large excess of the catalyst compared to the reactant.[27] New trends deal will the development of binary catalysts combining metal species with ionic liquids or organic bases [28-32]. These catalysts work by the synergistic activation of both the substrate and $CO_2$, or by the double activation of the substrate via the hydroxyl and alkyne groups. As a typical example, Han et al. reported on the selective synthesis of αCCs under solvent-free conditions by using a combination of $ZnI_2$ as catalyst and $NEt_3$ as cocatalyst at room temperature and low $CO_2$ pressure (10 bar).[28] However, a high catalyst loading (20 mol%) was required and the cocatalyst was used in equimolar amount with respect to the propargylic alcohol. AgOAc/tetraalkylammonium bromide salt[29], AgOAc/Schiff based ligands[30], AgI/$AcO^-$ catalysts[31] or AgOAc/DBU[32] were also described as catalytic systems. Although some of them were found very active for the selective formation of αCCs, one of the component of the binary catalyst, generally the base, was used in

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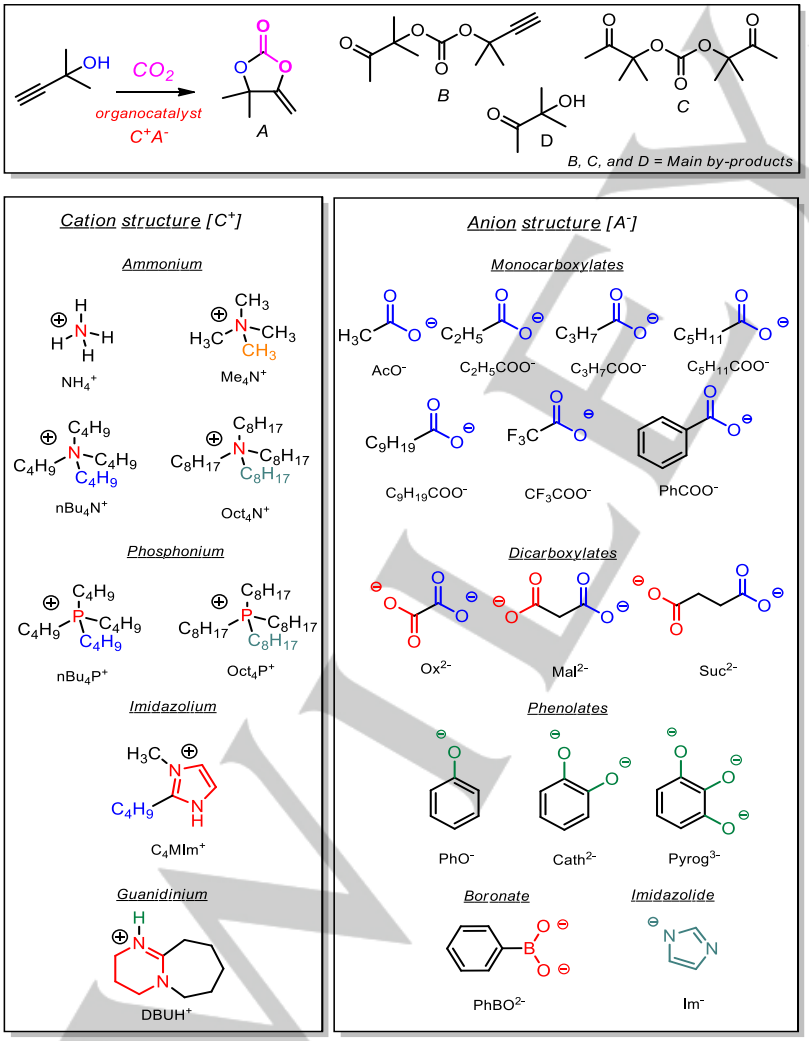
10.1002/cctc.201800063




equimolar amount or even in excess as compared to the propargylic alcohol. This large co-catalyst content was required to perform the reaction at low temperature (< 45 °C) and pressure (1-10 bar). Although huge progresses were made in the field of organocatalysis, the rational correlation between their structure and their influence on the reaction rate and selectivity is rarely addressed, the presence of side products being not deeply investigated.

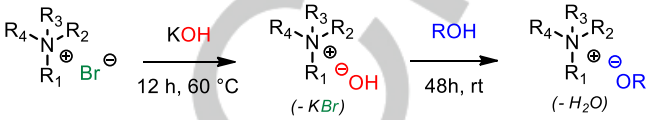
In this work, various organic salts (Scheme 1) were prepared and evaluated for the $CO_2$/alkynols coupling reaction. The objective is to identify the important structural parameters that dictate the performances of the catalyst in terms of both the rate and the selectivity of the reaction, while maintaining the catalyst loading low (5 mol%). Tetrabutylammonium acetate was chosen as a reference catalyst of moderate activity.[33] By tuning the structure of both the cation (ammonium, phosphonium, imidazolium or guanidinium) and anion ((di-)carboxylates, phenolates, boronate, imidazolide), the basicity of the catalyst was modulated, which strongly affected the catalytic activity.




**Scheme 1:** $CO_2$/propargylic alcohol coupling reaction: design of organocatalysts

## Results and Discussion

***1. Catalyst synthesis.*** Scheme 1 summarizes the library of organocatalysts based on ammonium and phosphonium salts with carboxylates, phenolates, boronate or imidazolate counter-anions that were prepared. The ammonium and phosphonium based catalysts were synthesized by a two-step process according to adapted procedures from the literature (Scheme 2).




**Scheme 2:** General strategy for the synthesis of organic catalysts. $R_1 = R_2 = R_3 = R_4 = -CH_3, -C_4H_9, -C_8H_{17}$. Nitrogen can be replaced by phosphorus.

The first step consisted in exchanging the halide anion of the quaternary ammonium/phosphonium salts by $OH^-$ anion by reaction with potassium hydroxide. Then, the quaternary ammonium/phosphonium hydroxide salt/IL was neutralized by addition of carboxylic acids of various structures, phenol derivatives, phenyl boronic acid or imidazole.[34-35] All synthetic procedures and characterizations are detailed in supporting information.

***2. Screening of the catalysts activity.*** The basicity of the catalyst has been shown crucial for the selective coupling of propargylic alcohols with $CO_2$.[24,25] In this study, we focused first on organocatalysts based on carboxylate anions; their basicity can be tuned by varying the structure of their alkyl substituent. The activity and selectivity of carboxylate salts towards the formation of αCCs was first screened using a model reaction between 2-methyl-3-butynol and $CO_2$ under solvent-free conditions at 50 bar, 80 °C for 6 h using 5 mol% of catalyst (Scheme 1).

Tetrabutylammonium acetate ($nBu_4NOAc$) was first tested as the reference catalyst. Figure S3 illustrates the $^1H$ NMR spectra of $nBu_4NOAc$, 2-methyl-3-butynol and the crude reaction mixture obtained after 6 h. Formation of αCC, 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (Scheme 1, product A) was attested by the appearance of peaks at 4.33 ppm and 4.77 ppm typical of the exocyclic olefinic group of the αCC, and one singlet at 1.61 ppm assigned to the two methyl groups. Meanwhile, complete consumption of 2-methyl-3-butynol was highlighted by the absence of any residual peaks of the reactant at 1.55, 2.16 and 2.44 ppm. However, the $^1H$ NMR spectrum of the crude sample also highlights the presence of two acyclic carbonates by-products. Sample B, formed by the regio-selective ring-opening of αCC with 2-methyl-3-butynol, shows typical resonances of methyl groups at 1.52, 1.72, 2.24 ppm, and one singlet at 2.54 ppm corresponding to the alkyne proton. By-product C produced by the addition of α-hydroxyketone D (formed

by hydrolysis of αCC) onto αCC is also observed by the presence of its characteristic methyl group peaks at 1.53 and 2.18 ppm. Then, the conversion of 2-methyl-3-butynol and the selectivity towards the formation of the (a)cyclic carbonates were determined by comparing the relative intensities of the integrations of characteristic peaks of each sample (see experimental section ESI2 for details). $nBu_4NOAc$ afforded a quantitative conversion of 2-methyl-3-butynol with the formation of αCC (product A) with a selectivity of 93 %.

The catalytic performance of all organocatalysts was then tested for the same model reaction. The conversion and the selectivity towards the formation of product A were benchmarked with the ones obtained for $nBu_4NOAc$. The influence of the structural parameters of the organocatalysts on their activity and selectivity is discussed in details below.

**Table 1.** Organocatalysts screening for the coupling of $CO_2$ with 2-methyl-3-butyn-1-ol.

| Entry | [C⁺] | [A⁻] | pKa* | Conv (%) | Selectivity (%) | | |
|---|---|---|---|---|---|---|---|
| | | | | | $S_A$ | $S_B$ | $S_C$ |
| 1 | $NH_4^+$ | $AcO^-$ | 4.78 | 0 | - | - | - |
| 2 | $Me_4N^+$ | $AcO^-$ | 4.78 | <6 | 93 | n.d. | n.d. |
| 3 | $nBu_4N^+$ | $AcO^-$ | 4.78 | 100 | 93 | 2 | 5 |
| 4 | $Oct_4N^+$ | $AcO^-$ | 4.78 | <4 | n.d. | n.d. | n.d. |
| 5 | $nBu_4P^+$ | $AcO^-$ | 4.78 | 11 | 92 | 8 | 0 |
| 6 | $Oct_4P^+$ | $AcO^-$ | 4.78 | 0 | - | - | - |
| 7 | $C_4MIm^+$ | $AcO^-$ | 4.78 | 16 | 100 | - | - |
| 8 | $DBUH^+$ | $AcO^-$ | 4.78 | 84 | - | 86 | 14 |
| 9 | $K^+$ | $AcO^-$ | 4.78 | 0 | - | - | - |
| 10[c] | $K^+$ | $AcO^-$ | 4.78 | 13 | 92 | - | 8 |
| 11[d] | $K^+$ | $AcO^-$ | 4.78 | 88 | 87 | 5 | 7 |
| 12 | $nBu_4N^+$ | $C_2H_5COO^-$ | 4.88 | 100 | 97 | 3 | - |
| 13 | $nBu_4N^+$ | $C_3H_7COO^-$ | 4.87 | 100 | 97 | - | 3 |
| 14 | $nBu_4N^+$ | $C_5H_{11}COO^-$ | 4.84 | 100 | 96 | - | 4 |
| 15 | $nBu_4N^+$ | $C_9H_{19}COO^-$ | 4.9 | 7 | 100 | - | - |
| 16 | $nBu_4N^+$ | $PhCOO^-$ | 4.19 | 95 | 98 | 2 | - |
| 17 | $nBu_4N^+$ | $CF_3COO^-$ | 0.05 | <5 | n.d. | n.d. | n.d. |
| 18[a] | $Me_4N^+$ | $Ox^{2-}$ | 1.23, 4.19 | 63 | 100 | - | - |
| 19[a] | $nBu_4N^+$ | $Ox^{2-}$ | 1.23, 4.19 | 100 | >99 | trace | - |
| 20[a] | $Oct_4N^+$ | $Ox^{2-}$ | 1.23, 4.19 | < 4 | n.d. | n.d. | n.d. |
| 21[a] | $nBu_4N^+$ | $Mal^{2-}$ | 2.83, 5.69 | 100 | >99 | trace | - |
| 22[a,*] | $nBu_4N^+$ | $Suc^{2-}$ | 4.16, 5.61 | 44 | 100 | - | - |
| 23 | $nBu_4N^+$ | $PhO^-$ | 9.89 | 100 | 90 | 3 | 7 |
| 24[a] | $nBu_4N^+$ | $Cath^{2-}$ | 9.3, 13 | 100 | 98 | 2 | - |
| 25[b] | $nBu_4N^+$ | $Pyrog^{3-}$ | n.d. | 100 | 90 | 10 | - |
| 26[a] | $nBu_4N^+$ | $PhBO^{2-}$ | n.d | 100 | 93 | 7 | - |
| 27 | $nBu_4N^+$ | $Im^-$ | 6.95 | 100 | 93 | 7 | - |
| 28 | $nBu_4N^+$ | $OH^*$ | / | - | - | - | - |
| 29 | $nBu_4N^+$ | $Br^-$ | / | - | - | - | - |

Conditions: T = 80 °C, P = 50 bar, t = 6 h, 0.03 mol of propargylic alcohol, 5 mol% of catalyst, volume of the cell = 20 ml.

* catalyst partly soluble

[a] *using 2.5 mol% of catalyst*

[b] *using 1.66 mol% of catalyst*

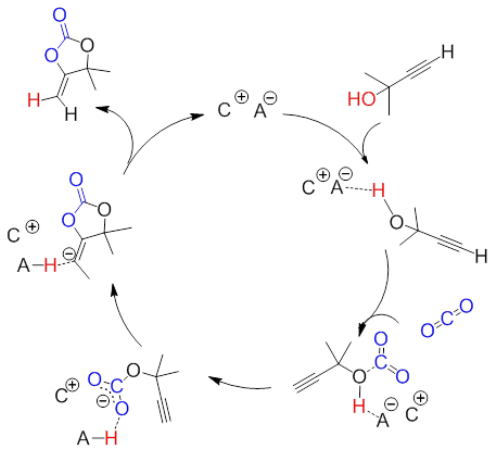
[c] *reaction in the presence of 18-crown-6, [KOAc]/[18-crown-6] =1, for 6h*

[d] *reaction in the presence of 18-crown-6, [KOAc]/[18-crown-6] =1, for 24h*

* pKa values in water

***3. Influence of the alkyl substituent of the ammonium.*** The influence of the nature of the alkyl chain of the ammonium cation and of its length on its catalytic performance was first evaluated for various ammonium bearing $AcO^-$ anion (Table 1, entries 1-4). As illustrated in Table 1, the evolution of the 2-methyl-3-butynol conversion was found strongly dependent on the alkyl chain length of the cation, e.g. 0 % with hydrogen, < 10 % with methyl or octyl, and 100 % with n-butyl. Interestingly, the same evolution pervades for the same ammoniums bearing oxalate counter-anion as attested by a maximum conversion of 100% with a $nBu_4N^+$ cation (Table 1, entries 18-20).

This trend was explained by the cation-anion interactions impacting the ion pair separation and consequently the catalyst activity. Electrostatic interactions between the acetate anion and $NH_4^+$ or cations with short alkyl substituents in $C_1$ are expected to be strong, which disfavours the ion pair separation and lowers the catalytic activity of the acetate. Indeed, the well accepted mechanism [33] involves the deprotonation of the hydroxyl group of the alkynol by a basic catalyst and the simultaneous nucleophilic attack of the so-produced alkoxide anion onto $CO_2$. This first step results in the formation of a cation-carbonate ionic pair and an acid. Then, the ring closure and formation of the α-methylene cyclic carbonate occur via an intramolecular nucleophilic addition of the carbonate anion onto the C≡C bond with the simultaneous pronation of the alkenyl anion by the acid (Scheme 3).



**Scheme 3.** Proposed general mechanism for the organocatalytic carboxylative coupling of $CO_2$ with propargylic alcohols with ammonium salts ($C^+A^-$)

From the optimized minimum energy structures of $nBu_4NOAc$ and $NH_4OAc$ catalysts calculated by the M06-2X functional[36] using the 6-311G(d,p) basis set (Figure 1), the presence of two supplementary hydrogen bonds for $NH_4OAc$ shortens the distance between the two ions of the ions pair from 4.22 Å for $nBu_4NOAc$ to 2.82 Å for $NH_4OAc$. This additional interaction observed with $NH_4OAc$ strongly hampers the catalytic activity of the acetate anion due to the energy needed to "break" this ion pair.

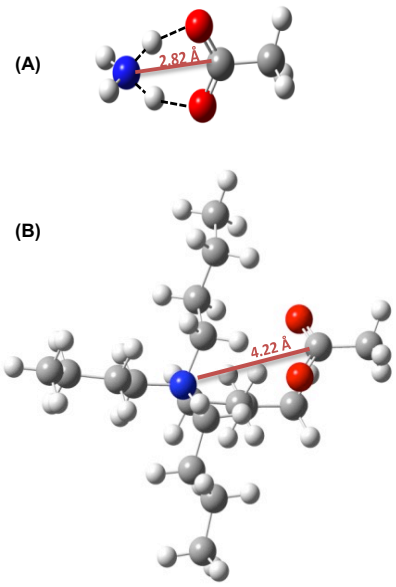



**Figure 1:** Optimized geometries (M06-2X/6-311G(d,p)) of the structures of $NH_4OAc$ (A) and $nBu_4NOAc$ (B).

In contrast, while substituents in $C_8$ should favour the ion pair separation, their bulkiness brings steric hindrance that is detrimental for the $CO_2$/2-methyl-3-butynol coupling reaction. The butyl group appears to offer the best compromise in terms of ion pair separation and steric hindrance with a quantitative conversion in 6 h. Note that the poor 2-methyl-3-butynol conversion (< 6 %) obtained with $NH_4^+$, $Me_4N^+$ or $Oct_4N^+$ prevents us from drawing any reliable conclusion regarding the influence of the alkyl chain length of the ammonium cation on the selectivity towards the formation of product A.

The crucial influence of the ion-pair separation on the catalyst activity was further confirmed experimentally by carrying out the coupling reaction in the presence of potassium acetate (KOAc) as catalyst. This acetate salt displayed no catalytic activity (Table 1, entry 9) under the experimental conditions that are optimal for $nBu_4NOAc$ (Table 1, entry 3). Importantly, the addition of 18-crown-6 ([KOAc]/[18-crown-6] = 1) activated this ammonium salt for the coupling reaction. Indeed, 13 and 90 % of the propargylic alcohol were converted after 6 and 24h, respectively, with a high selectivity (~ 87%) in αCC (product A) (Table 1, entries 10-11). The crown ether complexed the potassium cation, favoring the ion-pair separation and therefore the reaction.

***4. Influence of the nature of the cation.*** The nature of the cation on the activity of $AcO^-$-based organocatalysts was then evaluated. By substituting $nBu_4N^+$ for the phosphorous counterpart ($nBu_4P^+$), the 2-methyl-3-butynol conversion strongly decreased from 100 % to only 11 % (Table 1, entry 5), highlighting the importance of the nature of the cation on the catalytic performances. No catalytic activity was also noted for $Oct_4POAc$ (Table 1, entry 6). By using imidazolium acetate ($C_4MImAc$; Table 1, entry 7), a low conversion was also measured (16 %) with however the product A as the main compound. The catalytic performance of $nBu_4NOAc$ was then benchmarked with that of 1,8-diazabicyclo[5.4.0]-7-undecenium acetate (DBUHAc, Table 1, entry 8)[37] which was reported as a catalyst for the coupling of propargylic alcohols with $CO_2$ (although no data about the potential formation of by-products was available).[37] $nBu_4OAc$ was found slightly more active than DBUHAc as evidenced by a 2-methyl-3-butynol conversion of 100 % *vs* 84 %. However, the major difference between the two organocatalysts arises from the selectivity toward the formation of product A. While $nBu_4NOAc$ yielded product A with a selectivity of 93 %, by-product B was identified as the main compound with DBUHAc. This huge difference in selectivity is assumed to be the result of the acid-base equilibrium of DBUHA that releases DBU (a superbase) in the reaction medium. Indeed, DBU (and other organic superbases) were shown to promote the formation of the acyclic carbonate at the expense of the cyclic one.[25,38] Chen et al. also demonstrated that the increase of pKa of amines for the catalyzed propargylic alcohol/$CO_2$ reaction was found to increase the reaction rate but was detrimental to the selectivity.[24] This study highlights the impact of the cation structure of $AcO^-$ catalysts on their performances and further confirms that $nBu_4N^+$ cation should be privileged for tailoring efficient organocatalysts.

***5. Influence of the R group of the carboxylate.*** We then investigated the influence of the structure of the carboxylate on the activity of the catalyst based on $nBu_4N^+$ cation. Although increasing the length of the R alkyl chain of the carboxylate has only a very limited influence on the pKa value of the corresponding acid, the steric hindrance is expected to be increased and might affect the catalytic activity. For R substituents in $C_2$, $C_3$ or $C_5$ (Table 1, entries 12-14), the activity of the corresponding catalysts was similar to that of $nBu_4NOAc$ (Table 1, entry 3) with the quantitative conversion of 2-methyl-3-butynol into product A with a selectivity above 96 %. However, with a C9 substituent (Table 1, entry 15), a very poor conversion was noted (< 10%). This difference in catalytic activity is assumed to be the result of the steric hindrance induced by the C9 chain. Similarly to the case of the alkyl substituents of ammonium cations, there is therefore an optimum carboxylate chain length beyond which the conversion starts declining. Replacing acetate by a slightly less basic benzoate (Table 1, entry 16) led to a slightly lower 2-methyl-3-butynol conversion of 95% with a selectivity in product A of 98 %. When the even less basic trifluoroacetate anion was used (Table 1, entry 17), only traces (< 5 %) of 2-methyl-3-butynol were converted. This result highlights the crucial role of the basicity of the carboxylate anion on the performances of the organocatalysts.

***6. Influence of the nature of the anion.*** Tetrabutylammonium type organocatalysts composed of various anions (dicarboxylates, phenolate, catecholate, pyrogallolate, boronate, imidazolide)

were then prepared and their activity compared under identical experimental conditions (50 bar, 80 °C, 6 h). Oxalate ($Ox^{2-}$) was first tested as the anion (Table 1, entries 18-20). To take into account the presence of 2 carboxylate groups (and thus 2 $nBu_4N^+$) per oxalate, 2.5 mol% of catalyst was used instead of 5 mol% in order to compare the activity of the catalyst with the reference ($nBu_4NOAc$). 2-methyl-3-butynol was fully converted into product A with a selectivity superior to 99% by using $(nBu_4N)_2Ox$ (93 % for $nBu_4NOAc$ and full conversion), compared to 63 % conversion with 100 % selectivity for $(Me_4N)_2Ox$. Substituting the butyl or methyl groups of the ammonium by octyl ones was detrimental for the catalytic activity, only less than 4 % of the propargyl alcohol was converted (Table 1, entry 20).

We then investigated the influence of the spacer between the two carboxylate groups on the catalyst performances by testing tetrabutylammonium malonate and succinate (Table 1, entries 21 and 22). The former afforded full conversion of 2-methyl-3-butynol, with a similar selectivity for A than $(nBu_4N)_2Ox$. Although tetrabutylammonium succinate is also highly selective towards the formation of A, the 2-methyl-3-butynol conversion only reached 44 % under identical experimental conditions. This observation is at first glance surprising based on the higher basicity of succinate. However, the low solubility of this catalyst in propargylic alcohol might account for this difference of activity. The other catalysts were fully soluble in the reaction medium.

We then tested tetrabutylammonium phenolate ($nBu_4NOPh$) as potential catalyst (pKa of phenol = 9.8, Table 1, entry 23). A full conversion of 2-methyl-3-butynol was measured, however with a lower selectivity in A of 90 % as compared to 100% conversion with $(nBu_4N)_2Ox$ ($pKa_2$ of oxalate = 4.19) and 100 % selectivity in A. This result confirms that highly basic catalysts are very active but at the expense of the selectivity as previously discussed. Under identical experimental conditions, $nBu_4N^+$ with catecholate ($Cath^{2-}$), pyrogallolate ($Pyrog^{3-}$), phenylboronate ($PhBO^{2-}$) or imidazolide ($Im^-$) gave comparable results to $nBu_4NOPh$ in terms of conversion and selectivity (Table 1, entries 24-27). No catalytic activity was observed when the organic anion was substituted for the hydroxyl or bromide one (Table 1, entries 28-29).

The catalysts screening enabled us to identify the most efficient catalysts but full kinetics studies are required to class them according to their catalytic activity and selectivity. Therefore, kinetic studies of the organocatalyzed coupling of 2-methyl-3-butynol with $CO_2$ were carried out by online Raman spectroscopy under similar experimental conditions (i.e. P = 50 bar, T = 80 °C, catalyst loading of 5 or 2.5 mol% (the latter with oxalate based organocatalysts). The only difference compared to previous experiments arises from the addition of acetonitrile (acetonitrile/2-methyl-3-butyn-2-ol composition of 50/50 v/v) that served as an internal reference. Figure S5 shows the Raman spectra of the starting product, 2-methyl-3-butyn-2-ol, and the pure final one, product A, recorded by using a red ruby laser of λ = 785nm. The Raman spectrum of 2-methyl-3-butyn-2-ol shows two peaks at 2117 $cm^{-1}$ and 710 $cm^{-1}$ which are characteristic of the ν stretching and the δ C-H out of plane bending mode of the alkyne group, respectively. The Raman spectrum of product A shows a distinctive peak at 649 $cm^{-1}$, characteristic of the C=O out of plane bending vibration of the cyclic carbonate.

The kinetics of the reaction was therefore monitored by following the disappearance of the alkyne peak at 710 $cm^{-1}$, and the appearance of the peak at 649 $cm^{-1}$ characteristics of the cyclic carbonate as illustrated on a typical 3D superposition of the Raman spectra recorded with time for the reaction catalysed by $nBu_4NOAc$ (Figure 2a). The $CO_2$ peak intensity varied slightly at the early stages of the reaction and then reached a stable value once the propargylic alcohol/acetonitrile liquid phase was saturated by $CO_2$. The kinetic profile of each monitored reaction was obtained by plotting the evolution of the relative intensity of the cyclic carbonate peak at 649 $cm^{-1}$ with time.

Figure 2 shows the kinetic profiles recorded for reactions catalysed by $Me_4NOAc$, $nBu_4NOAc$, $(nBu_4N)_2Ox$ and $nBu_4NOPh$. Crucial information on the activity and selectivity of the catalysts was deduced from the slope of the kinetic curves (that is linked to the reaction rate) and from the intensity at which the plateau is reached (that is related to the content in product A).

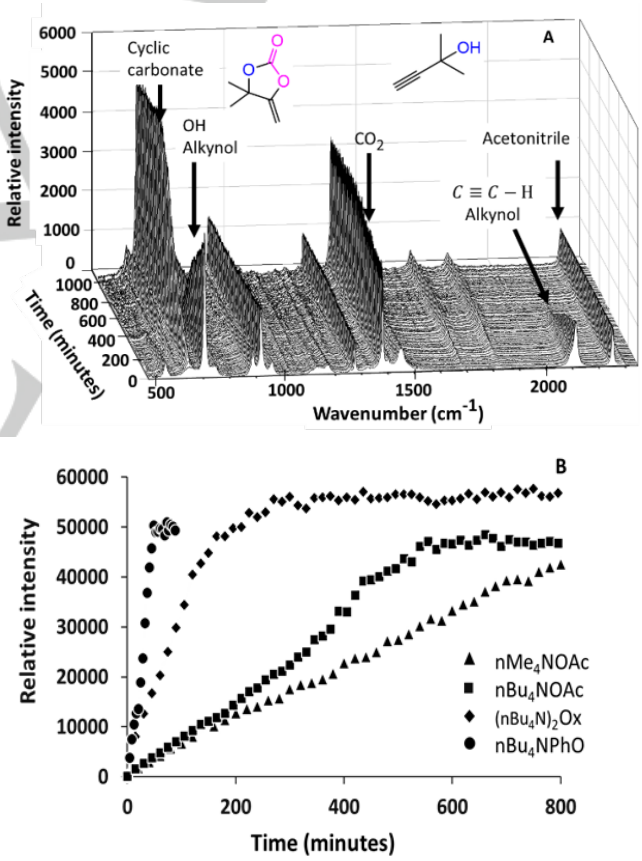



**Figure 2:** Addition of $CO_2$ to 2-methyl-3-butynol in the presence of various organocatalysts. (A) Evolution of the Raman spectra with time, (B) Comparison of the kinetic profiles. Conditions: T = 80 °C, p = 50 bar, t = 6 h, 0.03 mol (2.6 ml) of propargylic alcohol, 5 mol% of $nMe_4OAc$, $nBu_4OAc$ and $nBu_4OPh$ and 2.5 mol% for $(nBu_4N)_2Ox$, volume of the cell = 20 ml, v ACN = 2.6 ml.

These profiles could not be established for $(nBu_4N)_2Cath$ and $(nBu_4N)_3Pyrog$ due to fluorescence of the reaction medium. From

Figure 2, the organocatalysts were classified regarding their activity in the order $Me_4NOAc$ < $nBu_4NOAc$ < $(nBu_4N)_2Ox$ < $nBu_4NOPh$. The two latter organocatalysts ($nBu_4NOPh$ and $(nBu_4N)_2Ox$) were identified as the most active ones as attested by a higher slope and a plateau value that was reached after 50 min and 270 min, corresponding to a 12-fold and ~ 2.5-fold increase of the activity as compared to $nBu_4NOAc$, respectively. $Me_4NOAc$ was significantly less active and no plateau was reached after 800 mins of reaction.

The selectivity of the reaction in product A was estimated from the plateau value. With a relative intensity value of ~56000, $(nBu_4N)_2Ox$ was found to be the most selective catalyst with a quantitative formation of the cyclic carbonate A as confirmed by $^1H$ NMR spectroscopy of the reaction medium. All typical signals of product A were observed with no side product and the absence of any starting propargyl alcohol. With respective relative intensity values of ~50000 and ~ 49000, $nBu_4NOPh$ and $nBu_4NOAc$ were slightly less selective than $(nBu_4N)_2Ox$. By comparing the relative intensity values reached with these catalysts with the one for $(nBu_4N)_2Ox$, one estimates a selectivity towards product A of approximately 90 % that is in agreement with that reported for the catalyst screening experiments carried out under neat conditions (Table 1, entries 23 and 3).

It is worth noting that the kinetic profile of the cyclic carbonate formation for the $nBu_4NOAc$ catalyzed reaction displayed a peculiar shape that did not fit a pseudo-first order kinetics, in contrast to what is expected for a reaction carried out with an excess of $CO_2$. Indeed, the reaction rate increased with the consumption of the propargylic alcohol. This was previously explained by the solvation of $OAc^-$ by propargylic alcohol through hydrogen bonding.[33] This solvation shell stabilized $OAc^-$, that consequently lowered its catalytic activity as the result of a decrease of its pKa value. This hydrogen bonding solvation shell around $OAc^-$ was progressively weakened with the consumption of propargylic alcohol, thus leading to the increased activity of the counter-anion and of the reaction rate. Consequently, the observed unusual kinetic behaviour for this reaction was due to an evolution during the reaction of the hydrogen bond solvation shell formed by the propargylic alcohol around $OAc^-$. This observation on the rate of reaction was also made for the $CO_2$/2-methyl-3-butynol coupling catalyzed by $nBu_4NOPh$ and $(nBu_4N)_2Ox$.

### *7. Influence of reaction conditions.*

*Influence of the pressure.* Our groups reported on the phase behaviour of propargylic alcohols/$CO_2$ biphasic systems and highlighted that the concentration of $CO_2$ dissolved in the propargylic alcohol phase decreased with a decrease in pressure at a constant temperature.[39] This effect is reflected on the results we obtained as shown in the Table 2 (entries 1-6).

At a constant temperature of 80°C, reducing the pressure slows down the reaction rate as evidenced for experiments realized with $nBu_4NOAc$ catalyst for which the conversion which is close to 100% at 50 bar (Table 1, entry 19) drops to 20 and 11% at 15 and 5 bar respectively (Table 2, entries 4 and 1 respectively). For the other two catalysts, a decrease in the pressure is detrimental for the selectivity towards the formation of the cyclic carbonate, which decreases, especially at very low $CO_2$ pressure. The higher competition between the $CO_2$ fixation on propargylic alcohol, and the ring-opening of the αCC (product A) by unreacted propargylic alcohol could be proposed as a plausible explanation for this trend. Nonetheless, even at 5 bar, the $(nBu_4N)_2Ox$ catalysts remained quite selective as compared to $nBu_4NOPh$.

**Table 2.** Influence of the experimental parameters on the coupling reaction between $CO_2$ and 2-methyl-3-butynol.

| Entry | [C⁺] | [A⁻] | P (bar) | T (°C) | X(%)[b] | Selectivity (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | $S_A$ | $S_B$ | $S_C$ |
| 1 | $nBu_4N^+$ | $AcO^-$ | 5 | 80 | 11 | 100 | - | - |
| 2[a] | $nBu_4N^+$ | $Ox^{2-}$ | 5 | 80 | 100 | 89 | 5 | 6 |
| 3 | $nBu_4N^+$ | $PhO^-$ | 5 | 80 | 100 | 35 | 65 | - |
| 4 | $nBu_4N^+$ | $AcO^-$ | 15 | 80 | 20 | 95 | 5 | - |
| 5[a] | $nBu_4N^+$ | $Ox^{2-}$ | 15 | 80 | 100 | 94 | - | 6 |
| 6 | $nBu_4N^+$ | $PhO^-$ | 15 | 80 | 100 | 89 | 7 | 4 |
| 7 | $nBu_4N^+$ | $AcO^-$ | 50 | 60 | 16 | 100 | - | - |
| 8[a] | $nBu_4N^+$ | $Ox^{2-}$ | 50 | 60 | 24 | 100 | - | - |
| 9 | $nBu_4N^+$ | $PhO^-$ | 50 | 60 | 63 | 100 | - | - |

Conditions: T = 80 °C, p = 50 bar, t = 6h, 0.03 mol of propargylic alcohol, 5 mol% of catalyst, volume of the cell = 20 ml.

[a] *using 2.5 mol% of catalyst*

[b] *Conversion and selectivity determined by $^1H$ NMR*

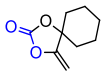
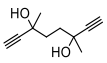
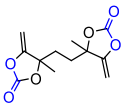
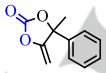
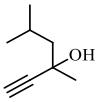
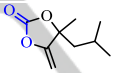
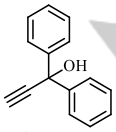
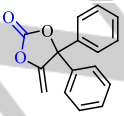
*Influence of the temperature.* The temperature can impact the reaction in two ways, i.e. by affecting the rate of the reaction, and by changing the solubility of $CO_2$ in the propargylic alcohol phase. We showed that for a constant pressure, the concentration of $CO_2$ dissolved in the alcohol phase decreases with the decrease in the temperature.[39] Entries 7 to 9 in Table 2 summarize the results obtained for experiments realized at 60°C and 50 bar for 6h using $nBu_4NOAc$, $(nBu_4N)_2Ox$ and $nBu_4NOPh$. As expected, lowering the temperature slowed down the reaction as the conversions close to 100% at 80°C with all catalysts decreased to 16, 24 and 63 by using respectively $nBu_4NOAc$, $(nBu_4N)_2Ox$ and $nBu_4NOPh$.

***8. Screening of the propargylic alcohols.*** In an effort to broaden the scope of α-methylene cyclic carbonates that could be produced by this synthetic approach, the $(nBu_4N)_2Ox$ promoted coupling of $CO_2$ with various propargylic alcohols precursors was investigated using the optimum experimental conditions, i.e. p = 50 bar, T = 80 °C for 6 h using 2.5 mol% of catalyst (relative to the alcohol). The results obtained are summarized in Table 3.

No αCC was formed from prop-2-yn-1-ol or but-3-yn-2-ol precursors, whereas 2-methyl-3-butynol was fully and selectively converted into product A under similar experimental conditions. These results can be explained by the Thorpe-Ingold effect (or "*gem effect*") which postulates that the mutual repulsion of gem di-methyl groups favour the cyclization.[40] When both methyl groups of 2-methyl-3-butynol were replaced by a bulkier cyclohexyl substituent, the conversion was low (12 %) but the reaction was also highly selective (Table 3, entry 4). These results

show that the steric hindrance induced by bulkier substituents may impede either the addition of $CO_2$ onto the alcohol, or the cyclization of the carbonate ion. Interestingly, a polymerizable bis-αCC[11] was synthesized from a dipropargylic alcohol with a conversion of 35 % and a selectivity above 99 % (Table 3, entry 5). When one of the methyl groups of 2-methyl-3-butynol was replaced by an ethyl group, the conversion decreased to 20% but the selectivity remained excellent (100%) (Table 3, entry 6). Complete conversion was however reached after 24 h of reaction when using 5 mol% catalyst (Table 3, entry 7). Under these conditions, other bulky propargylic alcohols were almost quantitatively converted into the corresponding cyclic carbonates with a high selectivity (60-96%) after only 6h of reaction (Table 3, entries 8-11). These experiments clearly highlight that the catalyst is active for the coupling reaction of $CO_2$ with a broad range of propargylic alcohols.

**Table 3:** Synthesis of various alkylidene 5-membered cyclic carbonate

| Entry | Reagent | Product | Conv.(%) | Selectivity (%) |
|---|---|---|---|---|
| 1 |  |  | 0 | 0 |
| 2 |  |  | 0 | 0 |
| 3 |  |  | 100 | 99 |
| 4 |  |  | 12 | 100 |
| 5[a] |  |  | 35 | 99 |
| 6 |  |  | 20 | 100 |
| 7[a,b] |  |  | 99 | 93 |
| 8[b] |  |  | 98 | 95 |
| 9[b] |  |  | 99 | 95 |
| 10[b] |  |  | 98 | 85 |
| 11 |  |  | 100 | 60 |

Conditions: T = 80 °C, p = 50 bar, t = 6 h, 0.03 mol of propargylic alcohols, 2.5 *mol% of* $(nBu_4N)_2Ox$, volume of the cell = 20 ml,
[a] experiment for 24 h
[b] *5 mol% of* $(nBu_4N)_2Ox$

## Conclusions

In this work, we tailored various organic salts that were tested as catalysts for the carboxylative coupling of $CO_2$ with propargylic alcohols. We have investigated the influence of the modulation of the structure of the organocatalyst (mainly the type and structure of the cation and anion) on the catalytic performances. Optimum activity resulted from the best compromise between ion-pair separation controlled by steric effects and the basicity of the anion. Low ion-pair separation might limit the catalytic activity because of stronger electrostatic interactions between the cation and the anion and a lower availability of the anion for the deprotonation of the alcohol. Organic salts with too basic anions increased the rate of the reaction but at the expense of the selectivity. Among the different salts that were tested, tetrabutylammonium oxalate appeared to be the most active catalyst for the 2-methyl-3-butynol/$CO_2$ coupling reaction with quantitative conversion of the starting product into the corresponding α-methylene cyclic carbonate with a remarkable selectivity (> 99 %) in less than 6h of reaction at 50 bar and 80 °C under solvent free conditions. Only 2.5 mol% of catalyst (compared to the propargylic alcohol) were required for this performance. This study clearly opens new avenues for conceiving efficient organocatalysts for $CO_2$/propargylic alcohol coupling reactions, with potentially less toxicity than metal based ones because carboxylate anions favour the biodegradability and decrease the toxicity of the corresponding organic salts.[41]

## Acknowledgements

All co-authors thank Prof. B. Gilbert for designing and setting up the probe that allowed to perform in-situ Raman spectroscopy under pressure, and for all his advices and his help for the comprehension of the reaction kinetics. Prof. Gilbert, who is co-author of this paper (and of many others with Liege's group), regrettably passed on the 17th on February 2018. The authors of Liège thank the "Region Wallonne" and the FEDER in the frame of the $CO_2$Green, Flycoat and Prostem projects, the "Belgian Science Policy" in the frame of the "Interuniversity Attraction Poles Programme (IAP VII/5) – Functional Supramolecular Systems" and the "Fonds National pour la Recherche Scientifique" (F.R.S.-FNRS) for financial supports. This work was partly supported by the Fonds de la Recherche Scientifique (FNRS) and the Fonds Wetenschappelijk Onderzoek – Vlaanderen (FWO) under EOS project n°O019618F (ID EOS: 30902231). C.D. is Research Director by F.R.S.-FNRS. We also thank computational facilities provided by the MCIA (Mesocentre de Calcul Intensif Aquitaine) of the University of Bordeaux financed by the "Conseil Regional d'Aquitaine".

**Keywords:** carbon dioxide • cyclic carbonate • organocatalyst

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10.1002/cctc.201800063

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*Bruno Grignard, Charlene Gabriela Ngassamtounzoua, Bernard Gilbert, Raphael Mereau, Christine Jerome, Thierry Tassaing, Christophe Detrembleur**

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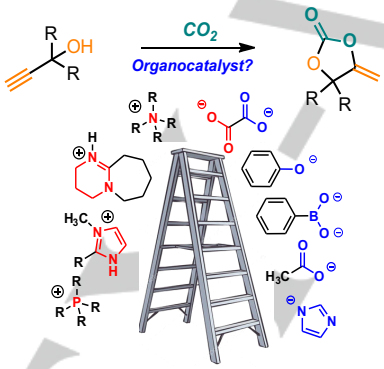
**Boosting the catalytic performance of organic salts for the fast and selective synthesis of α-alkylidene cyclic carbonates from $CO_2$ and propargylic alcohols**

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