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Supporting information (experimental procedures, characterization data and ^{1}H and ^{13}C NMR spectra) for this article is given via a link at the end of the document.

Abstract: Substituted vinylene carbonates were directly prepared from aromatic aldehydes following a one-pot Benzoin condensation / transcarbonation sequence under solvent-free conditions. The combination of a *N*-phenyl substituted triazolium salt NHC precursor and 4-dimethylaminopyridine (DMAP) was found essential to reach high yield and selectivity. The reaction scope was investigated with a range of aromatic aldehydes and the corresponding vinylene carbonates were obtained with 32-86% isolated yields (14 examples).

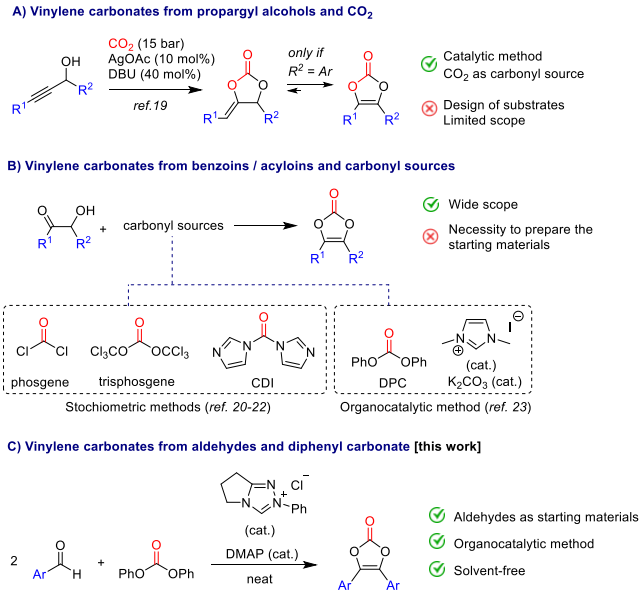
Introduction

Organic carbonates are environmentally-friendly and sustainable species that are the subject of intense research efforts. For instance, they can be used as electrolyte additives in lithium batteries,[1] as organic solvents[2] and for the production of polycarbonates[3] and polyurethanes.[4] The chemistry of organic cyclic carbonates has been developed extensively, due to the fact that they can be prepared through cycloaddition of epoxides with CO_2,[5] thus giving saturated species. On the opposite, the chemistry of unsaturated cyclic carbonates, *i.e.* vinylene carbonates, is considerably underdeveloped.

Unsubstituted vinylene carbonate (1,3-dioxol-2-one) is the parent member of the vinylene carbonate family. For instance, it can be used as an electrolyte additive in lithium batteries[6] or as a monomer to prepare poly(vinylenecarbonate),[7] a precursor of poly(hydroxymethylene) that could be used in 3D printing.[8] In organic chemistry, it is mainly used as a dienophile in Diels-Alder reactions.[9] Recently, the chemistry of vinylene carbonate has blossomed notably in annulation reactions[10] where it serves as acetylene,[11] acetaldehyde,[12] acetyl,[13] or ethynol[14] surrogates.

Substituted vinylene carbonates are also useful compounds that provide complementary applications. For example, 4,5-dimethyl-1,3-dioxol-2-one is the key precursor of a cleavable group that is used in prodrugs such as olmesartan medoxomil[15] and azilsartan medoxomil.[16] Recently, it was also demonstrated that functionalized dioxolone derivatives can be used to prepare excellent polymeric additives to make high-energy-density lithium-ion batteries.[17]

Only a few approaches to substituted vinylene carbonates have been reported in the literature. The silver-catalyzed cycloaddition of propargylic alcohols with CO_2 gives *exo*-vinylene carbonate intermediates (Scheme 1, a).[18] However, only a few of these species can be isomerized to vinylene carbonates,[19] thus limiting the scope of application. A wider range of vinylene carbonates can be obtained from benzoins and acyloins by reaction with carbonyl sources such as phosgene,[20] triphosgene[21] and carbonyl diimidazole (CDI) (Scheme 1, b).[22] However, these carbonyl sources are either too toxic or expensive to envision further utilization on the large scale. Moreover, our group has recently demonstrated that less toxic (but less reactive) diphenyl carbonate (DPC) can also be used as a carbonyl source, provided activation through organocatalysis.[23] This method is probably the most general in term of scope, however, it still requires the preliminary preparation of benzoins and acyloins. In this context, we report here the direct synthesis of vinylene carbonates from aldehydes. The reaction occurs through an unprecedented Benzoin condensation/transcarbonation sequence catalyzed by a mixture of a triazolium salt and 4-dimethylaminopyridine (DMAP).[24]



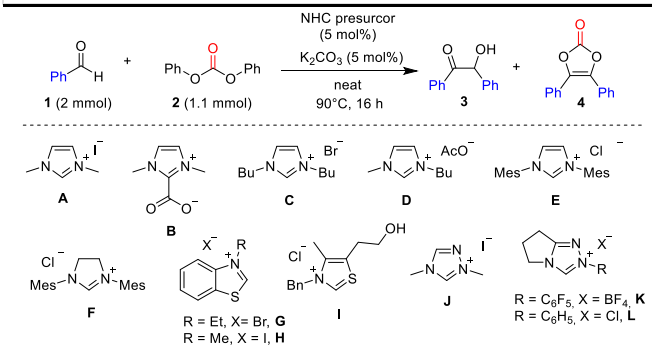
Scheme 1. Synthetic strategies to substituted vinylene carbonates.

Results and Discussion

Initial optimization reactions were performed using benzaldehyde **1** and diphenyl carbonate **2** as model substrates. The screening of catalysts was carried out in order to find a suitable species able to catalyze both transformations and was performed in the presence of K_2CO_3 in neat conditions (Table 1).

Considering that imidazolium salts were found effective to promote the formation of vinylene carbonates in our previous work,[23] optimization reactions were first carried out with these species. In sharp contrast, the use of NHC precursors **A-F** gave poor yields for either benzoin **3** or the desired vinylene carbonate **4** (entries 1-6). Benzothiazolium salts **G-H** and thiazolium salt **I** also gave poor yield of **4**, but slightly promote the formation of **3** with up to 10% yield (entries 7-9). Among triazolium salts, NHC precursor **J** did not catalyze the reaction (entry 10). On the contrary, the use of **K** led to formation of **4** with 9% yield along with 40% of intermediate **3** (entry 11). Vinylene carbonate **4** was also obtained with 10% yield with **L** but this catalyst proves to be more selective as only 2% of **3** was formed (entry 12). Consequently, this catalyst was selected for further optimization.

Table 1. Screening of NHC precursors.[a]

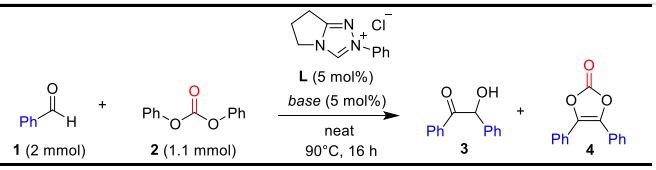


Entry	NHC precursor	Yield[b] of **3** (%)	Yield[b] of **4** (%)
1	**A**	1	0
2	**B**	0	0
3	**C**	0	1
4	**D**	0	1
5	**E**	4	6
6	**F**	0	0
7	**G**	7	1
8	**H**	3	0
9	**I**	10	5
10	**J**	0	0
11	**K**	40	9
12	**L**	2	10

[a] Reaction conditions: benzaldehyde **1** (2 mmol), diphenyl carbonate (DPC) **2** (1.1 mmol), NHC precursor (5 mol%), K_2CO_3 (5 mol%), 90 °C, 16 h. [b] Yields were determined by GC/FID with hexadecane as an internal standard.

Several bases (5 mol%) were next screened (Table 2). Using carbonates, the yield of **4** progressively increased from 0% with Li_2CO_3 to 38% with Cs_2CO_3, while the amount of intermediate **3** remained low (entries 1-5). These results could be explained by the better solubility of cesium carbonate in the neat reaction mixture. Organic bases such as triethylamine (TEA), triazabicyclodecene (TBD) and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) gave low yield (< 10%) for the desired product (entries 6-8). However, 4-dimethylaminopyridine (DMAP) gave an encouraging 57% yield (entry 9). Increasing its loading to 10 mol% allows reaching 99% yield of **4**, without any traces of benzoin intermediate (entry 10). This excellent result could be explained by the fact that DMAP acts as a base in the Benzoin condensation while also playing the role of a nucleophilic catalyst in the transcarbonation steps. By comparison, NHC precursor **K** gave 29% of **3** and 7 % of **4**, thus confirming the inferiority of this catalyst compared to **L** (entry 10, results in brackets). The catalyst loading of **L** was next decreased to 2 and 1 mol%. In these conditions, the desired vinylene carbonate was formed with only 85 and 57% yield (entries 11-12). However, the yield of **4** can also reached 99% when increasing the reaction time to 24 and 64 h, respectively (entries 11-12, results in brackets).

Table 2. Base optimization.[a]

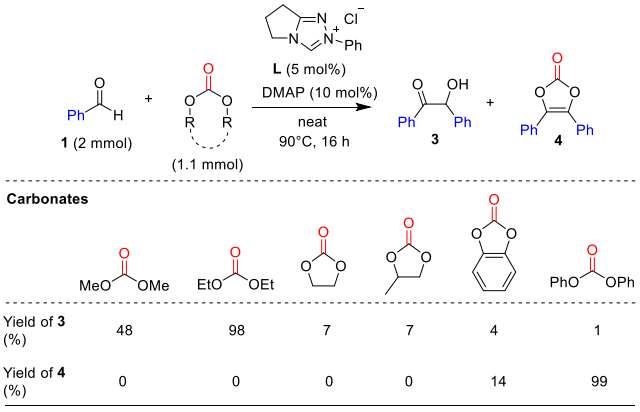


Entry	Base, loading (mol%)	Yield[b] of **3** (%)	Yield[b] of **4** (%)
1	Li_2CO_3 (5)	1	0
2	Na_2CO_3 (5)	3	5
3	K_2CO_3 (5)	2	10
4	Rb_2CO_3 (5)	1	19
5	Cs_2CO_3 (5)	2	38
6	TEA (5)	2	5
7	TBD (5)	1	10
8	DBU (5)	2	6
9	DMAP (5)	0	57
10	DMAP (10)	0 (29)[c]	99 (7)[c]
11[d]	DMAP (10)	0	85 (99)[f]
12[e]	DMAP (10)	0	57 (99)[g]

[a] Reaction conditions: benzaldehyde **1** (2 mmol), diphenyl carbonate (DPC) **2** (1.1 mmol), NHC precursor **L** (5 mol%), base (5 mol%), 90 °C, 16 h. [b] Yields were determined by GC/FID with hexadecane as an internal standard. [c] results in brackets obtained with **K** (5 mol%). [d] 2 mol% of **L**. [e] 1 mol% of **L**. [f] 24 h. [g] 64 h

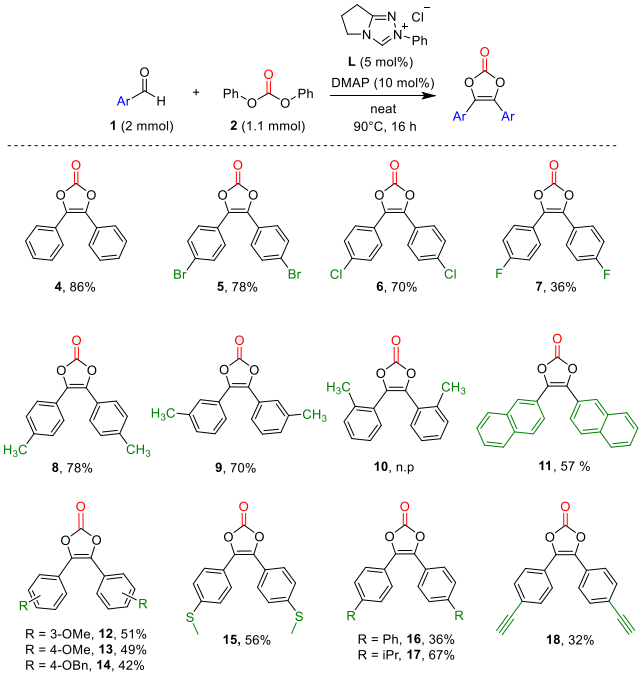
Several organic carbonates were next tested as a carbonyl source (Scheme 2). Using either dimethyl carbonate (DMC) or diethyl carbonate (DEC) as a carbonyl source, the desired product was not formed but benzoin intermediate **3** was obtained with 48% and 98% yield, respectively. These results indicate that DMC and DEC are only acting as solvents and are unable to act as carbonyl sources under these conditions. Ethylene carbonate (EC) and propylene carbonate (PC) were also tested as they directly arise from the cycloaddition of ethylene oxide or propylene oxide with CO_2. Similarly, no

vinylene carbonate was formed. Moreover, these species are also poor solvents for the transformation as benzoin was only obtained with 7% yield. Catechol carbonate gave **4** with only 14% yield. In sharp contrast, the use of diphenyl carbonate gave the desired product **4** with 99% yield. The better reactivity of DPC could be explained by the fact that the phenolate ion is by far a better leaving group than other alkoxides.



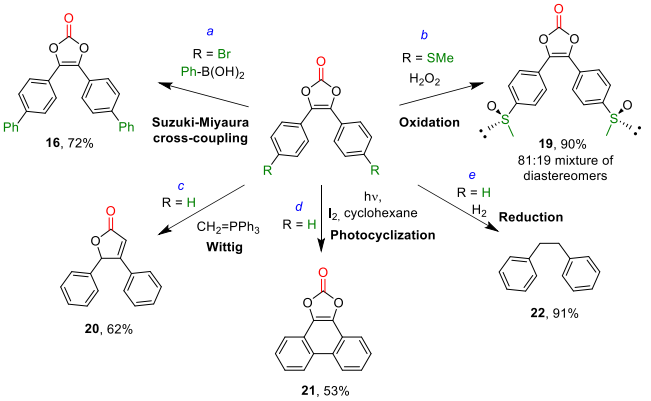
Scheme 2. Carbonates as carbonyl sources. Reaction conditions: benzaldehyde **1** (2 mmol), carbonate (1.1 mmol), NHC precursor **L** (5 mol%), DMAP (10 mol%), neat, 90 °C, 16 h. b Yields were determined by GC/FID with hexadecane as an internal standard.

The reaction scope was investigated with aromatic aldehydes under optimized conditions (Scheme 3). First, benzaldehyde gave **4** with a good isolated yield of 86 %. Benzaldehydes bearing halogens at the para position gave contrasting results. Bromo- and chloro- derivatives worked well with 70-78% yield for **5-6** while the fluoro derivative gave **7** with only 36% yield. These results are explained by the fact that the Benzoin condensation does not proceed well with aldehydes bearing strong electron-withdrawing substituents. This was also confirmed with the use of *para*-nitro and *para*-trifluorobenzaldehydes that did not convert at all under these conditions. *Para*- and *meta*-tolualdehydes gave the desired vinylene carbonates **8-9** with good yields (70-78%) while *ortho*-tolualdehyde did not furnish **10**, due to the fact that the Benzoin condensation is also sensitive to steric hinderance. This is also demonstrated with naphthaldehydes. No reaction occurred with α-naphthaldehyde while β-naphthaldehyde gave **11** with 57% yield. Aldehydes bearing electron-donating groups such as 3- or 4-anisaldehyde, 4-benzyloxy benzaldehyde and 4-(methylthio)benzaldehyde gave **12-15** with moderate yields (42-56%). The reaction also proceeds with 4-phenyl-, 4-isopropyl- and 4-ethynylbenzaldehydes and the corresponding vinylene carbonates **16-18** were isolated with 32-67% yield. The reaction was also attempted with aldehydes bearing free hydroxyl groups such as vanillin and 3-hydroxybenzaldehyde. In these cases, no conversion was observed indicating that the presence of acidic protons is deleterious for the reaction. Finally, aliphatic aldehydes were also tested but only aldolization products were observed under these conditions.



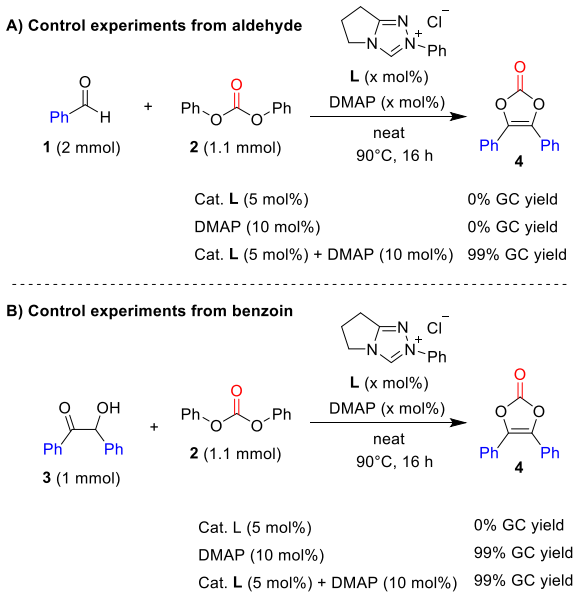
Scheme 3. Scope of aromatic aldehydes. Reaction conditions: aromatic aldehyde (2 mmol), diphenyl carbonate **2** (DPC) (1.1 mmol), NHC precursor **L** (5 mol%), DMAP (10 mol%), 90 °C, 16 h. n.p: no product.

The synthetic utility of substituted vinylene carbonates prepared through the developed methodology was next probed (Scheme 4). First, Suzuki-Miyaura cross-coupling of **5** (R=Br) with phenylboronic acid gave **16** with 72% yield. Oxidation of **15** (R = SMe) with H_2O_2 in the presence of acetic acid gave the corresponding bis-sulfoxide **19** as a 81:19 mixture of diastereomers in 90% yield. Other transformations were also investigated with vinylene carbonate **4** (R=H). Wittig reaction with methylenetriphenylphosphane afforded butenolide **20** with 62% yield.[25] Photocyclization in the presence of iodine gave 9,10-dihydrophenanthrene carbonate **21** with 53% yield. Finally, hydrogenation under 1 atm of hydrogen in the presence of palladium hydroxide gave **22** in 91% yield. These results show that vinylene carbonates offer a unique platform for further transformations.



Scheme 4. Synthetic applications of vinylene carbonates. See Supporting Information for experimental details.

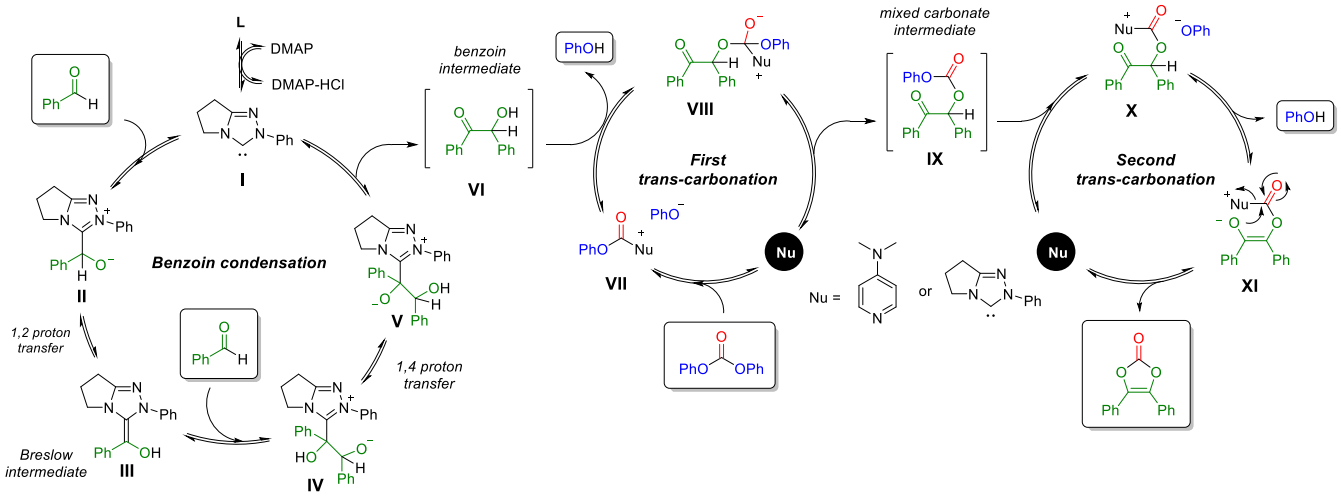
From a mechanism point of view, the reaction consists of three steps: i) formation of benzoin intermediate: ii) formation of a mixed carbonate intermediate through trans-carbonation iii) formation of the desired vinylene carbonate by a second trans-carbonation. So, some control reactions were performed to understand the role of the base and catalyst for each step. First, control experiments were performed from benzaldehyde (Scheme 5, A). The reaction was carried out with **L** alone and with DMAP alone and no conversion was observed in both cases. In contrast, the combination of triazolium **L** and DMAP led to full conversion of benzaldehyde and vinylene carbonate **4a** was obtained with an excellent 99% GC yield. These results show that DMAP acts as a base to generate the active species from **L**, which catalyzes the Benzoin condensation.



Scheme 5. Control experiments.

Considering that benzoins were formed as intermediates in this reaction, another series of control experiments was performed using benzoin as a starting material (Scheme 5, B). First, the reaction was performed with **L** alone and no conversion of benzoin was observed. On the contrary, when DMAP was used alone, a full conversion was reached and vinylene carbonate **4a** was obtained with 99% GC yield. Similarly, in the presence of both **L** and DMAP, **4a** was also obtained with 99% GC yield. This result suggests that the free carbene generated from **L** and DMAP could also catalyze the transcarbonation steps. This was also demonstrated when using catalyst **L** in the presence of Cs_2CO_3 as a non-nucleophilic base (see Table 2, entry 5). Moreover, we demonstrated that the formation of vinylene carbonates from benzoins can be catalyzed by NHCs.[23]

So, a reaction mechanism was proposed based on previous works[26] and the results of control experiments (Scheme 6). First, the triazolium salt **L** would be deprotonated by DMAP to give NHC **I**. Due to huge difference of pKa values of DMAP (pKa=9.6, 20°C in water)[27] and triazolium salt **L** (pKa=17.6, 25°C in water),[28] the direct deprotonation is unlikely but recent works have proposed other pathways, notably through an electrophilic aromatic substitution mechanism.[29] The nucleophilic addition of the NHC on the first aldehyde gives compound **II**, then Breslow intermediate[30] **III** after 1,2 proton transfer. Nucleophilic addition of **III** on a second aldehyde gives intermediate **IV**, which is converted to intermediate **V** by 1,4 proton transfer. Finally, benzoin **VI** is obtained after released of the free carbene. In the second step, diphenyl carbonate would be activated by a nucleophilic catalyst (either DMAP or NHC) to give intermediate **VII**. Trans-carbonation of **VII** with benzoin would afford **VIII** and release a first molecule of phenol. The mixed carbonate intermediate **IX** would be produced and the nucleophilic catalyst would be released. In the last step, in presence of the nucleophilic catalyst, **IX** would afford intermediate **X** that gives enolate intermediate **XI** and release a second molecule of phenol. Finally, the enolate **XI** would add onto the activated carbonyl group to form vinylene carbonate **4** through cyclization. In this mechanism, the mixed carbonate intermediate **IX** could also be produced by direct reaction of **IV** or **V** with diphenyl carbonate (not shown). Moreover, the last step is probably very fast as the mixed carbonate intermediate **IX** has never been detected under our reaction conditions.[31]



Scheme 6. Mechanism proposal.

Conclusion

In conclusion, we have developed an efficient catalytic method for the direct formation of vinylene carbonates from aromatic aldehydes. Good yields and selectivities were obtained using an original combination of triazolium salt **L** and DMAP, in which DMAP acts both as a base and a nucleophilic catalyst. The reaction scope was investigated with aromatic aldehydes and the corresponding vinylene carbonates were obtained with 32-86% isolated yields (14 examples). Post-functionalization and derivatization reactions were also reported, showing that vinylene carbonates are attractive platform molecules.

Experimental Section

General information. All reagents and solvents were commercially available and used without any further purification. Nuclear magnetic resonance spectra were recorded on a Brüker DRX 300, Brüker ALS 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz), Brüker ADVANCEIII 500, Brüker BBO probe, Brüker BBI probe (^{1}H: 500 MHz, ^{13}C: 125 MHz). Chemical shifts are given with reference to residual $CHCl_3$ central peaks: 7.26 ppm for proton, 77.16 for carbon, respectively. *J* values are given in Hertz (Hz). Abbreviations are defined as follows: s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublet, t = triplet, q = quadruplet, qt = quintet, hex = hexuplet, hept = heptuplet, m = multiplet.

General procedure for the preparation of vinylene carbonates. The aldehyde (2 mmol), diphenyl carbonate (DPC) (1.1 mmol), 4-dimethylaminopyridine (DMAP) (0.1 mmol, 10 mol%) and 2-phenyl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium chloride (0.05 mmol, 5 mol%) were introduced into a sample tube. The reaction mixture was heated at 90ºC under argon atmosphere (the conversion of aldehyde was followed by TLC). After 16 hours, the reaction mixture was cooled to room temperature and ethyl acetate (5 ml) was added. The resulting solution was washed twice with 1M NaOH (10 ml) and twice with brine (10 ml). The organic layer was dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography.

Acknowledgements

The authors thank the French National Agency for Research for financial support through a Ph.D. grant to K. Onida and a master grant to L. Ibrahimli (ANR-19-CE07-0006-ThermoPESO). The authors thank the Auvergne-Rhone-Alpes Region (SCUSI 2017 009361 01) for partial financial support.

Keywords: Aldehydes • Benzoin condensation • Diphenyl carbonate • Organocatalysis • Vinylene carbonates

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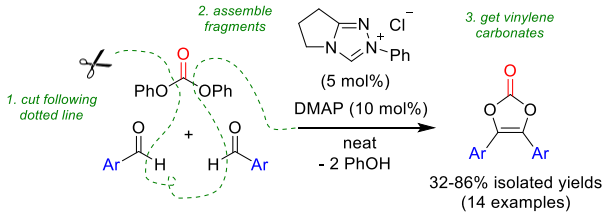
[31] Despite that the last step is probably very fast under the reported conditions, this transcarbonation step could also be catalyzed by either DMAP or the NHC species, so intermediates **X** and **XI** were shown in our mechanism proposal.

Entry for the Table of Contents



Substituted vinylene carbonates were directly prepared from aromatic aldehydes and diphenyl carbonate through an organocatalyzed Benzoin condensation / transcarbonation sequence under solvent-free conditions.

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