

One-pot stepwise synthesis of cyclic carbonates directly from olefins with CO₂ promoted by K₂S₂O₈/NaBr



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ABSTRACT

Efficient synthesis of cyclic carbonates from olefins using K₂S₂O₈ as oxidant and NaBr as “bromination” reagent has been developed through a reaction sequence involving hydroxybromination of olefins and subsequent carboxylation of the bromohydrin *in situ* generated with CO₂. This process provides a novel and convenient access to cyclic carbonates in a one-pot stepwise fashion. Representative olefins with different functional groups could react smoothly under relatively mild (3 MPa, 60 °C) and transition metal-free conditions to afford various cyclic carbonates.

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1. Introduction

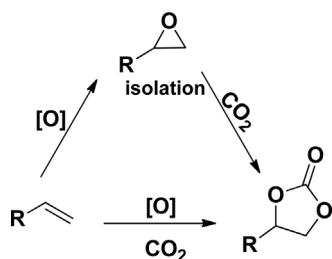
Carbon dioxide as an easily available renewable carbon resource is abundant, nontoxic, non-flammable [1–7]. Therefore, CO₂ chemistry has received much attention from the viewpoint of chemical synthesis. Upgrading CO₂ into value-added chemicals continues to be hot research area in terms of green chemistry and sustainable development [8–12]. In particular, cycloaddition of CO₂ with epoxides has already been developed to prepare cyclic carbonates, which have been widely used as polar aprotic solvents, electrolytes for lithium ion batteries, raw material for polycarbonates, polyurethanes, and intermediates for pharmaceutical/fine chemicals [13–15]. On the other hand, an attractive route to cyclic carbonates through oxidative carboxylation of olefins with CO₂, may evade the preliminary synthesis and tedious workup for isolation of the epoxidative intermediate (Scheme 1) [16].

Oxidative carboxylation of olefins with CO₂ to cyclic carbonates, as an economic and practical strategy, proceeds through the epoxidation of olefins and subsequent carboxylation reaction of epoxides with CO₂ (*path a*, Scheme 2). In 1962, the first example concerning oxidative carboxylation of olefins was reported by

Verdol [17], in which quaternary ammonium hydroxide/halide is used as cocatalyst with heavy metal (e.g. Co, Ni, V, et al.) salt. Recently, various processes for cyclic carbonates synthesis from olefins have successfully been developed by Aresta, [18,19] Jing, [20] and Jain [21] et al. respectively, involving CO₂ insertion into the metal-oxygen bond in the presence of metal complex (Nb, Ru, Co) and oxygen as the oxidant. Arai group [22–25] and Hu group [26] reported the one-pot synthesis of cyclic carbonates from aromatic olefins catalysed by the supported Au catalyst or molybdenyl acetylacetonate (MoO₂(acac)₂) with *tert*-butyl hydroperoxide (TBHP) as oxidant in the present of quaternary ammonium salt. Very recently, the mesoporous titanium-silicate Ti-MMM-E was introduced in the one-step oxidative carboxylation of styrene and 4-methylstyrene with TBHP in the presence of tetrabutylammonium bromide as cocatalyst [27]. Although the reaction runs readily according to *path a*, an expensive metal reagent for the epoxidation is still required. Particularly, numerous oxidative by-products (such as benzaldehyde and benzoic acid) are unavoidable in this epoxidation/cycloaddition pathway, leading to the formation of the target product in relatively low selectivity and yield.

Eligible strategy through the “bromohydrin” intermediate has proven to be more efficient than that *via* the epoxide intermediate pathway (*path b*, Scheme 2). In 2007, Li et al. developed an efficient catalytic system using N-bromosuccinimide (NBS) or Br[−]/H₂O₂ as the “bromination” reagent in conjunction with 1, 8-diazabicyclo

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Scheme 1. Oxidative carboxylation of olefins with CO₂ to cyclic carbonates.

[5.4.0]undec-7-ene (DBU) in water [28], in which DBU deprotonates the weakly acidic alcohol and neutralizes the hydrobromic acid *in situ* generated. A mechanism-guided design of a multi-step flow system was disclosed by Jamison et al., [29] analogously, DBU/NBS is also used in this hydroxybromination-carboxylation two-step sequential procedure. Recently, Jiang and co-workers have reported an electrochemical route for the direct conversion of CO₂ with olefins into cyclic carbonates, promoted by I₂ and NH₃ electrochemically *in situ* generated [30]. Although significant progress has been made in this regard, a hazardous, expensive “halohydrination reagent”, organic base or complicated work-up process are still needed. In this context, we have developed an environmentally friendly benign synthesis of styrene carbonate directly from styrene and CO₂ catalyzed by a binary system composed of sodium phosphotungstate and *n*-Bu₄NBr using 30% H₂O₂ as an oxidant, the selectivity could be controlled by subtly tuning the quantities of CO₂ and H₂O₂ [31].

Recently, Guo and co-workers have disclosed an efficient access to phenacyl bromides through the K₂S₂O₈-mediated tandem hydroxybromination and oxidation of styrene in aqueous media [32]. In terms of mechanistic consideration, K₂S₂O₈ is likely assumed to be a reasonable oxidant, leading to *in situ* formation of the bromohydrin. In this context, we envisioned the use of mild and easy-to-handle K₂S₂O₈ as oxidant and K₂CO₃ as “deprotonation reagent” to perform efficient synthesis of cyclic carbonates from olefins and CO₂ through the “bromohydrin” intermediate. The straightforward synthesis of cyclic carbonates from olefins could be regarded as the integration of two sequential reactions *i.e.* hydroxybromination of olefins without isolation of “bromohydrin” intermediate and carboxylation of bromohydrin with CO₂ in the presence of PEG [33]. Compared with traditional epoxidation process, olefins as starting materials could be cheaper and low toxic. Much importantly, this is an efficient and greener procedure without use of transition metal and hazardous or expensive “halohydrination reagent”.

2. Experimental

Olefins in this study were purchased from Aladdin or Alfa Aesar without further purification. PEG₁₀₀₀ were supplied from Aladdin and dried in vacuum oven at 80 °C for 24 h. CO₂ was commercially available with a purity of 99.99%. NaBr, K₂S₂O₈, K₂CO₃ were purchased from Tianjin Guangfu Fine Chemical Research Institute. The products were purified by silica gel column chromatography (200–300 mesh, 1:20 v/v ethyl acetate: petroleum as eluent). GC analyses were performed on Shimadzu GC-2014 equipped with a capillary column (RTX-17 30 m × 0.25 μm) and a flame ionization detector. GC–MS data were performed on Shimadzu 2014-QP2010 SE with a capillary column (Rtx@-5MS, 30 m × 0.25 μm). NMR spectra were recorded on a Bruker 400 in CDCl₃. ¹H and ¹³C NMR chemical shifts (δ) were given in ppm relative to CDCl₃ (7.26 ppm–77.0 ppm).

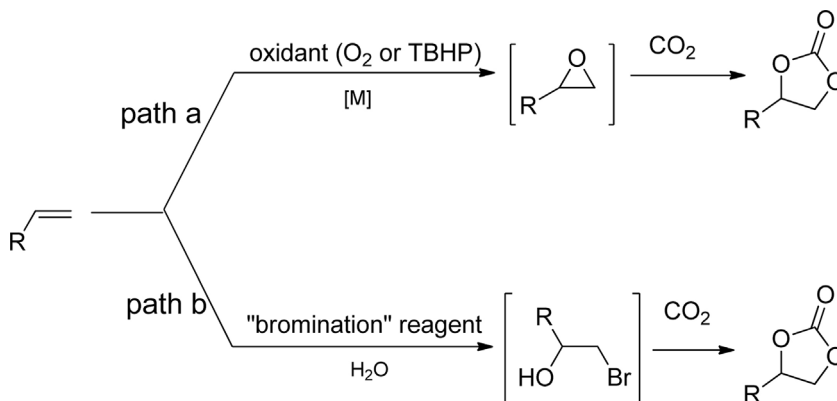
2.1. Synthesis of styrene carbonate from styrene and CO₂

A mixture of styrene (1 mmol, 0.1042 g), NaBr (1.2 mmol, 0.1235 g), K₂S₂O₈ (1.2 mmol, 0.3244 g) and H₂O (0.5 g) was placed in a 25 mL autoclave, equipped with an inner glass tube and heated to 60 °C for 5 h. Then the reactor was cooled in ice water and K₂CO₃ (1 mmol, 0.1382 g), PEG₁₀₀₀ (0.5 mmol, 0.5 g) was added. The flask was capped with a stopper and sealed. Then, the reaction mixture was stirred at 60 °C for 5 h under 3 MPa CO₂. After that, the reactor was cooled in ice water and the CO₂ was released slowly, the product was extracted with diethyl ether, and analyzed by gas chromatograph. Finally, the solvent was distilled off and the residue mixture was purified by silica gel column chromatography to get the styrene carbonate **1b**. The structure of products was further identified by using NMR and GC–MS techniques, which are consistent with those reported in the literature.

3. Results and discussion

3.1. Catalyst screening and optimization of the reaction conditions

Our study commenced with the reactions of styrene (**1a**) in the presence of K₂S₂O₈, NaBr and H₂O for 5 h, then K₂CO₃ and PEG (polyethylene glycol)₁₀₀₀ was added under CO₂ atmosphere in the second step as listed in Table 1. To our delight, 85% conversion of **1a** and 62% yield of styrene carbonate (**1b**) were obtained (entry 1). Besides, 1, 2-dibromoethylbenzene was also detected as by-product. The scope and limitation of this catalytic system were evaluated further. At first, the amount of NaBr was decreased to 0.8 equiv., leading to a slight decrease in activity with 58% yield of



Scheme 2. Two pathways to cyclic carbonates from olefins and CO₂.

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