



# Electrochemically catalyzed synthesis of cyclic carbonates from CO<sub>2</sub> and propargyl alcohols

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## ABSTRACT

A convenient and efficient electrochemical method has been developed for the synthesis of the  $\alpha$ -alkylidene cyclic carbonates from carbon dioxide (CO<sub>2</sub>) and propargyl alcohols at room temperature. The electrosynthesis was successfully carried out with a copper anode and a nickel cathode in an undivided cell containing *n*-Bu<sub>4</sub>NBr–MeCN electrolyte with a constant current under 3 MPa pressure of CO<sub>2</sub>, and the  $\alpha$ -alkylidene cyclic carbonates were obtained in good to excellent isolated yields in the secondary and tertiary terminal propargylic alcohols cases. The experimental results show that the electrogenerated Cu<sup>+</sup> ions and strong bases in situ could efficiently catalyze or promote the coupling reaction under the cooperation of electrolytic medium MeCN and supporting electrolyte *n*-Bu<sub>4</sub>NBr. The plausible mechanism of the coupling reaction was also discussed briefly.

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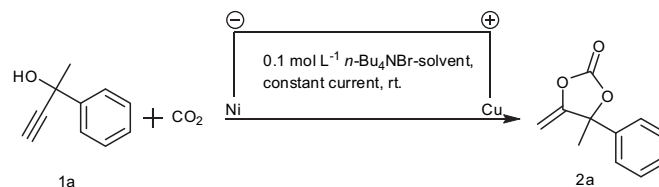
## 1. Introduction

The direct introduction of carbon dioxide, harmless, abundant, and recyclable source of carbon, into organic substrates may be considered as an attractive goal in organic synthesis. In recent years, considerable attention has been focused on the fixation of carbon dioxide (CO<sub>2</sub>) to organic substrates.<sup>1,2</sup> Among these investigations, the coupling reaction of CO<sub>2</sub> with propargyl alcohols is one of interesting topics because it can afford valuable cyclic carbonates, which are used as polar solvents, electrolytes in secondary batteries and as useful intermediates for the synthesis of functional carbonates, esters or oxazolidinone compounds, and polymers.<sup>3</sup> Up to now, various metal salts and organic compounds have been used to catalyze the coupling reaction of CO<sub>2</sub> with propargyl alcohols, such as copper,<sup>4,5</sup> silver,<sup>6</sup> phosphanes,<sup>7</sup> tri-*n*-butylphosphine,<sup>8</sup> *N*-heterocyclic carbene,<sup>9</sup> and iodine of *tert*-butyl hypoiodite (*t*-BuOI).<sup>10</sup> Most of these catalytic systems often required harsh reaction conditions, such as a high reaction temperature, because CO<sub>2</sub> is very stable molecule. In fact, CO<sub>2</sub> can react with some organic compounds through an electrochemical route at mild conditions. The electrochemical method has become one of the efficient routes of the fixation of CO<sub>2</sub> to various organic compounds, including alkenes,<sup>11–15</sup> alkynes,<sup>16,17</sup> ketones,<sup>18–21</sup> halides,<sup>22–29</sup> imines,<sup>30</sup> epoxides,<sup>31–33</sup> and heterocyclic compounds.<sup>34,29,35</sup> However, to our knowledge, the incorporation of CO<sub>2</sub> into propargyl alcohols via an electrochemical route has not ever been reported.

Al or Mg as a sacrificial anode was widely used in almost all the investigations,<sup>11–29,31–35</sup> including our previous work,<sup>36,37</sup> on the electrocarboxylations of CO<sub>2</sub> with organic substrates. Here, we further investigated the possibility of electrochemically coupling reaction of CO<sub>2</sub> with propargyl alcohols. We found that the electrochemical route with Al as a sacrificial anode was unsuccessful for the coupling reaction of CO<sub>2</sub> with propargyl alcohols. In this paper, we demonstrate a new and efficient electrochemical route (i.e., with copper as a sacrificial anode and Ni as cathode, and *n*-Bu<sub>4</sub>NBr–MeCN as electrolyte) for the coupling reaction. It was found that the electrogenerated Cu<sup>+</sup> ions and strong bases in situ could efficiently catalyze the coupling reaction under the cooperation of solvent MeCN, and the target product  $\alpha$ -alkylidene cyclic carbonates could be obtained in good to excellent yields at room temperature.

## 2. Results and discussion

The electrochemical synthesis of cyclic carbonates from propargyl alcohols and CO<sub>2</sub> follows the principle as shown in Scheme 1. With 2-phenylbut-3-yn-2-ol (**1a**) as a model compound, the



Scheme 1. Electrosynthesis of cyclic carbonates from propargylic alcohols and CO<sub>2</sub>.

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influence of the electrolytic conditions (solvents, electrode materials, conducting salts, and CO<sub>2</sub> pressure, substrate concentration, and electricity) was first investigated. Then the electrochemical reactions of other propargyl alcohols with CO<sub>2</sub> were further examined under the optimized conditions.

### 2.1. Influence of electrode materials and solvents

In our previous investigations,<sup>36</sup> the electrocarboxylations of aryl-substituted alkenes with CO<sub>2</sub> could be successfully carried out in *n*-Bu<sub>4</sub>NBr–DMF solution with Ni as the cathode and Al or Zn as a sacrificial anode, affording the corresponding 2-arylsuccinic acids in moderate to good yields (50–87%). Based on our previous results, the coupling reaction of CO<sub>2</sub> with propargyl alcohols was examined under the same conditions. Unfortunately, the results are unexpected, and the corresponding cyclic carbonate (**2a**) could not be obtained (Table 1, entries 1 and 2). When Al was replaced by Cu as a sacrificial anode, the target product **2a** could be obtained in 30% yield (Table 1, entry 3). Although the yield is very low, this indicates the possibility of electrochemically coupling reaction of CO<sub>2</sub> with propargyl alcohols at room temperature. Inspired by the successful result, we try to improve the yield of **2a** through changing electrolytic parameters (such as electrolytic media). When THF (tetrahydrofuran) or MeCN (acetonitrile) was chosen as electrolytic medium, the yield of **2a** rapidly increased to 76% and 86%, respectively (Table 1, entries 4 and 5). The experimental results mean that the Cu ions resulting from the oxidation of Cu anode and electrolytic medium MeCN or THF play an important role in the coupling reaction of CO<sub>2</sub> with propargyl alcohols. The excellent yield of the desired product could be obtained with MeCN or THF as solvent. The reason may be that the Cu ions generated at Cu anode could form complexes with MeCN<sup>38</sup> or THF,<sup>39</sup> which could efficiently catalyze the cyclic reaction. The detailed mechanism of influence of the solvent and anode materials would be further discussed in Section 3.4.

**Table 1**  
Influence of electrode materials and solvent on the electrochemical cyclization of propargyl alcohols with CO<sub>2</sub><sup>a</sup>

Entry	Cathode	Anode	Solvent	Yield <sup>b</sup> (%)
1	Ni	Al	DMF	0
2	Ni	Zn	DMF	0
3	Ni	Cu	DMF	30
4	Ni	Cu	THF	76
5	Ni	Cu	MeCN	86
6	Zn	Cu	MeCN	45
7	Al	Cu	MeCN	50
8	Cu	Cu	MeCN	59
9	Ag	Cu	MeCN	80

<sup>a</sup> Electrolytic conditions: room temperature, propargyl alcohol 0.1 mol L<sup>-1</sup>, solvent (35 mL), *n*-Bu<sub>4</sub>NBr (3.5 mmol), current density 10 mA cm<sup>-2</sup>, CO<sub>2</sub> 3 MPa and electricity 4 F mol<sup>-1</sup>.

<sup>b</sup> Isolated yield based on the starting propargyl alcohols (3.5 mmol).

In addition, the influence of different cathodes (Zn, Al, Cu, and Ag) was carefully studied, under the same experimental conditions (Cu anode, 35 mL of MeCN, 2.5 mmol of *n*-Bu<sub>4</sub>NBr, 0.1 mol L<sup>-1</sup> of propargyl alcohols, 10 mA cm<sup>-2</sup> of current density, 3 MPa of CO<sub>2</sub>, and 4 F mol<sup>-1</sup> of electricity, room temperature), and the results are summarized in Table 1. Indeed, the nature of cathode materials has a great impact on the yield of **2a**. The use of Zn, Al, and Cu cathodes gave **2a** in moderate yields (45%, 50%, and 59%, respectively, Table 1, entries 6–8), together with the formation of byproduct allyl alcohol (20–30%). Among the examined cathodes, Ni and Ag cathodes exhibit better results (86% and 80%, respectively, Table 1, entries 5 and 9), only the trace of byproduct allyl alcohol detected by GC–MS. The nature of cathode materials may affect the reduction of propargyl alcohols.

### 2.2. Influence of electricity and substrate concentrations as well as CO<sub>2</sub> pressure

Table 2 shows the influence of electricity, substrate concentrations, and CO<sub>2</sub> pressure on the electrosynthesis of cyclic carbonates from propargyl alcohol and CO<sub>2</sub>. As shown in Table 2, the yield of the target product strongly depends on the electricity (Q) supplied to the electrodes. When the electricity passed the cell increased from 1 to 4 F mol<sup>-1</sup>, the yield of the product increased rapidly from 38% to 88% (Table 2, entries 1–4). Further increasing the electricity, the yield of the target product increased slightly (Table 2, entry 5).

**Table 2**  
Influence of electricity, substrate concentration and CO<sub>2</sub> pressure on the electrochemical cyclization of propargyl alcohols with CO<sub>2</sub><sup>a</sup>

Entry	Electricity/(F mol <sup>-1</sup> )	c( <b>1a</b> )/(mol L <sup>-1</sup> )	P(CO <sub>2</sub> )/(MPa)	Yield <sup>b</sup> (%)
1	1	0.1	4	38
2	2	0.1	4	50
3	3	0.1	4	67
4	4	0.1	4	88
5	5	0.1	4	89
6	4	0.2	4	92
7	4	0.4	4	83
8	4	0.1	1	29
9	4	0.1	2	52
10	4	0.1	3	86
11	4	0.1	5	88

<sup>a</sup> Electrolytic conditions: room temperature, Ni cathode, Cu anode, MeCN (35 mL), *n*-Bu<sub>4</sub>NBr (3.5 mmol), current density 10 mA cm<sup>-2</sup>.

<sup>b</sup> Isolated yield based on the starting propargyl alcohols.

The yield of **2a** increases from 88% to 92% upon increasing in the initial concentration of the substrate from 0.1 to 0.2 mol L<sup>-1</sup> (Table 2, entries 4 and 6). However, when the electrolysis was conducted with a higher concentrated solution of propargyl alcohols, it led to the decrease of yield of the target product (83%, Table 2, entry 7). The further increase of concentration of propargyl alcohols may bring a negative effect, such as the increase of byproduct allyl alcohol.

As the CO<sub>2</sub> pressure increased from 1 to 3 MPa, the yield of the target product increased (Table 2, entries 8–10). Higher CO<sub>2</sub> pressure favors to the electrochemical cyclization reaction with propargyl alcohols and CO<sub>2</sub>, which may be related to the solubility of CO<sub>2</sub> in MeCN solvent. Practically, the amount of CO<sub>2</sub> at 3 MPa dissolved in MeCN solvent may greatly exceed that of propargyl alcohol. In order to confirm this point, the relevant experiment was carried out. CO<sub>2</sub> was charged into the cell to reach 3 MPa. Then, the quantity of CO<sub>2</sub> was determined via weighting after superfluous CO<sub>2</sub> was discharged from the cell. The result indicates that the amount of CO<sub>2</sub> dissolved in MeCN solvent is about 10 times as much as that of propargyl alcohol. So the influence of CO<sub>2</sub> pressure further increasing from 3 to 5 MPa becomes negligible (Table 2, entries 4, 10, and 11). Based on the experimental results, 3 MPa of CO<sub>2</sub> pressure appears to be more suitable for the electrosynthesis.

### 2.3. Electrochemical cyclization of other propargyl alcohols with CO<sub>2</sub>

Based on the above investigations, the optimal conditions of the electrochemical cyclization for propargyl alcohols with CO<sub>2</sub> are summarized as follows: Ni as the cathode and Cu as the anode, *n*-Bu<sub>4</sub>NBr–MeCN as the electrolyte, concentration of substrate 0.2 mol L<sup>-1</sup>, CO<sub>2</sub> pressure at 3 MPa, and electricity at 4 F mol<sup>-1</sup>.

Under the optimized reaction conditions, the electrochemical route is extended to examine the cyclization reaction of other propargyl alcohols (**1b–i**) with CO<sub>2</sub>. The obtained results were collected in Table 3. When tertiary propargyl alcohols (**1b–g**) were employed as substrates, such as aliphatic-substituted alcohols,

**Table 3**  
Electrochemical cyclization of propargyl alcohols with CO<sub>2</sub><sup>a</sup>

Entry	Substrate	Product	Yield <sup>b</sup> (%)
1			92
2			92
3			93
4			90
5			88
6			85
7			86
8			75
9			0
10			20 <sup>c</sup>
11			5 <sup>d</sup>

<sup>a</sup> Electrolytic conditions: room temperature, Ni cathode, Cu anode, propargyl alcohols 0.2 mol L<sup>-1</sup>, MeCN (35 mL), *n*-Bu<sub>4</sub>NBr (3.5 mmol), current density 10 mA cm<sup>-2</sup>, CO<sub>2</sub> 3 MPa and electricity 4 F mol<sup>-1</sup>.<sup>b</sup> Isolated yield based on the starting propargyl alcohols (7.0 mmol).<sup>c</sup> Determined by GC–MS.<sup>d</sup> Determined by GC–MS.

2-methylbut-3-yn-2-ol, 3-methylpent-1-yn-3-ol, 3,5-dimethylhex-1-yn-3-ol, 3-methylnon-1-yn-3-ol or five- or six-member-ring-substituted propargyl alcohols, the corresponding cyclic carbonates could be obtained in excellent yields (85–93%, Table 3, entries 1–7). The electrolysis with secondary propargylic alcohols **1h** in contrast to the tertiary propargyl alcohols gave the corresponding cyclic carbonate products **2h** in slightly decreasing yield (75%, Table 3, entry 8). It should be noted that when primary propargylic alcohol was used as substrate, the target product was not formed (Table 3, entry 9), and the internal propargyl alcohols afforded the corresponding products only in low yields (5–20%, Table 3, entries 10 and 11). The results suggest that the present electrochemical route could be specific to secondary and tertiary terminal propargylic alcohols.

## 2.4. Electrochemical reaction mechanism

According to the mentioned above results, Al or Zn as the sacrificial anode is not feasible at all for the cyclization process of propargyl alcohols with CO<sub>2</sub> (Table 1, entries 1 and 2). Only when Cu was used as the sacrificial anode, the cyclization process could be smoothly carried out. We deduced that the Cu metal ions generated at the anode may act as the catalytic role for the cyclization process. It is well known that Cu as the sacrificial anode is able to produce Cu<sup>2+</sup> or Cu<sup>+</sup> ions (i.e., Cu → Cu<sup>2+</sup> + 2e<sup>-</sup> or Cu → Cu<sup>+</sup> + e<sup>-</sup>). In the present system, which Cu metal ions can promote the cyclization reaction, Cu<sup>2+</sup> or Cu<sup>+</sup> ions? In order to better understand the electrocatalyzed cyclization process of propargyl alcohols with CO<sub>2</sub>, we further examined the reaction with CuBr or CuBr<sub>2</sub> as additive, and the obtained results are listed in the Table 4. Moreover, an inert carbon electrode was chosen as the anode to replace Cu electrode in order to avoid the interference from the metal ions electro-generated at anode. When the CuBr (copper(I) salt) was added into the electrolytic system, the cyclic carbonate could be obtained (Table 4, entry 1). However, the addition of CuBr<sub>2</sub> (copper(II) salt) does not activate the cyclization reaction at all (Table 4, entry 2). Thus, it could be inferred that the Cu<sup>+</sup> ions generated at the Cu anode catalyzed the cyclization reaction instead of Cu<sup>2+</sup> ions in the present electrolytic system. Besides, in contrast to the solvent DMF (Table 1, entry 3), it could be deduced that the high activity of the Cu(I) ion generated in situ is most probably due to the complex effect of the copper(I) cations with solvent MeCN<sup>38</sup> or THF.<sup>39</sup>

**Table 4**  
Influence of other parameters on the electrochemical cyclization of propargyl alcohols with CO<sub>2</sub><sup>a</sup>

Entry	Anode	Additive	Conducting salt	Yield <sup>b</sup> (%)
1	C	CuBr	<i>n</i> -Bu <sub>4</sub> NBr	14
2	C	CuBr <sub>2</sub>	<i>n</i> -Bu <sub>4</sub> NBr	0
3	—	CuBr	<i>n</i> -Bu <sub>4</sub> NBr	0 <sup>c</sup>
4	Cu	—	KBr	0
5	Cu	—	LiClO <sub>4</sub>	0
6	—	CuBr, Bu <sub>3</sub> N	—	27 <sup>d</sup>

<sup>a</sup> Electrolytic conditions: room temperature, Ni cathode, propargyl alcohols 0.1 mol L<sup>-1</sup>, MeCN (35 mL), conducting salt (3.5 mmol), additive (4 equiv), current density 10 mA cm<sup>-2</sup>, CO<sub>2</sub> 3 MPa and electricity 4 F mol<sup>-1</sup>.<sup>b</sup> Determined by GC–MS.<sup>c</sup> Without electric current passing through the cell.<sup>d</sup> Without electric current passing through the cell.

The formation of Cu(I) ions during the electrolysis is supported by the literature and our experimental results. For example, in the electrolytic system containing halogen ions (Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>), the oxidation of Cu anode could produce cuprous precipitates or complexes.<sup>40</sup> In our experiments, it was observed that a red deposit was formed when the distilled water was added to the solution after electrolyzed. The red deposit was proved to be metal copper,

which resulted from the disproportionation of Cu(I) ions in the aqueous solution (i.e.,  $\text{Cu}^+ \rightarrow \text{Cu} + \text{Cu}^{2+}$ ). The experimental result confirms the existence of Cu(I) ions in the present electrolytic system.

It was worthy to note that the cyclization reaction did not take place without electric current passing through the cell even in the presence of CuBr catalyst (Table 4, entry 3). This result indicates that the electrochemical activation is necessary for the cyclization reaction under the present conditions. In addition, if  $\text{LiClO}_4$  or KBr (instead of a  $\text{R}_4\text{N}^+$  salt) was used as supporting electrolyte, the electrolysis could also not afford the corresponding products (Table 4, entries 4 and 5). The result shows that  $n\text{-Bu}_4\text{NBr}$  not only conduces to the electric conduction but also promotes the formation of the corresponding cyclic carbonate. Based on the published work,<sup>41–43</sup> the electrochemical reduction of tetraalkylammonium cations  $\text{R}_4\text{N}^+$  at the cathode can generate a trialkylamine  $\text{R}_3\text{N}$  and alkyl radical  $\text{R}^\cdot$  ( $\text{R}_4\text{N}^+ + \text{e}^- \rightarrow \text{R}_4\text{N}^\cdot$ ,  $\text{R}_4\text{N}^\cdot \rightarrow \text{R}^\cdot + \text{R}_3\text{N}$ ). In the present system, since the  $\text{Br}^-$  ions of  $\text{Bu}_4\text{NBr}$  could react with the Cu(I) ions generated at the anode to form CuBr precipitates or complexes, the reduction of the corresponding  $\text{Bu}_4\text{N}^+$  ions becomes feasible. Our experimental results (GC–MS analysis) have confirmed the formation of  $\text{Bu}_3\text{N}$ . The formed  $\text{Bu}_3\text{N}$  could activate propargyl alcohols, then could react with carbon dioxide to generate a carbonate intermediate.<sup>5,6</sup> In addition, it should be noted that the cyclization reaction could only afford the cyclic carbonate in 27% yield (Table 4, entry 6) without electric current although the addition amount of CuBr and  $\text{Bu}_3\text{N}$  reached four equivalence of propargyl alcohol. This means that another key factor should further be considered for the activation of propargyl alcohols. As proposed in the literatures,<sup>41–43</sup> the alkyl radical  $\text{R}^\cdot$  resulted from the electrochemical reduction of  $\text{R}_4\text{N}^+$  cations could further be electroreduced to an alkyl anion  $\text{R}^-$  ( $\text{R}^\cdot + \text{e}^- \rightarrow \text{R}^-$ ). Compared with  $\text{Bu}_3\text{N}$ ,  $\text{R}^-$  alkyl anions have higher reactivity and stronger basicity. Thus,  $\text{R}^-$  alkyl anions more easily deprotonate the OH group of propargyl alcohol to give an active intermediate. The  $\text{R}^-$  alkyl anions may play a key role in the activation of propargyl alcohols. Since the concentration of the electrogenerated  $\text{R}^-$  alkyl anions is affected by the electricity supplied to the electrodes, the yield of cyclic carbonate (**2a**) increases with increasing electricity (Table 2, entries 1–4).

Based on the above-mentioned experimental results and analyses as well as literatures,<sup>5,6</sup> a plausible mechanism for the electrochemical incorporation of carbon dioxide into propargylic alcohols is outlined in Scheme 2. During the electrolysis, tetrabutylammonium cations  $\text{R}_4\text{N}^+$  on the surface of a nickel cathode first gets electrons to form tributylamine  $\text{R}_3\text{N}$  and the alkyl radical  $\text{R}^\cdot$ . Then, the alkyl radical  $\text{R}^\cdot$  further gets electrons to form alkyl anion  $\text{R}^-$ .  $\text{R}_3\text{N}$ , especially alkyl anion  $\text{R}^-$ , has enough strong basicity to deprotonate the OH group of propargyl alcohol to generate an intermediate **A**, followed by the reaction with carbon dioxide to

produce a carbamate anion intermediate **B**. Simultaneously the sacrificial copper anode is continuously oxidized to form complexes of copper(I) with MeCN tentatively represented as  $[\text{Cu}(\text{MeCN})_4]\text{Br}$ ,<sup>38</sup> which could activate a intramolecular ring-closing reaction taking place on the alkyne, to afford the corresponding cyclic carbonate with the release of the Cu(I) catalyst.

### 3. Experimental section for electrosynthesis of cyclic carbonates from propargyl alcohols and $\text{CO}_2$

#### 3.1. General methods

The electrolytic cell is the same as that reported previously.<sup>36</sup> Before the electrosynthesis, the anode and cathode were cleaned with detergent and diluted hydrochloric acid, followed by washing with distilled water, and then dried. In a typical experiment, dried acetonitrile solvent (35 mL), propargyl alcohols (3.5 mmol), and  $n\text{-Bu}_4\text{NBr}$  (3.5 mmol) were added to the cell in turn, followed by charging of  $\text{CO}_2$  into the desired pressure. The electrosynthesis was carried out in the high-pressure stainless-steel undivided cell fitted with a nickel sheet cathode (wet surface area  $6\text{ cm}^2$ ) and a copper sheet anode (wet surface area  $6\text{ cm}^2$ ) at a suitable constant current, under a continuously stirring condition. The electrolysis was ended after electricity  $4\text{ F mol}^{-1}$  of starting substrate was passed through the cell at room temperature. The electrolyte solution was mixed with distilled water (35 mL) and then extracted with (25 mL  $\times$  4) diethyl ether. The ether phase was washed three times with distilled water, and dried over anhydrous  $\text{MgSO}_4$ . After evaporation of ether, the obtained yellow crude product was dried in vacuum oven at  $40^\circ\text{C}$  and purified by chromatography on a silica gel column using light petroleum ether–ethyl acetate as eluent.

The obtained products were characterized by FTIR,  $^1\text{H}$  NMR, and mass spectra. FTIR spectra were measured by a TENSOR27 spectrometer. NMR spectra were recorded with a Bruker DRX-400 spectrometer using  $\text{CDCl}_3$  as the solvent and TMS as the internal standard. Mass spectra were recorded with a Shimadzu GC-MS-QP5050A spectrometer.

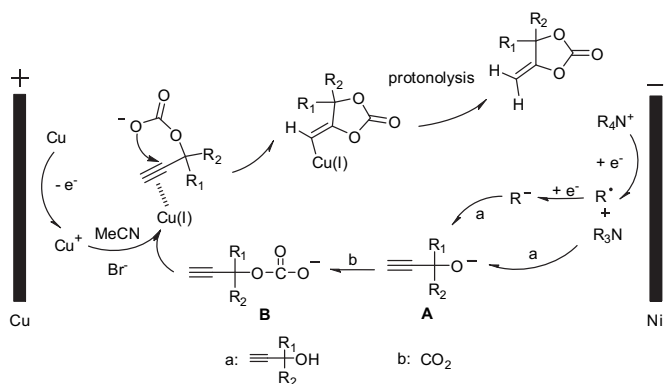
**3.1.1. 4-Methyl-5-methylene-4-phenyl-1,3-dioxolan-2-one (2a).** IR (neat):  $1820\text{ (C=O)}$ ,  $1684\text{ (C=C)}\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.475–7.366 (m, 5H), 4.93 (d,  $J=4\text{ Hz}$ , 1H), 4.45 (d,  $J=4\text{ Hz}$ , 1H), 1.95 (d,  $J=4\text{ Hz}$ , 3H). GC–MS:  $m/z$  (%) = 190 (2) ( $\text{M}^+$ ), 146 (6), 131 (14), 117 (100), 103 (36), 51 (15).

**3.1.2. 4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one (2b).** IR (neat):  $1837\text{ (C=O)}$ ,  $1640\text{ (C=C)}\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 4.78 (d,  $J=4\text{ Hz}$ , 1H), 4.31 (d,  $J=4\text{ Hz}$ , 1H), 1.61 (s, 6H). GC–MS:  $m/z$  (%) = 128 (4) ( $\text{M}^+$ ), 84 (27), 56 (72), 41 (100).

**3.1.3. 4-Ethyl-4-methyl-5-methylene-1,3-dioxolan-2-one (2c).** IR (neat):  $1832\text{ (C=O)}$ ,  $1687\text{ (C=C)}\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 4.82 (s, 1H), 4.27 (s, 1H), 1.94–1.89 (m, 1H), 1.79–1.74 (m, 1H), 1.59 (s, 3H), 0.99 (t,  $J=7.2$ , 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  157.5, 151.6, 87.6, 85.6, 33.4, 26.0, 7.4. GC–MS:  $m/z$  (%) = 142 (1) ( $\text{M}^+$ ), 97 (2), 70 (6), 56 (100).

**3.1.4. 4-Isobutyl-4-methyl-5-methylene-1,3-dioxolan-2-one (2d).** IR (neat):  $1831\text{ (C=O)}$ ,  $1685\text{ (C=C)}\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 4.76 (d,  $J=4\text{ Hz}$ , 1H), 4.25 (d,  $J=4\text{ Hz}$ , 1H), 1.82–1.75 (m, 2H), 1.66–1.61 (m, 1H), 1.54 (s, 3H), 0.95–0.92 (m, 6H). GC–MS:  $m/z$  (%) = 171 (2) ( $\text{M}^+$ ), 126 (5), 111 (28), 84 (47), 69 (100), 43 (41).

**3.1.5. 4-Hexyl-4-methyl-5-methylene-1,3-dioxolan-2-one (2e).** IR (neat):  $1830\text{ (C=O)}$ ,  $1685\text{ (C=C)}\text{ cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.79 (s, 1H), 4.28 (s, 1H), 1.89–1.83 (m, 1H), 1.74–1.67 (m, 1H), 1.58 (s, 3H), 1.39–1.28 (m, 8H), 0.87 (d,  $J=6.4\text{ Hz}$ , 3H).  $^{13}\text{C}$  NMR



Scheme 2. Proposed mechanism for  $\text{CO}_2$  incorporation into propargylic alcohols.



(CDCl<sub>3</sub>, 100 MHz):  $\delta$  157.9, 151.5, 87.2, 85.2, 40.6, 31.4, 29.0, 26.3, 22.9, 22.4, 13.8. GC–MS:  $m/z$  (%)=199 (2) (M<sup>+</sup>), 155 (6), 111 (49), 83 (61), 69 (65), 55 (100).

**3.1.6. 4-Methylene-1,3-dioxaspiro[4.4]nonan-2-one (2f).** IR (neat): 1833 (C=O), 1687 (C=C) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ =4.79 (d,  $J$ =4 Hz, 1H), 4.37 (d,  $J$ =4 Hz, 1H), 2.23 (d,  $J$ =8.4 Hz, 2H), 1.98–1.83 (m, 6H). GC–MS:  $m/z$  (%)=154 (1) (M<sup>+</sup>), 109 (4), 95 (12), 67 (100), 53 (15).

**3.1.7. 4-Methylene-1,3-dioxaspiro[4.5]decan-2-one (2g).** IR (neat): 1814 (C=O), 1683 (C=C) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ =4.76 (d,  $J$ =4 Hz, 1H), 4.30 (d,  $J$ =4 Hz, 1H), 2.01 (d,  $J$ =11.6 Hz, 2H), 1.78–1.59 (m, 8H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  158.6, 151.8, 86.2, 85.2, 36.8, 24.4, 21.6. GC–MS:  $m/z$  (%)=168 (1) (M<sup>+</sup>), 124 (8), 95 (17), 81 (61), 67 (100), 54 (47).

**3.1.8. 4-Methylene-5-pentyl-1,3-dioxolan-2-one (2h).** IR (neat): 1835 (C=O), 1688 (C=C) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ =5.25 (t,  $J$ =6.1 Hz, 1H), 4.32 (d,  $J$ =0.8 Hz, 2H), 1.59–1.55 (m, 1H), 1.45–1.40 (m, 1H), 1.37–1.30 (m, 6H), 0.96 (t,  $J$ =5.2 Hz, 3H). GC–MS:  $m/z$  (%)=170 (1) (M<sup>+</sup>), 127 (4), 83 (13), 69 (17), 55 (25), 28 (100).

#### 4. Conclusions

In conclusion, with nickel as the cathode and Cu as the anode and *n*-Bu<sub>4</sub>NBr–MeCN as the electrolyte, the electrochemical route has been applied to synthesize  $\alpha$ -alkylidene cyclic carbonate from propargyl alcohols and CO<sub>2</sub> at room temperature. The Cu<sup>+</sup> ions and strong bases electrogenerated in situ and solvent MeCN play a crucial role in the present electrochemical system. The electrochemical route is especially suitable for the cyclization reaction of secondary and tertiary terminal propargylic alcohols with CO<sub>2</sub>. The present work might be helpful to further extend the application scope of carbon dioxide.

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#### Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.10.039.

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