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Reusable Polymer-Supported Amine-Copper Catalyst for the Formation of α-Alkylidene Cyclic Carbonates in Supercritical Carbon Dioxide

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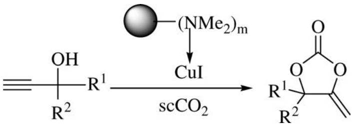
Keywords: Polymer-supported catalysts / Carbon dioxide fixation / Cyclic carbonates / Supercritical carbon dioxide / Cyclization / Copper

A green, simple and effective polymer-supported catalytic system has been developed for the cyclization of propargyl alcohols with carbon dioxide (CO_2). α-Alkylidene cyclic carbonates were obtained in satisfactory isolated yields in most cases. The catalyst could be recovered by simple filtration and reused several times without significant loss of activity.

Introduction

CO_2 is an environmentally benign and abundant C_1 resource, and therefore considerable attention has been focused on the fixation of carbon dioxide (CO_2) to organic substrates.[1] The formation of α-alkylidene cyclic carbonates from CO_2 and propargylic alcohol is an attractive route for the chemical fixation of CO_2 because α-alkylidene cyclic carbonates are useful building blocks in organic synthesis.[2] It has been reported that transition metals, including Cu,[3] Co,[4] Ru,[5] Pd[6] and Ag,[7] or tertiary phosphanes[8] are effective catalysts for the preparation of α-alkylidene cyclic carbonates. However, in most cases, the reactions have been accomplished under homogeneous catalytic conditions. Therefore, it is still desirable to search for a highly efficient, easily separating and recyclable catalytic system for this transformation.

Reviewing the developments in transition-metal-catalyzed reactions of CO_2 and propargylic alcohols,[3–7] we found that the desired cyclic carbonates were obtained in the presence of a stoichiometric amount of base. Amine resin, as a dual-purpose polymer-supported organic base and transition-metal ligand, is easily separated and recovered from the reaction mixture. Thus, we surmised that amine-resin-supported copper(I) iodide might be employed as an effective and reusable catalyst for the fixation reaction. On the other hand, the use of supercritical carbon dioxide ($scCO_2$) as a reactant and promising reaction medium has recently received much attention, not only because of its benign character, but also because of its greater activity and selectivity.[9,10] In this paper, we report on (dimethylamino)methyl-polystyrene-supported copper(I) iodide (DMAM-PS-CuI) as an efficient and environmentally benign heterogeneous catalyst for the cyclization of CO_2 and propargyl alcohols under supercritical conditions (Scheme 1).



Scheme 1. Carboxylative cyclization of propargyl alcohols with $scCO_2$ catalyzed by DMAM-PS-CuI.

Results and Discussion

The reaction of 2-methylbut-3-yn-2-ol (**1a**) with CO_2 was chosen as the model reaction to test the catalytic capability of DMAM-PS-CuI, and the results are summarized in Table 1. Initially, the amount of DMAM-PS-CuI was varied under 14 MPa of CO_2 at 40 °C; the results showed that an increase in the amount of catalyst enhanced the reaction yields (Table 1, Entries 1–4). Without any catalyst, this reaction did not take place even after 24 h (Table 1, Entry 1), whereas 48 % yield (by GC) of **2a** was obtained when 3 mol-% of DMAM-PS-CuI was added (Table 1, Entry 2). By further increasing the amount of DMAM-PS-CuI to 8 mol-%, the yield of **2a** sharply increased to 99 % (Table 1, Entry 4). Then the effect of the reaction pressure was examined; the results indicated that the pressure strongly influenced the carboxylative cyclization. When the pressure was increased from 14 to 18 MPa, the yield of **2a** slightly decreased (Table 1, Entries 4–6). However, reducing the pressure from 10 to 6 MPa had an obvious impact on the yield of **2a** (Table 1, Entries 9–11). The most suitable CO_2 pressure ranges from 12 to 16 MPa (Table 1, Entries 4, 7 and 8). The

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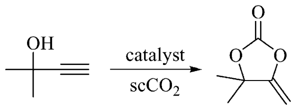
effect of temperature was also evaluated. The reactions at both 40 and 60 °C gave satisfactory results (Table 1, Entries 10 and 12). When the temperature was reduced to 30 or 25 °C, only small quantities of the desired product were obtained (Table 1, Entries 13 and 14). A yield of 77% was obtained with CuI alone as the catalyst and Et_3N (10 mol-%) as base (Table 1, Entry 15). This result thus shows that the Cu^I catalytic activity is significantly enhanced by fixing it to the polymer-supported base. We examined the ability of several other metal salts to activate the propargyl alcohol under a CO_2 pressure of 12 MPa. CuCl[3] and $AgBF_4$[7] afforded the cyclic carbonate in 73 and 81% yields, respectively (Table 1, Entries 16 and 17), $[Ru_3(CO)_{12}]$[5] showed little activity towards this reaction (Table 1, Entry 18), and $[Pd(OAc)_2]$[6] produced only a trace amount of the cyclic carbonate (Table 1, Entry 19).

Table 1. Formation of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (**2a**) from the reaction of 2-methylbut-3-yn-2-ol (**1a**) with CO_2.[a]



1a **2a**

Entry	Catalyst	Pressure [MPa]	Temp. [°C]	Yield [%][b]
1	–	14	40	0
2	DMAM-PS-CuI (3 mol-%)	14	40	48
3	DMAM-PS-CuI (5 mol-%)	14	40	77
4	DMAM-PS-CuI (8 mol-%)	14	40	99
5	DMAM-PS-CuI (8 mol-%)	16	40	98
6	DMAM-PS-CuI (8 mol-%)	18	40	96
7	DMAM-PS-CuI (8 mol-%)	13	40	99
8	DMAM-PS-CuI (8 mol-%)	12	40	99
9	DMAM-PS-CuI (8 mol-%)	10	40	97
10	DMAM-PS-CuI (8 mol-%)	8	40	84
11	DMAM-PS-CuI (8 mol-%)	6	40	53
12	DMAM-PS-CuI (8 mol-%)	12	60	99
13	DMAM-PS-CuI (8 mol-%)	12	30	46
14	DMAM-PS-CuI (8 mol-%)	12	25	22
15[c]	CuI (8 mol-%)	12	40	77
16[c]	CuCl (8 mol-%)	12	40	73
17[d]	$AgBF_4$ (8 mol-%)	12	40	81
18[c]	$[Ru_3(CO)_{12}]$ (8 mol-%)	12	40	46
19[c]	$[Pd(OAc)_2]$ (8 mol-%)	12	40	trace
20	$P(n\text{-}C_4H_9)_3$ (8 mol-%)	12	40	95
21	DMAM-PS-CuI (2nd)	12	40	96
22	DMAM-PS-CuI (3rd)	12	40	91
23	DMAM-PS-CuI (4th)	12	40	84
24	DMAM-PS-CuI (5th)	12	40	78
25[e]	CuI (8 mol-%)	12	40	48

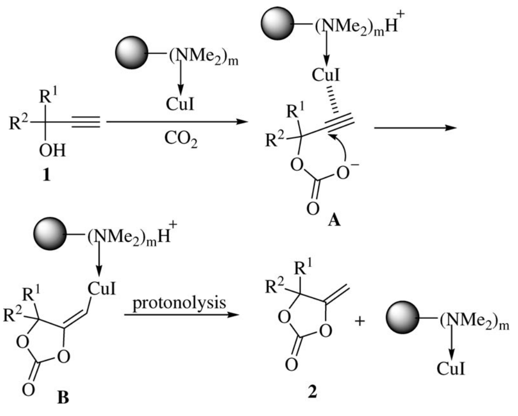
[a] Reaction conditions: 2-methylbut-3-yn-2-ol (**1a**) (1 mmol), DMAM-PS-CuI (1.21 mmol of CuI/g; 24.8 mg, 0.03 mmol CuI, 3 mol-%; 41.3 mg, 5 mol-%; 66 mg, 8 mol-%), 24 h. [b] Determined by GC. [c] Et_3N (24 mol-%) as base. [d] DBU (24 mol-%) as base. [e] DMAM-PS (50.5 mg, 4.8 mmol N/g, 24 mol-%) as base.

$P(n\text{-}C_4H_9)_3$[8] exhibited a comparable activity to that of the polymer-supported catalyst under the same reaction conditions (Table 1, Entry 20), but $P(n\text{-}C_4H_9)_3$ tends to be difficult to manipulate and recover compared with the heterogeneous catalyst.

Table 1 also shows the reusability of the supported catalyst (Entries 21–24). DMAM-PS-CuI could be recovered easily by simple filtration and reused after minimal treatment. The results showed that the reused DMAM-PS-CuI still retained its catalytic activity after multiple trials, but its catalytic capacity decreased with increasing reuse. To examine whether some leaching of Cu occurred during the reaction, the filtrate obtained after filtration was analyzed by ICP-AES which showed the amount of Cu present in the filtrate was less than 0.3% of the initial amount. For comparison with DMAM-PS-CuI, the cyclization of **1a** was performed with 8 mol-% of CuI and 24 mol-% of DMAM-PS; the product was obtained in only 48% yield (Table 1, Entry 25). It is suspected that physical destruction of the polymer matrix by stirring and leaching of Cu might be responsible for this decline.

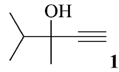
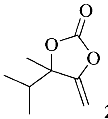
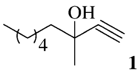
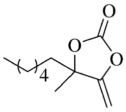
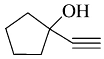
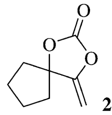
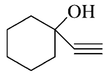
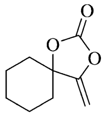
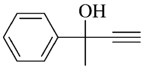
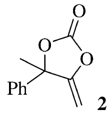
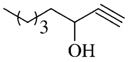
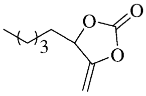
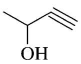
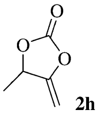
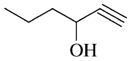
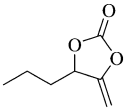
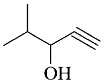
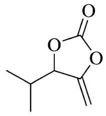
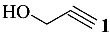
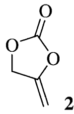
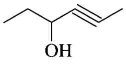
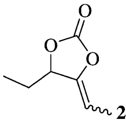
Under the optimized reaction conditions, other propargyl alcohols **1a**–**1k** were allowed to react with CO_2 and afforded the corresponding products in good to high yields. When tertiary propargyl alcohols **1b**–**1f** were employed, the aliphatic-substituted alcohols, whether 3,4-dimethyl-1-pentyn-3-ol, 3-methylnonyn-3-ol or five- or six-membered-ring-substituted propargyl alcohols, afforded the corresponding cyclic carbonates in good to excellent yields (Table 2, Entries 1–4). When the aliphatic substituent was replaced with an aromatic group such as phenyl, unfortunately, the desired product was not observed under the same conditions, and a large amount of unreacted starting material was recovered (Table 2, Entry 5). Note that secondary propargylic alcohols **1g**–**1j** gave the corresponding cyclic carbonate products **2g**–**2j** in high yields (Table 2, Entries 6–9). When primary and internal propargylic alcohols were used as the substrates, the desired products were not detected (Table 2, Entries 10 and 11), which suggests that the present methodology could be specific to aliphatic-substituted secondary and tertiary terminal propargylic alcohols.

A plausible mechanism for the incorporation of CO_2 into propargylic alcohols is postulated in Scheme 2, and it is similar to the mechanism reported previously for other cat-



Scheme 2. Proposed mechanism for CO_2 incorporation into propargylic alcohols catalyzed by DMAM-PS-CuI.

Table 2. Carboxylative cyclization of propargyl alcohols with $scCO_2$.[a]

Entry	Propargyl alcohol	Convension [%][b]	Product	Yield [%][c]
1	 **1b**	92	 **2b**	87
2	 **1c**	94	 **2c**	91
3	 **1d**	>99	 **2d**	97
4	 **1e**	>99	 **2e**	96
5	 **1f**	23	 **2f**	0
6	 **1g**	>99	 **2g**	95
7	 **1h**	>99	 **2h**	94
8	 **1i**	>99	 **2i**	94
9	 **1j**	>99	 **2j**	92
10	 **1k**	3	 **2k**	0
11	 **1l**	8	 **2l**	0

[a] Reaction conditions: propargyl alcohols (1 mmol), 66 mg of resin (1.21 mmol of CuI/g, 0.08 mmol of CuI, 8 mol-%), 14 MPa, 40 °C, 24 h. [b] Determined by GC. [c] Isolated yield.

alysts.[4,7] The first step of the reaction is the formation of carbonate intermediate **A** from **1** and CO_2 activated by the amine group of DMAM-PS-CuI. Then the intermediate **A** undergoes cyclization with the assistance of CuI to afford the corresponding cyclic carbonate and the release of the polymer-supported catalyst.

Conclusion

We have presented in this paper the cyclization of propargyl alcohols with CO_2 to α-alkylidene cyclic carbonates promoted by a polymer-supported catalyst containing cuprous iodide and amine functions under supercritical conditions. A tremendous advantage of using a polymer-supported catalyst for this transformation is that it can be easily recovered and reused after the reaction. The product can be separated easily from the system and continuous reactions might be achieved.

Experimental Section

General: NMR spectra were recorded with a Bruker DRX-400 spectrometer using $CDCl_3$ as solvent and TMS as the internal standard. GC analyses were performed with a GC-930 chromatograph (Shanghai Haixian Chromatograph Instrument Ltd. Co.). Mass spectra were recorded with a Shimadzu GCMS-QP5050A spectrometer. Elemental analyses were performed with a Vario EL Elemental Analyzer.

Materials: CO_2 was supplied by Guangzhou Gases Factory CO., Ltd. with a purity of 99.9%. The propargyl alcohols were purchased from Acros Organics and used without further purification. CuI was purchased from Aldrich Chemical Co. Resin (DMAM-PS) was obtained from Tianjin SHENTAI Chemical Industry Co., Ltd. The (dimethylamino)methyl-polystyrene-supported copper(I) iodide (DMAM-PS-CuI) was prepared according to procedures reported in the literature which gave the polymer a loading of 1.21 mmol CuI/g.[11]

Typical Experimental Procedure for the DMAM-PS-CuI-Catalyzed Reaction of CO_2 and Propargyl Alcohols: The reaction was carried out in an HF-15 autoclave. DMAM-PS-CuI (66 mg, 1.21 mmol of CuI/g, 0.08 mmol of CuI, 8 mol-%) and the propargyl alcohol (1 mmol) were added to the 15-mL autoclave in sequence. Liquid CO_2 was pumped into the autoclave by a cooling pump until the desired pressure was reached, and then the autoclave was heated by an oil bath under magnetic stirring for 24 h. After the reaction was finished, the autoclave was cooled to 0 °C. CO_2 was vented, and the residue was extracted with diethyl ether (10 mL). The resin was filtered, washed with CH_2Cl_2 (3×15 mL) and dried in vacuo at 40 °C. The collected filtrate was concentrated under reduced pressure. The product was purified by chromatography on a silica gel column using light petroleum ether/ethyl acetate as eluent.

4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one (2a):[8d] ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.59 (s, 6 H), 4.29 (d, J = 4.0 Hz, 1 H), 4.75 (d, J = 3.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 27.5, 84.6, 85.2, 151.2, 158.6 ppm. MS (EI, 70 eV): m/z (%) = 128 (4) $[M]^+$, 84 (46), 69 (22), 56 (96), 41 (100).

Supporting Information (see also the footnote on the first page of this article): Experimental procedures and analytical and spectral characterization data for all compounds.

Acknowledgments

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