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Poly(ethylene glycol): an Alternative Solvent for the Synthesis of Cyclic Carbonate from Vicinal Halohydrin and Carbon Dioxide

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Poly(ethylene glycol) (PEG) in this work proved to be an efficient reaction medium for the reaction of vicinal halohydrin with carbon dioxide in the presence of a base to synthesise cyclic carbonates. Notably, PEG-400 as an environmentally friendly solvent exhibits a unique influence on reactivity compared with conventional organic solvents. Various cyclic carbonates were prepared in high yield employing this protocol. The process presented here has potential applications in the industrial production of cyclic carbonates because of its simplicity, cost benefits, ready availability of starting materials, and mild reaction conditions.

Manuscript received: 17 December 2008. Final version: 27 March 2009.

Introduction

The correct choice of reaction media is considered as one of the central problems in chemical reactions, not only because unique reactivity and selectivity are often observed in the right solvent, but also because in many cases the general harm to the environment as well as to human beings of a organic solvent has a pivotal influence on its use on both a laboratory and industrial scale.^[1] With increasing regulatory pressure on using organic solvents, the development of an environmentally benign process is so desirable that various kinds of alternative solvents such as scCO₂,^[2] fluorous media,^[3] ionic liquids,^[4] and water^[5] have been explored as well as solvent-free processes.^[6] Furthermore, one of the key areas of green chemistry is the elimination of solvents in chemical processes or the replacement of a hazardous solvent with an environmentally benign one.^[7]

Poly(ethylene glycol)s (PEGs), also known as poly(ethylene oxide)s (PEOs) or poly(oxyethylene)s (POEs), are a family of water-soluble linear polymers formed by the interaction of ethylene oxide with water, ethylene glycol, or ethylene glycol oligomers. They have applications as textile auxiliaries, dispersants in toothpastes, oligomers in the manufacture of polyurethanes, and packing materials for food, etc.^[8] Our interest in PEG is as its use as an inexpensive, non-volatile, biologically acceptable, and eco-friendly solvent, which represents an interesting reaction medium for conventional solvent replacement.^[9] It has been discovered that its application as a reaction medium in organic syntheses has unique characters, as demonstrated by recently published reports.^[10]

Carbon dioxide is an easily available and renewable C1 building block as it has the advantages of high functionality, abundance, low cost, non-toxicity, and non-flammabilty. Nowadays, chemical transformation of CO₂ into useful organic chemicals has attracted ever-increasing attention from the point of view of environment protection and resource utilization.^[11] One of the most promising methodologies of CO₂ chemical fixation is the synthesis of five-membered cyclic carbonates, which have been widely used for various purposes, such as polar aprotic solvents, intermediates for organic and polymeric synthesis, chemical ingredients for pharmaceutical/fine chemicals in biomedical applications, and electrolytic elements of lithium secondary batteries.^[12] Therefore, great efforts have been devoted to producing cyclic carbonate through the cyclo-addition of an epoxide with CO₂ as a replacement of the conventional phosgene route.^[13] However, such a method requires the initial synthesis of an epoxide, which generally involves toxic or costly reagents and a tedious workup for separation.

Recently, we reported an environmentally 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.^[14] In terms of mechanistic considerations, a bromohydrin is assumed to be a intermediate in the single operation, thereby leading to the formation of cyclic carbonate with the aid of a base. We envisaged that there would be an alternative route to cyclic carbonate through the coupling of halohydrin and CO₂, thereby avoiding the pre-preparation of epoxides, which could still be obtained from the chlorohydrin route in most commercial processes.^[15] Indeed, Venturello et al. found that the reaction^[16a] of halohydrin with tetramethylammonium hydrogen carbonate in acetonitrile was preferentially carried out under a carbon dioxide atmosphere. Very recently, Kawanami and Ikushima^[16b] reported that organic carbonates were successfully prepared from vicinal halohydrins and CO2 in the presence of sodium hydroxide using ionic liquids as the reaction media at 120°C and a CO₂ pressure of 20 MPa. In a continuation of our work on the development of practical synthetic methodologies and green processes for organic carbonates and their derivatives using CO2 as a synthon through molecular activation,^[17] we demonstrate in the present



Scheme 1. Cyclic carbonates from halohydrin with CO₂.

Table 1. Synthesis of styrene carbonate from 2-bromo-2-phenylethanol and $\ensuremath{CO_2}$

 $\begin{array}{c} \mbox{Reaction conditions: 2-bromo-2-phenylethanol (0.2 g, 1 mmol), K_2CO_3} \\ (0.069 \mbox{ g}, 0.5 \mbox{ mmol}), \mbox{ solvent (2 mL), $PCO_2 $2 MPa} \end{array}$

Entry	Solvent	Base [mmol]	Time [h]	Temp [°C]	Conv. [%]	Yield ^A [%]
1	CH ₂ Cl ₂	0.5	3	50	0	0
2	THF	0.5	3	50	0	0
3	CHCl ₃	0.5	3	50	0	0
4	Dioxan	0.5	3	50	0	0
5	CH ₃ CN	0.5	3	50	45	45
6	DMF	0.5	3	50	72	72
7	H ₂ O	0.5	3	50	23	23
8	PEG-400	0.5	3	50	100	>99
9 ^B	H ₂ O/PEG-400	0.5	3	50	95	95
10	PEG-400	0.5	3	25	75	75
11	PEG-400	0.5	6	25	100	>99
12	PEG-1000	0.5	3	50	25	25
13 ^C	PEG-400	0.5	3	50	53	53
14	PEG-400	0	3	50	0	0
15^{D}	PEG-400	0.5	3	50	67	67
16 ^E	PEG-400	0.5	3	50	100	>99



^BThe volume ratio of H₂O to PEG-400, 1:1.

^CUsing NaOH as the base.

^DUsing Na₂CO₃ as the base.

^EUsing Cs₂CO₃ as the base.

work that vicinal halohydrin can be conveniently converted into cyclic carbonates by coupling with CO_2 in the presence of K_2CO_3 using PEG-400 (molecular weight 400) as an alternative solvent under mild reaction conditions (Scheme 1).

Results and Discussion

The cyclization of 2-bromo-2-phenylethanol with CO₂ into styrene carbonate was chosen as a bench reaction as shown in Table 1. Initially, solvent screening was carried out by using the reaction conditions of 3 h, 50°C, P_{CO2} 2 MPa. No conversion of vicinal bromohydrin was observed in the low polarity solvents such as dioxan, CH₃Cl, tetrahydrofuran (THF), and CH₂Cl₂ (Table 1, entries 1-4). With the increasing polarity of the solvents (H₂O > N,N-dimethylformamide (DMF) > CH₃CN),^[18] the yield of styrene carbonate increased except for with water (entries 5-7). Water showed poor performance probably owing to its poor solubility towards the reactants. PEG-400 as the reaction media gave full conversion with excellent selectivity under the otherwise identical reaction conditions (entry 8). Interestingly, the biphasic system also gave excellent results for cyclic carbonate synthesis with 95% yield under identical conditions (entry 9). It is distinct that the environmentally benign solvent PEG-400

Entry	Substrate	Product	Conv. [%]	Yield [%] ^A
1	CI Ph	O O Ph	100	>99
2	Br OH Ph	O O Ph	100	>99
3	HOCI		100	>99
4 ^B	CI	0	91	91
5 ^C	СІОН		100	>99
5C	OH CI CI		100	>99
7 ^D	OH Br		89	72

Table 2. Synthesis of various cyclic carbonatesReaction conditions: substrate (1 mmol), K2CO3 (0.069 g, 0.5 mmol),PEG-400 2 mL, PCO2 2 MPa, 50°C, 3 h

^ADetermined by GC using biphenyl as an internal standard.

^BThe reaction temperature was 80°C.

^CK₂CO₃ (0.138 g, 1 mmol) was used.

^D80°C, 12 h.

has a potential utility for the synthesis of styrene carbonate with high yield under mild reaction conditions.

Subsequently, we investigated the effect of the reaction temperature and the molecular weight of PEG. At 50°C, a 99% yield for styrene carbonate was attained, whereas room temperature showed low reaction rate (Table 1, entries 8, 10–12). However, PEG-1000 gave poor activity (entry 12), being presumably ascribed to the increased mass transport limitation of gaseous CO₂ in the highly viscous PEG with a long chain.^[19] Moreover, the base as an acid scavenger could have a great influence on the reaction. Indeed, the reaction did not occur at all without adding a base (entry 14). K₂CO₃ and Cs₂CO₃ performed better than Na₂CO₃ and NaOH under the otherwise identical conditions (entries 8, 13, 15, and 16). In the synthesis of cyclic carbonates, we chose K₂CO₃ as a base in terms of excellent yields, efficiency, and ease of workup.

In order to test the utility and generality of this process, we examined the coupling reaction of various vicinal halohydrins with CO₂ by performing the reaction with the established reaction conditions. The results are listed in Table 2. This protocol is easily found to be applicable to different types of vicinal halohydrins such as chlorohydrins, bromohydrins, and phenyl and alkyl-substituted halohydrins, to produce the corresponding cyclic carbonates (Table 2, entries 1–5). Note that the only side product was found to be the respective epoxide. Interestingly, α , γ -dichlorohydrin, derived from a biomass glycerol,^[20]

also gave excellent results by using this protocol (entry 6). It is worth mentioning that the present method could offer an efficient and feasible pathway for the internal carbonate (entry 7), which is difficult to prepare through other methods. Notably, internal cyclic carbonate is obtained exclusively as the *cis*-isomer, as determined by ¹H NMR, ¹³C NMR, and IR (cm⁻¹, KBr) spectroscopies ν (C=O): 1788 (s).^[17a,21]

As a consequence, in addition to its environmentally benign characteristics, the advantages of using PEG-400 as the reaction medium in the present study could be outlined as follows. First, it is assumed that PEG-400 can form complexes through coordinating the potassium cation such as crown ether does, which results in an increase in the basicity of K_2CO_3 .^[22] Second, the 'CO₂-expansion of PEG' effect^[10a,23] leads to changes in the physical properties of the reaction mixture, such as lowered viscosity, increased gas/liquid diffusion rates, and solubility of the reactants, thereby improving the synthetic process. Third, another merit of using PEG as a reaction media is the ease of product separation. In a typical experiment, cyclic carbonates were separated by extraction.

Conclusions

We have developed a viable alternative protocol for cyclic carbonate synthesis from vicinal halohydrins and CO_2 employing PEG-400 as a promising reaction medium. A high yield of cyclic carbonates together with excellent selectivity was achieved in mild reaction conditions. Moreover, the product can be easily separated by extraction. We feel that this would be a costeffective route to cyclic carbonate in an environmentally friendly manner. The broad scope of this method and further applications of PEG as reaction media to a wide set of organic reactions is currently under investigation in our laboratory.

Experimental

All vicinal halohydrins were prepared according to literature methods.^[24] Carbon dioxide with a purity of 99.99% was commercially available. All of the other reagents and catalysts used in this work were of analytical grade and were used as received without further purification. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury Plus 400 MHz or Bruker 300 MHz spectrometer, and at 100.4 or 75 MHz, respectively, in CDCl₃. Chemical shifts (δ) are given in ppm relative to tetramethylsilane (TMS). The solvent signals were used as references and the chemical shifts converted into the TMS scale (CDCl₃: $\delta_{\rm C}$ 77.0 ppm; residual CHCl₃ in CDCl₃: $\delta_{\rm H}$ 7.26 ppm). Gas chromatography (GC) analyses were performed on a Shimadzu GC-2014, equipped with a capillary column (RTX-5, $30\,\text{m} \times 0.25\,\text{mm}$) using a flame ionization detector. The products were characterized by comparison of their spectroscopic data with those of authentic samples.

General Procedure for the Reaction of Vicinal Halohydrin with CO₂

In a 50 mL inner volume stainless-steel autoclave equipped with a magnetic stirrer, substrate (1 mmol), K₂CO₃ (0.05 mmol, 0.069 g), and PEG-400 (2 mL) were added, and CO₂ (liquid, 2.0 MPa) was charged into the reactor at room temperature. The initial pressure was generally adjusted to 2 MPa at 50°C. The reactor was heated at that temperature for 3 h. After cooling, the products were separated by extraction with Et₂O (3 × 4 mL). (The PEG-400 was solidified when cooled to between -20° C and -10° C, followed by simple decantation of the Et₂O phase that contained the products.) The combined extracts were dried over $MgSO_4$ and concentrated under vacuum to give the product cyclic carbonate. The structures of the isolated products were also characterized by ¹H NMR and ¹³C NMR spectroscopy. Spectroscopic characteristics of the cyclic carbonates are as follows:

4-Phenyl-1,3-dioxolan-2-one

 $δ_{\rm H}$ 4.35 (400 MHz, CDCl₃) (t, 1H, *J* 8.4, OCH₂), 4.80 (t, 1H, *J* 8.4, OCH₂), 5.70 (t, 1H, *J* 8.0, OCH), 7.36 (d, 2H, *J* 7.6, Ph), 7.44 (d, 3H, *J* 6.4, Ph). $δ_{\rm C}$ (100.4 MHz, CDCl₃) 71.12, 77.95, 125.83, 129.22, 129.71, 135.78, 154.76. $ν_{\rm max}$ (KBr)/cm⁻¹ 1779, 1162, 1046, 756, 688. *m*/*z* (EI, 70 eV) 164 (M⁺), 119, 105, 90, 78, 65, 51, 39, 29.

4-Methyl-1,3-dioxolan-2-one

 $\delta_{\rm H}$ (400 MHz, CDCl₃) 1.43 (d, 3H, J 6.0, CH₃), 3.98 (t, 1H, J 8.4, OCH₂), 4.51 (t, 1H, J 8.4, OCH₂), 4.82 (m, 1H, CHO). $\delta_{\rm C}$ (100.4 MHz, CDCl₃) 19.15, 70.53, 73.49, 154.95. $\nu_{\rm max}$ (KBr)/cm⁻¹ 1791, 1184, 1120, 1076, 1052, 776. *m*/*z* (EI, 70 eV) 103 (M⁺), 57, 43.

1,3-Dioxolan-2-one

 $\delta_{\rm H}$ (400 MHz, CDCl₃) 4.50 (s, 4H, OCH₂). $\delta_{\rm C}$ (100.4 MHz, CDCl₃) 64.62, 155.55. $\nu_{\rm max}$ (KBr)/cm⁻¹ 1803, 1775, 1165, 1113, 1075. *m/z* (EI, 70 eV) 89 (M⁺), 43.

4-Chloromethyl-1,3-dioxolan-2-one

 $δ_{\rm H}$ (400 MHz, CDCl₃) 3.71 (dd, 1H, *J* 3.2, 12.0, ClCH₂), 3.80 (dd, 1H, *J* 5.2, 12.0, ClCH₂), 4.39 (dd, 1H, *J* 6.0, 8.4, OCH₂), 4.58 (t, 1H, *J* 8.4, OCH₂), 4.98 (m, 1H, CHO). $δ_{\rm C}$ (100.4 MHz, CDCl₃) 43.84, 66.83, 74.29, 154.28. $ν_{\rm max}$ (KBr)/cm⁻¹ 1800, 1168, 1112, 1073, 1044. *m/z* (EI, 70 eV) 137 (M⁺), 75, 43.

Cyclohexene Carbonate

 $\delta_{\rm H}$ (300 MHz, CDCl₃) 1.40–1.46 (m, 2H), 1.55–1.62 (m, 2H), 1.86–1.89 (m, 4H), 4.64–4.7 (m, 2H). $\delta_{\rm C}$ (75 MHz, CDCl₃) 19.1, 26.8, 75.7, 155.3. ν_{max} (KBr)/cm $^{-1}$ 1788, 1210, 1014. *m/z* (EI) 143 (M⁺), 97, 83, 79, 69, 55, 39.

Accessory Publication

¹H NMR and ¹³C NMR spectra, selected mass spectra, and IR spectra are available from the Journal's website.

Acknowledgements

Support of this work from National Science Foundation of China (no. 20421202, 20672504, and 20872073), the 111 project (B06005), and the Tianjin Natural Science Foundation is gratefully acknowledged. The authors also thank the referees for their valuable suggestions regarding revision.

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