



# Synthesis of 2-oxazolidinones/2-imidazolidinones from CO<sub>2</sub>, different epoxides and amino alcohols/alkylene diamines using Br<sup>-</sup>Ph<sub>3</sub><sup>+</sup>P-PEG<sub>600</sub>-P<sup>+</sup>Ph<sub>3</sub>Br<sup>-</sup> as homogenous recyclable catalyst

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## ARTICLE INFO

### Article history:

Received 3 November 2007

Received in revised form 6 March 2008

Accepted 12 March 2008

Available online 27 March 2008

### Keywords:

Carbon dioxide

Cyclic carbonates

2-Oxazolidinones

2-Imidazolidinones

Polyethylene glycol functionalized phosphonium salt

## ABSTRACT

Syntheses of various 2-oxazolidinones/2-imidazolidinones were carried out using polyethylene glycol functionalized phosphonium salt as an efficient homogenous recyclable catalyst via sequential addition of CO<sub>2</sub>, different epoxides and amino alcohols/alkylene diamines. The effects of various reaction parameters such as temperature, reaction time and catalyst concentration were investigated in detail. The catalyst was readily separated and reused. Excellent yields of 2-oxazolidinones/2-imidazolidinones and higher conversion of cyclic carbonates were observed.

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## 1. Introduction

Utilizing renewable resources is a prerequisite for a sustainable society. One easily available renewable carbon resource is carbon dioxide, which has the advantages of being nontoxic, abundant, and economical. In view of the sustainable chemistry and “green chemistry” concept, the synthesis of carbon dioxide-based industrially important chemicals has gained much interest [1,2]. However, due to the inert nature of carbon dioxide, its activation and incorporation into organic substances still remains a difficult task. The quest for certain molecules that can effectively act as a carbon dioxide fixation agents are required from an environmental viewpoint. Amino alcohols or diamines are worth investigating as an effective agent for the fixation of carbon dioxide into valuable chemicals such as 2-oxazolidinones and 2-imidazolidinones. 2-Oxazolidinones and 2-imidazolidinones have been extensively used for pharmaceuticals, cosmetics, pesticides, and so on [3–7]. They can be synthesized by reactions of amino alcohols or alkylene diamines with different reagents such as phosgene [8], urea [9,10], dialkyl carbonates [11,12], and a mixture of carbon monox-

ide and oxygen via oxidative carbonylation [13,14]. These systems suffer from various drawbacks such as the use of poisonous phosgene/carbon monoxide. The use of a mixture of CO/O<sub>2</sub> also has a risk associated with explosion hazards. As an alternative, dialkyl carbonates were used for the synthesis of 2-oxazolidinones and 2-imidazolidinones. However, it should be noted that currently dimethyl carbonate is mainly produced by phosgenation and oxidative carbonylation routes [15–18]. There are several reports on the direct synthesis of 2-oxazolidinones or 2-imidazolidinones by carbon dioxide and β-amino alcohols; aziridines or diamines [19–29]; however, essential requirement of toxic catalysts and high pressure or high temperature are limiting the application of these works. Hence there is sufficient scope for the development of active and recyclable homogeneous catalysts for this transformation. For the synthesis of 2-oxazolidinones/2-imidazolidinones many organic and inorganic compounds such as metal oxides, triphenylphosphine, carbon tetrachloride, amines, ionic liquids and inorganic bases, etc. have been utilized [21,22,29]. However, many of these catalysts suffer from disadvantages such as low stability, low catalyst activity and selectivity, etc. With homogeneous catalyst systems, catalyst/product separation and recyclability of the catalyst is also one of the major drawbacks. Hence in order to facilitate separation of catalyst, a large number of solid catalysts have been developed; unfortunately these solid catalysts have insufficient activity and most of them require polar solvent as an additive

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for attaining high activity and selectivity. This causes catalyst leaching and required additional product separation. The reaction rates are also lower for such heterogeneous catalysts and hence there is sufficient scope for the development of an active and recyclable catalyst system for this transformation.

In this work, we report the synthesis of 2-oxazolidinones/2-imidazolidinones via sequential addition of carbon dioxide, epoxide and amino alcohol/alkylene diamine catalyzed by  $\text{Br}^- \text{Ph}_3^+ \text{P-PEG}_{600} \text{P}^+ \text{Ph}_3 \text{Br}^-$  under mild conditions. In this direction, the work by He and co-workers using a novel,  $\text{PEG}_{600}(\text{NBu}_3\text{Br})_2$ , catalyst for the synthesis of cyclic carbonate via cycloaddition of epoxide and carbon dioxide [30] is one of important contribution. In another work they have also reported efficient synthesis of dimethyl carbonate from methanol, propylene oxide and carbon dioxide catalyzed by  $\text{PEG}_{600}(\text{PBu}_3\text{Br})_2$  [31] as a catalyst. This work demonstrates that such types of catalysts are useful for the synthesis of cyclic carbonates from carbon dioxide. Considering this prior art, in this work we observed that  $\text{Br}^- \text{Ph}_3^+ \text{P-PEG}_{600} \text{P}^+ \text{Ph}_3 \text{Br}^-$  shows excellent catalytic activity for the synthesis of 2-oxazolidinones and 2-imidazolidinones. The use of triphenylphosphonium bromide is advantageous as compared with tributylphosphonium bromide due to the issues related to stability, toxicity and handling of corresponding phosphines which are used as a precursors for the synthesis of these catalysts. To simplify the preparative procedure for 2-oxazolidinones and 2-imidazolidinones syntheses based on the two-step process from carbon dioxide (Scheme 1), namely to eliminate the separation of the cyclic carbonate and achieve catalyst recycling, we separately explored in detail the cycloaddition of various epoxide and carbon dioxide to form cyclic carbonate (Step 1) and also sequential addition of amino alcohol or alkylene diamine which leads to the formation of 2-oxazolidinones or 2-imidazolidinones (Step 2). The co-product obtained in Step 2 was diol which can be used as antifreeze agent.

## 2. Experimental

### 2.1. General

All chemicals were procured from the firms of repute and used without further purification/pre-treatment. The conversions and yields were based on GC analysis (Chemito 1000) using the external standard method. All products were characterized by GC–MS analysis (Shimadzu QP2010).

### 2.2. Catalyst preparation and characterization

To a solution of pyridine (7.9 g, 0.1 mol) in 500 ml of toluene, polyethylene glycol 600 ( $\text{PEG}_{600}$ ) (30 g, 0.1 mol) was added. To this

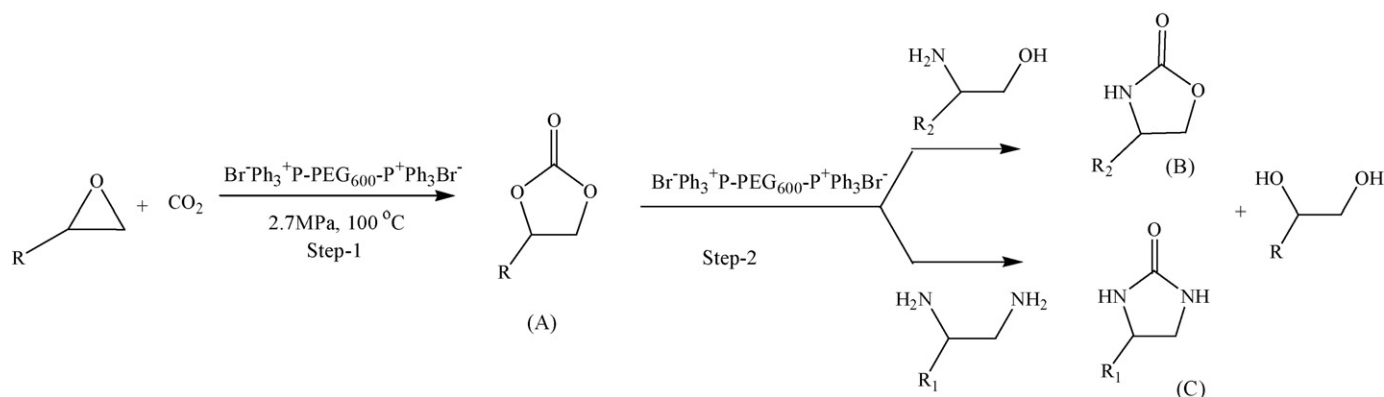
solution thionyl chloride (16 g, 0.14 mol) was slowly added with stirring, over a period of half an hour. The mixture was then refluxed for about 5 h. After cooling and filtering solid precipitate of pyridine hydrochloride, the solvent was removed in a vacuum. The residue was dissolved in dichloromethane and then treated with activated alumina. The procedure was repeated twice. The dichloromethane solution was filtered and evaporated to dryness to give  $\text{Cl}^- \text{PEG}_{600} \text{Cl}^-$  (23.5 g, 73%). To the  $\text{Cl}^- \text{PEG}_{600} \text{Cl}^-$  (10.0 g, 0.015 mol) prepared above, sodium bromide (10.3 g, 0.1 mol) was added and the mixture was heated to 120 °C in an oil bath for 12 h. After cooling, dichloromethane was added, the solution was filtered, and the solvent was removed in vacuo to obtain  $\text{Br}^- \text{PEG}_{600} \text{Br}^-$  (8.85 g, 78%). Finally, the above  $\text{Br}^- \text{PEG}_{600} \text{Br}^-$  (3.56 g, 0.003 mol) and triphenyl phosphine (1.290 g, 0.003 mol) were heated to 70 °C with stirring in an oil bath for 70 h. The residue was washed with petroleum ether at 60–80 °C and dried under vacuum to give  $\text{Br}^- \text{Ph}_3^+ \text{P-PEG}_{600} \text{P}^+ \text{Ph}_3 \text{Br}^-$  (5.08 g, 80%) [30–32]. The catalyst was characterized by  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ), which shows a peak at 23.32 ppm. This observation suggests that the phosphonium ion was formed in accordance with literature [31].

### 2.3. Typical experimental procedure for 2-oxazolidinones/2-imidazolidinones synthesis from epoxide, $\text{CO}_2$ and amino alcohol/alkylene diamine

Styrene oxide (25 mmol) and catalyst  $\text{Br}^- \text{Ph}_3^+ \text{P-PEG}_{600} \text{P}^+ \text{Ph}_3 \text{Br}^-$  (5 wt.%) were charged to a 100 ml stainless-steel high pressure reactor, then the reactor was heated to 100 °C, and was charged with carbon dioxide up to 2.7 MPa pressure and the reaction mixture was stirred for 3 h. After the completion of the reaction the reactor was cooled to room temperature. Carbon dioxide was vented out. After that to the same reactor without isolation of cyclic carbonate, amino alcohol (25 mmol) or alkylene diamine (25 mmol) was added and the reaction mixture was stirred at 60–100 °C for 3–5 h. After the completion of the reaction, the reaction mixture was cooled and 15 ml of ethanol was added. The catalyst was precipitated from the reaction mixture using diethyl ether. The precipitated catalyst was filtered and washed with 2 × 10 ml diethyl ether and was used for further recyclability study. The organic phase evaporated in a vacuum to yield the crude product. The product was further quantitatively analyzed by gas chromatography. The identification of the product was carried out via IR, GC–MS, and  $^1\text{H}$  NMR.

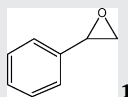
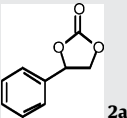

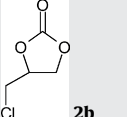
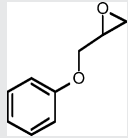
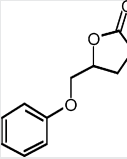
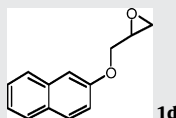
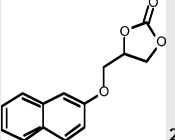
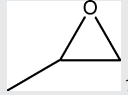
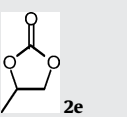
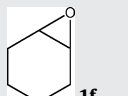
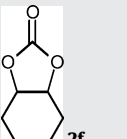
### 2.4. Spectral characteristics of the cyclic carbonates

**Table 1:** compound (2a):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  4.34 [t, J (H,H) = 8.21 Hz, 1H,  $\text{OCH}_2$ ], 4.82 [t, J (H,H) = 8.25 Hz, 1H,  $\text{OCH}_2$ ], 5.69



**Scheme 1.** Sequential synthesis of 2-oxazolidinones/2-imidazolidinones from carbon dioxide; epoxides and amino alcohols/alkylene diamines under mild conditions.

**Table 1**  
Synthesis of various carbonates catalyzed by  $\text{Br}^- \text{Ph}_3^+ \text{P-PEG-P}^+ \text{Ph}_3 \text{Br}^-$ <sup>a</sup>

Entry	Substrate	Product	Yield (%) <sup>b</sup>	Selectivity
1	 <b>1a</b>	 <b>2a</b>	98	99
2	 <b>1b</b>	 <b>2b</b>	98	99
3	 <b>1c</b>	 <b>3c</b>	98	99
4	 <b>1d</b>	 <b>2d</b>	98	99
5 <sup>c</sup>	 <b>1e</b>	 <b>2e</b>	60	99
6 <sup>c</sup>	 <b>1f</b>	 <b>2f</b>	75	99

<sup>a</sup> Reaction conditions: epoxides (25 mmol),  $\text{Br}^- \text{Ph}_3^+ \text{P-PEG}_{600} \text{-P}^+ \text{Ph}_3 \text{Br}^-$  (5 wt.%); temperature, 100 °C;  $\text{CO}_2$  pressure, 2.7 MPa; time, 3 h.

<sup>b</sup> Yield based on GC analysis.

<sup>c</sup> Reaction carried out at 120 °C temperature.

[t,  $J$  (H,H) = 7.79 Hz, 1H, OCH], 7.37 [d,  $J$  (H,H) = 7.6 Hz, 2H,  $\text{C}_6\text{H}_5$ ], 7.45 [d,  $J$  (H,H) = 7.6 Hz, 3H,  $\text{C}_6\text{H}_5$ ]. GC-MS:  $m/z$  = 164 ( $\text{M}^+$ ), 90, 78, 51.

**Table 1:** compound (**2b**):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  3.78 [dd,  $J$  (H,H) = 3.6 Hz,  $J$  (H,H) = 12.37 Hz, 1H, Cl- $\text{CH}_2$ ], 3.87 [dd,  $J$  (H,H) = 4.1 Hz,  $J$  (H,H) = 12.37 Hz, 1H, Cl- $\text{CH}_2$ ], 4.39 [dd,  $J$  (H,H) = 5.49 Hz,  $^2J$  (H,H) = 8.7 Hz, 1H, OCH<sub>2</sub>], 4.62 [t,  $J$  (H,H) = 9.16 Hz, 1H, OCH<sub>2</sub>], 5.07 [m, 1H, CHO]. GC-MS:  $m/z$  = 136.53 ( $\text{M}^+$ ), 87, 43. **Table 1:** compound (**2e**):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.43 [d,  $J$  (H,H) = 6.0 Hz, 1H,  $\text{CH}_3$ ], 4.059 [t,  $J$  (H,H) = 8.019 Hz, 1H, OCH<sub>2</sub>], 4.578 [t,  $J$  (H,H) = 8.249 Hz, 1H, OCH<sub>2</sub>], 4.91 [m, 1H, CHO]. GC-MS:  $m/z$  = 102 ( $\text{M}^+$ ), 87, 57, 43.

### 2.5. GC-MS (EI, 70 eV) of 2-oxazolidinones and 2-imidazolidinones

**Table 2** (entry **1**):  $m/z$  = 87 ( $\text{M}^+$ ), 59, 42; **Table 2** (entry **7**):  $m/z$  = 101 ( $\text{M}^+$ ), 84, 71, 56, 44; **Table 2** (entry **8**):  $m/z$  = 140 ( $\text{M}^+$ ), 100, 56, 42; **Table 2** (entry **9**):  $m/z$  = 115 ( $\text{M}^+$ ), 100, 72, 56, 42; **Table 3** (entry **1**):  $m/z$  = 86 ( $\text{M}^+$ ), 58, 42; **Table 3** (entry **7**):  $m/z$  = 100 ( $\text{M}^+$ ), 71, 56, 40.

## 3. Results and discussion

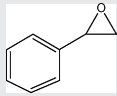
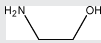
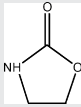
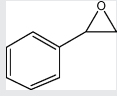

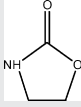


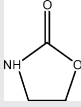
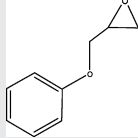

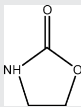
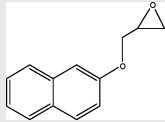
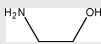
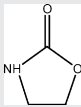
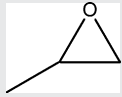
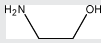
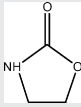


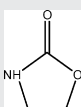
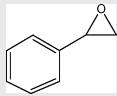
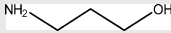

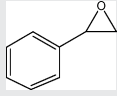
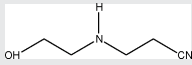
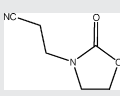
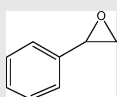
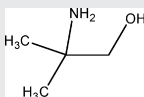
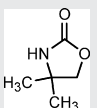
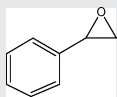
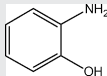
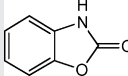
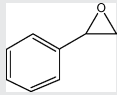
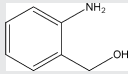
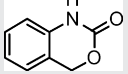
In the framework of our continuous effort to develop a simple and efficient route to organic carbonates from  $\text{CO}_2$

[33–37], we report herein, the synthesis of 2-oxazolidinones/2-imidazolidinones via sequential addition of carbon dioxide, epoxide and amino alcohol/alkylene diamine under mild reaction conditions (Scheme 1). The synthesis of cyclic carbonates (Step 1) and addition of amino alcohols/alkylene diamine (Step 2) was carried out sequentially without separation of cyclic carbonate obtained in Step 1, as described in the experimental section. We have explored cycloaddition of various epoxides and carbon dioxide to form cyclic carbonate separately (Step 1), followed by addition of amino alcohol / diamine in (Step 2).

### 3.1. Cycloaddition of $\text{CO}_2$ with styrene oxide

The cycloaddition reaction of styrene oxide (SO) and carbon dioxide was carried to obtain styrene carbonate (SC) using  $\text{Br}^- \text{Ph}_3^+ \text{P-PEG}_{600} \text{-P}^+ \text{Ph}_3 \text{Br}^-$  as a catalyst. The present protocol eliminates the use of air sensitive, pyrophoric and inflammable tributyl phosphine which is used as a precursor for catalyst preparation. Also use of aryl groups instead of alkyl groups is useful for structural modifications of catalyst as aryl group can be substituted easily. This can lead to tuning of catalyst with respect to electron density on phosphorous atom. Various reaction parameters such as catalyst concentration, temperature, time,  $\text{CO}_2$  pressure and also catalyst recyclability were studied in detail.

**Table 2**  
The synthesis of 2-oxazolidinones from different oxides and amino alcohols without isolation of cyclic carbonates<sup>a</sup>

Entry	Epoxides	Amino alcohols	Products	Yield <sup>b</sup> (%)
1 <sup>c</sup>				0
2				98
3				70
4				98
5				98
6				65
7				60
8				95
9				60
10				95
11				No reaction
12				No reaction

<sup>a</sup> Reaction conditions: epoxide (25 mmol), cat. Br<sup>-</sup>Ph<sub>3</sub><sup>+</sup>P-PEG<sub>600</sub>-P<sup>+</sup>Ph<sub>3</sub>Br<sup>-</sup> (5 wt.%), amino alcohol (25 mmol). Operation procedure: synthesis of cyclic carbonates at 100 °C, CO<sub>2</sub> 2.7 MPa, 3 h, the vessel was then cooled to room temperature CO<sub>2</sub> was vent off and then β-aminoalcohol was added reaction mixture stirred at 60–110 °C for 3 h.

<sup>b</sup> Yield determined by GC.

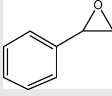

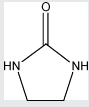
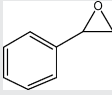

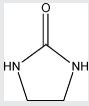
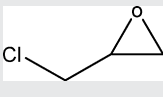

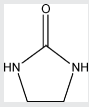
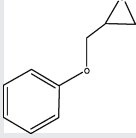

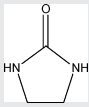
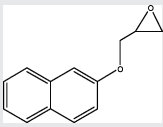

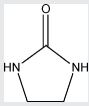
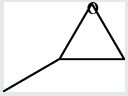

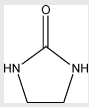

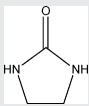
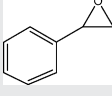
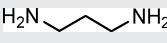
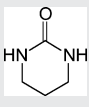
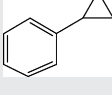

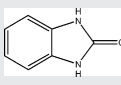
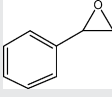

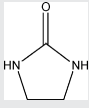
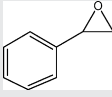

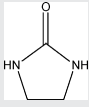
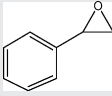

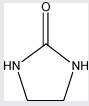
<sup>c</sup> Reaction carried out without catalyst.

### 3.1.1. Influence of catalyst concentration

In order to study the catalytic activity the reaction was carried out using PEG<sub>600</sub> alone with 2.7 MPa carbon dioxide at 100 °C for 3 h. PEG<sub>600</sub> was found inactive for the cycloaddition. When the

same reaction was carried out using Br<sup>-</sup>Ph<sub>3</sub><sup>+</sup>P-PEG<sub>600</sub>-P<sup>+</sup>Ph<sub>3</sub>Br<sup>-</sup> the reaction proceeded smoothly giving 98% yield and 99% selectivity performance. Accordingly, the phosphonium salts could be an active species for the reaction. The enhancement in the catalyst

**Table 3**  
The synthesis of 2-imidazolidinones from the different alkylene diamines and epoxides without isolation of cyclic carbonate<sup>a</sup>

Entry	Epoxides	Diamines	Products	Yield <sup>b</sup> (%)
1 <sup>c</sup>				0
2				85
3				65
4 <sup>d</sup>				75
5 <sup>d</sup>				75
6				60
7				60
8				85
9				No reaction
10 <sup>e</sup>				83
11 <sup>f</sup>				82
12 <sup>g</sup>				82

<sup>a</sup> Reaction conditions: epoxide (25 mmol), cat. Br<sup>-</sup>Ph<sub>3</sub><sup>+</sup>P-PEG<sub>600</sub>-P<sup>-</sup>Ph<sub>3</sub>Br<sup>-</sup> (5 wt.%), alkylene diamine (25 mmol), Operation procedure: synthesis of cyclic carbonates at 100 °C, CO<sub>2</sub> 2.7 MPa, for 3 h, the vessel was then cooled to room temperature CO<sub>2</sub> was vent off and then alkylene diamine was added reaction mixture stirred at 80 °C for 5 h.

<sup>b</sup> Yield determine by GC.

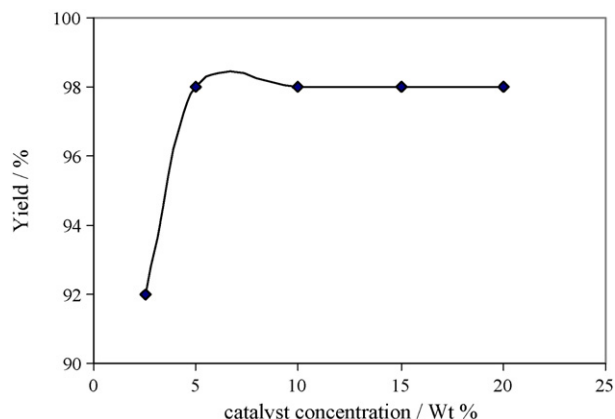
<sup>c</sup> Reaction carried out without catalyst.

<sup>d</sup> Reaction carried out at 100 °C.

<sup>e</sup> The second run of the catalyst recovered after run in (entry 2).

<sup>f</sup> The third run of the catalyst.

<sup>g</sup> The fourth run of the catalyst.



**Fig. 1.** Influence of catalyst concentration for cycloaddition of CO<sub>2</sub> with styrene oxide. Reaction conditions: styrene oxide (25 mmol), Br<sup>-</sup>Ph<sub>3</sub><sup>+</sup>P-PEG<sub>600</sub>-P<sup>+</sup>Ph<sub>3</sub>Br<sup>-</sup> (5–20 wt.%); temperature, 100 °C; CO<sub>2</sub> pressure, 2.7 MPa; time, 3 h. Yield of styrene carbonate determine by GC.

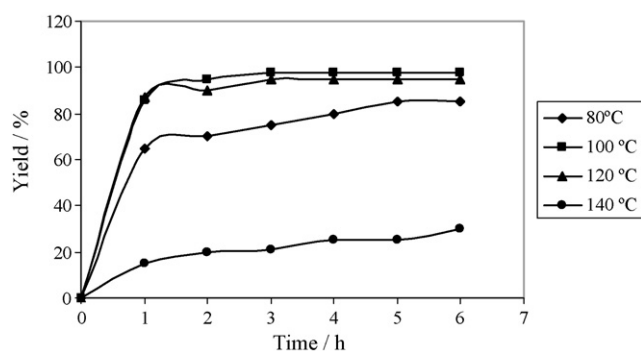
activity is due to change in the physical properties of the reaction mixture, such as lower melting points, lower viscosity, high diffusion rates, and increased solubility [38–41]. Various reaction parameters are discussed in detail for the cycloaddition of styrene oxide and carbon dioxide. The concentration of catalysts has strong influences on the yield of SC from CO<sub>2</sub> and SO. The catalyst amount was optimized by carrying out the reaction using 2.5, 5, 10, 15 and 20 wt.% of catalyst and it was observed that 5 wt.% of catalyst gave high yield (98%) and selectivity (99%). With further increase in the catalyst amount, change in the catalyst activity was not observed as shown in Fig. 1.

### 3.1.2. Influence of temperature/reaction time

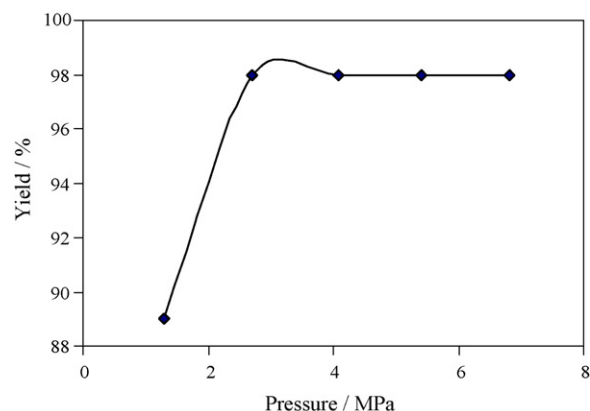
The influence of temperature on the yield of SC was investigated and the results obtained are shown in Fig. 2. The cycloaddition reaction of SO was carried out at various temperature and it was observed that temperature had a pronounced positive effect on the coupling reaction when the temperature was raised from 80 °C to 100 °C. The yield and selectivity of styrene carbonate increased with the increase in temperature from 80 °C to 100 °C.

However, with further increase in the temperature the yield and selectivity decreased due to the formation of by-products (mainly oligomers of reactive epoxides). From the experimental conditions mentioned above the optimal temperature was found to be 100 °C.

Effect of reaction time was also studied and it was observed that the PEG<sub>600</sub> functionalized catalysts exhibits high activity even at short reaction time as shown in Fig. 2. It can be seen that almost



**Fig. 2.** Influence of temperature/reaction time for cycloaddition of CO<sub>2</sub> with styrene oxide. Reaction conditions: styrene oxide (25 mmol), Br<sup>-</sup>Ph<sub>3</sub><sup>+</sup>P-PEG<sub>600</sub>-P<sup>+</sup>Ph<sub>3</sub>Br<sup>-</sup> (5 wt.%); CO<sub>2</sub> pressure, 2.7 MPa. Yield of styrene carbonate determine by GC.



**Fig. 3.** Influence of CO<sub>2</sub> pressure for cycloaddition of CO<sub>2</sub> with styrene oxide. Reaction conditions: styrene oxide (25 mmol), Br<sup>-</sup>Ph<sub>3</sub><sup>+</sup>P-PEG<sub>600</sub>-P<sup>+</sup>Ph<sub>3</sub>Br<sup>-</sup> (5 wt.%); temperature, 100 °C; time, 3 h. Yield of styrene carbonate determine by GC.

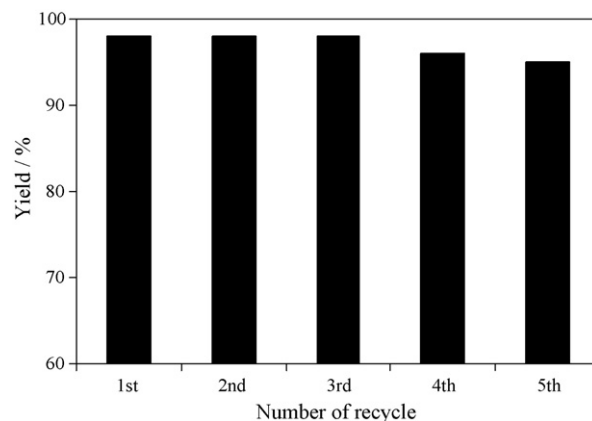
quantitative yield (98%) was achieved within 3 h. Further increase in the yield of SC was not observed after 3 h. Therefore, the reaction time of 3 h was optimal for the synthesis of SC at 100 °C.

### 3.1.3. Influence of CO<sub>2</sub> pressure

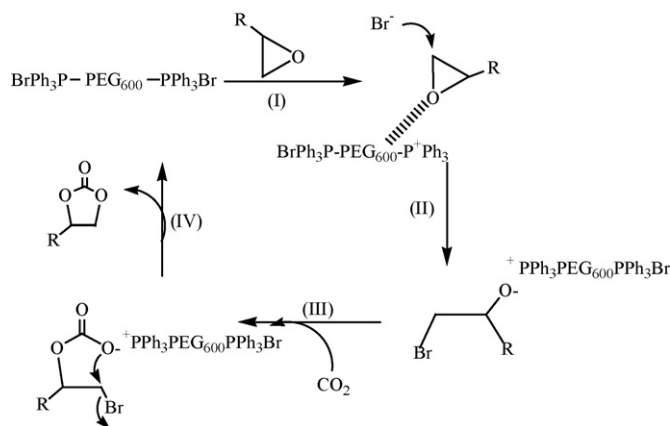
Essential requirement of high pressure is one of the drawbacks associated with using CO<sub>2</sub> as a reagent and a reaction medium in organic synthesis. It can be seen that pressure had no significant effect on the activity and selectivity in the pressure range of 2.7–6.8 MPa (see Fig. 3). It was observed that the higher yield of SC was obtained at lower pressure, i.e. 2.7 MPa. Indeed, the catalyst can be efficiently operated at 2.7 MPa. Even the pressure was reduced to below 1.3 MPa, the decline in activity was small.

### 3.1.4. Catalyst recyclability

The investigations on catalyst recyclability showed consistency of catalyst activity and selectivity. The SC formed is soluble in diethyl ether whereas Br<sup>-</sup>Ph<sub>3</sub><sup>+</sup>P-PEG<sub>600</sub>-P<sup>+</sup>Ph<sub>3</sub>Br<sup>-</sup>, being a salt, insoluble in ether. Hence, after each cycle Br<sup>-</sup>Ph<sub>3</sub><sup>+</sup>P-PEG<sub>600</sub>-P<sup>+</sup>Ph<sub>3</sub>Br<sup>-</sup> was separated from the reaction mixture by simple extraction using diethyl ether and reused for subsequent reaction. The yield of SC was consistent up to five cycles as shown in Fig. 4. Therefore, immobilization of a phosphonium salt on a soluble polymer (e.g. PEG<sub>600</sub>) provides an alternative pathway to realizing homogeneous catalyst recycling.



**Fig. 4.** Catalyst recyclability for cycloaddition of CO<sub>2</sub> with styrene oxide. Reaction conditions: styrene oxide (25 mmol), Br<sup>-</sup>Ph<sub>3</sub><sup>+</sup>P-PEG<sub>600</sub>-P<sup>+</sup>Ph<sub>3</sub>Br<sup>-</sup> (5 wt.%); temperature, 100 °C; CO<sub>2</sub> pressure, 2.7 MPa; time, 3 h. Yield of styrene carbonate determine by GC.



**Scheme 2.** Possible reaction path for  $\text{Br}^- \text{Ph}_3\text{P}^+ \text{-PEG}_{600} \text{-P}^+ \text{Ph}_3\text{Br}^-$  catalyzed cycloaddition of  $\text{CO}_2$  with epoxides (based on mechanism proposed by He and coworkers for  $\text{Br}^- \text{Bu}_3\text{N}^+ \text{-PEG}_{600} \text{-N}^+ \text{Bu}_3\text{Br}^-$  [30]).

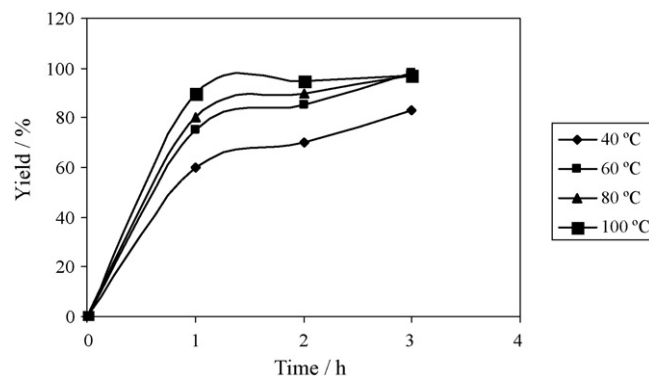
### 3.1.5. Substrate study

Under the optimized reaction conditions, cycloaddition of various terminal epoxides with  $\text{CO}_2$  was studied. The epoxides were converted to their corresponding cyclic carbonates with high yields. The results obtained are summarized in Table 1. Styrene oxide (**1a**), epichlorohydrin (**1b**), glycidyl phenyl ether (**1c**), and glycidyl naphthyl ether (**1d**) were good substrate to give cyclic carbonate in nearly 98% yield, while propylene oxide (**1e**), and cyclohexene oxide (**1f**) exhibited relatively low reactivity among the epoxide studied.

A possible reaction path for the  $\text{Br}^- \text{Ph}_3\text{P}^+ \text{-PEG}_{600} \text{-P}^+ \text{Ph}_3\text{Br}^-$  catalyzed cycloaddition of  $\text{CO}_2$  with epoxide is based on the mechanism proposed by He and co-workers for  $\text{Br}^- \text{Bu}_3\text{N}^+ \text{-PEG}_{600} \text{-N}^+ \text{Bu}_3\text{Br}^-$  catalyst which is shown in Scheme 2 [30]. The phosphonium salt part could be an active species for the reaction. The proposed reaction path involves the activation of epoxide ring by phosphonium cation (Step 1), followed by epoxide ring opening via nucleophilic attack of bromine at the least hindered carbon (Step 2) and insertion of  $\text{CO}_2$  into to P–O bond (Step 3) and subsequent cyclization via intermolecular nucleophilic attack (Step 4), leading to cyclic carbonate and regeneration of the catalyst (Scheme 2) [30].

### 3.2. Synthesis of 2-oxazolidinones/2-imidazolidinones from $\text{CO}_2$ , various epoxides and amino alcohol/alkylene diamine without cyclic carbonate separation

We report a novel method for synthesis of 2-oxazolidinones/2-imidazolidinones via sequential addition of  $\text{CO}_2$ , various epoxides and amino alcohol/alkylene diamine, in which the crucial point is the choice of the catalyst which can be active for both of the steps. Herein we wish to report  $\text{PEG}_{600}$  functionalized phosphonium salt as an effective catalyst for cyclic carbonate as well as 2-oxazolidinones/2-imidazolidinones synthesis under mild conditions. In order to study role of the catalyst the reaction was carried out in the absence of the catalyst and it was observed that formation of desired product did not take place (Tables 2 (entry 1) and 3 (entry 1)). However, when the same reaction was carried out using  $\text{Br}^- \text{Ph}_3\text{P}^+ \text{-PEG}_{600} \text{-P}^+ \text{Ph}_3\text{Br}^-$  the reaction proceeded smoothly giving 2-oxazolidinones and 2-imidazolidinones in 98% and 85% yields, respectively (Tables 2 (entry 2) and 3 (entry 2)). Hence, in order to establish the optimized reaction conditions, we examined the effect of temperature and reaction time on the 2-oxazolidinones synthesis.



**Fig. 5.** Influence of temperature/reaction time for the synthesis of 2-oxazolidinone from  $\text{CO}_2$ , styrene oxide and 2-amino ethanol. Reaction conditions: styrene oxide (25 mmol),  $\text{Br}^- \text{Ph}_3\text{P}^+ \text{-PEG}_{600} \text{-P}^+ \text{Ph}_3\text{Br}^-$  (5 wt.%), 2-amino ethanol (25 mmol). Operation procedure: synthesis of cyclic carbonate at 100 °C,  $\text{CO}_2$  2.7 MPa, 3 h, the vessel was then cooled to room temperature  $\text{CO}_2$  was vent off and then 2-amino ethanol was added and stirred the reaction mixture. Yield of 2-oxazolidinone determine by GC.

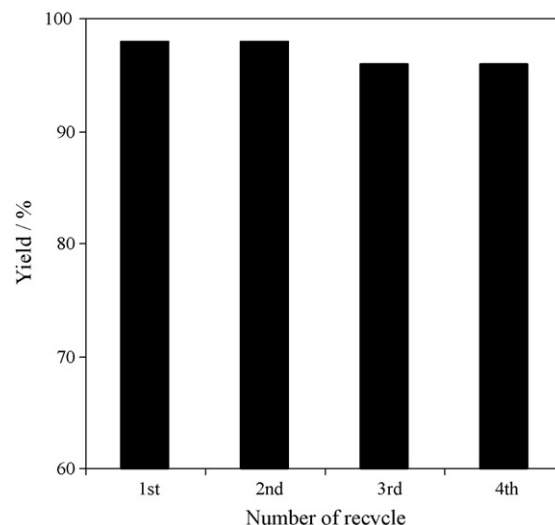
### 3.2.1. Influence of temperature/reaction time

It has been observed that the yield increases with increase in the reaction temperature. Above 60 °C, the 98% yield was achieved after 3 h. Typical results are shown in Fig. 5.

Thus the optimal temperature was found to be 60 °C. Effect of reaction time was also studied and it was observed that nearly quantitative yield (98%) was obtained within 3 h.

### 3.2.2. Catalyst recyclability

A catalyst recyclability study was carried out to investigate the consistency of the catalyst activity. After the completion of reaction, the reaction mixture was cooled and ethanol was added. The catalyst was precipitated from the reaction mixture using diethyl ether. The precipitated catalyst was filtered and washed with diethyl ether and reused for subsequent reaction. It is to be noted that the yield of 2-oxazolidinones was almost constant up to four recycle as shown in Fig. 6.



**Fig. 6.** Catalyst recyclability for synthesis of 2-oxazolidinone from  $\text{CO}_2$ , styrene oxide and 2-amino ethanol. Reaction conditions: styrene oxide (25 mmol),  $\text{Br}^- \text{Ph}_3\text{P}^+ \text{-PEG}_{600} \text{-P}^+ \text{Ph}_3\text{Br}^-$  (5 wt.%), 2-amino ethanol (25 mmol). Operation procedure: synthesis of cyclic carbonate at 100 °C,  $\text{CO}_2$  2.7 MPa, for 3 h, the vessel was then cooled to room temperature  $\text{CO}_2$  was vent off and then 2-amino ethanol was added reaction mixture stirred at 60 °C for 3 h. Yield of 2-oxazolidinone determine by GC.

### 3.2.3. Substrate study

Under the optimized reaction conditions it was found that this method was applicable to the synthesis of corresponding 2-oxazolidinones from different amino alcohols and cyclic epoxides. The results are summarized in Table 2. Styrene oxide, glycidyl phenyl ether, and glycidyl naphthyl ether were good substrates to give 2-oxazolidinone in nearly 98% (Table 2, entries 2, 4 and 5), while epichlorohydrin, propylene oxide, and cyclohexyl oxide exhibited relatively lower activity among the epoxides studied (Table 2, entries 3, 6 and 7). The reaction of 3-amino-1-propanol with styrene oxide gave 2-oxazolidinone in 95% yield (Table 2, entry 8). It can be seen that aliphatic amino alcohols shows high reactivity and gives excellent yields, while aromatic amino alcohols such as 2-amino phenol and 2-amino benzyl alcohol are found to be inactive. (Table 2, entries 11 and 12).

In view of the above results the same methodology was extended to the 2-imidazolidinones synthesis as presented in Table 3. Styrene oxide, glycidyl phenyl ether, and glycidyl naphthyl ether were good substrates to give 2-imidazolidinones quantitatively in above 70% yield (Table 3, entries 2, 4 and 5). The result showed that satisfactory yields of 2-imidazolidinones were obtained from the alkylene diamine. When the reaction was conducted with *o*-phenylenediamine as the substrate, the product of 2-hydroxybenzimidazole was not obtained (Table 3, entry 9). A series of catalytic cycles was examined to test the catalyst recycling. The consistent yields of 2-imidazolidinones as shown in Table 3 (entries 10, 11 and 12) were obtained. The catalyst gave high purity of 2-imidazolidinones without any additional purification procedure. Therefore, immobilization of a phosphonium salt on a soluble polymer (e.g. PEG<sub>600</sub>) provides an excellent alternative pathway to realizing homogeneous catalyst recycling.

## 4. Conclusions

We have developed a simple sequential procedure for the synthesis of 2-oxazolidinone/2-imidazolidinones from different oxides, CO<sub>2</sub>, amino alcohols and alkylene diamine. Excellent yields were achieved using the Br<sup>-</sup>Ph<sub>3</sub><sup>+</sup>P-PEG<sub>600</sub>-P<sup>+</sup>Ph<sub>3</sub>Br<sup>-</sup> as a catalyst under mild conditions. The complete conversion of styrene carbonate was reached under the optimized reaction conditions. This methodology represents a valuable and environmentally benign non-phosgene alternative for the synthesis of 2-oxazolidinone/2-imidazolidinones. The work-up procedure is simple and the catalyst can reused without loss of catalytic activity and selectivity.

## Acknowledgements

The financial support from Technical Education Quality Improvement Programme (TEQIP), Government of India is kindly acknowledged.

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