

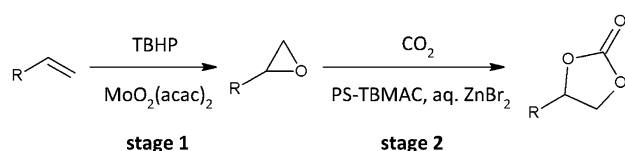


# Efficient Catalytic System Involving Molybdenyl Acetylacetonate and Immobilized Tributylammonium Chloride for the Direct Synthesis of Cyclic Carbonates from Carbon Dioxide and Olefins

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**Abstract** An effective direct method for preparing of cyclic carbonates from CO<sub>2</sub> and olefins in the presence of *tert*-butyl hydroperoxide as an oxidant was provided. The first stage, the epoxidation of olefins, was carried out using MoO<sub>2</sub>(acac)<sub>2</sub> as a catalyst (1h, 100 °C), and the second stage, the cycloaddition of CO<sub>2</sub> to the resulting epoxide, was proceeded in the presence of immobilized tributylmethylammonium chloride on a polystyrene cross-linked with divinylbenzene, and an aqueous solution of ZnBr<sub>2</sub> (100 °C, 0.9 MPa of CO<sub>2</sub>, 4 h). The proposed method allowed to obtain cyclic carbonates with high yields (50–77%) under mild conditions. Moreover, the immobilized catalyst could be reused at least five times without significant loss of its catalytic activity.

## Graphical Abstract



**Keywords** Carbon dioxide · Cyclic carbonates · Immobilization · Epoxidation · Cycloaddition

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## 1 Introduction

Inexpensive, readily available carbon dioxide plays an important role as a renewable raw material in several industrial processes. Among them, the synthesis of cyclic carbonates is of particular interest. The demand for cyclic carbonates continues to grow due to the wide range of their applications. They are used for polymer production e.g. non-isocyanate polyurethanes, polycarbonates; and as important intermediates in many processes for the preparation of fine chemicals. They are also employed as solvents, and components of electrolytes for lithium-ion batteries [1–4].

An important industrial method for preparing cyclic carbonate is by reaction of CO<sub>2</sub> with epoxides [5]. However, it is possible to carry out their synthesis from olefins and CO<sub>2</sub>. This method involves two stages: the epoxidation of olefins and the cycloaddition of CO<sub>2</sub> to the resulting epoxide. Due to the fact there is no need to isolate the epoxide, and the olefins are cheaper feedstock than epoxides, this method can be advantageous from an economic and environmental point of view. Although, the first report on this reaction appeared in 1962 [6], it has not yet been implemented on an industrial scale.

The direct synthesis of cyclic carbonates from carbon dioxide and olefins is typically conducted at temperature 30–150 °C and under pressure of CO<sub>2</sub> in the range of 1–15 MPa. Among others, metals, metal oxides, metal complexes, quaternary onium salts, and ionic liquids, are used as catalysts. Oxygen, hydrogen peroxide, alkyl hydroperoxides and urea hydroperoxide are usually used as oxidizing agents in the epoxidation stage [7, 8].

The synthesis of cyclic carbonates using alkyl hydroperoxides as oxidands is carried out mainly in the presence of metals, ionic liquids, and quaternary onium salts as

catalysts. Conducting the reaction using *tert*-butyl hydroperoxide (TBHP) as an oxidant and titanosilicate molecular sieves (TiMCM-41) and *N,N*-dimethylaminopyridine as a catalyst system in acetonitrile as a solvent, allowed to achieve conversion of olefin to epoxide only in the range of 13–44%, and 97–100% conversion of the resulting epoxide to cyclic carbonate with selectivities in the range 83–100% [9]. Arai et al. reported the synthesis of styrene carbonate (SC) from styrene (ST), TBHP and CO<sub>2</sub> using ionic liquids based on 1-*n*-alkyl-3-methylimidazolium or tetrabutylammonium cation as catalysts [10, 11]. The most effective catalyst was tetrabutylammonium bromide (TBAB), however, SC was obtained only in 38% yield (reaction conditions: 80 °C, a CO<sub>2</sub> pressure of 1 MPa). In 2005, the same group developed a method for preparation styrene carbonate, in which a silica-supported gold catalyst was used for the epoxidation of styrene with cumene hydroperoxide (CHP) or TBHP, while ZnBr<sub>2</sub> and TBAB were applied for the second stage of the process [12]. The reaction was carried out at the temperature of 80 °C and under the pressure of 1 MPa. The highest yield that has been achieved for styrene carbonate was 45%. Sun and co-workers proposed the catalyst system consisting of Au supported on Fe(OH)<sub>3</sub>, ZnBr<sub>2</sub> and TBAB for the synthesis of styrene carbonate using CHP as an oxidant [13]. Under reaction conditions of 80 °C, a CO<sub>2</sub> pressure of 4 MPa, styrene carbonate was obtained in yield of 53% after 10 h. In turn, the use of gold (0.01 wt%) supported on R201 resin functionalized with quaternary ammonium functional groups allowed to obtain styrene carbonate in 51% yield [14]. The reaction selectivity was 52%. Styrene carbonate can also be obtained in the reaction conducted in the presence of the MoO<sub>2</sub>(acac)<sub>2</sub>, TBAB catalytic system and TBHP as an oxidant [15]. The styrene epoxidation reaction was carried out for 1 h at the temperature of 100 °C. Next, the reaction of the resulting styrene oxide with carbon dioxide was conducted for 1 h (140 °C, CO<sub>2</sub> pressure of 3 MPa). SC was obtained in 68% yield whereas yields of other cyclic carbonates was in the range from 45 to 84%. 44% selectivity to SC at 57% styrene conversion was achieved in the reaction conducted with chromium-organic frameworks and TBAB as a catalyst system, at temperatures of 25–100 °C and a CO<sub>2</sub> pressure of 8–100 bar [16]. The ionic liquid 1-butyl-3-methylimidazolium bromide was used in a one-pot reaction (150 °C, 0.5 MPa of CO<sub>2</sub>, 6 h) allowed to obtain SC with 40% selectivity at 90% conversion of styrene, whereas SC was obtained with a selectivity of 63% at 99% conversion of styrene in the reaction conducted in a single reactor under different conditions for each step (epoxidation step: 100 °C, 16 h, cycloaddition step: 150 °C, 0.5 MPa, 6 h) [17]. Recently, polyoxometalate-based homochiral metal-organic frameworks were used as catalysts for enantioselective synthesis of cyclic carbonates in the presence

of TBHP as an oxidant [18]. Use of mild reaction conditions (50 °C, 0.5 MPa) but long reaction times (96 h) allowed for the preparation of cyclic carbonates with yields in the range 72–92% and the enantioselectivity of 55–80%. The catalyst could be used three times without a significant reduction in its activity. Gosh et al. used the catalyst system consisting of a manganese(III) complex of an amidamine ligand and TBAB for direct synthesis of cyclic carbonates [19]. The yields in the range of 10–48% were obtained under the reaction conditions: 100 °C, 250 psig of CO<sub>2</sub>, using acetonitrile as a solvent. Cyclic carbonates can be obtained with a selectivity of 44–68% at a conversion of olefin in the range of 62–98.5% using mesoporous titanium-silicate catalyst and TBAB as a cocatalyst [20]. The reaction conditions were relatively mild: 50–70 °C, a CO<sub>2</sub> pressure of 0.8 MPa, but the reaction time was 48 h.

The problems in above methods are usually not only unsatisfying yields of cyclic carbonates and low selectivities, but also long reaction time, often not easy synthesis of catalysts and their high price as well as difficulties associated with separation of the catalyst system and the inability to its reuse. It should also be emphasized that most of the described methods concerns only the synthesis of styrene carbonate.

Herein, we report an efficient one-pot procedure for the synthesis of cyclic carbonates directly from CO<sub>2</sub> and olefins using *tert*-butyl hydroperoxide as an oxidant. According to our previous studies, the reaction of CO<sub>2</sub> with epoxides could be carried out with high selectivities and yields in the presence of the catalyst system consisting of an immobilized quaternary ammonium salt on a polymeric carrier and an aqueous solution of zinc bromide(II) [21]. Therefore, this catalyst system was used for the second stage of the reaction of CO<sub>2</sub> with olefins, while molybdenyl acetylacetonate (MoO<sub>2</sub>(acac)<sub>2</sub>) was used as a catalyst for epoxidation of olefins.

## 2 Experimental

### 2.1 Chemical and Materials

Carbon dioxide (99.5%, from SIAD) was used without further purification. Bis(acetylacetonato)dioxomolybdenum(VI) (molybdenyl acetylacetonate, MoO<sub>2</sub>(acac)<sub>2</sub>), styrene (99%), styrene oxide (>97%), tributylamine (99%) were provided by Acros Organic. (Chloromethyl)ethylene carbonate, cyclohexene (99%), cyclohexene oxide (98%), 1-octene (98%), octane (>99%), ~5.5 M solution of *tert*-butyl hydroperoxide (TBHP) in decane, were purchased from Sigma Aldrich. Epichlorohydrin (>99%), tributylmethylammonium chloride (TBMAC) and tributylmethylammonium chloride polymer bound

(PS-TBMAC, 200–400 mesh; Cl loading: 1.2 mmol/g, polystyrene 1% cross-linked with DVB) were obtained from Fluka. Zinc bromide(II) (>98%) was bought from POCH S.A.

## 2.2 Instrumentation

The pressure reactions were carried out in 100 ml autoclave (EM-60-100-SS-HC) placed in a solid-state thermostat (EasyMax™ 102, Mettler Toledo). The pressure reactor was equipped with a mechanical stirrer (pitched-blade), temperature and pressure sensors and a rupture disc. Samples were analyzed by gas chromatography using PerkinElmer Clarus 500 chromatograph equipped with a flame ionization detector (FID) and a capillary column (SPB-5™: 30 m×0.25 mm×0.25 μm film thickness). GC-MS analyses were performed on a gas chromatography-mass spectrometry system (Agilent Technologies 7890 A GC system, Agilent Technologies 5975 C inert XL EI/CI MS System) equipped with a capillary column (HP5/MS-5: 30 m×0.25 mm×0.25 μm film thickness). Octane or nonane were used as the internal standards for the quantification of the formation of the products. The conditions of MS analysis were as follows: EI, ionization voltage 70 eV, ion source temperature 230 °C, m/z range 33–550. NMR spectra were recorded using a Varian 600 or 400 MHz for <sup>1</sup>H NMR and 150 or 100.6 MHz <sup>13</sup>C NMR. Elementary analyses were performed on a PerkinElmer 2400 series 2 CHNO/S analyzer. Infrared spectroscopy (IR) was conducted on a FT-IR spectrometer Mettler-Toledo IC10 with ATR probe. The parameters of the FT-IR spectrometer: measuring range: 4000–650 cm<sup>-1</sup>, resolution: 4, 8 or 16 cm<sup>-1</sup>, operating temperature range: from –80 to +200 °C.

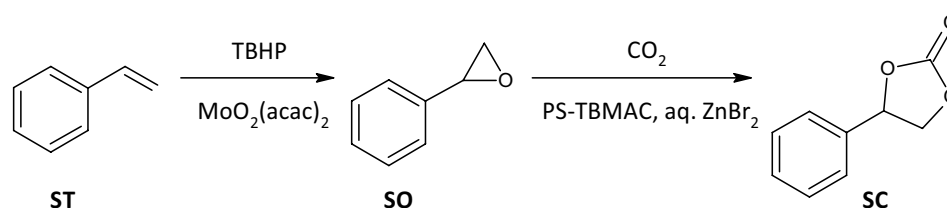
## 2.3 General Procedure of Cyclic Carbonates Synthesis

**Procedure 1** An olefin (58 mmol), MoO<sub>2</sub>(acac)<sub>2</sub> (0.058 mmol), TBHP (64 mmol), PS-TBMAC (0.58 mmol), an aqueous solution of ZnBr<sub>2</sub> (0.80 mmol of H<sub>2</sub>O, 0.16 mmol of ZnBr<sub>2</sub>), and an internal standard (0.4 g octane, or nonane, depending on the olefin used in the process) were added into an autoclave. The reactor was sealed and purged two times with carbon dioxide. Then, the reaction mixture was stirred (500 rpm) and heated up to 100 °C. After stabilization of the temperature, the autoclave was filled with carbon dioxide to the appropriate pressure (0.5–2.0 MPa). Process was conducted for 5 h. **Procedure 2:** An olefin (58 mmol), MoO<sub>2</sub>(acac)<sub>2</sub> (0.058 mmol), TBHP (64 mmol), PS-TBMAC (0.58 mmol) and an aqueous solution of ZnBr<sub>2</sub> (0.80 mmol of H<sub>2</sub>O, 0.16 mmol of ZnBr<sub>2</sub>), an internal standard (0.4 g octane, or nonane, depending on the olefin used in the process) were added into an autoclave.

The reactor was sealed and the reaction mixture was stirred (500 rpm) and heated up to 100 °C. After 1 h, the autoclave was filled with carbon dioxide to the appropriate pressure (0.9 MPa) and reaction was conducted for 4 h. **Procedure 3:** An olefin (58 mmol), MoO<sub>2</sub>(acac)<sub>2</sub> (0.058 mmol), TBHP (64 mmol), an internal standard (0.4 g octane, or nonane, depending on the olefin used in the process) were added into an autoclave. The reactor was sealed and the reaction mixture was stirred (500 rpm) at 100 °C for 1 h. After completion of the first stage of the process, the reactor content was cooled to room temperature. Then, the catalyst system required to carry out the second stage of the process, consisting of PS-TBMAC (0.58 mmol) and an aqueous solution of ZnBr<sub>2</sub> (0.80 mmol of H<sub>2</sub>O, 0.16 mmol of ZnBr<sub>2</sub>), was added. The reaction mixture was again heated up to the desired temperature (90–130 °C). After stabilization of the temperature, the autoclave was filled with carbon dioxide to the appropriate pressure (0.5–2.0 MPa) and reaction was conducted for 4 h. **Product isolation:** After the completion of the reaction, the mixture was cooled to room temperature and filtered to remove PS-TBMAC. The filtrate was concentrated and then extracted with ethanol (3×5 ml) in order to remove MoO<sub>2</sub>(acac)<sub>2</sub> which precipitated out as a solid. The organic phase was dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/chloroform). **GC Analysis:** On completion the reaction was cooled to room temperature and the excess carbon dioxide was vented. Then, the reaction mixture was diluted with 5 ml of ethyl acetate and sample of the reaction mixture (5 μl) was taken, dissolved in ethyl acetate (900 μl), and analyzed by gas chromatography. **Catalyst reusability:** After the completion of the reaction, the immobilized catalyst was simply recovered by filtration, washed with dichloromethane (6×5 ml). The filtrate was extracted with ethanol (3×5 ml) in order to extract MoO<sub>2</sub>(acac)<sub>2</sub>. The separated PS-TBMAC during the filtration was dried in vacuum and then reused for the next run.

## 3 Results and Discussion

The research was conducted on the example of a model reaction between styrene and carbon dioxide (Fig. 1). The first stage of the process, the epoxidation of styrene with 5.5 M solution of *tert*-butyl hydroperoxide in decane, was conducted in the presence of MoO<sub>2</sub>(acac)<sub>2</sub> as a catalyst. Based on our previous results [21], for the second step, the cycloaddition of CO<sub>2</sub> to styrene oxide (SO), the catalyst system consisting of an immobilized tributylmethylammonium chloride on a polystyrene cross-linked with divinylbenzene (PS-TBMAC) and an aqueous solution of

**Fig. 1** Model reaction between styrene and carbon dioxide**Table 1** The choice of procedure for conducting the direct synthesis of styrene carbonate from CO<sub>2</sub> and styrene

Entry	Procedure	Conversion of the styrene (%)	Yield <sup>a</sup> (%)		
			SO	BA	SC
1 <sup>b</sup>	1	79	8	17	22
2 <sup>b</sup>	2	82	11	19	43
3 <sup>b</sup>	3	96	8	11	67
4 <sup>c</sup>	3	94	21	6	42
5 <sup>d</sup>	3	92	6	23	51
6 <sup>e</sup>	3	94	8	25	57

Reaction conditions: styrene (58 mmol), 5.5 M solution of TBHP in decane (64 mmol), MoO<sub>2</sub>(acac)<sub>2</sub> (0.058 mmol), a quaternary ammonium salt (0.58 mmol), an aqueous solution of ZnBr<sub>2</sub> (0.80 mmol of H<sub>2</sub>O, 0.16 mmol of ZnBr<sub>2</sub>), 500 rpm. <sup>a</sup>Determined by GC. <sup>b</sup>PS-TBMAC. <sup>c</sup>TBMAC <sup>d</sup>TBAB without aqueous solution of ZnBr<sub>2</sub>. <sup>e</sup>TBAB. Procedure 1: all reagents including the catalyst system consisting of MoO<sub>2</sub>(acac)<sub>2</sub>, PS-TBMAC, aq. ZnBr<sub>2</sub>, were added simultaneously to the reactor. Process was conducted at 100 °C, under a CO<sub>2</sub> pressure of 0.9 MPa for 5 h. Procedure 2: the first stage of process was conducted in the presence of the catalyst system consisting of MoO<sub>2</sub>(acac)<sub>2</sub>, PS-TBMAC, aq. ZnBr<sub>2</sub>, at 100 °C for 1 h, after this time carbon dioxide (a CO<sub>2</sub> pressure of 0.9 MPa) was added to the reactor and the second step was conducted at 100 °C for 4 h. Procedure 3: the first stage of process was conducted in the presence of MoO<sub>2</sub>(acac)<sub>2</sub> as catalyst at 100 °C for 1 h, after this time carbon dioxide (a CO<sub>2</sub> pressure of 0.9 MPa) and the catalyst system consisting of PS-TBMAC (or TBMAC, TBAB) with or without an aqueous solution of ZnBr<sub>2</sub> were added to the reactor and the second step was conducted for 4 h

zinc bromide(II) (molar ratio of H<sub>2</sub>O to ZnBr<sub>2</sub> 5: 1), was applied.

### 3.1 The Impact of the Order of Reagent Introduction

The order in which reagents are added to a reactor can be crucial for the reaction of CO<sub>2</sub> with olefins. The introduction of all reagents: CO<sub>2</sub>, styrene, TBHP with the catalyst system consisting of MoO<sub>2</sub>(acac)<sub>2</sub>, PS-TBMAC and an aqueous solution of ZnBr<sub>2</sub>, allowed to obtain styrene carbonate with only 22% yield (Table 1, entry 1). The unreacted styrene oxide (8%) and benzaldehyde (BA) (17%) were also present in the reaction mixture. In this case, both stages of the process were carried out under the same conditions of temperature and pressure (procedure 1: 100 °C, the initial CO<sub>2</sub> pressure of 0.9 MPa, 500 rpm, 5 h). Sun et al. also observed that the presence of CO<sub>2</sub> has a negative

effect on the epoxidation reaction [14]. In contrast, Arai et al. found that the addition of carbon dioxide to the first reaction step results in improved yield both SO and SC [11]. A low yield of styrene carbonate was obtained possibly due to the fact that the epoxidation of styrene in the presence of CO<sub>2</sub> could allow the formation of the linear oligomers and polycarbonates, which in turn could impede the subsequent reaction of carbon dioxide with in situ formed epoxide [22, 23]. Therefore, in the next experiment, CO<sub>2</sub> was added to the reactor in the second step of the process. The first step proceeded at the temperature of 100 °C. Only after one hour carbon dioxide was added (0.9 MPa) and the reaction was carried out for additional 4 h (procedure 2). This resulted in about a two-fold increase in cyclic carbonate yield (43%) (Table 1, entry 2).

The quaternary ammonium salt with a halogen anion could catalyze the decomposition reaction of *tert*-butyl hydroperoxide and MoO<sub>2</sub>(acac)<sub>2</sub>, resulting in the formation of oxygen, *tert*-butanol and MoO<sub>2</sub>Br<sub>2</sub> [15]. Thus, in a further experiment CO<sub>2</sub>, PS-TBMAC and an aqueous solution of ZnBr<sub>2</sub> were added to the reaction system after one hour (procedure 3). The yield of cyclic carbonate was 67% (Table 1, entry 3).

In order to compare, a course of reaction in the presence of tributylmethylammonium chloride (TBMAC), which is a soluble counterpart of PS-TBMAC, the process was carried out according to the procedure 3. As can be seen from Table 1 (entry 4), the PS-TBMAC showed higher catalytic activity than its homogeneous counterpart. On the one hand, this might be due to the increased lipophilicity of quaternary ammonium salt immobilized onto the polymer carrier and thus easier contact of the reactants with active sites of the catalyst. On the other hand, the immobilized catalyst could show higher stability under reaction conditions. Based on the GC-MS analysis, it was found that during the process, 20% of TBMAC underwent decomposition to tributylamine, which could have a significant impact on reducing its activity. Moreover, a large amount of unreacted styrene oxide (an intermediate product) in the post-reaction mixture also confirmed the lower tributylmethylammonium chloride activity in the second stage of the process. By contrast, in the case of using PS-TBMAC, tributylamine was observed in an amount less than 1%.

Under the same conditions (procedure 3) the reaction in presence of TBAB as a catalyst of the second stage of the

**Table 2** The influence of temperature and CO<sub>2</sub> pressure on the second stage of the direct synthesis of styrene carbonate from CO<sub>2</sub> and styrene

Entry	Temperature of the 2 stage (°C)	CO <sub>2</sub> pressure (MPa)	Amount of the PS-TBMAC (% mol)	Conversion of ST (%)	Yield <sup>a</sup> (%)		
					SO	BA	SC
1	90	0.9	1.0	96	32	6	31
2	100	0.9	1.0	96	8	11	67
3	110	0.9	1.0	97	5	7	45
4	120	0.9	1.0	96	9	5	30
5	130	0.9	1.0	98	2	8	19
6	100	0.5	1.0	96	21	6	29
7	100	1.5	1.0	97	4	4	51
8	100	2.0	1.0	97	4	4	34
9	100	0.9	1.5	97	8	10	68
10	100	0.9	3.0	97	13	8	70

Reaction conditions: styrene (58 mmol), 5.5 M solution of TBHP in decane (64 mmol), MoO<sub>2</sub>(acac)<sub>2</sub> (0.058 mmol), PS-TBMAC, aqueous solution of ZnBr<sub>2</sub> (0.80 mmol of H<sub>2</sub>O, 0.16 mmol of ZnBr<sub>2</sub>), 500 rpm. The first step of process was conducted in the presence of MoO<sub>2</sub>(acac)<sub>2</sub> at 100 °C, 1 h; after this time carbon dioxide (a CO<sub>2</sub> pressure of 0.9 MPa) and the catalyst system consisting of PS-TBMAC and aq. ZnBr<sub>2</sub> were added to the reactor and the second step was conducted for 4 h. <sup>a</sup>Determined by GC

process (Table 1, entry 5), and the reaction with the catalyst system consisting of TBAB and aq. ZnBr<sub>2</sub>, were carried out (Table 1, entry 6). In both cases, the yield of SC was lower than that obtained in the case of using PS-TBMAC and aq. ZnBr<sub>2</sub>.

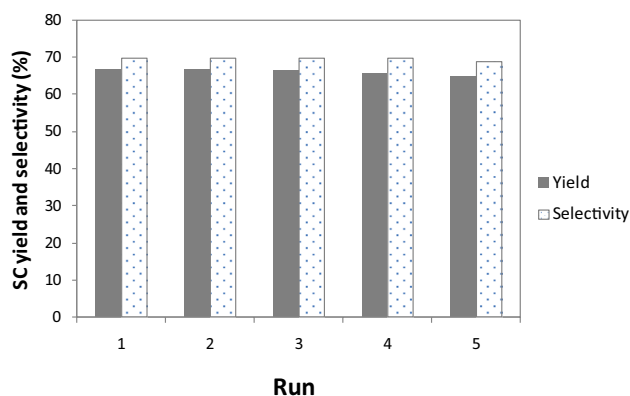
### 3.2 The Choice of Conditions of the Second Step of the Process

Conditions for carrying out the first reaction step using MoO<sub>2</sub>(acac)<sub>2</sub> as a catalyst, have been chosen on the basis of literature data (100 °C, 1 h) [15]. Whereas, the influence of temperature and CO<sub>2</sub> pressure on the course of the second stage of the reaction was examined. Optimal conditions for conducting the second stage of the direct synthesis of cyclic carbonates may be different from those we have specified for their synthesis from epoxides and CO<sub>2</sub> in the presence of PS-TBMAC [21], since in this case the reaction mixture is more complex. As shown in Table 2, the temperature increase from 90 to 100 °C in the second stage of the process caused more than two-fold increase in a yield of styrene carbonate. When the temperature raised, the rate of the reaction of carbon dioxide with in situ formed styrene oxide also increased. However, a further increase of temperature above 100 °C had an unfavorable effect on the reaction course.

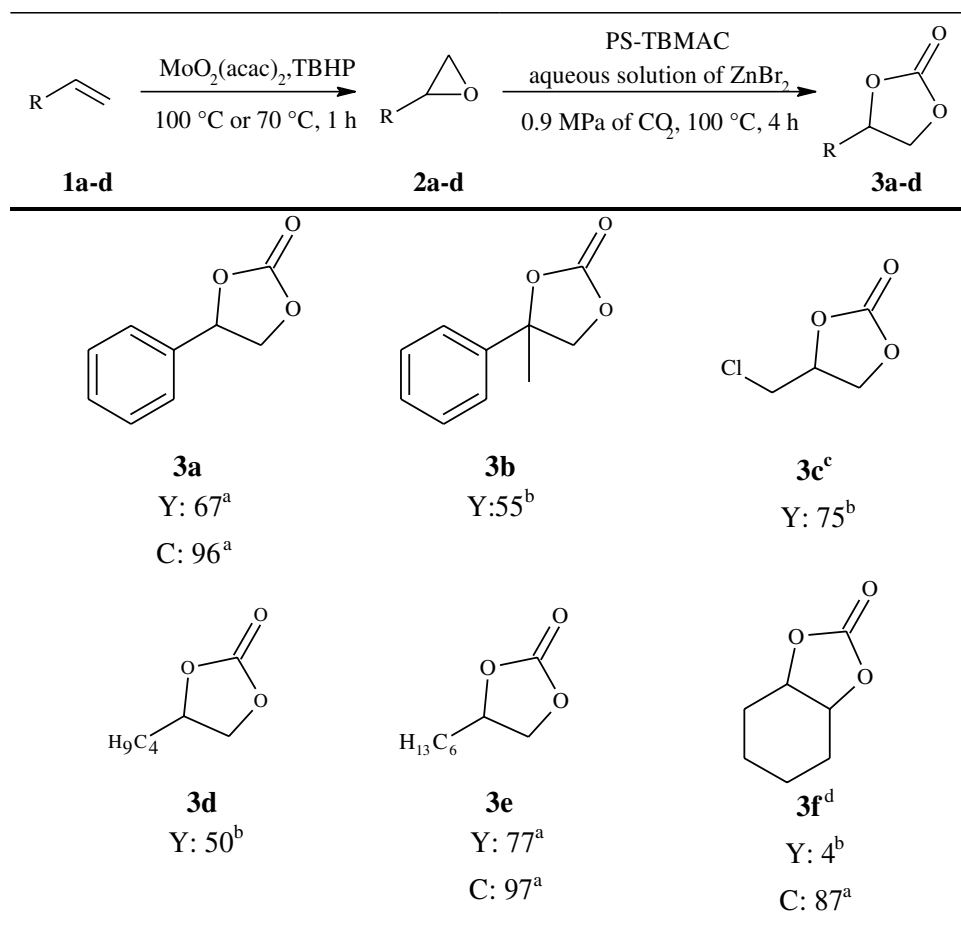
The styrene carbonate yield increased with pressure increasing from 0.5 to 0.9 MPa. However, a further increase in the CO<sub>2</sub> pressure resulting in lowered SC yield. This phenomenon has also been observed by other researchers. Some of them explain that too high concentration of carbon dioxide in the reaction mixture can hinder the interaction between styrene and catalyst [13].

Moreover, at high pressure of CO<sub>2</sub>, the formation of oligomers can be promoted [14].

The increase of the amount of immobilized catalyst in the studied range (1–3 mol% to styrene) has a negligible impact on the yield of styrene carbonate. It should also be emphasized that the excessive amount of the immobilized catalyst in the reaction system may impede mixing of the reaction mixture.



**Fig. 2** PC yield and selectivity in the reaction of CO<sub>2</sub> with styrene in the presence of recycled PS-TBMAC catalyst. Reaction conditions: styrene (58 mmol), 5.5 M solution of TBHP in decane (64 mmol), MoO<sub>2</sub>(acac)<sub>2</sub> (0.058 mmol), PS-TBMAC (0.58 mmol), aqueous solution of ZnBr<sub>2</sub> (0.80 mmol of H<sub>2</sub>O, 0.16 mmol of ZnBr<sub>2</sub>), 500 rpm. The first step of process was conducted in the presence of MoO<sub>2</sub>(acac)<sub>2</sub> at 100 °C, 1 h, after this time carbon dioxide (a CO<sub>2</sub> pressure of 0.9 MPa) and the catalyst system consisting of PS-TBMAC and aq. ZnBr<sub>2</sub> were added to the reactor and the second step was conducted for 4 h

**Table 3** Synthesis of various cyclic carbonates from olefins and CO<sub>2</sub>

Reaction conditions: olefin (58 mmol), 5.5 M solution of TBHP in decane (64 mmol), MoO<sub>2</sub>(acac)<sub>2</sub> (0.058 mmol), PS-TBMAC (0.58 mmol), aqueous solution of ZnBr<sub>2</sub> (0.80 mmol of H<sub>2</sub>O, 0.16 mmol of ZnBr<sub>2</sub>), 500 rpm. The first step of the process was conducted in the presence of MoO<sub>2</sub>(acac)<sub>2</sub> at 100 °C, 1 h; after this time carbon dioxide (CO<sub>2</sub> pressure of 0.9 MPa) and the catalyst system consisting of PS-TBMAC and aq. ZnBr<sub>2</sub> were added to the reactor and the second step was conducted for 4 h. Y—yield of cyclic carbonate (%), C—olefin conversion (%). <sup>a</sup>Determined by GC. <sup>b</sup>Determined by <sup>1</sup>H NMR. <sup>c</sup>Temperature of the first stage: 70 °C. <sup>d</sup>Cis-isomer, time of the second stage: 10 h

### 3.3 Studies on the Recycle of PS-TBMAC

Reusability of the catalyst is important from the economic point of view. Therefore, study on the recovery and reuse of the catalyst system was conducted. The process was performed under the optimized conditions described above (the first step at 100 °C for 1 h, the second step at 100 °C and under a pressure of 0.9 MPa CO<sub>2</sub> for 4 h).

The immobilized PS-TBMAC catalyst was separated from the reaction mixture by filtration, whereas molybdenyl acetylacetonate by extraction with ethanol and subsequent filtration of the precipitated catalyst. These catalysts with a fresh solution of zinc bromide were used for the next process for the preparation of styrene carbonate. However, the yield of styrene carbonate was lower than for the fresh catalyst system. This may be due to losses in the recovery of MoO<sub>2</sub>(acac)<sub>2</sub>, because it was used in very small amount

in the process. The recovery of MoO<sub>2</sub>(acac)<sub>2</sub> was only 48%. Therefore, in subsequent reactions, the addition of fresh MoO<sub>2</sub>(acac)<sub>2</sub> was used. It should be noted that if the reaction is conducted on a large scale, these losses may be negligible.

The results shown in Fig. 2, indicate that the PS-TBMAC catalyst exhibited high activity in five successive cycles of reaction. Cyclic carbonate yields in subsequent cycles ranged 65–67%.

### 3.4 Synthesis of Cyclic Carbonates from Selected Olefins and CO<sub>2</sub>

The cyclic carbonates from selected olefins and CO<sub>2</sub> in the presence of the developed catalytic system: MoO<sub>2</sub>(acac)<sub>2</sub>/PS-TBMAC/aqueous solution of ZnBr<sub>2</sub>, were synthesized. The first step of the process was carried out at 100 °C (or

at 70 °C for allyl chloride as a substrate) for 1 h, and the second stage at a temperature of 100 °C and a pressure of 0.9 MPa CO<sub>2</sub> for 4 h.

Cyclic carbonates were obtained in yields within a range of 50–77% (Table 3). Only in the case of cyclohexene as a substrate, despite the high conversion of CO<sub>2</sub>, carbonate yield was low (4%). It is most probably due to the fact that in situ generated 1,2-epoxy cyclohexane can undergo polymerization and copolymerization reaction with carbon dioxide [15]. It is necessary to emphasize that in many studies in the literature concerning the direct synthesis of cyclic carbonates from olefins and CO<sub>2</sub>, only the possibility of obtaining of styrene carbonate was examined.

#### 4 Conclusions

An effective one-pot method for the direct synthesis of cyclic carbonates from CO<sub>2</sub> and olefins in the presence of *tert*-butyl hydroperoxide as an oxidant using the system consisting of MoO<sub>2</sub>(acac)<sub>2</sub> and PS-TBMAC/aqueous solution of ZnBr<sub>2</sub>, was developed. Compared with the method described in the literature using MoO<sub>2</sub>(acac)<sub>2</sub>-TBAB as a catalytic system (the first step: 100 °C, 1 h, the second step: 140 °C, CO<sub>2</sub> pressure of 3 MPa, 1 h), our proposed method allows to achieve similar yields of cyclic carbonates under milder reaction conditions (100 °C, CO<sub>2</sub> pressure of 0.9 MPa) and enables easy separation of PS-TBMAC and its use several times without loss in its activity. The use of immobilized quaternary ammonium salt rather than its soluble counterpart, not only simplified the procedure for its removal from the reaction mixture, but also positively influenced the catalyst stability.

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