

Application of carbonate solvents in the telomerisation of butadiene with carbon dioxide

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Abstract

This contribution describes the synthesis of the δ -lactone 2-ethylidene-6-heptene-5-olide from the reactants 1,3-butadiene and carbon dioxide in carbonate solvents. Palladiumbis(acetylacetonate) in combination with the ligand triphenylphosphine is used as homogeneous catalyst. At a reaction temperature of 60–100 °C yields of the δ -lactone up to 50% can be achieved in a reaction time of 4 h. The use of green solvents like carbonates in this reaction is new, as mainly toxic nitrile solvents such as acetonitrile are known from literature till now.

In this work we examined in detail the application and the influence on the selectivity of linear carbonates (dimethyl and diethyl carbonate), cyclic carbonates (ethylene carbonate, propylene carbonate and butylene carbonate) and glycerol carbonate esters in the telomerisation of butadiene with carbon dioxide.

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1. Introduction

The first studies of the catalyzed reactions of 1,3-butadiene with carbon dioxide were carried out by the research groups of Inoue [1] and Musco [2] at the end of the 1970s and they succeeded in synthesizing lactones (1–3), 1,3,7-octatriene (4), acids (5 and 6) and esters (7 and 8) in small quantities. In the following years Braunstein et al. [3] and Behr et al. [4,5] examined the telomerisation of the δ -lactone 2-ethylidene-6-heptene-5-olide (1) in detail (Fig. 1).

The active catalyst was formed in situ from the catalyst precursor Pd(acac)₂ and the ligands tricyclohexylphosphine or triphenylphosphine. Behr et al. [4] showed in the eighties that the presence of nitrile groups may be crucial for higher yields of δ -lactone, which may be due to the formation of the unstable, but catalytic active catalyst intermediates Pd(NCR)_x(PR₃)_y.

Due to this so-called “nitrile effect” the nitrile groups can easily be displaced, which makes the required free coordination sites available for the first step of the catalyst cycle after their

secession. In the work of Behr et al. [6,7] acetonitrile proved to be the best solvent regarding yield and selectivity.

In further studies by Brehme [9,10] synthetic applications of δ -lactone were examined (Fig. 2). A broad variety of reactions like hydroformylation, hydroamination, hydroaminomethylation and hydrogenation leads to many different products like e.g. diols with possible use as cross-linkers in polymer industry.

In this work it is shown for the first time that also carbonate solvents provide high yields of δ -lactone (1) and that the use of different solvents gives the opportunity to distinctly influence the selectivity of the reaction.

2. Results

2.1. Comparison between acetonitrile and carbonate solvents

With standard test conditions using Pd(acac)₂, PPh₃ and different solvents at a reaction temperature of 80 °C and a reaction time of 4 h (Table 3 in Section 4) it is shown for the first time that the use of carbonate solvents results in higher yields of δ -lactone than reactions in acetonitrile. The following illustration (Fig. 3) shows the comparison between acetonitrile and different carbonate solvents.

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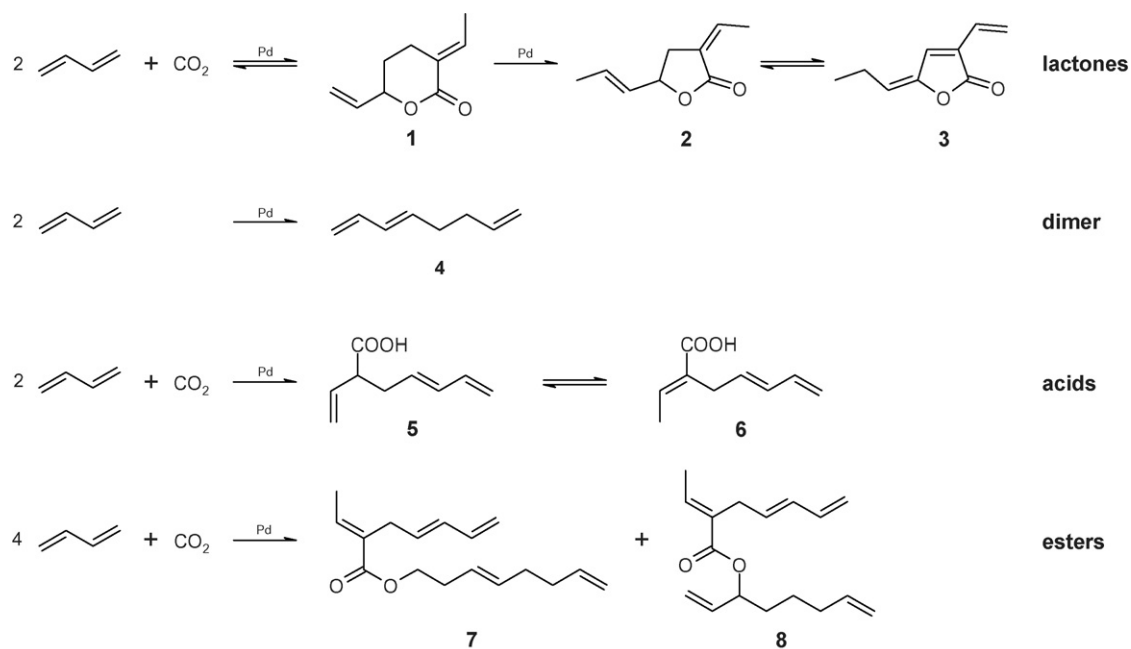


Fig. 1. Lactone (1) and side-products (2–8) in the telomerisation of butadiene with carbon dioxide.

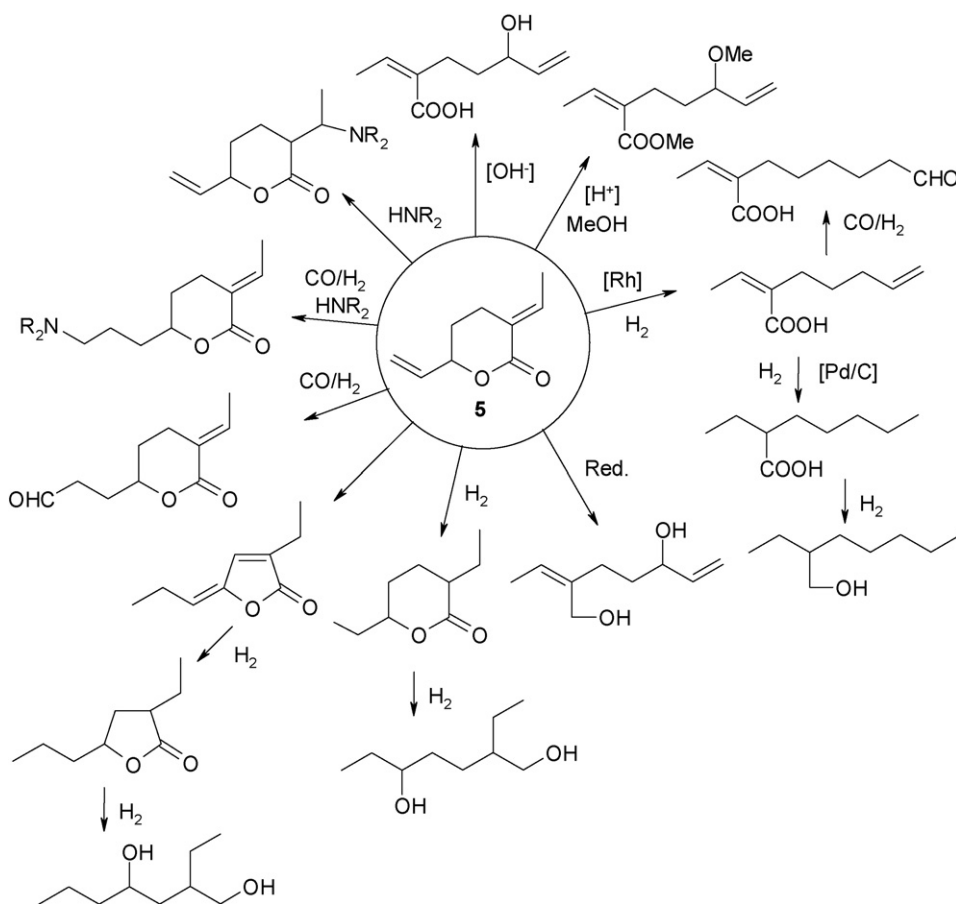


Fig. 2. Synthetic applications of δ -lactone (1) [8].

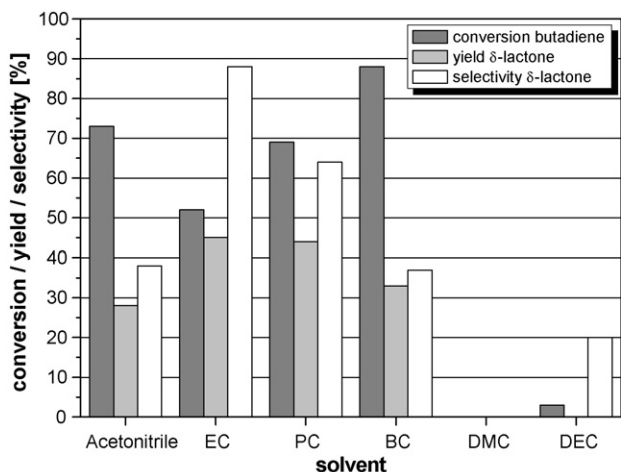


Fig. 3. Comparison between acetonitrile and carbonate solvents, EC: ethylene carbonate; PC: propylene carbonate; BC: butylene carbonate; DMC: dimethyl carbonate; DEC: diethyl carbonate ($\text{Pd}(\text{acac})_2$, PPh_3 , 4 h, 80°C).

Fig. 3 demonstrates that higher yields and selectivities can be obtained by using cyclic carbonates instead of acetonitrile. Here particularly ethylene carbonate (EC) is characterized by a high selectivity ($\sim 90\%$), which could be observed for the first time using PPh_3 in batch experiments in the telomerisation of butadiene and carbon dioxide [11].

When using linear carbonates such as dimethyl carbonate DMC and diethyl carbonate DEC only small conversions of butadiene are observed. All further investigations in the telomerisation therefore concentrated on the use and application of cyclic carbonates.

2.2. Variation of temperature

Since the reaction is partly limited by the amount of gaseous reactants in the solution, the temperature plays an important role for the performance of the telomerisation and was therefore investigated in more detail.

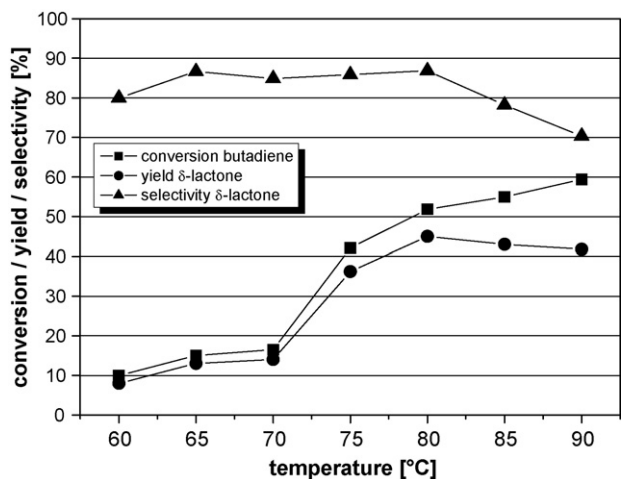


Fig. 4. Conversion of butadiene, yield and selectivity of δ -lactone 1 using the solvent ethylene carbonate EC ($\text{Pd}(\text{acac})_2$, PPh_3 , 4 h).

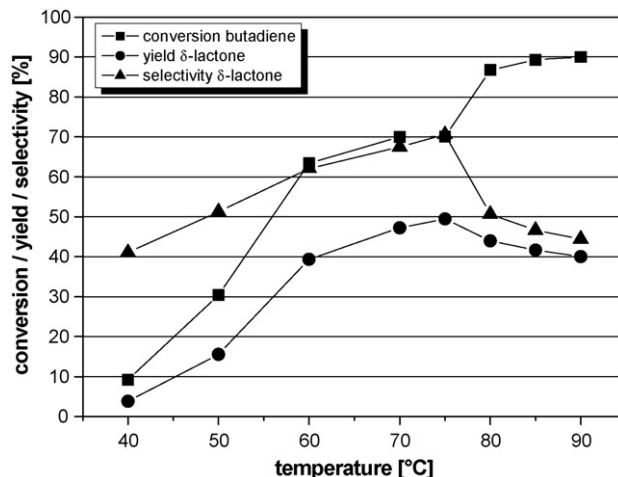


Fig. 5. Conversion of butadiene, yield and selectivity of δ -lactone 1 using the solvent propylene carbonate PC ($\text{Pd}(\text{acac})_2$, PPh_3 , 4 h).

2.2.1. Temperature variation in ethylene carbonate (EC)

As expected the conversion of butadiene increases with rising temperature (Fig. 4). The selectivity is almost constant within the range of 60 – 80°C , but decreases at higher temperatures. The highest yields of δ -lactone are likewise obtained at 80°C .

2.2.2. Temperature variation in propylene carbonate (PC)

Temperature variation in PC shows an optimum yield at 75°C , which is also the point of best selectivity. The conversion of butadiene generally rises with temperature. Fig. 5 shows that the selectivity for the δ -lactone is on the one hand controlled by kinetics of lactone-formation at temperatures lower than 60°C and on the other hand by kinetics of side-reactions of butadiene at temperatures above 80°C . The formation of δ -lactone reaches its maximum at temperatures around 80°C and decreases with rising temperature as it becomes thermodynamically more and more unfavorable [12]. Due to this decreasing lactone-formation a higher amount of butadiene is available in the liquid phase. This fact and the rising temperatures lead to

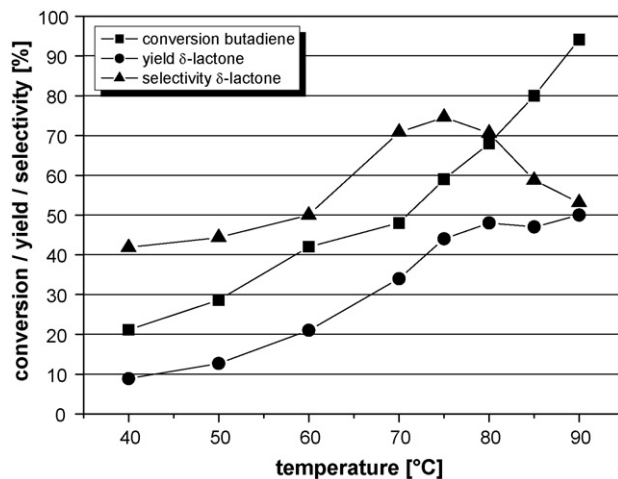


Fig. 6. Conversion of butadiene, yield and selectivity of δ -lactone 1 using the solvent butylene carbonate BC ($\text{Pd}(\text{acac})_2$, PPh_3 , 4 h).

an enhanced formation of diels–alder-products and butadiene dimers thus increasing the conversion significantly.

It is of particular importance that the thermodynamically stable starting compound carbon dioxide can be activated at such low temperatures by homogeneous catalysis. Already at 60 °C yields of the δ -lactone of 40% can be reached within 4 h.

2.2.3. Temperature variation in butylene carbonate (BC)

Fig. 6 shows the conversion of butadiene and the yield and selectivity of the δ -lactone as a function of temperature using the solvent butylene carbonate. The conversion is rising with temperature as noticed before and the yield of δ -lactone increases up to 50% at 80 °C. The highest selectivity of nearly 80% can be achieved at temperatures of 75–80 °C, similar to the use of PC. As in the case of PC conversion of butadiene is rising at higher temperatures because of the increasing formation of dimers.

Studies of the solubility of carbon dioxide and butadiene in various solvents showed similar solubility of these gases in EC as in PC and BC [12,13]. Therefore, we conclude that the amount of reactants dissolved in the solvent cannot be the only reason for the significant higher selectivities using EC.

2.3. Combination of solvents

As shown above the application of EC allows reaching higher selectivities than obtained so far with the examined catalyst system. By combination of EC with PC and combination of EC with BC the influence of EC on the selectivity was investigated in more detail. The main objective was to combine the high selectivities, which are attainable with EC, with the high conversions, which can be obtained with PC or BC.

2.3.1. Combination of ethylene carbonate and propylene carbonate

Fig. 7 shows the influence of the EC mass-fraction on the reaction. The additional use of EC in combination with PC seems to have no influence on selectivity, only pure EC gives higher selectivities compared to pure PC. The yield of the δ -lactone

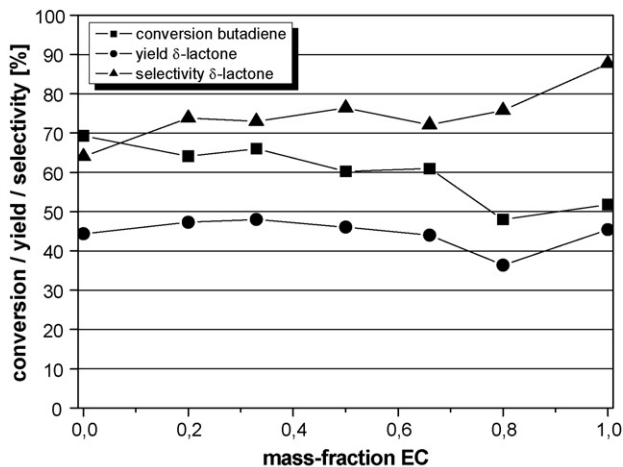


Fig. 7. Combination of the solvents ethylene carbonate and propylene carbonate (Pd(acac)₂, PPh₃, 4 h, 80 °C).

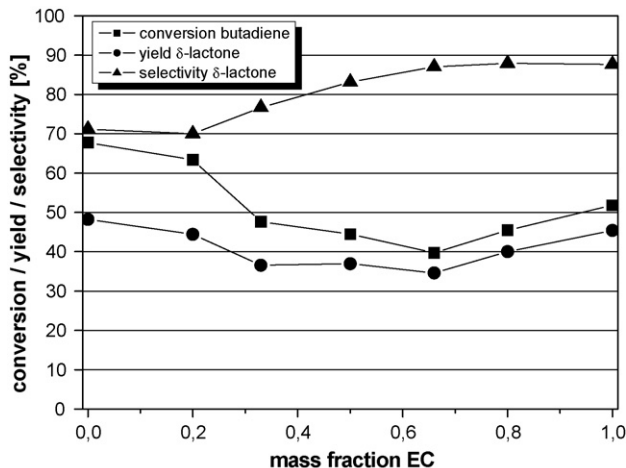


Fig. 8. Combination of the solvents ethylene carbonate and butylene carbonate (Pd(acac)₂, PPh₃, 4 h, 80 °C).

is nearly constant (40–50%), while the conversion of butadiene falls from 70% to 50% using pure EC.

2.3.2. Combination of ethylene carbonate and butylene carbonate

Fig. 8 shows the influence of EC/BC-mixtures on the telomerisation of butadiene with carbon dioxide. Selectivity is continually rising from 70% up to 90%. Conversion and yield are decreasing first and reach a minimum at a mass fraction of about 66% EC. Afterwards conversion and yield rise again to the value of pure EC.

Thus it can be concluded, that a combination of the solvents does not result in significant improvements of the reaction. However, once again the strong influence of EC on the selectivity could be confirmed by these experiments.

2.4. Continuous telomerisation in a miniplant

The miniplant in Fig. 9 contains all process-relevant steps of the technical continuously conversion of 1,3-butadiene with carbon dioxide including the recycle of the catalyst and the solvent acetonitrile [13,14].

The process can be described as follows: the gaseous butadiene is condensed at –20 °C and mixed with the catalyst phase in the vessel B1. The solution is then pumped into the reactor B2, which has a nominal value of 11 and is heated by an electrical steam jacket. Separately carbon dioxide is fed in by pressure control. After the reaction the unconverted gaseous reactants butadiene and carbon dioxide are separated from the liquid phase in the flash D1. Reaching the evaporator D2, the solvent acetonitrile is separated from the product solution and recycled into B1. The heavy-ends of the column, consisting of the product, side-products and the catalyst-phase are transferred into the evaporator D3, where the δ -lactone is separated.

The solvent acetonitrile has a much lower boiling point (82 °C at 1013 mbar) than the δ -lactone (76 °C at 0.13 mbar). As a consequence the acetonitrile has to be separated in an upstream distillation stage first before isolating the product.

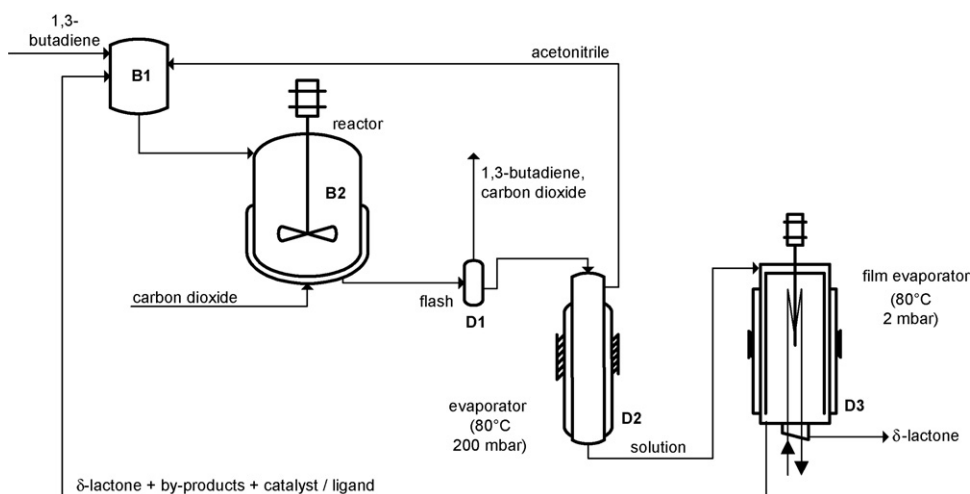


Fig. 9. Flow scheme of the telomerisation miniplant.

So the solvent is no more available after the product separation. To recycle the palladium catalyst in a continuously driven plant it has to be recycled with a part of the liquid product and the high-boiling side-products, which has a negative effect on the space–time–yield of the plant. Feeding the product back into the reactor might also lead to limitations in product yield because of a negative influence on the chemical equilibrium.

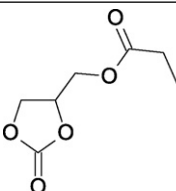
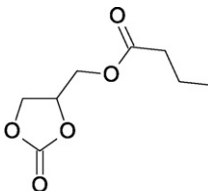
Due to the fact that the cyclic carbonates EC (238 °C at 1013 mbar), PC (242 °C at 1013 mbar) and BC (251 °C at 1013 mbar) have also lower boiling points than the δ -lactone their potential use in the miniplant was limited, as only higher-boiling solvents would allow an easier product separation and a better recycle of the catalyst phase. Hence, our further objective was to find solvents combining the positive benefits of the cyclic carbonates on catalysis with a higher boiling point allowing an easier separation of the δ -lactone and the catalytic solution.

2.5. Application of higher-boiling carbonate solvents

Considering these objectives we synthesized the asymmetric cyclic carbonate solvents glycerol carbonate propionate GCP (**9**) and glycerol carbonate butyrate GCB (**10**) (Table 1) and tested their activity in the telomerisation. Both esters **9** and **10** were synthesized by esterification of glycerol carbonate with the corresponding acid chlorides (see Section 4.3). Both solvents

Table 1

Chemical structures and boiling points (bp) of GCP and GCB

	bp (0.01 mbar) (°C)
 Glycerol carbonate propionate 9 (GCP)	126–128
 Glycerol carbonate butyrate 10 (GCB)	133–135

were liquids even below -20 °C and proved to be stable during the experiments.

First investigations in glycerol carbonate esters showed, that the telomerisation of butadiene with carbon dioxide can be carried out in these higher-boiling-solvents, but with lower yields of δ -lactone compared to EC, PC and BC (Table 2).

Table 2

Telomerisation in glycerol carbonate esters compared to other solvents (X = conversion of butadiene, Y = yield of δ -lactone **1**, S = selectivity of δ -lactone **1**) 4 h, 80 °C

Solvent	X (%)	Y (%)	S (%)	Dimer 4 (%)	Acids 5 and 6 (%)	Esters 7 and 8 (%)
CH ₃ CN	73	28	38	10	8	27
EC	52	45	88	2	1	3
PC	69	44	64	6	4	13
BC	88	33	37	8	4	42
GCP	34	22	65	5	2	3
GCB	46	23	49	3	7	12

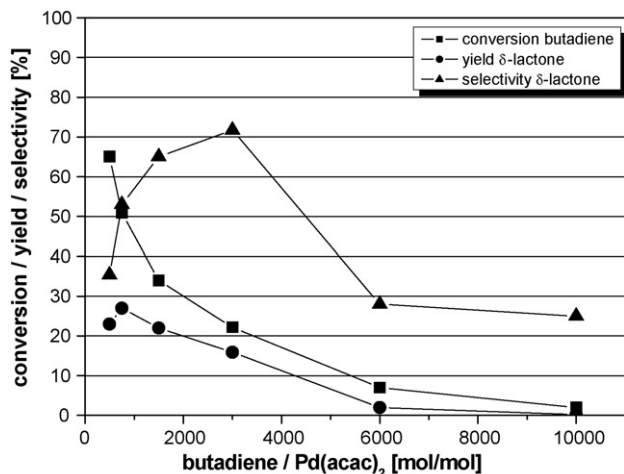


Fig. 10. Influence of catalyst concentration on the reaction in glycerol carbonate propionate (4 h/80 °C).

Using GCP conversions of 34% were achieved with yields of lactone up to 22%. The selectivities are as high as in PC. Using GCB the conversion of butadiene is higher (46%) while the yield is equal to GCP. This leads to worse selectivities using GCB.

However, the overall lower yields in GCP and GCB are negligible in the semi-technical miniplant due to the fact, that the essential recirculation of the δ-lactone using a low boiling solvent like PC or BC is no longer necessary.

Table 2 also shows the side-products formed and compares the selectivities achieved using GCP and GCB. Obviously the formation of acids and esters is preferred in GCB compared to GCP while the formation of dimers is lower using GCB.

In further investigations we studied the influence of the catalyst concentration on the selectivity of the reaction. It was known from preliminary investigations that the yield and selectivity of the lactone are highly dependent on the amount of catalyst but less dependent on the reaction temperature, ratio of catalyst to ligand and amounts and ratio of the starting compounds [12].

When GCP was used as solvent, with decreasing catalyst concentration the conversion of butadiene is decreasing, too (Fig. 10).

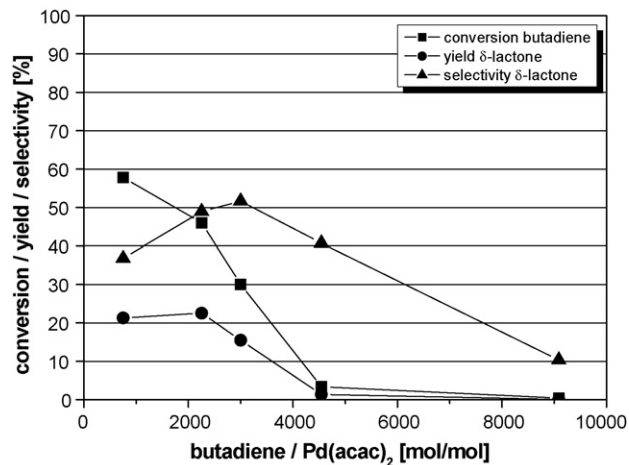


Fig. 11. Influence of catalyst concentration on the reaction in glycerol carbonate butyrate (4 h/80 °C).

There is an optimum in selectivity of the lactone between a butadiene/lactone ratio of 1500–3000. This corresponds to other examinations in the solvents CH₃CN, EC, PC and BC [12].

Similar results are observed in GCB, where an optimum selectivity of the δ-lactone is observed between a butadiene/catalyst ratio of about 3000 (Fig. 11). While the yield of the lactone is similar to the use of GCP, the selectivity of the lactone is lower using GCB.

Compared to the results in EC, PC and BC it can be concluded, that ester substituents on the cyclic carbonate solvent result in lower selectivities to the lactone.

3. Conclusions

For the first time it could be demonstrated that the telomerisation of butadiene with carbon dioxide can be accomplished in satisfying yields and reaction times using carbonate solvents. Contrary to the cyclic carbonates, the linear carbonates dimethyl carbonate and diethyl carbonate showed less activity in the telomerisation. Compared to the well-known results from literature with nitrile solvents, the results with the carbonate solvents proved to be much better. The selectivity of the lactone is highly dependent on the size of the additional substituent in the carbonate solvent. This fact was on the one hand observed in the cyclic carbonates containing additional alkyl groups like EC, PC and BC and on the other hand in the cyclic carbonates with different ester groups (GCP and GCB).

The screening tests with the higher-boiling carbonates make them attractive for further investigations. Although yields and selectivities are somewhat worse compared with ethylene carbonate, propylene carbonate and butylene carbonate, a nearly total removal of the δ-lactone should be realized by the use of the higher-boiling carbonates in a semi-technical scale. After optimization in the lab-scale the high-boiling carbonates will be further investigated in the miniplant-scale in continuous runs, especially the thermal separation of the δ-lactone as low boiling compound from the higher boiling solvent.

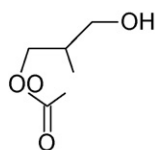
4. Experimental

4.1. Chemicals

The precatalyst Pd(acac)₂ was synthesized according to [5]. Triphenylphosphine was acquired from Acros (purity 99%) and used without further purification. Acetonitrile (purity 99%) was purchased from Riedel de Haen. Glycerol carbonate (purity 93.5%) as starting compound for glycerol carbonate propionate and glycerol carbonate butyrate was purchased from Huntsman GmbH. Pyridine (purity 99+%), propionyl chloride (purity 98%) and butyryl chloride (purity 98%) were acquired from Acros. Ethylene carbonate (EC purity 99+%), propylene carbonate (PC purity 99.5%) and butylene carbonate (BC purity 99%) were also purchased from Acros, dimethyl carbonate (DMC purity 99%) and diethyl carbonate (DEC purity 99%) were bought from Aldrich. Butadiene (purity 99.5%) and CO₂ (purity 3.5%) were acquired from Messer-Griesheim.

4.2. Instrumental

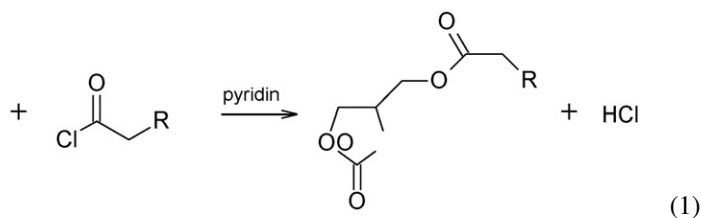
All batch reactions were carried out in 300 ml pressure vessels, model 4561 (Parr Instruments). The reactor consists of a steel bomb and a steel cover, which includes the armatures for filling and regulation. The reactor is certified for temperatures up to a maximum of 350 °C and pressures up to 207 bar,



4.4. Synthesis of higher-boiling glycerol carbonate ester

4.4.1. Synthesis of GCP

The synthesis of GCP (Eq. (1) with R = CH₃) was carried out according to Grahe [15] with 1.25 mol (=116 g) propionyl chloride, 1.3 mol (=154 g) glycerol carbonate and 0.13 mol (=10 g) pyridine:



whereby exceeding of the maximum pressure is prevented by a breaker plate. The system pressure can be read off a manometer attached at the reactor cover. The heating of the reactor up to the desired reaction temperature takes place using an electrical steam jacket. The temperature is measured by a thermocouple, which is attached to a PID automatic controller (Parr type 4842). Stirring was performed using a standard turbine type impeller.

The product sample was analyzed by GC (HP 6890) on a HP-5 phenylmethylpolysiloxan column (length 30 m, diameter 250 μm, layer thickness 0.25 μm) with undecylacetate as internal standard for the δ-lactone.

Spectroscopic data for the solvents was obtained by using coupled GC/MS analytics on the above mentioned instrument and column.

4.3. Experimental procedure

In a typical experiment amounts of catalyst and solvent as shown in Table 3 were weighed in a Schlenk tube. A 300 ml stainless steel autoclave was evacuated, purged with argon three times and left under vacuum. After that the homogeneous catalyst solution was transferred to the autoclave. To add the butadiene the vessel was cooled to -20 °C using an acetone bath and liquid nitrogen. In the last step the desired amount of carbon dioxide was added. Finally the autoclave was heated up to reaction temperature at a stirrer speed of 700 rpm.

After the desired reaction time the vessel was cooled down, unconverted gas was released to a flare and a sample was taken from the liquid phase.

All results obtained were reproduced for several times.

Glycerol carbonate and pyridine were filled into a 500 ml two-necked flask. The flask was connected to a reflux condenser which was linked to a washing bottle filled with 4N NaOH.

The second neck of the flask was connected to a drip funnel filled with propionyl chloride. In an ice bath and under constant stirring the propionyl chloride was dropped into the solution. After entire addition it was stirred until no more bubbles of produced HCl were observed in the washing bottle. Afterwards the ice bath was removed and the solution was stirred at 40 °C overnight. The product solution was washed in a separating funnel with 250 ml of 1N HCl solution to precipitate the pyridine as a salt. The solution was washed twice with distilled water to extract the pyridine salt from the product. After removing components like pyridine, propionyl chloride and residuals of glycerol carbonate in a fractional distillation the product GCP was obtained with a purity of 99.7+% (GC) (126 °C at 0.01 mbar) and an overall yield of 90%.

MS. (*m/e*): [M⁺] 144 (9) (-CH₂CH₃), 117 (0.5) (-C(O)CH₂CH₃), 100 (6) (-OC(O)CH₂CH₃), 87 (5) (-CH₂OC(O)CH₂CH₃), 75 (8), 57 (100).

4.4.2. Synthesis of GCB

The synthesis of GCB (Eq. (1) with R = CH₂CH₃) was carried out with 1.25 mol (=133 g) butyryl chloride, 1.30 mol (=154 g) glycerol carbonate and 0.13 mol (=10 g) pyridine.

The synthesis of GCB was performed identical to the synthesis of GCP. GCB was obtained with a purity of 99.5+% (GC) (135 °C at 0.01 mbar) and an overall yield of 90%.

MS. (*m/e*): [M⁺] 173 (2) (-CH₃), 160 (12) (-CH₂CH₃), 100 (5) (-OC(O)CH₂CH₂CH₃), 89 (5) (-CH₂OC(O)CH₂CH₂CH₃), 71 (100), 55 (11).

Table 3
Standard test conditions

Starting compounds	g	mol	Reaction conditions
Pd(acac) ₂	0.122	0.0004	<i>T</i> : 60–100 °C
PPh ₃	0.316	0.0012	<i>t</i> : 4 h
1,3-Butadiene	32.4	0.6	rpm: 700
Carbon dioxide	29.5	0.67	<i>p</i> : 30–40 bar
Solvent	60	–	

Acknowledgements

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