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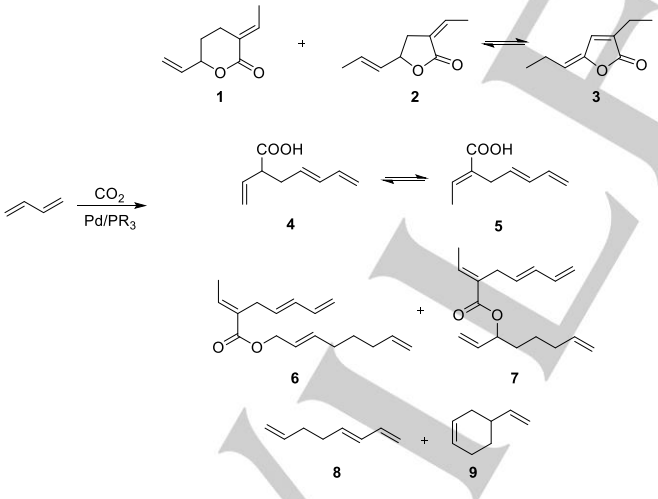
Telomerization of 1,3-Butadiene with Carbon Dioxide: a highly efficient process for δ-lactone generation

João M. Balbino,[a,b] Jairton Dupont*[a,c] and J. Carles Bayón*[b]

Abstract: A very efficient and selective telomerization of 1,3-butadiene with carbon dioxide leading to the δ-lactone (3-ethylidene-6-vinyltetrahydro-2*H*-pyran-2-one) was obtained using palladium acetate and *tris*(*p*-methoxyphenyl)phosphine as catalyst, in the presence of *p*-hydroquinone, *N,N*-diisopropylethylamine and acetonitrile. A high TON of 4500 with 96% selectivity to the δ-lactone was acquired after 5 h reaction at 70°C. The reaction was deactivated by the presence of different 1,3-dialkylimidazolium ionic liquids, possibly by the formation of stable and inactive Pd-imidazole-2-ylidene carbenes.

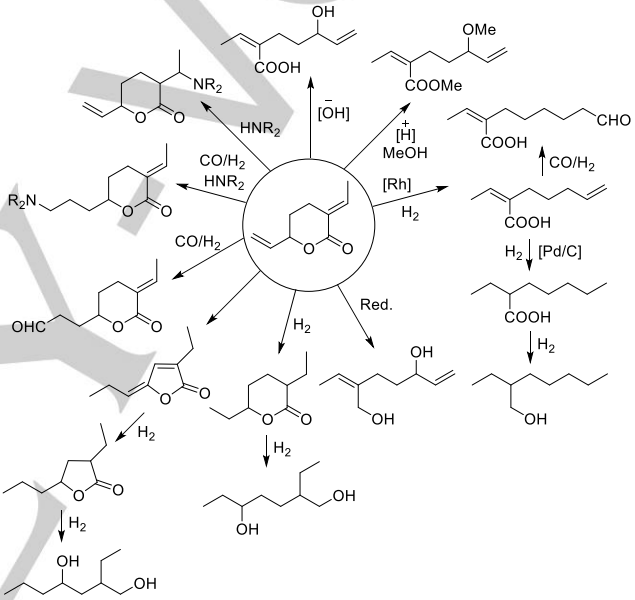
Introduction

The telomerization reaction of 1,3-dienes is a very important catalytic process due to its versatility and 100% atomic efficiency, which provides economic and ecological benefits.[1] The added value of the reaction is increased by using cheap and easily available feedstocks, as 1,3-butadiene and carbon dioxide.[2,3]
The catalytic reaction of 1,3-butadiene with CO_2 was first investigated by Inoue *et al.*[4,5] and Musco *et al.*[6,7] in the 1970s. They succeed in synthesize the lactones **1-3**, carboxylic acids **4** and **5**, esters **6** and **7**, and the usual butadiene dimers **8** and **9** in small quantities, as illustrated on Scheme 1.



Scheme 1. Telomerization of 1,3-butadiene with CO_2.

In subsequent years,[8-10] an intensive investigation of catalysts for this reaction demonstrated that systems constituted by palladium associated to phosphines as ligands lead to the best selectivities to the valuable δ-lactone 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one (**1**). This lactone presents a number of synthetic applications in reactions as hydroformylation, hydroamination, hydroaminomethylation and hydrogenation (Scheme 2), leading to many different products like saturated and unsaturated diols, as well as unsaturated hydroxyacids, with possible use as monomers for the polymer industry.[11,12]



Scheme 2. Synthetic applications of δ-lactone.[13]

A very selective scheme for the telomerization of 1,3-butadiene with carbon dioxide also includes, besides the Pd/phosphine catalyst, a tertiary amine with pK_b from 0 to 4 that boosts the δ-lactone selectivity, hydroquinone, which raises up reaction rate and allows to work with shorter time reaction, and a solvent containing nitrile groups, usually acetonitrile.[14]
The usually accepted mechanism for this reaction is illustrated on Scheme 3, based on detailed investigations by Behr *et al.*.[15,16] Oxidative coupling of two butadienes coordinated to the Pd(0) species **(A)** leads to the intermediate (1,8-η^1,η^1-2,7-octadiene)Pd(PR_3)$_2$ **(B)**. The double bonds of this complex are

[a] Institute of Chemistry, Federal University of Rio Grande do Sul, Avenida Bento Gonçalves, 9500, CEP-91501-970 Porto Alegre, RS, Brazil.
E-mail: jairton.dupont@ufrgs.br
[b] Department de Química, Universitat Autònoma de Barcelona, Bellaterra, 08193 Barcelona, Spain.
E-mail: joancarles.bayon@uab.cat
[c] School of Chemistry, University of Nottingham, University Park, Nottingham, UK, NG7 2RD
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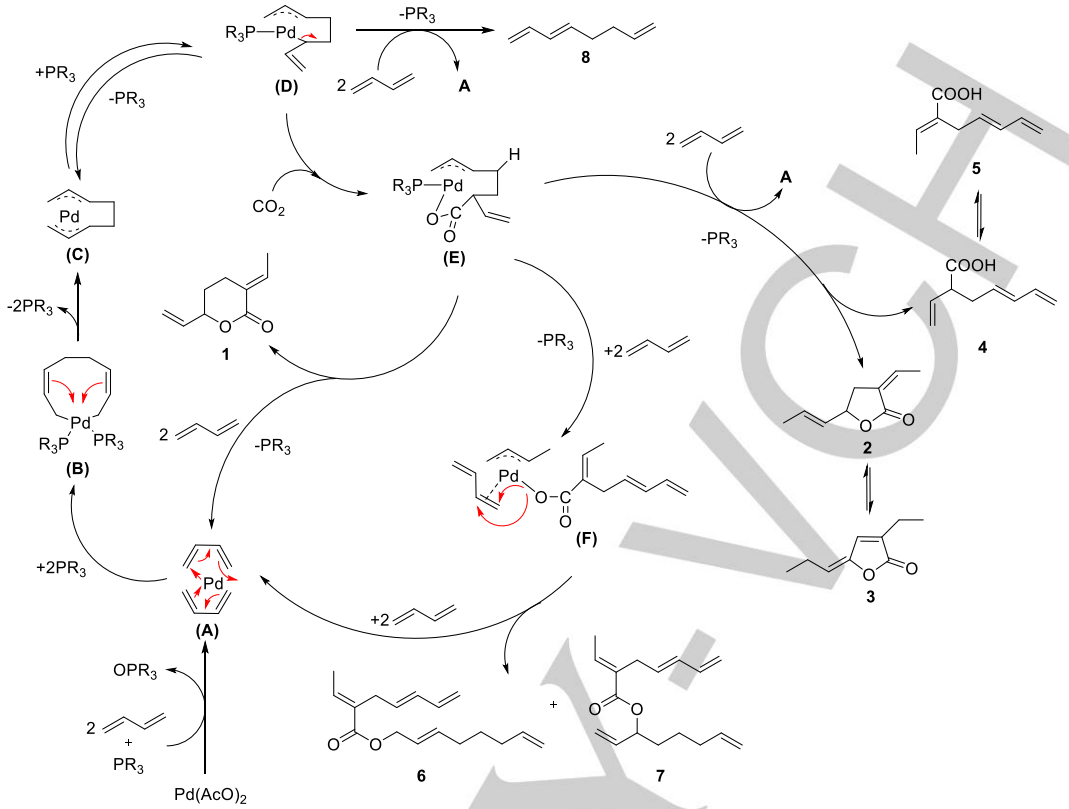


Scheme 3. Mechanism for the telomerization of 1,3-butadiene with CO_2.

rearranged, forming the *bis*-allyl complex (1,2,3,6,7,8-η^3,η^3-2,7-octadienyl)Pd **(C)**. This complex is then displaced by a phosphine to form the **D** intermediate (1,2,3,6-η^3,η^1-2,7-octadienyl)Pd(PR_3), which can follow two different paths. First and less important, allyl de-chelation can occur, leading to the formation of dimer **8**. Second, CO_2 can be inserted into the η^3,η^1-octadienyl chain, producing the key intermediate (1,2,3-η^3-6-CO_2-2,7-octadienyl)Pd(PR_3) **(E)**. The η^3-6-CO_2-octadienyl chain can then undergo an internal cyclization, which involves a Pd-O bond breaking followed by a new C-O bond formation, from the nucleophilic attack at 3- or 4- positions of the carbon chain, producing the lactones **1** or **2-3**, respectively. On the other hand, the carboxylate can abstract a proton at 4- position, leading to the formation of acids **4-5**. Alternatively, the allyl and phosphine ligands from species **E** can be displaced by two new butadiene molecules (one of them *via* transallylation), giving the intermediate (1,2,3-η^3-2-butenyl)(1,2-η^2-1,3-butadiene)Pd(6-CO_2-1,3,6-octratriene) **(F)**. Pd-O bond can then breaks up, allowing the nucleophilic attack at 1- or 2- positions of the η^2-butadiene chain, followed by its dimerization with the η^3-butenyl chain, leading to the formation of esters **6-7**.

For this catalytic cycle, the more basic is the phosphine, the easiest will be the displacement of η^3,η^3 intermediates **C** to η^3,η^1 **D**, thus facilitating the insertion of CO_2 and the consequent production of lactones.[17-19]

We report here the telomerization of 1,3-butadiene with CO_2 catalyzed by Pd/phosphine in the presence of *p*-hydroquinone, N,N-diisopropylethylamine (DIPEA) and acetonitrile as solvent. We also have investigated the effect of imidazolium ionic liquids in this reaction.

Results and Discussion

First, a series of triarylphosphines with different basicities (see Figure 1) were essayed as ligands for the Pd catalyst. All the reactions were pressurized with 30 bar of CO_2 and kept at 70°C for 5 h. In all of them, the major products obtained were lactones **1**-**3** and dimers **8**-**9**. Other minor products that added represented less than 1%. Vinylcyclohexene **9** was despised on TON and a selectivities calculation, since this is a thermal product of the reaction and it consumes approximately 0.1% of the total amount of butadiene.

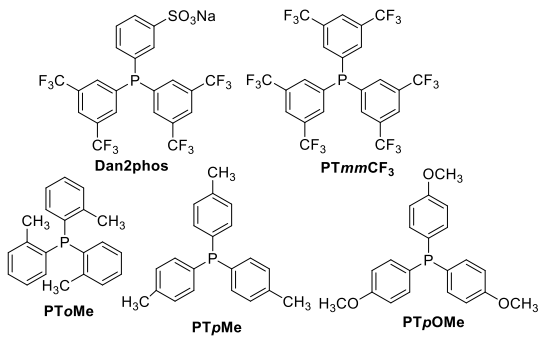


Figure 1. Structure of ligands used in the reactions reported in Table 1.

Table 1. Telomerization of butadiene with carbon dioxide using different phosphines.[a]

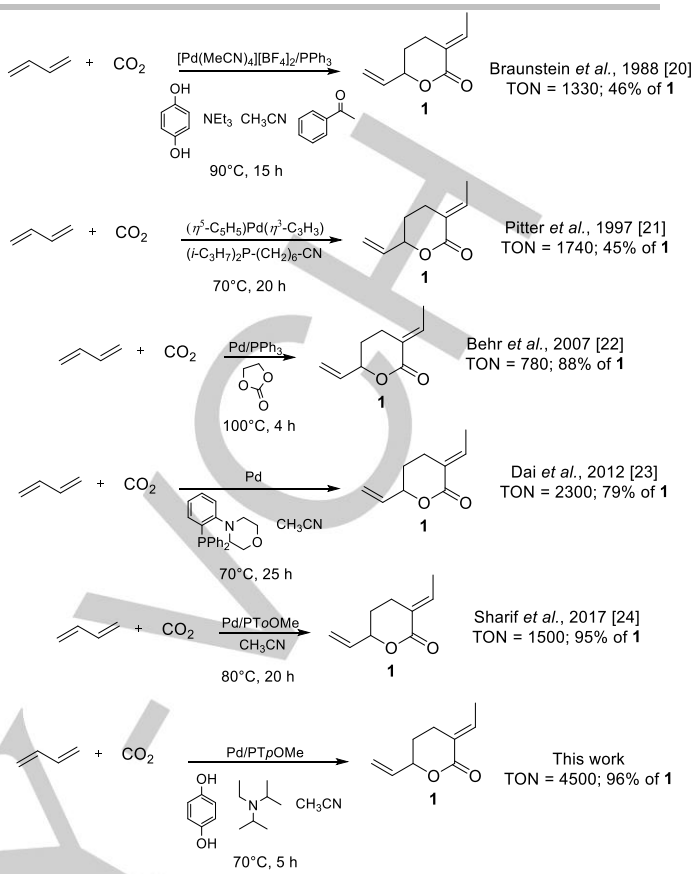
Entry	Phosphine	Selectivity (%)		TON
		8	1+2+3 (1/2+3)	
1	-	0.0	0.0	-
2	PPh_3	17.2	82.8 (93/7)	2200
3	NaTPPMS	67.4	32.6 (100/0)	60
4	Na_2TPPDS	37.4	62.6 (100/0)	90
5	Dan2phos	63.3	36.7 (100/0)	25
6	PT*mm*CF_3	35.5	64.5 (100/0)	360
7	PT*o*Me	51.6	48.4 (97/3)	930
8	PT*p*Me	15.9	84.1 (94/6)	2850
9[b]	PT*p*Me	53.3	46.7 (91/9)	930
10[c]	PT*p*Me	56.0	44.0 (79/21)	820
11[b],[c]	PT*p*Me	55.0	45.0 (91/9)	700
12[d]	PT*p*Me	60.2	39.8 (79/21)	220
13	PT*p*OMe	3.3	96.7 (99/1)	4500

[a]Reaction Conditions: $Pd(OAc)_2$ = 2.7 mg (1.2 10^{-2} mmol); phosphine/Pd = 3; *p*-hydroquinone = 33 mg (0.30 mmol); DIPEA = 77.4 mg (0.60 mmol); 4 mL of acetonitrile; C_4H_6 = 10.0 mL (120 mmol); 30 bar of CO_2; 70 °C; 5 h; 700 rpm. *n*-dodecane was added as an internal standard; 8 = octatriene; 1+2+3 = lactones; 1/2+3 is the ratio between δ-lactone and γ-lactone; TON = turnover number (mol of butadiene converted/mol of Pd after 5 h reaction); [b]reaction without hydroquinone; [c]reaction without DIPEA; [d]reaction without acetonitrile.

The reaction of 1,3-butadiene with CO_2 does not occur in the absence of a phosphine ligand (entry 1, Table 1). It shows very low activity in the presence of ionic phosphines such as NaTPPMS, Na_2TPPDS or Dan2phos (entries 3-5, Table 1). In the presence of the neutral triarylphosphines, catalytic activity and selectivity to δ-lactone increase with increasing ligand basicity (compare entries 2, 6, 8 and 13 of Table 1). Furthermore, the phosphine containing *ortho*-substituted methyl groups on the phenyl rings of the triphenylphosphine (PT*o*Me) leads to a reduction of both factors when compared to its analogue PT*p*Me (compare entries 7 and 8 of Table 1). This is due to the steric hindrance caused by the methyl groups in the arylphosphine that hampers the CO_2 insertion in the intermediate **D.**

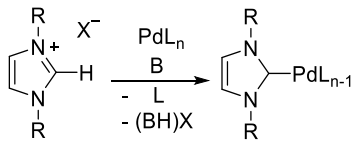
A remarkable TON of 4500 with 96% selectivity toward the valuable δ-lactone is obtained with the most basic phosphine essayed here, the *tris*-(*p*-methoxyphenyl)-phosphine (PT*p*OMe). To the best of our knowledge, this result is the best for the telomerization of 1,3-butadiene with carbon dioxide (Scheme 4) reported to date.[20-24]

In presence of Pd/PT*p*Me catalyst, but in the absence of any of the additional reagents (*p*-hydroquinone or *N,N*-diisopropylethylamine), there is a significant reduction in both the TON and the selectivity to δ-lactone (compare entry 8 with 9-11 of Table 1). These factors are also affected by the absence of the acetonitrile solvent (entry 12, Table 1), corroborating the importance of nitrile groups for this reaction.[16,25]



Scheme 4. Comparison of different reactions for the production of lactone **1**.

We have recently reported that the addition of an ionic liquid containing the 1,3-dialkylimidazolium cations to the telomerization reaction of butadiene and acetic acid has a remarkable effect in the Pd/phosphine catalyst performance.[26] On the other hand, it is known that the addition of these type of ionic liquids to the telomerization reaction of 1,3- butadiene with methanol leads to the complete deactivation of the catalyst,[27] likely by the formation of a catalytically inactive Pd-carbene species. The formation of this species requires a basic media to deprotonate C2-H position of the imidazolium cation (Scheme 5),[28-30] as the one provided by the methoxide used as co-catalyst in the telomerization with methanol.

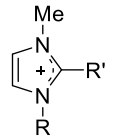


Scheme 5. Carbene formation from 1,3-dialkylimidazolium ionic liquids and Pd catalyst in the presence of base.

This deactivation also takes place in the telomerization of 1,3-butadiene with carbon dioxide that requires the presence of *N,N*-diisopropylethylamine. Thus, the Pd/PT*p*OMe catalyst is deactivated by the presence of different 1,3-dialkylimidazolium ionic liquids (Table 2). Although no evidence of carbene species have been found in the NMR analysis of the reaction mixtures, the fact that the deactivation is significantly less important in the presence of the ionic liquid containing the 1,2,3-trialkylimidazolium cation $BMMImBF_4$ (compare entries 13 and 18 of Table 2), which blocks the formation of carbenes at the active C2 position, supports the hypothesis of the formation of

these carbene species in the case of ionic liquids non-substituted at the C2 position.[31,32]

Table 2. Telomerization of butadiene with carbon dioxide in the presence of different imidazolium ionic liquids.[a]



BMIm$^+$: R = Bu; R' = H

MeOIm$^+$: R = $CH_2CH_2OCH_3$; R' = H

BMMIm$^+$: R = Bu; R' = CH_3

Entry	Ionic Liquid	Selectivity (%)		TON
		8	1+2+3 (1/2+3)	
13	-	3.3	96.7 (99/1)	4500
14	$BMImBF_4$	20.1	79.9 (100/0)	80
15	$BMImPF_6$	0.0	100.0 (100/0)	30
16	BMImCl	0.0	0.0	0
17	MeOImAcO	0.0	100.0 (100/0)	25
18	$BMMImBF_4$	3.1	96.9 (99/1)	1630

[a]Reaction Conditions: $Pd(OAc)_2$ = 2.7 mg (1.2 10^{-2} mmol); PT*p*OMe/Pd = 3; *p*-hydroquinone = 33 mg (0.30 mmol); DIPEA = 77.4 mg (0.60 mmol); 4 mL of acetonitrile; C_4H_6 = 10.0 mL (120 mmol); 30 bar of CO_2; 70 °C; 5 h; 700 rpm. *n*-dodecane was added as an internal standard; 8 = octatriene; 1+2+3 = lactones; 1/2+3 is the ratio between δ-lactone and γ-lactone; TON = turnover number after 5 h reaction.

Conclusions

The telomerization of 1,3-butadiene with carbon dioxide to δ-lactone is readily achieved by using $Pd(OAc)_2$ plus *tris*-(*p*-methoxyphenyl)-phosphine in the presence of *p*-hydroquinone, *N,N*-diisopropylethylamine and acetonitrile. A remarkably high TON of 4500 with 96% selectivity to the valuable δ-lactone was obtained after 5 h reaction at 70°C. This is the highest catalytic activity reported so far for this reaction. The telomerization was deactivated by the presence of different 1,3-dialkylimidazolium ionic liquids, likely by the formation of inactive Pd-carbene species.

Experimental Section

Materials

1,3-butadiene (Linde 2.5), carbon dioxide (Linde 4.5), *p*-hydroquinone (Panreac Sintesis), N,N-diisopropylethylamine (Fluka), acetonitrile (Scharlau), $Pd(OAc)_2$ (Aldrich), PPh_3 (Acros Organics), PT*o*Me (Avocado), PT*p*Me (Fluka) and PT*p*OMe (Aldrich) were used without further purification. Phosphines NaTPPMS,[33] Na_2TPPDS,[34] PT*mm*CF_3 and Dan2phos[35] (currently commercially available from Strem), and ionic liquids $BMImBF_4$, $BMImPF_6$, BMImCl and $BMMImBF_4$,[36] and MeOImAcO[26]**Fehler! Textmarke nicht definiert.** were prepared according to reported procedures.

Telomerization reactions

The telomerization reactions in a batch system were carried out in a 50 mL magnetically stirred stainless steel reactor provided with a glass vessel. The temperature reaction was controlled with a thermocouple dipped inside the reaction and a heating unit. 1 mL of 12 mM solution of $Pd(AcO)_2$ in dichloromethane was added to the reactor glass and the solvent was evaporated under reduced pressure. Then the desired quantities of phosphine, *p*-hydroquinone, N,N-diisopropylethylamine, ionic liquid and *n*-dodecane (internal standard) were added to the glass vessel and the reactor was closed and purged with nitrogen. 4 mL of acetonitrile was transferred to the reactor under a flow of nitrogen gas with the aid of a syringe. The reactor was frozen in liquid nitrogen and then butadiene was liquefied in a flask cooled in a bath at –78°C and the desired amount of the diene was transferred to the reactor *via* syringe. The reactor was heated to room temperature with the aid of a heating gun, then it was connected to the heating unit. Finally, the reactor was connected to the gas line for carbon dioxide loading up to a pressure of 30 bar, held constant by a backpressure valve. Once the working temperature was reached, the stirring was turned on. The pressure reactor was carefully checked along the reaction to warrant that enough liquid butadiene remains in the reactor. After the reaction time, heating and stirring were turn off, the reactor was immersed in an ice bath and the remaining butadiene/CO_2 was vented in a hood. The obtained mixture was diluted in CH_2Cl_2 and analyzed using (GC-FID) Hewlett Packard 5890 Series II and GC-MS Hewlett Packard G1800A GCD System, both equipped with HP5 columns. 4-vinylcyclohexene and δ-lactone (3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one) were used to calculate the response factors to dimers and lactones, respectively. *n*-dodecane (Sigma Aldrich) was used as an internal standard. The TON was calculated from the mols of butadiene converted, excluding the amount of vinylcyclohexene formed, and the mols of Pd catalyst used.

Acknowledgements

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Keywords: butadiene, telomerization, carbon dioxide, δ-lactone, 3-ethylidene-6-vinyltetrahydro-2*H*-pyran-2-one, ionic liquid.

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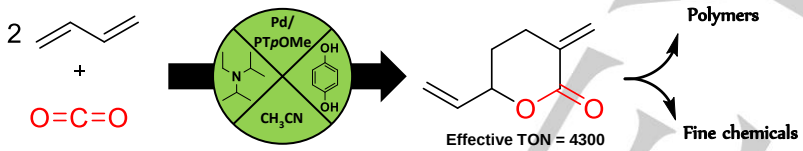

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Title

A Pd catalyst plus *tris*-(*p*-methoxyphenyl)-phosphine in the presence of *p*-hydroquinone, *N,N*-diisopropylethylamine and acetonitrile is the best system for the telomerization of butadiene with carbon dioxide reported till now.