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ARTICLE

Selective Palladium-catalysed Synthesis of Diesters: Alkoxycarbonylation of a CO_2-butadiene derived δ-lactone

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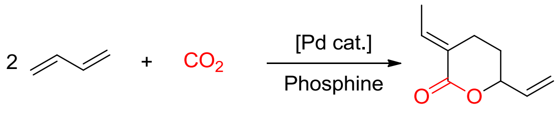
Novel unsaturated C_{10} diesters are produced via alkoxycarbonylation of δ-lactone **1** (3-ethylidene-6-vinyltetrahydro-2*H*-pyran-2-one), derived from the telomerization of CO_2 and butadiene. Key for the selective valorization of **1** is the use of a catalytic system based on $PdCl_2$, a chelating phosphine bearing electron-withdrawing groups and an acidic promoter. The unsaturated C_{10} methyl diester can be easily hydrogenated on Pd/C under mild conditions to afford its corresponding saturated diester. Subsequent hydrogenation using the homogeneous $[Ru(acac)_3]$/Triphos catalysts gives 2-ethyloctane-1,8-diol in high yield. The overall procedure allows synthesizing new building blocks for the manufacturing of renewable polymers and polymers processing materials.

Introduction

One of the most important tasks for 21st century scientists is to provide practical ways to substitute fossil-based feedstocks by renewables. In this context, an important challenge for organic chemistry and the chemical industry is the effective use of carbon dioxide. Indeed, this area is of actual interest and many efforts have been spent in the past decades to develop synthetic methodologies employing CO_2 as a raw material.[1-4] Clearly, one promising way of using CO_2 is its inclusion into polymers. As an example, processes based on the reaction of CO_2 and epoxides to produce polycarbonates and polyethercarbonates have been commercialised in recent years.[5, 6] So far, they remain the only polymers that include CO_2 of practical and commercial interest.

Although different olefins are known to react with carbon dioxide in the presence of specific metal complexes, in nearly all cases the release of the olefin-CO_2 adduct requires additional stoichiometric reagents leading to large amount of wastes.[3] Thus, direct olefin/CO_2 polymerization or the synthesis of monomers derived from them in a sustainable and economical way continues to be a very difficult task.

An exception to the above described reactivity is the catalytic telomerisation reaction of 1,3-dienes with carbon dioxide. Already in 1976, Inoue and co-workers[7] reported the first studies on this reaction. Further studies by the groups of Behr, Dinjus and Braunstein evidenced that, using a tertiary mono-phosphine and a Pd(0) precursor, δ-lactone **1** (3-ethylidene-6-vinyltetrahydro-2*H*-pyran-2-one) can be obtained with good selectivity (Scheme 1).[8-13] Recently, we became also interested in this transformation and demonstrated improved efficiency using a palladium/tris-(o-methoxyphenyl)-phosphine catalytic system.[14]



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Scheme 1 Synthesis of δ-lactone **1** by telomerization of butadiene and CO_2.

As pointed out by Behr and co-workers straightforward valorisation of **1** to other monomers, polymers and plasticizers offers interesting possibilities for the development of new sustainable materials.[15] Although 1,3-butadiene is currently mainly obtained as a by-product of steam cracking process to ethylene, it can be also produced from renewable feedstocks.[16, 17] In 2014, the group of Nozaki renewed the interest in the chemistry of lactone **1** reporting on the synthesis of polymers either by lactone **1** polymerization or by one-pot/two-step co/terpolymerisation of carbon dioxide and 1,3-dienes via lactone intermediate.[18, 19]

Before this last discovery, **1** had been particularly studied by Behr and co-workers in a variety of reactions such as hydrogenation, hydroformylation, hydroaminometylation, hydroamination, alcoholysis and hydrolysis affording carboxylic acids and esters, diols as well as functionalised lactones. Some of these compounds are of interest to produce polymers and polymer-related materials. In particular, diols and hydroxy-carboxylic acids are potential monomers for polyester and polyurethane chemistry while both monocarboxylic acid and alcohols can be used in plasticizers production. [15]

Concerning the reactivity of **1**, it is clear from the reactions listed above that it can undergo carbonylation reactions. However attempts to perform an alkoxycarbonylation of **1** using $Pd(OAc)_2$/triphenylphosphine as the catalyst and *p*-toluenesulfonic acid (PTSA) as promoter, unexpectedly, resulted only in its alcoholysis and no carbonylation product was detected.[15] Nevertheless, di- or tri-esters derived from carbonylation of **1** could be building blocks of high potential interest for the polymer industry.

In this paper, we report for the first time a successful catalytic system for the alkoxycarbonylation of **1**. In particular, we have developed a high yielding one pot procedure for the synthesis of C_{10} unsaturated diesters from **1**. We also report the catalytic hydrogenation of the so obtained diesters to their saturated form and to diol. Both the diesters and diol derived from the reaction are relevant building blocks for the synthesis of polyesters.

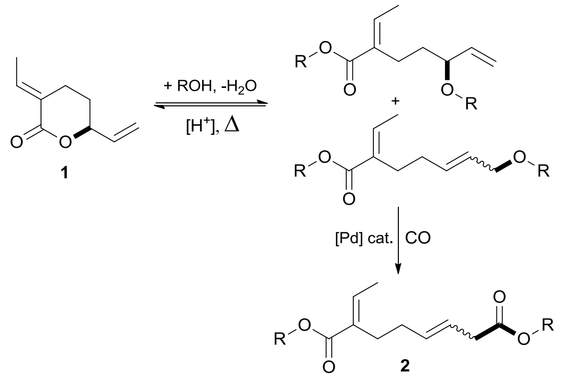
Results and discussion

Diesters from CO_2-derived δ-lactone 1

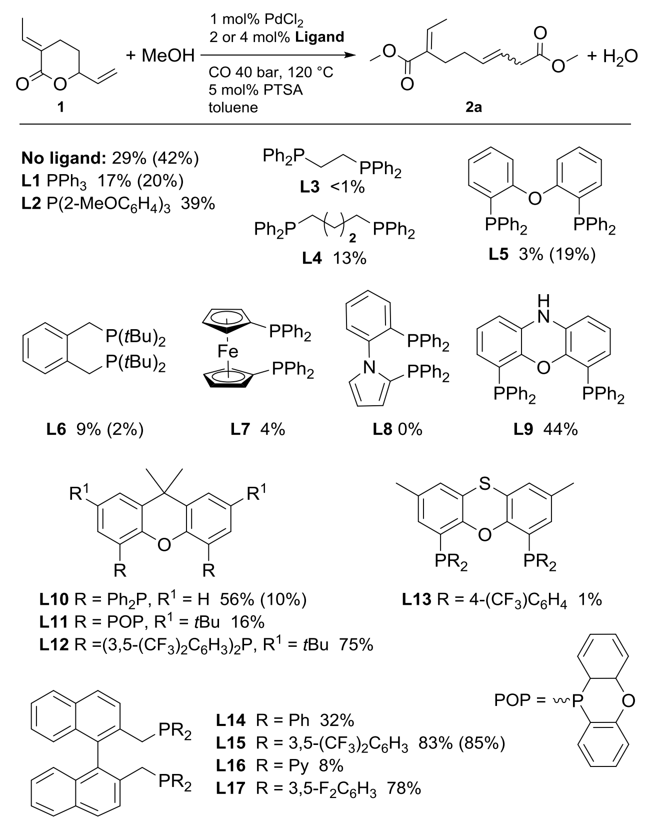
Typical catalytic hydroesterification reactions of olefins are performed using a palladium compound (such as $Pd(OAc)_2$, $PdCl_2$, $Pd(dba)_2$) in combination with a mono- or diphosphine, an alcohol and an acidic promoter. The application of such catalytic systems to the alkoxycarbonylation of **1** on the terminal olefinic bond, seems an easy task at a first sight. However, preliminary tests evidenced that when **1** is heated in toluene in the presence of a primary alcohol and an acid, alcoholysis to a mixture of non-cyclic isomeric products readily takes place also in the absence of palladium. The opening of the lactone to yield different esters cannot be avoided even without acidic promoter if a palladium/phosphine catalyst is present. These observations confirm the general reactivity of **1** with H-Y type substrates (as water, alcohols, amines or silanes) reported by the group of Behr.[15]

Given that non-selective alcoholysis cannot be easily suppressed, we decided to take advantage of that, developing a straightforward procedure for the synthesis of diester **2** through a novel domino alcoholysis/allylic substitution/carbonylation reaction (Scheme 2).[20] In fact, alcoholysis of **1** and subsequent allylic substitution yields a mixture of esters bearing an allylic ether moiety that can be carbonylated further on to the unsaturated diester **2**. Interestingly the synthesis of 2-ethylideneoctanedioic acid, an α,ω unsaturated diacid related to **2**, from lactone **1** was previously reported by the group of Behr in a Ph.D. dissertation.[15, 21] However, this reaction requires a three steps procedure: an initial rhodium/phosphine catalysed hydrogenolysis of lactone **1** to a mixture of isomeric unsaturated C_9-carboxylic acids followed by rhodium/phosphite catalysed isomerization/hydroformylation of one double bond with syngas and finally oxidation of the obtained aldehyde.

To develop a more efficient direct methoxycarbonylation procedure of **1** to **2a**, we initially examined the effect of different phosphines (**L1**-**L17**; Scheme 3) in combination with $PdCl_2$ as precatalyst and PTSA as acidic promoter. Conversion of δ-lactone **1** is complete in all cases. The reaction takes place even in the absence of a phosphine, however metallic palladium is always present at the end thus indicating the need for a ligand to stabilise the catalytic system. Monodentate phosphines (**L1** and **L2**) did not lead to appreciable improvements of the catalytic performance, although only a small amount palladium black was detected at the end of the reaction. Then, different bisphosphines were tested. Most of them (**L3**-**L8**) gave low or no selectivity in the desired product **2a** mainly due to the formation of catalytic systems unable to carbonylate the allylic position of the intermediately formed esters. Surprisingly when **L6** was used, the conversion of the mixture on non-cyclic esters was almost complete but no major products could be identified by GC-MS. ESI-MS evidenced the formation of higher molecular weight products. The large bite-angle ligand Xantphos (**L10**) allowed to obtain **2a** in fair yield, when the reaction was performed for 5 h. A drop in the yield of **2a** was noticed upon prolonging the reaction time to 20 h. A dispersion of products was formed, mainly due to further carbonylation of the double bonds of **2a**. It should be anyway noted that, as for **L6**, no other major byproducts could be detected by GC. This can be explained by the formation of oligomeric products. Encouraged by the results obtained with **L10** we tested other ligands with larger bite-angles. Hence, phosphines of the Xantphos (**L9**-**L13**) and NaPhos (**L14**-**L17**) families were employed.



Scheme 2 Formation of esters of 7-ethylideneoct-3-enedioic acid **2** by alkoxycarbonylation of δ-lactone 1.



Scheme 3 Palladium-catalysed alkoxycarbonylation of the allylic position of δ-lactone 1. Investigation of different phosphine ligands. Reaction conditions: **1** (1.0 mmol), PdCl$_2$ (1 mol%), monodentate ligand (4 mol%) or bidentate ligand (2 mol%), PTSA (5 mol%) toluene (2 mL), MeOH (0.25 mL, 6 mmol), CO (40 bar), 120°C for 5 h; yields determined by GC analysis using hexadecane as the internal standard; number in parenthesis indicates yield after 20h. Yield is given as sum of E and Z isomers. Substrate **1** conversion was complete in all cases.

Interestingly, good yields were obtained with those substituted with electron-withdrawing groups (**L12**, **L15** and **L17**), with the only exception of **L13**. IPhos (**L15**) was identified as the best ligand affording **2a** in very good yield in a short reaction time. Notably, in this case, even prolonging the reaction to 20h the yield of **2a** remained almost constant.

To further improve the reaction, we studied the effect of different parameters on the methoxycarbonylation of **1** using **L15** as ligand (Table 1). At first the effect of the amount of acid on the reaction was explored. A strong increase in the yield of **2a** was noticed with the increase of the amount of PTSA from 1 mol% to 10 mol%, after which a plateau was reached (entries 1-4). No variation was detected changing the identity of the acid to methanesulfonic acid (MSA, entry 5). Hydrochloric acid instead gave much worse results, probably because of its volatility. Sulfuric acid afforded the same yield obtained with PTSA (10 mol%) albeit with just 5 mol% (compare entry 7 with entry 3). Notably, the source of palladium is crucial for the outcome of the reaction. Thus, several commonly used palladium(0) and (II) precursors were investigated. [Pd(dba)$_2$] and Pd(OAc)$_2$ (entries 9-10) afforded **2a** in poor yield, while PdCl$_2$(CH$_3$CN)$_2$ gave the same outcome as PdCl$_2$ (entry 7-8).

Table 1. Palladium-catalysed methoxycarbonylation of δ-lactone **1** to **2a**: optimization of the reaction conditions.[a]

Entry	Precatalyst (mol%)	Solvent	Acid (mol%)	CO (bar)	t (h)	Y[b] (%)
1	PdCl$_2$ (1)	toluene	PTSA (1)	40	5	58
2	PdCl$_2$ (1)	toluene	PTSA (5)	40	5	83
3	PdCl$_2$ (1)	toluene	PTSA (10)	40	5	89
4	PdCl$_2$ (1)	toluene	PTSA (15)	40	5	90
5	PdCl$_2$ (1)	toluene	MSA (5)	40	5	84
6	PdCl$_2$ (1)	toluene	HCl (5)	40	5	33
7	PdCl$_2$ (1)	toluene	H$_2$SO$_4$ (5)	40	5	89
8	PdCl$_2$(CH$_3$CN)$_2$ (1)	toluene	H$_2$SO$_4$ (5)	40	5	88
9	Pd(dba)$_2$ (1)	toluene	H$_2$SO$_4$ (5)	40	5	16
10	Pd(OAc)$_2$ (1)	toluene	H$_2$SO$_4$ (5)	40	5	19
11	PdCl$_2$ (1)	CH$_3$CN	H$_2$SO$_4$ (5)	40	5	37
12	PdCl$_2$ (1)	THF	H$_2$SO$_4$ (5)	40	5	45
13	PdCl$_2$ (1)	MeOH	H$_2$SO$_4$ (5)	40	5	39
14[c]	PdCl$_2$ (0.5)	toluene	H$_2$SO$_4$ (5)	40	3	86
15	PdCl$_2$ (0.5)	toluene	H$_2$SO$_4$ (5)	40	3	89
16[d]	PdCl$_2$ (0.5)	toluene	H$_2$SO$_4$ (5)	40	3	87
17	PdCl$_2$ (0.5)	toluene	H$_2$SO$_4$ (5)	30	3	89
18	PdCl$_2$ (0.5)	toluene	H$_2$SO$_4$ (5)	20	3	87
19[e]	PdCl$_2$ (0.5)	toluene	H$_2$SO$_4$ (7.5)	30	3	91[f]
20[g]	PdCl$_2$ (0.17)	toluene	H$_2$SO$_4$ (1.7)	30	5	80

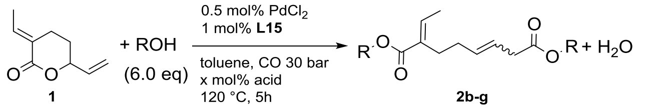
[a]Reactions conditions: **1** (1.0 mmol), [Pd] (x mol%), **L15** (2x mol%), solvent (2 mL), MeOH (0.25 mL, 6 mmol), CO, 120°C. [b] Determined by GC analysis using hexadecane as the internal standard. Yield is given as sum of E and Z isomers. E/Z ratio ranges from 3.6 to 4.2. [c] 130 °C. [d] 110 °C. [f] MeOH (0.50 mL, 12 mmol), isolated yield 90%. [g] **1** (3.0 mmol), MeOH (0.75 mL, 18 mmol).

Apparently, the presence of chloride ion seems necessary to ensure the formation of a sufficiently stable catalytically active species as previously noticed in our group for other carbonylation reactions of conjugated dienes[22, 23] and allylic alcohols.[24] Changing the reaction medium from toluene to either aprotic polar solvents (entries 11-12) or to a protic one (entry 13) led to a decrease of the yield of the desired product. In the range of temperature between 110 °C and 130 °C and of CO pressure between 20 and 40 bar only small variations of the yield of **2a** were detected. A minor improvement was observed increasing both the amount of sulfuric acid and methanol, allowing to reach a 91% yield. We were pleased to notice that increasing the amount of lactone and MeOH still a good catalyst activity can be achieved at 0.17 mol% loading (entry 20). It should be noted that even under the best condition yield could not be improved to more than 91%. No formation of other major side products was noticed by GC analysis. However traces of doubly carbonylated products as well as a number of unidentified components were found in very small amount. Due to their retention times in the GC, it can be argued that they are related to isomerized esters formed by initial alcoholysis of the lactone that are preferentially subjected to side reaction instead of being carbonylated.

Next, we examined the scope of the alkoxycarbonylation of the allylic position of **1** by using different alcohols (Table 2). Primary aliphatic alcohols gave excellent yields (entries 1-2). Notably, the alcohol most frequently used in plasticizers production, 2-ethylhexanol,[25] gave the diester **2c** in essentially quantitative yield. Both benzyl and isopropyl alcohols yielded the corresponding diesters **2d**-**e** (entries 3-4) in good yields while *tert*-butanol and phenol did not afford the desired product at all (entries 5-6). The lack of selectivity in these cases is not surprising considering that the first step of the process involves an alcoholysis reaction which often proceeds sluggishly with tertiary alcohols or phenols.

Finally, to demonstrate the scalability of the process, we performed a multi-gram scale methoxycarbonylation of **2a** (Scheme 4). Using a low catalyst loading ($PdCl_2$ = 0.15 mol%, **L15** = 0.3 mol%) and the concentrations of the other reagents used in entry 20, Table 1, a 81% isolated yield of dimethyl 7-ethylideneoct-3-enedioate **2a** was obtained.

Table 2. Palladium-catalysed alkoxycarbonylation of δ-lactone **1** to **2** using different alcohols.[a]



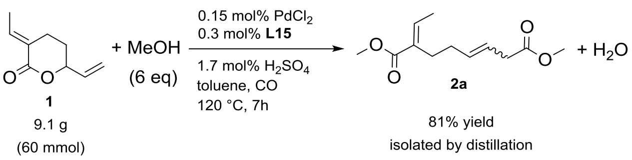
Entry	Alcohol	Acid (mol%)	Product	Yield (%)[b]
1	^{n}BuOH	H_2SO_4 (5)	**2b**	90 (E/Z = 3.8)
2	2-Ethylhexanol	H_2SO_4 (5)	**2c**	99 (E/Z = 4.2)
3	$PhCH_2OH$	PTSA (10)	**2d**	73 (E/Z = 4.5)
4	^{i}PrOH	H_2SO_4 (5)	**2e**	64 (E/Z = 2.3)
5	^{t}BuOH	PTSA (10)	**2f**	-
6	PhOH	PTSA (10)	**2g**	-

[a] Reactions conditions: **1** (1.0 mmol), [Pd] (0.5 mol%), **L15** (1 mol%), ROH (6 mmol), 30 bar CO in toluene (2 mL) for 5h. [b] Determined by GC analysis using hexadecane as the internal standard. Yield is given as sum of E and Z isomers.

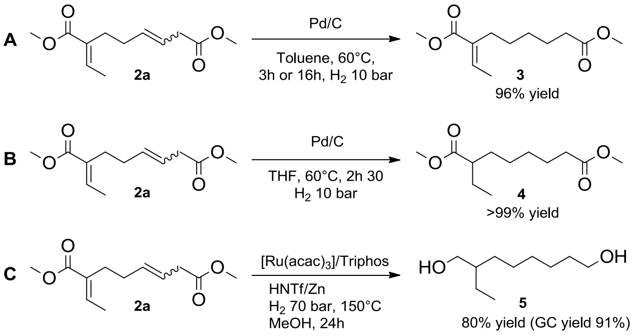
Hydrogenation of dimethyl 7-ethylideneoct-3-enedioate (2a)

Unsaturated esters obtained by alkoxycarbonylation of **1** are valuable platform chemicals themselves; however the corresponding saturated esters and the resultant diols are of interest for applications, too. In order to transform 2 into saturated esters or diols catalytic hydrogenations were performed.

At first, commercial Pd/C (10 wt%) was used as catalyst to hydrogenate the unsaturated diester **2a**. Mild reaction conditions (10 bar H_2, 60 °C), previously reported by Behr and co-workers for the reduction of lactone **1** to 3,6-diethyltetrahydro-2*H*-pyran-2-one,[26] were used. We noticed a marked solvent effect on the chemoselectivity of the hydrogenation. When the reaction was performed in toluene, reduction of the di-substituted double bond was attained within 3 h. However, the conjugated tri-substituted double bond was not reduced even after 16 h (Scheme 5-A). Complete reduction of olefinic bonds of **2a** to yield **4** was instead accomplished in 2.5 h using THF as the solvent (Scheme 5-B). The latter diester **4** is of potential industrial interest for plasticizer applications and as co-monomer in combination with diamines and diols to yield respectively polyamides and polyesters. On the other hand, the presence of a single unsaturation makes **3** comparable to α,β-unsaturated esters, e.g. acrylic and tiglic acid derivatives, which are of interest for the preparation of different functional materials.



Scheme 4 Multi-gram scale synthesis of **2a** from δ-lactone **1**



Scheme 5 Hydrogenation of diester **2a**.

To further illustrate the versatility of **2** as a building block for polymers, we studied its hydrogenation to diol **5**. Synthesis of **5** can be performed by reduction of **4** using $LiAlH_4$ as stoichiometric reagent, a classical method used in laboratory organic synthesis. However, when we performed this reaction, we found that the separation and purification of **5** from byproducts was difficult. Anyhow, such methodology is clearly not environmental compatible and nowadays not applicable to a bulk scale industrial production; thus, a catalytic hydrogenation was investigated.

Ester and carboxylic acid moieties are challenging functional groups for hydrogenation reactions. In industrial processes their hydrogenation is generally performed over heterogeneous catalysts at high pressures and temperatures.[27, 28] However, recently homogenously catalysed hydrogenation of carboxylic acid derivatives has experienced significant developments.[29-31]

Hence, we applied two different commercially available ruthenium based catalysts to the reduction of **2a** to **5**: a Noyori type ruthenium catalyst firstly reported by Saudan at al. for the hydrogenation of esters[32] (**c1**, Table S1) and the tetrahydroborato form of the ruthenium PNP pincer complex named Ru-MACHO™ (**c2**, Table S1) discovered by Kuriyama and co-workers at Takasago company.[33] In both cases, reaction conditions commonly used for these catalytic systems were employed (Table S1, entries 1 and 2). Unfortunately, even after 22h only traces of diol were present using **c1** as the catalyst and just 8 % yield was obtained using **c2**. Promising results were instead obtained using ruthenium complexes of 1,1,1-*tris*-(diphenylphosphinomethyl)ethane (Triphos). This was the first homogenous catalyst reported by Elsevier for the hydrogenation of esters.[34, 35] In the last decade this catalytic system has been further employed by different groups.[36] Moving from the reduction of oxalic acid, which was carried out in methanol in the presence of zinc powder, many modifications have been introduced. For example, Cole-Hamilton and Mecking studied the effect of water, MSA and zinc and solvent in the reduction of natural oil-derived diesters.[37] In addition, Leitner and co-workers reported a strong dependence of the selectivity for biogenic acids reduction upon change of ionic or acid additives.[38] The same group described the use of the defined complex [Ru(Triphos)(TMM)] **c3** (TMM = trimethylenemethane) instead of the *in situ* formed system from [Ru(acac)$_3$]/Triphos (**c4** in Table S1, acac = acetylacetonate). Interestingly they found that the addition of acidic additives lowers the selectivity towards benzyl alcohol in the hydrogenation of benzoic acid.[39] Recently, also the use of Lewis acids as promoters in the reductive etherification of esters was reported by some of us.[40] Here, we started our investigation using both **c4** in combination with MSA in methanol (entry 3, Table S1) and **c3** in THF in the absence of any additive (entry 4, Table S1). The first system yielded 35% of diol **5** while the latter afforded mainly a mixture of the esters **3** and **4**. Encouraged by the result obtained with MSA we tested sodium methoxide and bis(trifluoromethane)sulfonimide (HNTf$_2$) as additives. The use of HNTf$_2$ (10 mol%) afforded 69% yield of **5** (entry 5, Table S1). Finally, the desired full reduction of **2a** to diol **5** was obtained under relatively mild conditions in 91% yield (80% isolated) upon reduction of the amount of HNTf$_2$ to 5 mol% and addition of 5 mol% of metallic zinc (entry 7, Table S1).

Experimental

General procedures

All commercial reagents were ordered from Alfa Aesar, Aldrich, TCI or Strem. Unless otherwise stated, commercial reagents were used without purification. δ-Lactone **1** was synthesised as previously reported and kept under an Ar atmosphere after distillation.[14] PTSA was used as monohydrate. Pd/C 10 wt% was purchased from Aldrich (product n. 205699). [Ru(Triphos)(TMM)] was synthesised as previously reported in the literature.[39] Toluene, THF and methanol were collected from The Solvent Purification System by M BRAUN and used under standard Schlenk technique. Acetonitrile, *n*-butanol, 2-ethylhexanol, benzyl alcohol and *i*-propanol were dried using standard techniques and kept under an Ar atmosphere. Analytical data of literature known compounds were in accord with reported data. NMR spectra were recorded on Bruker AV-300, Bruker Fourier 300 or Bruker AV-400 NMR spectrometers. Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet) and br. s (broad singlet). All measurements were carried out at room temperature unless otherwise stated. Mass spectra were recorded on an Agilent 6890/5973 GC-MS. High resolution mass spectra (HRMS) were recorded on Agilent 6210 Time-of-Flight LC/MS (Agilent) with electrospray ionization (ESI). The data are given as mass units per charge (m/z) and intensities of signals are given in brackets. For GC analyses, Agilent HP-7890A chromatograph equipped with a FID instrument and a HP-5 column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 µm film thickness) was used. Unless otherwise stated, the products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, (Merck) using gradient elution from heptane to heptane/AcOEt = 8:2.

Alkoxycarbonylation of δ-lactone (1) to diesters (2)

General procedure. Alkoxycarbonylation experiments on 1-3 mmol scale were performed in a 4 mL vial placed inside a 300 mL stainless steel Parr autoclave. Molar ratios and experimental conditions are reported in the captions of Scheme 2, Table 1 and Table 2. In a typical reaction, palladium precursor (0.01 mmol, 1 mol%), ligand (0.02 mmol, 2 mol%), δ-lactone **1** (152 mg, 1.0 mmol) and a magnetic stirring bar were placed in a 4 mL vial. When catalyst loading was lower than 1 mol%, a stock solution of PdCl$_2$ and **L15** was prepared by mixing them in toluene and stirring the mixture overnight. The vial was then sealed, connected to the atmosphere with a needle and evacuated and refilled with argon for three times. Solvent (2.0 mL) and a solution of the acidic promoter in the appropriate alcohol, were injected into the vial by syringe (in the case of phenol and *tert*-butanol, the alcohol and the acid were added by weight). The autoclave was flushed three times with CO, pressurised to the required pressure and then placed in a preheated aluminium block. After the reaction time, the autoclave was cooled with ice water to room temperature and the pressure was carefully released. The reaction mixture was analysed by gas-chromatography using hexadecane as the internal standard. The diesters **2** were isolated from the reaction mixture by column chromatography.

Gram-scale methoxycarbonylation to 2a. The reaction was performed in an Hastelloy-C 100 mL Parr autoclave. PdCl$_2$ (16.1 mg, 9.1 × 10^{-2} mmol), **L15** (215 mg, 0.18 mmol) and **1** (9.11 g, 60 mmol) were weighed in a Schlenk flask. The flask was purged with argon. Toluene (40 mL) and a solution of H$_2$SO$_4$ (95 mg) in MeOH (15 mL) were added. The mixture was stirred for 1h under argon and then transferred to the autoclave previously purged with argon. The autoclave was flushed three times with CO, pressurised to 50 bar and then heated to 120 °C for 7 h. The autoclave was then cooled with ice water and vented. The volatiles were evaporated under rotary evaporation and the crude was distilled under vacuum (0.25-0.20 mbar) collecting the fraction between 80-85°C. Purity was checked by gas-chromatography. 10.95 g (81% yield) of **2a** were obtained as a colourless liquid.

Hydrogenation of diester 2a

Synthesis of (*E*)-dimethyl 2-ethylideneoctanedioate, 3. Pd/C 10 wt% (2.8 mg), **2a** (0.5 mmol) and a magnetic stirring bar were added to a 4 mL vial. The vial was then sealed, connected to the atmosphere with a needle and evacuated and refilled with argon for three times. Toluene (2 mL) was added and the vial placed inside a 300 mL stainless steel Parr autoclave. The autoclave was flushed three times with nitrogen, pressurised with hydrogen to 10 bar and then heated to 60 °C for 3 h. The autoclave was cooled with an ice bath and vented. The reaction mixture was filtered through Celite, the solvent evaporated and the crude purified by column chromatography affording **3** as a colorless liquid in 96% yield.

Synthesis of dimethyl 2-ethyloctanedioate, 4. Pd/C 10 wt% (3.1 mg), **2a** (1.4 mmol) and a magnetic stirring bar were added to a 4 mL vial. The vial was then sealed, connected to the atmosphere with a needle and evacuated and refilled with argon for three times. THF (3 mL) was added and the vial placed inside a 300 mL stainless steel Parr autoclave. The autoclave was flushed three times with nitrogen, pressurised with hydrogen to 10 bar and then heated to 60 °C for 2.5 h. The autoclave was cooled with an ice bath and vented. The reaction mixture was filtered through Celite and the solvent evaporated affording pure **4** as a colorless liquid in >99% yield.

Synthesis of 2-ethyloctane-1,8-diol 5. $[Ru(acac)_3]$ (4.0 mg, 0.01 mmol), Triphos (12.5 mg, 0.02 mmol) and zinc (1.6 mg, 2.5×10^{-2} mmol) were weighed in a 4 mL vial in the air. The vial was then sealed, connected to the atmosphere with a needle and evacuated and refilled with argon for three times. **2a** (0.5 mmol) and 2 mL of a stock solution of $HNTf_2$ (7.0 mg, 2.5×10^{-2} mmol) in methanol were added. The vial was placed inside a 300 mL stainless steel Parr autoclave and the autoclave was flushed three times with nitrogen, pressurised with hydrogen and heated. After 24 h, the autoclave was cooled with ice water and vented. The crude mixture was analysed by gas-chromatography. The product was purified by column chromatography on silica gel (gradient elution from CH_2Cl_2 to CH_2Cl_2/MeOH 9:1).

Conclusions

For the first time the synthesis of valuable unsaturated diesters **2** from δ-lactone **1** is described. Key to success for the selective esterification/allylic substitution/alkoxycarbonylation domino sequence of **1** is the use of specific palladium catalysts based on $PdCl_2$ and chelating diphosphines substituted with electron-withdrawing groups. The resulting unsaturated diesters can be selectively hydrogenated under mild conditions either to the mono-unsaturated diesters or to the saturated one, both of which are relevant building blocks for the synthesis of functional materials or plasticizers. Moreover, we show that such diesters can be also hydrogenated to 2-ethyloctane-1,8-diol **5** that offers new possibilities for the synthesis of polymers. In general, the overall process constitutes a new way to building blocks from δ-lactone **1**, which is derived from CO_2 and butadiene, thus representing a new step towards renewable polymers.

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41