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The Palladium Catalyzed Carbonylative Telomerization of Butadiene : One Pot Catalytic and Atom-Economical Synthesis of Unsaturated Esters from Agrobased Alcohols and Polyols.

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Dedication ((optional))

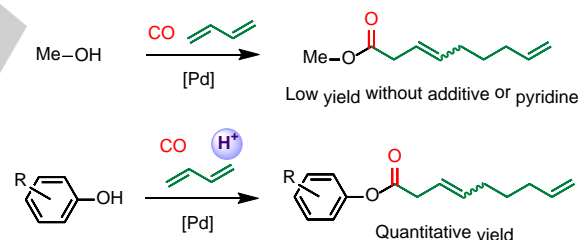
Abstract: The palladium catalysed carbonylative telomerization reaction of alcohols with butadiene allows an efficient and atom-economical access to unsaturated alkyl nona-3,8-dienoate esters. The reaction has been studied on the point of view of the nature of the catalyst (phosphine and acid) with ethanol. Commercially available triarylphosphines and carboxylic acids associated to a simple palladium precursor appear as the best combination for the insitu generation of the catalyst. The reaction conditions have been further optimized and the carbonylative telomerization reaction has been efficiently applied to the full transformation of several industrially relevant agrobased monoalcohols and polyols.

Introduction

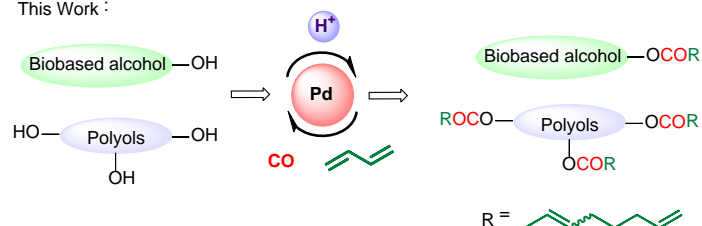
Among the numerous synthetic methods for esters synthesis, metal-catalyzed carbonylation reactions are of strong interest, being highly atom economical as well as highly efficient.^[1] Saturated and unsaturated esters are for example respectively obtained from the hydroesterification of olefins^[2] or dienes with an alcohol.^[3] The hydroesterification of ethylene, thanks to the development of effective catalytic systems, has found industrial application as an intermediate synthetic step towards methylmethacrylate.^[4] The reaction with olefins has also been applied to the conversion of agrobased polyols for the synthesis of plasticizers.^[5] The hydroesterification reaction that incorporates butadiene yields C5 unsaturated esters^[3] that can be further chemically modified thanks to the versatile reactivity of the double bond. Interestingly, the carbonylative coupling reaction of 2 equivalents of 1,3-butadiene followed by the nucleophilic attack of an alcohol yields alkyl nona-3,8-dienoates (Scheme 1).^[6] This carbonylative version of the telomerization reaction^[7] encompasses several advantages such as high atom-economy and the use of industrially accessible reactants (butadiene, CO, alcohols). All of these are already produced on large scale from agro-resources: This further strengthens the attractiveness of such transformation in a context of efficient biomass upgrading.^[8] Moreover, the butadiene coupling

reactions advantageously lead to the formation of two unsaturations and thus open the way to further functionalization. This herein considered transformation applied with simple alcohols is promoted by palladium-based catalysts. After early works reported by Tsuji, Billups and Knifton,^[9] it did not attract significant attention in the literature. The reaction was only recently used for the synthesis of C21 monoesters from β -myrcene under neutral conditions^[10] and in an intermediate step for the synthesis of diesters from butadiene with pyridine as solvent.^[11] We recently reported that the reaction can be efficiently employed for the functionalization of phenols, natural phenols and a polyphenolic biopolymer such as Kraft lignin.^[12] This study revealed that with phenolic nucleophiles, acidic conditions are greatly enhancing the yield of products. Bearing in mind the synthetic potential of this reaction in the field of biomass upgrading, we turned our attention toward the synthesis of unsaturated esters from the catalytic transformation of agrobased aliphatic alcohols and polyols.

Previous work :



This Work :



Scheme 1 The carbonylative telomerization reaction.

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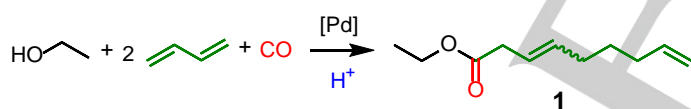
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Results and Discussion

The catalytic procedure previously developed for the transformation of phenols was first evaluated with ethanol as a simple biobased aliphatic alcohol. We more particularly focused our attention on the choice of the palladium-based precatalyst

and of the acid co-catalyst used as these were key-parameters in the case of phenols conversion. It should be noticed that ethanol is not used as solvent but as a stoichiometric reagent. The very polar solvent dioxane has been selected as the solvent of reaction as it is able to solubilize polyols^[5a] 4 equivalents of butadiene were used per ethanol in order to counterbalance the possible butadiene oligomerization and thus favor full conversion of the alcohol. The catalyst was generated in situ from the combination of halide-free Pd(OAc)₂ and four equivalents of PPh₃. The E isomer was obtained in all cases as the major isomer, the E/Z proportion varied with the reaction conditions from 85%/15% to 70%/30%.^[13] In the case of ethanol, both weak and strong acids were evaluated as co-catalysts (Table 1, entries 1-4). Acetic acid, benzoic acid and 2-chlorobenzoic acid showed a high efficiency and yields up to 94 % could be obtained with the latter one. 4-bromobenzoic acid afforded a very low amount of product. Indeed, in contrast to the C-Cl bond in 2-chlorobenzoic acid, the C-Br bond is very reactive toward Pd(0) species. This reactivity is typically used in carbonylation reactions of arylbromide derivatives that lead to the formation of HBr.^[14] The strong acid thus contributed to poisoning of the catalyst as exemplified by the catalytic reactions performed with TFA and PTSA as acid cocatalysts (Table 1, entries 5-6). With these two acids, very low yields in product of reaction were obtained. Strong acids are indeed expected to favour the formation of palladium hydride species through the protonation of low valent Pd(0) species. This reactivity prevents the oxidative coupling of two butadiene units, a key step in the catalytic cycle of the carbonylative telomerization reaction.

Table 1. Carbonylative telomerization of butadiene with ethanol: Influence of the acid ^[a]



Entry	Acid	pK _a	Yield ^[b]
1	Acetic acid	4.76	83 %
2	Benzoic acid	4.19	82 %
3	4-bromobenzoic acid	3.97	2 %
4	2-chlorobenzoic acid	2.92	94 %
5	TFA	0.23	8 %
6	PTSA	-6.5	< 1 %
7	-	-	30 %

[a] Conditions: Ethanol (0.58 mL, 10 mmol), butadiene (3.5 mL, 40 mmol), Pd(OAc)₂ (11.1 mg, 0.05 mmol), PPh₃ (52.8 mg, 0.2 mmol), acid (1.5 mmol), dioxane (3.0 mL), 30 bar CO, T = 90°C, t = 20h; [b] NMR Yield with trimethoxybenzene as internal reference.

The impact of the ligand used to stabilize the catalyst under acidic conditions was also studied. We were more particularly interested in comparing air-stable triarylphosphines with different electronic and steric properties on this catalytic reaction (Table 2). Benzoic acid has been used as co-catalyst for this study.

Triarylphosphines featuring electron-donating groups on the *para* position of the aryl groups showed higher efficiencies, as higher yields were obtained with P(*p*-MeOC₆H₄)₃ and P(*p*-MeC₆H₄)₃ (compare entry 1 with entries 2 and 3). Sterically hindered phosphines led to very low catalytic activities as shown from the catalytic runs involving tris(2,4,6-trimethoxyphenyl)phosphine and tris(2,4,6-trimethylphenyl)phosphine (entries 4 and 5). This contrasts with the results obtained in the case of the (non-carbonylative) telomerization reaction that is efficiently promoted with the sterically hindered P(*o*-MeOC₆H₄)₃ ligand.^[15] This family of ligands doesn't prevent the oxidative coupling step of two butadiene units. However, one can expect that in the case of the carbonylative telomerization reaction, the presence of CO will compete with the coordination of sterically hindered phosphines and thus favour the formation of unstable under-coordinated palladium species. A diphosphine, namely dppb (1,4-bis(diphenylphosphino)butane), has been evaluated as ligand, affording the targeted product in low yield, while the product results from butadiene ethoxycarbonylation (ethylpent-3-enoate) has been isolated as main compound.^[16] A phosphine-free catalytic reaction didn't show any formation of the products of reaction (entry 8).

Table 2 Carbonylative telomerization of butadiene with ethanol: Influence of the ligand.^[a]

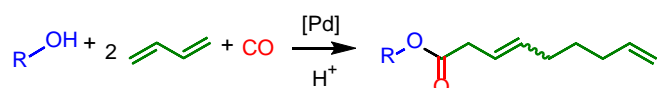
Entry	Ligand	Yield ^[b]
1	PPh ₃	82%
2	P(<i>p</i> -MeOC ₆ H ₄) ₃	91%
3	P(<i>p</i> -MeC ₆ H ₄) ₃	93%
4	P(2,4,6-(OMe) ₃ C ₆ H ₂) ₃	<1%
5	P(2,4,6-Me ₃ C ₆ H ₂) ₃	<1%
6	P(C ₆ F ₅) ₃	<1%
7	dppb ^[c]	7%
8	-	<1%

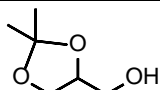
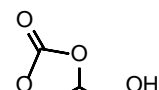
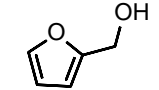
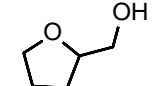
[a] Conditions: ethanol (0.58 mL, 10 mmol), butadiene (3.5 mL, 40 mmol), Pd(OAc)₂ (11.1 mg, 0.05 mmol), ligand (0.2 mmol), benzoic acid (183.2 mg, 1.5 mmol), dioxane (3.0 mL), 30 bar CO, T = 90°C, t = 20 h; [b] NMR Yield with trimethoxybenzene as internal reference; [c] dppb ligand : 0.1 mmol.

The PPh₃/Pd(OAc)₂/benzoic acid combination was selected for further applications, as it involves readily available constituents while affording high yields. It was thus used to promote the catalytic conversion of bio-based monoalcohols through the carbonylative telomerization reaction (Table 3). Glycerol is a triol that can be readily converted into a monoalcohol by protecting two hydroxyl groups through the formation of an acetal with acetone (as solketal)^[17] or carbonate (as glycerol carbonate).^[18] Thus, solketal has been reacted and efficiently converted by carbonylative telomerization in the corresponding unsaturated ester with 81 % isolated yield (Table 3, entry 1). On the other hand, the monoester derived from glycerol carbonate has been obtained in very low yield, most probably because of the

carbonate opening reactions under acidic conditions (Table 3, entry 2). We then probed the efficiency of the transformation on furfuryl alcohol^[19] and tetrahydrofurfuryl^[20] alcohol, which are agrobased compounds derived from pentoses issuing from the hemicellulosic feedstock.^[21] Simple processes are used for the production of these derivatives at the industrial scale. Interestingly, the carbonylative telomerization of butadiene has been very efficiently applied to the conversion of these two alcohols, the furfuryl and tetrahydrofurfuryl esters have been isolated with respectively 94 % and 81 % isolated yield (entries 3 and 4).

Table 3. Carbonylative telomerization reaction with agrobased monoalcohols.^[a]



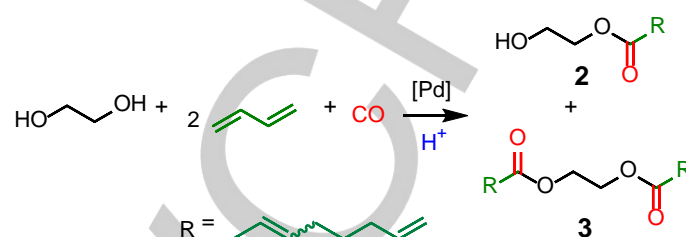
Entry	Alcohol (R-OH)	Isolated Yield ^[b]
1		81 %
2		13 %
3		94 %
4		81 %

[a] Conditions: alcohol (10 mmol), butadiene (3.5 mL, 40 mmol), Pd(OAc)₂ (11.1 mg, 0.05 mmol), PPh₃ (52.8 mg, 0.2 mmol), acid (1.5 mmol), 40 bar CO, dioxane (3.0 mL), T = 90°C, t = 20 h; [b] purified by silica gel column chromatography.

The conversion of alcohols by carbonylative telomerization has been extended to polyols. With such derivatives, selectivity issues related to substitution degrees are expected. The reaction has been studied in depth with a simple model polyol, ethylene glycol, in order to further optimize the reaction conditions (CO pressure, temperature, see Table 4). The very simple PPh₃/Pd(OAc)₂/benzoic acid catalytic combination has been used for this study. The ethylene glycol conversion and the selectivity into mono-/diesters have been determined by GC and ¹H NMR analyses performed on the crudes of reaction. The variation of the CO pressure has an impact on the reaction yield. Almost quantitative yields of diester were obtained at 20 and 40 bar of CO (Table 4, entries 1 and 2, respectively). At 50 bar, the reaction is not complete and a mixture of monoester and diester is obtained (entry 3). This is likely to be due to the competition for active sites on the catalyst between the CO and butadiene molecules, favoring CO at higher pressure. Consequently, high

CO pressure slows down the butadiene from dimerising. With 0.5% of catalyst in respect to the hydroxyl groups, the reaction can be setup at lower reaction temperatures without loss of yield (entries 4-6)

Table 4. Carbonylative telomerization reaction with ethylene glycol.^[a]



Entry	T (°C)	CO (bar)	EG conv (%) ^[b]	Y2 (%) ^[b]	Y3 (%) ^[b]
1	90	20	100	0	97
2	90	40	100	0	97
3	90	50	100	35	65
4	90	30	100	0	93
5	80	30	100	0	97
6	70	30	100	0	99

[a] Conditions: Ethylene glycol (0.56 mL, 10 mmol), butadiene (6.2 mL, 70 mmol), benzoic acid (366.4 mg, 3 mmol), Pd(OAc)₂ (0.1 mmol), PPh₃ (0.4 mmol), dioxane (3.0 mL), t = 20 h. [b] Yields were calculated by using both the NMR spectra and the GC chromatograms of the products.

The conversion of ethylene glycol and selectivity towards the different products of reaction have been monitored and plotted in function of the reaction time (See Figure 1). The conversion profile gives evidence of an activation period which is likely due to the *in situ* formation of the actual catalyst.

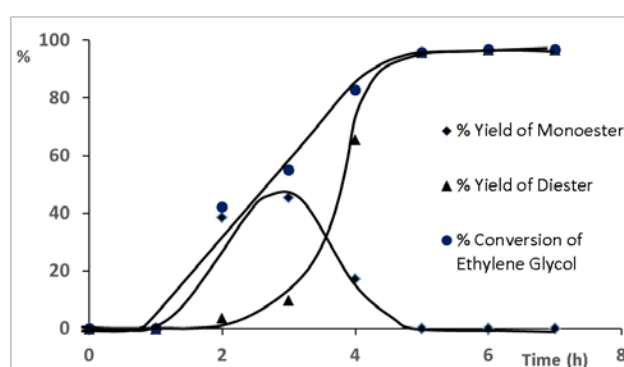
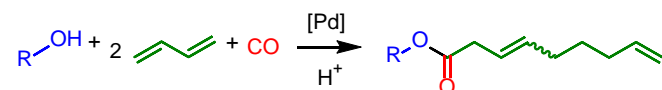


Figure 1. Carbonylative telomerization reaction with ethylene glycol. Reaction conditions : Ethylene glycol (1.6 mL, 0.029 mol), butadiene (7 eq. per ethylene glycol), benzoic acid (0.3 eq./ethylene glycol), dioxane (9.0 mL), Pd(OAc)₂ (0.01 eq./ethylene glycol), PPh₃ (4 eq./Pd), undecane (1.0 mL), 25 bar CO, T = 90°C.

After 1 hour, the ethylene glycol starts to be converted into its monoester. The yield in monoester rapidly reaches a maximum of 42 % after 2.5 hours, after which it is converted into diester, reaching full selectivity after 5 hours. At the maximum rate of ethylene glycol conversion, the turn over frequency of the reaction is 40 mol.h⁻¹.

Following this, the scope of the carbonylative telomerization reaction has been extended to polyols derived from agrosources (diols, triols and tetraols, Table 3).

Table 3. Carbonylative telomerization of butadiene with agrobased polyols. ^[a]

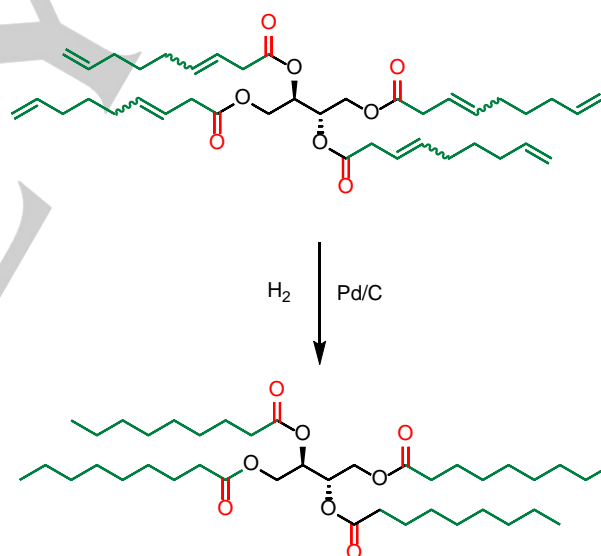


Entry	Polyol	Isolated Yield ^[b]
1		76 %
2		86 %
3		81 %
4		94 %
5		94 %
6		86 %
7		36 %

^[a] Conditions: polyol (10mmol), butadiene (3.5 eq per hydroxyl group), Pd(OAc)₂ (0.5% mol per hydroxyl group), PPh₃ (4 eq/Pd), benzoic acid (0.15 eq per hydroxyl group), 40 bar CO, dioxane (3.0mL), T = 90°C, t = 20h; ^[b] Isolated yield of the per-esterified product : diester for entries 1-5, triester for entry 6, tetraester for entry 7.

In addition, as further substrates, 1,3-propanediol, 1,4-butanediol and 2,3-butanediol have been selected, as they are accessible from bio-based resources. The first two, 1,3-propanediol and 1,4-butanediol, which are primary alcohols, show a similar behaviour with the model substrate ethylene glycol regarding their reactivity towards carbonylative telomerization. The corresponding diesters were obtained with 76 % and 86 % isolated yields (Table 3, entries 1 and 2).

Conversely, 2,3-butanediol bears more sterically hindered secondary alcohols, which should hinder its efficient conversion. However, to our delight, the corresponding diester was obtained with a 81 % yield, comparable to that obtained with 1,3-propanediol and 1,4-butanediol (Table 3, entry 3). This prompted us to study the catalytic conversion of the anhydrohexitols isomannide and isosorbide (secondary alcohols). Isosorbide is particularly relevant as this chiral diol is industrially produced from glucose through a hydrogenation / dehydration two-steps process. ^[22] Among its various applications, ^[23] it is used as a precursor for the production of isosorbide-based diesters that are relevant bio-based plasticizers. ^[24] Isomannide and isosorbide show a very interesting reactivity: they are fully converted into the corresponding diesters that can be isolated in high yield (Table 3, entries 4 and 5). This synthetic pathway is attractive as it allows the synthesis of isosorbide diesters from butadiene and carbon monoxide according to a highly atom-economical process, a major advance compared to prior methods. Finally, higher polyols were also converted according to the same protocol. Glycerol that bears both primary and secondary alcohols functions was fully converted into the corresponding triester in high isolated yield. Erythritol was also converted in the corresponding tetraester with 36 % isolated yield.



Scheme 2 Hydrogenation of the erythritol tetraester. Reaction conditions : erythritol tetraester (100 mg, 0.15 mmol), Pd/C (6.4 mg, 0.04 eq.), 30 bar H₂, 1:1 DCM: methanol (2 mL), 40°C, 5 days.

The ¹H-NMR spectrum of this compound showed a high complexity due to the presence of Z/E mixtures. In order to get simpler ¹H NMR spectra and thus better assess the structure of the tetraester, the isolated compound was fully hydrogenated with Pd/C catalyst into the tetranonanoate derivative of erythritol (Scheme 2). The ¹H NMR of this species is fully in line with a symmetric structure (see Supporting Information). Beyond the interest in product characterization, this demonstrates how the

unsaturated chains can be further converted, affording additional compounds following the carbonylative telomerization reaction.

Conclusions

In this contribution, we have shown that the carbonylative telomerization reaction is an efficient catalytic transformation for the synthesis of esters from agrobased alcohols, CO and butadiene. The most efficient system in our hand combines palladium acetate, a monophosphine ligand and an acid. Weak acids are particularly efficient co-catalysts: benzoic acid or acetic acid can be used for instance, affording excellent catalytic performances. Regarding the ligand associated to palladium, non-sterically hindered triarylphosphines that bear electron-donating groups on the para-position give superior yields in products of reaction with ethanol as model substrate. In order to provide the synthetic community with a simple catalytic system which comprises readily accessible and economically competitive constituents, we optimized reaction conditions with the $\text{PPH}_3/\text{Pd}(\text{OAc})_2/\text{benzoic acid}$ combination. With a metal loading of 0.5%, this has been efficiently used to convert several monoalcohols, diols and higher polyols, which are mostly derived from agroresources. Industrially-relevant alcohols with primary or secondary alcohols such as isosorbide and glycerol have been efficiently converted in the corresponding diester and triester with high isolated yields. On the top of that, glycerol and erythritol can also be converted into their fully esterified analogue. Thus, we have demonstrated that a wide range of alcohols can be efficiently combined with carbon monoxide and butadiene to selectively yield the corresponding esters with C9 side chains. The substrate scope described here comprises a significant share of biosourced alcohols. Combined with the considered reaction high atom-economical character, it highlights the sustainable character of this approach. This is of high interest, especially when targeting novel products that can find industrial applications, from plasticizers to detergents, with a lesser environmental impact compared to fossil fuel-derived analogues.

Acknowledgements ((optional))

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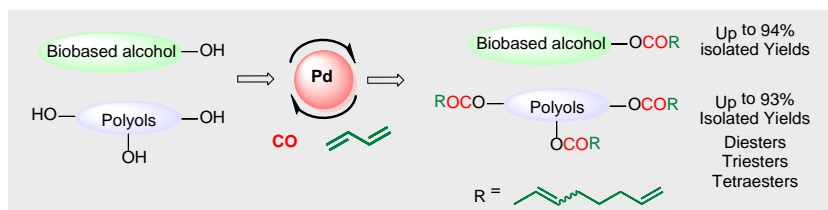
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Title

The palladium catalysed carbonylative telomerization reaction of agro-based alcohols with butadiene allows an efficient and atom-economical access to the corresponding unsaturated alkyl nona-3,8-dienoate esters.