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Research Paper

Palladium-catalyzed methoxycarbonylation of a commodity CO_2-sourced δ-valerolactone

Hussein Tabaja [a], Bruno Grignard [b], Christophe Detrembleur [b,c], Matthias Beller [d], Sophie M. Guillaume [a,*], Jean-François Carpentier [a,*]

[a] Univ Rennes, CNRS, Institut des Sciences Chimiques de Rennes, Rennes F-35042, France
[b] Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liege, Sart-Tilman B6a, Liege 4000, Belgium
[c] WEL Research Institute, Avenue Pasteur 6, Wavre 1300, Belgium
[d] Leibniz Institute for Catalysis e. V. at the University of Rostock, Rostock 18059, Germany

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ABSTRACT

The methoxycarbonylation of 3-ethylidene-6-vinyltetrahydro-2*H*-pyran-2-one (EVP), a commodity δ-valerolactone prepared by telomerization of CO_2 with butadiene, is reported. The py^{t}bpx ligand proved instrumental to achieve successful formation of the new carbonylation product **11**.

1. Introduction

Carbon dioxide (CO_2) is a carbon source which is not only stable and available in large amounts, which yet features also a regenerative character due to its integration in a natural cycle. It is therefore quite an attractive building block for 'green chemistry'. Among the many processes using CO_2 as a C1 feedstock described over the past decades, the telomerization of CO_2 with butadiene has attracted a large interest [1,2]. This reaction, initially reported in the 1970s [3], leads to a highly functionalized δ-valerolactone, namely 3-ethylidene-6-vinyltetrahydro-2*H*-pyran-2-one (EVP, 1). This telomerization reaction has been intensively investigated and optimized over the years to reach a selectivity for EVP above 95 % [1]. It is best performed using homogeneous palladium catalysts bearing tris(*p*- or *o*-methoxyphenyl)phosphine (TOMPP) [4], as developed at a miniplant scale by the group of Behr, with recycling of by-products and achieving an overall butadiene conversion of 45 % [1]. Although EVP did not find by itself an application yet, it constitutes an attractive platform molecule with various reactivities thanks to its lactone group and two terminal and internal C=C double bonds. Many molecular and macromolecular conversion processes have been investigated from EVP to access new secondary products of potential industrial relevance [1].

One particular interest of EVP is its use as monomer [5]. Direct chain-growth polymerization of EVP, either by ring-opening polymerization (ROP) of the lactone or by radical processes involving the C=C bonds have been described; yet, their implementation often turned out more difficult than anticipated [6,7]. Another possible strategy implies the further hydroesterification of EVP to access diesters and triesters which could serve in turn as di/trifunctional monomers for step-growth polymerizations (via reactions with diols, diamines, etc.). Yet, to date, only a limited number of reports on the carbonylation of EVP has been published. The group of Behr reported that the Rh-Biphephos-catalyzed hydroformylation of EVP proceeds readily (0.1 mol % Rh, 90 °C, 5 bar syngas) and selectively at the terminal vinyl group to provide the corresponding linear aldehyde in 95 % yield [1]. This was successfully extended to hydroaminomethylation of EVP by using the same Rh-Biphephos catalyst system in the presence of morpholine [1]. On the other hand, Behr *et al.* reported on unsuccessful attempts to perform hydroesterification of EVP in the presence of 0.4 mol- % of $Pd(OAc)_2$, a PPh_3-to-Pd ratio of 4:1, a tenfold excess of *p*-toluenesulfonic acid (PTSA) as promotor, 35 bar CO at 75 °C for 2 h with the pure alcohol as solvent. In fact, in all experiments, no carbonylation product but only the products of (acid-catalyzed) alcoholysis/ring opening of EVP were formed (*i.e.*, **6** and **8**, in Scheme 2) in quantitative conversion with primary alcohols and a much lower one with secondary alcohols [1]. The authors noted that "*the assumption that the* C=C *double bonds of the cleaved δ-lactone are no more active for any carbonylation reaction was disproved by successful hydroformylation of the isolated cleavage product yielding the corresponding linear aldehyde*" [1]. Thus, the reason why

* Corresponding authors.
E-mail addresses: sophie.guillaume@univ-rennes.fr (S.M. Guillaume), jean-francois.carpentier@univ-rennes.fr (J.-F. Carpentier).

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palladium remains inactive remained unclear. In 2017, Beller *et al.* showed that effective conversion of EVP into unsaturated C10 diesters **10** (as *E/Z* mixtures) can be achieved through a domino alcoholysis/allylic substitution/carbonylation reaction using different primary alcohols (Scheme 1) [8]. The use of a catalytic system based on a Pd precursor bearing chloride ions (typically $PdCl_2$), a chelating phosphine bearing electron-withdrawing groups (IPhos) and an acidic promoter (PTSA, or methylsulfonic acid (MSA), or H_2SO_4), proved to be the key for the selective conversion of EVP, with yields in **10** up to 91 %.

In the present work, we have re-investigated the methoxycarbonylation of EVP using different catalyst systems based on phosphine-type ligands which have recently offered remarkable performances in challenging carbonylation reactions [9–12]. We demonstrate that the use of a unique diphosphine, py^{t}bpx ("LikatPhos") in combination with $Pd(OAc)_2$ and an acidic promoter, enables generating an effective catalyst system that provides in significant yields another type of carbonylation product, namely the methoxylated diester compound **11** (Scheme 1).

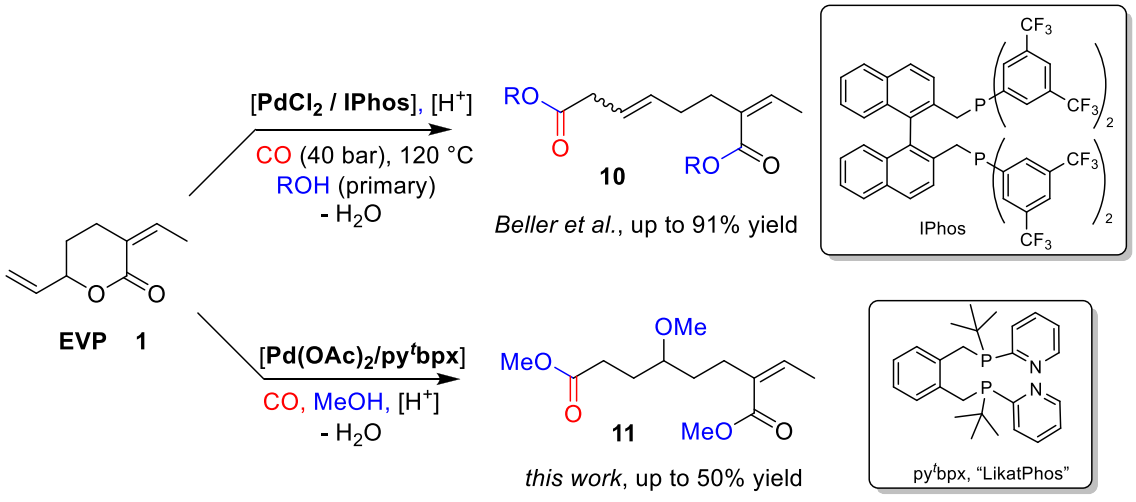
2. Results and discussion

The hydroesterification of EVP was explored using Pd catalyst precursors combined with an acidic promotor (trifluoroacetic acid (TFA), *p*-toluenesulfonic acid (PTSA), or methylsulfonic acid (MSA)) and several phosphine ligands including a reference one (PPh_3) and ubiquitous ones which have been reported much more effective in alkoxycarbonylation reactions of C=C and C≡C bonds: 2-pyridyldiphenylphosphine (2-$PyPPh_2$) [9], Xantphos [10], 1,2-bis(di-*tert*-butylphosphinomethyl) benzene (1,2-DTBPMB) [11], and 1,2-bis((*tert*-butyl(pyridin-2-yl)phosphanyl)methyl)benzene (py^{t}bpx, "LikatPhos") [12] (Chart 1). For the sake of simplicity, we decided to use methanol as nucleophile in these carbonylation reactions of EVP, even though – as aforementioned – a primary alcohol would necessarily induce concomitant or even preliminary alcoholysis of the lactone ring.

2.1. Preliminary identification of the nature of the different reaction products and intermediates

Crude mixtures resulting from the methoxycarbonylation of EVP proved actually complex in composition, due to the diversity of the products formed and the presence of several isomers associated to the positioning of the C=C bonds in several of these compounds. The different products identified are depicted in Scheme 2. Their analysis was performed by a combination of different techniques: high-resolution mass-spectroscopy with electrospray ionization (ESI-HRMS), GC–MS with electronic impact (EI) ionization, and $^1H/^{13}C$ NMR spectroscopy (see the Supp. Info.). The nature of the main products was confirmed by (HR)MS and NMR analyses after isolation by column chromatography and/or by comparison with data from previous reports [8] or independently prepared pure compounds.

In fact, in line with previous reports [1,8], in all reactions performed in the present study, almost all the detected products resulted from the ring opening of the lactone ring. Compounds **2**/**3**, arising from 'direct' mono-methoxycarbonylation of EVP, *i.e.* without ring opening, were almost always observed in minute amounts (0–4 mol %). Also, the bis-methoxycarbonylated compound **4** was detected only once as traces by HRMS (see Fig. S13 in the Supp. Info.). The main carbonylation product that could be successfully prepared under optimized conditions is methoxy-diester **11**; it results from the methoxycarbonylation of allylic methyl ether **8** (*vide infra*), itself arising from the corresponding allylic alcohol **6** obtained upon methanolysis of EVP [1]. These three compounds – **6, 8** and **11** – were authenticated by GC–MS / HRMS techniques, and **6** and **11** were independently isolated from reaction mixtures and further characterized by 1D and 2D NMR spectroscopy (see



Scheme 1. Diester products **10** and **11** resulting from the methoxycarbonylation of EVP (**1**) with different catalyst systems (Beller *et al.*, [8] and this work).

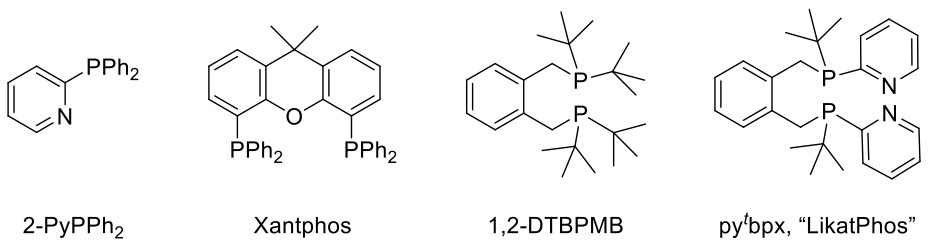
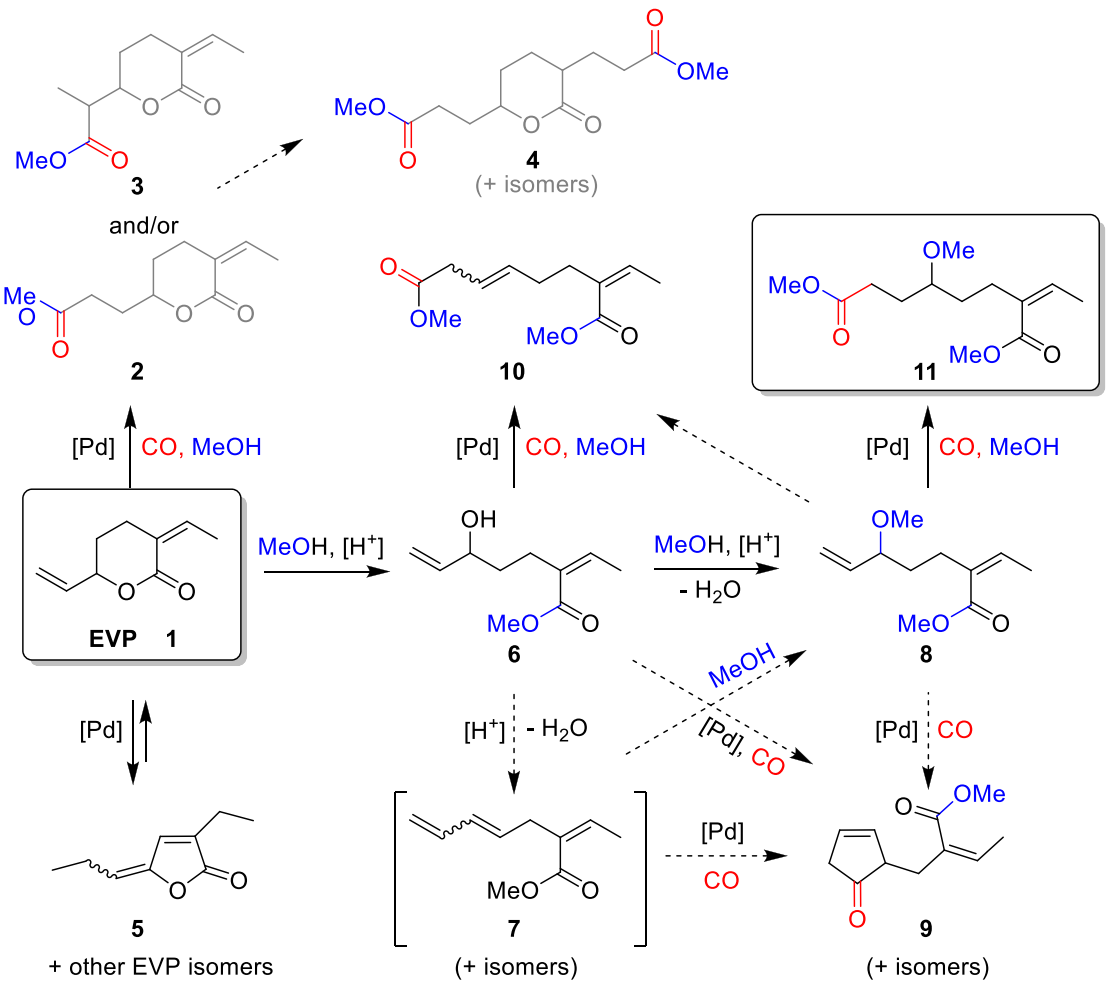


Chart 1. Ligands explored in the present study on Pd-catalyzed methoxycarbonylation of EVP.



Scheme 2. Main products formed in the Pd-catalyzed hydroesterification of EVP (**1**) in methanol. Note that different C=C bond position isomers may be envisioned for several products such as EVP isomerization products **5**, as well as **7** and **9**.

Figs. S2,S3,S7,S10–S12 in the Supp. Info.). Another carbonylation product observed by GC–MS, in significant yet smaller amounts than **11**, is diester **10** (Fig. S10)[1]; this is the product described and optimized by Beller *et al.* [8] that results from allylic substitution/carbonylation of allylic alcohol **6** and/or ether **8** [10]. The diene **7** was observed by GC–MS(EI); it results from dehydration of **6**, which is promoted by the acidic reaction medium; it also forms in the GC injector and/or upon EI ionization by demethoxylation of **8**. EVP isomers **5**, previously reported by Behr *et al.* in other Pd-catalyzed reactions of EVP [1], and several isomers of a putative cyclopentenone **9** (not isolated, identified by GC–MS; see Fig. S11) are the main products that account for the balance of the reaction.

2.2. Confirmation of the nature of reaction products via subsequent hydrogenation of reaction mixtures

In order to further corroborate the identity of the aforementioned products formed in the methoxycarbonylation of EVP and to ensure the validity of the analytical protocols, the subsequent hydrogenation of a representative crude reaction mixture (Table 1, entry 18; *vide infra*) was conducted (Scheme 3). Using Pd/C as catalyst, in methanol, with 50 bar H_2 at room temperature, all regular C=C bonds were fully hydrogenated, while those in α position of the ester groups (*i.e.* the crotonate-type ones) were only slightly affected under these conditions. Thus, the mono- or di-hydrogenated analogues of **6**–**10**, namely **6-H$_2$**, **7-H$_4$**, **8-H$_2$**, **9-H$_2$** and **10-H$_2$**, were produced, analyzed by GC–MS and HRMS, and, for some of them, further isolated by column chromatography and characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (see Figs. S4–S6 and S15,S16 in the Supp. Info.). Besides, small amounts of **8-H$_4$** and **11-H$_2$** were formed, as corroborated by ^{1}H NMR, HRMS and GC–MS.

2.3. Methoxycarbonylation catalysis

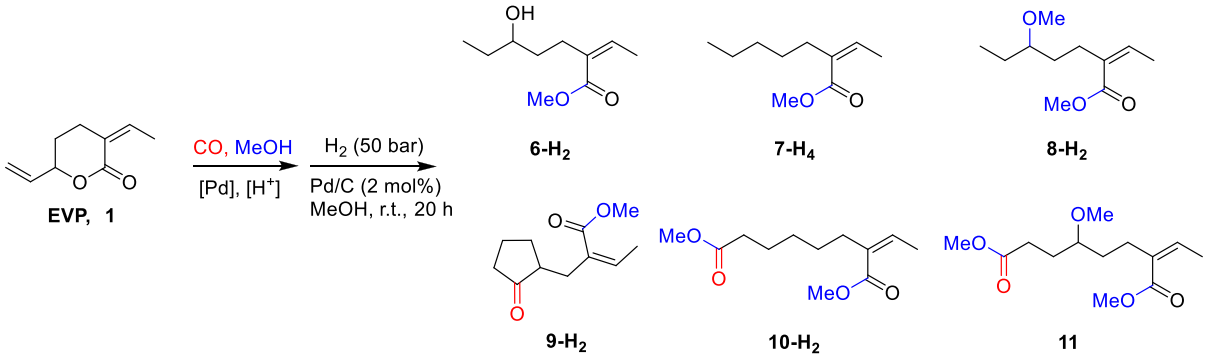
With these analytical protocols in hands, we explored the methoxycarbonylation of EVP under a variety of conditions; the most representative results obtained are gathered in Table 1. Initial attempts conducted with simple ligands like PPh_3 or 2-$PyPPh_2$ combined with Pd$(OAc)_2$, Pd$(acac)_2$ or $PdCl_2$ in the presence of various acidic/protic promotors under a range of reaction conditions (70–140 °C) returned no or minimal amounts ($\leq$ 2 mol %) of methoxycarbonylation products **2, 3, 10** and **11** (entries 2–6). Besides variable amounts of EVP isomers, and ring-opening products **6, 7** and **8**, cyclopentenone derivative **9** (as a mixture of isomers) was formed in *ca.* 25 % yield (as determined by GC analysis; Table 1, entries 4, 5). Compound **9** presumably originates from the carbonylation of diene **7** or its parent allylic alcohol **6**; for instance, Larock *et al.* have reported the carbonylation of dienyl triflates to

[1] As described by Beller *et al.*, diester **10** occurs as the linear isomer depicted in Scheme 2 (as a mixture of *E* and *Z* isomers), since the carbonylation reaction of allyl alcohols/ethers proceeds through typical π-allyl/Pd intermediates, and only the linear carbonylation product has been shown to be produced both from the linear and the branched allyl alcohols/ethers (see [8,10]).

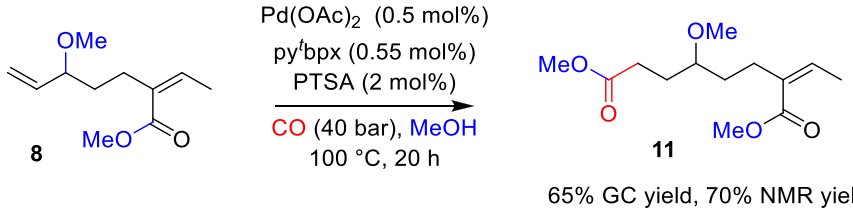
Table 1
Pd-catalyzed methoxycarbonylation of EVP (**1**).[a].

Entry	Pd precursor (mol %)	Ligand (mol %)	Additive (mol %)	MeOH (mL)	Solvent (mL)	Temp (°C)	Time (h)	EVP conv (%)	**5**	**2/3**	**6**	**7**	**8**	9	10	11
1	–	–	–	2	–	120	20	23	–	–	23	–	–	–	–	–
2	$Pd(OAc)_2$ (1.5)	PPh_3 (8)	PTSA (4)	2	Toluene (2)	100	20	80	18	–	–	6	53	3	–	–
3	$Pd(acac)_2$ (1)	2-$PyPPh_2$ (4)	–	2	–	120	20	80	38	–	33	3	–	6	–	–
4	$Pd(acac)_2$ (5)	2-$PyPPh_2$ (20)	–	2	–	120	20	100	52	2		12	5	25	–	–
5	$PdCl_2$ (1)	2-$PyPPh_2$ (8)	H_2O 1 drop	0.5	Dioxane (1.5)	120	20	100	66	–	–	7	–	27	–	–
6	$Pd(acac)_2$ (0.05)	2-$PyPPh_2$ (0.4)	PTSA (0.8)	2	–	120	20	47	–	–	35	4	8	–	–	–
7	$Pd(OAc)_2$ (1)	Xantphos (1.1)	TFA (1)	2	Toluene (12)	105	22	96	57	1	–	6	13	19	–	–
8	$Pd(OAc)_2$ (1)	Xantphos (1.1)	TFA (10)	0.3	Toluene (12)	105	22	98	27	2	–	54	–	15	–	–
9	$Pd(OAc)_2$ (2)	Xantphos (2.2)	TFA (10)	0.3	Toluene (12)	105	22	99	41	2	–	20	–	36	–	–
10	$Pd(OAc)_2$ (1)	Xantphos (1.1)	PTSA (4)	2	Toluene (2)	100	22	100	–	–	–	9	86	5	–	
11	$Pd(OAc)_2$ (1)	DTBPMB (1.1)	PTSA (4)	2	Toluene (2)	100	22	82	–	2	39	4	34	–	3	
12	$Pd(OAc)_2$ (0.5)	DTBPMB (0.55)	PTSA (2)	2	Toluene (2)	100	22	100	–	4	77	3	10	–	6	–
13	$Pd(OAc)_2$ (1)	py^{t}bpx (1.1)	TFA (1)	2	Toluene (12)	100	22	8	–	–	8	–	–	–	–	–
14	$Pd(OAc)_2$ (1)	py^{t}bpx (1.1)	MSA (4)	2	Toluene (2)	100	22	100	–	–	–	4	52	18	2	24
15	$Pd(OAc)_2$ (1)	py^{t}bpx (1.1)	PTSA (4)	2	Toluene (2)	120	22	100	–	–	–	28	52	5	–	15
16	$Pd(OAc)_2$ (1)	py^{t}bpx (1.1)	PTSA (1)	2	Toluene (2)	100	22	70	–	13	6	36	8	5	2	–
17	$Pd(OAc)_2$ (1)	py^{t}bpx (1.1)	PTSA (8)	2	Toluene (2)	100	22	100	–	2	9	26	7	29	–	27
18	$Pd(OAc)_2$ (0.5)	py^{t}bpx (0.55)	PTSA (2)	2	Toluene (2)	100	22	100	–	4	–	5	17	13	8	53[b]
19[c]	$Pd(OAc)_2$ (0.5)	py^{t}bpx (0.55)	PTSA (2)	4	-[c]	100	22	100	–	1	5	2	73	–	4	15
20	$Pd(OAc)_2$ (0.5)	py^{t}bpx (0.55)	PTSA (2)	2	THF (2)	100	22	100	–	3	5	2	73	4	–	13
21	$Pd(acac)_2$ (0.5)	py^{t}bpx (0.55)	PTSA (2)	2	Toluene (2)	100	22	100	–	13	13	2	52	8-	–	12
22[d]	$Pd(OAc)_2$ (0.5)	py^{t}bpx (0.55)	PTSA (2)	2	Toluene (2)	100	22	100	–	–	6	2	87	–	–	5[d]

[a] General conditions unless otherwise stated: EVP (0.60 g, 4.0 mmol), $Pd(OAc)_2$ (0.020 mmol, 0.5 mol % vs. EVP), ligand (0.022 mmol, 0.55mol %), additive (e.g. PTSA, 13.8 mg, 0.080 mmol, 2.0 mol %), methanol (2.0 mL) + co-solvent (e.g. toluene, 2.0 mL), 40 bar CO; conversion of EVP and relative selectivities (normalized at 100 %) of the main products formed, as determined by GC–MS and GC-FID (see the Experimental section).
[b] 48 % yield for **11** as determined by ^{1}H NMR of the crude reaction mixture, see the Supp. Info, Fig. S9.
[c] Reaction performed in neat MeOH.
[d] Reaction performed at 5 bar CO.



Scheme 3. Subsequent hydrogenation of a representative crude reaction mixture (Table 1, entry 18) to deliver the mono- or di-hydrogenated analogues of **6**–**10**, namely **6-H$_2$**, **7-H$_4$**, **8-H$_2$**, **9-H$_2$** and **10-H$_2$** (only the products resulting from the hydrogenation of simple C=C bonds are depicted, as the crotonate groups were only minorly affected under these conditions).



Scheme 4. Direct methoxycarbonylation of allyl ether **8*** into compound **11** (* a 93:7 mixture of **8** and EVP was used); other compounds observed include **6** (10 %), remaining **8** (11 %) and **10** (14 %) (GC yields).

cyclopentenones catalyzed by $Pd(OAc)_2$ in the presence of pyridine [13]. Experiments conducted with Xantphos returned essentially similar results, with **9** as the main product (up to 36 % GC yield, entry 9) when using TFA as protic/acidic promotor; with PTSA as promotor, small amounts (5 % GC yield) of **9** were observed besides large amounts of the parent allylic ether **8** (entry 10). Hence, all of these carbonylation reactions of EVP performed with PPh_3, 2-$PyPPh_2$ or Xantphos revealed neither effective nor selective. This is line with previous report on related chemistry [8].

Of interest, 1,2-DTBPMB has been reported over the years as one of the best ligands for achieving the Pd-catalyzed alkoxycarbonylation of various unsaturated compounds [11]. It is in particular best known for

the Lucite Alpha process toward methyl methacrylate developed by Eastham *et al.*, via methoxycarbonylation of ethylene using the Shell catalyst system $Pd(OAc)_2$/2-$PyPPh_2$/$MeSO_3H$ pioneered by Drent and co-workers for the methoxycarbonylation of alkynes [9]. However, when applied in the methoxycarbonylation of EVP, 1,2-DTBPMB returned also surprisingly disappointing results (Table 1, entries 11, 12). In fact, although the parallel, undesired isomerization of EVP could be almost completely tamed down (**5** $\leq$ 1 mol % GC yield), only minor amounts of the methoxycarbonylation product **10** were formed ($\leq$ 6 mol % GC yield). Depending on the amount of PTSA present in the medium, the reaction stagnated essentially at the intermediate products, that is allylic alcohol **6** (at low PTSA concentration) or its methoxylated derivative **8** (at higher PTSA concentration).

Use of the related py^{t}bpx ligand [12] allowed much better performance for the desired carbonylation process, with formation of the methoxylated diester **11**. With this Pd/ligand system, water or TFA (Table 1, entry 13) proved ineffective promotors and the formation of **11** was observed only upon using the more acidic MSA (entry 14) or PTSA (entries 15–17); this is line with previous observations in related alkene carbonylation processes with other state-of-the-art Pd/(di)phosphine catalyst systems assisted with acidic promoters [8,9,11,12,14]. The PTSA-to-$Pd(OAc)_2$/py^{t}bpx ratio proved quite important: formation of **11** was observed only if PTSA was in excess (2–8 equiv; entries 14,15,17), in sharp contrast to an experiment conducted at a 1:1:1 ratio (entry 16).[2] The concentration of the acidic promoter in the reaction medium seems also to play an important role on the product distribution: at high PTSA concentration (8 mol %, entry 17), the formation of **11** is plagued by the formation of equal amounts of side-product **9** (27 % *vs*. 29 % GC yields, respectively). Under the optimized conditions, conducted using 0.5 mol % of $Pd(OAc)_2$/py^{t}bpx with 4 equiv (2.0 mol %) of PTSA (entry 18), compound **11** could be obtained in up to 53 % GC yield. The latter value is consistent with that determined by ^{1}H NMR analysis of the crude reaction mixture (*i.e.* 48 % NMR yield, see the Supp. Info, Fig. S9). Changing the reaction medium from methanol-toluene solutions to either neat methanol (hence more protic, entry 19) or using an aprotic polar solvent (THF, entry 20) led to a decrease of the yield of **11**. Also, replacing the palladium precursor $Pd(OAc)_2$ by $Pd(acac)_2$ or reducing the CO pressure at 5 bar reduced the catalytic activity, resulting also in lower yields for **11** (compare entries 18, 21 and 22).

Of note, in most reactions conducted with the $Pd(OAc)_2$-py^{t}bpx-PTSA system, the final reaction mixtures were essentially clear, deep yellow-colored, but did always contain variable, usually small amounts of Pd black, indicating partial catalyst decay. The reactions conducted in neat MeOH and in THF led to larger amounts of Pd black.

The $Pd(OAc)_2$-py^{t}bpx-PTSA system has also been probed in the ethoxycarbonylation of EVP using EtOH instead of MeOH. Detailed results are reported in the Supporting Information (Scheme S2, Figs. S19–S21). This resulted in a similar speciation as the one observed in the methoxycarbonylation of EVP, that is the formation of the ethoxy analogous products, namely allyl alcohol **6-OEt** (6 %), diene **7-OEt** (12 %), allyl ether **8-OEt** (54 %), and of the two ethoxycarbonylated products **10-OEt** (15 %) and **11-OEt** (12 %). Hence, this reaction with EtOH proceeded somewhat more slowly than with MeOH, returning lower amounts of **11-OEt** and larger amounts of the putative intermediate allyl ether **8-OEt** (54 %).

2.4. Mechanistic considerations

Considering the large amounts of allyl ether compound **8** generated under the acidic reaction conditions (see Table 1), we envisioned that this compound could be an intermediate towards the carbonylation product **11**. Actually, we checked that **8**, independently prepared from EVP [15], is converted to **11** in 65 %(GC)–70 %(NMR) yield under the optimized catalytic conditions (Scheme 4). This latter yield in **11** from methoxycarbonylation of **8** is higher than that obtained from EVP (up to ca. 50 %); this can be rationalized by the decreased formation of unwanted products **6** and **7** that arise from EVP and also by the prevented formation of **9** (which is not observed in process of Scheme 4).

The above results (Table 1 and Scheme 4) indicate that the methoxycarbonylation of EVP mediated by the $Pd(OAc)_2$/py^{t}bpx/H^+ (H^+ = PTSA, MSA) system always generates preferentially the methoxy-diester compound **11** as compared to the unsaturated diester **10**; they also suggest that product **11** is obtained by methoxycarbonylation of intermediate **8**. Previously, Beller *et al.* suggested that, in the methoxycarbonylation of EVP mediated by the $PdCl_2$/IPhos/H^+ ($H^+ = H_2SO_4$, PTSA, MSA) system under otherwise very similar reaction conditions than those used in the present study (Scheme 1), unsaturated diester **10** originates from the allylic substitution/carbonylation of allylic ether **8** [8]. The fact that the methoxy group in allylic ether **8** is retained in methoxy-diester product **11** suggests that methoxycarbonylation with the $Pd(OAc)_2$/py^{t}bpx/H^+ does not proceed through π-allyl-Pd species, but rather by direct methoxycarbonylation of the terminal C=C bond via a regular 'hydride mechanism' involving a Pd–H species (acid-promoted; see Scheme S1 in the Supp. Info.) [16]. Hence, the different selectivity (towards **11** or **10**) observed in the two different processes would originate from a different reactivity of each catalyst system towards the same intermediate compound **8**. Beller *et al.* stated that the presence of chloride ions in the palladium precursor is apparently necessary for selective formation of **10**, presumably to ensure the formation of a sufficiently stable catalytically active species [8]. This is not the case with $Pd(OAc)_2$ and this may contribute to a different reactivity. Another obvious, possibly more important parameter of the catalyst system is the diphosphine ligand. IPhos, identified among the NaPhos family as the best ligand to afford **10** from EVP [8], bears electron-withdrawing groups. Conversely, py^{t}bpx, another large bite angle, yet more basic diphosphine was designed to bear both sterically hindered and amphoteric groups on the P-atoms [12]; in particular, the 2-pyridyl group [17] is aimed at acting as a proton-shuttle for the alcohol, to facilitate in turn the (rate-determining) alcoholysis of the Pd–acyl species [18] (Scheme S1). We surmise this is the key feature that enables the formation of **11** from EVP via **8** with the py^{t}bpx-based system.

In conclusion, we have established another methoxycarbonylation reaction of the important platform compound EVP. Remarkably, upon using a palladium catalyst based on the 2-pyridyl-substituted py^{t}bpx ligand and $Pd(OAc)_2$ as precursor, the latter process provides a different carbonylation derivative than that previously reported. The formation of methoxy-diester product **11**, in selectivities up to *ca.* 50 % from EVP but up to *ca.* 70 % from previously prepared allyl ether **8**, shall pave the way towards other carbonylation-type transformation processes of the important EVP and related allyl ethers.

CRediT authorship contribution statement

Hussein Tabaja: Writing – original draft, Investigation, Formal analysis, Data curation. **Bruno Grignard:** Writing – original draft, Funding acquisition, Conceptualization. **Christophe Detrembleur:** Writing – original draft, Funding acquisition, Conceptualization. **Mathias Beller:** Conceptualization. **Sophie M. Guillaume:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Formal analysis, Conceptualization. **Jean-François Carpentier:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Funding acquisition, Formal analysis, Conceptualization.

[2] Note that under these less acidic conditions, expectedly, a maximal 13% selectivity for **2**/**3**, *i.e.* the mono-methoxycarbonylation of EVP without ring opening of the δ-lactone was reached.

Declaration of competing interest

The authors have nothing to declare.

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Supplementary materials

Supporting Information available: General conditions, typical procedure for methoxycarbonylation of EVP, synthesis and NMR, GC–MS, ESI-HRMS characterization of reaction compounds (39 pages).

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2025.115376.

Data availability

Data will be made available on request.

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