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Catalytic carbonylation of 4-penten-1-ol to ε-caprolactone and oligocaprolactone

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Abstract

A catalyst consisting of $Pd_2(dba)_3$ + 2 XANTPhos (dba = dibenzylideneacetone, XANTPhos = 9,9-dimethyl-4,5-bis(diphenylphosphino) xanthene) in toluene catalyzes the alkoxycarbonylation of 4-penten-1-ol to form the cyclic products ε-caprolactone and 2-methylvalerolactone, as well as oligocaprolactone. The conversion and selectivity observed using this catalyst is higher than that observed with other reported systems with the regioselectivity for terminal carbonylation exceeding 70%.

Keywords: ε-Caprolactone; Carbonylation; Palladium catalyst; Carbon monoxide; Lactones

1. Introduction

Transition metal-catalyzed carbonylation reactions have been extensively studied for the formation of both small molecules and polymeric materials [1–7]. Of particular interest has been the use of palladium-based catalysts for the formation of esters and lactones. Recently, research has been done on a methoxycarbonylation system utilizing (D*t*BPX)Pd(dba) + MSA as a promoter (D*t*BPX = bis(di-*tert*-butylphosphino)-ortho-xylene, MSA = methanesulfonic acid) for the synthesis of methyl propionate from ethene, CO and methanol [8–12]. In contrast to this intermolecular esterification of alkenes, most of the research on lactone formation to date has focused on the formation of five-membered rings from the intramolecular carbonylation of allylic alcohols [13–22].

One particularly important lactone that is not a five-membered ring is ε-caprolactone. This lactone is used as a monomer for the production of numerous polyester-based products including sutures and plasticizers [23–25]. Currently, ε-caprolactone is synthesized mainly by the Baeyer–Villiger oxidation of cyclohexanone via a peroxyacid or hydrogen peroxide [26–29]. From an industrial standpoint, this is an undesirable process because it is not catalytic and the oxidation reaction results in the formation of a stoichiometric amount of acid, as well as some overoxidized byproducts [30–33].

Interestingly, there are some examples of the synthesis of seven-membered lactones by intramolecular cyclocarbonylation reactions. In one example, Alper and co-workers reported that 2-allylphenols could be selectively cyclocarbonylated to five- or seven-membered lactones using a catalyst consisting of either $[(Cy_3P)_2Pd(H)(H_2O)][BF_4]$ or $Pd(OAc)_2$ + 4 eq. dppb (dppb = 1,4-bis(diphenylphosphino)butane) in toluene, under an atmosphere of CO/H_2 [34,35]. More importantly, it was found in the patent literature that a catalyst system consisting of $(Ph_3P)_2PdCl_2$ + 4 eq. $SnCl_2$ in MIBK (MIBK = methyl isobutyl ketone) under an atmosphere of pure CO could catalyze the cyclocarbonylation of 4-penten-1-ol for the synthesis of ε-caprolactone with up to 77% selectivity [36]. However, few details of the reaction, its products, or how it compares to other alkoxycarbonylation systems were given.

Recently, there have been numerous reports in the patent literature of attempts to find a new route towards the synthesis of ε-caprolactone starting with 1,3-butadiene according to the proposed reaction shown in Scheme 1 [37–51].

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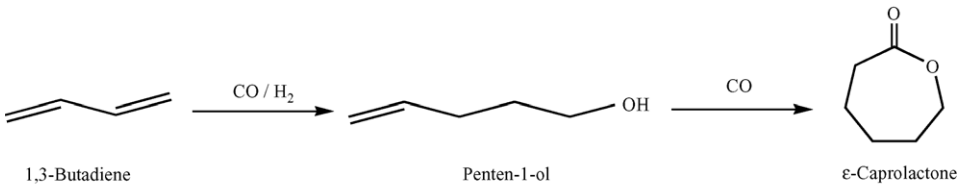


Scheme 1. Proposed synthesis of ε-caprolactone via a two-step sequence from 1,3-butadiene, carbon monoxide, and dihydrogen.

In this reaction sequence, the synthesis of ε-caprolactone is potentially catalytic and utilizes the relatively cheap starting materials of 1,3-butadiene, dihydrogen and carbon monoxide. With the exception of the $(Ph_3P)_2PdCl_2 + 4\,SnCl_2$ system, there are no reports to date on a possible catalyst for the second step of the above synthetic scheme. Herein we report progress towards a new synthetic method for the preparation of ε-caprolactone and polycaprolactone via the carbonylation of 4-penten-1-ol.

2. Experimental

2.1. Materials

Toluene (ACS Grade) was dried over a Grubbs-type purification system and stored over molecular sieve packets (Aldrich) [52]. 4-Penten-1-ol (99%, Acros), *cis*-3-penten-1-ol (97+%, GFS), ε-caprolactone (99%, Acros) and 1,1,2,2-tetrachloroethane (TCE, 99%, Aldrich) were dried over CaH_2, distilled and degassed (freeze, pump, thaw) three times prior to use. Polycaprolactone (average 10k M_w, Aldrich), hexanes (ACS grade, EMS), isopropanol (ACS grade, EMS), toluene-d_8 ("100.0%", Aldrich) and triethylamine (99%, EM Science) were used as received. Tris(dibenzylideneacetone)dipalladium (0) ($Pd_2(dba)_3$), palladium (II) acetate ($Pd(OAc)_2$), tetrakis(acetonitrile)palladium(II) tetrafluoroborate ($(MeCN)_4Pd(BF_4)_2$), 9,9-dimethyl-4,5-bis (diphenylphosphino)xanthene (XANTPhos), alpha, alpha'-bis(di-*tert*-butylphosphino)-*ortho*-xylene (97+%) (D*t*BPX), tricyclohexylphosphine (97+%) (PCy_3), and 1,4-bis(diphenylphosphino)butane (dppb) were purchased from Strem and used as received. 2-Methylvalerolactone [53–55] and 2-ethylbutyrolactone [56] were synthesized according to literature procedures.

2.2. General experimental methods

All ^{1}H NMR (at ambient temperature), ^{13}C NMR (at ambient temperature), and ^{31}P NMR (at −80 °C) spectra were obtained on a Bruker DPX-300 spectrometer using an external capillary standard of 1,4-dioxane referenced to 66.9 ppm (^{13}C NMR) or standard of Xantphos referenced to −17.5 ppm (^{31}P NMR). Gas chromatography analysis was obtained on an Agilent 5890 Series II GC using a RTX-5 split capillary column (Restek) connected to an FID detector. Gel permeation chromatography was obtained on a Shimadzu size exclusion chromatograph using a flow rate of 1 mL/min and a three-column bed (Styragel HR 7.8 mm × 300 mm columns with a 5 μm bead size: 100–10,000, 500–30,000 and 5000–6,000,000 Da), a Shimadzu RID 10A differential refractometer and SPD-10A UV–vis detector. Samples were run in $CHCl_3$ at ambient temperature and calibrated to polystyrene standards obtained from Aldrich. All work involving air- and/or water-sensitive compounds was carried out using standard Schlenk and/or dry box techniques under a dinitrogen atmosphere.

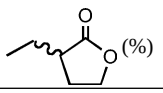
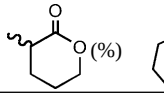
2.3. Synthesis of transesterification product

In a 100 mL round bottom flask, 100 mmol ε-caprolactone, 100 mmol 4-penten-1-ol and 200 mmol triethylamine were refluxed overnight. The products were then dissolved in 100 mL 5% HCl (aq) and purified by liq/liq extraction (3× 100 mL hexane). The slightly reddish solution was reduced under vacuum and purified by column chromatography (15% isopropanol: 85% hexanes). ^{1}H NMR ($CDCl_3$) (ppm): 5.72 (m, 1H), 4.96 (td, 2H), 4.01 (t, 2H), 3.53 (t, 2H), 2.25 (t, 2H), 2.01 (q, 3H), 1.56 (m, 6H), 1.32 (m, 2H); ^{13}C NMR ($CDCl_3$) (ppm) 173.77, 138.17, 115.57, 64.25, 62.14, 34.56, 32.88, 30.64, 28.47, 26.01, 25.37.

2.4. General procedure for the carbonylation of penten-1-ol

A mixture of 0.050 mmol $Pd_2(dba)_3$, 0.10 mmol XANTPhos, 10 mmol penten-1-ol, 2.0 mmol TCE (GC standard), and 15 mL toluene was added to a thin-necked glass liner. A small sample was removed for initial GC analysis. The glass liner was then placed in a 125 mL Parr high-pressure reactor, sealed and charged with 300 psi CO. The reactor was then placed on a 140 °C oil bath (100 °C internal temperature) for 3 h. The high pressure reactor was then removed from the oil bath, cooled in an ice bath, depressurized and analyzed by GC. To determine the polymer content of the reaction, the sample was subsequently placed in a scintillation vial, reduced under vacuum, dissolved in $CDCl_3$ and analyzed by ^{13}C NMR spectroscopy.

Table 1
Carbonylation of 4-penten-1-ol: comparison of catalyst systems[a]

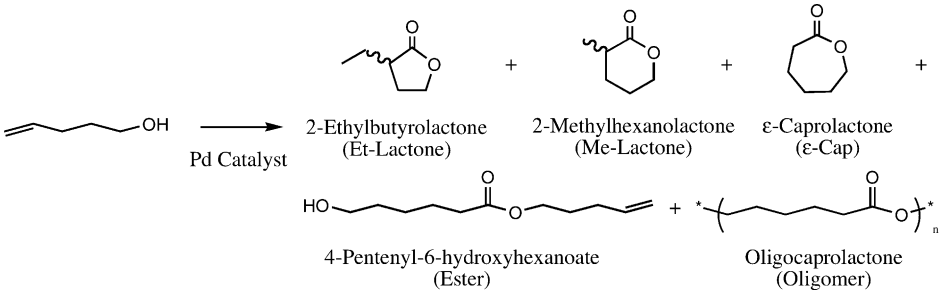
Run	Catalyst[a]	Solvent	Conversion[b] (%)	 (%)	 (%)	 (%)	Ester (%)	Oligomer[c] (%)
1	$Pd_2(dba)_3$ + XANTPhos	Toluene	62	0	17	16	13	16
2	$Pd(OAc)_2$ + XANTPhos	Toluene	41	0	11	10	18	2
3	$(MeCN)_4Pd(BF_4)_2$ + XANTPhos	Toluene	78	13	23	6	15	21
4	$Pd(OAc)_2$ + 4 dppb + 300 psi H_2	Toluene	<5	–	–	–	–	–
5	$(MeCN)_4Pd(BF_4)_2$ + 2 PCy_3 + 300 psi H_2	Toluene	<5	–	–	–	–	–
6	$(COD)PdCl_2$ + 2 PPh_3 + 4 $SnCl_2$	Toluene	27	5	3	3	16	0
7	$(COD)PdCl_2$ + 2 PPh_3 + 4 $SnCl_2$	MIBK	36	2	3	8	1	22
8	$Pd_2(dba)_3$ + D*t*BPX + 2 MSA	Toluene	<5	–	–	–	–	–
9	$Pd_2(dba)_3$ + D*t*BPX + 2 MSA	Anisole	99.5[d]	0	0.5	4.5	0.1	0

[a] Reaction conditions: 1% catalyst loading, 10 mmol 4-penten-1-ol, 0.2 mmol TCE (GC Std), 15 mL solvent, 300 psi CO, 100 °C, 3 h.
[b] Conversion determined by gas chromatography of the remaining penten-1-ol isomers. Lactone and ester products determined by gas chromatography.
[c] Oligomeric products determined by ^{13}C NMR analysis. Gel permeation chromatography analysis of the oligomeric species indicated that they all had a $M_w < 600$ as calibrated to polystyrene standards.
[d] 91.5% of the starting 4-penten-1-ol converted to valeraldehyde.

3. Results and discussion

3.1. Carbonylations of 4-penten-1-ol: comparison of catalytic systems

A catalyst system consisting of $Pd_2(dba)_3$ + 2 XANTPhos was found to produce ε-caprolactone and oligocaprolactone from 4-penten-1-ol in moderate yield and moderate selectivity in comparison to the other cyclic lactone products as shown in Eq. (1) (products of the Pd(II)-catalyzed carbonylation of 4-penten-1-ol). A comparison to other known carbonylation systems is shown in Table 1.



(1)

Since the ε-caprolactone, the ester, and oligocaprolactone are all formed through alkoxycarbonylation with the terminal regioselectivity, the desired regioselectivity for carbonylation exceeds 70% for entries 1 and 2, Table 1. The Alper system, which is useful for the cyclocarbonylation of 2-allylphenols, gave very low yields with the present substrate (entries 4 and 5). More importantly, the use of $(Ph_3P)_2PdCl_2$ (produced in situ from addition of $(COD)PdCl_2$ + 2 PPh_3) + 4 $SnCl_2$ under similar reaction also resulted in low yield and selectivity (entry 6). Moreover, using the more coordinating solvent of MIBK (methyl isobutyl ketone) reported in the patent did not result in a significant improvement (entry 7).

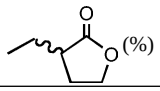
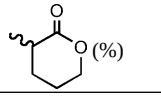
The current catalysts for the methoxycarbonylation of ethene to produce methyl propionate all utilize a sterically bulky bidentate phosphine-coordinated palladium catalyst that is activated by the addition of a strong acid such as a sulfonic acid to produce a palladium-hydride species, usually in an ether solvent [1–3,8–12,39–44,50–51]. The role of the ether solvents seems to be very important in stabilizing the acidic species as the same reaction run in toluene versus anisole resulted in very different results (entry 8 versus entry 9). However, the addition of acid to this catalyst species resulted in a very active alkene isomerization catalyst, isomerizing over 90% of the initial 4-penten-1-ol species to valeraldehyde.

3.2. The carbonylation of 4-penten-1-ol: variations of the catalyst system and mechanistic considerations

In order to further probe the reactivity of this carbonylation system, a series of control reactions were performed and are summarized in Table 2.

In the Alper systems for the cyclocarbonylation of allylphenol, the use of H_2 was necessary, presumably to form the starting palladium-hydride. In contrast, the $Pd_2(dba)_3$ + 2 XANTPhos system does not require the use of H_2, although its addition did significantly increase the substrate conversion without affecting the regioselectivity (Table 2, entry 1 versus entry 2).

Table 2
Variations in the catalyst system[a]

Entry	Catalyst system variation	Conversion (%)	 (%)	 (%)	 (%)	Ester (%)	Oligomer (%)
1	None (4-penten-1-ol as substrate, 300 psi CO, no acid)	62	0	17	16	13	16
2	300 psi CO and 300 psi H_2	98	0	31	27	9	35
3	*cis*-3-Penten-1-ol as substrate	16	2	6	1	6	1
4	*cis*-3-Penten-1-ol as substrate, 0.2 mmols MSA added	87	25	28	0	8	26
5	2 eq. MSA added to Pd catalyst	99	4	9	3	6	77
6	ε-Caprolactone as substrate	<5	–	–	–	–	–
7	5 mmol 4-penten-1-ol and 5 mmol ε-caprolactone as substrates	56	0	4	43	5	4
8	Ester as substrate[b]	22	0	0	0	17	5
9	ε-Caprolactone as substrate, no Pd catalyst, 0.2 mmol MSA added	96	0	0	4	0	92
10	ε-Caprolactone as substrate, no Pd catalyst, 0.4 mmols $SnCl_2$ added	98	0	0	10	0	90

[a] Where not specified, reaction conditions same as in Table 1.
[b] 2.60 mmol starting material.

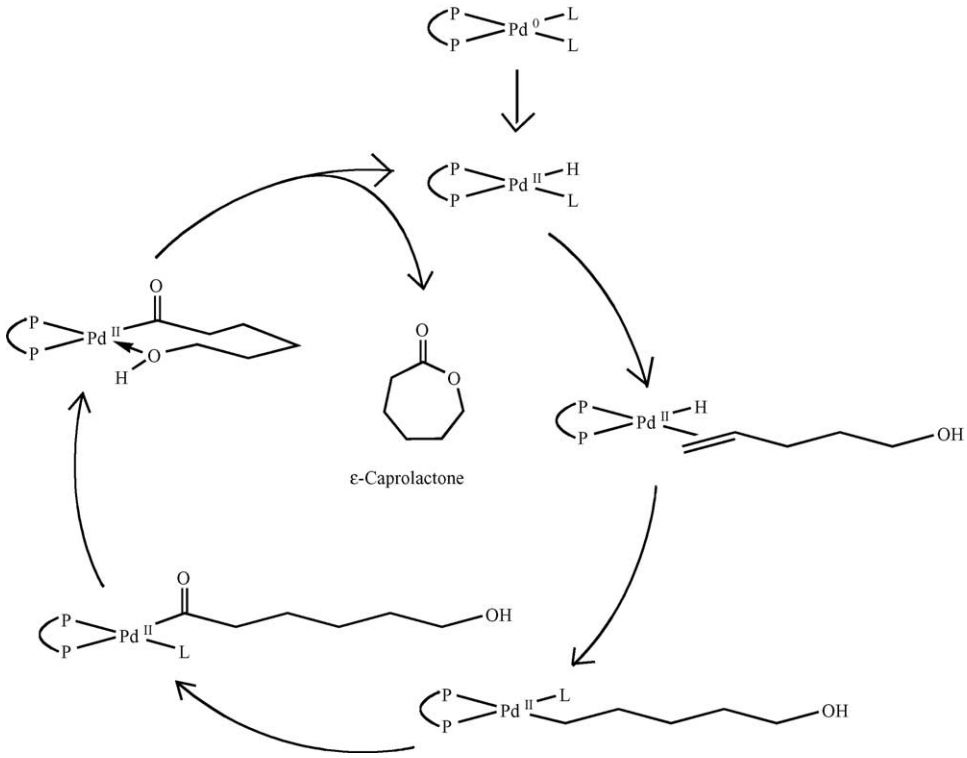
In comparison to the reactivity of the terminal 4-penten-1-ol, use of the internal isomer *cis*-3-penten-1-ol produced a significantly lower amount of carbonylation products and with a higher selectivity toward the five- and six-membered lactone rings (entry 3). This suggests that the rate of isomerization of the C=C bond is slow compared to the carbonylation reaction. In order to promote the isomerization, an acid was added to increase the concentration of palladium(II)-hydride species. Acids are also frequently added to palladium catalyst systems as promoters such as in the methoxycarbonylation systems [8–12]. Addition of 2 eq. MSA to *cis*-3-penten-1-ol as a substrate did significantly increase its reactivity, but still failed to produce the desired regioselectivity (entry 4). In comparison, the addition of 2 eq. MSA to 4-penten-1-ol resulted in increased conversion, predominantly to the oligocaprolactone (entry 5).

A reasonable mechanism for the $Pd_2(dba)_3 + 2$ XANTPhos carbonylation system is similar to that proposed by Alper and co-workers for the cyclocarbonylation of 2-allylphenols [34]. Shown in Scheme 2, the reaction starts with the formation of a palladium(II)-hydride species via oxidative addition of adventitious water or the ROH group. This palladium-hydride species then coordinates and inserts the vinyl functionality to form a palladium-alkyl species, which is subsequently carbonylated to form a palladium(II)-acyl species. This species then undergoes intramolecular nucleophilic attack by the alcohol functionality, producing ε-caprolactone and regenerating the palladium(II)-hydride species.

The six- and five-membered lactone ring products are also formed by a similar mechanism as shown in Scheme 3. Formation of the six-membered two-methylvalerolactone isomer could result from either initial palladium-hydride mediated isomerization of the terminal alkene or by initial 2,1-insertion of the alkene into the Pd-hydride bond. The five-membered two-ethylbutyrolactone isomer can be formed analogously.

The carbonylation of 4-penten-1-ol also results in the formation of open-chain oligomeric products. Gel permeation chromatography analysis of these species indicate that they are low molecular weight oligomers with a $M_w < 600$ versus polystyrene standards. These oligoesters are formed via competitive intermolecular versus intramolecular nucleophilic attack on the Pd-acyl species according to Scheme 4 [57]. In the case of intermolecular nucleophilic attack, the resulting ester species also contains an alkene functionality, this can potentially coordinate to the Pd catalyst to be carbonylated, producing higher molecular weight oligomeric species.

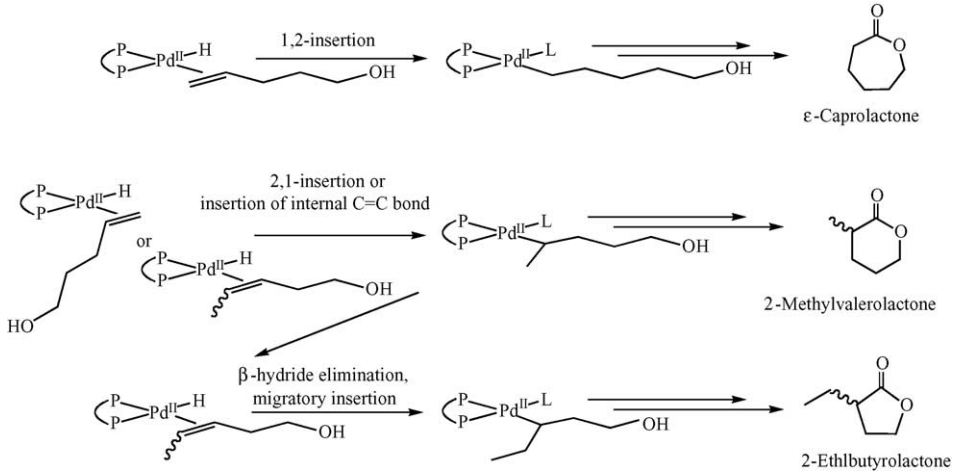
It is also conceivable that the oligomeric species could be formed by ring opening polymerization of the initially synthesized ε-caprolactone (Scheme 5). Because palladium(II) is an electrophilic species, the metal center may coordinate to ε-caprolactone, initiating cationic polymerization (Scheme 5, path a) [58–65]. Alternatively, the electrophilic palladium(II) species could interact with the penten-1-ol species to form a palladium(II)-alkoxy species which are known to initiate ring-opening polymerization (Scheme 5, path b) [66–67]. In order to determine if palladium species present in the catalytic system are able to initiate ring opening polymerization, a series of control reactions starting with ε-caprolactone were run. In one reaction, ε-caprolactone was heated in the presence of the catalyst system (Table 2, entry 6). This resulted in no decrease in the concentration of ε-caprolactone or the formation of oligomeric species, suggesting that the catalyst system itself was not able to initiate ring-opening polymerization of the ε-caprolactone (Scheme 5, path a). However, it is also possible that the palladium catalyst served to activate ε-caprolactone toward nucleophilic attack by the penten-1-ol in solution, resulting in ring opening polymerization (Scheme 5, path b). To test this possibility, an equimolar amount of ε-



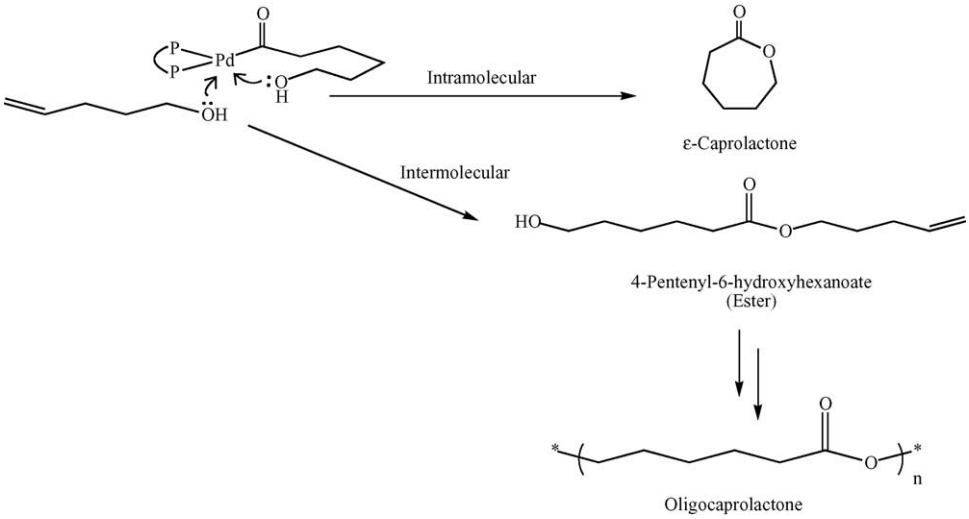
Scheme 2. Proposed mechanism for the cyclocarbonylation of 4-penten-1-ol to form ε-caprolactone.

caprolactone and 4-penten-1-ol were heated in the presence of the palladium catalyst under catalytic conditions (Table 2, entry 7). If the formation of oligomeric species resulted from ring opening polymerization of the ε-caprolactone in solution, then this reaction should have resulted in a formation of a greater amount of oligomeric species in comparison to the standard reaction because of the greater initial concentration of ε-caprolactone. If, on the other hand, the ε-caprolactone is not susceptible to ring opening polymerization under these conditions, then there should be no extra oligomers formed. Indeed, no decrease in the quantity of ε-caprolactone was observed, suggesting that the oligomeric species are a result of direct competitive intermolecular versus intramolecular nucleophilic attack on the Pd-acyl species (Scheme 4).

Although the above results suggest that palladium species present in the reaction mixture are not electrophilic enough to activate the ε-caprolactone towards ring opening polymerization, it is well known that Brønsted and strong Lewis acids can initiate ring opening polymerization of ε-caprolactone (Scheme 5, reaction c) [68–71]. To test the possibility that ε-caprolactone formed in situ might be polymerized by the MSA or $SnCl_2$ cocatalyst, ε-



Scheme 3. Proposed mechanism of formation of isomeric lactones.

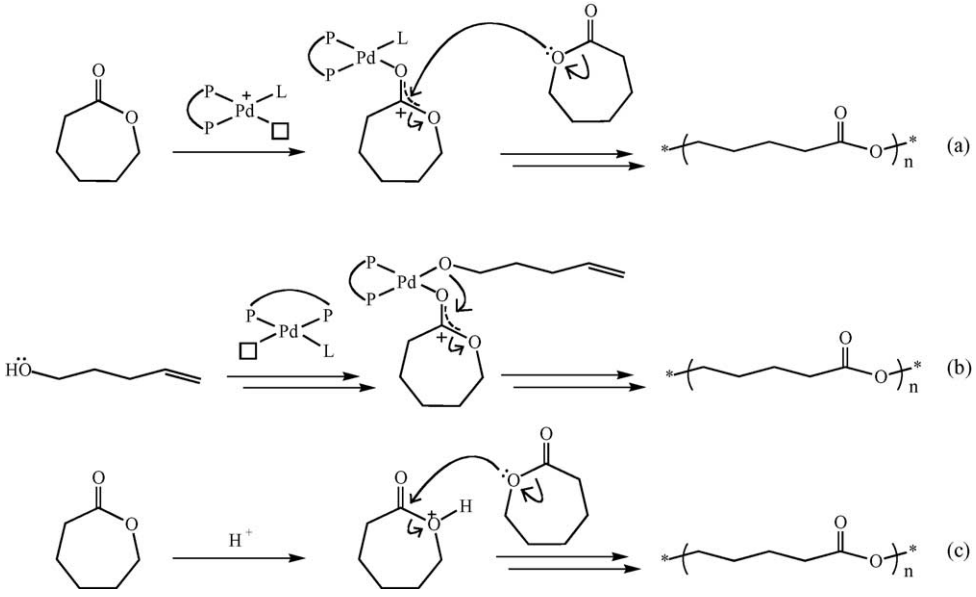


Scheme 4. Intermolecular vs. intramolecular nucleophilic attack for the formation of oligomeric species vs. ring-closed products.

caprolactone was heated with either MSA or $SnCl_2$ without the palladium catalyst under reaction-like conditions (Table 2, entries 9 and 10). As expected, the presence of these acids result in the ring-opening polymerization of ε-caprolactone.

In light of the above results, one important advantage of the $Pd_2(dba)_3$ + 2 XANTPhos system over several other reported alkoxycarbonylation systems is that it does not require the use of an acid cocatalyst, resulting in lower yields of oligomeric products. Nevertheless, some oligomeric species are formed via competitive intermolecular nucleophilic attack on the Pd-acyl intermediate.

Finally, in order to probe the nature of the palladium species present in some of the systems described, the reaction mixtures were examined by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of the product mixture from Run 2, Table 1 consisted of a dominant singlet at 8.5 ppm, and a doublet of doublet (4.9 and 1 ppm, J_{P-P} = 59 Hz) The former corresponds to the *trans* coordination of the two phosphorus atoms of XANTPhos. Furthermore, the chemical shift is consistent with that of a (Xantphos)Pd(acyl)$^+$ species [57]—a likely resting stage for the catalyst system (see Scheme 2). The minor doublet of doublet corresponds to a palladium species with *cis* coordination of the Xantphos ligand. When D*t*BPX was used as the ligand, the species formed quantitatively was (D*t*BPX)Pd(CO) [72]. The persistence and stability of this species is consistent with the very poor catalytic activity shown by this system.



Scheme 5. Possible mechanisms of oligocaprolactone formation from ε-caprolactone formed in situ.

4. Conclusion

As a proposed new method for the synthesis of ε-caprolactone, we have demonstrated the viability of a catalytic system consisting of $Pd_2(dba)_3$ + 2 XANTPhos for the carbonylation of 4-penten-1-ol in toluene. The conversion and selectivity observed using this catalyst is higher than that observed with other reported systems with the regioselectivity for terminal carbonylation exceeding 70%. Since in the present system C=C bond isomerization is slower than carbonylation, the use of bulkier ligands that favor 1,2-alkene insertion may further increase the product regioselectivity.

Acknowledgement

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