

# Revisiting the Palladium-Catalyzed Carbonylation of Allyl Alcohol: Mechanistic Insight and Improved Catalytic Efficiency

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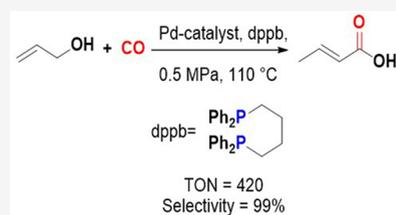
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**ABSTRACT:** Although crotonic acid (CA) is in high demand due to its use in various industrial applications, the preparation of CA currently requires a multi-step process from the petrochemical cracking of ethane with a very low overall yield and poor selectivity. An atom economical, one-step, carbonylation of readily accessible allyl alcohol to CA is one of the attractive approaches. In this study, the direct carbonylative transformation of allyl alcohol to CA was analyzed in detail to detect the reaction intermediates and propose a reaction mechanism. Following the reaction mechanism, the process was optimized to synthesize CA *via* the direct carbonylation of allyl alcohol with improved efficiency and productivity (TON = 420) under mild reaction conditions using Pd-based catalytic systems.



## INTRODUCTION

Crotonic acid (CA), an unsaturated carboxylic acid, is widely used in the preparation of the active drug molecule, Crotamiton, a scabicide agent, as well as in the production of cosmetics and hair styling products such as Cevian, Mowilith, Gelva, and Vinac.<sup>1–5</sup> In addition, CA derivatives are used in the coating, plasticizer, adhesive, flocculant, and agrochemical industries.<sup>1,4,6–8</sup>

The industrial synthesis of CA currently requires a multi-step process with a very low overall yield (30%) that involves the selective oxidation of crotonaldehyde, which is a byproduct of the petrochemical cracking of ethane to ethylene.<sup>1,8,9</sup> Given the demand for CA, a facile and efficient method to produce CA in high yields is desired. Various nonindustrial methods of CA synthesis have been developed, including dehydration of 2-hydroxybutyric acid, isomerization of 3-butenic acid, oxycarbonylation of propene, bacterial fermentation, and pyrolysis of poly(3-hydroxybutyrate).<sup>1,7,8</sup> However, these procedures often require harsh reaction conditions or result in poor yields.<sup>7</sup>

From an industrial point of view, an atom economical, one-step, carbonylative transformation of allyl alcohol to CA is an attractive alternative to the above strategies because allyl alcohol and carbon monoxide are readily accessible. However, the poor leaving ability of the hydroxyl group and the H<sub>2</sub>O byproduct causes poor selectivity,<sup>10</sup> leading to the formation of a mixture of products including unsaturated acids, butenoic acid derivatives, cyclized lactones, and unsaturated esters (Scheme S1).<sup>11–16</sup> Thus, the carbonylation of allyl alcohol derivatives, in general, suffers from obvious drawbacks, such as high CO pressures, poor selectivity, or/and low yield. Interestingly, Alper et al. reported the selective carbonylation of allyl alcohol to CA in 93% yield with a turnover number (TON) of 23.3 using Pd(dba)<sub>2</sub> (dba = bis(dibenzylideneacetone)) and 1,4-bis(diphenylphosphino)-

butane (dppb) as a catalytic system at 190 °C for 48 h under 40 bar CO in dimethoxyethane (DME).<sup>17</sup> Following this, in-depth research and a comprehensive understanding of the reaction mechanism are in demand to improve the selectivity and productivity of CA synthesis. Additionally, a detailed mechanistic study is crucial to develop additional catalysts for this transformation.

Therefore, in this study, to identify the reaction intermediates, the carbonylation of allyl alcohol to CA was monitored by <sup>1</sup>H NMR spectroscopy under different time intervals, and a mechanism for the reaction was proposed on the basis of the intermediates observed during the process. In addition, following the reaction mechanism, the reaction conditions were optimized to produce CA with the highest TON of 420 under low CO pressure (5 bar) at 110 °C in benzene (Scheme 1).

## Scheme 1. Pd-Catalyzed Carbonylation of Allyl Alcohol to CA



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Table 1. Pd(OAc)<sub>2</sub>-Catalyzed Carbonylative Transformation of Allyl Alcohol to CA in Different Solvents<sup>a</sup>

entry	solvent	conversion (%)	selectivity (%)				TON for CA <sup>b</sup>
			$\gamma$ -butyrolactone	allyl ester	3-butenic acid	crotonic acid	
1	benzene	>99	<1	ND	ND	99	24
2	dioxane	>99	ND	ND	23	77	17
3	DME	>99	ND	<1	30	70	16
4	THF	>99	2	8	30	60	12
5	CH <sub>2</sub> Cl <sub>2</sub>	70	43	ND	20	37	5

<sup>a</sup>Reaction conditions: 0.1 M allyl alcohol (1 mmol, 10 mL of solvent), 4 mol % Pd(OAc)<sub>2</sub>, 4 mol % dppb, 50 bar CO, 110 °C, 18 h. <sup>b</sup>Determined using <sup>1</sup>H NMR using mesitylene as an internal standard; TON for CA = mol of CA formed per mol of Pd.

## RESULTS AND DISCUSSION

It has been reported that a catalytically active Pd<sup>0</sup> complex can be spontaneously formed from a Pd<sup>II</sup> precursor in the presence of phosphine ligands.<sup>18,19</sup> Therefore, the allyl alcohol carbonylation was initially performed with the readily available, air-stable Pd(OAc)<sub>2</sub> and dppb in different solvents under 50 bar CO at 110 °C for 18 h in a 100 mL stainless steel tube reactor (Table 1, entry 1–5). The crude carbonylation products from each reaction were analyzed by <sup>1</sup>H NMR spectroscopy with mesitylene as an internal standard. The <sup>1</sup>H NMR spectral results showed that a mixture of products including CA, 3-butenic acid, allyl esters of CA and 3-butenic acid, and  $\gamma$ -butyrolactone (GBL) were formed in different ratios in different solvents studied (Scheme S1). Interestingly, a 99% conversion of allyl alcohol and 99% selectivity to CA was observed upon using the nonpolar solvent benzene (Table 1, entry 1). When ethereal solvents such as 1,4-dioxane, dimethoxyethane (DME), and tetrahydrofuran (THF) were used, the selectivity toward CA was decreased to 77, 70, and 60%, respectively (Table 1, entries 2–4). 3-Butenoic acid was formed as the byproduct in both 1,4-dioxane and DME; however, in the case of THF, along with 3-butenic acid (30%), the allyl ester of CA (8%) and a negligible amount of GBL (2%) were also formed. The use of CH<sub>2</sub>Cl<sub>2</sub>, a noncoordinating polar solvent, resulted in a reduced conversion (70%) and very low selectivity for CA (37%) that was observed along with the formation of GBL (43%) and 3-butenic acid (20%) (Table 1, entry 5). These byproducts are believed to be the intermediates during the carbonylative transformation of allyl alcohol to CA (*vide infra*). The large excess of the ethereal solvents might interfere with the allyl alcohol coordination to the Pd-site and might reduce the reaction rate, resulting in the incomplete conversion of the observed intermediates to CA. Whereas, the coordination of allyl alcohol is expected to be facilitated in benzene and a complete conversion of allyl alcohol to CA is observed. However, the reason for the formation of GBL as a major product in the CH<sub>2</sub>Cl<sub>2</sub> solvent is currently not clear. Thus, for the complete carbonylative transformation of allyl alcohol to CA, benzene was used as the solvent in subsequent experiments.

CA yield was unaffected by varying the CO pressure in the range 5–50 bar; reactions at a low CO pressure (5 bar) resulted in similar conversion rates (93% yield, TON = 23.3) to those at a higher CO pressure (50 bar), under otherwise identical reaction conditions (Table 2, entry 1). It may originate from the fast CO insertion in this transformation, and low CO pressure is enough to effectuate the transformation.

The reaction temperature significantly influenced the reactivity and outcome of the Pd-catalyzed carbonylative

Table 2. Pd(OAc)<sub>2</sub>-Catalyzed Carbonylative Transformation of Allyl Alcohol to CA<sup>a</sup>

entry	CO (bar)	T (°C)	time (h)	S/C	CA yield (%) <sup>b</sup>	TON <sup>c</sup>
1	5	110	18	25	93	23.3
2	5	80	18	25	48	12.0
3	5	140	18	25	90	22.5
4	5	110	48	100	92	92.0
5	5	110	48	250	63	157.5

<sup>a</sup>Reaction conditions: 1 mmol of allyl alcohol, 10 mL of benzene, ligand = dppb, Pd/dppb = 1:1. <sup>b</sup>CA yield, calculated using <sup>1</sup>H NMR spectroscopy. <sup>c</sup>TON = mol of CA formed per mol of Pd.

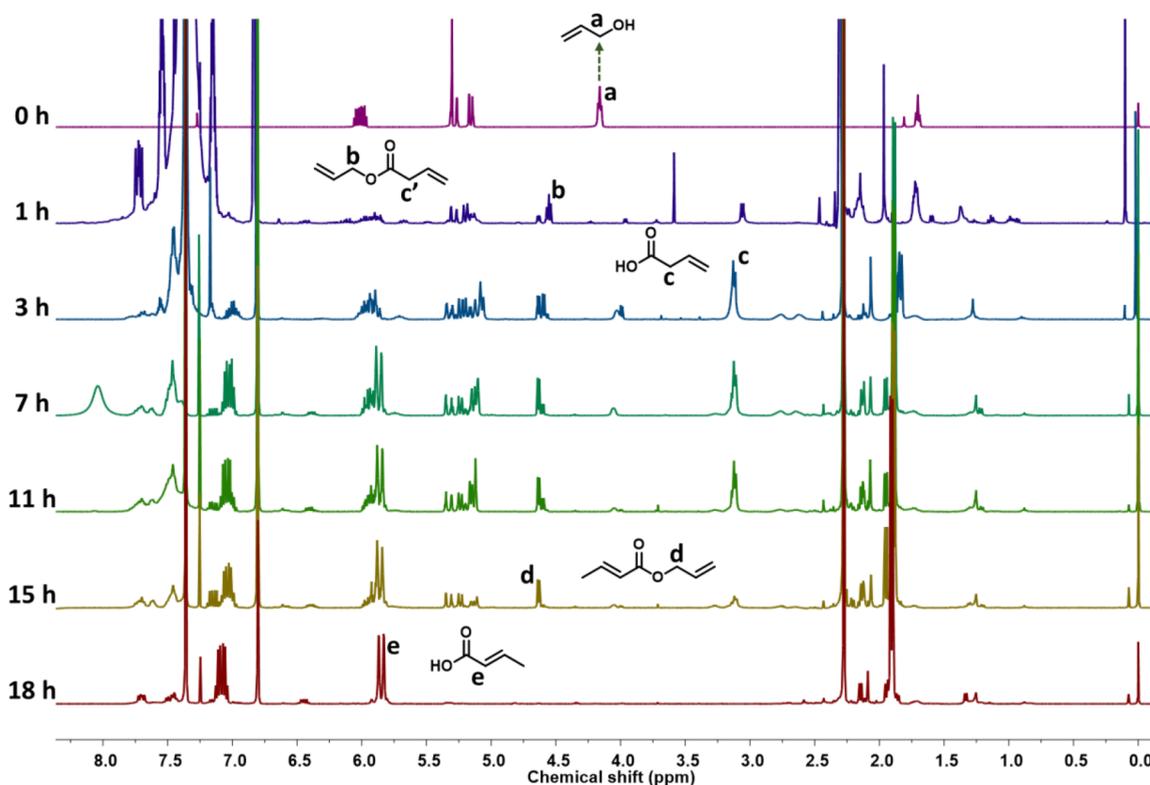
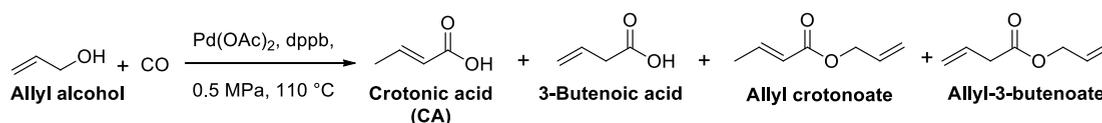
transformation of allyl alcohol to CA. At a slightly lower temperature (80 °C), the yield of CA was reduced to 48% with a TON of 12.0 (Table 2, entry 2). It is noticeable that homogeneous Pd complexes tend to form Pd-black at elevated temperatures. Similarly, the formation of Pd-black has been observed frequently in Pd(OAc)<sub>2</sub>/dppb-catalyzed carbonylation of allyl alcohol to CA (Figure S1).

In line with this, the TON for CA was reduced to 22.5 at a higher temperature of 140 °C, due to undesired side reactions and Pd-black formation (Table 2, entry 3). In this study, the optimum reaction temperature was 110 °C.

To improve the productivity of the Pd(OAc)<sub>2</sub>/dppb catalytic system, the substrate to catalyst (S/C) ratio was increased from 25 to 100 and 250. Interestingly, a yield of 92% CA with a TON of 92.0 was obtained with an S/C ratio of 100 in 48 h (Table 2, entry 4). Additionally, with an S/C ratio of 250, only a 63% yield of CA was obtained after 48 h, possibly because of the gradual decomposition of active Pd-species into Pd-black (Table 2, entry 5). Here, the use of heterogeneous phosphine-based ligands as supports for the Pd precursors may help to avoid both the aggregation of leached Pd metal and the formation of Pd-black in the carbonylation reaction.

To further understand the mechanism of the conversion of allyl alcohol to CA, detailed <sup>1</sup>H NMR analysis of the reaction mixture obtained at different time intervals was performed using the Pd(OAc)<sub>2</sub>/dppb catalytic system at 5 bar CO in benzene. Structures of the intermediates and product are shown in Scheme 2, which were determined by comparing their <sup>1</sup>H NMR spectra to those of synthesized standard samples or literature data. Peak assignments were made using the structures shown in the inset of Figure 1 and in Figure S2. Product amounts were estimated by integrating the area of the peaks assigned to the corresponding products. In particular, the content of allyl 3-butenate, 3-butenic acid, allyl crotonate, CA, and allyl alcohol/ether were calculated according to the integrated areas of peaks b, c, d, e, and a/f, respectively (Figure 1 and Figure S2).

**Scheme 2. Structures of the Intermediates and Products Formed at Different Reaction Times during the Pd(OAc)<sub>2</sub>/dppb-Catalyzed Carbonylative Transformation of Allyl Alcohol to CA**

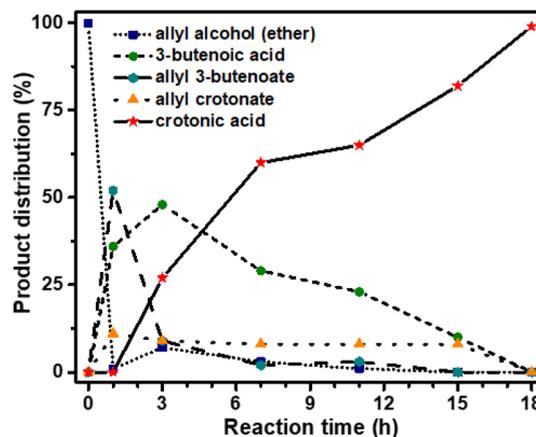


**Figure 1.** <sup>1</sup>H NMR spectra of generated intermediates at different reaction times during the Pd(OAc)<sub>2</sub>/dppb-catalyzed carbonylative transformation of allyl alcohol to CA.

After 1 h, the methene signal at 4.16 ppm (a) of allyl alcohol disappeared, suggesting that almost all of the allyl alcohol was consumed. Concurrently, new signals at 4.60 ppm (b), 4.63 ppm (d), and 3.05 ppm (c + c') were detected, indicating the formation of allyl 3-butenate (52%), allyl crotonate (11%), 3-butenic acid (36%), respectively, as well as negligible CA formation. As the reaction time extended to 3 h, the decreasing relative intensity of the signal at 4.60 ppm suggested the decomposition of allyl 3-butenate. In addition, according to signals at 3.05, 7.1, and 4.0 ppm, 3-butenic acid (48%), CA (27%), and allyl alcohol/ether (7%) were formed. As reaction time increased further (>3 h), the ratio between the signals at 7.1 and 3.05 ppm gradually increased, indicating increasing CA and decreasing 3-butenic acid yields. The signal at 4.63 ppm, attributable to allyl crotonate, remained at approximately 8%, then started to decrease after 15 h. The complete conversion of the intermediates into CA was observed after 18 h.

Figure 2 shows the distribution of all possible products of allyl alcohol carbonylation at different reaction times. Based on these results and previous reports, a possible reaction mechanism was proposed (Scheme 3). It is reported that Pd<sup>0</sup> species (1) is generated from the reduction of Pd(OAc)<sub>2</sub> by phosphine ligand and CO at an elevated temperature.<sup>18–20</sup>

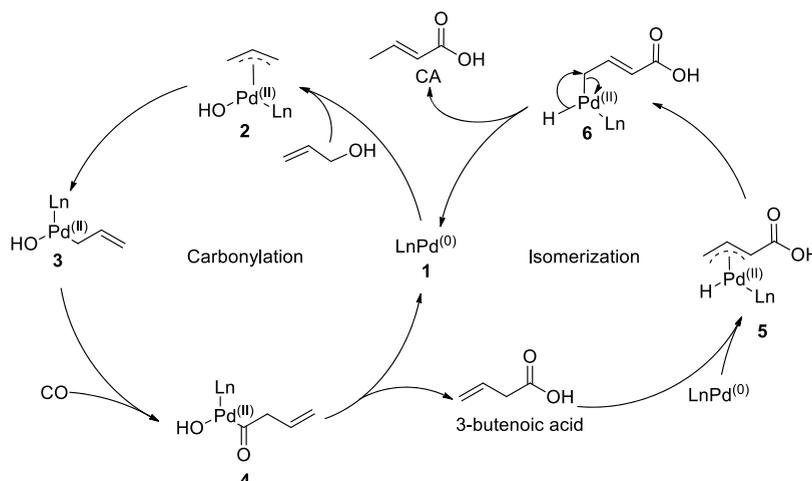
The oxidative addition of allyl alcohol to the Pd<sup>0</sup> species 1 leads to the ( $\pi$ -allyl)palladium intermediate, 2, thus activating



**Figure 2.** Product distribution for allyl alcohol carbonylation as a function of reaction time.

the C–O bond in the allyl alcohol. The species 2 subsequently rearranges to the alkyl-Pd<sup>II</sup> intermediate 3.<sup>13</sup> Then, the coordination and insertion of CO with 3 lead to the formation of the Pd-acyl intermediate 4. Reductive elimination of 4 affords 3-butenic acid and regenerates the catalytically active Pd<sup>0</sup> species 1. The as-formed 3-butenic acid undergoes

Scheme 3. Proposed Reaction Pathway of Allyl Alcohol Carbonylation to CA



isomerization to drive the equilibrium toward the stable, conjugated carboxylic acid CA *via* intermediate **6**. The lower bond dissociation energies ( $DH_{298}$ )<sup>21,22</sup> of C–O (~80 kcal/mol) and C–H (~90 kcal/mol) bonds in comparison with the O–H bond of the allylic system (~105 kcal/mol) and carboxylic systems (~112 kcal/mol) may facilitate the activation of C–O and C–H bonds during the formation of the species **1** and **5**, respectively. The intermediates **3** and **4** are in equilibrium with allyl ether and allyl-3-butenate, respectively, in the presence of allyl alcohol.

Based on the <sup>1</sup>H NMR analysis results at different time intervals and the proposed mechanism, the final step of the Pd-catalyzed carbonylation of allyl alcohol to CA involves the isomerization of 3-butenic acid to CA. Therefore, the isomerization of 3-butenic acid to CA was then studied using Pd(OAc)<sub>2</sub>/dppb as the catalyst. Interestingly, the 3-butenic acid was completely converted to CA within 2 h in the absence of CO (Scheme S2). However, when 3-butenic acid was treated with dppb in the absence of a Pd species, no isomerization was observed, indicating the importance of the Pd species for the isomerization step.

From the above mechanism, the carbonylative transformation of allyl alcohol to CA should also be catalyzed by Pd<sup>0</sup> precursors. Hence, to further confirm the reactivity of Pd<sup>0</sup> as a catalytic species in the conversion of allyl alcohol to CA, a series of Pd<sup>0</sup> sources were investigated as catalysts (Table 3 and Figure S3).

Commercially available Pd/C was initially tested with allyl alcohol and CO (5 bar) in the presence of dppb. The Pd/C-dppb system produced only a 20% yield of CA, likely due to the heterogeneous nature of the catalyst. Therefore, soluble homogeneous Pd<sup>0</sup> sources such as Pd(PPh<sub>3</sub>)<sub>4</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>, and Pd(dba)<sub>2</sub> were investigated. However, in an initial trial with Pd(PPh<sub>3</sub>)<sub>4</sub> without the dppb ligand, no product was detected (Table 3, entry 2). On the contrary, 94% CA formation was observed during the carbonylation of allyl alcohol upon using Pd(PPh<sub>3</sub>)<sub>4</sub> along with dppb as a catalytic system (Table 3, entry 3). Moreover, the other Pd<sup>0</sup> precursors, such as Pd<sub>2</sub>(dba)<sub>3</sub> and Pd(dba)<sub>2</sub>, were also catalyzed the carbonylation of allyl alcohol to CA upon being used in combination with dppb with the formation of 90 and 93% of CA, respectively (Table 3, entries 4 and 5). It has been reported that the addition of the phosphine ligand assisted the heterolytic cleavage of allyl alcohol into a cationic Pd-allyl intermediate

Table 3. Effect of Different Pd Sources on the Carbonylative Transformation of Allyl Alcohol to CA<sup>a</sup>

entry	Pd precursor	ligand	S/C	time (h)	CA yield (%) <sup>b</sup>	TON
1	Pd/C	dppb	25	18	20	5.0
2 <sup>c</sup>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	–	25	18	0	0
3	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dppb	25	18	94	23.5
4	Pd <sub>2</sub> (dba) <sub>3</sub>	dppb	25	18	93	23.3
5	Pd(dba) <sub>2</sub>	dppb	25	18	94	23.5
6 <sup>d</sup>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dppe	25	18	80	20
7 <sup>e</sup>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	PPh <sub>3</sub>	25	18	89	22.3
8	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dppb	100	48	96	96.0
9	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dppb	500	48	84	420.0

<sup>a</sup>Reaction conditions: 1 mmol of allyl alcohol, 10 mL of benzene, 110 °C, 0.5 MPa CO, Pd/dppb = 1:1. <sup>b</sup>CA yield, calculated using <sup>1</sup>H NMR spectroscopy. <sup>c</sup>Reaction was performed without dppb. <sup>d</sup>dppe = bis(diphenylphosphino)ethane; Pd/dppe = 1:1. <sup>e</sup>Pd/PPh<sub>3</sub> = 1:2

and hydroxide anion in aqueous medium.<sup>23,24</sup> In accordance with the previous studies, these results suggest that the addition of dppb may facilitate the formation and stabilization of the corresponding ( $\pi$ -allyl)palladium intermediate **2** from allyl alcohol in nonaqueous medium in the initial step. To further confirm the effect of phosphine ligand, other phosphine-based ligands such as bis(diphenylphosphino)ethane (dppe) and the monodentate ligand PPh<sub>3</sub> were used along with Pd(PPh<sub>3</sub>)<sub>4</sub> in the carbonylation of allyl alcohol (Table 3, entry 6 and 7). Interestingly, both the dppe and PPh<sub>3</sub> were found to be comparatively active for the transformation of allyl alcohol to CA with a conversion efficiency of 80 and 89%, respectively, which suggests that the addition of phosphine ligands is needed for the initial allyl alcohol activation. The higher catalytic activity found for the Pd(PPh<sub>3</sub>)<sub>4</sub>/dppb system might originate from the effective stabilization of the Pd-catalytic center by dppb ligand than the other labile ligands such as dba or PPh<sub>3</sub>.

Thus, the Pd(PPh<sub>3</sub>)<sub>4</sub>/dppb catalytic system is highly efficient for this transformation. Increasing the S/C ratio to 100 resulted in a 96% CA yield (Table 3, entry 8). Additionally, a further high increment in the S/C to 500 resulted in a record high TON of 420.0 for the conversion of allyl alcohol to CA in 48 h (Table 3, entry 9).

## CONCLUSIONS

In this paper, we have proposed simple and efficient catalytic systems for preparing CA. The Pd<sup>0</sup>-dppb catalytic systems are highly effective for the carbonylation of allyl alcohol to CA under very low CO pressures. The system presented herein affords excellent selectivity as well as desirable CA yields. Detailed <sup>1</sup>H NMR analysis of the reaction process reveals that allyl alcohol is consumed rapidly and that the isomerization of 3-butenic acid to CA plays a key role in driving the equilibrium toward the target product. However, the formation of Pd-black must be avoided to improve productivity in this transformation. We propose that Pd-based catalysts show promise for application in the industrial synthesis of CA

## EXPERIMENTAL SECTION

**General Considerations.** All reagents and materials used in this study were obtained from commercial sources and were used as received unless mentioned otherwise. The solvents used in this study were dried using traditional methods. Conversions of allyl alcohol to crotonic acid (CA) were determined by <sup>1</sup>H NMR spectroscopy using an Ascend 400 MHz instrument (Bruker).

**General Procedure for Carbonylation of Allyl Alcohol.** In a glovebox, a solution of Pd(OAc)<sub>2</sub> (9 mg, 0.04 mmol) and dppb (17 mg, 0.04 mmol) in 5 mL of benzene was charged to a homemade 100 mL stainless steel tube reactor and stirred at 20 °C for 20 min. Allyl alcohol (58 mg, 1.0 mmol) dissolved in 5 mL of benzene was added, then the reactor was flushed three times with CO and pressurized to 5 bar with CO. The autoclave was immersed in a preheated oil bath, and the reaction mixture was stirred for 18 h at 110 °C. The pressure was released after the reactor was cooled to room temperature and the crude reaction mixture was analyzed by <sup>1</sup>H NMR spectroscopy.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.0c00117>.

Schemes of possible products and isomerization pathways and figures of images of formations, <sup>1</sup>H NMR spectra, and effects of transformation (PDF)

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### Author Contributions

<sup>‡</sup>S.P. and J.J. contributed equally to this work.

### Notes

The authors declare no competing financial interest.

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