

Palladium clay catalyzed regio- and stereospecific synthesis of β,γ -unsaturated acids by the carbonylation of allylic alcohols

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Abstract

Palladium acetate immobilized on montmorillonite is an effective catalyst for the carbonylation of secondary allylic alcohols with carbon monoxide, in the presence of triphenylphosphine and an acid promoter, affording β,γ -unsaturated acids in 39–56% isolated yields. The reaction is regio- and stereospecific.

Keywords: Palladium; Clay; Regiospecificity; Stereospecificity; Unsaturated acids; Carbonylation; Allylic alcohols

1. Introduction

The carbonylation of allylic alcohols is of significant academic and industrial interest as a method to produce unsaturated acids. It is also of considerable potential for the manufacture of fatty acids, fragrance materials, and polymers [1,2].

Few publications have appeared on the conversion of allylic alcohols to form unsaturated acids in spite of the ready availability of starting materials, as the reaction requires a high pressure of carbon monoxide. In most cases, homogeneous catalysts are used [3–9], and lactones [10,11], unsaturated esters [7] or acids [12–14] are formed in these reactions. The carbonylation of allyl alcohol in the presence of acetic acid affords 3-butenic acid [15]. The reaction occurs without isomerization of the carbon–carbon

double bond. However, carbonylation does take place with concurrent double bond migration using $1/2$ $\text{PdCl}_2/\text{PPh}_3$ at very high pressures (237 atm) [8].

In order to make the catalyst recovery more facile, clays such as montmorillonite have recently been used as supports for catalytic reactions [16–22]. We wish to report that montmorillonite–bipyridinylpalladium(II) acetate (Pd–clay), is a useful catalyst for the direct carbonylation of allylic alcohols to β,γ -unsaturated acids.

2. Results and discussion

Treatment of an allylic alcohol (**1**) with carbon monoxide (600 to 800 psi) in benzene in the presence of a catalytic amount of Pd–clay (250: 1 ratio of 1/Pd–clay), HCl and triphenylphosphine, at 125–180°C for 48 to 72 h,

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Table 1
Pd-clay catalyzed carbonylation of α -vinylbenzyl alcohol^a

Entry	CO (psi)	T (°C)	PPh ₃ /Pd	c-HCl (ml)	Yield (%) ^b
1	600	125	5	0.05	30
2	600	125	5	0.3	50
3	600	180	5	0.3	53
4	800	180	5	0.3	53
5 ^c	600	180	16	0.3	50
6	800	180	5	—	NR ^d

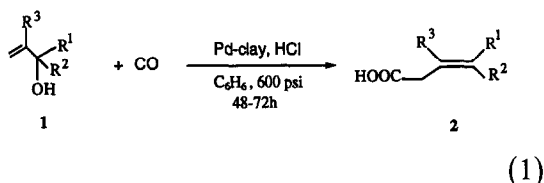
^a Reaction conditions: Pd-clay 30 mg (0.006 mequiv.); α -vinylbenzyl alcohol (1.5 mmol); benzene (10 ml); reaction time 72 h.

^b Isolated yield.

^c Pd-clay 30 mg (0.006 mequiv.), Ru₃(CO)₁₂ (0.014 mmol); PPh₃ (0.1 mmol); α -vinylbenzyl alcohol (2 mmol); benzene (10 ml), reaction time, 48 h.

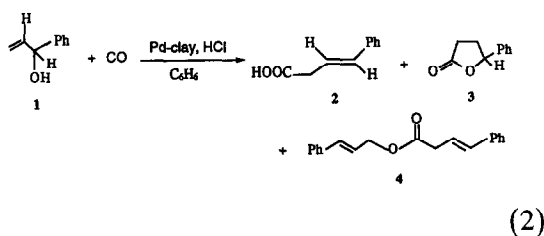
^d NR = no reaction.

affords the corresponding β,γ -unsaturated acid (**2**) in 39–56% isolated yield (Eq. 1).



The effect of various reaction conditions on the carbonylation reaction was examined in the case of α -vinylbenzyl alcohol **1** ($R^1 = \text{Ph}$, $R^2 = R^3 = \text{H}$) and the results are summarized in Table 1.

After 72 h, the reaction was complete and gave the unsaturated acid **2**, $R^1 = \text{Ph}$, $R^2 = R^3 = \text{H}$. Only a small amount of lactone **3** (less than 10% yield), and the ester **4** (20% yield) are formed as secondary products (Eq. 2).



The presence of an acid promoter is essential for significant catalytic activity. When the amount of HCl is too low (0.05 ml), the reaction

proceeds very slowly (Table 1). Only 30% of acid was isolated after 72 h. Montmorillonite has both Brønsted and Lewis acidic sites corresponding to a Hammett acidity function (H_0) value of +1.5 to -3.0 [16](a). This low catalytic activity can be explained by the reduction of the Brønsted acidity during the preparation of the catalyst by treatment with SOCl₂ [16](b). Note that the yields rise slightly with increasing reaction temperature (125 to 180°C) at a given concentration of HCl.

It has been previously shown that the combination of Ru₃(CO)₁₂ with palladium-clay can enhance the reactivity, increasing the surface acidity of the clay [17]. In the case of α -vinylbenzyl alcohol, after 48 h of reaction, in the presence of Pd-clay and Ru₃(CO)₁₂, the isolated yield of acid is 50% but the reaction is less selective, with other unidentified products formed as well. The best results were realized (53% isolated yield of **3**) when α -vinylbenzyl alcohol was reacted at 180°C, 800 psi of carbon monoxide and 0.3 ml of concentrated hydrochloric acid.

A series of allylic alcohols were carbonylated under the conditions described above, and the results are presented in Table 2.

The β,γ -unsaturated acids were isolated in 39–56% yield from secondary allylic alcohols,

Table 2
Pd-clay catalyzed carbonylation of allylic alcohols^a

1	Entry	Yield of 2 ^b (%)
R ¹ , R ² , R ³		
Ph, H, H	a	53
Ph, H, CH ₃	b	56
C ₆ H ₁₁ , H, H	c	51
C ₃ H ₇ , H, H	d	48
C ₂ H ₅ , H, H	e	46
CH ₃ , H, H	f	39
CH ₃ , CH ₃ , H	g	25 ^c
Ph, CH ₃ , H	h	

^a Reaction conditions: Pd-clay 30 mg (0.006 mequiv.); substrate (1.5 mmol); PPh₃ (0.1 mmol), c-HCl (0.3 ml), benzene (10 ml); reaction time, 72 h.

^b Isolated yield.

^c The corresponding lactone was formed in this case.

and the reaction is regio- and stereospecific, with the *Z*-isomer formed as the only product for all cases of **2** in which geometric isomers exist. No isomeric α,β -unsaturated acid was formed in these reactions. Only a small amount of lactone was observed as a secondary product in some of these reactions.

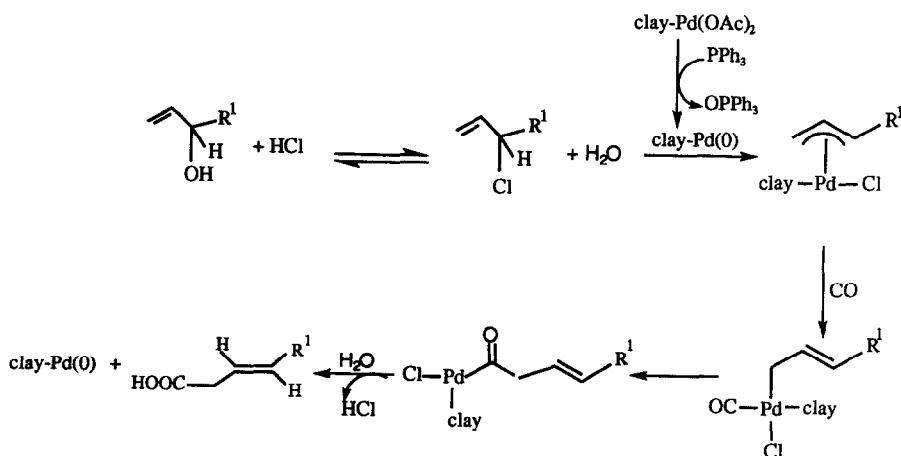
Under the same conditions, benzylic tertiary allylic alcohols such as 2-phenyl-3-buten-2-ol (entry h), 2-phenyl-3-methyl-3-buten-2-ol (**1**, $R^1 = \text{Ph}$, $R^2 = \text{H}$, $R^3 = \text{CH}_3$) or α -vinylidibenzyl alcohol (**1**, $R^1 = \text{Ph}$, $R^2 = \text{Ph}$, $R^3 = \text{H}$) afforded only uncharacterized non-carbonylated materials, and other decomposition products. However, 2-methyl-3-buten-2-ol (entry g) can be carbonylated and affords only the corresponding lactone in 25% isolated yield.

To our knowledge, this reaction is the first, direct, efficient carbonylation of allylic alcohols to β,γ -unsaturated acids, using a palladium–clay catalyst. Moreover, the formation of black palladium is minimal using Pd–clay. In contrast, using homogeneous $\text{Pd}(\text{OAc})_2$ as the catalyst resulted in decomposition of the catalyst affording large quantities of black palladium, and the β,γ -unsaturated acid is formed in much lower yield relative to that realized using the palladium–montmorillonite system (eg. **2**, $R^1 = \text{Ph}$, $R^2 = R^3 = \text{H}$ was obtained in 53% using Pd–clay, and in 25% yield using $\text{Pd}(\text{OAc})_2$). In

addition, the amount of Pd in solution after one run was 22 ppm (determined by atomic absorption spectroscopy). Furthermore, the Pd–clay was reused four times without significant leaching, for the carbonylation of **1**, $R^1 = \text{Ph}$, $R^2 = R^3 = \text{H}$.

A possible mechanism for the conversion of allylic alcohols to β,γ -unsaturated acids is outlined in Scheme 1. It is conceivable that the allylic alcohol reacts with HCl to give the corresponding chloride, which initiates the catalytic cycle. This kind of reaction is easy particularly at high temperatures [23]. Oxidative addition of the chloride compound to a palladium(0) species (probably formed by reduction) [21] can result in the formation of a π -allylpalladium chloride complex. Such synthesis of allylpalladium complexes from the reaction of allylic chlorides have been reported in the literature [24]. Insertion of carbon monoxide into the Pd–C bond generates an acylpalladium intermediate. Hydrolysis of the latter will give the β,γ -unsaturated acid and regenerate the palladium(0) species.

Evidence for the participation of an allylic chloride in the reaction pathway was obtained using 3-chloro-1-butene (allylic chloride compound equivalent to entry f) under identical conditions to those for the allylic alcohol with and without HCl. The same β,γ -unsaturated acid **2**, $R^1 = \text{CH}_3$, $R^2 = R^3 = \text{H}$ was obtained in



45% and 30% isolated yield, respectively (compared with 39% using the alcohol and HCl). Clearly, the increase in yield using HCl indicates that, in addition to the conversion of alcohol to chloride, hydrochloric acid plays a role in the catalytic cycle leading to the acid.

It is important to note that even if the reaction proceeds via an allylic chloride intermediate, no base is needed to produce the β,γ -unsaturated acid with complete stereospecificity. Most of the examples presented in the literature require strong bases or alkoxides [7](b), [25].

Tertiary allylic alcohols are readily transformed into tertiary chlorides by the use of hydrochloric acid even at room temperature [23]. The lack of carbonylation of these compounds may be due to the fact that the π -allylpalladium complex is not generated because of the absence of allylic hydrogen atoms.

3. Conclusion

Palladium acetate immobilized on montmorillonite is an effective catalyst for direct carbonylation of secondary allylic alcohols in the presence of triphenylphosphine, carbon monoxide and hydrochloric acid to give β,γ -unsaturated acids in reasonable yields.

4. Experimental section

4.1. General

The palladium–clay was prepared according to a literature method [16](b), [18] and characterized by elemental analysis and X-ray diffraction.

All solvents were dried and distilled prior to use. The following spectrometers were used to obtain spectral data: Gemini 200 and Varian XL 300 for NMR; VG 7070E for mass spectral; Bomem MB 100-C15 for infrared data.

4.2. Synthesis of allylic alcohols

Most of the allylic alcohols used were prepared by Grignard reaction using vinylmagnesium bromide and either benzaldehyde (entry a), acetophenone (entry h), or cyclohexancarboxaldehyde (entry c) in THF at 0°C. After hydrolysis and extraction with ether, the allylic alcohol was obtained and purified by column chromatography (eluant hexane/ethyl acetate 95/5). Except for one new allylic alcohol, all of the known alcohols were identified by comparison of spectral data with literature results.

4.2.1. $CH_2=CHCH(OH)C_6H_{11}$ (a)

(a) 1H NMR: ($CDCl_3$) δ 0.89–1.80 (m, 11H), 1.87 (s, 1H), 3.81 (t, 1H, $J_{H-H} = 6$ Hz), 5.11–5.25 (m, 2H) ppm. ^{13}C NMR: ($CDCl_3$) δ 25.6, 25.9, 28.3, 28.6, 43.3, 77.6, 115.2, 139.7 ppm. HRMS Calcd: 140.1197, Found: 140.1220.

4.3. General procedure

A 45 ml stainless steel autoclave (Parr instruments) was used as a batch reactor. In a typical run, 30 mg of Pd–clay (0.006 mol Pd), 8.6 mg of PPh_3 (0.03 mmol), 1.5 mmol of olefin, 10 ml of benzene and 0.3 ml of concentrated HCl were charged into the reactor. The autoclave was purged three times with CO, and pressurized to the desired level. The reactor was then placed in an oil bath maintained at constant temperature. After the reaction, the autoclave was cooled to room temperature, the reaction mixture was filtered, and the solvent was removed by rotary evaporation. Each experiment was repeated twice. Purification was effected by one of two methods, either directly by HPLC (to recuperate the lactone and the ester when those were formed), or the crude material was diluted with ether (20 ml), extracted with 0.5 N NaOH (3×15 ml), and the combined organic phase was washed with water (3×20 ml), dried ($MgSO_4$), filtered, and concentrated to give the product. Further purification, if necessary, was effected by HPLC (column JAIGEL 2H). Pure

acids were characterized by comparison of NMR (^1H , ^{13}C), IR and high resolution mass spectral data with literature results, except for the following acid which is new.

4.3.1. $\text{C}_6\text{H}_{11}\text{CH}=\text{CHCH}_2\text{COOH}$ (**2c**)

^1H NMR: (CDCl_3) δ 0.96–2.01 (m, 11H), 3.05 (d, 2H), 5.4–5.5 (m, 2H) ppm. ^{13}C NMR: (CDCl_3) δ 25.9, 26.1, 32.7, 32.8, 37.9, 40.6, 118.3, 141.2, 178.7 ppm. IR (neat) $\nu(\text{CO}) = 1709\text{ cm}^{-1}$. HRMS Calcd: 168.1216, Found: 168.1163.

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