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A simple catalytic system for the substitutive carbonylation of allyl alcohols to β,γ -unsaturated acids or esters

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Abstract

Allyl alcohols can be efficiently carbonylated to β,γ -unsaturated acids or esters in dimethylacetamide (DMA) or MeOH/DMA mixtures under relatively mild conditions (80°C, 50–100 atm) using a simple catalytic system consisting of palladium iodide in the presence of thiourea as ligand. In the case of but-2-ene-1,4-diol, selectivation to methyl 5-hydroxypent-3-enoate, 3,6-dihydro-1,2-pyrone or dimethyl hex-3-enedioate may be achieved.

Keywords: Carbonylation; Allyl alcohols; Carboxylic acids; Esters; Palladium

1. Introduction

Palladium-catalyzed substitutive carbonylation of allylic compounds is a very useful method for the synthesis of β,γ -unsaturated carboxylic acids derivatives [1–3]. Although efficient methods for the carbonylation of allyl carbonates [4], esters [5,6], halides [7,8], amines [9] and ethers [10,11] under relatively mild conditions have been recently developed, very few methods are known for allyl alcohols, in spite of their greater availability. Moreover, the reaction usually requires high temperature and carbon monoxide pressure (70–130°C, 15–200 atm) [12–15]. Recently a new method has been re-

ported which allows the reaction under milder conditions (75–100°C, 15–25 atm); however, the presence of stoichiometric amounts of titanium(IV) isopropoxide and lithium chloride is essential for the reaction [16].

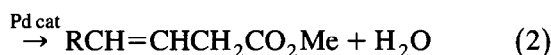
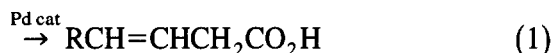
Now we report a very simple catalytic procedure for the substitutive carbonylation of allyl alcohols under relatively mild conditions. A preliminary account, limited to dimethyl 2-hydroxymethylbut-2-ene-1,4-dioate, was published recently [17].

2. Results and discussion

Our method consists of the reaction of allyl alcohols in dimethylacetamide (DMA) or MeOH/DMA mixtures at 80°C and 50–100 atm of carbon monoxide in the presence of PdI₂

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and thiourea (tu) as ligand (3–6 mol per mol of palladium) [Eqs. (1, 2)].



For example, by reacting 3-phenylprop-2*E*-ene-1-ol (19 mmol) in DMA (19 ml) in the presence of PdI₂ (0.38 mmol) and tu (1.14 mmol) under 50 atm of initial carbon monoxide pressure at 80°C for 15 h, 4-phenylbut-3*E*-enoic acid was obtained in 81% yield (run 1, Table 1). Using MeOH as solvent under the same conditions, the carbonylation reaction was slowed down, and after 15 h methyl 4-phenylbut-3*E*-enoate **1** was obtained in 46% yield at 54% conversion. 1,1-Dimethoxy-3-phenylpropane **2** (2%) and 3-methoxy-1-phenylprop-1*E*-ene **3** (6%) were formed as by-products (run 2). However, when the reaction was carried out in MeOH:DMA mixtures, higher yields in ester could be obtained (runs 3, 4, 5).

When palladium chloride was used in place

of palladium iodide, the substrate conversion and product yields were rather low (run 6). The presence of the thiourea ligand is essential in order to achieve good selectivities in the carbonylated product, the use of PdI₂ alone (in conjunction with KI to favour its solubilization) affording 3-methoxy-1-phenylprop-1*E*-ene as the main product (63% yield, run 7). On the other hand, complexes Pdtu₂I₂ [18] and Pdtu₄I₂ [19] led to less satisfying results (runs 8 and 9). A carbonylation product of thiourea, methyl thioallophanate H₂N(CS)NHCO₂Me, was also detected in the reaction mixture.

Table 2 lists the results obtained with different allyl alcohols. 3-Phenylprop-2*E*-ene-1-ol gave the best yield (92%, run 10). But-1-ene-3-ol and but-2-ene-1-ol gave the same product, methyl pent-3-enoate (runs 11 and 12), which is consistent with the involvement of a common π-allyl intermediate. Carbon monoxide insertion occurs exclusively at the less substituted carbon of the allyl moiety (runs 12 and 13). Electron withdrawing substituents on the double bond are compatible (run 14).

Of particular interest is the reaction of but-2-ene-1,4-diol. The carbonylation of this diol (*Z*:*E* = 95:5) under the usual conditions gave a

Table 1
Carbonylation of 3-phenylprop-2*E*-ene-1-ol

Run	Catalyst	Solvent	Conversion (%) ^a	Yields (%) ^a		
				1	2	3
1	PdI ₂ + 3tu	DMA	100	81 ^b	0	0
2	PdI ₂ + 3tu	MeOH	54	46	2	6
3	PdI ₂ + 3tu	MeOH/DMA = 2.2	70	66 ^c	3	1
4	PdI ₂ + 3tu	MeOH/DMA = 3.75	74	68 ^d	3	3
5	PdI ₂ + 3tu	MeOH/DMA = 5.3	60	58 ^e	2	0
6	PdCl ₂ + 3tu	MeOH	23	14	1	0
7	PdI ₂ + 10KI	MeOH/DMA = 3.75	100	36 ^f	traces	63
8	Pdtu ₂ I ₂	MeOH/DMA = 3.75	63	62 ^g	traces	0
9	Pdtu ₄ I ₂	MeOH/DMA = 3.75	57	54	3	0

Conditions: *T* = 80°C, initial CO pressure = 50 atm; *t* = 15 h, substrate:Pd = 50:1, substrate concentration = 1 mmol/ml of solvent.

^a Based on starting 3-phenylprop-2*E*-ene-1-ol, by GLC.

^b Free acid.

^c 4% free acid.

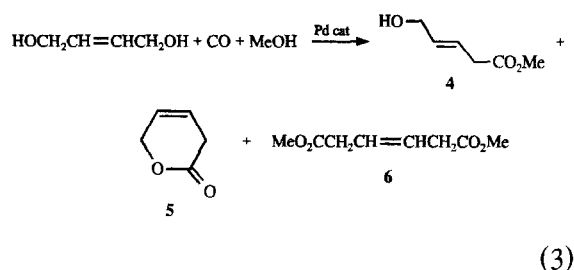
^d 2% free acid.

^e 1% free acid.

^f 2% free acid.

^g 1% free acid.

mixture of products **4**–**6** deriving from mono- and disubstitutive carbonylation [Eq. (3)].



The yields in methyl 5-hydroxypent-3*E*-enoate **4**, 3,6-dihydro-1,2-pyrone **5** and dimethyl hex-3-ene-1,6-dioate **6** were 10, 7 and 41%, respectively (run 15). Similar results were obtained starting from but-2*E*-ene-1,4-diol (run 16). In both cases, butadiene was formed as a by-product due to a competitive reduction process. Product **4** is an intermediate in the formation of **6**, in fact if it is isolated and subjected to carbonylation under the same conditions it affords **6** in good yields (run 17).

The ability to obtain products **4**–**6** in a very simple way starting from a readily available substrate is attractive, the known methods for the synthesis of **4** [20] and **5** [21] being more laborious.

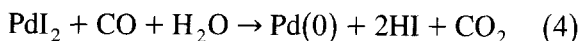
Product **6** is a precursor of adipic acid, and in recent years several methods have been developed for its synthesis by dicarbonylation of but-2-ene-1,4-diol and its derivatives [15,22–27]. An 80% yield in the corresponding diacid was obtained using PdCl₂ in the presence of an excess of PBu₄Cl (17 mmol per mol of palladium) in *N*-methyl-pyrrolidone as solvent at 100°C and 125 atm of CO [15]; no selectivation towards monocarbonylated products **4** and **5** was reported, however. Under our conditions a completely selective dicarbonylation reaction may be achieved working at 100 atm of CO. For example, by reacting butenediol at 80°C and initial carbon monoxide pressure = 100 atm for 6 h, only **6** is obtained (57% yield), butadiene being formed as by-product (run 18, Table 3). On the other hand, the use of a tu: Pd ratio = 6

alters the product distribution in favour of monocarbonylated products **4** and **5** (run 19); no butadiene is formed in this case. Therefore increasing the tu: Pd ratio has two effects: the second carbonylation step is slowed down and the competitive process leading to butadiene formation is hindered.

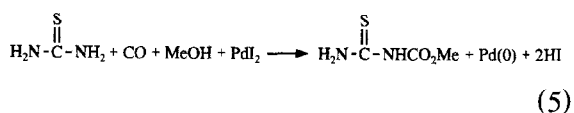
Working in DMA or DME (1,2-dimethoxyethane) as solvent, in the absence of methanol (runs 20 and 21), no formation of monomeric acids was observed, and lactone **5** was formed, even though in low yields (13–30%). Unidentified oligomeric products were present in the reaction mixture.

As already mentioned, the carbonylation process probably involves the formation of a π-allyl intermediate, analogous to what was previously reported for the substitutive carbonylation of allylic substrates [1–3] (Scheme 1; unreactive ligands are omitted). Such an intermediate could be formed by oxidative addition of the allyl iodide (from allyl alcohol + HI) to a Pd⁰ species or by direct interaction between the allyl alcohol and an H-Pd-I species. Carbon monoxide insertion followed by methanol or water attack leads to product formation and to regeneration of the catalytically active species.

The way by which Pd(0) + HI or H-Pd-I species are formed deserves some comment. A likely pathway consists of the oxidation of CO to CO₂ in the presence of traces of water according to Eq. (4).



This process probably involves the formation of an I-Pd-COOH species, which then decomposes to H-Pd-I and CO₂ as known for Pt [28] and for many other transition metal complexes [29]. Also the tu ligand can play a role, based on its ability to undergo oxidative carbonylation according to Eq. (5).



On the other hand, no formaldehyde or 3-phenylprop-2-enal or their acetals were detected in the reaction mixture in methanol, so palladium reduction by alcohol oxidation, as observed by

Portnoy and Milstein [30], does not seem to play a significant role under our conditions.

The H–Pd–I species is likely to be responsible for the formation of product **2**, via isomer-

Table 2
Carbonylation of various allyl alcohols in the presence of PdI₂ + 3tu

Run	Substrate (<i>E:Z</i>)	Conv. (%) ^a	Product (% yield ^a ; <i>E:Z</i> ^b)
10		95	
11	$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$ (95:5)	87	$\text{CH}_3\text{CH}=\text{CHCH}_2\text{CO}_2\text{Me}$ (71; 74:26)
12		98	$\text{CH}_3\text{CH}=\text{CHCH}_2\text{CO}_2\text{Me}$ (88; 75:25)
13		97	$\text{H}_2\text{C}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CO}_2\text{Me}$ (89; 82:18)
14		95	
15	$\text{HOCH}_2\text{CCH}=\text{CHCH}_2\text{OH}$ (5:95)	98	$\text{MeO}_2\text{CCH}_2\text{CH}=\text{CHCH}_2\text{CO}_2\text{Me}$ (41 ^e ; 76:24)
16		98	$\text{MeO}_2\text{CCH}_2\text{CH}=\text{CHCH}_2\text{CO}_2\text{Me}$ (40 ^f ; 78:22)
17		62	$\text{MeO}_2\text{CCH}_2\text{CH}=\text{CHCH}_2\text{CO}_2\text{Me}$ (50 ^g ; 75:25)

Conditions: $T = 80^\circ\text{C}$, initial CO pressure = 50 atm; $t = 15$ h, substrate: Pd = 25:1, substrate concentration = 1 mmol/ml of solvent (MeOH:DMA = 3.75).

^a Based on starting allyl alcohol, by GLC.

^b Determined by GLC.

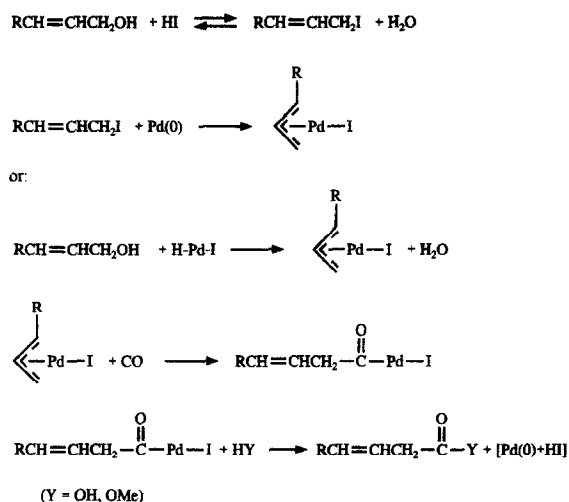
^c 7% free acid; 1,1-dimethoxy-3-phenylpropane **2** was also produced in 3% yield.

^d Dimethyl methylenebutane-1,4-dioate (19% yield) was also produced.

^e Methyl 5-hydroxypent-3-*E*-enoate **4** (10% yield), 3,6-dihydro-1,2-pyrone **5** (7%), dimethyl adipate (1%) and butadiene (35%) were also formed.

^f **4** (10% yield), **5** (8%), dimethyl adipate (1%) and butadiene (35%) were also formed.

^g Dimethyl adipate was also produced in 1% yield.



Scheme 1.

ization of 3-phenylprop-2*E*-ene-1-ol to 3-phenylpropanal and acetalization. Methanol attack on the less substituted carbon of the allyl system accounts for the formation of methyl ether **3**; accordingly, no conversion of 3-phenylprop-2*E*-ene-1-ol to its methyl ether **3** was observed in the absence of palladium under the reaction conditions.

Butadiene formation can be explained by Pd(0)-induced reductive dehalogenation of the 1,4-diiodobut-2-ene in equilibrium with the diol, analogously to what has been reported for the reaction between 1,4-dichlorobut-2-ene and Ni(0) [20,31,32] [Eq. (6)]:

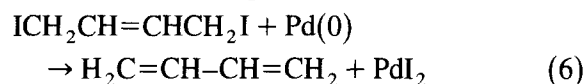


Table 3

Carbonylation of but-2-ene-1,4-diol (*Z*:*E* = 95:5) in the presence of PdI₂ + 3tu

Run	Catalyst	Solvent	Time (h)	Conversion (%) ^a	Yields (%) ^a		
					4	5	6
18	PdI ₂ + 3tu	MeOH:DMA = 3.75	6	100	0	0	57 ^b
19	PdI ₂ + 6tu	MeOH:DMA = 3.75	8	80	52	13	9 ^c
20	PdI ₂ + 3tu	DMA	8	100	0	30	0
21 ^d	PdI ₂ + 4tu + 5KI ^e	DME	24	81	0	13	0

Conditions: *T* = 80°C, initial CO pressure = 100 atm; substrate: Pd = 25: 1, substrate concentration = 1 mmol / ml of solvent.

^a Based on starting butenediol, by GLC.

^b *E*:*Z* = 74:26; dimethyl adipate (1%) and butadiene (38%) were also formed.

^c *E*:*Z* = 74:26.

^d Substrate: Pd = 50.

^e 5 moles of KI per mol of palladium were added to favour the dissolution of the catalyst in DME.

In conclusion, substitutive carbonylation of allyl alcohols to β,γ-unsaturated acids or esters can be carried out using a very simple catalytic system, consisting of PdI₂ in the presence of thiourea as ligand, under relatively mild conditions. In the case of but-2-ene-1,4-diol selectivity to the monocarbonylated products **4** and **5** or to the dicarbonylated product **6** has been achieved.

3. Experimental

3.1. General

Organic starting materials 3-phenylprop-2*E*-ene-1-ol, but-2-ene-1-ol (*E*:*Z* = 95:5), but-1-ene-3-ol, hexa-1,5-diene-3-ol, but-2-ene-1,4-diol (*E*:*Z* = 5:95) and products 4-phenylbut-3*E*-enoic acid, pent-3-enoic acid (*E* + *Z* mixture), hex-3-ene-1,6-dioic acid (*E* + *Z* mixture), dimethyl methylenebutane-1,4-dioate, 1,2,3-prop-2*E*-enetricarboxylic acid and 1,2,3-prop-2*Z*-enetricarboxylic acid were commercial products (Aldrich, Fluka). Dimethyl 2-hydroxymethylbut-2*Z*-ene-1,4-dioate [33], but-2*E*-ene-1,4-diol [34], Pd(tu)₂I₂ [18] and [Pd(tu)₄]I₂ [19] were prepared according to literature procedures. 1,1-Dimethoxy-3-phenylpropane [35], 3-methoxy-1-phenylprop-1*E*-ene [36], methyl hepta-3*E*,6-dienoate [37], methyl 5-hydroxypent-3*E*-enoate

[20] and 3,6-dihydro-1,2-pyrone [21] were compared with those reported in the literature.

Product mixtures were analyzed by TLC (SiO_2) or by GLC using capillary columns with polymethylsilicone + 5% phenylsilicone (HP-5) or TPA-modified polyethylene glycol (HP-FFAP) as the stationary phase. Quantitative determination of the products was carried out by GLC with an internal standard.

Products deriving from 3-phenylprop-2-ene-1-ol, hexa-1,5-diene-3-ol and but-2-ene-1,4-diol were separated by column chromatography (Merck silica gel 60, 70–230 mesh) using appropriate n-hexane–ethyl acetate mixtures as eluent, after filtration from palladium metal and elimination of MeOH and/or DMA at reduced pressure. Products deriving from but-2-ene-1-ol and but-1-ene-3-ol were separated by Kugelrohr distillation.

3.2. Carbonylation procedure

In a typical experiment a 300 ml stainless steel autoclave (Parr) was charged with 274 mg (0.76 mmol) of PdI_2 , 174 mg (2.29 mmol) or 350 mg (4.60 mmol) of thiourea and the appropriate allyl alcohol (19 mmol) dissolved in a mixture of MeOH (15 ml) and DMA (4 ml). The autoclave was pressurized with CO (10 atm), stirred for about 1 min and then the CO was released. The charging and releasing of CO was repeated three times to eliminate any air in the autoclave. The system was eventually charged with CO (50 or 100 atm), heated at 80°C and stirred for the required time.

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