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Preliminary communication

Carbonylation of organic allyl moieties.

II *. A bi-functional Pd—HCl catalyst for the carbonylation of methoxyoctadienes

M.C. Bonnet, D. Neibecker, B. Stitou, and I. Tkatchenko *

Laboratoire de Chimie de Coordination du CNRS **, *205, route de Narbonne, 31077 Toulouse Cedex (France)*

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Abstract

In the presence of hydrogen chloride, methoxyoctadienes resulting from the telomerisation of butadiene and methanol are converted into methyl nona-3,8-dienoate. The availability of protons as well as chloride ligands is essential for a smooth and selective reaction.

The carbonylation of unsaturated substrates provides a powerful method for the introduction of a –C(O)– unit into organic substrates. It has been shown that butadiene can be alkoxycarbonylated in the presence of palladium catalysts in a highly chemo- and regio-selective process to yield either pent-3-enoic or nona-3,8-dienoic acid esters, depending on the nature of the counter-anion present [1]. The carbonylation of allyl ethers has scarcely been studied. Tsuji et al. [2] used palladium(II) chloride for the conversion of simple allyl ethers (eqn 1). Medema et al. [3] suggested the use of bis[(η^3-allyl)chloropalladium], **1a**, in toluene or carbon tetrachloride. However, as reported by Poirier et al. [4], carbonylation of methoxyhexadecatetraenes [5] in the presence of carbon tetrachloride, although giving higher rates of conversion, led to lower selectivities owing to the addition of the solvent to one of the double bonds of these compounds. High selectivities are achieved in toluene in the presence of complex **1b**, but at the expense of activity. Several other group 8–10 metal complexes have been used, but with low activities and/or selectivities [6]. We report here preliminary results on the influence of chloride sources on the carbonylation of models for a methoxyhexadecatetraene, viz. 1-

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* Part 1: see ref. 4.

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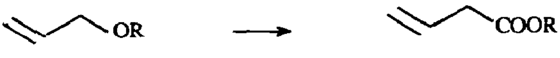
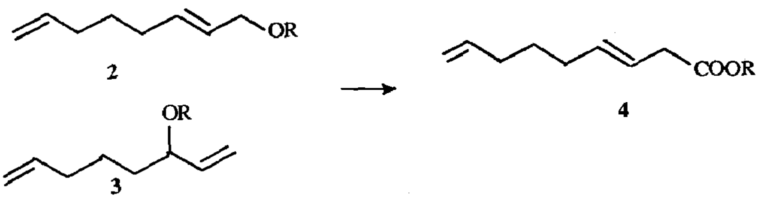

(1)

R = Me, Et, C_3H_5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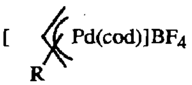
3

4

(2)

a, R = Me ; **b**, R = Et ; **c**, R = i-Pr ; **d**, R = Ph


1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a, R = H; **b**, R = Me-2

methoxy-octa-2,7-diene, **2a**, and 3-methoxy-octa-1,7-diene, **3a**, which are converted into methyl nona-3,8-dienoate, **4a** (eq. 2).

Inspection of Table 1 shows that in toluene, ionic complexes such as **5**, zerovalent compounds such as bis(dibenzylideneacetone)palladium, and palladium(II) acetate, are inactive in the carbonylation of these ethers. However, addition of one equivalent of bis(triphenylphosphine)iminium chloride, [PPN]Cl to **5**, induces the conversion of the starting materials into **4a**. The best results are observed with bis(η^3-

Table 1

Carbonylation of the ether mixtures **2a**+**3a**: Influence of catalyst precursor, solvent and reaction conditions (catalyst: 0.5 mmol; {**2a**+**3b**}: 50 mmol; solvent: 8 ml)

Catalyst	Ratio Pd/Additive	Solvent	Reaction time (h)	Reaction temperature (°C)	**4** (%)	**2a**+**3a** (%)
5	–	PhMe	72	100	0	92
5+[PPN]Cl	1/1	PhMe	72	100	67	29
5+[PPN]Cl	1/5	PhMe	72	100	7	90
1b	–	PhMe	72	100	75	21
1b	–	PhMe	168	100	79	18
1b	–	AcOEt	168	100	70	23
1b	–	NMP	120	100	24	71
1b	–	DMF	144	100	14	85
1b	–	MeOH	120	100	55	39
1b	–	AcOH	168	100	49	43
1b	–	–	120	100	52	43
1b	–	PhMe	72	80	44	56
1b+$P(OPh)_3$	1/1	PhMe	72	100	28	69
1b+PPh_3	1/1	PhMe	72	100	14	84

Table 2

Carbonylation of ether mixtures **2**+**3**: Influence of acids (catalyst: **1b**, 0.5 mmol; solvent: toluene, 8 ml; T 100 °C; P_{CO} 30 bar; time 3 d)

Ethers	Additive	Ratio Pd/Additive	**4** (%)	**2**+**3** (%)
2a+**3a**	Et_3N	1/1	8	88
2a+**3a**	HCl	1/5	81	9
2b+**3b**	–	–	29	67
2b+**3b**	HCl	1/5	71	20
2c+**3c**	–	–	0	100
2c+**3c**	HCl	1/5	71	29
2d+**3d**	–	–	63	37

methallyl-chloropalladium), **1b**. Addition of phosphanes sharply lowers the product yields. Under the standard conditions used, no carbonylation of octa-1,3,7-triene is observed, suggesting that this olefin does not participate in the reaction. Indeed, no octa-1,3,7-triene is detected during or after the carbonylation reaction.

The reaction takes place in various solvents (Table 1), but is strongly inhibited by the use of aprotic dipolar solvents, suggesting that they may be coordinated to the palladium centre, preventing activation of the ethers. It is noteworthy that acetic acid can also be used as solvent, and its use leads only to the methyl ester: no mixed anhydride (or its expected derivative, ethyl acetate) which might arise from the reaction of a nonadienoyl-palladium moiety with acetate ions is detected in the reaction mixture. There is no improvement in the yield of **4a** if reactions are prolonged after 3 days. The optimal conditions are 3 days, 100 °C, and 30 bar of carbon monoxide, with a palladium to substrate ratio of 1 : 100.

The fall in the yield of **4a** on going from triphenylphosphite to triphenylphosphine suggested to us that the interaction of **1b** with some of the reactants produces hydrogen chloride, which in turn enhances the catalytic activity. A clear-cut indication of the intervention of an acid in this catalytic reaction is given by the inhibiting effect of one equivalent of triethylamine (Table 2). Addition of anhydrous hydrogen chloride should thus favour the carbonylation process. The effect is rather small in the case of methoxy ethers. A much more pronounced influence is observed for ethoxy- and isopropoxy-octadienes, since in the absence of any added HCl, carbonylation of **2b** + **3b** is less important than that of **2a** + **3a**, whereas no transformation of **2c** + **3c** is observed (Table 2).

The formation of only one product from both isomers **2** or **3** supports the participation of an η^3-octadienyl palladium species as catalyst. The formation of this intermediate is presumably assisted by the protonation of the oxygen atom of the ethers. The formation of allyl species has been reported in the case of zero-valent nickel [7] and palladium [8] complexes for the better leaving groups phenate and acetate, respectively.

The catalysts described above thus behave as bi-functional catalysts: HCl acts as catalyst for the C–O bond cleavage, and palladium as catalyst for the carbonylation reaction itself. Further studies are in progress aimed at delineating the specific roles of H^+ and Cl^- (since an excess of chloride ion inhibits the reaction (Table 1)) and also establishing the origin of HCl from **1**.

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