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INTER- AND INTRAMOLECULAR DI-ALKOXYCARBONYLATION OF 3-BUTENOLS CATALYZED BY PALLADIUM(II)

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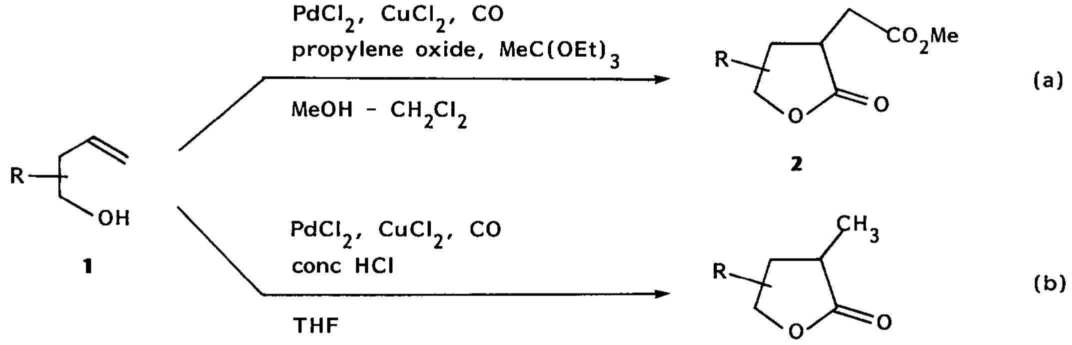
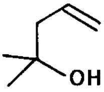
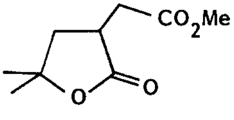
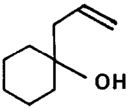
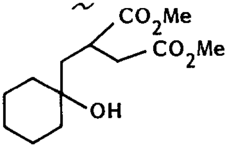
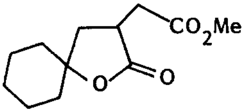
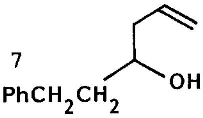
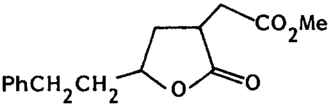
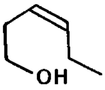
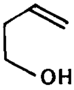
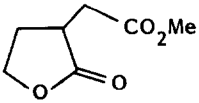
Summary: Palladium(II) salt catalyzes the inter- and intramolecular di-alkoxycarbonylation of 3-butenols to provide γ-butyrolactone 2-acetic acid esters under 1 atm of carbon monoxide.

Recently we[1] and Semmelhack[2] have shown that 4-pentenols undergo the palladium(II) catalyzed oxycarbonylation to provide tetrahydrofuran 2-acetic acid esters. 3-Butenols show the completely different reactivity. Here we report the first example of inter- and intramolecular di-alkoxycarbonylation of 3-butenols, which gives rise to γ-butyrolactone 2-acetic acid esters by the catalysis of Pd(II) salt under 1 atm of carbon monoxide (Eq. a). The reaction is reminiscent of the succinate formation by the di-alkoxycarbonylation of olefins reported by Tsutsumi,[3a] Fenton,[3b] and Stille,[3c] and also of the γ-butyrolactone formation by the hydrocarbonylation of γ,δ-unsaturated alcohols reported by Alper (Eq. b)[4] and Norton[5] (vide infra).



The present di-alkoxycarbonylation can be performed by usig $PdCl_2$ (0.01 - 0.5 equivalents) and $CuCl_2$ (3 equivalents) under 1 atm of CO in methanol or in a methanol-dichloromethane mixed solvent at an ambient temperature. Results are summarized in Table I. The reaction is quite dependent both on the kinds and the amounts of additives. In the presence of 0.4 equivalents of ethyl orthoacetate (EOA), 1-allylcyclohexanol (1b) was converted to 1-(2',3'-dicarbomethoxypropyl)cyclohexanol (3b) in 57% yield (entry 5), while addition of 5 equivalents of N,N,N',N'-tetramethylurea (TMU) into this reaction mixture caused a dramatic

Table I. Palladium Catalyzed Inter- and Intramolecular Double Carbonylation of 3-Butenols **1**[a]

entry	3-butenol	$PdCl_2$	Additives		Solvent	product[b]
		(mmol)	HCl Quencher (mmol)	$MeC(OEt)_3$ (mmol)	$MeOH/CH_2Cl_2$ (mL/mL)	(% yield)
1	 1a	0.5	TMU (5)	0.4	3/3	 2a (70%)
2	**1a**	0.1	PO (3)	---	3/6	**2a** (26%)
3	**1a**	0.1	PO (5)	---	3/6	**2a** (47%)
4	**1a**	0.1	PO (5)	0.4	3/6	**2a** (72%)
5	 1b	0.5	-----	0.4	5/0	 3b (57%)
6	**1b**	0.5	TMU (5)	0.4	5/0	 2b (70%)
7	 1c	0.5	TMU (5)	0.4	3/3	 2c (63%)
8	**1c**	0.1	PO (5)	0.4	3/6	**2c** (97%)[c]
9	 1d	0.1	PO (5)	0.4	3/6	**2d** (22%), **4d** (28%)[d]
10	 1e	0.1	PO (5)	0.4	3/6	 2e (76%)
11	**1e**[e]	0.01	PO (4)	0.2	2/4	**2e** (72%)

(Table I, continued)

a) Usual reaction conditions (except for entry 11) are as follows: 3-butenol (1 mmol), $PdCl_2$ (indicated amount), $CuCl_2$ (3 mmol), HCl quencher (TMU = N,N,N',N'-tetramethylurea, PO = propylene oxide, indicated amounts), ethyl orthoacetate (indicated amount) under 1 atm of CO at an ambient temperature for 1 day.

b) Isolated yield by means of column chromatography on silica gel.

c) A diastereomeric mixture in a 3 : 1 ratio.

d) See Scheme I.

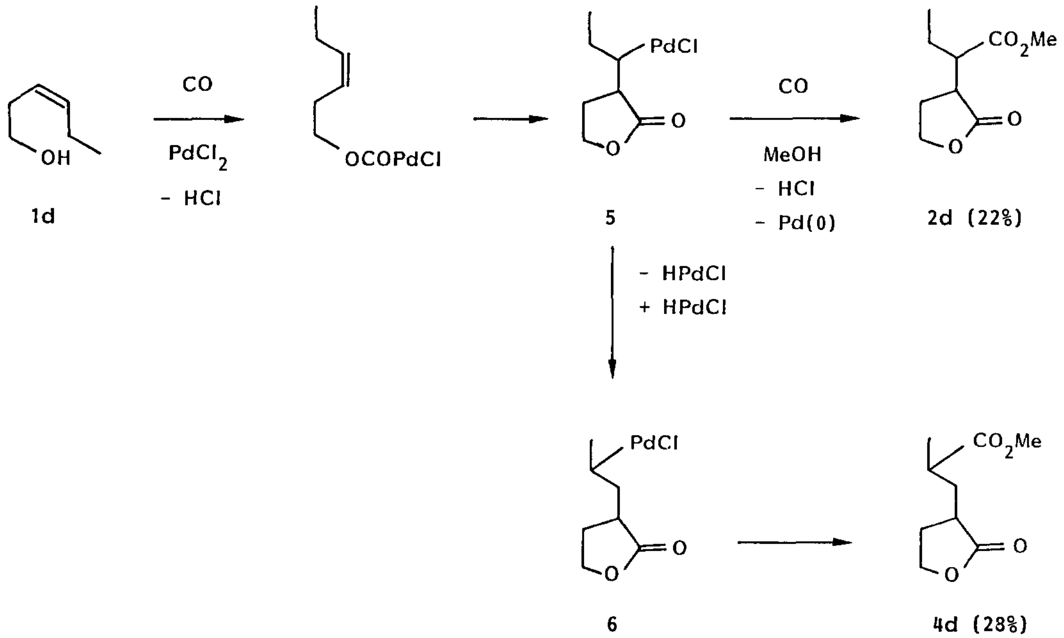
e) See the experimental part in the text.

change of product, and γ-butyrolactone (2b) was obtained in 70% yield (entry 6). In the absence of these additives, the reaction becomes complex and 3b was obtained in low yield as a mixture with other unidentified product(s). Propylene oxide (PO) is by far the superior additive to TMU. With this, the γ-butyrolactone (2c, as a 3:1 diastereomeric mixture) was obtained in a quantitative yield even by the use of a smaller amount of catalyst (cf. entries 7 and 8). By comparison of entries 1 - 4, it is apparent that both additives, PO and EOA, cooperate to increase the turn-over number of the catalyst system. Although the roles of these additives are not yet clear,[6] PO and TMU may serve as the quenchers of HCl produced in the reaction. As a matter of fact, the water layer obtained during the extractive work-up of entry 2 is acidic, while the water layer of entry 4 is neutral. In this context, it is noteworthy that the above mentioned hydrocarbonylation (Eq. b) is only successful when it is performed in the presence of conc. HCl.[4] Furthermore, the reaction behavior of the present reaction makes marked contrast to the palladium catalyzed di-alkoxycarbonylation of olefins.[3] These reactions provide succinates under basic conditions, while under neutral (or acidic) conditions 3-alkoxypropionates prevail.[3c]

Although the longer reaction time is neccessary for the completion of the reaction, the amount of $PdCl_2$ may be reduced to 0.01 equivalents to a substrate (entry 11). Typical experiment under the optimized conditions is as follows (entry 11): Into a 100 mL, two necked round bottom flask, equipped with a CO balloon and a septum cap, containing a magnetic stirring bar, $PdCl_2$ (18 mg, 0.1 mmol), and $CuCl_2$ (4.04 g, 30 mmol) was introduced a solution of 3-butenol (720 mg, 10 mmol), propylene oxide (2.32 g, 40 mmol), and ethyl orthoacetate (324 mg, 2 mmol) in 40 mL of dichloromethane and 20 mL of methanol. During stirring, the color of the reaction mixture turns from deep green to yellowish brown. After stirrig for 6 days at an ambient temperature, low-boiling materials were evaporated and the residue was filtered through a cellulose column to remove inorganics and washed with ethyl acetate. The filtrate was washed with aq. $NaHCO_3$ (20 mL) and the basic water layer was extracted with ethyl acetate (15 mL x 2). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated. γ-Butyrolactone 2-acetic acid methyl ester 2e was obtained in 72% yield (1.14 g) by kugelrohr distillation of the residue under the reduced pressure (120°C/ 0.3 mmHg). 2e: IR (neat film, cm^{-1}) 1735 and 1765; ^1H NMR ($CDCl_3$, ppm) 1.75 - 2.31 (m, 1 H), 2.31 - 2.75 (m, 2 H), 2.75 - 3.19 (m, 2 H), 3.72 (s, 3 H), and 4.06 - 4.56 (m, 2 H); ^{13}C NMR ($CDCl_3$, ppm) 28.2, 34.1, 35.6, 51.6, 66.3, 171.3, 177.7.

By the carbonylation of cis-3-hexenol (1d) were provided two kinds of products. One is the expected lactone 2d (as a single stereoisomer) and the other is its regioisomer 4d (entry 9, Scheme I). These observations indicate that the reaction presumably proceeds according to Scheme I, which is characterized by the first intramolecular carbonylation (lactonization forming an intermediate 5) followed by the intermolecular carbonylations at the β-position to the lactone carbonyl to give 2d and at the γ-position to give 4d. An intermediate 6 might be derived from 5 by an elimination-addition of hydridopalladium species.[3c]

Scheme I. Intramolecular Oxycarbonylation followed by Intermolecular One



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4) H. Alper and D. Leonard, J. Chem. Soc., Chem. Commun., 511 (1985).
5) E. G. Samsel and J. R. Norton, J. Am. Chem. Soc., 106, 5505 (1984).
6) Ethyl orthoacetate may serve as a drying agent of water in the catalyst system.[6b,6c]

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