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Hydroxycarbonylation of vinyl acetate with formic acid: pathway to lactic acid and lactates

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General information

^{1}H and ^{13}C NMR spectra were recorded on Bruker AM300 spectrometer (300.13 and 75.48 MHz, respectively) in $CDCl_3$. Chemical shifts data were reported as δ in units of parts per million (ppm) relative to residual $CHCl_3$ peak: ^{1}H (δ = 7.26 ppm), ^{13}C (δ = 77.16 ppm).

Vinyl acetate (VA **1**, 99+%, stabilized) was purchased from Acros Organics and distilled before use. All solvents were dried and distilled using standard procedures and kept over NaA molecular sieves. $Pd(OAc)_2$ [S1], $Pd(acac)_2$ [S2], $PdCl_2(PPh_3)_2$ [S3] and $Pd(dba)_2$ [S4] were prepared according to the literature procedures.

Experimental procedure for hydoxycarbonylation of vinyl acetate

A 50 mL steel autoclave equipped with glass lining and magnetic stirrer was charged with VA **1** (0.2 mL, 2.17 mmol), appropriate amounts of catalyst precursor, ligand, HCOOH in a solvent (3 mL). The system was purged three times with CO, pressurized and heated to the desired temperature. The reaction was performed under stirring (600 rpm) for 4 h. After that, the reactor was chilled to room temperature, depressurized and opened, the mixture was analyzed chromatographically on an Avtokhrom 3700 instrument (Alltech™ quartz capillary column 60 m × 0.25 mm, stationary phase SE-30, FID, argon as a carrier gas) using *n*-nonane as an internal standard. For quantitative determination of carboxylic acids, they were converted into their methyl esters by treating the sample with ether solution of diazomethane.

To identify the products, the reaction mass was extracted with water. The water layer was rinsed with heptane, separated and carefully evaporated in air. The solid colourless residue was thus obtained. Analysis revealed **2a** with small impurity of isomer **2′a** (ratio ≈ 20:1). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ): 8.67 (br s, 1H), 5.08 (q, 1H), 2.12 (s, 3H), 1.51 (d, 3H). $^{13}C\{^{1}H\}$ NMR (75.48 MHz, $CDCl_3$, δ): 176.3, 170.8, 68.4, 20.7, 16.9.

References

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Table S1. Effect of solvent on VA **1** hyroxycarbonylation. Conditions: VA (0.2 mL, 2.17 mmol), 0.3% $Pd(OAc)_2$, HCOOH (0.1 mL, 1.2 equiv.), 3% PPh_3, solvent (3 mL). *T* 80°C, *P* 3 bar, 4 h.

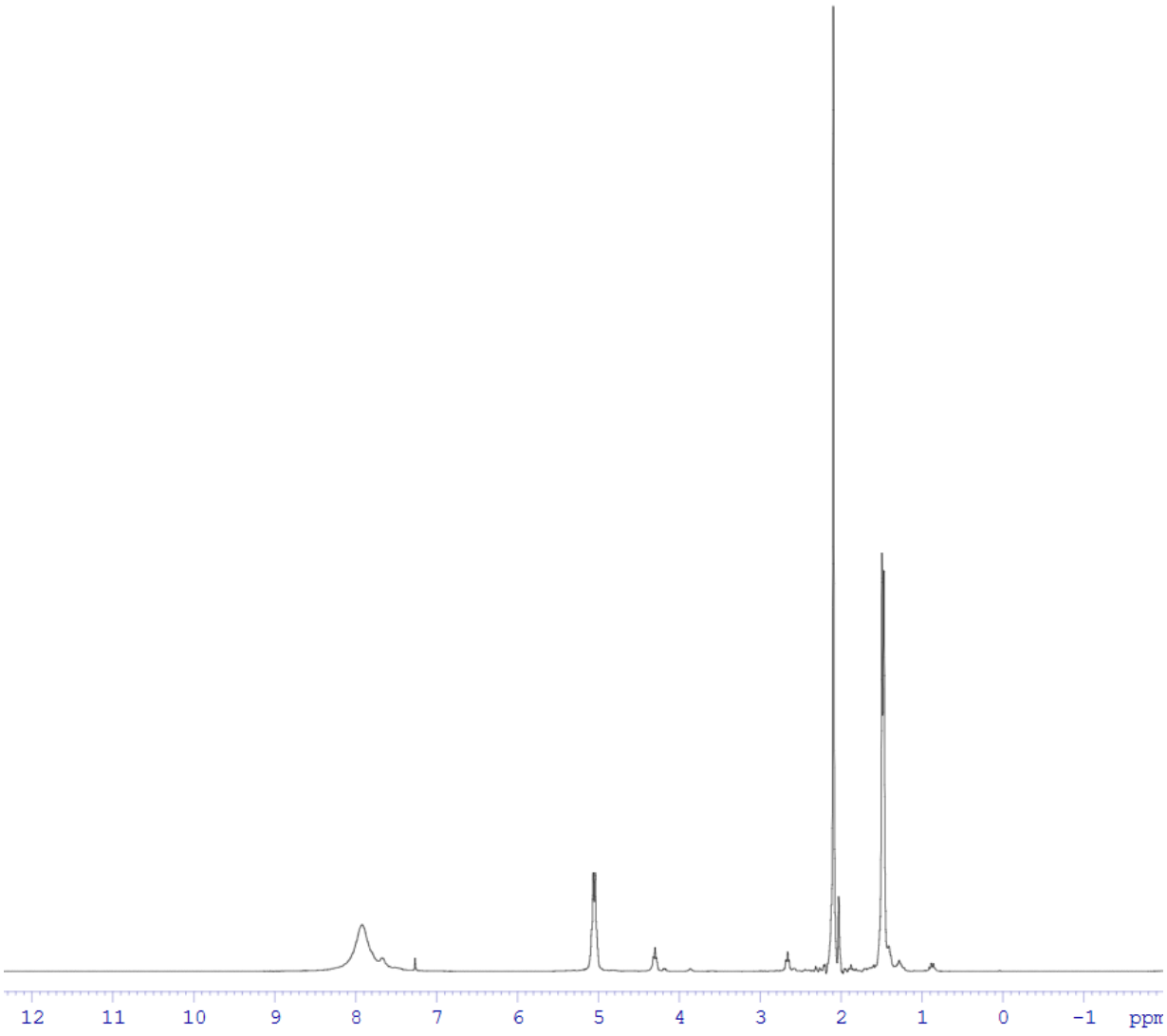
Entry	Solvent	VA conversion, %	Yield of **2a**, %
1	Benzene	57.1	23.5
2	Toluene	67.6	35.3
3	*o*-Xylene	36.8	14.6
4	*p*-Xylene	36.8	16.1
5	PhCl	83.3	64.1
6 [a]	PhCl	67.1	50.1
7 [b]	PhCl	50	11.2
8	MeCN	40.5	2.2
9	MeC(O)Et	45.2	7.1
10	Pyridine	16.6	0
11	MeOH	22.2	5.5
12	Heptane	65.6	0
13	THF	20.9	6.8
14	1,4-dioxane	21.6	6.8
15	DCM	40.9	18.2
16	EtOAc	16.6	0
17 [c]	Bu_4NBr	33.3	11.7 (+1.7% of **2′a**)

[a] With $Pd(dba)_2$

[b] 90% HCOOH was used

[c] no PPh_3

2-Acetoxypropanoic acid 2a, ^{1}H NMR



2-Acetoxypropanoic acid 2a, ^{13}C NMR