

## CARBONYLATION OF 1-NONENE ON Pd(II) COMPLEXES IN ALCOHOLS AT LOW CO PRESSURE

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The alkoxy carbonylation of olefins catalyzed by palladium complexes is a promising method for the synthesis of carboxylic acids [1-3]. The dilution of the alcohol solvent by acetone gives an increase in the yield and selectivity of the carbonylation of 1-nonene in methanol at low CO pressure (13-24 atm) [4]. In this regard, it was of interest to evaluate the effect of acetone on the carbonylation of olefins in other aliphatic alcohols.

The carbonylation of 1-nonene in alcohols or mixtures of alcohols and acetone was carried out according to our previous procedure [4] at 90°C and 13 and 24 atm CO pressure in the presence of catalytic amounts of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.9 mole % relative to 1-nonene). The reaction time was 6 h. The yields of the major products, namely, esters of decanoic (I) and α-methylpelargonic acids (II), were determined by gas-liquid chromatography.

Table 1 shows that the total yield of the reaction products in normal alcohols increases in the series: PrOH < BuOH < HeptOH (Nos. 1, 4, and 10), while the selectivity hardly changes. An increase in the CO pressure from 13 to 24 atm does not have a marked effect on the reaction (compare Nos. 4 and 5 and 10 and 11). The reaction in these alcohols proceeds better than in methanol, in which the yield was only 40% and the selectivity was 58% for P<sub>CO</sub> 13 atm [4]. Esters of α-ethyloctanoic acid (III), which are the products of the carbonylation of 2-nonene arising due to isomerization of 1-nonene in the reaction mixture, are virtually absent, while the yield of (III) is 5% in methanol [4].

The introduction of a small excess of PPh<sub>3</sub> into butanol, as expected [1, 2], leads to an increase in selectivity (compare Nos. 4 and 6). However, in contrast to the effect of PPh<sub>3</sub> in methanol, in which the improvement in selectivity is accompanied by an increase in the yield of isomer (I), an excess of the ligand in butanol inhibits the formation of both isomers.

TABLE 1. The Yield and Selectivity (S) of the Carbonylation of 1-Nonene in Alcohols and Alcohol-Acetone Mixtures at 90°C Catalyzed by PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (P<sub>CO</sub> 13 atm)

Number	Alcohol	V <sub>ac</sub> /V <sub>al</sub> <sup>a</sup>	Yield of esters			S <sup>b</sup>
			(I)	(II)	total	
1	PrOH	0	47	25	74 <sup>c</sup>	64
2	PrOH	0.5	42	28	71 <sup>c</sup>	59
3	PrOH	2	40	31	71	56
4	BuOH	0 <sup>d</sup>	61	28	89	69
5	BuOH	0	61	32	93	66
6	BuOH	0 <sup>e</sup>	42	6	48	88
7	BuOH	0.5	46	35	81	57
8	BuOH	2	41	35	76	54
9	BuOH	5	31	29	60	52
10	HeptOH	0 <sup>d</sup>	62	31	93	67
11	HeptOH	0	67	32	99	69
12	HeptOH	2	35	33	68	51

<sup>a</sup>Acetone-alcohol volumetric ratio.

<sup>b</sup>Ratio of the yield of isomer (I) to the total yield %.

<sup>c</sup>Including 2% (No. 1) and 1% (No. 2) isomer (III).

<sup>d</sup>P<sub>CO</sub> 24 atm.

<sup>e</sup>Twofold molar excess of PPh<sub>3</sub> relative to PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.

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The addition of acetone also has different effects on the reaction in different alcohols. Thus, upon the dilution of methanol by acetone to give a 1:2 volumetric ratio, the total ester yield increases [4], while this yield is hardly affected upon the dilution of propanol by acetone (Nos. 1-3). The total ester yield is significantly reduced upon the addition of acetone to butanol and heptanol (Nos. 4, 7, 8, and 10, 12). In this case, the yield of isomer (I) is increased from 23% to 57% in the reaction of 1-nonene with methanol, while this yield drops upon the addition of acetone to the other alcohols; this reduction in the yield is more pronounced with increasing molecular mass of the alcohol. On the other hand, going from the alcohol to 1:2 alcohol-acetone gives an increase in the yield of isomer (II), which is the greatest for methanol (by 15%) and least in heptanol (by only 2%). Thus, the selectivity of the hydrocarboalkoxylation of 1-nonene in all the alcohols studied with the exception of methanol deteriorates upon the addition of acetone.

We should note that the yields in 1:5 mixtures of methanol and butanol with acetone are 62% and 60%, respectively, while the selectivities are 53% and 52% in these solvent mixtures, respectively. This result, which relates to a medium whose macroscopic properties are largely determined by acetone, is in accord with the conclusion of Knifton [1] that the reaction step involving the alcohol does not control the rate of regioselectivity of the olefin carbonylation reaction.

Since the addition of acetone most often has opposite effects on the yields of isomers (I) and (II), we may assume that the mechanisms for the formation of the linear and branched products of the carbonylation of olefins are different [4]. Without discussing the effect of the medium and ligand on the yield and selectivity, we note that the difference in the effects of  $\text{PPh}_3$  in methanol (an increase in the total activity of the palladium catalyst) and in butanol (a decrease in this activity) may be explained taking account of the different types of palladium intermediates in these alcohols. Thus, in the carbonylation of propene in methanol, Temkin [5] isolated acyl and carbomethoxyl complexes of palladium which are intermediates in the carbonylation steps proceeding by hydride and alcoholate mechanisms, respectively, while in butanol, on the acyl palladium complex was isolated [2]. On the basis of data for analogous platinum complexes [6], we may assume that  $(\text{ROOC})\text{PdCl}_2$  ( $\text{L} = \text{PPh}_3$ ) complexes are less active in olefin carbonylation than the acyl complexes. It is not excluded that  $\text{Ph}_3\text{P}$  inhibits the formation of  $(\text{ROOC})\text{PdCl}_2$  from  $\text{PdCl}_2\text{L}_2$ , thereby leading to an increase in the concentration of the more active forms of the palladium catalyst in methanol for low  $\text{PPh}_3/\text{Pd}$  ratios, while in butanol, in which the fractions of low-activity forms is initially small, an excess of ligand L, as usual [1, 4], reduces the catalyst activity. The observed effects of acetone may possibly be explained by similar reasons.

#### CONCLUSIONS

1. The yields of the products of the carbonylation of 1-nonene in normal alcohols upon catalysis by palladium (II) complexes and low carbon monoxide pressures increases with increasing molecular mass of the alcohol, while the selectivity remains virtually the same.

2. The dilution of the alcohol by acetone does not affect the yields of the carbonylation of 1-nonene in 1-propanol but causes a decrease in this yield in 1-butanol and 1-heptanol. The selectivity decreases upon the addition of acetone to all the alcohols studied.

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