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A NOVEL SYNTHESIS OF LEVULINIC ESTERS FROM 4-ALKOXY-2-BUTANONE USING RHODIUM CATALYSTS

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The catalytic carbonylation reactions of ethers and alcohols in the presence of homogeneous catalysts were already studied by many workers. For example, the carbonylations of ethers such as diethyl ether and THF by using iron, nickel and cobalt catalysts were reported.1,2,3) Recently, it was found that acetic acid is selectively synthesized from methanol and carbon monoxide using rhodium catalyst under mild condition.4,5)

We attempted to synthesize levulinic acid by hydroformylation and hydrocarboxylation of methyl vinyl ketone (MVK) using usual catalysts, e.g., palladium, rhodium, cobalt, nickel, but unfortunately, this attempt was unsuccessful. Next, we have tried to synthesize levulinic esters by the carbonylation reaction of 4-alkoxy-2-butanone, which is easily obtained from MVK and alcohols, and found that this reaction proceeds smoothly under mild conditions by using rhodium catalyst.

In the most of runs, the mixture of the ether (60 mmol), solvent (40 ml), rhodium complex (2 mmol) and iodide (35 mmol) is charged in a stainless-steel (SUS 316) autoclave and carbon monoxide of 150 kg/cm^2 (initial pressure) is introduced, reaction being carried out at 90-150°C for 5-8 hrs.

The results are listed in the table.

Table Carbonylation of 4-alkoxy-2-butanone*

Reactant	Catalysts	Reaction Temp. (°C)	Conversion of Reactant (%)	Yield**		
				EL (mol%)	LA (mol%)	EL+LA (mol%)
4-Ethoxy-2-butanone	$RhCl(PPh_3)_3$ 2 mmol CH_3I 35 mmol	120	100	12.9	26.7	39.6
	$RhCl_3 \cdot 3H_2O$ 2 mmol $P(n\text{-}Bu)_3$ 6 mmol CH_3I 35 mmol	120	100	21.9	11.6	33.5
	$[RhCl(CO)_2]_2$ 1 mmol CH_3I 35 mmol	120	100	22.7	1.7	24.4
	$[Rh(CH_3COO)_2]_2$ 1 mmol I_2 12 mmol	120	85	19.1	0	19.1
	$RhCl(CO)(PPh_3)_2$ 4 mmol	120 150	5	0	0	0
	NiI_2 6 mmol CH_3I 35 mmol	200	100	trace	-	trace
	$Fe(CO)_5$ 10 mmol CH_3I 35 mmol	200	100	trace	-	trace
	$[Co(CO)_4]_2$ 3 mmol CH_3I 35 mmol	200	100	0	0	0
4-Methoxy-2-butanone	$RhI(CO)(PPh_3)_2$ 2 mmol CH_3I 35 mmol	120	100	-	10.1***	10.1
4-Hydroxy-2-butanone	$[RhCl(CO)_2]_2$ 2 mmol CH_3I 35 mmol	120	90	-	trace	trace

* Reactant: 60 mmol, solvent(toluene or benzene): 40 ml, CO pressure: 150 kg/cm^2

** EL: ethyl levulinate, LA: levulinic acid, ML: methyl levulinate

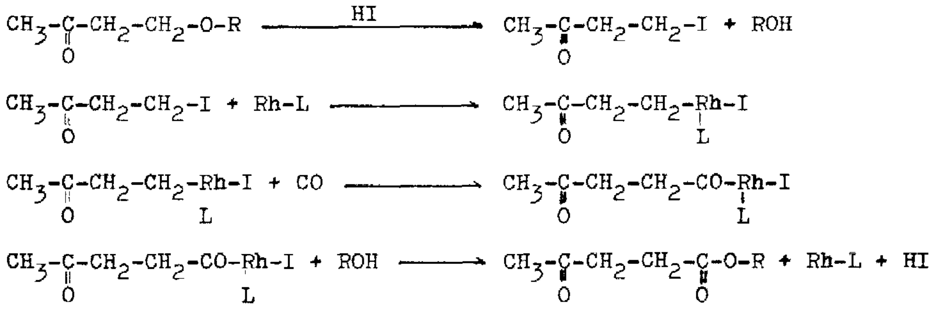
*** ML+LA

The carbonylation of 4-alkoxy-2-butanone using homogeneous rhodium/iodide catalysts was found to produce both levulinic acid and alkyl levulinate. The yield of free levulinic acid remarkably increases when the rhodium complexes having tertiary phosphine ligands, e.g., PPh_3, $P(n\text{-}Bu)_3$, are used. There was no formation of acetic acid but formation of small amount of ethyl acetate. The gaseous products obtained consisted of hydrogen, methane, ethane, ethylene, propylene and butanes in addition to the unreacted carbon monoxide.

In the presence of rhodium/iodide catalyst, carbon monoxide was inserted into the ethers containing additional functional groups, e.g., -CO, -OH, -COOR, -CN, under milder conditions than usual ethers containing no additional functional groups, e.g., diethyl ether, THF etc.[6] On the other hand, the carbonylation of 4-hydroxy-2-butanone does not proceed under this reaction condition as shown in the table.

These results seem to show that this carbon monoxide insertion reaction does not proceed via 4-hydroxy-2-butanone.

The following reaction scheme is proposed.



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-O-R \xrightarrow{HI} CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-I + ROH \qquad (1)$$

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-I + Rh-L \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{L}{|}}{Rh}-I \qquad (2)$$

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{L}{|}}{Rh}-I + CO \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CO-\underset{\underset{L}{|}}{Rh}-I \qquad (3)$$

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CO-\underset{\underset{L}{|}}{Rh}-I + ROH \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-O-R + Rh-L + HI \qquad (4)$$

(L: ligands)

It is considered that the ether bond is cleaved into 4-iodo-2-butanone and alcohol by hydriodic acid, and then oxidative addition reaction occurs between 4-iodo-2-butanone and Rh(I) complex to form a six-coordinate alkyl-rhodium(III) species. Rapid insertion of carbon monoxide into the alkyl-rhodium bond occurs, to yield an acyl-rhodium(III) complex. Finally, reaction is completed by reaction of the acyl-rhodium(III) complex with the alcohol to yield alkyl levulinate and the original rhodium(I) complex.[7] The formation of hydriodic acid is deduced from reaction of iodine or methyl iodide with solvent or reactants.[8] Free levulinic acid may be produced by pyrolysis or hydrogenolysis of levulinic ester.

Iron, nickel, and cobalt compounds are practically inactive for the carbonylation of 4-ethoxy-2-butanone. In this case, 4-ethoxy-2-butanone is decomposed to methyl vinyl ketone and ethanol. Methyl vinyl ketone is hydrodimerized to 2,7-octanedione⁹⁾ and then 2,7-octanedione undergoes rapid cyclodehydration to produce 1-acetyl-2-methylcyclopentene-1.¹⁰⁾

Further investigations of this new type reaction, are being carried out in our laboratory.

References and notes

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6) The carbonylation of diethyl ether or THF does not proceed under similar mild conditions to this experiment. This carbonylation does not proceed below 170°C.

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