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Palladium(II)-Catalyzed Cyclocarbonylation of Enol Ester of Acetone. A Novel Synthesis of 1,3-Dioxolan-4-one

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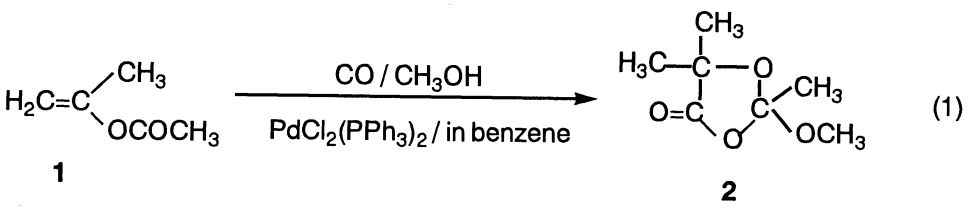
The cyclocarbonylation of isopropenyl acetate(**1**) to produce 2-methoxy-2,5,5-trimethyl-1,3-dioxolan-4-one(**2**) by use of palladium(II)-phoshine catalyst with methanol in benzene solution was studied at 100 °C under 200 atm of CO. Conversion of **1** up to 98% and yield to **2** as high as 67% were attained.

In general, the carbonylation of olefinic carbon in the presence of an alcohol catalyzed by transition metals can take place to afford saturated esters or β-alkoxy esters. However, catalytic carbonylation of carbonyl carbon has so far received much less attention.

We previously reported that a rhodium-phosphine complex is a very efffective catalyst for the hydrocarbonylation of formaldehyde to afford glycolaldehyde.[1] Murai and co-workers have reported that a new catalytic reaction system of $HSiR_3/Co_2(CO)_8/CO$ can bring about incorporation of CO into aliphatic aldehydes[2] and cyclobutanones.[3]

During our continued research to develop the method for carbonylation of the carbonyl carbon in aldehyde and ketone derivatives, we found that the palladium(II)-catalyzed carbonylation of isopropenyl acetate(**1**), which is an enol ester of acetone, gives 2-methoxy-2,5,5-trimethyl-1,3-dioxolan-4-one(**2**) in high selectivity.



1 **2** (1)

It is interesting to compare the present reaction with previously reported palladium(II)-catalyzed cyclocarbonylation of an unsaturated alcohols to lactones.[4]

We wish to report here the preliminary results of this attractive carbonylation of **1** to **2**, which is a new synthetic method for 1,3-dioxolan-4-one ring compounds based on a palladium-catalyzed reaction of an enol ester with CO.

The representative results under various conditions using $PdCl_2(PPh_3)_2$ as a catalyst are shown in Table 1. A typical experimental procedure was as follow: 40 ml glass tube charged with **1** (2 mmol), methanol (2.5 mmol), 2,6-lutidine (0.1 mmol), $PdCl_2(PPh_3)_2$ (0.1 mmol), and benzene (5 ml) was placed in an autoclave,

which was pressurized with CO of 200 atm, and then the mixture was heated with stirring for 5.5 h at 100 °C. GC analysis revealed the formation of **2** as a main product together with small amounts of methyl 2-acetoxyisobutyrate(**4**) and methyl 3-acetoxybutyrate(**5**). The main product **2** isolated by column chromatography on silica gel was identified by the comparison of the ^{1}H and ^{13}C NMR and GC-MS fragmentation pattern with those of an authentic compound prepared from the reaction of 2-hydroxyisobutyric acid and trimethyl orthoacetate.[5)]

The reaction was largely dependent on the conditions. First, we screened catalytic effects of various palladium complexes such as $PdCl_2(PhCN)_2$, $PdCl_2(AsPh_3)_2$, $PdCl_2(PBu_3)_2$, $Pd(OAc)_2{\cdot}2PPh_3$, $PdCl_2$(dppe), $Pd(PPh_3)_4$, and $PdCl_2(PPh_3)_2$ for the reaction at 80 °C and 100 atm of CO: then it was found that only $PdCl_2(PPh_3)_2$ showed the catalytic activity enough to promote the reaction. Other transition metal

Table 1. Carbonylation of Isopropenyl Acetate with $PdCl_2(PPh_3)_2$[a)]

Run	CH_3OH/**1** mol/mol	Base/Pd mol/mol	Temp °C	CO atm[b)]	Conv. of **1**/%	Products yield/%[c)] **2**	**3**	**4**	**5**	Select. of **2**/%[d)]
1	0	0	100	200	6.0	0	0	0	0	
2	0.5	0	100	200	11.2	6.7	0	0.5	0.2	59.8
3	1.25	0	100	200	69.7	46.3	0	0.8	1.6	66.4
4	2.4	0	100	200	82.8	32.7	1.1	1.1	1.7	39.5
5	3.7	0	100	200	81.4	12.5	5.7	1.2	1.3	15.4
6	9.9	0	100	200	80.6	2.8	12.0	0.9	1.3	3.5
7	1.25	0.5	100	200	38.4	26.4	0	4.8	1.4	68.8
8	1.25	1.0	100	200	42.0	33.6	0	3.2	2.3	80.0
9	1.25	2.5	100	200	5.5	2.9	0	0.3	0	52.7
10	1.25	1.0[e)]	100	200	51.0	38.0	0	4.7	1.7	74.5
11	1.25	1.0[f)]	100	200	54.0	43.7	0	3.2	1.4	80.9
12	1.25	1.0[g)]	100	200	46.4	40.1	0	1.0	0	86.4
13	1.25	1.0	100	100	43.7	31.1	0	3.0	2.9	71.2
14	1.25	1.0	100	160	61.7	48.3	0	4.0	2.9	78.3
15	1.25	1.0	100	250	45.0	31.4	0	3.5	1.4	69.8
16	1.25	1.0	80	200	16.1	10.8	0	0.9	0.4	67.1
17	1.25	1.0	120	200	35.6	10.3	0	3.3	6.2	28.9
18	1.25	1.0	140	200	36.1	0.6	0	1.1	6.0	1.7
19[h)]	1.25	1.0	100	200	98.7	67.0	0	7.0	4.0	67.9

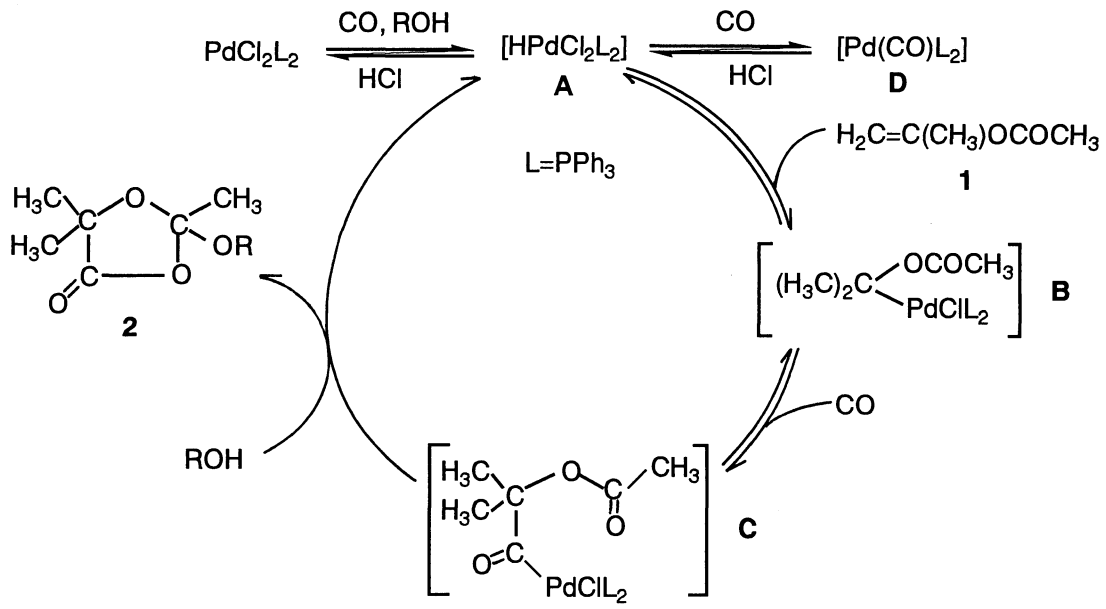
a) All reactions were run with 2.0 mmol of **1** and 0.1 mmol of $PdCl_2(PPh_3)_2$ in 5 ml benzene for 5.5 h. b) Initial pressure at room temperature. c) Determined by GC and based on **1** employed. d) Yield of **2**/Conversion %. e) Pyridine was used. f) Tributhylamine was used. g) Sodium butyrate was used. h) Reaction for 15.5 h.

complexes such as $NiCl_2(PPh_3)_2$ and $RhCl(PPh_3)_3$ were catalytically ineffective.

Next, we surveyed the effects of reaction variables on the product yield and selectivity. No reaction proceeded at all in the absence of methanol, and **1** was recovered almost unchanged(run 1). A slightly excessive amount of methanol to **1** gave the best yield of **2**. However, at still higher MeOH/**1** ratio, methyl 2-hydroxyisobutyrate(**3**) was produced instead of **2**, presumably via an in situ methanolysis of **2**(runs 2-6).

Addition of 2,6-lutidine in an equivalent amount to the catalyst improved the selectivity of **2**. However, the use of an excess of the base remarkably retarded the reaction(runs 7-9). Other bases such as pyridine, tributylamine, and sodium butyrate were almost as effective as 2,6-lutidine(runs 10-12). The reaction did not take place below 60 °C. The best result with respect to the yield and selectivity of the desired product(**2**) was achieved with the reaction carried out under 160 atm of CO and at 100 °C(runs 13-18). At higher temperature, the catalyst lost its activity by reduction to palladium metal. The catalytic reaction was complete within 15.5 h, and afforded **2** in 67% yield along with much smaller amounts of hydroesterification products, **4** and **5**(run 19). Use of ethanol in place of methanol afforded the corresponding dioxolanone, 2-ethoxy-2,5,5-trimethyl-1,3-dioxolan-4-one, in 41.5% yield under similar conditions.

It is noteworthy that an in situ IR spectra[6] of a solution of $PdCl_2(PPh_3)_2$ in methanol-chloroform under 100 atm of CO at 100 °C without **1** exhibited an only new absorption at 2050 cm^{-1} which is characteristic of hydridopalladium(II).[8] Thus, it could be safely concluded that the reaction proceeds via a hydridopalladium species(**A**) in the presence of alcohol under the atmospher of pressurized CO. It is known that $PdCl_2(PPh_3)_2$ can abstract hydrogen from alcohols to form a hydride complex under these conditions.[9] The complex **A** is also known to undergo a facile reduction to a carbonyl complex(**D**) under higher pressure of CO,[9] which would decrease the catalytic activity of this system(run 15).



Scheme 1.

As shown in Scheme 1, the proposed mechanism on this reaction is closely related to that of the hydroesterification of ordinary olefins[10] except for the ring closure step of acylpalladium complex(**C**). In the ring closure step leading to **2**, the acetoxy carbonyl oxygen, which is in a sterically favorable position, could serve as a nucleophile toward the strongly electrophilic acylpalladium carbon; simultaneous nucleophilic attack by a methanol molecule on the carbonyl carbon of the acetoxy group would lead to the ring-closing.

References

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5) The authenic compound was prepared by a method analogous to N. Cohen, B. L Banner, A. J. Laurenzano, and L Carozza, Org. Synth., Coll. Vol. VII, **1990**, 297. **2**: ^{1}H NMR($CDCl_3$) δ 3.26 (3H, s), 1.64 (3H, s), 1.48 (3H, s), and 1.43 (3H, s); ^{13}C NMR($CDCl_3$) δ 174.7, 120.5, 78.6, 49.4, 25.3, 24.8, and 24.4. GC-MS m/z 129 (M^+-OCH_3), 101, and 59.
6) In situ IR spectra were taken by the use of a high pressure IR cell designed in our laboratory.[7] Since benzene has absorption at 1800-2000 cm^{-1} region, we chose chloroform as the solvent for the measurement.
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