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Cobalt-catalyzed Hydroesterification of Formaldehyde Dialkyl Acetals

Kazuhisa Murata,* Akio Matsuda, and Takashi Masuda
National Chemical Laboratory for Industry, Tsukuba Research Center,
Yatabe, Tsukuba, Ibaraki 305
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Synopsis. $Co_2(CO)_8$-organic amine system was found to be an effective catalyst for the production of alkoxyacetic ester from formaldehyde dialkyl acetals and CO; this is the first example of homogeneous hydroesterification of acetal.

Alkoxyacetic ester is not only a good ether/ester type solvent, but also an important intermediate for preparing ethylene glycol by hydrolysis and hydrogenation. The ester is produced when formaldehyde dialkyl acetals(acetals) are allowed to react with CO in the presence of (solid) acid catalyst (Eq. 1).[1]

$$(RO)_2CH_2 \xrightarrow{CO} ROCH_2COOR \qquad (1)$$

1 (R=Me(**a**), Et(**b**), i-Pr(**c**))

$$\xrightarrow{CO/H_2} ROCH_2CHO \qquad (2)$$

Also, the ester is obtained by the reaction of formaldehyde with alkyl formate under CO pressure using acid catalyst.[2] In the presence of cobalt catalyst, acetals react with CO/H_2 gas to give alkoxyacetaldehyde (Eq.2).[3] However, in these three processes the yields of product are low. $Co_2(CO)_8$-organic amine system is well known to catalyze the hydroesterification of olefin to give the corresponding carboxylic ester.[4] These findings prompt us to study the cobalt-catalyzed hydroesterification of acetals, yielding alkoxyacetic ester (**1**). We describe here some of our results.

As shown in Table 1, basic solutions prepared *in situ* from $Co_2(CO)_8$ were found to be active catalysts for the hydroesterification of acetals under CO pressure. The reaction proceeded smoothly with no induction period. Ethyl ethoxyacetate (**1b**) was produced from formaldehyde diethyl acetal in 91% yield (*ca.* 910% based on cobalt atom) when the reaction was carried out in dioxane in the presence of γ-picoline under CO pressure of 150 K/cm² at 160 °C (Run 6). Methyl methoxyacetate (**1a**) and isopropyl isopropoxyacetate (**1c**) were obtained from formaldehyde dimethyl acetal and formaldehyde diisopropyl acetal, respectively, in high yields (Runs 4,9). Besides γ-picoline/dioxane(solvent) system, some amine/solvent combinations are also effective (Runs 1—3). The use of γ-picoline solvent was unfavorable(11% yield (**1a**)). The use of CO/H_2 gas in place of CO reduced the yield of **1b**[5] (Run 7).

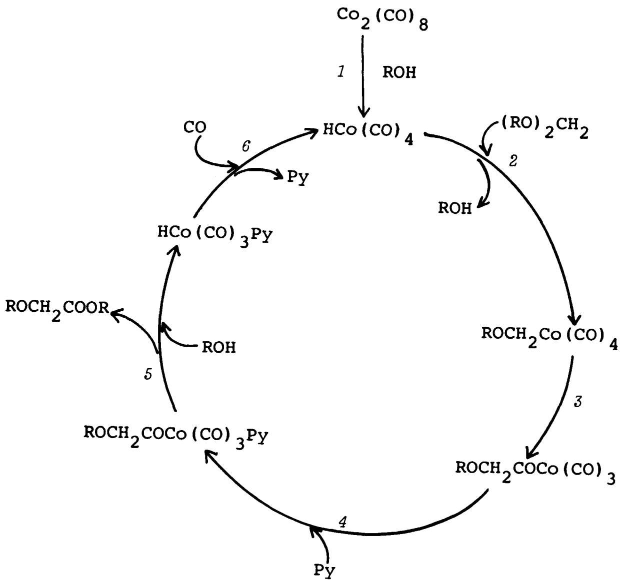

Fig. 1. A possible scheme.

Table 1. Hydroesterification of formaldehyde dialkyl acetals
$Co_2(CO)_8$ 2 mmol, γ-picoline 30 mmol, H_2O 5 mmol, CO 150 Kg/cm² (initial), 160 °C, 5 h.

Run No.	Solvent (mL)		Acetal $CH_2(OR)_2$/alcohol (mmol) /(mmol)	Conv. (%)[a]	Yield of ester/%[b]
1	THF	15	R=Me(50)/MeOH(100)	65	50(**1a**)
2	Benzene	15	R=Me(50)/MeOH(100)	65	57(**1a**)
3	Monoglyme	15	R=Me(50)/MeOH(100)	62	51(**1a**)
4	Dioxane	15	R=Me(50)/MeOH(100)	68	57(**1a**)
5[c]	THF	15	R=Me(50)/MeOH(100)	—	—
6	Dioxane	15	R=Et(40) /EtOH(80)	95	91(**1b**)
7[d]	Dioxane	15	R=Et(20) /EtOH(40)	97	59(**1b**)
8	Dioxane	15	R=Et(40) / —	90	73(**1b**)
9	Dioxane	15	R=i-Pr(40)/i-PrOH(80)	89	46(**1c**)

a) Acetal reacted/acetal initially introduced. b) Ester produced/acetal initially introduced. c) Without γ-picoline. d) CO 100 Kg/cm², H_2 100 Kg/cm².

TABLE 2. EFFECT OF SOME ORGANIC AMINES
$Co_2(CO)_8$ 2 mmol, amine 10 mmol, H_2O 5 mmol, formaldehyde dimethyl acetal 50 mmol, MeOH 100 mmol, THF 15 mL, CO 150 Kg/cm², 160 °C, 5 h.

Run No.	Amine	Conv./%[a]	Yield of ester/**1a**, %
1	Pyridine	40	10
2	Pyridine(40 mmol)	70	50
3	γ-Picoline	54	44
4	β-Picoline	46	28
5	3-Pyridinol	65	47
6	4-Pyridinol	26	12
7	2,4-Lutidine	34	0.4
8	2,4,6-Collidine	13	1.3
9	3-Cyanopyridine	—	—

a) See footnote of Table 1.

Organic amines are essential as catalyst component;[6] the ester, **1a** was not produced at all in the absence of amine (Table 1, Run 5). Pyridine or its derivatives such as γ-picoline, 3-pyridinol are generally favorable (Table 2, Runs 1—6). The yield of ester, **1a** increased with the increase in amine concentration(pyridine 10—60 mmol, γ-picoline 10—30 mmol).

Other metal carbonyl catalysts such as $Rh_4(CO)_{12}$, $Ru_3(CO)_{12}$, $Fe(CO)_5$, $Mo(CO)_6$, and $Cr(CO)_6$ were examined for this reaction of acetals under the same conditions as that of $Co_2(CO)_8$ catalyst, but neither of these catalysts gave carbonylation products.

A possible scheme by which the production of alkoxyacetic ester can be explained, is illustrated in Fig. 1, where pyridine(Py) is used as amine. In this scheme, pyridine participates in alkoholysis step 5, as is the case of the cobalt-catalyzed hydroesterification of olefin.[4] Steps 2 and 3 have been already given in the hydroformylation of acetals (Eq. 2).[3] The absence of EtOH resulted in the appearance of induction period (*ca.* 30 min) and in the drop of **1b** yield (Table 1, Run 8), indicating that, under CO conditions, EtOH takes part in step 1. Based on the scheme, scavenging of $HCo(CO)_4$ from the reaction mixture will stop the catalytic cycle. In fact, when sodium carbonate (4 mmol) is initially added to Run 4(Table 1), the yield of **1a** was only 3%.

Experimental

Materials. Solvents and amines were obtained commercially and used with no further purification. Formaldehyde dimethyl acetal and formaldehyde diethyl acetal were purchased from Tokyo Kasei Kogyo CO., LTD. Formaldehyde diisopropyl acetal was synthesized from aqueous formalin and 2-propanol using *p*-toluenesulphonic acid as catalyst.

Reaction Procedure. A catalyst solution prepared from $Co_2(CO)_8$(2 mmol), amine(10—60 mmol), acetal(40—50 mmol), alcohol(80—100 mmol), and H_2O(5 mmol) in dioxane(15 cm³) was placed in a stainless-steel autoclave (50 cm³), which was subsequently charged with CO (150 Kg/cm²). After the reaction, the vessel was cooled to room temperature and the catalyst solution was analyzed by GLC. Satisfactory spectral data were obtained for alkoxyacetic esters.

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References

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5) $EtOCH_2CH_2OH$(4%), $EtOCH_2CH(OEt)_2$(7%), and trace amount of ethoxyacetaldehyde were detected by GLC analysis as by-products.

6) After the reaction of Run 4 (Table 1), >99% of γ picoline was confirmed by GLC.