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DIRECT SYNTHESIS OF 1,4-BUTANEDIOL FROM ALLYL ALCOHOL USING CARBON MONOXIDE AND WATER IN THE PRESENCE OF $Rh_6(CO)_{16}$-PROPANEDIAMINE SYSTEM

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$Rh_6(CO)_{16}$-propanediamine system catalyzes a direct route to 1,4-butanediol from allyl alcohol under the water gas shift reaction condition. Using an aminopyridine in place of the diamine gives γ-butyrolactone in a good yield.

We have studied the water gas shift reaction (WGSR) and its application to organic synthesis.1) Rhodium carbonyl cluster catalysts show a high activity for reduction of carbonyl functions, but not for olefinic ones, indicating that a hydride species generated in situ has a strong nucleophilic character. Furthermore, the carbonylation of common olefins under the WGSR condition gives exclusively the corresponding alcohols of one additional carbon without aldehydes.1c) We here describe the selective formation of 1,4-butanediol from allyl alcohol. Recently much attention has been paid to 1,4-butanediol as a useful raw material.2) The processes for 1,4-butanediol via allyl alcohol mostly consist of two successive reactions of hydroformylation and hydrogenation.3) The present reaction without formation of a branched diol, 2-methyl-1,3-propanediol gives a direct route to 1,4-butanediol from allyl alcohol.

Typical results of the allyl alcohol carbonylation are summarized in Table 1. The scrutiny of the additive effect reveals that diamines, especially N, N'-tetramethyl-1,3-propanediamine are effective for the 1,4-butanediol formation. The yield of the diol is dependent on temperature, CO pressure, and H_2O concentration. A suitable choice of these conditions attains 72% yield of the diol. Interestingly, 4-dimethylaminopyridine in place of the diamine gives γ-butyrolactone in a good yield. γ-Butyrolactone may be formed by intramolecular cyclization of a metal acyl intermediate. On the other hand, the diamine as a bidentate ligand prevents the coordinating activation of a hydroxyl function, which allows a hydride attack on an acyl moiety to give the diol. Markownikoff addition of M-H on the olefinic bond leads to isomerization products of propanal and propanol. Triethylamine and KOH which are often used as bases in the WGSR facilitate the isomerization.

It should be noted that a suitable choice of the additive can control the formation of 1,4-butanediol or γ-butyrolactone. The reaction of other allyl alcohols and homoallyl alcohols are under investigation.

Table 1. Carbonylation of Allyl Alcohol Using CO and H_2O[a]

Additive	Conditions			Conversion (%)	Yield of Products (%)			
	Temp (C°)	P_{CO} (atm)	H_2O (mmol)		1,4-Butanediol	Butyrolactone	Propanal	Propanol
TMPDA[b]	50	10	56	79	42	6	4	15
TMPDA	60	10	56	100	59	10	1	27
TMPDA	100	10	56	100	23	10	3	54
TMPDA	60	5	56	100	45	22	1	29
TMPDA	60	20	56	100	65	6	1	25
TMPDA	60	10	10	18	1	3	4	5
TMPDA	60	10	100	100	72	8	1	19
4-DMAP[c,d]	80	5	30	100	0	36	32	20
4-DMAP[e]	50	10	56	100	21	68	0	11
Et_3N	60	10	56	27	2	2	14	4
KOH	60	10	56	14	0	0	6	6

a) The reaction procedure is similar to that in a previous paper.[1c] Allyl alcohol (3 mmol); $Rh_6(CO)_{16}$(0.05 mmol); additive(15 mmol); 2-ethoxyethanol(0.5 ml); 5 h.
b) TMPDA: N,N'-tetramethyl-1,3-propanediamine. c) 2-Ethoxyethanol(3 ml); 10 h.
d) 4-DMAP: 4-dimethylaminopyridine. e) 2-Ethoxyethanol(3 ml); 48 h.

References

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