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Oxidation-Reduction Hydration of Olefins with Molecular Oxygen and 2-Propanol Catalyzed by Bis(acetylacetonato)cobalt(II)

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In the presence of a catalytic amount of bis(acetylacetonato) cobalt(II), various olefins are hydrated with oxygen and secondary alcohol to afford the corresponding alcohols together with alkanes and ketones via Oxidation-Reduction process. Effect of additives in the present hydration reaction shows that 2,6-lutidine and 2-picoline inhibit the production of alkanes in a large extent to result in the better yielding of alcohols.

The selective O_2 oxidation of olefins to monooxygenated compounds by a single oxygen atom transfer is one of the current interests, and recently, several catalysts combined with some reducing reagents have been reported. For example, Tabushi$^{1)}$ has reported that the oxidation of olefins with oxygen by the use of (tetraphenylporphyrin)manganese(III) complex / $NaBH_4$ (or colloidal Pt-H_2) gives the corresponding epoxides. Okamoto$^{2)}$ and Inoue$^{3)}$ have reported that the oxidation of conjugated olefins, such as styrene, with air by the use of (tetraphenylporphyrin) cobalt(II) complex / Et_4NBH_4 (or $NaBH_4$) gives the corresponding alcohols. Drago$^{4)}$ and Nishinaga$^{5)}$ have reported that the oxidation of olefins with oxygen by the use of [bis(salicylidene-γ-iminopropyl)methylamine]cobalt(II) complex / primary alcohol gives the corresponding ketones, as major products, along with alcohols.$^{6)}$

In this communication, we would like to report a unique hydration reaction of olefins with molecular oxygen in 2-propanol by using a catalytic amount of bis(acetylacetonato)cobalt(II) (Co(acac)$_2$).

Since Co(II) complexes readily absorb O_2,$^{7)}$ we first examined the O_2 oxidation of 4-phenyl-1-butene as a model substrate to know the effects of Co(II) complexes and solvents. As shown in Table 1, the reaction proceeds smoothly to give 4-phenyl-2-butanol as a major product along with 1-phenylbutane and 4-phenyl-2-butanone, when Co(acac)$_2$ was used in secondary alcohol, such as 2-propanol or cyclopentanol. On the contrary, when primary alcohol such as ethanol, or tertiary

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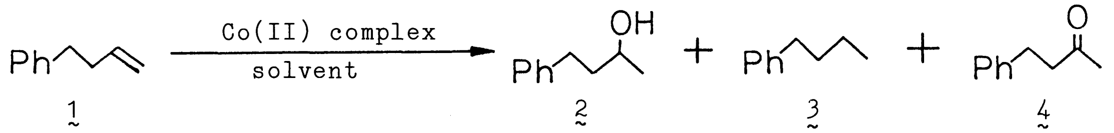
Table 1. Examination of Cobalt(II) Complexes and Solvents[a)]



Entry	Cobalt(II) complex	Solvent	Conversion /%[b)]	Yield /%[b)]		
				2	**3**	**4**
1	Co(salen)[c)]	2-propanol	0	0	0	0
2	Co(acacen)[d)]	2-propanol	0	0	0	0
3	$Co(acac)_2$	2-propanol	100	46	17	8
4	$Co(acac)_2$	cyclopentanol	100	45	16	9
5	$Co(acac)_2$	ethanol	0	0	0	0
6	$Co(acac)_2$	t-butyl alcohol	0	0	0	0

a) Reaction conditions; 4-phenyl-1-butene 2 mmol, Co(II) complex 0.4 mmol, solvent 10 ml, 75 °C, 1 h. b) Determined by GC. c) Co(salen); (N,N'-disalicylidene-ethylenediaminato)cobalt(II). d) Co(acacen); [N,N'-bis(1-methyl-3-oxobutylidene)-ethylenediaminato]cobalt(II).

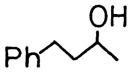
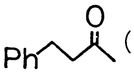
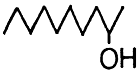
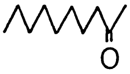
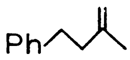
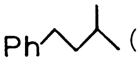
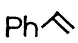
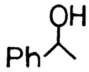
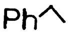
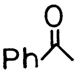
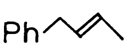
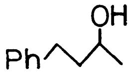
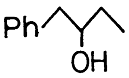
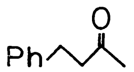
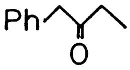
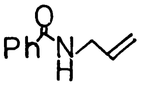
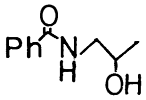
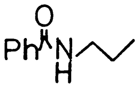
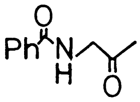
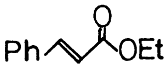
alcohol such as t-butyl alcohol, was used as solvent, no reaction took place. It is interesting to point out that the present reaction produces an alcohol as a major product, directly from olefin under mild conditions via simultaneous transfer of oxygen and hydrogen even under oxidative condition. Therefore, this reaction is considered as "Oxidation-Reduction Hydration".

Next, the reaction of various olefins was studied, and the results are shown in Table 2. In every case except entry 7, the hydration took place to produce alcohols and alkanes. Ketones were always formed as minor products except in the case of exo-olefin (entry 3). In entries 1, 2, 3, 4, and 6, a hydroxy group was introduced in more substituted carbon according to the Markownikov rule. However, concerning 1,2-disubstituted olefin (entry 5), a hydroxy group was introduced without regio-selection. In the case of olefin having amide group (entry 6), the present reaction similarly afforded the corresponding three amides.

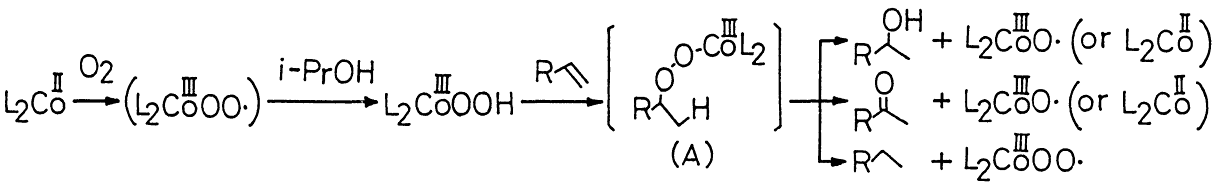
At present, it is assumed that the active species, $L_2Co(III)OOH$, is initially generated from $L_2Co(III)OO\cdot$[7)] and 2-propanol, and the hydroperoxide readily reacts with olefins according to the Markownikov rule to form the second intermediate (A), which in turn decomposes to alcohols, alkanes and ketones, respectively, as depicted in Scheme 1.

A typical procedure is described for the hydration of 4-phenyl-1-butene; 4-phenyl-1-butene (2.0 mmol) and bis(acetylacetonato)cobalt(II) (0.4 mmol) in 2-propanol (10 ml) were stirred at 75 °C under an oxygen atmosphere for 1 h. 2-Propanol was then removed under reduced pressure. The residue was purified by thin layer chromatography (silica gel) to give 4-phenyl-2-butanol (46%), 1-phenylbutane (17%) and 4-phenyl-2-butanone (8%).

Table 2. Hydration of Various Olefins[a)]

Entry	Substrate	Products (Yield /%)[b)]		
1		 (46)[c)]	 (17)[c)]	 (8)[c)]
2		 (45)[c)]	 (22)[c)]	 (7)[c)]
3		 (37)[d)]	 (25)[d)]	
4		 (48)[e)]	 (2)[e)]	 (24)[e)]
5		 (18)[e)]  (19)[e)]	 (19)[e)]	 (7)[e)]  (7)[e)]
6		 (38)[d)]	 (28)[d)]	 (18)[d)]
7		No Reaction		

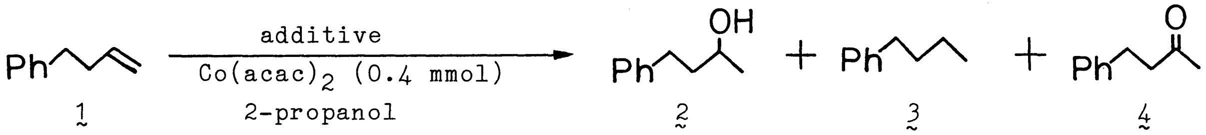
a) Reaction conditions; substrate 2 mmol, Co(acac)$_2$ 0.4 mmol, 2-propanol 10 ml, under O$_2$ atmosphere, 75 °C, 1 h. b) All the products gave satisfactory ^{1}H-NMR and IR spectra. c) Determined by GC. d) Isolated yield. e) Ratio of GC area.



Scheme 1.

Next, based on the reported evidence,[8)] the addition of several amine bases was tried in order to increase the yield of alcohols. Various amine bases which are able to coordinate on Co(acac)$_2$ were screened in the hydration of 4-phenyl-1-butene, and as shown in Table 3, these additives inhibited production of alkane to improve the yield of alcohol. Particularly, 2,6-lutidine and 2-picoline gave better results; (60% yield of alcohol). The additive may coordinate to cobalt atom of the catalyst. The strength of coordination of additives to cobalt influences

Table 3. Effect of Various Additives[a)]



Entry	Additive (Amount /mmol)	Conversion /%[b)]	Yield /%[b)]		
			2	3	4
1	none	100	46	17	8
2	pyridine (0.4)	87	53	5	9
3	2,6-lutidine (0.4)	97	61	7	6
4	2-picoline (0.4)	98	60	7	7
5	4-methoxypyridine (0.4)	75	48	3	6
6	2,6-lutidine (0.2)	100	56	11	7
7	2,6-lutidine (0.8)	81	53	3	5

a) Reaction conditions; 4-phenyl-1-butene 2 mmol, $Co(acac)_2$ 0.4 mmol, 2-propanol 10 ml, under O_2 atmosphere, 75 °C, 1 h. b) Determined by GC.

the yield of alcohol; for example, 4-methoxypyridine having electron-donating substituent caused relatively low conversion of olefin. Instead, 2,6-lutidine and 2-picoline caused high conversion probably because of steric hindrance around the nitrogen atom. When the amount of additive was used less than that of $Co(acac)_2$, the yield of alkane became higher. The use of more additive allowed the conversion of olefin to decrease because of the coordination of two 2,6-lutidine molecules onto $Co(acac)_2$ prevents the interaction with O_2.

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