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Bis(trifluoroacetylacetonato)cobalt(II) Catalyzed Oxidation-Reduction Hydration of Olefins

Selective Formation of Alcohols from Olefins

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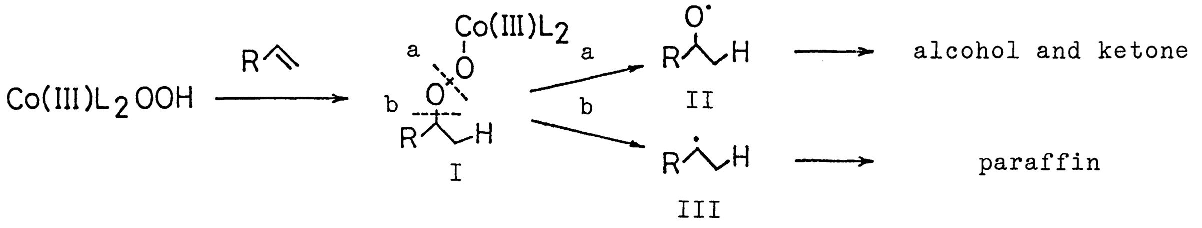
Various olefins are hydrated with molecular oxygen (oxidant) and a secondary alcohol (reductant) in the presence of a catalytic amount of bis(trifluoroacetylacetonato)cobalt(II) in good yields.

Oxidation of olefins with molecular oxygen and transition metal complexes have been investigated[1-3] extensively in recent years, however, there still remains an important problem which involves the control of the direction of the reaction: In most cases, a complicated mixture of oxygenated compounds results under the above reaction conditions.

In the previous communication,[4] we have reported that alcohols are formed as major products directly from olefins by the treatment with oxygen (oxidant) and 2-propanol (reductant) in the presence of a catalytic amount of bis(acetylacetonato) cobalt(II). In the above reaction, however, the yield of alcohol is not suffiucient because of accompanying by-products as paraffin and ketone.

As mentioned previously,[4] we assumed that active species in the above reaction is Co(III)L_2OOH in turn decomposes into II or III, respectively (Scheme 1). Therefore, i) the activity of catalyst and ii) the yields of alcohols which are determined by the mode of the decomposition shown in Scheme 1 are considered to be influenced greatly on the structure of ligands of Co(II) complexes.

In this communication, improvement of the selectivity in the formation of



Scheme 1.

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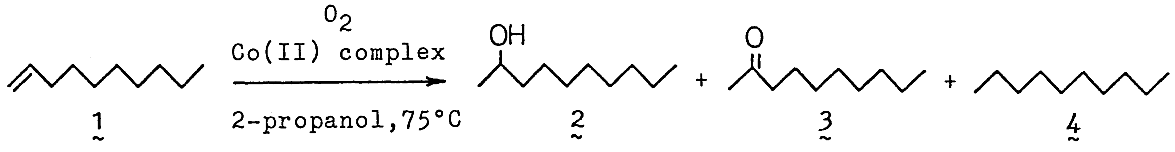
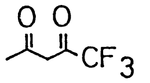
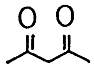
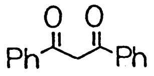
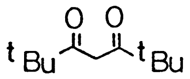
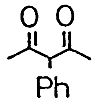
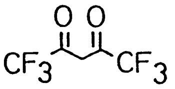
alcohols was attempted by screening the effect of the structure of β-diketones, ligands of Co(II) complexes, in order to establish an effective method for synthesis of alcohols from various olefins.

At first, the reactions of 1-decene with molecular oxygen in 2-propanol were tried by heating a stirred mixture in the presence of a catalytic amount of Co(II) complex (Scheme 2). As shown in Table 1, some bis(β-diketonato)cobalt(II)



Scheme 2.

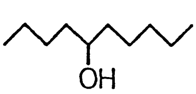
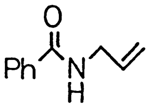
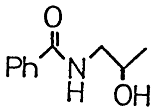
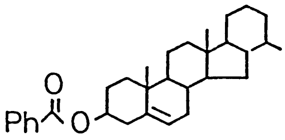
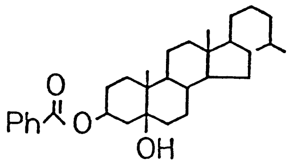
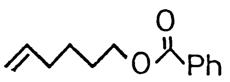
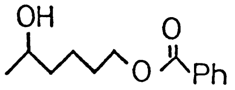
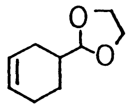
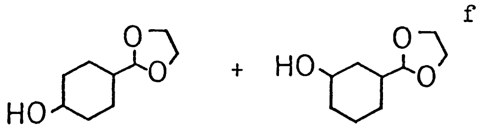
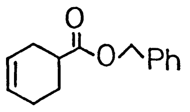
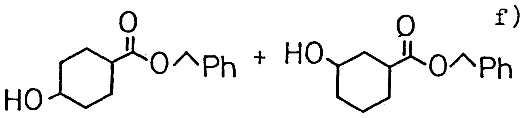
Table 1. Comparison of Yields for Oxidation-Reduction Hydration of 1-Decene Catalyzed by Co(II) Complexes[a)]

Ligand		Reaction time /h	Conversion /%	Yield /%		
				2	3	4
1,1,1-Trifluoroacetyl acetone		15	100	81	13	2
Acetylacetone		2	100	45	7	22
Dibenzoylmethane		2	100	52	12	32
Dipivaloylmethane		8	100	59	25	0
3-Phenylacetylacetone		No Reaction				
1,1,1,5,5,5-Hexafluoro acetylacetone		No Reaction				

a) Reaction conditions; 1-decene (2.0 mmol) and Co(II) complex (0.40 mmol) were heated in 10 ml of 2-propanol at 75 °C under O_2 atmosphere. Analysis of products were carried out by gas chromatography.

showed catalytic activities for the present reaction, and, in the case of using bis(trifluoroacetylacetonato)cobalt(II) as a catalyst, the formation of paraffin was almost suppressed and the yield of alcohol was improved up to 80%.5) When bulky complex such as bis(dipivaloylmethanato)cobalt(II) was used, the formation of paraffin was also controlled, however, the yield of ketone was increased unexpectedly.6) On the other hand, bis(hexafluoroacetylacetonato)cobalt(II) having

Table 2. Bis(trifluoroacetylacetonato)cobalt(II) Catalyzed Hydration of Olefinsa)

Entry	Substrate	Reaction time /h	Productb)	Yield /%
1		15		87c)
2		30	 f)	78d)
3		4	 f)	78c)
4		6		91c)
5		8	 f)	82c)
6		16	 f) (1 : 1)	74c,e)
7		16	 f) (1 : 1)	82c,e)

a) Reaction conditions; Co(II) complex was used 20 mol% for substrate. The reaction was carried out in 2-propanol at 75 °C under O_2 atmosphere. b) All the products gave satisfactory NMR and IR spectra. c) Isolated yield. d) Determined by gas chromatography. e) Mixture of stereoisomers. f) In entries 2, 3, 5, 6, and 7, the corresponding ketones were formed in 18%, 11%, 12%, 7%, and 15% yields, respectively.

strong electron-withdrawing group in ligand, and bis(3-phenylacetylacetonato) cobalt(II) having substituent on 3-position of acetylacetone, showed no catalytic activity.

Of these ligands screened, it is noted that bis(trifluoroacetylacetonato) cobalt(II) is an excellent catalyst for the selective formation of alcohol.

Next, according to a similar procedure, the present Oxidation-Reduction Hydration was applied to various olefins. As shown in Table 2, various olefins were converted to the corresponding alcohols in good yields. Especially, exo-olefins and trisubstituted olefins afforded alcohols in 87% and 91% yields, respectively, without accompanying ketones (see entries 1 and 4). Furthermore, olefins bearing unstable substituents toward an acid or a base (i.e. amide, acetal, or ester) gave the corresponding alcohols also in good yields without destroying these substituents as shown in entries 3, 4, 5, 6, and 7.

A typical procedure is described for the hydration of cholesteryl benzoate; a mixture of cholesteryl benzoate (1.0 mmol) and bis(trifluoroacetylacetonato) cobalt(II) (0.20 mmol) in 2-propanol (10.0 ml) was stirred at 75 °C for 8 h under O_2 atmosphere. Then solvent was removed under reduced pressure, and the residue was purified by preparative TLC (silica gel) to yield the corresponding alcohol (91%).

It is noted that, in the presence of a catalytic amount of bis(trifluoroacetylacetonato)cobalt(II), various olefins smoothly react with molecular oxygen (oxidant) and 2-propanol (reductant) to afford the corresponding alcohols in good yields under mild reaction conditions.

References

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2) T. Okamoto and S. Oka, J. Org. Chem., 49, 1589 (1984).
3) A. Nishinaga, T. Yamada, H. Fujiura, K. Ishizaki, H. Ihara, and T. Matsuura, Abstract of 20th Symposium on Oxidation, Tokyo, Nov. 1986, p.83; A. Nishinaga, H. Yamato, T. Abe, and K. Matsuura, Tetrahedron Lett., 29, 6309 (1988).
4) T. Mukaiyama, S. Isayama, S. Inoki, K. Kato, T. Yamada, and T. Takai, Chem. Lett., submitted.
5) In this case, we considered that the formation of paraffin could be controlled by fission of O-O bond (a: Scheme 1). Of six ligands examined, trifluoroacetylacetone having electron-withdrawing substituent, lowered electron density of O-O bond to increase of the yield of alcohol.
6) In the case of sterically hindered ligand, it was postulated that O-O bond distance would be lengthened to decrease the formation of paraffin because of preferentially O-O bond fission. The details are now under investigation.

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