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A Convenient Method for the Stereoselective Preparation of trans-2-Hydroxymethyltetrahydrofurans by the Oxidative Cyclization of 5-Hydroxy-1-alkenes with Molecular Oxygen Catalyzed by Cobalt(II) Complex

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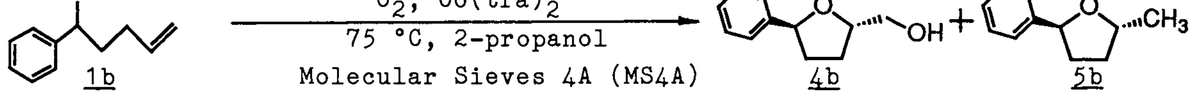
In the presence of a catalytic amount of bis(1-morpholinocarbamoyl-4,4-dimethyl-1,3-pentanedionato)cobalt(II), various 5-hydroxy-1-alkenes are converted to the corresponding 2-hydroxymethyltetrahydrofurans in good yields with extremely high trans selectivities by the oxidative cyclization with molecular oxygen. The yields of cyclization products are improved by addition of hydroperoxide.

Derivatives of 2-hydroxymethyltetrahydrofuran are one of the useful intermediates for the synthesis of natural products and several preparative methods have been reported. For example, 2-hydroxymethyl-5-methyltetrahydrofuran (4a) was produced as a mixture of cis and trans isomers (ratio=1:1) by oxidative cyclization with m-CPBA[1)] or by oxymercuration reaction[2)] of 5-hydroxy-1-hexene. Also, 4a was obtained by oxymercuration reaction of 5,6-epoxy-1-hexene.[3,4)] However, it was shown there that one isomer of 4a could not be obtained stereoselectively.

Previously, we have reported "oxidation-reduction hydration"[5)] of olefins with O_2 catalyzed by bis(1,3-diketonato)cobalt(II) in 2-propanol. In the course of our continuing study, it was found that 5-hydroxy-5-phenyl-1-pentene (1b) was oxidized with O_2 in the presence of bis(trifluoroacetylacetonato)cobalt(II) (Co(tfa)$_2$) under above hydration conditions to afford cyclization products, 2-hydroxymethyl-5-phenyltetrahydrofuran (4b) and 2-methyl-5-phenyltetrahydrofuran (5b) in 21% and 24% yields, respectively (Scheme 1). In addition, it is interesting to note that 4b and 5b were obtained with extremely high trans selectivities (>99%). In this communication, we would like to describe the stereoselective preparation of trans-2-hydroxymethyltetrahydrofurans by oxidative cyclization of 5-hydroxy-1-alkenes catalyzed by bis(1,3-diketonato)cobalt(II).

First, the effect of the reaction temperature and that of structure of ligand



Scheme 1.

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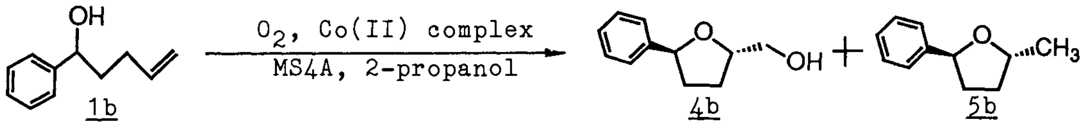
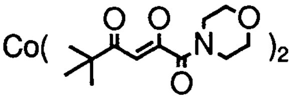
of Co(II) complexes on the formation of 2-hydroxymethyltetahydrofuran (4b) was examined by taking the oxidative cyclization of 5-hydroxy-5-phenyl-1-pentene (1b) as a model reaction. The results are summarized in Table 1.

Table 1. Cyclization of 5-Hydroxy-5-phenyl-1-pentene[a]



Entry	Co(II)	Temperature /°C	Additive (Equivalent vs. 1b)	Time /h	Yield /%[b] 4b[f]	Yield /%[b] 5b[f]
1	$\mathrm{Co(tfa)_2}$	75	None	4	21	24
2	$\mathrm{Co(tfa)_2}$	50	None	8	55	0
3	$\mathrm{Co(acac)_2}$[c]	50	None	1	29	0
4	$\mathrm{Co(modp)_2}$[d]	50	None	0.5	62	0
5	$\mathrm{Co(modp)_2}$	50	t-BuOOH (0.5)	0.5	64	0
6	$\mathrm{Co(modp)_2}$	50	t-BuOOH (1.0)	0.5	73	0
7	$\mathrm{Co(modp)_2}$	50	CHP (1.0)[e]	0.5	71	0

a) Reaction conditions; 5-hydroxy-5-phenyl-1-pentene 2.0 mmol, Co(II) complex 0.4 mmol, solvent (2-propanol) 20 ml, MS4A[6] 1 g, 1 atm. O_2. b) Determined by GC.
c) $\mathrm{Co(acac)_2}$; bis(acetylacetonato)cobalt(II).
d) $\mathrm{Co(modp)_2}$; bis(1-morpholinocarbamoyl-4,4-dimethyl-1,3-pentanedionato)cobalt(II).[7] e) CHP; cumene hydroperoxide.
f) In all cases, trans selectivities of 4b and 5b are 99%.



$\mathrm{Co(modp)_2}$

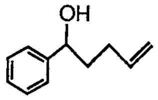
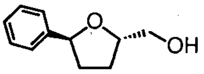
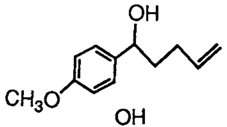
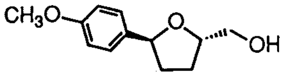
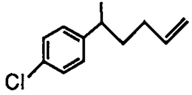
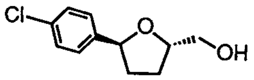
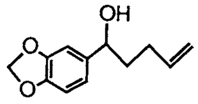
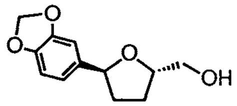
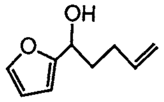
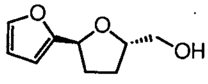
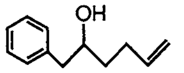
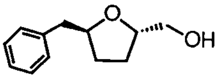
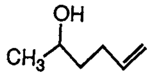
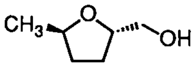
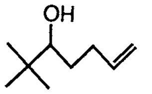
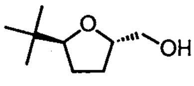
It was found then that the yield of 4b is depended on the reaction temperature. As shown in Table 1, when the reaction was carried out at 50 °C by using $\mathrm{Co(tfa)_2}$ as a catalyst, the yield of desired product 4b increased to 55% without accompanying 5b (Entry 2). By the use of $\mathrm{Co(acac)_2}$ as a catalyst, however, the cyclization reaction afforded the product 4b only in 29% yield (Entry 3). The cyclization of 1b with O_2 was effectively promoted by $\mathrm{Co(modp)_2}$ to yield 4b in 62% (Entry 4).

Further, it was found that hydroperoxides are effective to improve the yield of 4b. As shown in Entries 6 and 7, by addition of an equimolar amount of t-butyl hydroperoxide or cumene hydroperoxide, the yield of 4b increased to 71~73%.

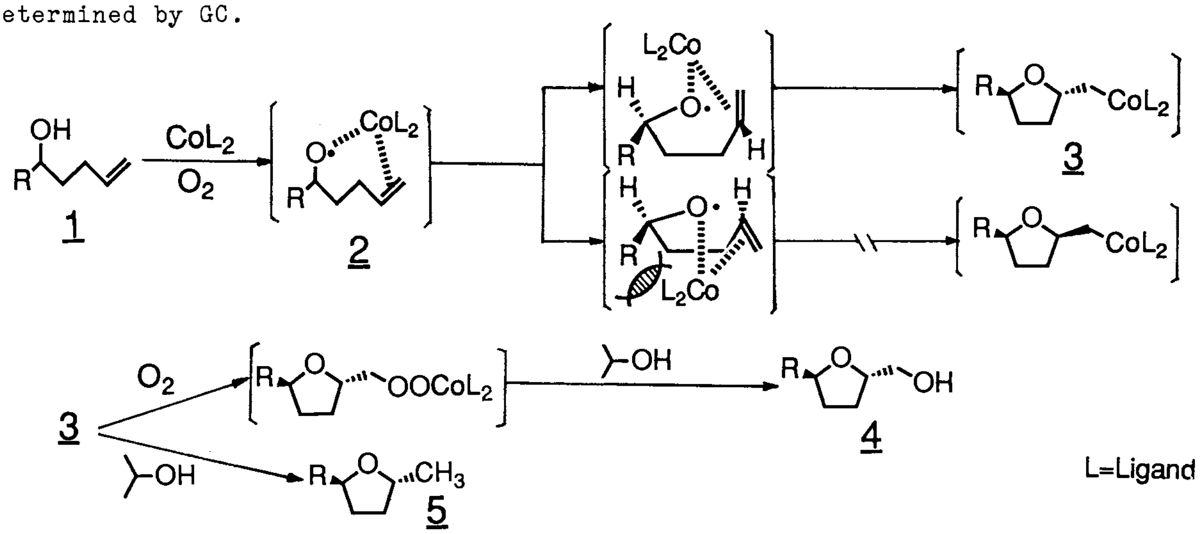
Thus, the above mentioned procedure was successfully applied to the stereoselective preparation of trans-2-hydroxymethyltetrahydrofurans from several 5-hydroxy-1-alkenes (see Table 2). And it should be pointed out that all the products are obtained with extremely high trans selectivities.

A mechanism of the formation of trans-2-hydroxymethyltetrahydrofuran is assumed as follows; initially, by the reaction of 5-hydroxy-1-alkene (1) with Co complex and O_2, a radical intermediate (2) which interacts to Co complex in the coordination sphere[8] is formed.

Table 2. Preparation of Various 2-Hydroxymethyltetrahydrofurans[a)]

Entry	Substrate	Product[b)]	Yield[c)] /%	Trans sel.[d)] /%
1			73	99
2			69	99
3			60	99
4			79	99
5			62	99
6			69	97
7			53	99
8			55	>99

a) Reaction conditions; substrate 2.0 mmol, $Co(modp)_2$ 0.4 mmol, 2-propanol 20 ml, t-butyl hydroperoxide 2.0 mmol, Molecular Sieves 4A 1.0 g, 1 atm. O_2, 50 °C, 0.5 h. b) All products gave satisfactory ^{1}H-NMR and IR spectra. c) Isolated yield. d) Determined by GC.



Scheme 2.

Then, 2 is converted to a cyclized intermediate (3) with trans relation between 2 and 5 positions located substituents, R- and -CH_2CoL_2, because of less steric repulsion between substituent R- and CoL_2 in the step of radical cyclization.$^{9)}$ Insertion of O_2 into Co-C bond of 3 yields cobalt peroxide$^{10)}$ which is in turn changed to 2-hydroxymethyltetrahydrofuran (4) by reductive cleavage with 2-propanol as depicted in Scheme 2. On the other hand, 2-methyltetrahydrofuran (5) is formed by the abstraction of a hydrogen atom from the solvent (2-propanol).

The role of hydroperoxide is not yet made clear. However, it is confirmed that hydroperoxide participates before the cyclization step, based on the results that addition of hydroperoxide has no influence on stereoselectivity of 4. Accordingly, it is reasonable to assume that hydroperoxide accelerates the generation of the radical intermediate (2).

A typical procedure is described for the preparation of 2-hydroxymethyl-5-phenyltetrahydrofuran (4b); to a 2-propanol solution (20 ml) of 5-hydroxy-5-phenyl-1-pentene (324 mg, 2.0 mmol) was added Co(modp)$_2$ (220 mg, 0.4 mmol), MS4A (activated powder 1.0 g) and t-butyl hydroperoxide (180 mg, 2.0 mmol). After being stirred for 0.5 h at 50 °C under O_2 atmosphere, MS4A was removed by filtration. Then saturated sodium thiosulfate solution (5 ml) was added to the reaction mixture to decompose residual peroxides completely and the mixture was stirred for another 1 h at room temperature. After usual work-up, 4b (260 mg, 73%) was obtained. The trans selectivity of 4b was determined to be 99% by the GC analysis.

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