

**THE HYDRIDOPENTACYANOCOBALTATE ANION INDUCED DEOXYGENATION  
OF ALLYLIC ALCOHOLS USING  $\beta$ -CYCLODEXTRIN AS A PHASE TRANSFER AGENT**

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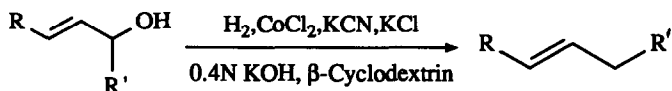
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*Summary:*  $\beta$ -Cyclodextrin promotes the deoxygenation of allylic alcohols to olefins using hydrogen and the *in situ* generated hydridopentacyanocobaltate anion. Internal olefins, of trans-stereochemistry, are the principal reaction products (i.e., no cis-products are formed).

The hydridopentacyanocobaltate anion is an effective catalyst for several reduction processes. For instance,  $\text{HCo}(\text{CN})_5^{-3}$  catalyzes 1,2- or 1,4-addition of hydrogen to conjugated dienes, depending on whether a surfactant<sup>1</sup> or phase transfer catalyst is used and, in the latter case, on the type of phase transfer agent.<sup>2,3</sup> If  $\beta$ -cyclodextrin<sup>4</sup> is used as the latter, then 1,2-addition is the normal mode of  $\text{HCo}(\text{CN})_5^{-3}$  catalyzed addition of hydrogen to a 1,3-diene<sup>3</sup>.

In 1978, Funabiki and co-workers<sup>5</sup> described the conversion of allylic alcohols to olefins catalyzed by  $\text{HCo}(\text{CN})_5^{-3}$ . The catalyst was generated *in situ* from cobalt chloride and potassium cyanide, followed by treatment with hydrogen. The authors reported that trans and cis-2-butene were obtained from the deoxygenation of  $\text{C}_4$ -allylic alcohols, and that the isomer distribution is dependent on the ratio of  $\text{CN}^-/\text{Co}$ . We now present results on the  $\beta$ -cyclodextrin promoted deoxygenation of allylic alcohols, a process which differs in several important respects when compared with the findings of Funabiki and co-workers<sup>5</sup>.

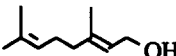
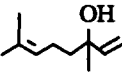
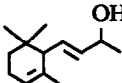
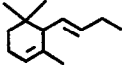
The  $\text{HCo}(\text{CN})_5^{-3}$  anion, generated from  $\text{CoCl}_2$ ,  $\text{KCN}$  [5.2/1.0 ratio of  $\text{CN}^-/\text{Co}$ ],  $\text{KCl}$ ,  $\beta$ -cyclodextrin and 0.4 N potassium hydroxide, followed by exposure to hydrogen, induced the deoxygenation of trans-2-hexen-1-ol to give trans-2-hexene in 91% yield and 1-hexene in 4% yield. Interestingly, use



of either a 6.0/1.0 or 7.0/1.0 ratio of  $\text{CN}^-/\text{Co}$  resulted in no reaction. This result is in marked contrast to the previously described method which afforded the terminal olefin as the main product (using a  $\text{CN}^-/\text{Co}$  ratio of 6.0/1.0)<sup>5</sup>. Furthermore, in no case were cis-olefins detected in any of the reactions described herein, while variable amounts of such alkenes were previously obtained as reaction by-products. Another distinguishing feature of the two methods is that, although a homoallylic alcohol such as 3-hexen-1-ol is inert under the phase transfer conditions, 3-buten-1-ol is readily converted to trans-2-butene as the main product<sup>5</sup>.

TABLE 1

Hydrogenolysis of Allylic Alcohols Using  $\text{HCo}(\text{CN})_5^{-3}$  and  $\beta$ -Cyclodextrin<sup>a</sup>

Substrate	Reaction temp. °C	Products	Yield <sup>b</sup> %
2-Hexen-1-ol <sup>c</sup>	r.t.	trans-2-hexene, 1-hexene,	91 4
2-Hexen-1-ol <sup>d</sup>	r.t.	trans-2-hexene, 1-hexene,	66 4
1-Hexen-3-ol	r.t.	trans-2-hexene, 1-hexene,	82 4
Cinnamyl alcohol	r.t.	trans-1-phenyl-propene 3-phenyl-1-propanol	87 (80) 12 (11)
Cinnamyl alcohol <sup>d</sup>	r.t.	trans-1-phenyl-1-propene 3-phenyl-1-propanol	67 (62) 13 (12)
Cinnamyl alcohol <sup>e</sup>	r.t.	trans-1-phenyl-1-propene 3-phenyl-1-propanol	(6) (3)
Cinnamyl alcohol <sup>f</sup>	r.t.	trans-1-phenyl-1-propene 3-phenyl-1-propanol	16 29
Cinnamyl alcohol <sup>g</sup>	r.t.	trans-1-phenyl-1-propene 3-phenyl-1-propanol	79 12
3-Nonen-2-ol <sup>h</sup>	70	trans-3-nonene trans-2-nonene	45 2
4-Phenyl-3-buten-2-ol	r.t.	trans-1-phenyl-1-butene trans-1-phenyl-butene 4-phenyl-2-butanol	51 7 13
	70	-	
	70	-	
 (1)	70		(40)

<sup>a</sup>Reaction conditions: substrate (5 mmol), 0.4 N KOH (10 mL), 5.5%  $\beta$ -cyclodextrin,  $\text{CoCl}_2$  (1.65 mmol), KCN (8.55 mmol), KCl (3.60 mmol). <sup>b</sup>GC yield except for those given in parenthesis which are isolated yields. <sup>c</sup>Using a 4.8/1.0 ratio of CN/Co gave trans-2-hexene in 91% yield and 1-hexene in 5% yield. Use of a 6.0/1.0 or 7.0/1.0 ratio of CN/Co gave only recovered 2-hexen-1-ol. <sup>d</sup>No  $\beta$ -cyclodextrin. <sup>e</sup>Use of  $\text{N}_2$  instead of  $\text{H}_2$ . <sup>f</sup>Using  $\text{H}_2\text{O}$  instead of 0.4N KOH. <sup>g</sup>0.8N KOH. <sup>h</sup>2.5 mmol of substrate,  $\text{CoCl}_2$  (0.82 mmol), KCN (4.27 mmol), KCl (1.80 mmol), 0.4 N KOH (10 mL).

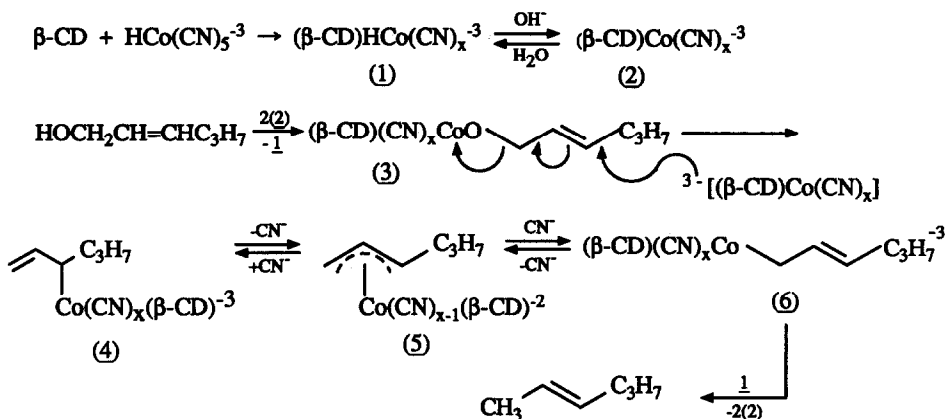
The results obtained for the  $\text{HCo}(\text{CN})_5^{-3}$  mediated deoxygenation of a variety of allylic alcohols is presented in Table 1. While cinnamyl alcohol afforded trans-1-phenyl-1-propene in 80% yield and 3-phenyl-1-propanol in 11% yield, the yield of trans-1-phenyl-1-propene decreased to 62% in the absence of  $\beta$ -cyclodextrin [12% 3-phenyl-1-propanol was also formed]. The behavior of 2-hexen-1-ol with and without  $\beta$ -cyclodextrin mirrored that of cinnamyl alcohol. Clearly, while  $\beta$ -cyclodextrin is not essential for this biphasic reaction, its presence is beneficial in promoting olefin formation. Note that trans-1-phenyl-1-propene does not arise by dehydration of 3-phenyl-1-propanol followed by double bond isomerization, since the alcohol is recovered unchanged when subjected to reaction conditions identical to those used for cinnamyl alcohol.

The hydrogenolysis reaction is applicable to other primary and secondary allylic alcohols, including  $\alpha$ -ionol (**1**), affording olefins in reasonable yields [Table 1]. Tertiary allylic alcohols, as well as those having a trisubstituted double bond, do not react under these conditions.

Optimum results were realized using a 3/1 ratio of substrate/ $\text{Co}(\text{CN})_5^{-3}$ , a 4.8-5.2/1.0 ratio of CN/Co, an 18.2/1.0 ratio of substrate/ $\beta$ -cyclodextrin, and 0.4N potassium hydroxide. Use of higher or lower concentrations of KOH gave inferior results, as did the replacement of  $\beta$ -cyclodextrin by its  $\alpha$ - or  $\gamma$ -homologs. Concerning the latter, trans-1-phenyl-1-propene was obtained in 70% yield and 3-phenyl-1-propanol in 26% yield when  $\alpha$ -cyclodextrin (5.5%) was used instead of  $\beta$ -cyclodextrin in the deoxygenation of cinnamyl alcohol (compare with entry 4 of Table 1 where the yield of olefin, and the olefin/alcohol product ratio is higher). Interestingly, use of  $\gamma$ -cyclodextrin under identical conditions afforded trans-1-phenyl-1-propene in only 3% yield and 3-phenyl-1-propanol in 15% yield.

A possible pathway for the deoxygenation process is outlined in Scheme 1 (illustrated for 2-hexen-1-ol). It is conceivable that  $\beta$ -cyclodextrin can form an adduct with  $\text{HCo}(\text{CN})_5^{-3}$  generating **1** in which the metal is in the cavity of the cycloamylose and is bound via oxygen atoms, analogous to copper and manganese salts.<sup>6</sup> Deprotonation of **1** would afford **2** which can then react with the organic substrate to give **3**. Reaction of the latter with **2** would afford **4**. Conversion to the isomeric  $\sigma$ -allyl complex **6** may occur via a  $\pi$ -allyl intermediate (**5**). Reaction of **6** with **1** would give the product and regenerate **2**. The poor results obtained using  $\gamma$ -CD may be due to the fact that the cobalt anion, rather than being in the cavity of  $\gamma$ -CD, is attached "externally" to two oxygens of  $\gamma$ -CD, giving a less catalytically active species.

## SCHEME 1



The following general procedure was used:

In a 25 mL three-necked flask equipped with a condenser, gas inlet and pressure-equalizing dropping funnel, was placed 0.393 g [1.65 mmol] of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.312 g [0.275 mmol] of  $\beta$ -cyclodextrin, and 5 mL of 0.4N KOH. A mixture of 0.557 g [8.55 mmol] of KCN and 0.268 g [3.60 mmol] of KCl in 5 mL of 0.4N KOH was placed in the dropping funnel. The apparatus was purged three times with hydrogen, following which the cyanide solution was rapidly added to the stirred solution in the flask. After half an hour, 5 mmol of substrate was added, and the reaction mixture was stirred under hydrogen for one day [see Table 1 for reaction temperatures]. Work-up was effected by careful neutralization using 10% HCl, and then extraction with ether. Depending on the nature of the product, the ether extract was dried ( $\text{MgSO}_4$ ) and distilled, or subjected to rotary evaporation followed by silica gel column chromatography. The products were identified by comparison of spectral data and gc retention times with authentic materials.

In conclusion  $\beta$ -cyclodextrin can promote the  $\text{HCo}(\text{CN})_5^{-3}$  induced hydrogenation of allylic alcohols to olefins under mild conditions. Only the trans-olefin is formed where the potential exists for the production of cis and trans-isomers.

#### Acknowledgements

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