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Kyoto University
Cobalt-catalyzed Conversion of Aliphatic Olefins to Alcohols by $O_2$ and BH$_4^-$

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KEY WORDS: Oxygenation/ Olefin/ Secondary alcohol/ Cobalt complex/ Catalysis/

Oxygenation of aryl substituted olefins in the presence of cobalt(III) complex catalysts and BH$_4^-$ attracted attention as a unique hydration of olefins into alcohols under the basic reaction conditions and also as a transition-metal catalyzed reaction of molecular oxygen under the reductive conditions relevant to oxygenases.

\[
\begin{align*}
\text{CH} &= \text{CH}_2 + \text{O}_2 + \text{BH}_4^- + \text{Co}^{III} + \text{OH} \\
&\rightarrow \text{R-CH-CH}_3 \\
\end{align*}
\]

Although the reaction of aryl substituted olefins is not fast at room temperature and requires several days for completion, it is accepted as a synthetic method since the yield of product alcohol is generally high and the regioselectivity for benzyl alcohol-type product is quantitative. However, it was also reported that the reaction of 1-hexene, an aliphatic olefin, showed almost no regioselectivity. To clarify the scope and limitation of this reaction, we examined several aliphatic olefins by the catalysis of bis(dimethylglyoximato)chloro(pyridine) cobalt(III), CoCl(DH)$_2$(py), as summarized in Table 1. The reactivity of cyclohexene was low compared with styrene by a factor of about 1/100, and steric crowding of substrate olefin further depressed the reactivity. A better result was obtained with meso-tetraphenylporphyrinatocobalt(II), CoTPP, as the catalyst instead of CoCl(CH$_3$(py), but it was still insufficient for the synthetic purpose. Illumination by room fluorescent light had an acceleration effect on the oxygenation of cyclohexene, contrary to the results of aryl substituted olefins. With respect to the selectivity, differentiation between endo- and exo-double bonds was moderately attained in the reaction of 4-vinylcyclohexene. The double bond located on the side chain was preferred over the endocyclic double bond by a factor of 4/1 probably because of the steric reason. However, the regioselectivity of the reaction, represented by the ratio of the yields of secondary alcohol over primary alcohol, which was 100/0 with aryl olefins, was disappointingly low showing virtually no selectivity with all aliphatic olefins examined except for 1-meth...
Cobalt-catalyzed Conversion of Aliphatic Olefins to Alcohols by O$_2$

Table 1. Oxygenation of Aliphatic Olefins$^a$)

<table>
<thead>
<tr>
<th>Olefin</th>
<th>Time</th>
<th>Yield of ROH$^b$)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene</td>
<td>14 hr</td>
<td>16% (0.6)</td>
<td>—</td>
</tr>
<tr>
<td>4-Vinylcyclohexene</td>
<td>21 hr</td>
<td>12% (0.7)</td>
<td>endo/exo=1/4</td>
</tr>
<tr>
<td>4-Methylcyclohexene</td>
<td>21 hr</td>
<td>25% (1.1)</td>
<td>3/-4-Methylcyclohexanol=1/1</td>
</tr>
<tr>
<td>4-Methylcyclohexene$^c$</td>
<td>25 hr</td>
<td>85% (3.8)</td>
<td>3/-4-Methylcyclohexanol=1/1</td>
</tr>
<tr>
<td>1-Methylcyclohexene</td>
<td>12 day</td>
<td>40% (1.7)</td>
<td>1/-2-Methylcyclohexanol=7/93</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>21 hr</td>
<td>16% (0.8)</td>
<td>1/-2-Hexanol=45/55</td>
</tr>
<tr>
<td>1-Hexene$^d$</td>
<td>12 hr</td>
<td>3300% (3.6)</td>
<td>1/-2-Hexanol=45/55</td>
</tr>
<tr>
<td>Isoprene</td>
<td>7 day</td>
<td>45% (3.3)</td>
<td>2-Methyl-3-butene-2-ol/2-Methyl-1-butene-3-ol=1/1</td>
</tr>
</tbody>
</table>

$a)$ Olefin, 1 ml; catalyst, 150 mg; NaBH$_4$, 50 mg; dimethoxyethane, 5 ml, room temperature; dark.

$^b)$ Yields based on the amount of catalyst. Values in the parenthesis show the yields based on the amount of substrate used.

$c)$ Under room fluorescent light.

$d)$ Catalyst (Co(TPP)), 6 mg; Et$_4$NBH$_4$, 145 mg, no solvent was used.

Thermolysis.

Now it can be concluded that the cobalt-catalyzed oxygenation of aliphatic olefins in the presence of BH$_4^-$ is of little value in organic synthesis. However, the results are helpful for understanding of the reaction mechanism. Following are the major differences of aliphatic olefins in the oxygenation compared with aromatic olefins; 1) low reactivity, 2) low regioselectivity, and 3) acceleration by light. According to our previous proposal,$^1)$ the reactive intermediate of the present oxygenation is an organocobalt complex (Eqs 2–4).

\[
\begin{align*}
\text{CH}_3 \\
\text{RCH} = \text{CH}_2 + \text{HCoLn} & \rightleftharpoons \text{RCHCoLn} \\
\text{CH}_3 & \text{CH}_3 \\
\text{RCHCo}^{\text{iii}}\text{Ln} & \rightarrow \text{RCH}^- + \text{Co}^{\text{iii}}\text{Ln} \quad \text{O}_2 \quad \text{RCHOOCO}^{\text{iii}}\text{Ln} \\
\text{CH}_3 & \text{CH}_3 \\
\text{RCHOOCO}^{\text{iii}}\text{Ln} + \text{BH}_4^- & \rightarrow [\text{RCHOOH}] \\
\text{CH}_3 & \text{CH}_3 \\
\text{RCHOH} + \text{RCH} = \text{O} & \rightarrow \text{RCHOH}
\end{align*}
\]

(105)
olefins. The difference of stabilization energies between radicals on $C_\pi (A)$ and $C_\pi (B)$ in Figure 1 (hence that of the corresponding energies of C-Co bonds) should be small for radicals generated from aliphatic olefins compared with those of aryl substituted olefins. If the regioselectivity is determined at the stage of the formation of C-Co bond, then the observed selectivity is the result of competition between the stability of the generated radical species and the steric interaction of the alkyl group with other ligands of the metal complex. The stabilization of radical A must exceed the steric repulsion for the aryl substituted olefins but not for aliphatic olefins.

EXPERIMENTAL

Catalysts were prepared according to the method in literature. Experimental procedures of oxygenation were similar to those of the previous publication except that the reaction was carried out in dimethoxyethane rather than in dimethoxyethane-2-propanol.

REFERENCES

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