EFFECT OF SELENIUM ON THE CATALYTIC REACTIVITY OF IRON(II) CHLORIDE IN THE REDUCTION OF AROMATIC EPOXIDE TO OLEFIN

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Selenium enhances the catalytic reactivity of $FeCl_2 \cdot 4H_2O$ during the reduction of aromatic epoxides to olefins with sodium borohydride in ethanol. The yield of olefin was the highest when the catalyst Fe:Se ratio was 1:1.

KEYWORDS selenium; iron chloride; catalyst; epoxide; olefin; reduction; borohydride

While chalcogens such as Se and S are known to have strong poisoning effects on metal catalysis,[1)] the complexes of metal and sulfur atoms such as nonheme iron-sulfur proteins and their model complexes are efficient electron transfer catalysts.[2,3)] This implies that chalcogens may enhance the catalytic reactivity of metals. To the best of our knowledge, such an effect by selenium has received little attention.[4)]

Recently, we have reported that sodium selenite (Na_2SeO_3) affects the catalytic reactivity of metal salts during the reduction of nitrobenzene with sodium borohydride ($NaBH_4$).[5)] While it decreases the reactivity of some metal salts, it increases the reactivity of some other metal salts such as $FeCl_2$, $CuCl_2$, $HgCl_2$, and $MoCl_5$. Here we report that the combination of $FeCl_2$ and Se catalyzed the reduction of aromatic epoxides to olefins with $NaBH_4$.

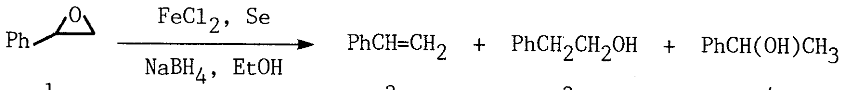
A typical procedure is as follows: $FeCl_2 \cdot 4H_2O$ (0.1 mmol) in ethanol[6)] (40 ml) was added to metallic selenium (0.1 mmol) and $NaBH_4$ (50 mmol) at 0 °C with stirring. After 5 min, epoxide (10 mmol) in ethanol[6)] (10 ml) was added and the resulting mixture was stirred at 30 °C for 20 h under an argon atmosphere. Then the reaction mixture was diluted with water (100 ml) and the products were extracted with ether and purified by silica-gel column chromatography.

The reduction of 2-phenyloxirane (1) with a $FeCl_2$—Se catalyst was examined. It is generally accepted that the reduction of epoxides with $NaBH_4$ is slow and gives alcohol.[7)] Indeed, Table I shows that the reaction without a catalyst (Entry 1) or with only $FeCl_2$ or Se (Entry 2 or 3) proceeded slightly to give mainly α-phenethyl alcohol (4). The use of a $FeCl_2$—Se catalyst increased the reduction rate of 1 and enhanced the formation of styrene (2) and β-phenethyl alcohol (3). The yield of 2 was the highest with a Fe:Se ratio of 1:1 (Entry 5) and lower than that of 3 when Fe < Se (Entries 6 and 7). These results show that $FeCl_2$ and Se are essential in the present reaction and imply that the active species for the formation of 2 may contain Fe and Se in the ratio of 1:1.[8)]

The reduction of other aromatic epoxides with the $FeCl_2$-Se catalyst proceeded like the reduction of 1. Table II shows the results concerning the olefin synthesis. It seems that gem- and cis-diphenyloxirane and an epoxide attached to an electron-withdrawing group (CO_2Et) are readily reduced (Entries 3-5). Vic-diaryloxiranes gave mixtures of cis and trans olefins (Entries 5-7). Both cis- and trans-2,3-diphenyloxirane gave mixtures of cis- and trans-stilbene with the same cis:trans ratio. This shows that the deoxygenation proceeds via ring opening followed by free rotations about the carbon-carbon bond originally part of the epoxide system.[9)] On the other hand, when the aliphatic epoxides (5α,6α-epoxycholestan-3β-ol and 1,2-epoxycyclododecane) were treated in ethanol for 2 h in the same manner as the aromatic ones, the reaction proceeded scarcely at all and traces of or no corresponding olefins were detected by TLC or by GLC respectively.

Instead of $NaBH_4$ in EtOH, $NaBD_4$ in EtOD or in EtOH was used to reduce 1 with the $FeCl_2$—Se catalyst (Table III). No "D" styrene was detected under either condition. This shows that 2 is not produced from α- or β-phenethyl alcohol by dehydration.[10)] However, the β hydrogen of 3 was "D" under the $NaBD_4$—EtOD condition and "H" under the $NaBD_4$—EtOH one. It shows that the β-"H" of 3 comes from the solvent EtOH and the

Table I. Effect of Selenium on the Catalytic Reactivity of $FeCl_2$ during the Reduction of 2-Phenyloxirane (1)[a)]

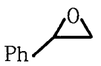
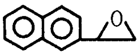
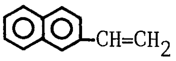
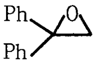
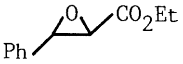
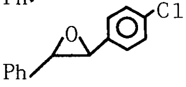
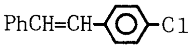


1 2 3 4

Entry	Catalyst (mmol) $FeCl_2 \cdot 4H_2O$	 Se	Yield[b)] (%) 2 + 3 + 4	Molar ratio 2	 : 3	 : 4
1	–	–	35	0	20	80
2	0.1	–	30	0	20	80
3	–	0.1	35	0	17	83
4	0.1	0.05	90	51	32	17
5	0.1	0.1	91	60	27	12
6	0.1	0.2	93	41	47	12
7	0.1	0.4	91	37	45	18

a) Reaction time is 2 h. Other conditions are described in the text.
b) Yield was based on 1 and determined by GLC.

Table II. $FeCl_2$–Se Catalyzed Reduction of Epoxides to Olefins[a)]

Entry	Epoxide	Olefin	Ratio of cis:trans	Yield[b)] (%)
1		$PhCH=CH_2$	—	55[c)]
2			—	29
3		$Ph_2C=CH_2$	—	50
4		$PhCH=CHCH_2OH$	13:87	53
5		PhCH=CHPh	12:88	45
6		PhCH=CHPh	12:88	18
7			19:81	22

a) Reaction time is 20 h except for Entry 1 (2 h). Other reaction conditions are described in the text. b) Isolated yield of olefin. c) Yield was determined by GLC.

Table III. Deuterium Experiments

Conditions[a)]	Product[b)]		
	<u>2</u>	<u>3</u>	<u>4</u>
$NaBD_4$ EtOD	$PhCH{=}CH_2$	$Ph\text{-}CHD\text{-}CH_2\text{-}OH^{c)}$	$Ph\text{-}CH(OH)\text{-}CH_2D^{d)}$
$NaBD_4$ EtOH	$PhCH{=}CH_2$	$Ph\text{-}CH_2\text{-}CH_2\text{-}OH^{e)}$	$Ph\text{-}CH(OH)\text{-}CH_2D^{f)}$

a) The reaction time was 2 h. Other reaction conditions are described in the text. b) Determined by GC-MS. c) The deuterium content (%D) was calculated from GC-MS peak intensity. %D = 91. d) %D = 84. e) %D = 8. f) %D = 81.

reaction intermediate has an anion or radical at the β position.

In conclusion, selenium enhances the catalytic reactivity of $FeCl_2$ during the reduction of aromatic epoxides. Such an effect of selenium is of current interest in the biological field. Recently, it has been reported that selenium is contained in [FeNiSe] hydrogenase, coordinates to the active nickel site, and may influence its catalytic reactivity.[11)] The effect of selenium in promoting metal activity may open a new way to use selenium compounds in organic synthesis. The application for the reduction of other functional groups is now being investigated in this laboratory.

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6) Ethanol was the best solvent for the formation of styrene (2) from 2-phenyloxirane (1) during the preliminary experiments using the following solvents: Water, methanol, ethanol, n-propanol, isopropanol, tetrahydrofuran (THF), ethyl acetate, chloroform, benzene, ethanol-water (1:1), ethanol-THF (1:1), ethanol-ethyl acetate (1:1), ethanol-chloroform (1:1), and water-THF (1:1).

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8) There were black solids in the reaction mixture. When FeSe was used as a catalyst, the result was the same as that in the reaction without a catalyst. It is possible that the active species may be a selenium-iron-boron complex since the Se-$NaBH_4$ complex and metal-$NaBH_4$ complex are reported in the literature: M. Miyashita, M. Hoshino, and A. Yoshikoshi, Tetrahedron Lett., 29, 347 (1988); J. A. Cowan, ibid., 27, 1205 (1986).

9) cis- and trans-Stilbene were not isomerized under the same reaction conditions.

10) No styrene was produced from α- or β-phenethyl alcohol with $NaBH_4$ in EtOH in the presence of $FeCl_2$–Se catalyst.

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