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Epoxidation of Alkenes with O_2 Catalyzed by $EuCl_3$ under Ambient Conditions

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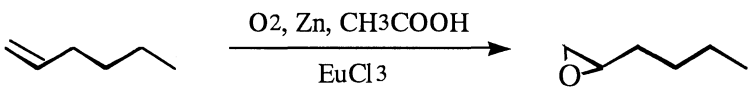
$EuCl_3$ dissolved in a mixture of propanoic acid and 1,2-dichloroethane catalyzed the epoxidation of 1-hexene (81.4% selectivity, 5.34% yield for 1 h) with O_2 in the presence of Zn powder at 40 ^oC. The epoxidation was also catalyzed by $LaCl_3$ (0.75% yield) and $SmCl_3$ (0.57% yield), but $CeCl_3$ (0.08% yield) was inactive. Epoxidations of styrene and cyclohexene were also promoted by the $EuCl_3$-catalytic system.

We have very recently reported that the rare earth salts catalyze the partial oxidation of alkanes (hexane, cyclohexane, and adamantane) with O_2 in the liquid phase at ambient temperature.[1] $EuCl_3$ was the most active catalyst for the mono-oxygenation of alkanes among the rare earth salts tested. In this work, we report that the same catalytic systems are also suitable for epoxidation of alkenes as shown in Scheme 1.

Scheme 1.



A simple, one-step synthesis of epoxides is one of the most attractive themes for the researchers in academic fields as well as in chemical industry. Some reaction systems for the epoxidations with O_2 using transition metal complexes were reported.[2, 3] However, it is desired to develop a new catalytic system for one-step epoxidation of alkenes with O_2 under mild conditions. Our reaction system was catalyzed by a simple rare earth salt such as chloride. Components of our reaction system are resemble to those of the Gif-Orsay-Texas system,[4] except for solvent (CH_2Cl_2) and catalyst ($EuCl_3$). However, the epoxidation of 1-hexene does not proceed in the Gif-Orsay-Texas system.

Table 1 shows experimental results for the epoxidation of 1-hexene catalyzed by some rare earth salts at 40 °C for 1 h. The standard procedure for the epoxidation was as follows. Rare earth salt of 30 μmol was dissolved in a mixed-solution of acetic acid (2 ml) as a proton donor, dichloromethane (2 ml) as a solvent in a three-necked flask with a reflux condenser. After 1-hexene (1 ml) and Zn powder (1 g) as an electron donor had been added to the solution, the reaction was started by stirring the solution and slurry under a stream of O_2 as an oxidant (10 ml•min^{-1} at 1 atm). The products were extracted from the crude reaction mixture and were analyzed by GC-technique. The yields of products were evaluated on the basis of the 1-hexene converted. Fairly good yields of epoxide were observed for most of rare earth salts shown in Table 1, but catalytic activities for $Eu_2(SO_4)_2$, EuF_3 and $CeCl_3$ were quite low. The yield of the epoxide for $EuCl_3$ was the highest among the rare earth catalysts tested. The products other than 1,2-epoxyhexane were 1-hexanal, 1,2-hexane-diol,

Table 1. Epoxidation of 1-hexene catalyzed by various rare earth salts[a)]

Catalyst	Yield of epoxide / %	Selectivity to epoxide / %	TON [b)]
$LaCl_3$	0.75	74.0	2.7
$CeCl_3$	0.08	55.8	0.4
$SmCl_3$	0.57	73.3	2.1
$EuCl_3$	3.39	65.8	13.8
$Eu(NO_3)_3$	2.25	67.1	8.9
$Eu_2(CO_3)_3$	1.76	73.9	6.3
$Eu(CH_3COO)_3$	1.19	61.1	5.2
$Eu(ClO_4)_3$	0.77	38.2	5.4
$Eu_2(SO_4)_3$	0.20	62.7	0.8
EuF_3	0.16	65.2	0.7
blank	0.06	50.1	-

a) Reaction temperature was 40 ℃, reaction time 1 h, rare earth salts 30 μmol, 1-hexene 1 ml, CH_3COOH 2 ml, CH_2Cl_2 2 ml, Zn powder 1 g, and O_2 10 ml•min^{-1} at 1 atm.
b) Turn over number for the sum amount of the products.

1-hexene-3-ol, 1-hexanol, 2-hexanol, some C6 oxygenates and CO_2. The formation of CO_2 of 35 μmol was detected in the gas phase during the epoxidation using $EuCl_3$ catalyst. The selectivity to the epoxide for $LaCl_3$ was the highest and that for $EuCl_3$ was fairly good. The order of TON (turn over number for total amount of the products) was $EuCl_3$ > $Eu(NO_3)_3$ >$Eu_2(CO_3)_3$ > $Eu(ClO_4)_3$ > $Eu(CH_3COO)_3$ > $LaCl_3$ > $SmCl_3$ > $Eu_2(SO_4)_3$ > EuF_3> $CeCl_3$ ≈ blank. $EuCl_3$ is the most active catalyst for the oxidation of 1-hexene. These orders for catalytic activities were true also for the oxidation of cyclohexane.[1)]

Table 2 shows the effects of some solvents on the epoxidation using $EuCl_3$. When solvents of 1,2-dichloroethane, dichloromethane, acetone, diethyl ether were used for the epoxidation, the yields of the epoxide became larger than that without solvent, and the selectivities and the TON were improved. The maximum yield (4.38%) was obtained when 1,2-dichloroethane was used. Thus, 1,2-dichloroethane was the most suitable solvent for the epoxidation of 1-hexene.

Effects of some carboxylic acids on the epoxidation were also examined using dichloromethane, as shown in Table 3. The order of the yields of the epoxide obtained for the acids was acetic acid ≈ propanoic acid > butyric acid > isobutyric acid >> trifluoroacetic acid. In the case of trifluoroacetic acid, the epoxide was not produced, but 1-hexanal (1.19% yield) and 1-hexene-3-al (0.78% yield) were obtained as the major products. The selectivity to the epoxide was improved by using butyric acid and propanoic acid, which were larger than

Table 2. Effect of solvents for the epoxidation of 1-hexene catalyzed by $EuCl_3$[a)]

Solvent	Yield of epoxide / %	Selectivity to epoxide / %	TON [a)]
CH_2Cl_2	3.38	65.8	13.8
$(CH_2Cl)_2$	4.38	74.2	15.7
$(CH_3)_2CO$	2.84	66.7	11.4
$(C_2H_5)_2O$	1.44	70.0	5.5
CH_3CN	1.10	48.7	6.0
C_5H_5N	0.03	5.9	1.3
without	1.23	52.2	6.3

a) Reaction temperature was 40 ℃, reaction time 1 h, $EuCl_3$ 30 μmol, 1-hexene 1 ml, CH_3COOH 2 ml, solvent 2 ml, Zn powder 1 g, O_2 10 ml•min^{-1} at 1 atm.
b) Turn over number for the total amount of the products.

Table 3. Effect of carboxylic acids for the epoxidation of 1-hexene catalyzed by $EuCl_3$[a)]

Carboxyric acid	Yield of epoxide / %	Selectivity to epoxide / %	TON [b)]
CH_3COOH	3.38	65.8	13.8
C_2H_5COOH	3.34	77.1	11.6
C_3H_7COOH	2.15	80.6	7.1
$(CH_3)_2CHCOOH$	0.57	58.3	2.6
CF_3COOH	0	0	7.0

a) Reaction temperature was 40 ℃, reaction time 1 h, $EuCl_3$ 30 μmol, 1-hexene 1 ml, carboxylic acid 2 ml, CH_2Cl_2 2 ml, Zn powder 1 g, O_2 10 ml•min^{-1} at 1 atm.
b) Turn over number for the total amount of the products.

that for acetic acid. Thus, a good yield to the epoxide was obtained by using of propanoic acid. This result was also different from that obtained for the oxidation of cyclohexane, i.e., the product yield in the case of propanoic acid was less than 40 % of that for acetic acid.[1)]

As described above, the most suitable solvents and carboxylic acids for the epoxidation of 1-hexene ($(CH_2Cl)_2$, C_2H_5COOH) were different from those for the oxidation of cyclohexane (CH_2Cl_2, CH_3COOH). When 1,2-dichloroethane and propanoic acid were used for the epoxidation of 1-hexene, the maximum yield of 5.34% and TON of 17.6 were obtained in the present work.

In order to get information for the active oxygen species generated on $EuCl_3$-system, the epoxidations of more reactive alkenes (styrene and cyclohexene) than 1-hexene were carried out under the standard reaction conditions. Epoxidation of styrene to styrene oxide proceeded as shown in Table 4, but the selectivity to styrene oxide was fairly low compared with that observed for 1-hexene. The selectivities to benzyl alcohol (33%) and benzaldehyde (28%) were greater than that to the epoxide. Acetophenone (14% selectivity) and phenyl acetaldehyde (7% selectivity) were also produced. When the reaction temperature decreased to 10 °C from 40 °C (standard conditions), the selectivity to styrene oxide increased up to 38%. However, the selectivity to the sum of benzyl alcohol and benzaldehyde (50%) was fairly high at 10 °C. Oxidation of cyclohexene by $EuCl_3$ catalyst also proceeded under the standard conditions. The selectivity to cyclohexene oxide was low comared with that observed for 1-hexene. Main product was cyclohexanone (28% selectivity) and other major products were 2-cyclohexene-1-ol (11% selectivity) and 2-cyclohexene-1-one (10% selectivity). The active oxygen species generated in the catalytic system of $EuCl_3$ was so reactive as to oxidize C-H bond of alkanes.[1] Thus, it is not surprising that two allyl positions of cyclohexene have been easily oxidized. As described above, reactivity of the active oxygen species generated in the catalytic system in this work must be so strong for reactive alkenes that the selective epoxidations do not occur.

Further investigations are needed to clarify the nature of the active oxygen species generated in the $EuCl_3$ system, $LaCl_3$ system and $SmCl_3$ system.

Table 4. Epoxidation of styrene and cyclohexene with O_2 catalyzed by $EuCl_3$[a)]

Reactant	Yield of epoxide /%	Selectivity to epoxide /%	TON [b)]
styrene	0.33	15.6	6.1
cyclohexene	1.40	23.8	19.2

a) Reaction temperature was 40 ℃, reaction time 1 h, $EuCl_3$ 30 μmol, alkene 1 ml, CH_3COOH 2 ml, CH_2Cl_2 2 ml, Zn powder 1 g, O_2 10 ml•min^{-1} at 1 atm.

b) Turn over number of $EuCl_3$ for the total amount of the products.

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