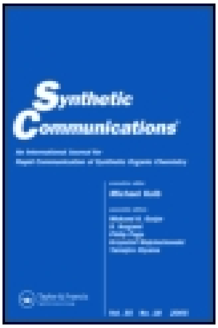

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A Novel Method for Epoxidation of Cyclohexene Catalyzed by Fe_2O_3 with Molecular Oxygen and Aldehydes

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A Novel Method for Epoxidation of Cyclohexene Catalyzed by Fe_2O_3 with Molecular Oxygen and Aldehydes

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Abstract: A novel method for the epoxidation of cyclohexene using molecular oxygen (1atm) and aldehyde in the presence of Fe_2O_3 is presented. The yields of epoxide highly increased by using this method.

Epoxidation of olefins is one of the most important reactions in organic synthesis. However, oxidants generally used in this type of oxidation such as hydrogen peroxide or organic peracid, are potentially explosive[1]. Recently, researches are actively in progress to find safer and simpler oxidation process, much interest has been focused on the direct epoxidation of olefins by combined use of molecular oxygen and aldehyde in the presence of catalyst under mild reaction conditions[2,3,4]. Several transition metal catalysts, such as Ni(II), cobalt(II) and Fe(III) complex, are effective for this purpose and have been extensively studied[3,4,5,6]. It is essential that an aldehyde is present as reductant during this type of reactions. Addition of some proper additive, such as 4A molecular sieves, can effectively accelerate the reaction[7,8].

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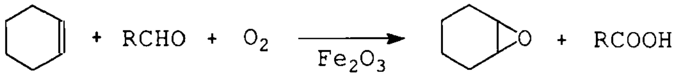
In the previous communication[9], we reported our results of the Baeyer-Villiger oxidation of cyclohexanone to ε -caprolactone with molecular oxygen (1atm) and benzaldehyde in the presence of Fe_2O_3. As shown in the following equation, our subsequent study revealed that Fe_2O_3 behaved as an excellent catalyst for epoxidation of cyclohexene, although successful results were obtained in previous literature only when some metal complexes were used. The present system is in safety, compared with usual method of empolyed expoxidation reagents such as m-chloroperbenzoic acid (mCPBA).

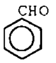
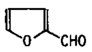


A typical procedure is as follows:

Method 1: A mixture of cyclohexene (10.mmol) or cyclohexanone (10.mmol), Fe_2O_3 (2mmol), aldehyde (30.0mmol) and 1,2-dichloroethane (60ml) was placed into a four-necked flask with a reflux condenser, and was vigorously stirred. Oxygen was bubbled into the stirred solution at 40 ℃ for 6h. The reaction mixture was washed with saturated $NaHCO_3$ solution, dried over Na_2SO_4, and filtered. The products in 1,2-dichloroethane were then analyzed by GC and were identified by ^1H NMR and ^{13}C NMR.

As shown in Table 1, it is interesting to note that some aldehydes were quite effective for the Baeyer-Villiger oxidation of cyclohexanone, but were much less effective for the epoxidation of cyclohexene. For instance, benzaldehyde was found to be remarkably effective for the Baeyer-Villiger oxidation of cyclohexanone, while only a small amount of epoxide was detected in the same reaction system for the epoxidation of cyclohexene.

Table 1 Effect of the kind of aldehydes on Baeyer-Villiger oxidation and epoxidation

aldehyde	$(CH_3)_2CHCHO$	CH_3CH_2CHO	$CH_3(CH_2)_5CHO$		
yield[a] (%) of ε -caprolactone	14.1	15.4	71.3	97.2	53.0
yield[b] (%) of 1,2-epoxycyclohexane	72.4	3.6	32.0	0.8	trace

a: 10.0mmol cyclohexanone, 30.0mmol aldehyde, 60ml 1,2-dichloroethane,O_2 bubbling at 40℃ for 6h.

b: 10.0mmol cyclohexene, 30.0mmol aldehyde,60ml 1,2-dichloroethane,O_2 bubbling at 40℃ for 6h.

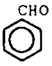
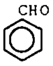
It has been suggested[10] that peracid was formed, though its amount is very small, in the present system with aldehyde and oxygen in the presence of Fe_2O_3. If this is true, epoxidation may occur in similar systems. In order to gain insight into this question, a competing reaction with both cyclohexene (5mmol) and cyclohexanone (5mmol) in the presence of benzaldehyde and Fe_2O_3 was performed. It was found that the yield of ε -caprolactone decreased remarkably from 97.2% to 10.1%, whereas the yield of 1,2-epoxycyclohexane remained almost the same (0.7%).

Compared with the result of benzaldehyde in Table 1, it seems that the formation of peracid may be hampered by the presence of olefinic compound. So we designed a new procedure for this reaction as described in the following paragraph.

Method 2: First, oxygen was bubbled into the mixture of aldehyde (30.0mmol) and 1,2-dichloroethane (60ml) in the presence of Fe_2O_3 (2mmol) for 4.5h under vigorously stirring. Then the olefin was added to the above system . Other conditions were the same as the previous procedure. The products in the 1.2-dichloroethane were analyzed by GC.

As shown in Table 2, for the epoxidation of cyclohexene using method 2 the yield of 1,2-epoxycyclohexane increased from 0.8% (method 1) up to 99.7%. In the case of n-heptaldehyde , the yield of 1,2-epoxycyclohexane using method 2 for only 3h was much higher than that of using method 1 for 6h.

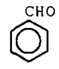
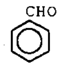
Table 2 Epoxidation of cyclohexene

aldehyde			$CH_3(CH_2)_5CHO$	n-$CH_3(CH_2)_5CHO$
reaction time(h)	3	6	3	6
yield[a] (%) of 1,2-epoxycyclohexane	-	0.8	-	32.0
yield[b] (%) of 1,2-epoxycyclohexane	89.6	99.7	51.0	-

a: method 1;b: method 2

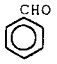
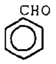
The above method 2 has also been successfully applied to the epoxidation of styrene. The results are listed in Table 3.

Table 3 Epoxidation of styrene

aldehyde			$(CH_3)_2CHCHO$	$(CH_3)_2CHCHO$	$CH_3(CH_2)_5CHO$	n-$CH_3(CH_2)_5CHO$
reaction time (h)	3	6	3	6	3	6
yield[a] (%) of styrene oxide	-	trace	-	4.3	-	trace
yield[b] (%) of styrene oxide	25.2	76.1	21.6	43.0	23.1	44.2

a: method 1;b: method 2

Table 4 Effect of additive on epoxidation of cyclohexene

aldehyde		
reaction time (h)	3	6
yield[a] (%) of 1,2-epoxycyclohexane	-	no product
yield[b] (%) of 1,2-epoxycyclohexane	99.9	-

a: method 1, benzoyl chloride 3.2 mmol

b: method 2, benzoyl chloride 3.2mmol

Our observations suggest that aldehyde is oxidized by oxygen in the presence of the catalyst to produce peracid, whereas this conversion may be hampered by the presence of some kind of olefins. By using method 2, this disadvantage can be avoided. In our previous communication[8], we also reported addition of benzoyl choride to the above oxidation system could accelerate the Baeyer-Villiger oxidation of cyclohexanone highly efficiently. It is noteworthy that addition of benzoyl chloride to the above oxidation system could also accelerate the epoxidation of cyclohexene, but only with method 2. The results are listed in Table 4. When using method 1, no product was detected. Although it is premature to explain clearly this effect at the stage, the role of additive may be to promote the yield of perbenzoic acid derived from oxidation of benzaldehyde. It was reported by Bafford[11] that acyl halides were used in preparation of peroxy compounds with aldehydes, molecular oxygen and acid acceptors. Further work is in progress in order to give a explanation for the effect of benzoyl chloride.

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