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A CONVENIENT SYNTHESIS OF EPOXIDES FROM OLEFINS USING MOLECULAR OXYGEN IN THE ABSENCE OF METAL CATALYSTS

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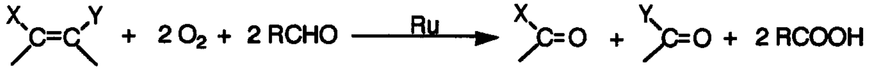
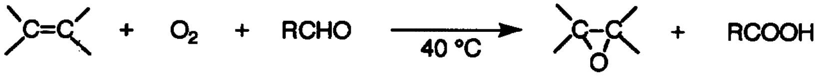
Key Words: Epoxidation, Olefin, Molecular oxygen, Aldehyde

Summary: The system consisting of molecular oxygen and aldehydes (e.g., isobutyraldehyde and pivalaldehyde) oxidizes various olefins to give epoxides in high yields at 40 °C for 3 - 6 h.

Recently, we have reported that the system consisting of molecular oxygen, aldehydes, and ruthenium dioxide is an effective reagent for oxidative cleavage of olefinic double bonds (Eq. 1): peracids from autoxidation of aldehydes oxidize ruthenium dioxide to give ruthenium compounds with higher oxidation state, e.g., RuO_4, which act as catalysts for the oxidative cleavage reaction.[1] When the above oxygenation of olefins was carried out *in the absence of the ruthenium compounds*, epoxidation selectively occurred. Many reports describe epoxidation of olefins using combinations of various oxidants (e.g., H_2O_2 and t-BuOOH) and metal catalysts,[2,3] but little is known concerning selective synthesis of epoxides from olefins with molecular oxygen as an oxygen donor.[4-6] Here, we report a convenient synthetic method of epoxides from olefins using molecular oxygen and aldehydes in the absence of metal catalysts (Eq. 2).



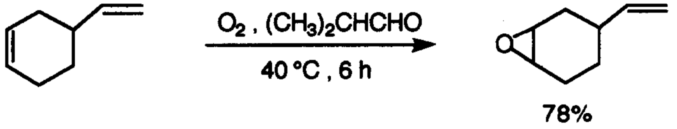
(1)



(2)

A typical reaction procedure of the epoxidation of olefins is as follows. Oxygen was bubbled into a solution of isobutyraldehyde (24 mmol) and 1,2-dichloroethane (100 ml) at 40 °C for 30 min.[7] A 1,2-dichloroethane solution (10 ml) of 2-octene (8 mmol) was added and the resulting mixture was stirred with bubbling of oxygen at 40 °C for 2.5 h. After successive treatment with Na_2SO_3 and $NaHCO_3$, isobutyric acid was removed by extraction into the aqueous solution. The oxygenation products in 1,2-dichloroethane were then analyzed by GC and 2,3-epoxyoctane of 0.90 g was isolated by Kugelrohr distillation.

Representative results of this epoxidation procedure are shown in Table 1. All olefins studied except for styrenes (C=C cleavage, Run 16) and allylic alcohols (no reaction, Run 18) were selectively oxidized to give epoxides using molecular oxygen in the presence of aldehydes without metal catalysts. Carboxylic acids were also formed as a by-product from the starting aldehydes, but were simply removed by extraction with aqueous base. One atom of molecular oxygen is incorporated into the olefinic double bond to form an epoxide and the other oxygen atom is consumed in oxidation of the aldehyde to carboxylic acid. In essence, the aldehydes activate molecular oxygen to lead to selective epoxidation of olefins even without metal catalysts. Of the C_2-C_5 aldehydes studied, pivalaldehyde was found to be the most effective for the epoxidation (Run 5). The reaction of internal olefins using only a stoichiometric amount of the pivalaldehyde yielded the corresponding epoxides, quantitatively (Run 7). However, in the case of acetaldehyde, a large amount of the aldehyde had to be used to attain a high yield of the epoxide (Run 2). Halogenated solvents like 1,2-dichloroethane and tetrachloromethane[4)] were the most effective for the epoxidation (Run 6). Alcohols were poor solvents. This oxidizing reagent consisting of aldehyde and molecular oxygen showed higher reactivity for an internal olefinic double bond than for the external one; 4-vinylcyclohexene gave exclusively 1,2-epoxy-4-vinylcyclohexane (Eq. 3).



(3)

This epoxidation appears to proceed stereospecifically; cis-2-octene gave selectively cis-2,3-epoxyoctane, while the trans epoxide was exclusively formed from the reaction of trans-2-octene (Runs 6 and 8). A similar stereospecific epoxidation was also observed in the cases of (E)- and (Z)-stilbene, respectively.[8] Therefore, we think that the epoxidation of olefins did not occur by acylperoxy radical species, but rather by peracids generated from autoxidation of aldehydes.[9]

Recently, thianthrene 5-oxide (SSO) has been used as a mechanistic probe for assessing the electronic character of oxygen-transfer agents.[10] We also have applied the SSO method to our oxidant system of molecular oxygen and aldehydes (Eq. 4). The oxidant that attacks preferentially the sulfide "S" site of the SSO to give the bis(sulfoxide) (SOSO) acts as an electrophile, as has been also observed in the reaction using m-CPBA as the oxidant.[11]

Table 1. Epoxidation of olefins using molecular oxygen and aldehydes[a]

Run	Olefin	Aldehyde[b]	Reaction time (h)	Yield of epoxide[c] (%)
1	1-octene	CH_3CHO (3)	6	8
2		CH_3CHO (25)	6	80
3		$(CH_3)_2CHCHO$ (3)	6	47
4		$(CH_3)_2CHCH_2CHO$ (3)	6	42
5		$(CH_3)_3CCHO$ (3)	6	75
6[d,e]	cis-2-octene	$(CH_3)_2CHCHO$ (3)	3	quantitative
7		$(CH_3)_3CCHO$ (1.2)	3	quantitative
8[f]	trans-2-octene	$(CH_3)_2CHCHO$ (3)	3	quantitative
9	2-methyl-1-pentene	$(CH_3)_2CHCHO$ (3)	3	80
10		$(CH_3)_3CCHO$ (1.4)	3	79
11	2-methyl-2-pentene	$(CH_3)_2CHCHO$ (3)	3	quantitative
12	cyclopentene	$(CH_3)_2CHCHO$ (3)	6	85
13	cyclohexene	$(CH_3)_2CHCHO$ (3)	3	87
14	cyclooctene	$(CH_3)_2CHCHO$ (3)	3	quantitative
15	1-methylcyclohexene	$(CH_3)_2CHCHO$ (3)	3	quantitative
16	p-chlorostyrene	$(CH_3)_2CHCHO$ (3)	6	70[g]
17	2-norbornene	$(CH_3)_2CHCHO$ (3)	3	quantitative
18	4-methyl-3-penten-1-ol	$(CH_3)_3CCHO$ (3)	3	no reaction

[a] Olefin (2 mmol), aldehyde, 1,2-dichloroethane (30 ml), O_2 bubbling, 40 °C.

[b] Molar ratio of aldehyde and olefin in parenthesis.

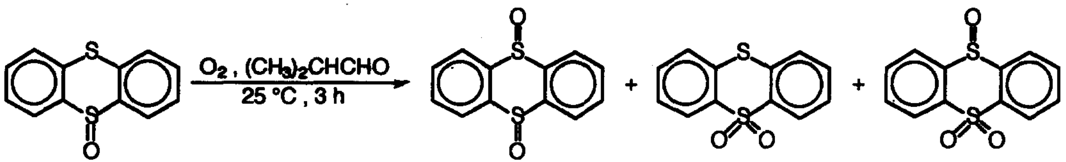
[c] Determined by GC analysis.

[d] Olefin (cis/trans = 97/3), epoxide (cis/trans = 85/15, 89/11 at 30 °C).

[e] Use of tetrachloromethane in place of 1,2-dichloroethane gave also a 83% yield of the epoxide.

[f] Olefin (trans, 100%), epoxide (trans/cis = 97/3).

[g] p-Chlorobenzaldehyde was obtained in 22% yield.



SSO SOSO 46% SSO$_2$ 27% SOSO$_2$ 10%

The system consisting of aldehyde and molecular oxygen is a very convenient oxidizing reagent for common olefins. We are currently investigating the detailed characteristics of the present epoxidation and the behavior of molecular oxygen in relation to the epoxidation mechanism.[12]

References and Notes

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7. After the 30 min pretreatment, iodometric titration showed that the reaction mixture involved 5 mmol of active oxygen.
8. (E)-Stilbene was oxidized exclusively to (E)-stilbene oxide (30%), while (Z)-stilbene afforded only the (Z)-oxide at 35% conversion.
9. Although there are very few reports on selective synthesis of epoxides from olefins using molecular oxygen and aldehydes,[6] the mechanism for the epoxidation has been extensively studied. For a review of the epoxidation mechanism, see: Filippova, T.V.; Blyumberg, E.A. Russ. Chem. Rev., **1982**, 51, 582.
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11. SOO (1 mmol) was allowed to react in the presence of isobutyraldehyde (2 mmol) under O_2 atmosphere in CH_2Cl_2 (8 ml) at 25 °C for 3 h. Product distribution was determined by HPLC measurement.
12. For preliminary kinetic study, the O_2 absorption rate for reaction of 2-octene with isobutyraldehyde is dependent on second order of concentration of the aldehyde: $-\frac{d[O_2]}{dt}=k[\text{aldehyde}]^2[O_2]^0[\text{olefin}]^0$
The rate expression is similar to that of autoxidation of acrolein with a cobalt catalyst: Takenouchi, T,; Osa, T.;.Misono, A. Yukagaku (Oil Chemistry), **1972**, 189.

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