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Epoxidation of Terminal Alkenes with Oxygen and 2-Ethyl Hexanal, without Added Catalyst or Solvent

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Abstract:

Two terminal alkenes, 1-decene and methyl 10-undecenoate, were epoxidized with oxygen using 2-ethyl hexanal as coreactant without any added solvent. Under optimal conditions, the yield of methyl 10,11-epoxyundecanoate was 98.7%. 2-Ethyl hexanal was oxidized mainly to 2-ethyl hexanoic acid and also formed some byproducts. The tested metal complexes retarded the epoxidation reaction slightly and increased the amount of byproducts of 2-ethyl hexanal.

Introduction

The epoxidation of alkenes by molecular oxygen in the presence of a catalyst and aldehyde has been intensively studied (Scheme 1).[1−15] Several research groups have also reported on epoxidation procedures in the absence of catalyst.[16−19] In both the presence and the absence of catalyst, the solvent is thought to be essential for the reaction. Chlorinated or perfluorinated solvents are recommended because of their capacity to dissolve molecular oxygen.

However, chlorinated solvents constitute a serious environmental problem in large-scale production, and perfluorinated solvents do not always allow reactions to be performed in a homogeneous phase. In view of these drawbacks, we set out to test 2-ethyl hexanal as solvent because the oxidation product of the aldehyde, 2-ethyl hexanoic acid, is itself in industrial use. In these preliminary experiments, the reaction proceeded well without additional solvent. A practical method for preparative isolation of the product is still under investigation.

Scheme 1. **Epoxidation of alkenes with oxygen aldehyde as coreactant**

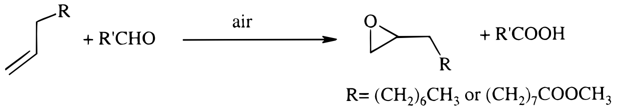

Table 1. **Epoxidation of 1-decene (experiments 1−8) and methyl 10-undecenoate (experiments 9−12) with procedure A**

expt	*T* (°C)	solvent (mL)	aldehyde/ alkene[c]	epoxide (%) at 6 h	epoxide (%) final	reaction time (h)
1	rt	20	3/1[a]		4.9	7.5
2	rt	20	6/1[a]	6.9	16.2	24
3	40	20	6/1[a]	21.6	47.9	22
4	40	20	6/1[b]	31.9	59.3	21
5	40	10	6/1[b]	41.2	63	24
6	40		6/1[b]	21.6	45.4	24
7	40		4.5/1[b]	19.0	19.0	6
8	60		4.5/1[b]	38.7	42	8
9	60		4.5/1[b]	38.7	38.7	6
10	40	10	6/1[b]	34.0	54.6	24
11	40		6/1[b]	18.4	32.5	24

[a] Aldehyde, 2-methyl propanal. [b] Aldehyde, 2-ethyl hexanal. [c] The aldehyde/alkene ratio is the final ratio of added substances.

Results and Discussion

We chose to carry out the air epoxidations on two representative terminal alkenes, 1-decene and methyl 10-undecenoate, using 2-ethyl hexanal and 2-methyl propanal as aldehydes. The influence of solvent and metal complexes was studied as well as the mode of addition of the reactants at different temperatures. The results are summarized in Tables 1 and 2.

We found that, under proper conditions, these terminal alkenes can be epoxidized in good to excellent yields using air oxidation with 2-ethyl hexanal as aldehyde, without added solvent or catalyst. Although terminal alkenes react more sluggishly in epoxidation reactions than do internal ones, this reaction was clean and could be optimized to yield methyl 10,11-epoxyundecanoate at 98.7%. 2-Ethyl hexanal is less volatile than the 2-methyl propanal often used in this type

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Table 2. **Epoxidation of 1-decene with procedure C (experiments 12−15) and methyl 10-undecenoate with procedure b (experiments 16−18)[a]**

expt	aldehyde/ alkene[c]	epoxide (%)		reaction time (h)
		at 4 h	final	
12	1/1	38.0	38.0	4
13	1/1	18.8	37.0	8
14	2/1	42.3	71.2	8
15	3/1	28.5	48.6	8
16	7/1	67.5	89.7	8
17	13.2/1	65.3	98.7	11
18	8.7/1	39.7	39.7	4

[a] Continuous addition of aldehyde, temperature 60 °C. [b] The aldehyde/alkene ratio is the final ratio of added substances.

of epoxidations, and it allows higher reaction temperatures while eliminating the need for added solvent. 2-Ethyl hexanal also appeared to be slightly more effective in inducing epoxidations than was 2-methyl propanal (Table 1, experiments 3 and 4).

The mode of addition of the reactants, as well as the proportions of alkene and aldehyde, was important for obtaining high conversions. In the first set of experiments, the aldehyde was allowed to react with air from 10 to 15 min before the addition of the alkene. The aldehyde was used in excess: the initial molar aldehyde-to-alkene ratio was 3/1, and the rest of the aldehyde was added in portions after 4 and 8 h, bringing the ratio to the final value shown in Table 1. The results in Table 1 show that the reaction is slower in the absence of solvent (dichloroethane): in experiments 5 and 6, the conversions to epoxide after 6 h were 41.2% with solvent and 21.6% without. This effect could be offset, however, through use of higher temperature in epoxidations without solvent (60 °C instead of 40 °C, experiment 8). A reaction temperature of 60 °C was found to be optimal; at higher temperatures the amount and number of byproducts from the aldehyde started to increase.

In a second series of experiments (Table 2), we found that continuous addition of aldehyde gives higher conversions of alkene to epoxide at a given aldehyde-to-alkene ratio. With discontinuous addition (experiments 8 and 9) and an aldehyde-to-alkene ratio of 4.5/1, the conversion of alkene to epoxide at 6-h reaction time was 38.7% for both alkenes. With continuous addition of aldehyde and an aldehyde-to-alkene ratio 4.2/1, the conversion after 3 h was 47.3%. After 5 h of reaction and an aldehyde-to-alkene ratio of 6.5/1, the conversion was already 73.5% (experiment 17).

An increase in the rate of addition of aldehyde increased the rate of epoxidation. When the amount of alkene was 45 mmol and the rate of aldehyde addition 6.6 mmol/h (experiment 13), the conversion of epoxide was 37% after 8 h, and when the rate was 11.15 mmol/h (experiment 14), the conversion increased to 71.2% measured after 8 h.

The best conversion of alkene to epoxide, 98.7%, was obtained when a 2/1 mixture of aldehyde and methyl 10-undecenoate (10 mmol) was allowed to react with oxygen for 1 h, after which aldehyde was added continuously for about 10 h at a rate of addition 11.15 mmol/h (procedure B) (experiments 16 and 17). Further increase in the rate of addition of aldehyde (22.3 mmol/h) led to a lowering of epoxide conversions (experiment 18) (Figure 1).

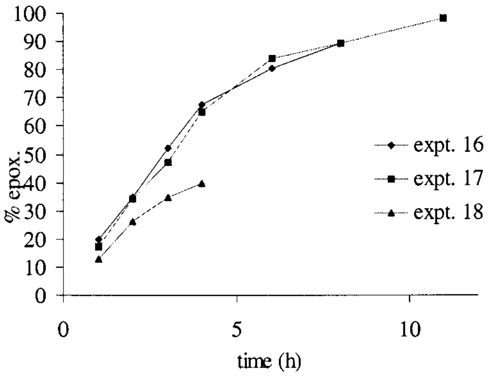

Figure 1. **Progress of epoxidation of methyl 10-undecenoate as a function of time using procedure B. The rate of addition in experiment 18 is twice that in experiments 16 and 17. Aldehyde-to-alkene ratios at the end of the reaction were 7/1 (experiment 16), 13.2/1 (experiment 17), and 8.7/1 (experiment 18).**

The oxidation reaction of alkene and aldehyde begins with autoxidation of the aldehyde to acyl peroxy radicals and peracids, which then react with the alkenes to form epoxide and acid.[20] Radical reactions are difficult to control, and byproducts such as 3-heptanol, 3-heptanone, and 3-heptyl formate were detected in the reaction of 2-ethyl hexanal and terminal alkenes. The same products were also found along with heptane in previous work on the autoxidation reaction of 2-ethyl hexanal.[21−24]

Varying the rate of addition of aldehyde did not significantly affect the amount of aldehyde byproducts. In experiments where the final aldehyde-to-alkene ratio was 3/1, the amount of byproducts was 10−20% after 8 h. Under the same conditions but with a final aldehyde-to-alkene ratio of 2/1 or 1/1, the amount was still the same. Even in a synthesis with a final aldehyde-to-alkene ratio of 13.2/1, after 11 h of reaction, about 16% of the aldehyde had reacted to byproducts. With added metal complexes, the amount of substances other than 2-ethyl hexanoic acid was more significant.

Catalytic activity of several metal complexes was tested in the reaction. The tested metal complexes, $Co(NO_3)_2{\cdot}6H_2O$, $Co(OAc)_2{\cdot}4H_2O$, $Ni(OAc)_2{\cdot}4H_2O$, $Fe(OAc)_2$, and $Mn(OAc)_2{\cdot}2H_2O$, did not increase the epoxidation rate; in fact, the reaction rate in the presence of metal complex was slightly lower. The conversion to epoxide after 6 h was between 22 and 26.8%. The progress of epoxide formation during the reaction is shown in Figure 2.

The addition of metal complexes changed the composition of the oxidation byproducts of 2-ethyl hexanal. Without metal complex, the main byproduct was 3-heptyl formate, whereas with metal complex, the main byproducts were 3-heptanol and 3-heptanone and no or only traces of 3-heptyl formate. Addition of acetic acid did not affect either the reaction rate

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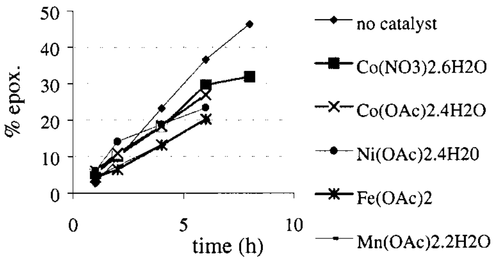

Figure 2. **Effect of metal complexes in alkene epoxidation, procedure C.**

or the product composition. The amount of byproducts was greater in the presence of all metal complexes except $Fe(OAc)_2$ relative to the reactions where no metal complex was added. In the presence of metal complex, 17−28% of 2-ethyl hexanal was converted to products other than 2-ethyl hexanoic acid in 4 h, and the amount continued to increase during the experiment. For example, in the case of $Co(NO_3)_2\cdot 6H_2O$, the amount of byproducts of the aldehyde was about 39% after 8 h of reaction (aldehyde-to-alkene ratio, 2/1).

Conclusions

The epoxidation of terminal alkenes 1-decene and methyl 10-undecenoate with air and 2-ethyl hexanal as solvent and coreactant proved to be an excellent synthesis route. Continuous addition of the aldehyde gave the highest epoxidation rates, and up to a certain point, faster addition of aldehyde to the reaction mixture speeded up the epoxidation. The transformation of alkene to epoxide was clean, and no byproducts of the alkene were detected at low temperatures (60 °C). Under optimal conditions, the yield of epoxide was 98.7%. The main product of the oxidation of 2-ethyl hexanal was 2-ethyl hexanoic acid, but some other products were also formed. Metal complexes in the synthesis increased the amount of byproducts and did not advance the epoxidation.

Experimental Section

General. 2-Methyl propanal (Merck) and 2-ethyl hexanal (Aldrich) were dried, distilled and kept under inert atmosphere before use. Methyl 10-undecenoate (Pfaltz & Bauer), 1-decene (Merck), and dichloroethane (Merck) were kept over molecular sieves and distilled before use. The metal complexes, $Co(NO_3)_2\cdot 6H_2O$ (Merck), $Co(OAc)_2\cdot 4H_2O$ (J.T. Baker), $Ni(OAc)_2\cdot 4H_2O$ (Fluka), $Fe(OAc)_2$ (Aldrich), and $Mn(OAc)_2\cdot 2H_2O$, were used as obtained from the supplier. In some cases, 1 mL of glacial acetic acid was added. Gas chromatographic analyses were performed on an HP 6890 instrument: 15-m HP5 column; carrier gas, helium; initial column temperature, 40 °C; final column temperature 280 °C; progress rate, 9 °C/min. The epoxides were identified by comparison with authentic samples. (For preparation, see below.) Decane was used as standard to calculate the exact amount of epoxide present in the reaction mixture. The oxidation products of 2-ethyl hexanal, 1-decene, and methyl 10-undecenoate were identified by GC−mass spectrometry by comparison with library spectra.

Epoxidation of Alkene with Air with Aldehyde as Coreactant. *Procedure A.* The reaction vessel, equipped with a condenser, was charged with 2-methyl propanal or 2-ethyl hexanal (30−60 mmol), and 10−20 mL of dichloroethane if solvent was used. Magnetic stirring (1250 rpm) and air bubbling through a needle (70 mL/min) to solution were started, and 1-decene or methyl 10-undecenoate (5−10 mmol) was added to the vessel after 10 min. The alkene-to-aldehyde ratio was 1/3 in the beginning, with a final ratio of added alkene and aldehyde of 1/6. The rest of the aldehyde was added during the reaction in two equal portions at 4 and 8 h. Both reaction temperatures and times varied.

Procedure B. To the reaction vessel equipped with condenser was added 20 mmol of 2-ethyl hexanal. Stirring (1250 rpm) and air bubbling (70 mL/min) were commenced. After 10 min, methyl 10-undecenoate (10 mmol) was added to the vessel. Continuous addition of aldehyde to the reaction was begun after 1 h.

Procedure C. 1-Decene (45 mmol) was charged to the reaction vessel; stirring (1250 rpm) and air bubbling (70 mL/min) were commenced. After 10 min, continuous aldehyde addition was begun. If metal complex was used, it was added to the reaction after air bubbling was started. The temperature in procedures B and C was 60 °C if not otherwise mentioned.

Synthesis of 1,2-Epoxy Decane and Methyl 10,11-Epoxyundecanoate with Use of *m*-CPBA as Oxidizing Agent. A 50-mL two-neck, round-bottomed flask equipped with a condenser was charged with 1-decene or methyl 10-undecenoate and 20 mL of dichloroethane. *m*-Chlorobenzoic acid (1 g) in dichloroethane (3 mL) was added dropwise (1 h) to the ice-cooled solution of alkene. The reaction mixture was first maintained for 15 h at room temperature and then refluxed for 1 h at 45 °C. Ether (10 mL) was added to generate a clear solution. The solution was washed with 2 × 20 mL of 5% $NaHCO_3$, 2 × 20 mL of 2% NaOH, and 2 × 20 mL of brine and then dried with $MgSO_4$. The solvent was removed in a rotary evaporator to yield 1,2-epoxydecane, [85% (GC 6.3 min), purity 94%; ^{13}C NMR (200 MHz, $CDCl_3$) analysis δ 14.1 (C-10), 22.8 (C-9), 26.0 (C-8), 29.3 (C-7), 29.5 (C-6), 29.6 (C-5), 31.9 (C-4), 32.6 (C-3), 47.0 (C-1), 52.4] and (C-2) methyl 10,11-epoxyundecanoate [88% (GC 12.4 min), purity 99%; ^{13}C NMR (200 MHz, $CDCl_3$) analysis δ 26.0 (C-3), 27.1 (C-8), 30.1, 30.2, 33.6 (C-9), 35.1 (C-2), 48.0 (C-11), 51.4 ($COOCH_3$), 52.4 (C-10), 174.6 (C-1)].

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