

Epoxidation of Fatty Acid Esters with Aqueous Hydrogen Peroxide in the Presence of Molybdenum Oxide-Tributyltin Chloride on Charcoal Catalyst

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The epoxidation of fatty acid esters was carried out with a 30% aqueous hydrogen peroxide in the presence of a molybdenum oxide-tributyltin chloride on a charcoal catalyst in 2-propanol at 50°C. Such inner olefins as ethyl erucate and ethyl oleate gave good yields of 77 and 76%, respectively. Ethyl elaidate, a trans-form of ethyl oleate, was less reactive (40% yield). Several vegetable oils such as rapeseed oil, olive oil, soybean oil, cottonseed oil, corn oil, and linseed oil were oxidized with the oxirane oxygen contents of 5.3 to 3.5%.

Epoxy fatty acid esters have been used for the plasticizer of a poly(vinyl chloride) resin since it was found by Greenspan et al.¹⁾ Among various oxidation processes, an in situ method using acetic acid and a highly-concentrated hydrogen peroxide is practical.²⁾ However, epoxidation with peracetic acid or performic acid tends to open the oxirane rings. Also, it has some difficulties to separate acid catalysts from the reaction products. Furthermore, hydrogen peroxide of a high concentration is dangerous to handle. Therefore, the use of 30% aqueous hydrogen peroxide in place of organic peroxy acids is favorable.

Hitherto, we have studied the epoxidation of C₅–C₈ alkenes using 30% aqueous hydrogen peroxide as an oxidizing agent. We used molybdenum oxide on charcoal under the presence of organotin compounds as cocatalysts.³⁾ The catalyst system was applied on several unsaturated fatty acid esters to give epoxides in good yields. The epoxidation was selectively carried out and the separation of the catalyst was easily performed by filtration.

Results and Discussion

Epoxidation of Various Unsaturated Fatty Acid Esters. Previously, we found that certain alkenes such as cyclopentene, cyclohexene, cyclooctene, 1-octene, and 2-octene were epoxidized selectively in high yields in the presence of molybdenum blue (MB), a type of mixed acids of Mo(V) and Mo(VI),⁴⁾ and tributyltin chloride on charcoal.³⁾ In this paper we applied the catalyst for the epoxidation of various unsaturated fatty acid esters. Then, the epoxidation of ethyl erucate, ethyl oleate, ethyl elaidate, ethyl linoleate, ethyl 2-hexenoate, and ethyl 3-hexenoate was carried out with 30% aqueous hydrogen peroxide in 2-propanol solvent for 15 h at 50°C. Results are shown in Table 1. In all the substrates examined, products were the epoxidized fatty acid esters and recovered materials as was confirmed by the analyses of HPLC and flash chromatography. The epoxidation of unsaturated fatty acid esters of cis-form such as ethyl erucate, ethyl oleate, and ethyl linoleate afforded higher yields than those of the trans-form; it was considered that the activity to the cis-form was higher

Table 1. Epoxidation of Various Unsaturated Fatty Acid Esters with 30% H₂O₂ in the Presence of Molybdenum Oxide–Bu₃SnCl–Charcoal (DMFBA) Catalyst^{a)}

Material	Epoxide yield/%
Ethyl erucate	77
Ethyl oleate	76
Ethyl elaidate	40
Ethyl 10-undecenoate	29
Ethyl linoleate	56
Ethyl 2-hexenoate	0
Ethyl 3-hexenoate	0

a) Substrate (3.0 mmol), 30% H₂O₂ (1.8 ml, 17.6 mmol), 1.25% MB-charcoal (0.4 g), Bu₃SnCl (50 mg, 0.15 mmol), and 2-propanol (12 ml) were used. The reaction was carried out at 50°C for 15 h. DMFBA; *N,N*-dimethylformamide dibutyl acetal.

than that of the trans-form owing to a steric effect.

Ethyl 10-undecenoate, an ester including a terminal double bond, gave a lower yield than those of inner ones. On the other hand, unsaturated fatty acids which included a double bond near the carbonyl group, such as ethyl 2-hexenoate or ethyl 3-hexenoate, did not epoxidized at all.

Recently, it has been reported that a pair of isomers, methyl oleate and methyl elaidate, were epoxidized using excess molar ratios of aqueous hydrogen peroxide in the presence of iron(III) acetylacetonate.⁵⁾ The epoxidation has took place to give trans-isomer in high yields either from methyl oleate or methyl elaidate. In our reaction system, a double bond was epoxidized by keeping its configuration. This tendency has also been reported in the epoxidation using *m*-chloroperbenzoic acid.⁵⁾

In the epoxidation of ethyl linoleate, the oxidation rate of one double bond was faster than that of others. The monoepoxides were selectively separated from ethyl linoleate and the oxirane ring was confirmed by elemental analyses; NMR spectra though the epoxidized site could not be determined. The epoxidation of α,β -unsaturated acids has been carried out using hydrogen peroxide in the presence of tungstic acid in an alkaline media.⁶⁾ The active species for the reaction systems were suggested to be HOO[–] which reacted at the electron-poor double bond of α,β -unsaturated

Table 2. Epoxidation of Various Vegetable Oils Using 30% H₂O₂ in the Presence of Molybdenum Oxide-Bu₃SnCl-Charcoal (BSA) Catalyst^{a)}

Oil (Iodine number)	Iodine number	Oxirane oxygen/%	Erc ^{c)}	Constitution ^{b)}		
				Ole ^{d)}	Li ₂ ^{e)}	Li ₃ ^{f)}
Rapeseed oil (104)	42	3.9	45—55	12—18	12—16	7—9
Olive oil (81)	12	4.0	0	65—85	4—15	0
Soybean oil (139)	45	5.3	0	15—33	43—56	5—11
Cottonseed oil (121)	59	3.5	0	15—36	34—55	0
Corn oil (127)	57	3.6	0	19—49	34—62	0
Linseed oil (152)	75	4.6	0	13—38	5—29	26—58

a) Oil (3 g), 30% H₂O₂ (6 ml, 58.7 mmol), 1.25% MB-charcoal (0.8 g), Bu₃SnCl (100 mg, 0.3 mmol), and 2-propanol (24 ml) were used. The reaction was carried out at 50°C for 15 h. b) These constitutions were quoted from JP IX and Yushi Kagaku Binran (ed by Chemical Society of Oil and Fats, 1971). c) Erucic acid. d) Oleic acid. e) Linoleic acid. f) Linolenic acid. BSA; *N,O*-bis(trimethylsilyl)acetamide.

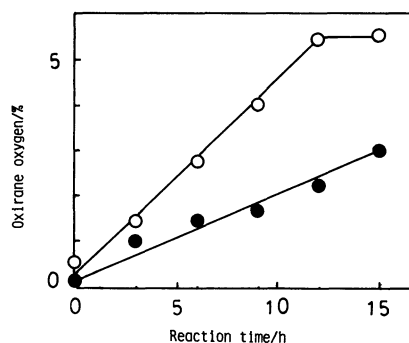


Fig. 1. Oxirane oxygen (%) vs. reaction time in the epoxidation of ethyl erucate and soybean oil with 30% H₂O₂ in the presence of molybdenum oxide-Bu₃SnCl-charcoal (DMFBA) catalyst. O: Soybean oil, ●: ethyl erucate. Substrate (2 g), 30% H₂O₂ (3 ml), 1.25% molybdenum oxide-charcoal (0.8 g), Bu₃SnCl (100 mg), and 2-propanol (19 ml) were used. DMFBA; *N,N*-dimethylformamide dibutyl acetal.

acids.

Epoxidation of Various Vegetable Oils. In the plastic industries, soybean oil and oleic acid derivatives are used as a plasticizer. Therefore, we epoxidized various vegetable oils such as rapeseed oil, olive oil, soybean oil, corn oil, cottonseed oil, and linseed oil with 30% aqueous hydrogen peroxide in the presence of molybdenum oxide-tributyltin chloride-charcoal catalyst.

In the oxidation of soybean oil and ethyl erucate, a linear increase of oxirane oxygen according to the reaction time to give the values of 5.6 and 3.0%, respectively (Fig. 1). Also, various vegetable oils were oxidized. Results are shown in Table 2. According to Japanese Pharmacopoeia IX, rapeseed oil contains an erucic acid ester as the main component, and was expected to give a high yield of epoxides since ethyl erucate gave the epoxide in good yield (Table 1). However, the oil gave a poor yield. For this result, it was supposed that the rapeseed oil used in our experiment did not contain erucic acid ester according to the history of the recent process.⁷⁾ On the other hand, olive oil which contains an oleic acid ester as a main com-

ponent was epoxidized in high yield.

Vegetable oils which have linoleic or linolenic acid as a main component gave rather low yields. In our experiments, the epoxidized soybean oil contained 5.3% oxirane oxygen. Other epoxidized vegetable oils, such as olive oil or linseed oil, could also be used as a plasticizer.

Experimental

Materials. Aqueous hydrogen peroxide (30%) (Hayashi Pure Chemicals), ethyl oleate, ethyl erucate, ethyl linoleate, 2-hexenoic acid, 3-hexenoic acid, tributyltin chloride (Tokyo Chemical Industry), elaidic acid, *N,N*-dimethylformamide dibutyl acetal (DMFBA), and *N,O*-bis(trimethylsilyl)acetamide (BSA) (Wako Pure Chemicals) were purchased. Charcoal (DC-5200w) was kindly provided by Dia Catalysts & Chemicals.

Esterification. 2-Hexenoic acid, 3-hexenoic acid, and elaidic acid (1 g) were respectively esterified with ethanol (10 ml) in the presence of two drops of concd H₂SO₄ at room temperature for 6 h. After the ethanol was evaporated off under reduced pressure, the reaction solution was diluted with water (20 ml). The product was extracted with ether and dried with anhydrous Na₂SO₄. The evaporation of ether gave an oily product.

Pretreatment of Charcoal. Charcoal powder (1 g) was treated with DMFBA or BSA (50 mg) in cyclohexane (20 ml) by stirring at 50°C. After 2 h, the charcoal was filtered off, washed with hexane, and dried.

Preparation of Catalyst. The molybdenum oxide-charcoal catalyst was prepared by fixing MB which was prepared from molybdenum powder and H₂O₂^{4,8)} on pretreated charcoal (65 mesh) by stirring overnight at room temperature. The catalyst was separated by filtration and dried.

Epoxidation Procedure. Into the dispersed 2-propanol solution of the molybdenum oxide-charcoal catalyst (0.4 g), Bu₃SnCl (50 mg) was added. After 30 min, additional 2-propanol (10 ml), substrate (1 g), and 30% aqueous hydrogen peroxide (2 ml) were added. The reaction was carried out at 50±1°C in an oil bath under magnetic stirring.

Analyses of Products. After the reaction, the catalyst was filtered off and 2-propanol was evaporated from the reaction solution. Then, the reaction mixture was extracted with ether and dried. After the removal of ether, the residue was subjected to flash chromatography by passing it through a

Kieselgel 60 column. Elution with benzene-hexane (9:1, v/v) and evaporation of the solvents gave epoxides.

The melting point was uncorrected. NMR spectra were recorded on a Varian XL-200 spectrometer with tetramethylsilane (TMS) as an internal standard. The chemical shifts and coupling constants (J) are given in δ and Hz, respectively.

cis-Ethyl 13,14-Epoxydocosanoate. Colorless crystals (mp 26–27°C). ^1H NMR (CDCl_3) 0.88 (3H, t, $J=6$ Hz, CH_3), 1.00–1.72 (34H, m, CH_2), 2.28 (3H, t, $J=8$ Hz, CH_3), 2.90 (*cis*-2H, m, CH),⁹⁾ 4.13 (2H, q, $J=8$ Hz, CH_2). Found: C, 75.55; H, 12.30%. Calcd for $\text{C}_{22}\text{H}_{44}\text{O}_3$: C, 75.33; H, 12.12%.

cis-Ethyl 9,10-Epoxyoctadecanoate. Colorless oil. ^1H NMR (CDCl_3) 0.92 (3H, t, $J=6$ Hz, CH_3), 1.12–1.76 (32H, m, CH_2), 2.32 (3H, t, $J=8$ Hz, CH_3), 2.95 (*cis*-2H, m, CH),⁹⁾ 4.18 (2H, q, $J=8$ Hz, CH_2). Found: C, 73.53; H, 11.82%. Calcd for $\text{C}_{20}\text{H}_{42}\text{O}_3$: C, 73.57; H, 11.73%.

trans-Ethyl 9,10-Epoxyoctadecanoate. Colorless oil. ^1H NMR (CDCl_3) 0.90 (3H, t, $J=6$ Hz, CH_3), 1.06–1.76 (32H, m, CH_2), 2.31 (3H, t, $J=8$ Hz, CH_3), 2.68 (*trans*-2H, m, CH),⁹⁾ 4.17 (2H, q, $J=8$ Hz, CH_2). Found: C, 73.23; H, 11.74%. Calcd for $\text{C}_{20}\text{H}_{42}\text{O}_3$: C, 73.57; H, 11.73%.

Ethyl 10,11-Epoxyundecanoate. Colorless oil. ^1H NMR (CDCl_3) 1.12–1.90 (16H, m, CH_2), 2.32 (3H, t, $J=8$ Hz, CH_3), 2.42–2.60 (1H, m, CH), 2.72–3.02 (2H, m, CH_2), 4.17 (2H, q, $J=8$ Hz, CH_2). Found: C, 68.10; H, 10.75%. Calcd for $\text{C}_{13}\text{H}_{24}\text{O}_3$: C, 68.38; H, 10.59%.

Ethyl Epoxyoctadecenoate. Colorless oil. ^1H NMR (CDCl_3) 0.90 (3H, t, $J=6$ Hz, CH_3), 1.08–1.73 (24H, m, CH_2), 2.38 (3H, t, $J=8$ Hz, CH_3), 2.93 (2H, m, CH), 4.13 (2H, q, $J=8$ Hz, CH_2), 5.33–5.63 (2H, m, CH). Found: C, 73.77; H, 11.10%. Calcd for $\text{C}_{20}\text{H}_{37}\text{O}_3$: C, 74.03; H, 11.18%.

Iodine Numbers of Vegetable Oils. Iodine numbers of vegetable oils were obtained by the titration with 0.1 M[†]

sodium thiosulfate after oils were treated with iodine trichloride.¹⁰⁾

Oxirane Oxygens of Vegetable Oils. Oxirane oxygens of vegetable oils were estimated by titration with 0.1 M HBr/AcOH in benzene using 0.1% Crystal Violet as an indicator.¹¹⁾

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[†] 1 M=1 mol dm⁻³.