

Hydrolysis of Mono- and Diepoxyoctadecanoates by Alumina

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ABSTRACT: In this study it is shown that the epoxide derivative of oleic acid, methyl 9,10-epoxyoctadecanoate, is readily hydrolyzed to a diol when exposed to a commercial preparation of neutral alumina. Comparison of ^1H and ^{13}C NMR spectra of the diol with those of standards showed that the product was the *threo* isomer. When methyl 9,10-12,13-diepoxyoctadecanoate was treated with alumina, a mixture of dihydroxytetrahydrofuran regioisomers, methyl 9,12-epoxy-10,13-dihydroxystearate and methyl 10,13-epoxy-9,12-dihydroxystearate, was obtained. These results show that alumina is an unsuitable support for epoxidation catalysts. However, alumina-catalyzed hydrolysis of fatty epoxides is an efficient way to synthesize polyhydroxy materials, and these materials are suitable for several industrial applications.

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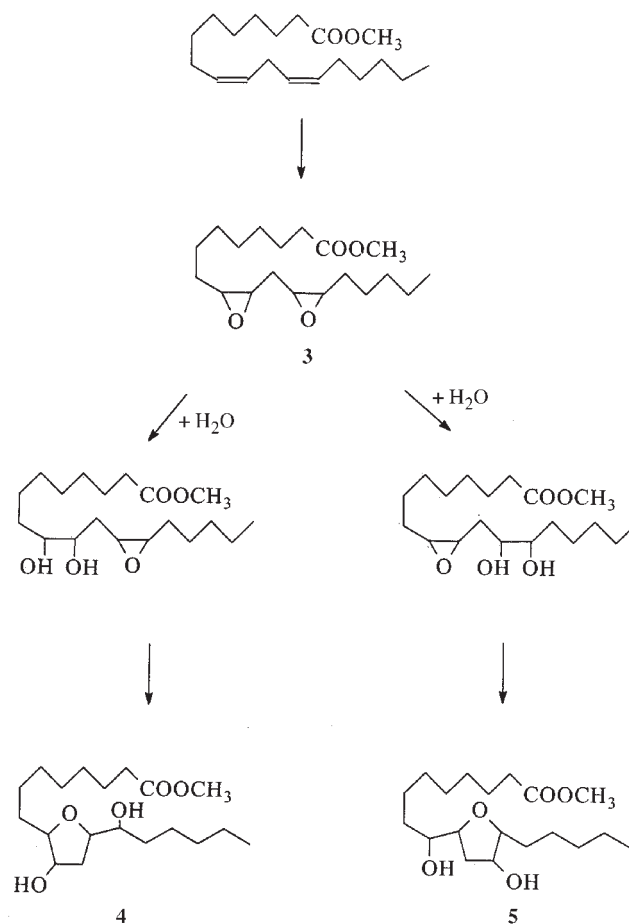
KEY WORDS: Alumina, methyl 9,10-12,13-diepoxyoctadecanoate, methyl 9,10-dihydroxyoctadecanoate, methyl 9,12-epoxy-10,13-dihydroxyoctadecanoate, methyl 10,13-epoxy-9,12-dihydroxyoctadecanoate, methyl 9,10-epoxyoctadecanoate.

Heterogeneous catalysts are easily recovered and reused in continuous processes, and because of this, there is a continuing search for ways to prepare heterogenized catalysts (1). Epoxidation is an important industrial process, and epoxidized FA derivatives are used as plasticizers and plastic stabilizers (2). Recent research efforts have focused on the use of transition metal complexes for epoxidation, and some of these catalysts have been supported or heterogenized on alumina (3,4). However, prior work showed that alumina is an effective catalyst for oxirane ring opening by oxygen- and nitrogen-containing nucleophiles (5,6). This raises the possibility that heterogeneous catalysis by alumina might be effective in promoting epoxide hydrolysis. Accordingly, we exposed methyl 9,10-epoxyoctadecanoate and methyl 9,10-12,13-diepoxyoctadecanoate to neutral alumina and found that the epoxides are readily hydrolyzed to FA derivatives with hydroxy groups that are useful in a wide variety of applications. Generally, dilute acid treatment is used for the hydrolysis of epoxides. However, alumina is superior to such acid treatment because it is easily removed from the product. Also, for industrial use, alumina is preferred because it is safe, low in cost, and has a long shelf life.

MATERIALS AND METHODS

Chemicals. *t*-Butyl hydroperoxide (70%), oleic acid, and methyl linoleate were from Sigma Chemical (St. Louis, MO). Methyl (\pm)-*threo*-9,10-dihydroxyoctadecanoate and methyl (\pm)-*erythro*-9,10-dihydroxyoctadecanoate were purchased from Larodan Fine Chemicals AB (Malmö, Sweden). Oxone ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), 1,1,1-trifluoroacetone, and aluminum oxide (activated, neutral, Brockmann 1, 150 mesh, 58Å) were purchased from Aldrich (Milwaukee, WI). Trimethylsilyl (TMS) derivatives were prepared using *N,O*-bis(trimethylsilyl)-trifluoroacetamide from Pierce (Rockford, IL).

Preparation of fatty epoxides. Methyl 9,10-epoxyoctadecanoate **1** was prepared by the epoxidation of oleic acid with *t*-butyl hydroperoxide by using immobilized peroxygenase as the catalyst followed by methylation as described previously (7). Methyl 9,10-12,13-diepoxyoctadecanoate **3** (Scheme 1) was prepared as follows: Methyl linoleate (100 mg), 3 mL ace-



SCHEME 1

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tonitrile, 1,1,1-trifluoroacetone (300 μ L), and 2 mL 40 mM Na_2EDTA were combined in a 50-mL glass-stoppered Erlenmeyer flask. The flask was cooled in a 5°C water bath, and 195 mg NaHCO_3 and 0.7 g oxone were added. The reaction flask was shaken vigorously for 6 h. After the addition of 10 mL H_2O , the product was extracted with 50 mL diethyl ether. The ether fraction was washed with 2×20 mL H_2O , dried with anhydrous Na_2SO_4 , and the ether removed under a stream of nitrogen.

Epoxide hydrolysis. Methyl 9,10-epoxyoctadecanoate **1** (5 mg), neutral alumina (115 mg), and cyclohexane (0.6 mL) were placed in a 1.7-mL glass HPLC vial with a screw cap. The vial was attached to laboratory rotator (radius of 17 cm) and rotated at 3.5 revolutions per minute. At the indicated time, the contents of the vial were filtered through a sintered glass funnel and the alumina was washed sequentially with 5 mL each of methanol, dichloromethane, and diethyl ether. Hydrolysis of methyl 9,10-12,13-diepoxyoctadecanoate **3** was conducted in an identical manner except that 230 mg neutral alumina was used. Alternatively, the epoxides **1** and **3** were hydrolyzed by placing them in a 0.6-mL mixture of THF/water (3:2, vol/vol) containing 1% HClO_4 and agitating the mixture. At the indicated time, the product was partitioned between 20 mL diethyl ether and 20 mL H_2O . The ether layer was washed with 2×20 mL portions of 2% NaHCO_3 .

Chromatographic and instrumental methods. ^1H and ^{13}C NMR spectra were obtained as described previously (8).

Epoxidized fatty methyl esters were analyzed by RP-HPLC. Solutions of the methyl esters in dichloromethane were filtered through 13-mm, 0.45- μm syringe filters (PVDF; Scientific Resources, Eatontown, NJ). Dichloromethane was removed under a stream of nitrogen, and the filtered products were dissolved in 1 mL isopropanol. Reaction mixtures were separated on two Symmetry 3.5 μm C_{18} reversed-phase columns (150 \times 2.1 mm and 50 \times 2.1 mm) (Waters, Milford, MA) connected in series. Quantification of hydrolyzed epoxide products was made using a Vorex MK III ELSD (Alltech, Deerfield, IL) operated at 55°C, and with N_2 as the nebulizing gas at a flow rate of 1.5 L/min. Mobile phase composition and gradient were 0–5 min $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (40:60, vol/vol); 5–30 min $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (40:60, vol/vol) to CH_3CN (100); 30–54 min CH_3CN (100). The flow rate was 0.25 mL/min. Products were characterized by HPLC with mass detection using EI-MS (Thermabeam Mass Detector; Waters) and atmospheric pressure chemical ionization (APCI) HPLC-MS (Micromass ZMD; Waters). The EI-MS detector was set to scan in the mass range of m/z 55–600 at 1000 amu/s and had an ionization energy of 70 eV. Ionization source, nebulizer, and expansion region temperatures were 200, 64, and 75°C, respectively. When using the APCI-MS, the HPLC gradient contained 0.1% formic acid, and the APCI-MS detector was set to scan in the mass range of m/z 150–550 at 400 amu/s. The corona, cone, and extractor voltages were 3700, 20, and 5 eV, respectively. The source and APCI heater temperatures were 150 and 400°C, respectively.

Structural confirmation of hydrolysis products. (i) *Methyl threo-9,10-dihydroxyoctadecanoate (2)*. Retention time (RT): 18.2 min; IR: 3280 (hydroxy), 1702 (carbonyl) cm^{-1} ; APCI-

MS (not derivatized): m/z (obs. fragment, intensity), 390 ($[\text{M} + 1 + 18 (\text{H}_2\text{O}) + 41 (\text{CH}_3\text{CN})]^+$, 10.5%), 348 ($[\text{M} + 18]^+$, 14.7%), 331 ($[\text{M} + 1]^+$, 100%); EI-MS: m/z (obs. fragment, intensity), 187 ($[\text{HOCH}(\text{CH}_2)_7\text{COOCH}_3]^+$, 40.5%), 155 ($[\text{M} + 187 - 32 (\text{CH}_3\text{OH})]^+$, 100%); APCI-MS (bis-TMS ether): m/z (obs. fragment, intensity), 475 ($[\text{M} + 1]^+$, 100%); EI-MS: m/z (obs. fragment, intensity), 259 ($[\text{TMSOCH}(\text{CH}_2)_7\text{COOCH}_3]^+$, 57.4%), 215 ($[\text{M} - 259]^+$, 66.7%); ^1H NMR: (400 MHz, C_6H_6 , δ_{H}) 1.16 (*t*, $J = 6.8$ Hz, 3H, CH_3), 1.40–1.90 (*m*, 24H, CH_2), 2.38 (*t*, $J = 7.4$ Hz, 2H, 2- H_2), 3.49 (*bs*, 2H, 9- H , and 10- H), 3.61 (*s*, 3H, COOCH_3); ^{13}C NMR: (100 MHz, C_6H_6 , δ_{C}) 15.0 (C-18), 23.8, 25.9, 26.6, 26.8, 30.0, 30.2, 30.5, 30.7, 30.8, 33.0, 34.8, 51.6 (COOCH_3), 75.3 (C-9 and C-10), 174.3 (C-1); (100 MHz, CDCl_3 , δ_{C}) 14.1 (C-18), 22.7, 24.9, 25.5, 25.6, 29.0, 29.1, 29.3, 29.4, 29.5, 29.7, 31.9, 33.6, 34.1, 51.4 (COOCH_3), 74.5 (C-9 and C-10), 174.3 (C-1).

(ii) *Methyl 9,12-epoxy-10,13-dihydroxystearate (4) and methyl 10,13-epoxy-9,12-dihydroxystearate (5)*. Peak I: RT 5.9 min; Peak II: RT 9.4 min; IR (I): 3468 (hydroxy), 1738 (carbonyl), 1174 (C–O–C) cm^{-1} ; IR (II): 3388, 1738, 1171 cm^{-1} ; APCI-MS (not derivatized) (I): 404 ($[\text{M} + 1 + 18 + 41]^+$, 15.4%), 362 ($[\text{M} + 18]^+$, 25.6%), 346 ($[\text{M} + 2]^+$, 28.2%), 345 ($[\text{M} + 1]^+$, 100%); APCI-MS (II): m/z (obs. fragment, intensity), 362 ($[\text{M} + 18]^+$, 16.0%), 346 ($[\text{M} + 2]^+$, 28.0%), 345 ($[\text{M} + 1]^+$, 100%); EI-MS (I): m/z (obs. fragment, intensity), 308 ($[\text{M} - 18 - 18]^+$, 0.9%), 295 ($[\text{M} - 31(\cdot\text{OCH}_3) - 18]^+$, 1.1%), 277 ($[\text{M} - 31 - 18 - 18]^+$, 0.9%), 187 ($[\text{HO}=\text{CHC}_6\text{H}_{12}\text{COOCH}_3]^+$, 100%), 157 ($[\text{M} - 187]^+$, 23.7%), 155 ($[\text{M} + 187 - 32]^+$, 87.6%), 139 ($[\text{C}_8\text{H}_{16}\text{COOCH}_3 - 32]^+$, 11.9%), 113 ($[\text{C}_7\text{H}_{12}\text{OH}]^+$, 63.2%); EI-MS (II): m/z (obs. fragment, intensity), 308 ($[\text{M} - 18 - 18]^+$, 1.3%), 295 ($[\text{M} - 31(\cdot\text{OCH}_3) - 18]^+$, 2.1%), 277 ($[\text{M} - 31 - 18 - 18]^+$, 1.6%), 187 ($[\text{HO}=\text{CHC}_6\text{H}_{12}\text{COOCH}_3]^+$, 64.4%), 157 ($[\text{M} - 187]^+$, 16.9%), 155 ($[\text{M} + 187 - 32]^+$, 100%), 139 ($[\text{C}_8\text{H}_{16}\text{COOCH}_3 - 32]^+$, 13.8%), 113 ($[\text{C}_7\text{H}_{12}\text{OH}]^+$, 39.7%); APCI-MS (bis-TMS ether) (I): m/z (obs. fragment, intensity), 490 ($[\text{M} + 2]^+$, 46.7%), 489 ($[\text{M} + 1]^+$, 100%), 417 ($[\text{M} - \text{TMSOH} + 18 + 1]^+$, 2.0%), 399 ($[\text{M} - \text{TMSOH} + 1]^+$, 1.3%); APCI-MS (II): m/z (obs. fragment, intensity), 490 ($[\text{M} + 2]^+$, 41.6%), 489 ($[\text{M} + 1]^+$, 100%), 417 ($[\text{M} - \text{TMSOH} + 18 + 1]^+$, 9.1%), 399 ($[\text{M} - \text{TMSOH} + 1]^+$, 2.6%); EI-MS (I): m/z (obs. fragment, intensity), 315 ($[\text{M} - \text{C}_6\text{H}_{12}\text{OTMS}]^+$, 2.6%), 259 ($[\text{M} - \text{TMSOC}_8\text{H}_{15}\text{COOCH}_3]^+$, 91.9%), 229 ($[\text{M} - 259]^+$, 4.8%), 173 ($[\text{M} - 315]^+$, 100%); EI-MS (II): m/z (obs. fragment, intensity), 315 ($[\text{M} - \text{C}_6\text{H}_{12}\text{OTMS}]^+$, 1.1%), 259 ($[\text{M} - \text{TMSOC}_8\text{H}_{15}\text{COOCH}_3]^+$, 100%), 229 ($[\text{M} - 259]^+$, 10.7%), 173 ($[\text{M} - 315]^+$, 77.3%); NMR: (see Tables 1 and 2).

RESULTS AND DISCUSSION

Methyl 9,10-epoxyoctadecanoate **1** was prepared from oleic acid. Monoepoxide **1** was exposed to alumina, and analysis by RP-HPLC showed that a single product was formed that had an RT of 18.2 min. The MS data and the ^1H and ^{13}C NMR spectra given in the Materials and Methods section show that a 1,2-diol was formed with hydroxy groups on C-9 and C-10. Furthermore, comparison of the carbon and proton shifts with

TABLE 1
¹H NMR and ¹³C NMR of Methyl 9(12)-oxy-10,13-dihydroxystearate and Methyl 10(13)-Oxy-9,12-dihydroxystearate^a (peak I, RT on RP-HPLC: 5.9 min)

Chemical shift (400 MHz, C ₆ D ₆ , δ _H)	Number of protons	Appearance	Assignment	Coupling constant (Hz)
1.14 and 1.15	3H	<i>t</i>	CH ₃ CH ₂ -	<i>J</i> = 7.0, <i>J</i> = 7.0
1.40–1.96	22H	<i>m</i>	-CH ₂ -	
2.34 and 2.36	2H	<i>t</i>	-CH ₂ COOCH ₃	<i>J</i> = 7.6, <i>J</i> = 7.4
3.51	1H	<i>m</i>	-CH-OH	
3.60	3H	<i>s</i>	-COOCH ₃	
3.75	1H	<i>dt</i>	-CH-OH	<i>J</i> = 7.0, <i>J</i> = 2.9
4.06	1H	<i>d</i>	-HC(O)-CH-OH (H-13 or H-9)	<i>J</i> = 3.6
4.24	1H	<i>td</i>	-HC(O)-CH-OH (H-10 or H-12)	<i>J</i> = 6.4, <i>J</i> = 9.2

¹³C NMR (100 MHz, C₆D₆, δ_C): 14.9 (CH₃CH₂-), 23.7, 23.7, 25.9, 25.9, 26.5, 26.7, 27.1, 27.2, 30.0, 30.1, 30.2, 30.6, 33.0, 33.1, 34.5, 34.7, 38.8, 51.6 (-COOCH₃), [74.1, 74.8 (-CH-OH)], [81.2, 83.6 (-HC(O)-CH-OH)], 174.1 (-COOCH₃). ¹³C NMR (100 MHz, CDCl₃, δ_C): 14.1 (CH₃CH₂-), 22.7, 25.0, 25.4, 25.6, 26.1, 26.3, 29.0, 29.1, 29.2, 29.2, 29.6, 32.0, 32.1, 33.4, 34.2, 38.1, 51.4 (-COOCH₃), [73.5, 74.1 (-CH-OH)], [80.2, 82.5 (-HC(O)-CH-OH)], 174.1 (-COOCH₃).

^aAbbreviation: RT, retention time.

those obtained from commercial preparations of methyl (±)-*threo*- and *erythro*-9,10-dihydroxyoctadecanoate shows that the *threo* isomer **2** was formed exclusively. Thus, *anti* addition occurred during oxirane ring opening. The time course of hydrolysis showed that nearly complete hydrolysis of the starting epoxide was obtained in less than 4 h.

Methyl 9,10-12,13-diepoxyoctadecanoate **3** was prepared from methyl linoleate (Scheme 1). Diepoxide **3** was treated with alumina, and the progress of the reaction was followed by RP-HPLC. The peak corresponding to the diepoxide **3** (RT 18.4 min) disappeared, and two product peaks arose at RT 5.9 min (Peak I) and 9.4 min (Peak II). APCI-MS spectra of both products were nearly identical, as were the spectra of their silylated derivatives (see the Materials and Methods section). The base peaks in the APCI-MS spectra for Peak I and Peak II are at *m/z* 345 (M + H⁺), and the base peaks in the APCI-

MS spectra of silylated Peak I and Peak II are at *m/z* 489 (M + H⁺). The indicated M.W. are consistent with the formation of a mixture of dihydroxytetrahydrofuran derivatives, methyl 9(12)-oxy-10,13-dihydroxystearate **4**, and methyl 10(13)-oxy-9,12-dihydroxystearate **5**, derived from intramolecular cyclization (Scheme 1). EI-MS of the free and silylated derivatives of both products shows that two regioisomers are present in both HPLC fractions. In particular, in the silylated derivatives, the intense peak at *m/z* 259 (86.8%) clearly shows the presence of a hydroxyl group at C-9, whereas the intense peak at *m/z* 173 (100%) shows the presence of a hydroxyl group at C-13. The two product fractions were separated by preparative TLC using a published method (9). Data from the ¹H and ¹³C NMR spectra of the two fractions are shown in Tables 1 and 2. They indicate that both product fractions contained complex mixtures of regio- and stereoisomers. Our

TABLE 2
¹H NMR and ¹³C NMR of Methyl 9(12)-oxy-10,13-dihydroxystearate and Methyl 10(13)-oxy-9,12-dihydroxystearate (peak II, RT on RP-HPLC: 9.5 min)^a

Chemical shift (400 MHz, C ₆ D ₆ , δ _H)	Number of protons	Appearance	Assignment	Coupling constant (Hz)
1.14	3H	<i>m</i>	CH ₃ CH ₂ -	
1.40–2.2	22H	<i>m</i>	-CH ₂ -	
2.34 and 2.36	2H	<i>t</i>	-CH ₂ COOCH ₃	<i>J</i> = 7.4, <i>J</i> = 7.2
3.41	1H	<i>m</i>	-CH-OH	
3.61	3H	<i>s</i>	-COOCH ₃	
3.67	1H	<i>dt</i>	-CH-OH	<i>J</i> = 2.8, <i>J</i> = 6.8
3.93	1H	<i>d</i>	-HC(O)-CH-OH (H-13 or H-9)	<i>J</i> = 9.6
4.09	1H	<i>m</i>	-HC(O)-CH-OH (H-10 or H-12)	

¹³C NMR (100 MHz, C₆D₆, δ_C): 14.9 (CH₃CH₂-), 23.7, 25.9, 26.7, 26.9, 27.2, 27.3, 30.0, 30.1, 30.2, 30.3, 30.7, 32.8, 33.2, 34.8, 35.3, 39.5, 51.6 (-COOCH₃), [72.5, 74.4 (-CH-OH)], [79.9, 80.0, 85.2 (-HC(O)-CH-OH)], 174.1 (-COOCH₃). ¹³C NMR (100 MHz, CDCl₃, δ_C): 14.0 (CH₃CH₂-), 22.6, 24.8, 24.9, 25.7, 25.9, 25.9, 26.1, 28.8, 29.0, 29.1, 29.3, 29.6, 31.7, 32.0, 34.1, 34.4, 38.8, 51.4 (-COOCH₃), [71.6, 73.9, 74.0 (-CH-OH)], [79.1, 84.3, 84.3 (-HC(O)-CH-OH)], 174.3 (-COOCH₃).

^aSee Table 1 for abbreviation.

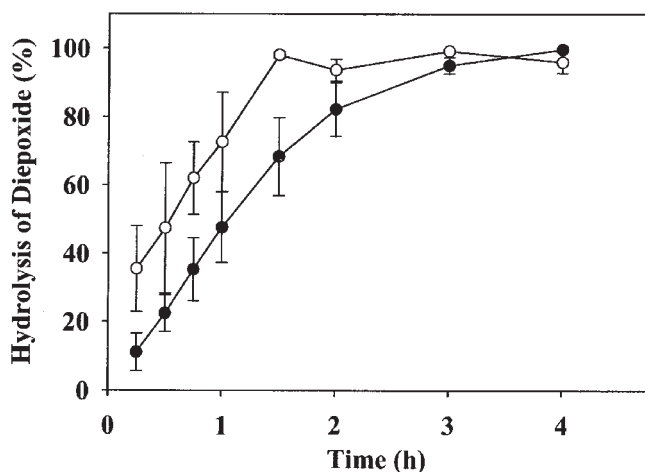


FIG. 1. Time course for the hydrolysis of methyl 9,10-12,13-diepoxyoctadecanoate **3** (5 mg) with 230 mg alumina in 0.6 mL cyclohexane (○) and 1% perchloric acid in 0.6 mL THF/H₂O (3:2, vol/vol) (●).

results are similar to those obtained by Hammock's group (10,11) when they investigated products obtained from fatty diepoxide hydrolysis using low levels of epoxide hydrolase; they reported that the fraction with a short RT in RP-HPLC contained side chains that were in the *trans* configuration across the THF ring, whereas the fraction with a longer RT contained side chains in the *cis* configuration. Weber *et al.* (12) also have reported on the synthesis of methyl dihydroxy-tetrahydrofuran octadecanoates from the treatment of epoxides of plant oils and epoxides of methylated fatty esters using sulfuric acid-activated bleaching earth.

Figure 1 shows the time course of hydrolysis of methyl 9,10-12,13-diepoxyoctadecanoate **3** with alumina and with a low concentration (1%) of perchloric acid (HClO₄). The concentration of perchloric acid was kept low to eliminate ester hydrolysis during the study period. One can observe in Figure 1 that alumina hydrolysis was complete in 1.5 h, whereas perchloric acid hydrolysis took somewhat longer. The products of perchloric acid hydrolysis were identical to the products obtained from alumina hydrolysis.

Our results show that unmodified alumina catalyzes the hydrolysis of epoxides, and therefore its use as a support for epoxidation catalysts should be avoided. At this time, the structure of the surface of alumina has not been completely described (13). However, it is known that the surface contains free hydroxyl groups, which may act as nucleophiles for the promotion of hydrolysis. Posner (5) speculated that rate acceleration by alumina for nucleophile addition is provided by an entropy of activation when a reactant and a reagent are adsorbed close to each other. Also, the alumina may activate the epoxide by forming a complex with aluminum atoms. In those studies of transition metal epoxidation catalysts that have used alumina as a catalyst support, an appreciable amount of the product was found as diols, which are the hydrolyzed epoxide products. The hydrolysis has been ascribed to the acidity of the catalyst, but the results presented here show that hydroly-

sis by the alumina support should be considered as a contributing factor. Hydrolyzed fatty epoxides are useful for a variety of applications such as polymers, high-temperature greases, and boundary lubricants for aluminum metal working (14). In those cases where hydrolyzed material is the desired product, the most efficient process would be to conduct epoxidation in the presence of alumina, and in this way obtain the hydrolyzed material directly without isolating the intermediate epoxide.

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