✻Epoxidation of Methyl 4-Hydroxy-*trans*-2-hexadecenoate

M.S. AHMAD, Jr., A. RAUF and **S.M. OSMAN,** Department of Chemistry,
Aligarh Muslim University, Aligarh-202001, India

ABSTRACT

Reaction of methyl 4-hydroxy-*trans*-2-hexadecenoate (**1b**) with *m*-chloroperbenzoic acid (1.0 mol) in chloroform yielded methyl 4-hydroxy-*trans*-2,3-epoxyhexadecanoate (**2**) in 32% yield. Reaction with 2 mol afforded both methyl 4-oxo-*trans*-2-hexadecenoate (**3**) (15.3%) and (**2**) (65.8%). The presence of an allylic hydroxyl group in the α,β-unsaturated ester enhances the yield of the epoxidation product (**2**) as well as the keto compound (**3**). The structures of individual reaction products were established by elemental analyses as well as by spectral studies.

INTRODUCTION

It is well known that epoxidation of α,β-olefinic fatty acid or ester with peracids gives only poor yields of epoxide (1). The natural occurrence of epoxy glycerides and their use as stabilizers and plasticizers have focused interest on long-chain epoxy acids (2). The stereochemistry involved in their formation and transformation have further attracted attention to the chemistry of epoxy acids. The reaction of olefinic esters with *m*-chloroperbenzoic acid in chloroform to give epoxy compounds is well known (2). This reaction is quantitative and makes the epoxides synthetically valuable. The *cis*-epoxide which results from epoxidation of β-hydroxyolefinic acid gives hydroxy epoxide whereas γ-hydroxyolefinic acid furnishes 9,12-epoxides (3).

In continuation of our synthetic studies on the reaction of long-chain α,β-unsaturated acids or esters (4-10), this work describes the first preparation of the epoxide of an allylic hydroxy fatty ester, methyl 4-hydroxy-*trans*-2-hexadecenoate. However, Ansari et al. (11) have recently reported the formation of only methyl-3-oxo-4-hydroxy ester from the corresponding methyl 4-hydroxy-*trans*-2-octadecenoate.

EXPERIMENTAL PROCEDURES

All melting points were observed on a Kofler apparatus and are uncorrected. Infrared (IR) spectra were obtained with a Perkin-Elmer 621 spectrophotometer in KBr. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian A60 spectrometer. Chemical shifts are reported as δ (ppm) relative to tetramethylsilane (TMS). The samples were run as 10% solution in chlorofrom-d. The abbreviations "s, m, d, t and br" denote singlet, multiplet, doublet, triplet and broad, respectively. Mass spectra were measured with an AE1 MS-9 mass spectrometer. Thin layer chromatographic (TLC) plates were coated with Silica Gel G, and a mixture of petroleum ether/ether/acetic acid (70:30:1, v/v) was used as developing solvent. The spots were visualized by charring after spraying with a 20% aq solution of perchloric acid. Light petroleum refers to a fraction bp 40-60 C.

MATERIALS AND METHODS

4-Hydroxy-*trans*-2-hexadecenoic acid (1a) (mp 70-71 C), was prepared from *trans*-2-hexadecenoic acid and its structure and geometry was established by combustion data and spectral analysis (7).

Epoxidation of 1b (2)

Reaction of *m*-chloroperbenzoic acid with methyl 4-hydroxy-*trans*-2-hexadecenoate (**1b**) was done by the following procedure of Gunstone and Jacobsberg (2), and by additional heating of the reaction mixture. To the solution of methyl ester (600 mg, 0.0021 mol) in chloroform (10 mL), *m*-chloroperbenzoic acid (365 mg, 1 mol) in chloroform (5 mL) was added with shaking. The mixture was kept at room temperature for 48 hr and examined by direct TLC. It was found that the formation of product is not sufficient; therefore, it was refluxed for 4 hr on a water bath. The mixture was cooled and the solvent was removed under reduced pressure, extracted with ether and shaken with a saturated solution of sodium sulfite (8 mL) to destroy excess of peroxide. The organic layer was then shaken with 5% aq sodium bicarbonate to remove *m*-chloroperbenzoic acid and dried over anhyd sodium sulfate. The reaction mixture (540 mg) was chromatographed over a column of silica gel (10.0 g) and the elution was done with petroleum ether containing increasing amounts of ethyl ether; each fraction of 10 mL was collected. Elution with petroleum ether (88:12, v/v) gave the starting material (**1b**) (360 mg, 66.6%) mp 56-57 C.

Further elution with a mixture of petroleum ether/ether (86:14, v/v), gave methyl 4-hydroxy-*trans*-2,3-epoxyhexadecanoate (**2**) (172 mg, 32%) as a colorless solid, mp 48-49 C. Analysis: calcd. for $C_{17}H_{32}O_4$: C, 67.96; H, 10.73. Found: C, 67.89; H, 10.72%.

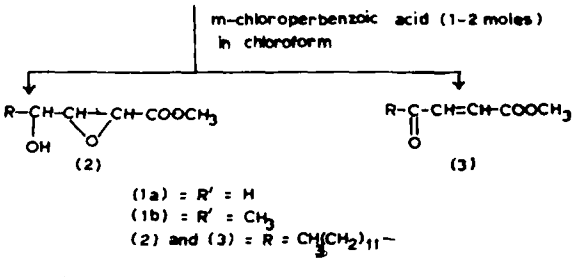
The same reaction, when done with 2 mol of *m*-chloroperbenzoic acid afforded **3** (84 mg, 15.3% with petroleum ether/ether 97:3, v/v) as a solid, mp 64-65 C (lit. mp 65-66 C) (7). Analysis: calcd. for $C_{17}H_{30}O_3$: C, 72.29; H, 10.71. Found: C, 72.23; H, 10.65%.

Subsequent elution with a mixture of petroleum ether/ether (90:10, v/v) gave **1b** (107 mg, 19.6%).

Further elution with petroleum ether/ether (89:11, v/v) gave the epoxide **2** (362 mg, 65.8%).

RESULTS AND DISCUSSION

This communication describes the result (Scheme I) of epoxidation of methyl 4-hydroxy-*trans*-2-hexadecenoate (**1b**). The structures of the individual reaction products were established by elemental analyses as well as by spectral studies.



SCHEME I

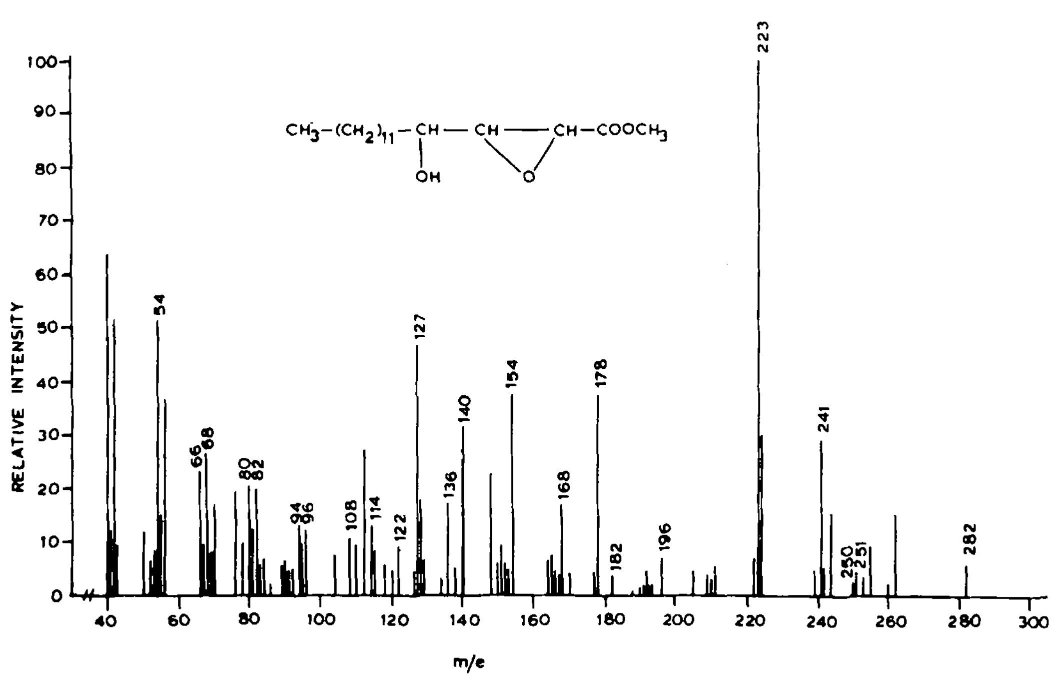
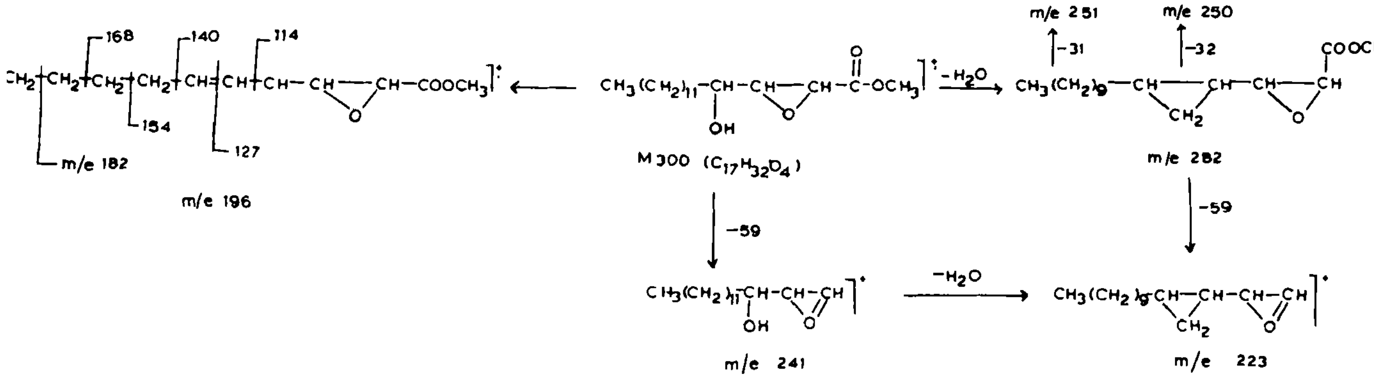


FIG. 1. Mass spectrum of compound 2.

Compound 2 obtained as a solid (mp 48-49 C) analyzed correctly for $C_{17}H_{32}O_4$. Picric acid TLC did not rule out the presence of epoxy group. Its IR spectrum gave bands at 3380-3290 (OH), 1730 (-$\underline{C}$OOCH$_3$), 1195, 1150, 1120, 1070, 1040, 1010 (C-O), 880 sharp, 830 and 820 cm^{-1} (epoxy ring). The NMR spectrum further confirmed the structure as methyl 4-hydroxy-*trans*-2,3-epoxyhexadecanoate (2) by the characteristic signals at 3.74 s (3H, COOC$\underline{H}_3$), 3.72 br,m (1H, C$\underline{H}$-OH, merging in part with signal of protons methyl ester; 3.4 br,s (1H, -CH-C$\underline{H}$-COOCH$_3$), 3.2 br,s
\ /
O
(1H, -C$\underline{H}$-CH-COOCH$_3$), 2.42 br (1H, O$\underline{H}$, disappeared on
\ /
O
addition of D_2O), 1.3 br,s (chain-C$\underline{H}_2$) and 0.86 t (3H, terminal -C$\underline{H}_3$). After D_2O shake the signal at δ 2.42 disappeared with a small change in the signal at δ 3.72. The mass spectrum of compound 2 (Fig. 1) gave no molecular ion peak at 300 ($C_{17}H_{32}O_4$), but showed the peaks at m/e 282 (M-H_2O), m/e 251 (282-31), 250 (M-32), 241 (M-59), 223 (241-18 or 282-59), 196 (282-86), 182 (196-14), 168 (182-14), 154 (168-14), 140 (154-14), 136 (168-32), 127 (140-13), 122 (136-14), 114 (127-13), 108 (140-32), 96 (122-26), 94 (108-14), 82 (114-32), 80 (108-28) and other low ion peaks. The mass spectral fragmentation of 2 is given in Scheme II.

Epoxidation of 1b with 2.0 mol of *m*-chloroperbenzoic acid yielded an additional product, methyl 4-oxo-*trans*-2-hexadecenoate (3), (15.3%) together with 2, (65.8%). Compound 3 was also obtained as a white solid product, mp 64-65 C (lit. mp 65-66 C) (7). The elemental analysis of 3 corresponded to the molecular formula $C_{17}H_{30}O_3$. This composition suggests that a conjugated dioxoalkenoate was formed. Its UV spectrum (λ max 220 nm) shows it to have S-*trans*, S-*trans* conformation. Its IR spectrum gave bands



$$\text{m/e } 168 \xrightarrow{-32} \text{m/e } 136 \xrightarrow{-14} \text{m/e } 122 \xrightarrow{-26} \text{m/e } 96$$
$$\text{m/e } 154 \xrightarrow{-32} \text{m/e } 122 \xrightarrow{-14} \text{m/e } 108 \xrightarrow{-26} \text{m/e } 82$$
$$\text{m/e } 140 \xrightarrow{-32} \text{m/e } 108 \xrightarrow{-CO} \text{m/e } 80 \xrightarrow{-14} \text{m/e } 66$$
$$\xrightarrow{-13} \text{m/e } 127 \xrightarrow{-31} \text{m/e } 96 \xrightarrow{-CO} \text{m/e } 68$$
$$\text{m/e } 114 \xrightarrow{-32} \text{m/e } 82 \xrightarrow{-28} \text{m/e } 54$$

SCHEME II

at 1730 ($-C=C-\underline{C}OOCH_3$), 1665 ($CO-C=C$), 1645 ($C=C$), 1270, 1210, 1190 ($C-O$), and 995 (*trans* olefin). Its NMR spectrum gave a doublet centered at δ 7.05 (1H, J=16 Hz, ascribable to a proton β to ester carbonyl) a doublet of the same magnitude at δ 6.54 (1H, J=16 Hz, *trans* olefinic proton) ascribable to a proton α to ester carbonyl, 3.88 s (3H, $-COOC\underline{H}_3$), 2.5 m (2H, $-C\underline{H}_2-CO-CH=CH-$), 1.3 br,s (chain-$C\underline{H}_2$), and 0.9 t (terminal $-C\underline{H}_3$). The mass spectrum of compound 3 absolutely resembled that of methyl 4-oxo-*trans*-2-hexadecenoate reported earlier (7). The mass spectrum of 3 gave the molecular ion at m/e 282 ($C_{17}H_{30}O_3$) followed by other salient ion peaks at m/e 251 (M-31), 250 (M-32), 223 ($M-COOCH_3$), 169 (δ-cleavage between C-8, C-9), 155 (γ-cleavage between C-7, C-8), 141 (β-cleavage between C-6, C-7), 137 (155-18), 128 (McLafferty, cleavage base peak), 113 (cleavage between C-4, C-5) and other low mass ion peaks.

ACKNOWLEDGMENTS

We thank W. Rahman for providing necessary facilities and M.S. Ahmad for helpful discussion. The Council of Scientific and Industrial Research (CSIR), New Delhi, furnished financial support.

REFERENCES

1. Swern, D., Organic Reactions, John Wiley and Sons, Inc., New York, NY, 7:378 (1953).
2. Gunstone, F.D., and F.R. Jacobsberg, Chem. Phys. Lipids 9:26 (1972).
3. Abbot, G.G., and F.D. Gunstone, Ibid. 7:290 (1971).
4. Ansari, A.A., and S.M. Osman, JAOCS 53:118 (1976).
5. Ansari, A.A., F. Ahmad and S.M. Osman, Ibid. 55:541 (1976).
6. Ansari, A.A., F. Ahmad and S.M. Osman, Fette Seifen Anstrichm. 79:328 (1977).
7. Ahmad, M.U., M.S. Ahmad and S.M. Osman, JAOCS 55:491 (1978).
8. Ahmad, M.U., M.S. Ahmad, Jr., and S.M. Osman, Ibid. 55:669 (1978).
9. Ahmad, M.S., Jr., M.U. Ahmad and S.M. Osman, Ibid. 56:867 (1979).
10. Ahmad, M.S., Jr., and S.M. Osman, Ibid. 57:363 (1980).
11. Ansari, A.A., B. Schmitz and H. Egge, Chem. Phys. Lipids 29:45 (1981).

[Received July 1, 1981]

✱Reaction of Lithium Naphthalene with Carboxylic Acids Containing the Dichlorocyclopropane Ring System

SHOJI WATANABE, TSUTOMU FUJITA, KYOICHI SUGA and **SATOSHI INOKI,**
Department of Applied Chemistry, Faculty of Engineering, Chiba University,
Yayoicho, Chiba, Japan 260

ABSTRACT

Carboxylic acids containing the dichlorocyclopropane ring system react with lithium naphthalene to give dechlorinated products. For example, from the reaction of 9,10-dichloromethylene octadecanoic acid and lithium naphthalene, a mixture of 9,10-nonadecadienoic acid as a main product and unidentified minor products were obtained.

INTRODUCTION

The selective dichlorocarbene reaction with phase-transfer catalyst is well known (1). The conversion of the easily accessible carboxylic acids containing the dichlorocyclopropane ring system into other useful products has been a subject of some interest. Their dechlorination is not well known, however, except for reactions of the following compounds. Reactions which serve this purpose include reduction with sodium in liquid ammonia (2), formation of allenes from 1,1-dibromocyclopropanes (3), reaction of magnesium turnings with 9,9-dibromobicyclo [6,1,0] nonane (4), reaction of butyllithium with 13,13-dichlorobicyclo [10,1,0] tridecane (5), the reaction of 1,1-dichlorocyclopropanes with base to obtain the allenic compounds (6) and a dichlorocyclopropane ring opening with base (7).

Recently, it was reported that lithium naphthalene in tetrahydrofuran solution is an excellent reagent for various synthetic organic reactions (8). In connection with our earlier works, an interesting reaction between lithium naphthalene and various carboxylic acids containing the dichlorocyclopropane ring is described in this short Communication.

EXPERIMENTAL PROCEDURES

Methyl esters of oleic acid, erucic acid, undecylenic acid and 3-methyl-3-butenoic acid were used in commercial samples.

Reaction of Methyl Oleate [1] with Chloroform

Forty g of 50% sodium hydroxide solution was added by drops with stirring at a room temperature to a mixture of methyl oleate [1] (23 g), chloroform (60 g) and cetyltrimethylammonium chloride (0.4 g). The mixture was stirred for 5 hr at 60 C. After the mixture was acidified with 50% sulfuric acid, it was extracted with diisopropyl ether. The ether extracts were washed with water, dried over anhyd. sodium sulfate and distilled to give crude methyl 9,10-dichloromethylene octadecanoate [2a]. This [2a] was hydrolyzed with methanol and sodium hydroxide in the usual way to give crude 9,10-dichloromethylene octadecanoic acid [2b] (18 g). The crude product was molecularly distilled with a pot still to give 8 g of 9,10-dichloromethylene octadecanoic acid [2b], bath temperature 150-155 C at 0.1 mm Hg, mp 85-87 C (recrystallized from *n*-hexane). Infrared (IR) (cm^{-1}): 3200-3500, 1710 ($-COOH$); nuclear magnetic resonance (NMR) 9.9 (1H, s, $-COOH$), 2.30 (2H, bt, $-C\underline{H}_2COOH$), 1.80 (2H, bm, $-\underset{\substack{\diagdown\ \diagup \\ C \\ \diagup\ \diagdown \\ Cl\ \ Cl}}{C\underline{H}-C\underline{H}}-$), 1.30 (26H, bs, $-CH_2-$), 0.92 (3H, t, CH_3-).