2-Ethoxyalkanoic Acid: A Co-product during Synthesis of Long Chain α, β-Unsaturated Acid

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ABSTRACT

A co-product occurring during synthesis of long chain α,β-unsaturated acid by dehydrohalogenation of α-halogenated acid by alcoholic alkali, previously unidentified, has been characterized as 2-ethoxyalkanoic acid. Its structure has been established by combustion data as well as by spectral methods.

INTRODUCTION

Myers (1) reported an improved procedure for the preparation of *trans*-2-octadecenoic acid by dehydrohalogenation of 2-iodostearic acid with alcoholic alkali. By this procedure, the unsaturated acid was obtained along with 2-hydroxystearic acid, as the result of concurrent substitution at the 2-position. These acids were separated by fractional crystallization from petroleum ether due to the lower solubility of the hydroxy acid. All attempts to find *cis*-2-octadecenoic acid in the crystallization liquors, either by fractional crystallization or by chromatographic separation were unsuccessful. The latter technique yielded only further amounts of *trans* acid and 2-hydroxystearic acid, together with a small amount of an unidentified material (mp 48-52 C). Palameta and Prostenik (2) modified this procedure and gave a novel method for the quantitative separation of 2-hydroxystearic acid from *trans*-2-enoic acid through copper chelate formation. These authors during their investigation did not detect the minor side product of the reaction.

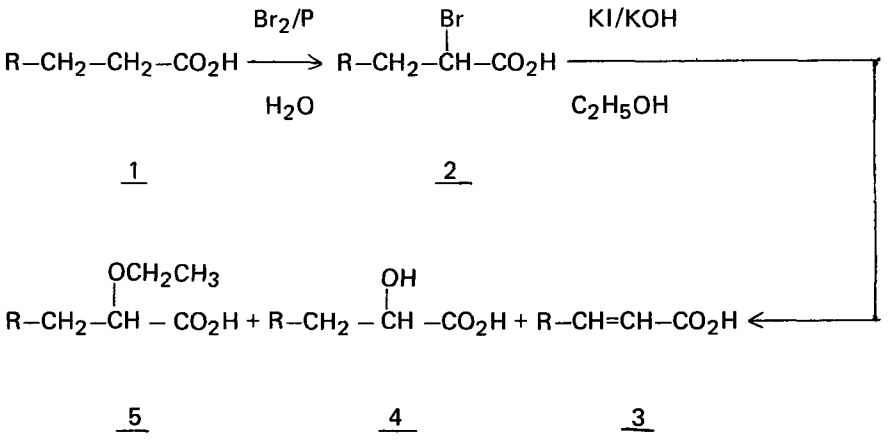
In a continuing study on the reactions of long chain α,β-unsaturated acids/esters reported from this laboratory (3–7), an attempt was made to isolate the minor product of the reaction. This present paper deals with the proof of structure of the previously unidentified minor product as 2-ethoxyalkanoic acid [5].

EXPERIMENTAL PROCEDURES

Melting points were observed on a Kofler apparatus and are uncorrected. Infrared (IR) spectra were obtained with a Perkin-Elmer 621 spectrophotometer (liquid film or 1% solutions in carbon tetrachloride). Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ using a Varian XL-100 (100 MHz). Chemical shifts were measured in ppm downfield from internal tetramethylsilane (δ = 0). The abbreviations "s,d,m,q,br, and t" denote "singlet, doublet, multiplet, quartet, broad, and triplet," respectively. Mass spectra (MS) were measured with an Varian MAT-311 (A) mass spectrometer at 70 eV. Analytical thin layer chromatography (TLC) was carried out on glass plates (20 x 5 cm) with a layer of Silica Gel G (0.25 mm wet thickness). Mixtures of diethyl ether and petroleum were normally used as developing solvents. The abbreviation PE 10, for example, indicates a mixture of diethyl ether (10%) and petroleum (90%) by volume. Light petroleum refers to a fraction of bp 40–60 C. Separated components on analytical plates were made visible by spraying with an aqueous solution (20%) of perchloric acid by heating at 120 C for 15 min.

MATERIALS AND METHODS

α,β-Unsaturated acids of C_{16}, C_{18} and C_{22} chain length [3a,b,c] were prepared from palmitic, stearic and behenic acids, respectively, according to the procedure of Palameta and Prostenik (2). The reaction product obtained after evaporation of the solvent revealed three distinct spots on TLC. The 2-hydroxyhexadecanoic, -octadecanoic, and -docosanoic acids [4a,b,c] were separated as their copper chelates by treatment with cupric acetate in 95% ethanol, slightly acidified with acetic acid. The remaining two components obtained after removal of 2-hydroxyalkanoic acids were fractionated by Silica Gel (BDH, 60-120 mesh)



1a to 5a ; R = $CH_3(CH_2)_{12}$-

1b to 5b ; R = $CH_3(CH_2)_{14}$-

1c to 5c ; R = $CH_3(CH_2)_{18}$-

SCHEME I.

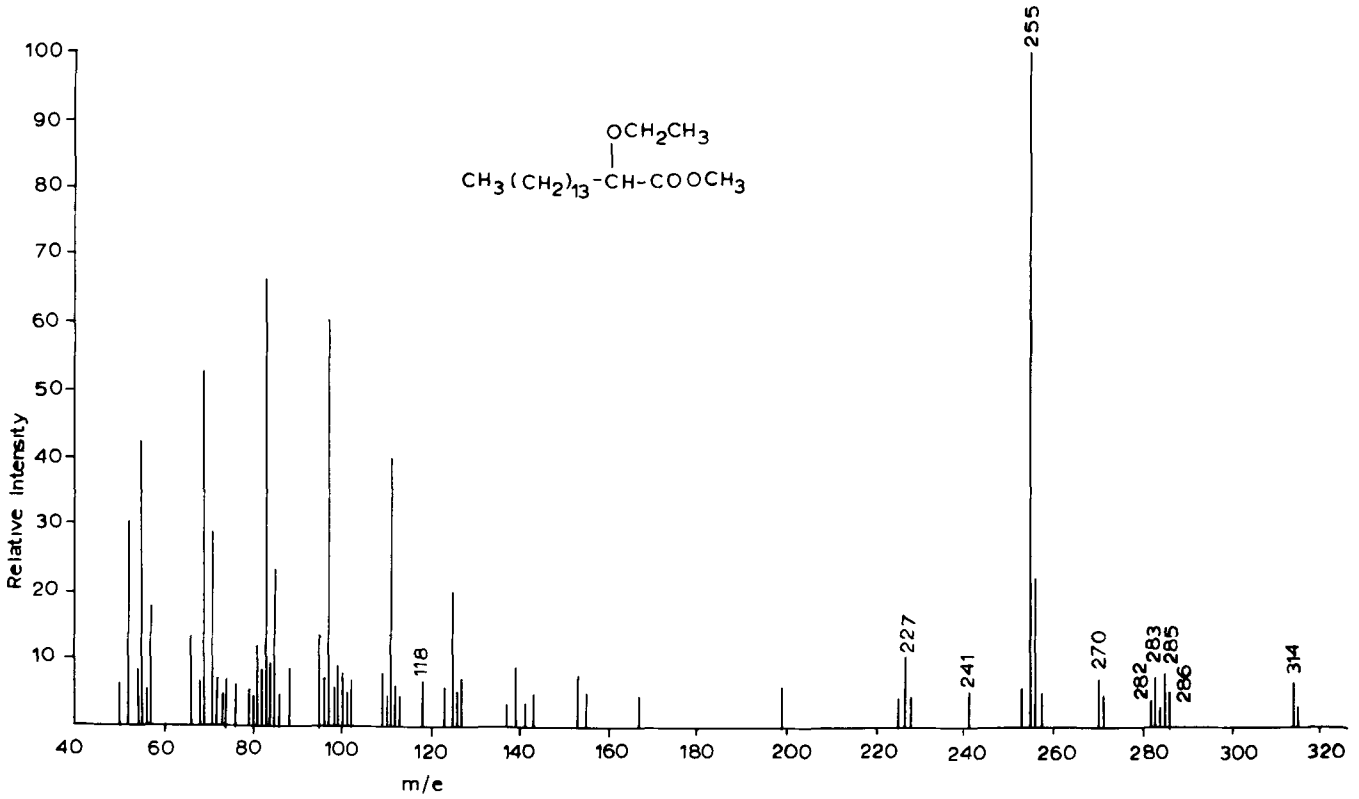


FIG. 1. Methyl 2-ethoxy hexadecanoate.

column chromatography to afford the individual components, i.e., *trans*-2-hexadecenoic, -octadecenoic, and -docosenoic acids [3a,b,c] and 2-ethoxyhexadecanoic, -octadecanoic, and -docosanoic acids [5a,b,c].

The 2-ethoxyalkanoic acids [5a,b,c] were isolated by elution with PE 10 after removal of *trans*-2-enoic acids [3a,b,c] with PE 5. The pure 2-ethoxyalkanoic acids obtained in yields ranging from 1.3 to 1.7% by recrystallization from light petroleum to constant melting point. They were white, odorless, crystalline solids soluble in the common organic solvents.

RESULTS AND DISCUSSION

Our general approach is typified in Scheme I. The *trans*-2-enoic acids of C_{16}, C_{18}, and C_{22} chain length were prepared according to the procedure of Palameta and Prostenik (2). The structures of *trans*-2-enoic and 2-hydroxy acids [3 and 4] were already established by their spectral studies (3). The present paper deals with the proof of structure of the previously unidentified material (1) which is obtained as a co-product [5] of the reaction.

The structure of 2-ethoxy compounds [5a,b,c] of the three parent acids was deduced from spectral studies of their methyl esters [5a',b',c'] and is consistent with proximate analyses. Carbon and hydrogen values determined for the three 2-alkoxy alkanoic acids and their methyl esters were all in agreement with calculated values. The methyl esters of the α-alkoxy C_{16} and C_{18} acids were liquid. Melting points of the other compounds were determined as follows: α-alkoxy acids (C_{16}:40C; C_{18}:45C; C_{22}:63C), α-alkanoic acid methyl ester (C_{22}:35-6C). Since the IR and NMR spectra are consistent with the same structure, it is convenient to discuss them all together. Interestingly, the IR spectra gave two bands of almost equal intensity in the carbonyl region, i.e., at 1750 and 1730 cm^{-1} which can be attributed to $-\underset{\displaystyle O-C_2H_5}{\underset{|}{CH}}-COOCH_3$; the appearance of two bands in the carbonyl region might be attributed to internal hydrogen bonding of ethoxy methylene hydrogen to carbonyl oxygen. (One of the referees suggested this which is gratefully acknowledged.) The other bands were observed at 1190, 1160, 1120, 1080, 1010 cm^{-1} (C–O). The NMR spectrum was found more helpful in arriving at its correct structure. It gave signals at

$$\delta\ 3.8t(1H,-CH_2-\underset{\displaystyle \underline{H}}{\underset{|}{\overset{\displaystyle OCH_2CH_3}{\overset{|}{C}}}}-COOCH_3,\ J = 6\ Hz),$$

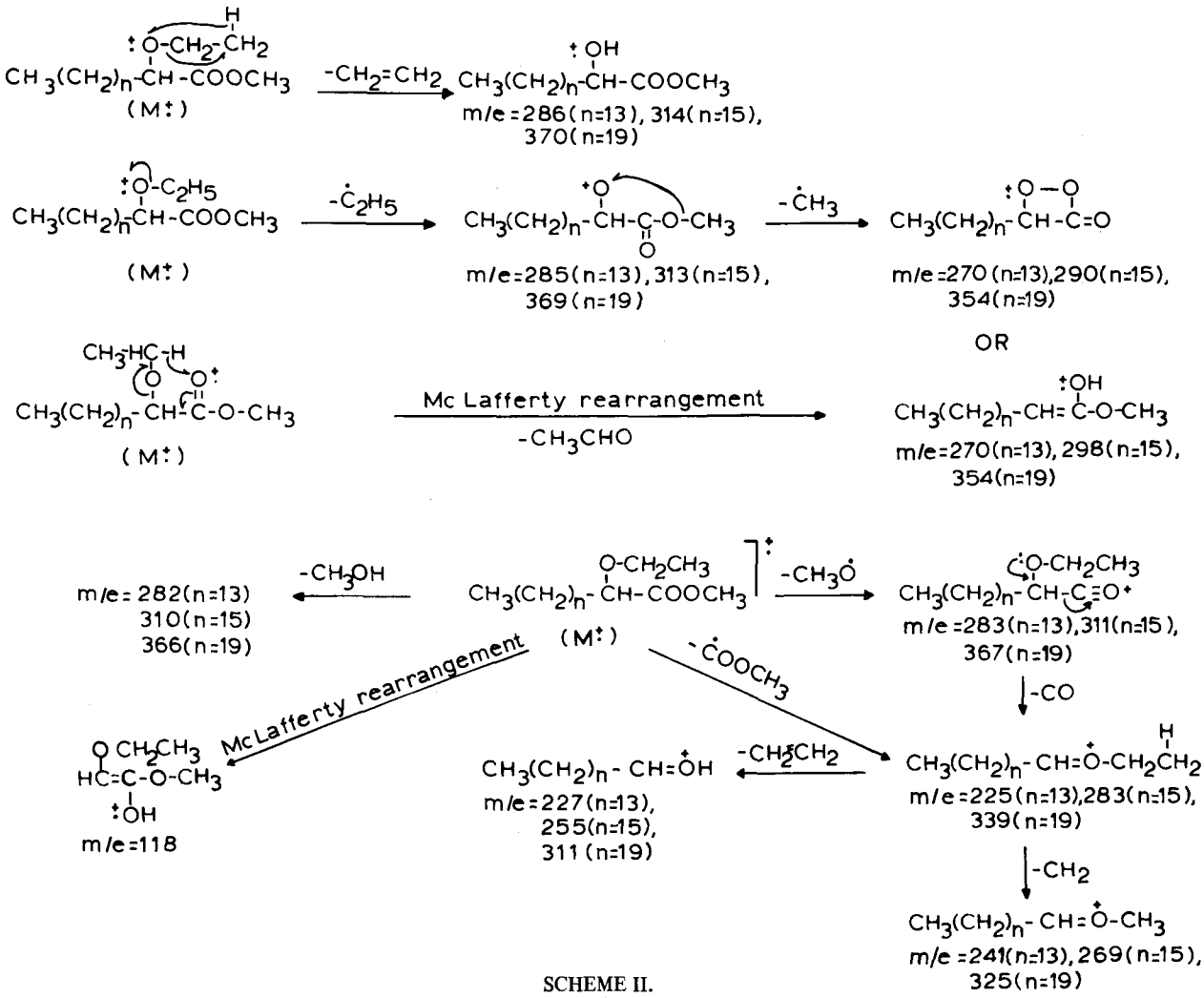
$$3.7s\ (3H,-COOC\underline{H}_3),$$

$$3.5q\ (2H,-OC\underline{H}_2-CH_3,\ J = 6\ Hz),$$

$$1.7m\ (2H,-C\underline{H}_2-\underset{\displaystyle OC_2H_5}{\underset{|}{CH}}-COOCH_3),$$

1.25br,s (chain $-CH_2$), 1.15t (3H, $-OCH_2-CH_3$, J=6 Hz, the downfield part of the triplet merging with chain $-CH_2$ signal), and 0.9t like (3H, terminal $-CH_3$). From these data, the esters [5a',b',c'] were formulated as methyl 2-ethoxyhexadecanoate, -octadecanoate, and -docosanoate, respectively. This formulation was further supported by mass spectrometry. As an illustrative example the mass spectrum of methyl 2-ethoxyhexadecanoate (Fig. 1) is recorded. Of greater interest for diagnostic purposes are the ions m/e 118 and 255 (M-59)[cf.8] which indicates the position of the substituent $-OC_2H_5$ at C_2 atom of the chain. The fragment ions m/e 283 ($M-OCH_3$) and 282 ($M-CH_3OH$) are prominent, which are of common occurrence. The genesis of important fragment ions are outlined in Scheme II.

From the foregoing discussion it is convincingly clear that the compound [5] is 2-ethoxyalkanoic acid. The



SCHEME II.

formation of [5] from [2] as one of the minor side products of the reaction is self-explanatory.

ACKNOWLEDGMENTS

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