*Simmons-Smith Reaction of Allylic Hydroxylated Long Chain α, β-Unsaturated Esters

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ABSTRACT

The reaction of methyl 4-hydroxy-*trans*-2-hexadecenoate [1*b*] with diiodomethane in the presence of zinc-copper couple yielded methyl 4-methoxy-*trans*-2,3-methylenehexadecanoate [2] in a 70% yield, together with methyl 4-hydroxy-*trans*-2,3-methylenehexadecanoate [3] (∿20%). The presence of an allylic hydroxyl group in the α,β-unsaturated ester increases the yield of the cyclopropanation product. The formation of *o*-methyl ether reveals the dual role of cyclopropanation and etherification by S.S. reagent of a hydroxylated olefinic compound.

INTRODUCTION

Cyclopropanation of the double bond in olefinic fatty acids has been reported recently (1-4). Because long chain fatty acids with an allylic hydroxyl group do not occur naturally, a study of the reactivity of the synthetically prepared acids would reveal their importance in fatty acid chemistry.

In continuation of our earlier work on the reaction of long chain α,β-unsaturated acids (5-10), this study on cyclopropanation of allylic hydroxy fatty acid was undertaken to study the influence of an ester carbonyl adjacent to the double bond as well as the role of the hydroxyl group during cyclopropanation. This communication reports that S.S. reagent plays a dual role, both in cyclopropanation and etherification of a multifunctional compound, like allylic hydroxylated olefinic fatty acids.

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 CCl_4. 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% solutions in chloroform-d. The abbreviations "s,m and br" denote singlet, multiplet and broad, respectively. Thin layer chromatographic (TLC) plates were coated with Silica Gel G, and a mixture of petroleum ether/ether/acetic acid (80:20:1, v/v/v) was used as developing solvent. The spots were visualized by charring after spraying with a 20% aqueous solution of perchloric acid. Light petroleum refers to a fraction of bp 40-60 C.

MATERIALS AND METHODS

4-Hydroxy-*trans*-2-hexadecenoic acid (1*a*) (mp 70-71 C), was prepared from *trans*-2-hexadecenoic acid and the structure of this acid and its geometry was established by IR, NMR and mass spectrometry (MS) (8).

Cyclopropanation of [1*b*]

The Christie and Holman procedure (11) was followed for the S.S. reaction of the acid [1*b*]. To zinc-copper couple in anhydrous ether (25 ml) was added a solution of diiodomethane (10 ml) and methyl 4-hydroxy-*trans*-2-hexadecenoate [1*b*] (0.5 g) in anhydrous ether (12 ml). The solution was refluxed for 4 hr.

The crude product (0.48 g) after the usual workup was chromatographed over a column of silica gel (8.0 g) and the elution was carried out with petroleum ether containing increasing amounts of ethyl ether; each fraction of 10 ml was collected. Elution with petroleum ether/ether (99:1, v/v) gave methyl 4-methoxy-*trans*-2,3-methylenehexadecanoate [2] (0.33 g, ca. 70%) as an oil. Analysis: Calcd. for $C_{19}H_{36}O_3$: C, 73.03; H, 11.61. Found: C, 73.84; H, 11.60% (spectral values are recorded in Results and Discussion).

Subsequent elution with a mixture of petroleum ether/ether (95:5, v/v), gave methyl 4-hydroxy-*trans*-2,3-methylenehexadecanoate [3] (0.09 g, ca. 20%) as an oil. Analysis: Calcd. for $C_{18}H_{34}O_3$: C, 72.44; H, 11.49. Found: C, 72.41; H, 11.46%.

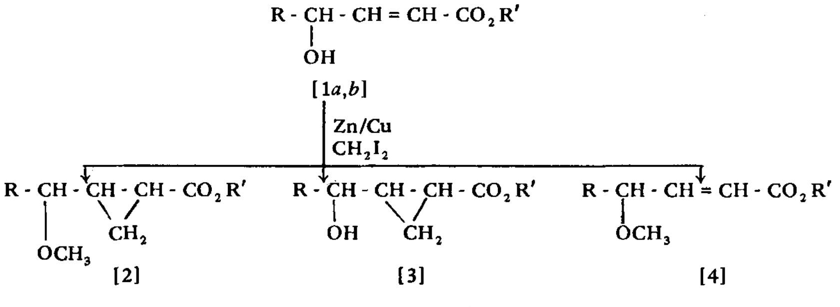
Further elution with petroleum ether/ether (90:10, v/v) gave the starting material [1*b*] (0.05 g, ca. 10%) mp and mmp 70-71 C.

RESULTS AND DISCUSSION

This work describes the result (Scheme I) of cyclopropanation of methyl 4-hydroxy-*trans*-2-hexadecenoate [1*b*]. The structures of the reaction products were determined by combustion and spectroscopic data.

The compound [2] obtained as a homogeneous oil (TLC) analyzed correctly for $C_{19}H_{36}O_3$. This composition suggested that besides cyclopropanation, the hydroxyl group was also methylated. This assumption was further supported by IR and NMR spectra. The IR spectrum gave

SCHEME I



(1a): $R = CH_3(CH_2)_{11}$-; $R' = H$
(1b) (2) (3) and (4): $R = CH_3(CH)_2)_{11}$-; $R' = CH_3$

bands at 3040 w (ring C-H, Str, $\text{-}\underset{\underset{CH_2}{\diagdown\diagup}}{CH - CH}\text{-}$), 1720 ($\underline{C}OOCH_3$), 1190, 1160, 1090, 1025 cm^{-1} (C-O). The band at 1025 and 3040 cm^{-1} in the IR spectrum established the presence of cyclopropane moiety and a prominent band at 1160 cm^{-1} indicated the C-O stretching of an ether function. The assigned structure of methyl 4-methoxy-*trans*-2,3-methylenehexadecanoate [2] was further confirmed by the NMR spectrum. It gave signals at δ 3.66 s (3H, -COOC$\underline{H}_3$), 3.6 s (3H, -O-C$\underline{H}_3$), 3.35 (1H, -C$\underline{H}$-OCH$_3$), 1.69 m (1H, $\text{-}\underset{\underset{CH_2}{\diagdown\diagup}}{CH - C\underline{H}}\text{-COOCH}_3$), 1.3 br,s (chain-C$\underline{H}_2$) and 0.85 m (6 protons, $\text{-}\underset{\underset{C\underline{H}_2}{\diagdown\diagup}}{C\underline{H} - CH}\text{-COOCH}_3$; and terminal -C$\underline{H}_3$).

Compound [3] was also obtained as an oil analyzed for $C_{18}H_{34}O_3$. This composition can give rise to 2 possible structures [3 and 4], which can be derived from [1*b*] under the reaction conditions. The IR and NMR spectra of the product support structure [3]. The IR spectrum gave bands at 3430 (OH), 3030 w (ring C-H, Str, $\text{-}\underset{\underset{CH_2}{\diagdown\diagup}}{CH - CH}\text{-}$), 1725 ($\underline{C}OOCH_3$), 1175, 1025 (C-O). The NMR spectrum gave signals at δ 4.55 br (1H, O$\underline{H}$, disappeared on D_2O addition), 3.65 s (3H, -COOC$\underline{H}_3$), 3.5 m (1H, C$\underline{H}$-OH), 1.71 m (1H, $\text{-}\underset{\underset{CH_2}{\diagdown\diagup}}{CH - C\underline{H}}\text{-COOCH}_3$), 1.3 br,s (chain-C$\underline{H}_2$) and 0.9 m (6 protons, $\text{-}\underset{\underset{C\underline{H}_2}{\diagdown\diagup}}{CH - CH}\text{-COOCH}_3$; and terminal -C$\underline{H}_3$).

In both cases one of the cyclopropane protons appeared downfield (δ 1.69 and δ 1.71), which is understandable since one cyclopropane proton is α to the ester carbonyl group. After addition of D_2O the spectrum of [3] was slightly modified.

In conclusion, it may be added that it has been reported that the ester carbonyl suppresses cyclopropanation of the conjugated double bond (3) and the yields are ca. 20-25%. However, the presence of an allylic hydroxyl group increases the double bond reactivity of the α,β-unsaturated ester and this might be one of the reasons for the formation of cyclopropane derivative in high yield ($\sim$90%) in relatively less reaction time.

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.

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[Received December 4, 1979]

Detection of Goat Body Fat in Ghee by Differential Thermal Analysis[1]

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ABSTRACT

The differences in the melting diagrams and crystallization patterns of goat body fat and ghee, as determined by differential thermal analysis, provide a basis for the determination of adulteration in cow or buffalo ghee. The new endothermic peak on the melting diagram in samples having more than 10% goat body fat can be used for qualitative detection and the crystallization diagram can be used for quantitative estimation.

INTRODUCTION

Ghee (clarified butterfat) is a popular indigenous product in India prepared from cream or butter by a heat clarification process (1-3). Like butter, ghee is sometimes adulterated with animal or vegetable fat; a common adulterant is animal body fat (4, 5). In the past, several methods have been tried to detect such adulteration based on color test (6) or chromatography (7, 8). This paper offers a method for detecting goat body fat in ghee using differential thermal analysis (DTA).

MATERIALS AND METHODS

Milk samples were obtained from a cow or buffalo maintained as National Dairy Research Institutes herds. Ghee samples were prepared either from cow milk or buffalo

TABLE I

Mixtures of Ghee and Goat Body Fat Analyzed by Differential Thermal Analysis

Sample no.	Sample composition
1	Goat body fat (pure)
2	Buffalo ghee (pure)
3	Cow ghee (pure)
4	Buffalo ghee + 5% goat body fat
5	Buffalo ghee + 10% goat body fat
6	Buffalo ghee + 20% goat body fat
7	Cow ghee + 5% goat body fat
8	Cow ghee + 10% goat body fat
9	Cow ghee + 20% goat body fat

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[1] NDRI (India) Publication No. 79-314.