

✶Oxidative Cyclization of Unsaturated Fatty Acids with Lead Tetraacetate

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ABSTRACT

The reaction of 10-undecenoic acid with lead tetraacetate (LTA) in the presence of acetic acid and anhydrous potassium acetate gave a eutectic mixture of 10(11)-acetoxy-11(10)-methylundecanoic acid (25%), 10,11-diacetoxyundecanoic acid (15%) and 5-(ω -carboxy-octyl) γ -butyrolactone (45%). Similar reaction with *cis*-9-octadecenoic acid yielded a eutectic mixture of 9(10)-acetoxy-10(9)-methyl-octadecanoic acid (20%) and 4(5)-(ω -carboxyheptyl)-5(4)-octyl γ -butyrolactone (40%). In the reaction with *trans*-2-enoic acids (C_{16} and C_{18}), products obtained were: 1,2-diacetoxypenta- and heptadecane (27%), 3-acetoxyhexa- and octadecanoic acid (31%) and 2-(2-penta- and heptadecyl) succinic anhydride (23%), respectively. The structures of individual compounds were characterized by spectral methods.

INTRODUCTION

Publications (1–3) on the reaction of lead tetraacetate (LTA) with olefins are abundant, but use of LTA oxidative cyclization of olefins to produce γ -lactones is relatively unexplored (4). Only sporadic reports (5) have appeared dealing with long-chain terminal γ -lactones involving carboxylic function. The recent applications of fatty lactones as insect attractant and growth stimulant (6, 7) as well as in the lubricant industry (8) have attracted interest in the chemistry of γ -lactones. As part of our continuing study of the derivatization of aliphatic compounds related to fats, the synthesis of chain-substituted lactones, not hitherto reported,^a has been undertaken with the hope of preparing new fatty acid derivatives for possible industrial utilization. The present work describes the results of oxidative cyclization of olefinic acids by LTA, yielding long-chain oxygen-containing cyclic derivatives.

EXPERIMENTAL PROCEDURES

Melting points were observed on a Kofler apparatus and are uncorrected. Infrared (IR) spectra were obtained with a Perkin-Elmer 621 spectrophotometer (CCl_4/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 abbreviations s, d, m, br and t denote singlet, doublet, multiplet, broad and triplet, respectively. Mass spectra were measured with an AEIMS-9 mass spectrometer. Thin layer chromatographic (TLC) plates were coated with silica gel. Spots were detected by charring after spraying with a 20% aqueous solution of perchloric acid.

MATERIALS AND METHODS

The 10-undecenoic acid and *cis*-9-octadecenoic acid were made available commercially. *trans*-2-Enoic acids of C_{16} and C_{18} chain length were prepared according to the procedure of Palameta and Prostenik (9). The 2-enoic structure of the two parent acids and their geometry were established by IR and NMR, as discussed in an earlier communication (10).

Reaction of 10-Undecenoic Acid (I) with LTA

To the solution of 10-undecenoic acid (1 g; 5.4 mmol) in glacial acetic acid (20 mL) were added LTA (4.8 g; 10.8 mmol) and 10 g of anhydrous potassium acetate. The reac-

tion mixture was refluxed for 26 hr and filtered. Acetic acid was removed on reduced pressure and the reaction mixture was extracted with ether, washed with 5% aq sodium bicarbonate, water and dried. After evaporation of the solvent, a deep yellow liquid was obtained which showed four distinct spots on TLC plate along with the starting material. The reaction product was passed over a column of Silica Gel G and three products (II, 25%; III, 15% and IV, 45%) (see Table I) were eluted successively with a mixture of petroleum ether/ethyl acetate (86:14, 86:14 and 84:16, v/v), respectively.

10(11)-Acetoxy-11(10)-methylundecanoic acid (II). Analysis: Calc. for $C_{14}H_{26}O_4$: C, 65.11; H, 9.84. Found: C, 65.10; H, 9.83%. IR: 1740 ($OC(=O)CH_3$), 1710 ($COOH$), 1240 (acetate), 1060 and 1010 cm^{-1} (C–O).

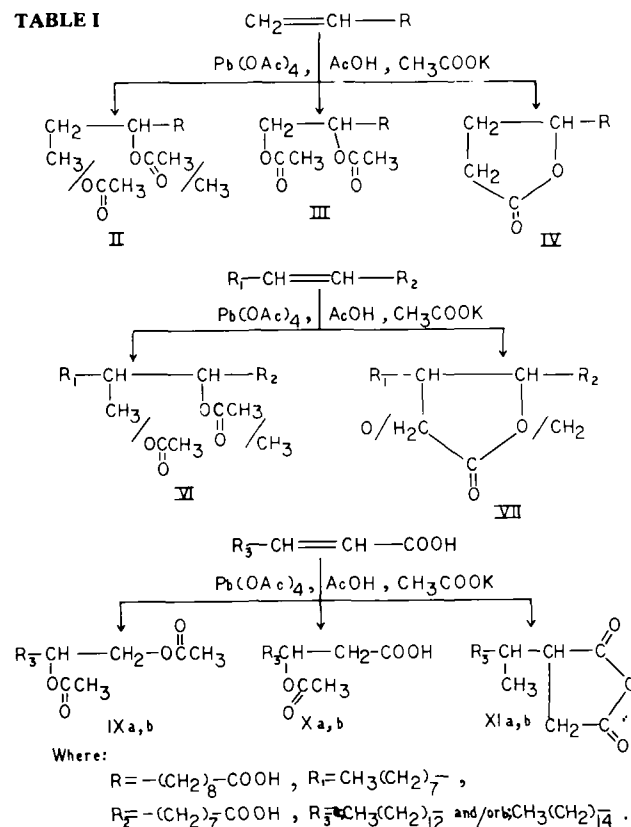
10,11-Diacetoxyundecanoic acid (III). Analysis: Calc. for $C_{15}H_{26}O_6$: C, 59.93; H, 8.69. Found: C, 59.92; H, 8.68%. IR: 1740 ($OC(=O)CH_3$), 1710 ($COOH$), 1240 (acetate), 1060 and 1010 cm^{-1} (C–O).

5-(ω -Carboxy-octyl) γ -butyrolactone (IV, mp 74 C). Analysis: Calc. for $C_{13}H_{22}O_4$: C, 64.46; H, 9.09. Found: C, 64.45; H, 9.07%. IR (KBr): 1740 (lactone carbonyl), 1690 ($COOH$), 1170, 1090 and 1070 cm^{-1} (C–O).

Reaction of *cis*-9-Octadecenoic Acid (V) with LTA

A mixture of *cis*-9-octadecenoic acid (1 g; 3.6 mmol), LTA (3.2 g; 7.2 mmol), glacial acetic acid (20 mL) and 6.6 g of

TABLE I



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anhydrous potassium acetate was refluxed for 29 hr and the usual work-up yielded an oily yellowish product. It showed four distinct spots on TLC along with the spot of unreacted acid. Purification by Silica Gel G column chromatography as usual gave two major products (**VI**, 20% and **VII**, 40%) in a mixture of petroleum ether/diethyl ether (96:4 and 95:5, v/v), respectively.

9(10)-Acetoxy-10(9)-methyl-octadecanoic acid (VI). Analysis: Calc. for $C_{21}H_{40}O_4$: C, 70.71; H, 11.23. Found: C, 70.69; H, 11.22%. IR: 1745 (OCOCH_3), 1710 (COOH), 1230, 1090 and 1000 cm^{-1} (C—O).

4(5)-(ω -Carboxyheptyl)-5(4)-octyl γ -Butyrolactone (VII). Analysis: Calc. for $C_{20}H_{36}O_4$: C, 70.00; H, 11.75. Found: C, 69.90; H, 11.74%. IR: 1760 (lactone carbonyl); 1710 (COOH), 1060 and 1010 cm^{-1} (C—O).

Reaction of *trans*-2-Enoic (C_{16} and C_{18}) Acids (**VIII a, b**) with LTA

As a general method, *trans*-2-enoic acid (3.93 mmol) taken in glacial acetic acid (20 mL) was refluxed with LTA (7.86 mmol) and 7.2 g anhydrous potassium acetate for 35 hr. Final work-up afforded a brownish viscous oil. TLC showed four spots along with the unreacted acid. Silica Gel G column chromatographic separation yielded three homogeneous products (**IX a, b** 27%; **X a, b** 31%; **XI a, b** 23%) using a mixture of petroleum ether/diethyl ether (99:1, 94:6 and 94:6, v/v).

1,2-Diacetoxypentadecane (IX a). Analysis: Calc. for $C_{19}H_{36}O_4$: C, 69.51; H, 10.97. Found: C, 69.50; H, 10.96%.

1,2-Diacetoxiheptadecane (IX b). Analysis: Calc. for $C_{21}H_{40}O_4$: C, 70.78; H, 11.20. Found: C, 70.77; H, 11.18%. IR (**IX a, b**): 1730 (OCOCH_3), 1230 (acetate), 1070 and 1010 cm^{-1} (C—O).

3-Acetoxyhexadecanoic acid (X a). Analysis: Calc. for $C_{18}H_{34}O_4$: C, 68.78; H, 10.82. Found: C, 68.77; H, 10.81%.

3-Acetoxyoctadecanoic acid (X b). Analysis: Calc. for $C_{20}H_{38}O_4$: C, 70.98; H, 11.11. Found: C, 70.97; H, 11.10%. IR (**X a, b**): 1730 (OCOCH_3), 1705 (COOH), 1240 (acetate), 1060 and 1000 cm^{-1} (C—O).

2-(2-Pentadecyl) succinic anhydride (XI a). Analysis: Calc. for $C_{19}H_{34}O_3$: C, 73.54; H, 10.06. Found: C, 73.53; H, 10.05%.

2-(2-Heptadecyl) succinic anhydride (XI b). Analysis: Calc. for $C_{21}H_{38}O_3$: C, 70.75; H, 11.20. Found: C, 70.74;

H, 11.19%. IR (**XI a, b**): 1760 and 1810 cm^{-1} (—C—O—C—), 1080 and 1020 cm^{-1} (C—O).

RESULTS AND DISCUSSION

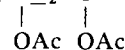
The present work describes the results (Table I) of the reaction of LTA on 10-undecenoic, *cis*-9-octadecenoic, *trans*-2-hexa- and octadecenoic acids and a proof of structure of the products by combustion and spectroscopic data.

The two major products in the treatment of 10-undecenoic acid (**I**) with LTA are α -methyl- β -acetate adduct (25%) and γ -lactone (45%). One minor product was identified as diacetate adduct (15%).

The structure of methylacetate adduct was established as 10(11)-acetoxy-11(10)-methylundecanoic acid. The

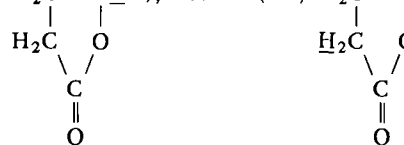
elemental analysis corresponded to the formula $C_{14}H_{26}O_4$. Its IR spectrum gave bands at 1730 cm^{-1} (OCOCH_3), 1700 cm^{-1} (COOH) and 1240 cm^{-1} (acetate). The C—O stretching vibrations appeared at 1060 and 1000 cm^{-1} . The NMR gave signals at δ 4.8 m (CHOCOCH_3), 4.2 d ($\text{CH}_2\text{—OCOCH}_3$), 2.0 s (3H, OCOCH_3), 1.4 m merged in part with chain methylene (1H, — CHCH_3), 1.3 br, s (chain CH_2) and 0.9 m for branched methyl group. The appearance of NMR signals at δ 4.8 (1H) and 4.2 (2H) clearly suggests the presence of two isomers, i.e., 10-acetoxy-11-methylundecanoic and 11-acetoxy-10-methylundecanoic acids in the product (**II**), which were found to be 67 and 33%, respectively on NMR basis.

The minor product (**III**) corresponded to formula $C_{15}H_{26}O_6$. This compound showed bands at 1740 cm^{-1} (OCOCH_3), 1710 cm^{-1} (COOH) and 1240 cm^{-1} (acetate). C—O stretching appeared at 1060 and 1010 cm^{-1} . NMR spectrum was very informative in establishing the structure of **III**. It gave signals at δ 4.9 m (1H, — CHCOCH_3), 4.2 d, d (2H, $J=6$ and 4 Hz , $\text{CH}_2\text{—CH—}$), 2.1 s (6H 2X OCOCH_3).



From these evidences, the structure of **III** was formulated as 10,11-diacetoxyundecanoic acid.

Identity of 5-(ω -carboxyoctyl) γ -butyrolactone (**IV**) was confirmed by its elemental analysis. It had IR (KBr) bands at 1740 cm^{-1} (lactone carbonyl) and 1690 cm^{-1} (COOH). Additional bands at 1170 , 1090 and 1070 cm^{-1} were attributable to the carbon oxygen stretching. The NMR signals at δ 4.5 (1H, $\text{H}_2\text{C—CH—}$), 2.4 m (4H, $\text{H}_2\text{C—CH—}$) and

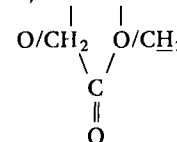


($\text{CH}_2\text{—COOH}$) further support its structure.

The above structure of **IV** was further confirmed by its mass spectrum as shown in Scheme 1 (Fig. 1).

When *cis*-9-octadecenoic acid (**V**) was treated similarly with LTA, the major products were methylacetate adduct (**VI**, 20%) and γ -lactone (**VII**, 40%) along with minor product which remained unidentified in 17% yield. Elemental analysis of **VI** corresponded to formula $C_{21}H_{40}O_4$. In its IR spectrum, bands at 1745 cm^{-1} (OCOCH_3), 1710 cm^{-1} (COOH), 1230 , 1090 and 1000 cm^{-1} were observed. In NMR spectrum, it displayed signals at δ 4.9 (— CH—OCOCH_3), 2.1 s (3H, OCOCH_3) and 1.4 m partly merged with chain methylene (1H, CHCH_3). From these data, the presence of methyl and acetate groups in the molecule is confirmed. However, the internal double bond position suggests the product (**VI**) as an isomeric mixture of 9(10)-acetoxy-10(9)-methyl-octadecanoic acid.

Another product 4(5)-(ω -carboxyheptyl)-5(4)-octyl γ -butyrolactone (**VII**) exactly corresponded to formula $C_{20}H_{36}O_4$ by its combustion data. Its IR spectrum gave peaks at 1760 cm^{-1} (lactone carbonyl), 1710 cm^{-1} (COOH), 1060 and 1010 cm^{-1} (C—O). The structure **VII** finds further support from its NMR spectrum. It gave a multiplet signal centered at δ 4.0 (1H), which is ascribed to one methine proton. Other signals were observed at δ 2.3m (4H, — CH—CH— and



CH_2COOH) and at 1.3 br, s (chain — CH_2).

The mass spectrum of this compound showed a molecular ion peak at m/z 340. The other important fragments are detailed in Scheme 2 (Fig. 2).

LTA OXIDATION OF OLEFINIC ACIDS

The C_{16} (VIII a) and C_{18} (VIII b) *trans*-2-enoic acids when similarly refluxed with LTA in acetic acid gave some very unusual products instead of the usual products obtained from terminal and internal olefinic acids. Since the IR and NMR spectra are consistent with the same structure, it is convenient to discuss them all together.

Compounds (IX a, b 27%) analyzed for $C_{19}H_{36}O_4$ and $C_{21}H_{40}O_4$, respectively. In their IR spectra bands at 1730 ($OC(=O)CH_3$), 1230 (acetate), 1070 and 1010 cm^{-1} (C—O) were observed. The NMR spectrum displayed signals at δ 4.8 m (1H, $-\text{CHOC(=O)CH}_3$), 4.0 d (2H, $\text{CH}_2\text{OC(=O)CH}_3$) and 2.0 s (6H, $2 \times \text{OC(=O)CH}_3$). From these data the compounds (IX a, b) were formulated as 1,2-diacetoxypenta- and heptadecane, respectively.

As an illustrative example, the mass spectrum of 1,2-diacetoxypentadecane is recorded. The mass spectral fragmentation is given in Scheme 3 (Fig. 3).

Compound (X a, b 31%) analyzed for $C_{18}H_{34}O_4$ and $C_{20}H_{38}O_4$, respectively. Their IR spectra gave bands at 1730 ($OC(=O)CH_3$), 1705 ($COOH$), 1240 (acetate), 1060 and 1000 cm^{-1} (C—O). NMR spectra gave bands at δ 4.8 m (1H, $-\text{CHOC(=O)CH}_3$), 2.4 d (CH_2COOH), 2.0 s (3H,

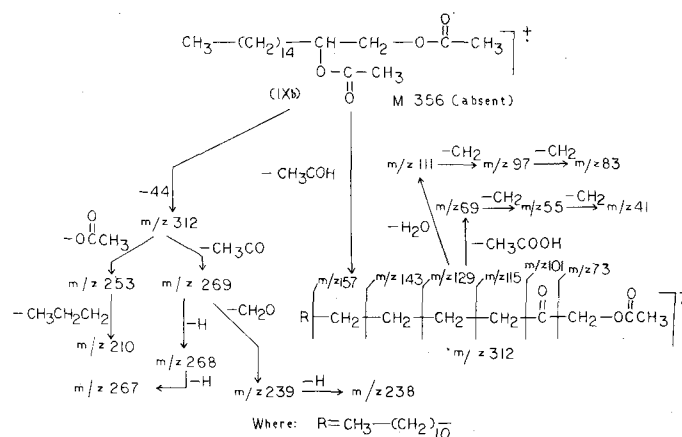
$OC(=O)CH_3$) and 1.3 br, s (chain CH_2). From the above spectral evidences compounds X a, b were identified as 3-acetoxypentadeca- and octadecanoic acids. This structure was further substantiated by the mass spectrum, geneses of which are given in Scheme 4 (Fig. 4).

The third compound (XI a, b 23%) corresponded to formula $C_{19}H_{34}O_3$ and $C_{21}H_{38}O_3$, respectively. Infrared spectrum was the main source to reach the structure of this compound. It showed peaks at 1760 and 1810 (anhydride linkage) of equal intensity. C—O stretchings appeared at 1080 and 1020 cm^{-1} . The NMR gave signals at δ 2.3 m (3H, $-\text{CH}-\text{C}(=\text{O})_2$), 2.0 m (1H, $\text{CH}-\text{CH}_3$), 1.3 br, s (chain

CH_2) and 0.9 m (6H, $2 \times \text{CH}_3$).

Further the mass spectrum corroborated this structure as given in Scheme 5 (Fig. 5).

The formation of (IX a, b; X a, b and XI a, b) can be rationalized in terms of mechanistic sequence given in Table II.



SCHEME 3

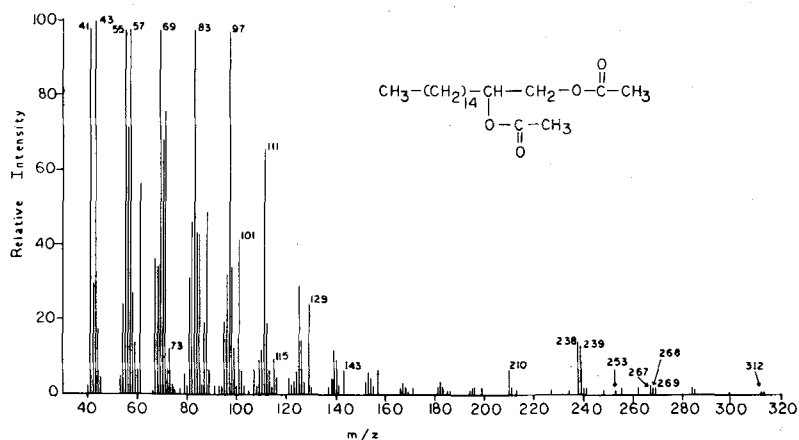


FIG. 3. Mass spectrum of 1,2-diacetoxypentadecane (IX b).

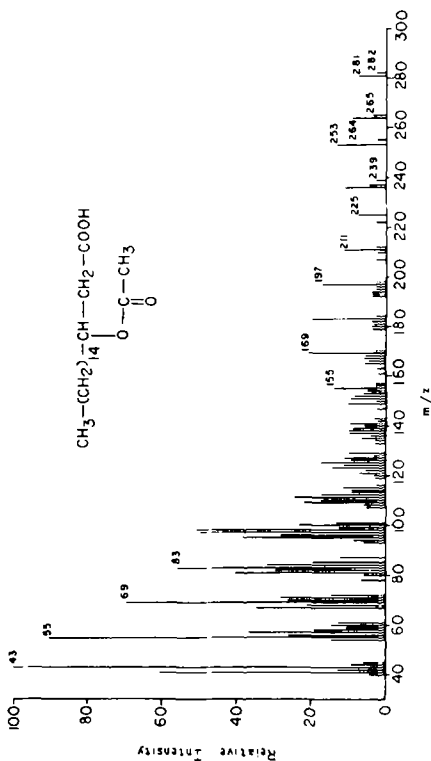
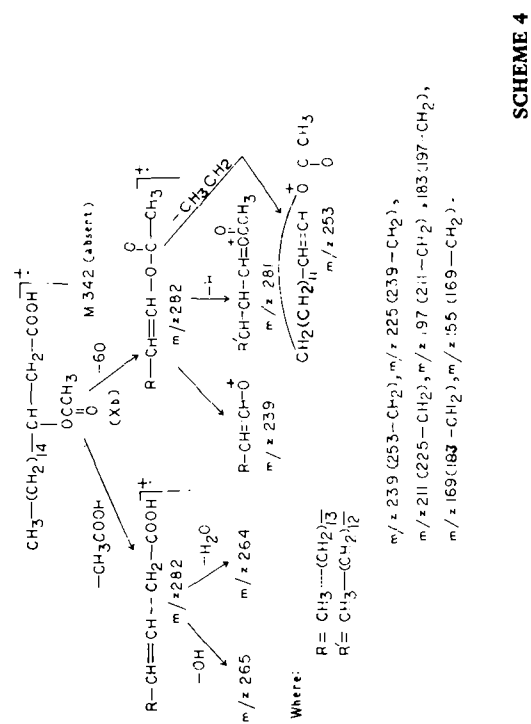
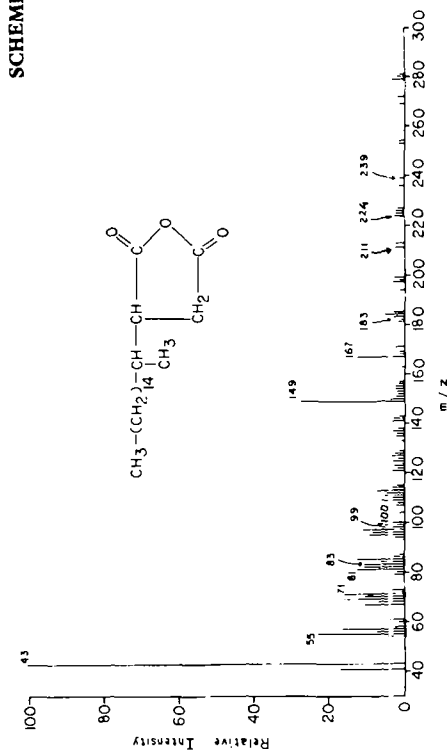
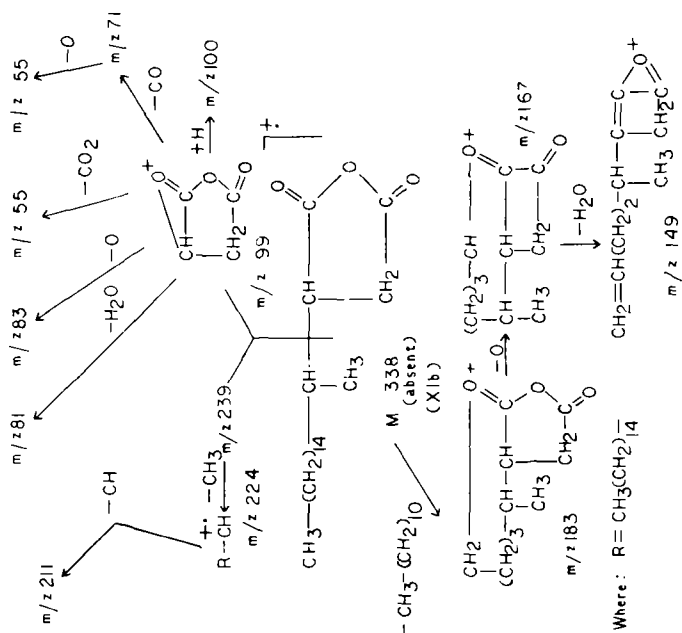
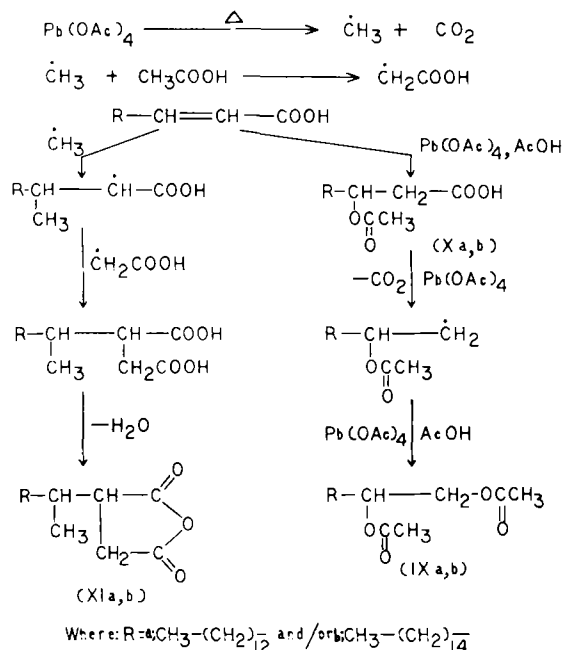


TABLE II



It is envisaged that β -acetate (X a, b) is formed quantitatively and preferentially in respect of α -acetate on steric grounds by the acetic acid addition. This β -acetate in presence of LTA undergoes decarboxylation (11) and the radical formed is converted into carbonium ion. Now the acetate ion interacts with the carbonium ion to form 1,2-

diacetoxy-penta- and heptadecane (IX a, b). The formation of XI a, b is supposed to be by addition of $\dot{\text{C}}\text{H}_3$ at the β -position and as the secondary radical is resonance stabilized by the adjacent carboxylic group the attack of carboxymethyl radical takes place which on subsequent dehydration results in XI a, b.

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Optimization of Industrial Vegetable Oil Hydrogenators

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ABSTRACT

A method to optimize the operation of industrial vegetable oil hydrogenators is proposed. The hydrogenation data from an operating plant are used to fit a simple mathematical model which is then used to select values for temperature and hydrogen pressure such that a desired product is obtained in minimum hydrogenation time. Methodology is suggested whereby any nonoptimal operation can be changed to optimal operation in a few trials.

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Nomenclature: E = activation energy, kcal/kg mol; IV = iodine value; k_L - reaction rate constant for linoleate hydrogenation, $\text{sec}^{-1} \text{atm}^{-0.5} (\text{kg cat}/100 \text{ kg oil})^{-1}$; k_O = reaction rate constant for oleate hydrogenation, $\text{sec}^{-1} \text{atm}^{-1} (\text{kg cat}/100 \text{ kg oil})^{-1}$; k^0 = preexponential factor; k_B = hydrogen mass transfer coefficient, $\text{kg mol sec}^{-1} \text{atm}^{-1} (\text{kg oil})^{-1}$; [L] = linoleate concentration, $\text{kg}/100 \text{ kg oil}$; m = catalyst concentration, $\text{kg}/100 \text{ kg oil}$; N = hydrogen mass transfer rate, $\text{sec}^{-1} (\text{kg mol}/\text{kg oil})$; [O] = oleate concentration, $\text{kg}/100 \text{ kg oil}$; p_{H_2} = hydrogen pressure in liquid phase, atm; $p_{\text{H}_2}^0$ = hydrogen pressure in gas phase, atm; R = reaction rate, $\text{sec}^{-1} (\text{kg}/100 \text{ kg oil})$; R_g = gas constant, $\text{kcal kg mol}^{-1} \text{K}^{-1}$; [S] = stearate concentration, $\text{kg}/100 \text{ kg oil}$; s = linoleate to oleate ratio; T = absolute temperature, K; x_i = optimization variables. Greek symbols: ϵ = tolerance; θ = hydrogenation time, min. Subscripts: d = desired value; L = linoleate, O = oleate; S = Stearate; t = trial value; o = initial value.

INTRODUCTION

Modeling and computer simulation of vegetable oil hydrogenation has attracted a lot of attention over the years. Presently, models with various degrees of sophistication are available. Design of a full-scale unit on the basis of laboratory data alone can seldom be considered optimal, due to the inherent empiricism in the hydrogenation models. In the present work, a methodology is suggested whereby the data from an operating unit can be used to optimize its performance in a few steps.

OPTIMIZATION METHODOLOGY

A simplified reaction scheme was earlier shown to fit the hydrogenation data from industrial hydrogenators (1,2). A simple procedure to estimate the parameters in the model was presented (2). The simplified nature of the model and the subsequent estimation of the model parameters from plant data necessitate that the search for optimum operating variables be restricted to the immediate neighborhood of the prevailing operational practice. The possibility of the actual optimum lying far outside such a restricted domain, however, cannot be ruled out. The search for this optimum can be carried out in steps by a procedure logically similar to the evolutionary operation (3) as follows.