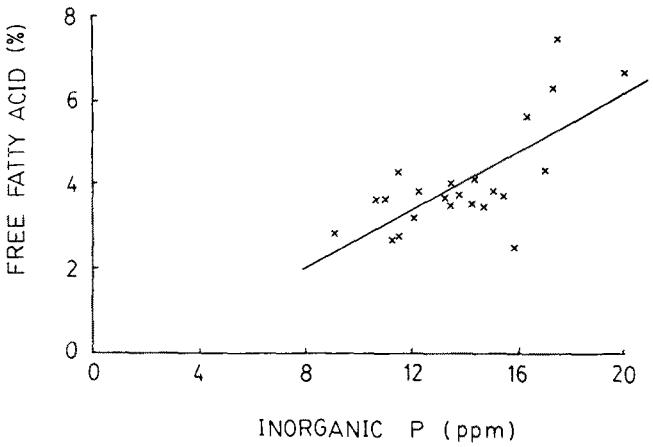

FIG. 1. FFA/inorganic phosphorus correlation.

in crude palm oil and probably also in refined palm oil which has been treated with phosphoric acid, routine quality control using this method would be preferable as ashing and/or acid digestion are not necessary.

ACKNOWLEDGMENT

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A Convenient Preparaton of γ-Lactones and Dialkyltetrahydrofurans From the Reaction of Fatty Acids with Epoxides Using Lithium Naphthalenide

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ABSTRACT

Fatty acids reacted with epoxides using lithium naphthalenide in the presence of diethylamine to give corresponding 4-hydroxy acids. These 4-hydroxy acids easily tended to cyclize into their corresponding γ-lactones by refluxing in benzene. Reduction of these γ-lactones with lithium aluminum hydride followed by intramolecular dehydration with potassium bisulfate afforded corresponding dialkyl tetrahydrofuran derivatives in high yields. For example, 4-methyl-2-(8-nonenyl) γ-butyrolactone (III) was obtained from 10-undecylenic acid and propylene oxide. 2-Methyl-4-(8-nonenyl) tetrahydrofuran (IV) was produced from (III). 2-Methyl-4-(8-nonenyl) and 2-ethyl-4-(8-nonenyl) tetrahydrofurans are woody smelling and may be used as perfumery materials.

INTRODUCTION

As perfumery and flavor materials, various alcohols, aldehydes, ketones, ethers, esters and lactones are available (1). Syntheses of compounds containing those functional groups are widely investigated, and extensive preparation methods for lactones are well known (2-9).

Preparation methods for γ-lactones from lower fatty acids and epoxides also are reported (10-13). However, reactions of higher fatty acids and epoxides are not well investigated. Recently, we reported that lithium naphthalenide is an excellent reagent for various synthetic organic reactions (14-16). In connection with these studies of lithium naphthalenide, we now report the reaction of higher fatty acids and epoxides using lithium naphthalenic in the presence of diethylamine. A variety of new γ-butyro lactones were obtained, and the conversion of these butyrolactones to tetrahydrofuran derivatives was performed by the reduction with lithium aluminum hydride followed by intramolecular dehydration with potassium bisulfate.

EXPERIMENTAL

Reaction of 10-Undecylenic Acid (I) with Propylene Oxide (II)

To 0.1 mol (12.8 g) of naphthalene in 150 ml of tetrahydrofuran, 0.2 mol (1.4 g) of metallic lithium cutting was added, and the mixture was agitated at room temperature in an atmosphere of dry nitrogen. After 1 hr, 0.2 mol (14.6 g) of diethylamine was added. After agitation for 1 hr, 0.1 mol (18.4 g) of 10-undecylenic acid, I, in tetrahydrofuran (100 ml) was slowly added. After 2 hr, 0.2 mol (11.6 g) of propylene oxide II was added to the reaction mixture, which was left overnight. The mixture was refluxed for an additional 8 hr. The acidic materials were separated as reported previously (11) to give a mixture of unreacted I and the 4-hydroxy acid. The acidic material mixture was dissolved in 300 ml of benzene, refluxed for 8 hr and cooled to room temperature. The benzene solution

was washed with saturated sodium carbonate solution (100 ml × 2) and water, and dried over anhydrous sodium sulfate. After the benzene was removed, the residue was distilled under vacuum to give 18.8 g of 4-methyl-2-(8-nonenyl) γ-butyrolactone III (yield 84%) boiling at 103-107 C/1 mmHg. IR(cm^{-1}): 1770, 1640, 990, 910; ^1H NMR (δ, ppm): 1.10 (3H, d, J=6.0Hz, $C\underline{H}_3CH$), 1.42-1.65 [14H, m, $(CH_2)_6$, $C\underline{H}_2CHCOO$], 2.10-2.35 (2H, m, $CH_2C{=}C$), 2.41-2.82 (1H, m, CHCOO), 4.41-4.86 (1H, m, CHO−), 4.96-5.38 (2H, m, $-CH{=}C\underline{H}_2$), 5.60-6.12 (1H, m, $-C\underline{H}{=}CH_2$); MS m/e M^+ 224.

The same technique was used to prepare a series of γ-lactones. The results are listed in Table I.

Reduction and Dehydration of 4-Methyl-2-(8-nonenyl) γ-butyrolactone (III)

To lithium aluminum hydride (25 mmol, 0.95 g) in 150 ml of dry ethyl ether, III (25 mmol, 5.60 g) in 50 ml of dry ethyl ether was added dropwise with stirring at 0 C. It was agitated for an additional 4 hr at the same temperature. The reaction mixture was decomposed with 50 ml of ice water and acidified with 100 ml of 10% (v/v) sulfuric acid. The ether was washed with water and dried with anhydrous sodium sulfate. The solvent was removed and the residue was transferred into 50 ml of Claisen flask which contained 10 mmol (1.36 g) of potassium bisulfate. The flask was kept at 180 C under a pressure of 20 mmHg for 2 hr. Then the mixture was distilled under vacuum to give 4.73 g of 2-methyl-4-(8-nonenyl) tetrahydrofuran IV (yield 90%) boiling at 90-92 C/3 mmHg. IR (cm^{-1}): 1640, 1110, 990, 910; ^1H NMR (δ, ppm): 1.15 (3H, d, J=6.1Hz, $C\underline{H}_3CH$), 1.25-1.40 [14H, m, $(CH_2)_6$, $CH_3CHC\underline{H}_2$), 1.45-2.48 (3H, m, $C\underline{H}CH_2O-$, $C\underline{H}_2C{=}C$), 3.01-3.42 (1H, m, $CH_3C\underline{H}O-$), 3.60-4.14 (2H, m, CH_2O-), 4.70-5.15 (2H, m, $-CH{=}C\underline{H}_2$), 5.43-6.14 (1H, m, $-C\underline{H}{=}CH_2$); MS m/e M^+ 210.

The same technique was applied to other γ-lactones and prepared a series of tetrahydrofuran derivatives. The results are listed in Table I.

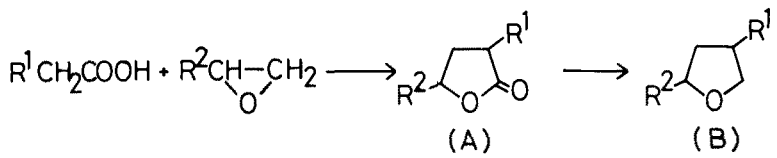
Oxidation of 4-Methyl-2-(8-nonenyl) γ-butyrolactone (III)

A mixture of palladium (II) chloride (2.0 mmol, 0.35 g), cupric chloride (5.0 mmol, 0.67 g), dimethylformamide (20 ml) and water (4 ml) was stirred at room temperature in a current of oxygen. To this solution, III (20 mmol, 4.48 g) was added dropwise and the reaction mixture was stirred for 20 hr at room temperature under a stream of oxygen gas. The reaction mixture was treated in the usual way to give 3.90 g of 4-methyl-2-(8-oxononyl) γ-butyrolactone VI (yield 81%), boiling at 149-152 C/4 mmHg. IR (cm^{-1}): 1770, 1710; ^1H NMR (δ ppm): 0.92 (3H, d, J=6.2Hz, $C\underline{H}_3CH$), 1.02-1.89 [14H, m, $(CH_2)_6$, $C\underline{H}_2CHCOO$], 2.14 (3H, s, CH_3CO), 2.25-2.75 (3H, m, CHCOO, CH_2CO), 4.22-4.82 (1H, m, CHO−); MS m/e M^+ 240.

The same technique was used for the oxidation of IV and 3-methyl-4-(8-oxononyl) tetrahydrofuran, V was obtained in 80% yield, Bp 115-118 C/4 mmHg; IR (cm^{-1}): 1710, 1110; ^1H NMR (δ, ppm): 1.10 (3H, d, J=6.0Hz, $C\underline{H}_3CH$), 1.17-2.01 [15H, m $(CH_2)_6$, $CH_3CHC\underline{H}_2C\underline{H}$), 2.04 (3H, s, CH_3CO), 2.32 (2H, t, J=6.4Hz, $C\underline{H}_2COCH_3$), 2.96-3.45 (1H, m, $CH_3C\underline{H}CO$), 3.67-4.15 (2H, m, CH_2O-); MS m/e M^+ 226.

TABLE I

Preparation of γ-Lactones and Tetrahydrofurans



Fatty acids	Epoxide R¹	Epoxide R²	γ-Lactones (A) (yield %)	Tetrahydrofurans (B) (yield %)
Capric acid	$CH_3(CH_2)_7$	Me	bp 111-114 C/1 mmHg (86)	bp 116-120 C/18 mmHg (92)
Lauric acid	$CH_3(CH_2)_9$	Me	bp 138-141 C/1 mmHg (82)	bp 109-111 C/3 mmHg (96)
Myristic acid	$CH_3(CH_2)_{11}$	Me	bp 141-143 C/1 mmHg (81)	bp 135-136 C/1 mmHg (96)
Palmitic acid	$CH_3(CH_2)_{13}$	Me	bp 149-153 C/1 mmHg (81)	bp 136-139 C/2 mmHg (96)
Stearic acid	$CH_3(CH_2)_{15}$	Me	bp 156-158 C/1 mmHg (82)	bp 138-140 C/2 mmHg (95)
Oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_6$	Me	bp 158-160 C/1 mmHg (72)	bp 134-137 C/2 mmHg (90)
Linoleic acid	$CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_6$	Me	bp 160-164 C/0.5 mmHg (86)	bp 146-149 C/1 mmHg (94)
Linolenic acid	$CH_3(CH_2CH{=}CH)_3(CH_2)_6$	Me	bp 169-171 C/0.5 mmHg (89)	bp 136-139 C/0.5 mmHg (93)
10-Undecylenic acid	$CH_2{=}CH(CH_2)_7$	Me	bp 103-107 C/1 mmHg (84)	bp 90-92 C/3 mmHg (90)
10-Undecylenic acid	$CH_2{=}CH(CH_2)_7$	Et	bp 139-141 C/1 mmHg (77)	bp 97-99 C/3 mmHg (91)
10-Undecylenic acid	$CH_2{=}CH(CH_2)_7$	$AllylOCH_2-$	bp 152-154 C/1 mmHg (83)	bp 116-118 C/2 mmHg (81)
10-Undecylenic acid	$CH_2{=}CH(CH_2)_7$	$n\text{-}ButylOCH_2-$	bp 157-159 C/1 mmHg (89)	bp 129-132 C/2 mmHg (96)

[a]The yields are based on fatty acids used.
[b]The yields are based on γ-lactones used.

Reduction and Dehydration of 4-Methyl-2-(8-oxononyl) γ-butyrolactone (VI)

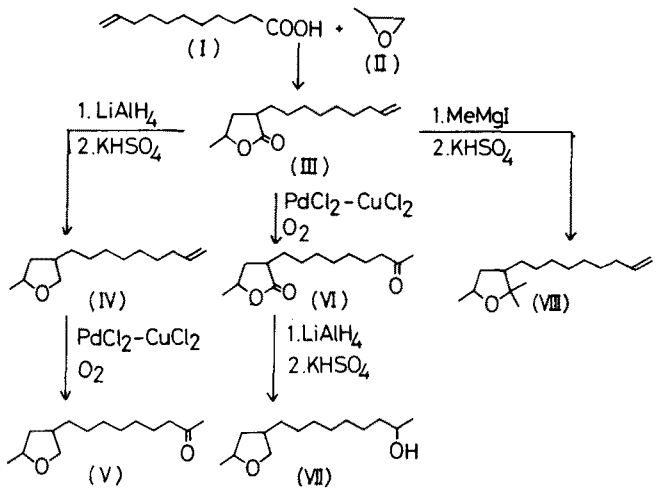
Reduction and dehydration of VI was carried out by the above mentioned method and 2-methyl-4-(8-hydroxynonyl) tetrahydrofuran, VII, was obtained in 77% yield. Bp 77-79 C/4 mmHg; IR (cm^{-1}): 3350, 1110; ^1H NMR (δ, ppm): 1.03 (3H, d, J=6.4Hz, $C\underline{H}_3CH$), 1.12 (3H, d, J=6.2Hz, $C\underline{H}_3CH-$), 1.22-1.70 [14H, m, $(CH_2)_6$, $CH_3CHC\underline{H}_2$], 1.70-2.59 (3H, m, $C\underline{H}_2CHOH$, $C\underline{H}CH_2O-$), 3.01-3.49 (2H, m, $-C\underline{H}O \times 2$), 3.51 (1H, s, OH), 3.58-4.12 (2H, m, CH_2O); MS m/e M^+ 228.

Reaction of 4-Methyl-2-(8-nonenyl) γ-butyrolactone (III) with Methylmagnesium Iodide

Methylmagnesium iodide solution prepared from magnesium (0.1 mol, 2.43 g) and methyl iodide (0.1 mol, 1.42 g) in 200 ml of ethyl ether was slowly added to a solution of III (25 mmol, 5.60 g) in 50 ml of ethyl ether at 0 C in an atmosphere of dry nitrogen. After stirring for 5 hr at 0 C, the reaction mixture was treated as reported previously (17). Crude product was dehydrated with potassium bisulfate as in the above mentioned method and 2,2,5-trimethyl-3-(8-nonenyl) tetrahydrofuran, VIII, was obtained in 89% yield. Bp 92-94 C/1 mmHg; IR (cm^{-1}): 1645, 990, 910; ^1H MNR (δ, ppm): [6H, s, $(CH_3)_2C$], 1.13 (3H, d, J=6.1Hz, $C\underline{H}_3CH$) 1.20-1.83 [14H, m, $(CH_2)_6$, $CH_3CHC\underline{H}_2$], 1.83-2.33 [3H, m, $(CH_3)_2C\underline{C}H$, $CH_2C=C$], 3.59-4.30 (1H, m, $CH_3C\underline{H}O-$), 4.82-5.28 (2H, m, $-CH=C\underline{H}_2$), 5.46-6.31 (1H, m, $-C\underline{H}=CH_2$); MS m/e M^+ 238.

RESULTS AND DISCUSSION

We have reported previously that various γ-lactones can be prepared from the reaction of carboxylic acids and epoxides using lithium naphthalenide, and these lactones are sweet smelling (11-13). In these reactions, lithium diethylamide is formed from lithium naphthalenide and diethylamine, and it reacts with carboxylic acids to proceed lithium α-lithiocarboxylates. These carboxylates react with epoxide to give 4-hydroxy acids. In the absence of diethylamine, 4-hydroxy acids cannot be obtained. This paper concerns a reaction of higher fatty acids, such as myristic acid, palmitic acid and stearic acid, with propylene oxide to give γ-lactones, and preparation of tetrahydrofuran derivatives from these γ-lactones. We have found that γ-lactones and tetrahydrofuran derivatives were obtained in high yields. For example, 4-methyl-2-(8-nonenyl) γ-butyrolactone III was obtained by the reaction of 10-undecylenic acid I and propylene oxide II as shown in the Experimental section. Other γ-lactones were prepared in high yields, and the results are listed in Table I. However, these γ-lactones were not sweet smelling. The γ-lactones were converted to tetrahydrofuran derivatives by reduction with lithium aluminum hydride followed by intramolecular dehydration with potassium bisulfate. For example, 2-methyl-4-(8-nonenyl) tetrahydrofuran IV was obtained from 4-methyl-2-(8-nonenyl) γ-butyrolactone III. Tetrahydrofuran derivative IV prepared from 10-undecylenic acid, I, and propylene oxide, II, was woody smelling. So, for preparing sweet smelling compounds, the reactions of I with other



Scheme I

epoxides were examined, and corresponding γ-lactones and tetrahydrofurans were obtained (Table I). Furthermore, γ-lactones containing carbonyl group VI, tetrahydrofuran derivatives containing carbonyl group V, hydroxy group VII and terminal vinyl group VIII were prepared from 10-undecylenic acid I and propylene oxide II (Scheme I).

In these products, tetrahydrofuran derivative IX derived from I and 1,2-butylene oxide was woody smelling, and compond VIII prepared from γ-lactone III with methylmagnesium iodide followed by intramolecular dehydration was weak woody smelling. These products IV, VIII and IX may be used as perfumery materials.

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