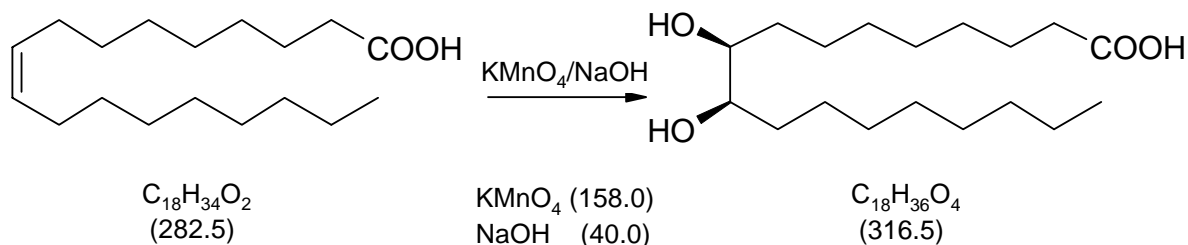


3011 Synthesis of erythro-9,10-dihydroxystearic acid from oleic acid



Literature

A. Lapworth und E. N. Mottram, *J. Chem. Soc.*, **1925**,1628-31

Classification

Reaction types and substance classes

addition to alkenes, oxidation, cis-hydroxylation
alkene, alcohol, natural product

Work methods

stirring with magnetic stir bar, filtering, recrystallizing, extracting

Instruction (batch scale 10 mmol)

Equipment

5 L beaker or Erlenmeyer flask, heatable magnetic stirrer, magnetic stir bar, suction flask, Buechner funnel, mortar, desiccator

Substances

oleic acid (techn. 90%) (oleic acid, pure: mp 16 °C, bp 193 °C/1.6 hPa)	3.14 g (equivalent to 10.0 mmol pure oleic acid)
potassium permanganate	2.50 g (15.8 mmol)
sodium hydroxid	3.14 g (78.5 mmol)
hydrochloric acid (conc., 36%)	94 mL
sodium sulfite or sodium disulfite	
petroleum ether (bp 60-80 °C)	about 200 mL
ethanol (bp 78 °C) for recrystallizing	

Reaction

3.14 g (10.0 mmol) oleic acid (techn. 90%) are added to a solution of 3.14 g (78.5 mmol) NaOH in 320 mL water in a 5 L beaker with a magnetic stir bar. The mixture is heated under

stirring until a clear solution is formed. After the addition of 2.5 L ice-cold water, 250 mL 1% potassium permanganate solution are added within 1 minute under stirring at a temperature of 10 °C. After 5 minutes so much solid sodium sulfite oder sodium disulfite is added, that the excess of potassium permanganate is reduced. Afterwards the solution is acidified with 94 mL conc. hydrochloric acid. The solution becomes colourless, and a colourless fluffy precipitation is formed.

Work up

The precipitation is sucked off and dried. Crude yield: 3.01 g, mp 81-88 °C

The crude product is washed with 50 mL petroleum ether (60-80 °C) and dried under reduced pressure. The dried product is powdered in a mortar and digested with 100-150 mL petroleum ether in a beaker. Thus the sturated carboxylic acids contained in the oleic acid as impurities are removed. The dihydroxystearic acid is insoluble in petroleum ether. It is sucked off and recrystallized from ethanol.

Yield: 2.74 g (8.70 mmol, 87%); mp 132 °C; colourless powder

Comments

The given amounts of reactants must be strictly observed, otherwise the oleic acid molecule can be cleaved at the double bond.

Waste management

Recycling

The petroleum ether filtrate is collected and redistilled.

Waste disposal

Waste	Disposal
aqueous filtrate	neutralize with sodium hydroxide solution, then: aqueous waste, neutral to alkaline, containing heavy metals
mother liquor from recrystallization	organic solvents, halogen free

Time

1 hour

Break

After sucking off the crude product and before recrystallizing

Degree of difficulty

Easy

Instruction (batch scale 1 mmol)

Equipment

500 mL beaker or Erlenmeyer flask, heatable magnet stirrer, magnetic stir bar, suction flask, Buechner funnel, mortar, desiccator

Substances

oleic acid (techn 90%) (oleic acid, pure: mp 16 °C, bp 193 °C/1.6 hPa)	314 mg (equivalent to 1.00 mmol pure oleic acid)
potassium permanganate	250 mg (1.58 mmol)
sodium hydroxide	314 mg (7.85 mmol)
hydrochloric acid (conc., 36%)	9.5 mL
sodium sulfite or sodium disulfite	
petroleum ether (bp 60-80 °C)	about 20 mL
ethanol (bp 78 °C) for recrystallizing	

Reaction

314 mg (1.00 mmol) oleic acid (techn. 90%) are added to a solution of 314 mg (7.85 mmol) NaOH in 32 mL water in a 500 mL beaker with a magnetic stir bar. The mixture is heated under stirring until a clear solution is formed. After the addition of 250 mL ice-cold water, 25 mL 1% potassium permanganate solution is added within 1 minute under stirring at a temperature of 10 °C. After 5 minutes so much solid sodium sulfite or sodium disulfite is added, that the excess of potassium permanganate is reduced. Afterwards the mixture is acidified with 9.5 mL conc. hydrochloric acid. The solution becomes colourless, and a colourless fluffy precipitation is formed.

Work up

The precipitation is sucked off and dried. Crude yield: 301 mg; mp 81-88 °C.

The crude product is washed with 5 mL petroleum ether (60-80 °C) and dried under reduced pressure. The dried product is powdered in a mortar and digested with 10-15 mL petroleum ether in a beaker. Thus the saturated carboxylic acids contained in the oleic acid as impurities are removed. The dihydroxystearic acid is insoluble in petroleum ether. It is sucked off and recrystallized from ethanol.

Yield: 260 mg (0.820 mmol, 82%); mp 132 °C; colourless powder

Comments

The given amounts of reactants must be strictly observed, otherwise the oleic acid molecule can be cleaved at the double bond.

Waste management

Recycling

The petroleum ether filtrate is collected and redistilled.

Waste disposal

Waste	Disposal
aqueous filtrate	neutralize with sodium hydroxide solution, then: aqueous waste, neutral to alkaline, containing heavy metals
mother liquor from recrystallization	organic solvents, halogen free

Time

1 hour

Break

After sucking off the crude product and before recrystallization

Degree of difficulty

Easy

Analytcs**TLC**

TLC-conditions:

adsorbant:

TLC-aluminium foil, Merck silica gel 60 F₂₅₄

eluent:

acetic acid ethyl ester

visualisation:

2.7 g KMnO₄ and 18 g K₂CO₃ are added to a solution of 216 mg NaOH in 18 mL water. Then 256 mL water are added in several portions.

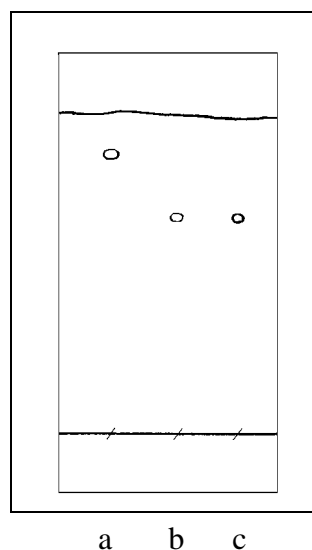
The TLC aluminium foil is dipped in this solution and then slightly warmed with a hot air dryer. The substances become visible as yellow spots

R_f (oleic acid)

0.87

R_f (product)

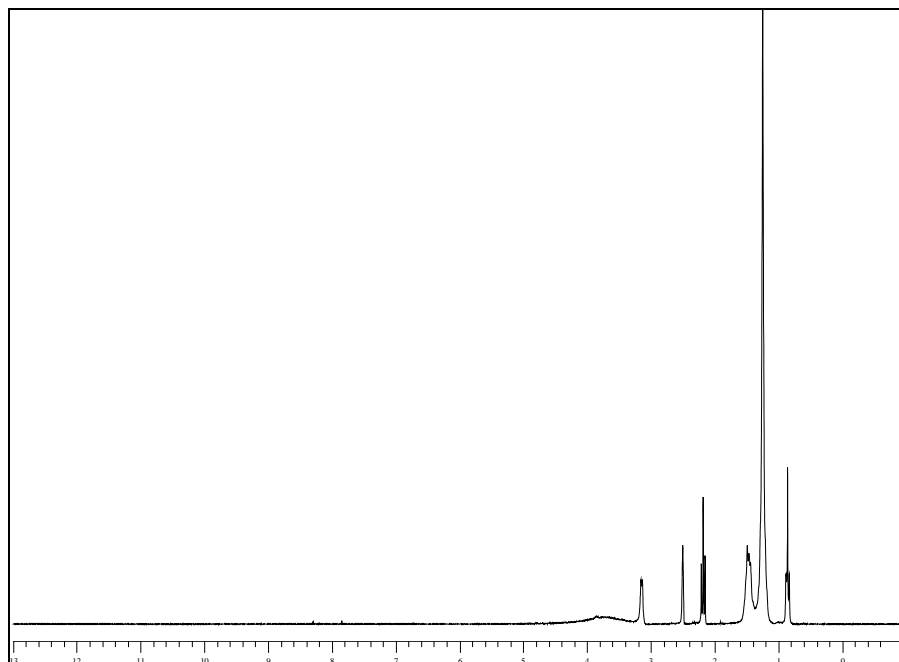
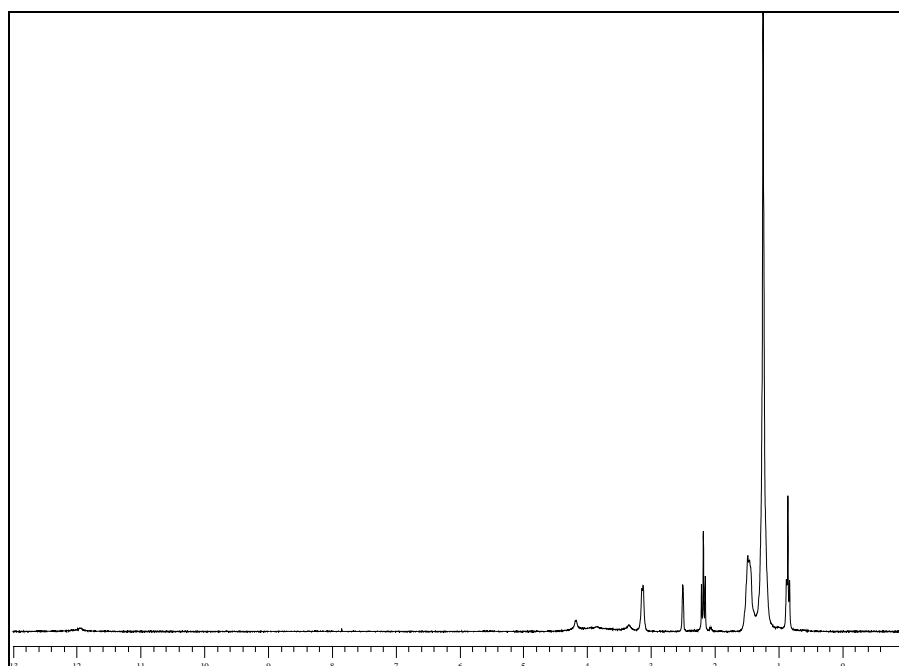
0.67



a: oleic acid

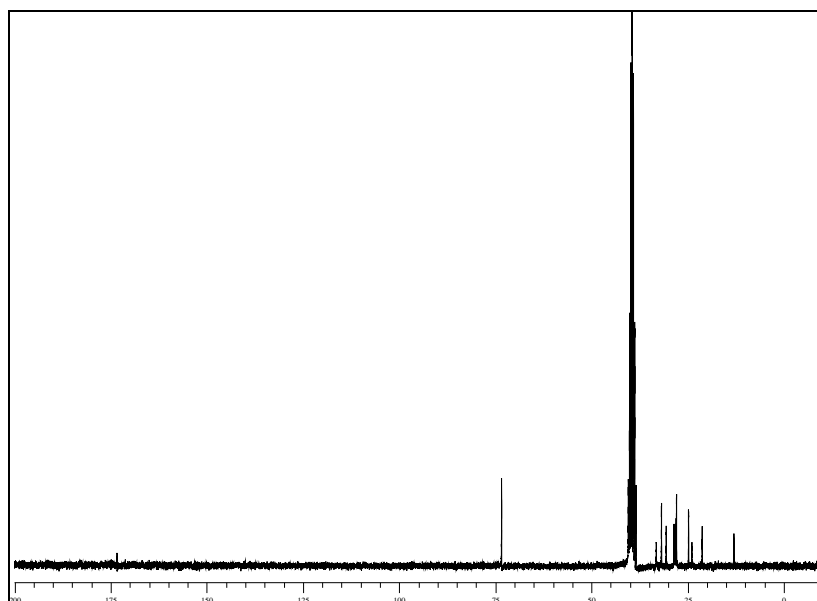
b: crude product

c: pure product

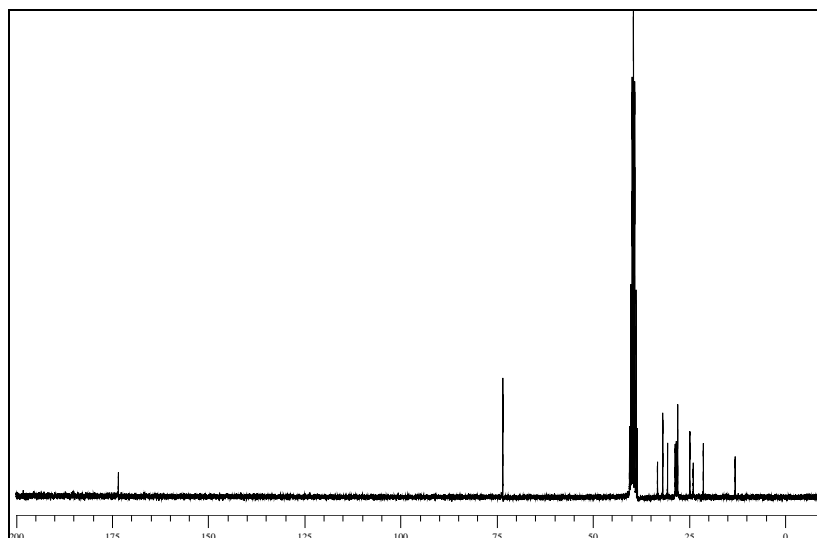
^1H NMR spectrum of the crude product (250 MHz, DMSO- D_6) **^1H NMR spectrum of the pure product (250 MHz, DMSO- D_6)**

δ (ppm)	Multiplicity	Number of H	Assignment
0.86	t, $^3J = 6.4$ Hz	3	CH_3
1.2 - 1.6	m	26	remaining CH_2
2.18	t, $^3J = 7.3$ Hz	2	$\text{CH}_2\text{-COOH}$
3.25	m	2	CH-OH

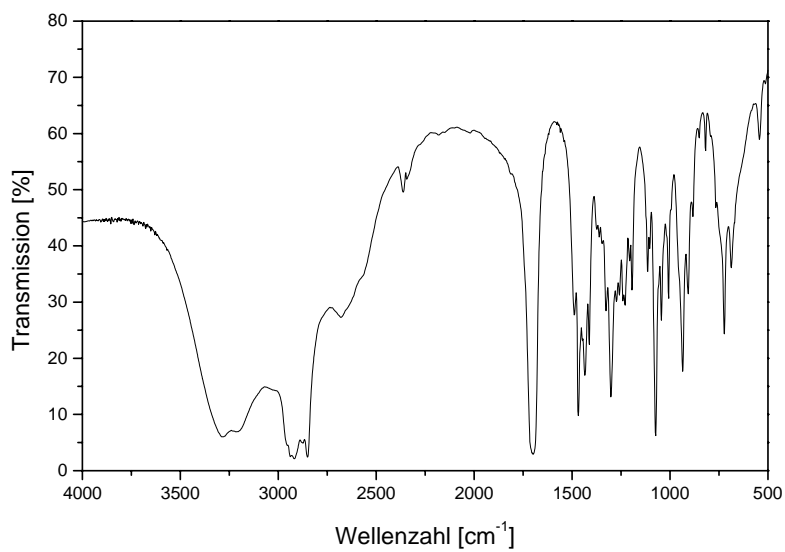
^{13}C NMR spectrum of the crude product (62.5 MHz, DMSO- D_6 , bei 373 °K)



^{13}C NMR spectrum of the pure product (62.5 MHz, DMSO- D_6 , bei 373 °K)



δ (ppm)	Assignment
13.0	CH_3
21.2	$\text{CH}_2\text{-CH}_3$
23.9	
24.8	
27.9	
28.0	
28.3	
28.4	
28.6	
30.6	
31.8	
33.2	$\text{CH}_2\text{-COOH}$
73.4	CH-OH
173.4	COOH
38.5-40.5	solvent

IR spectrum of the pure product (KBr)

(cm ⁻¹)	Assignment
3500-2500	O-H-valence, alcohol and acid C-H-valence, alkane
1716	C=O-valence, carboxylic acid