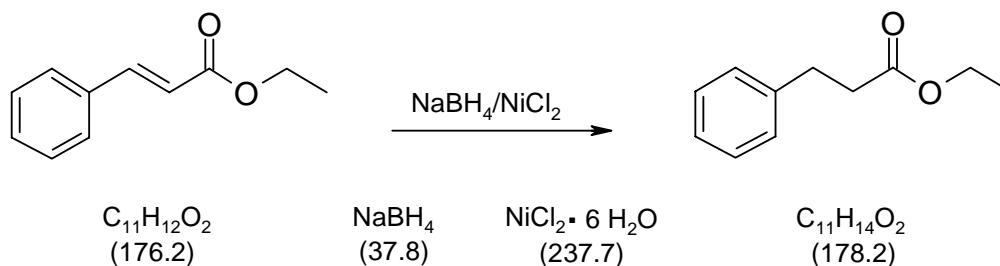


3023 Hydrogenation of cinnamic acid ethyl ester to 3-phenylpropionic acid ethyl ester



Literature

S.-K. Chung, *J. Org. Chem.* **1979**, *44*, 1014

Classification

Reaction types and substance classes

hydrogenation, reduction, addition to alkenes
 carboxylic acid ester, alkene, complex metal hydride

Work methods

stirring with magnetic stir bar, extracting, shaking out, filtering, evaporating with rotary evaporator, distilling under reduced pressure, use of an ice cooling bath, heating with oil bath

Instruction (batch scale 100 mmol)

Equipment

500 mL three-neck flask, reflux condenser, heatable magnetic stirrer, magnetic stir bar, internal thermometer, bubble counter, separating funnel, powder funnel, suction flask, Buechner funnel, distillation apparatus, rotary evaporator, vacuum pump, ice bath, oil bath

Substances

cinnamic acid ethyl ester (bp 271 °C)	17.6 g (16.8 mL, 100 mmol)
sodium borohydride	7.56 g (200 mmol)
nickel(II) chloride hexahydrate	2.38 g (10.0 mmol)
ethanol (bp 78 °C)	410 mL
<i>tert</i> -butyl methyl ether (bp 55 °C)	350 mL
water	220 mL
Celite (filter help)	
sodium sulfate for drying	

Reaction

17.6 g (16.8 mL, 100 mmol) cinnamic acid ethyl ester together with 2.38 g (10.0 mmol) nickel(II) chloride hexahydrate in 360 mL ethanol are filled in a 500 mL three-neck flask with magnetic stir bar, internal thermometer and reflux condenser with bubble counter. Then, 7.56 g (200 mmol) sodium borohydride are added in small portions over a powder funnel through the free opening of the flask, whilst the temperature of the reaction mixture is kept at 20 °C by means of an ice bath. After complete addition of the sodium borohydride the mixture is stirred for further 90 minutes at 50 °C internal temperature. Then, also as a signal for the end of reaction, no further gas evolution should be visible.

Work up

The reaction mixture is cooled down to room temperature and sucked off over a Buechner funnel with Celite, the filter cake is washed with 50 mL ethanol. The solvent is evaporated from the filtrate at a rotary evaporator. To the residue 150 mL water are added and this mixture is extracted five times with 70 mL *tert*-butyl methyl ether each. The organic phase is washed with 70 mL water and then dried over sodium sulfate. The drying agent is filtered off and the solvent is evaporated. Crude yield: 16.4 g

The crude product is distilled under reduced pressure.

Yield: 13.4 g (75.2 mmol, 75%); colourless liquid, bp 118 °C (12 hPa)

Comments

In order to remove the excessive sodium borohydride, the work up should directly follow the completed hydrogenation, otherwise 3-phenylpropanol is formed through further reduction of the product (see analytics).

Waste management**Recycling**

The evaporated solvents ethanol and *tert*-butyl methyl ether are collected and redistilled.

Waste disposal

Waste	Disposal
filter cake	solid waste, free from mercury
aqueous phase	solvent water mixtures, containing halogen, containing heavy metals
distillation residue	organic solvents, halogen free
sodium sulfate	solid waste, free from mercury

Time

4 - 5 hours

Break

After shaking out with *tert*-butyl methyl ether

Degree of difficulty

Medium

Instruction (batch scale 10 mmol)

Equipment

100 mL three-neck flask, reflux condenser, heatable magnetic stirrer, magnetic stir bar, internal thermometer, bubble counter, separating funnel, powder funnel, suction flask, Buechner funnel, distillation apparatus, rotary evaporator, vacuum pump, ice bath, oil bath

Substances

cinnamic acid ethyl ester (bp 271 °C)	1.76 g (1.68 mL, 10.0 mmol)
sodium borohydride	0.756 g (20.0 mmol)
nickel(II) chloride hexahydrate	0.238 g (1.00 mmol)
ethanol (bp 78 °C)	45 mL
<i>tert</i> -butyl methyl ether (bp 55 °C)	50 mL
water	20 mL
Celite (filter help)	
sodium sulfate for drying	

Reaction

1.76 g (1.68 mL, 10.0 mmol) cinnamic acid ethyl ester together with 0.238 g (1.00 mmol) nickel(II) chloride hexahydrate in 35 mL ethanol are filled in a 100 mL three-neck flask with magnetic stir bar, internal thermometer and reflux condenser with bubble counter. Then, 0.756 g (20.0 mmol) sodium borohydride are added in small portions over a powder funnel through the free opening of the flask, whilst the temperature of the reaction mixture is kept at 20 °C by means of an ice bath. After complete addition of the sodium borohydride the mixture is stirred for further 90 minutes at 50 °C internal temperature. Then, also as a signal for the end of reaction, no further gas evolution should be visible.

Work up

The reaction mixture is cooled down to room temperature and sucked off over a Buechner funnel with Celite (filter help), the filter cake is washed with 10 mL ethanol. The solvent is evaporated from the filtrate at a rotary evaporator. To the residue 10 mL water are added and this mixture is extracted five times with 10 mL *tert*-butyl methyl ether each. The organic phase is washed with 10 mL water and then dried over sodium sulfate. The drying agent is filtered off and the solvent is evaporated. Crude yield: 1.69 g

The crude product is distilled under reduced pressure.

Yield: 1.35 g (7.52 mmol, 76%); colourless liquid, bp 118 °C (12 hPa)

Comments

In order to remove the excessive sodium borohydride, the work up should directly follow the completed hydrogenation, otherwise 3-phenylpropanol is formed through further reduction of the product (see analytics).

Waste management**Recycling**

The evaporated solvents ethanol and *tert*-butyl methyl ether are collected and redistilled.

Waste disposal

Waste	Disposal
filter cake	solid waste, free from mercury
aqueous phase	solvent water mixtures, containing halogen, containing heavy metals
distillation residue	organic solvents, halogen free
sodium sulfate	solid waste, free from mercury

Time

About 4 hours

Break

After shaking out with *tert*-butyl methyl ether

Degree of difficulty

Medium

Analytics**GC**

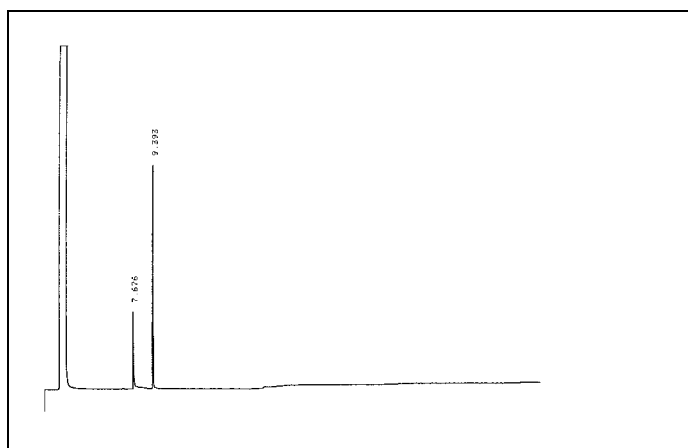
Sample preparation:

One drop from the crude or pure product is diluted with 1 mL *tert*-butyl methyl ether, from this solution 1 μ L is injected.

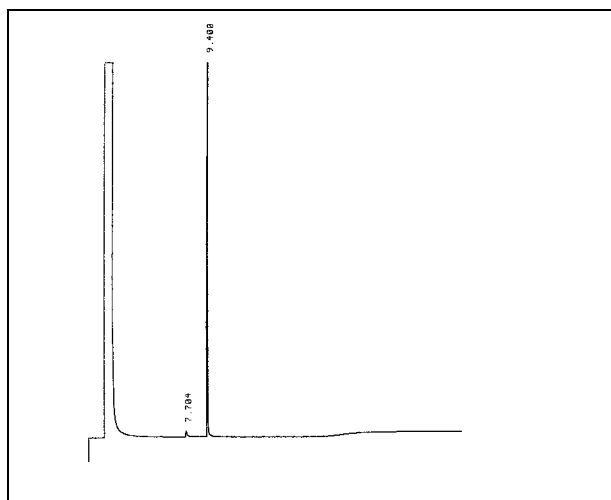
GC-conditions:

column: Macherey and Nagel, SE-54, 326-MN-30705-9, length 25 m, ID 0.32 mm, DF 0.25 μ m
 inlet: Gerstel KAS with control unit, injector temperature 250 $^{\circ}$ C;
 split injection 1:20, injected volume 1 μ L
 carrier gas: nitrogen, pre-column pressure 62 kPa, rate 1.04 mL/min
 oven: start temperature 100 $^{\circ}$ C (1 min), 10 $^{\circ}$ C/min, final temperature 250 $^{\circ}$ C (30 min)
 detector: FID, 275 $^{\circ}$ C

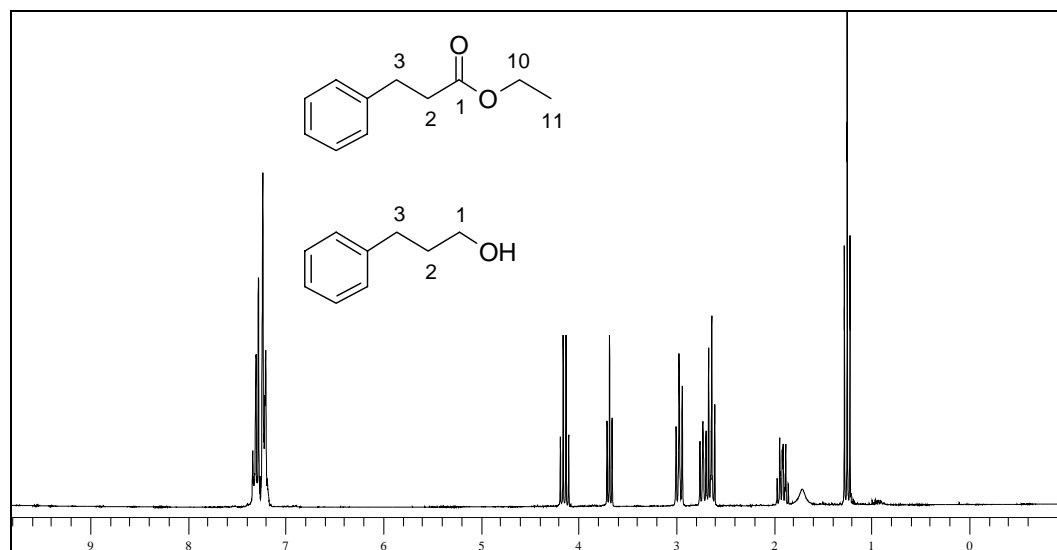
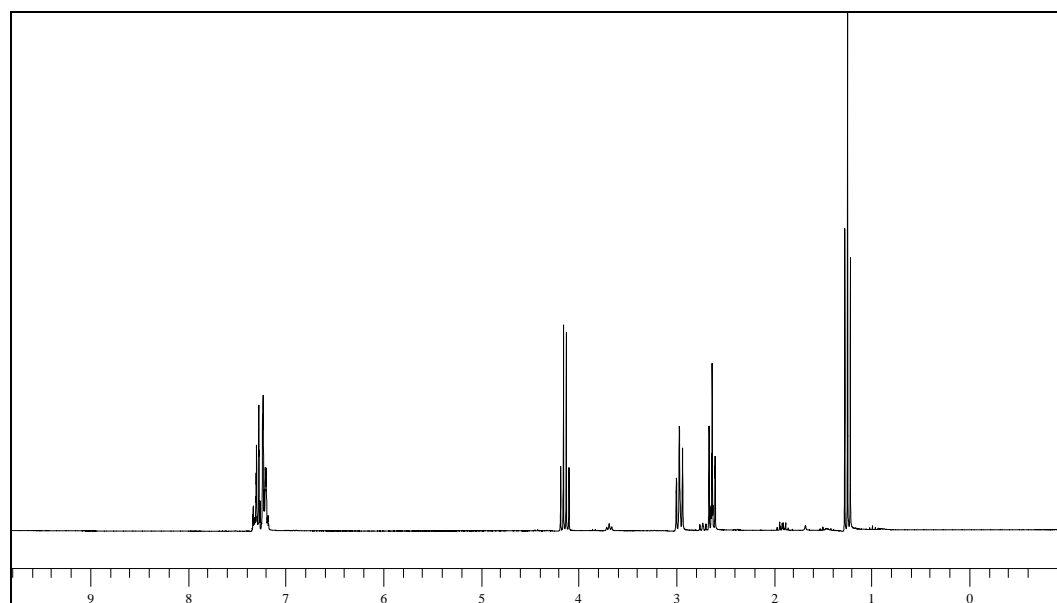
Percent concentration was calculated from peak areas.

GC of the crude product

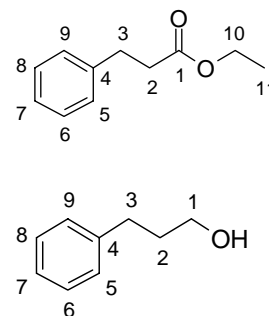
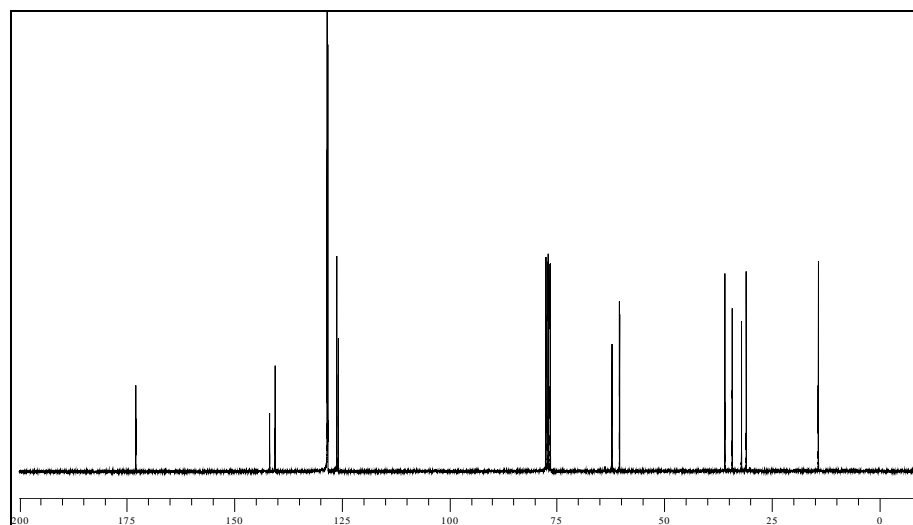
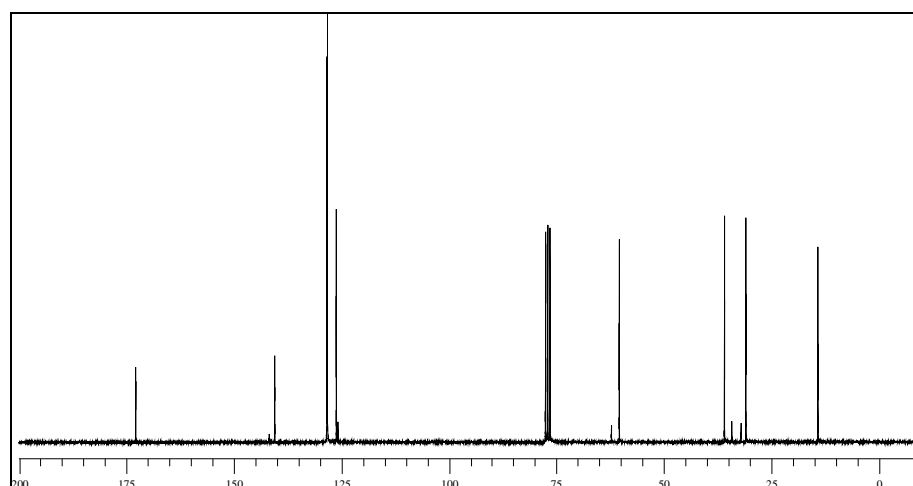
Retention time (min)	Substance	Peak area %
9.39	product (3-phenylpropionic acid ethyl ester)	74
7.68	side product (3-phenylpropanol, determined with GC/MS)	26

GC of the pure product

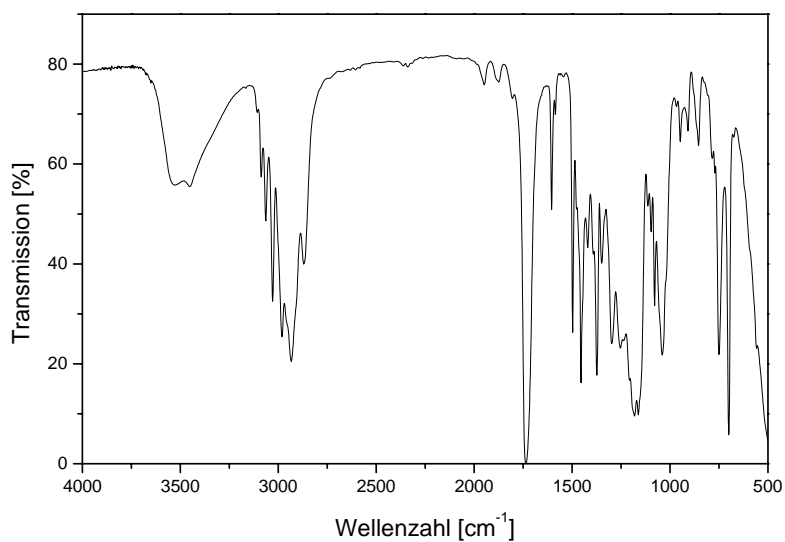
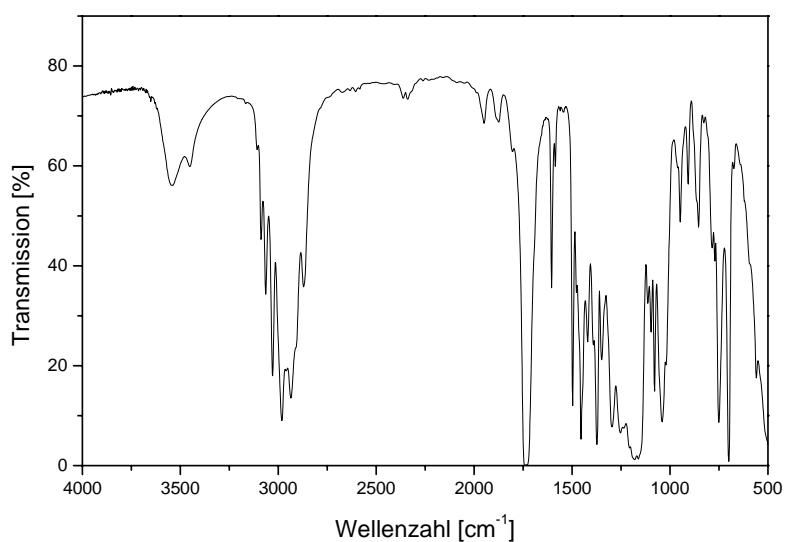
Retention time (min)	Substance	Peak area %
9.40	product (3-phenylpropionic acid ethyl ester)	98
7.70	side product (3-phenylpropanol, determined with GC/MS)	2

^1H NMR spectrum of the crude product (250 MHz, CDCl_3) **^1H NMR spectrum of the pure product (250 MHz, CDCl_3)**

δ (ppm)	Multiplicity	3-Phenylpropionic acid ethyl ester		3-Phenylpropanol	
		Number of H	Assignment	Number of H	Assignment
1.25	t, $^3J=7.1$	3	11-H		
1.91	m			2	2-H
2.63	m	2	2-H		
2.73	m			2	3-H
2.97	m	2	3-H		
3.68	t, $^3J=6.4$			2	1-H
4.14	q, $^3J=7.1$	2	10-H		
7.17-7.35	m	5	CH arene	5	CH arene

¹³C NMR spectrum of the crude product (62.5 MHz, CDCl₃)**¹³C NMR spectrum of the pure product (62.5 MHz, CDCl₃)**

δ (ppm)	Assignment	
	3-Phenylpropionic acid ethyl ester	3-Phenylpropanol
14.1	C-11	
30.9	C-3	
32.0		C-2
34.1		C-3
35.9	C-2	
60.3	C-10	
62.1		C-1
125.8		C-7
126.2	C-7	
128.2–128.4	C-5/C-9, C-6/C-8	C-5/C-9, C-6/C-8
140.5	C-4	
141.8		C-4
172.9	C-1	
76.5-77.5	solvent	

IR spectrum of the crude product (film)**IR spectrum of the pure product (film)**

(cm^{-1})	Assignment
3554, 3464	O-H-valence
3088, 3064, 3030	C-H-valence, arene
2983, 2873, 2939	C-H-valence, alkane
1745	C=O-valence, ester
1604, 1496	C=C-valence, arene