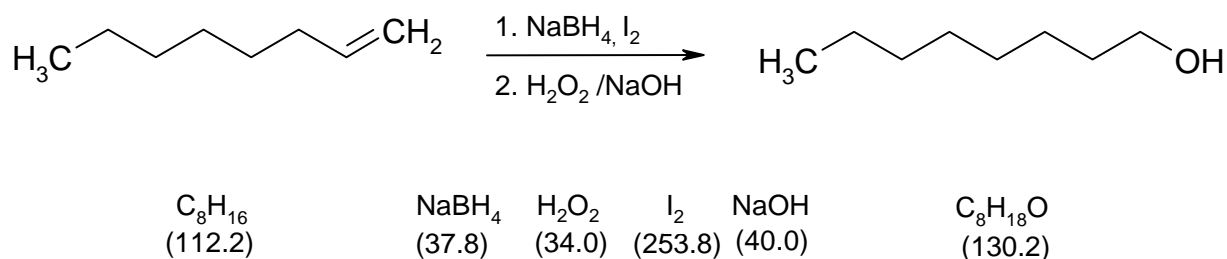


### 3001 Hydroboration/oxidation of 1-octene to 1-octanol



#### Literature

A.S. Bhanu Prasad, J.V. Bhaskar Kanth, M. Periasamy, *Tetrahedron* **1992**, 48, 4623

#### Classification

##### Reaction types and substance classes

addition to alkenes, hydroboration, oxidation  
alcohol, alkene

##### Work methods

working with moisture exclusion, stirring with magnetic stir bar, adding dropwise with addition funnel, shaking out, extracting, filtering, evaporating with rotary evaporator, distilling under reduced pressure, use of cooling bath, heating with oil bath

#### Instruction (batch scale 100 mmol)

##### Equipment

500 mL three-neck flask, drying tube, heatable magnetic stirrer, magnetic stir bar, internal thermometer, addition funnel with pressure balance, separating funnel, rotary evaporator, distillation apparatus, vacuum pump, ice bath, ice/sodium chloride cooling bath

##### Substances

1-octene (bp 121 °C)	11.2 g (15.6 mL, 100 mmol)
sodium borohydride ( $\text{NaBH}_4$ )	1.77 g (46.8 mmol)
tetrahydrofuran (dry) (bp 66 °C)	260 mL
iodine	4.72 g (18.6 mmol)
hydrogen peroxide (30%) (bp 107 °C)	20.4 mL (22.6 g, 200 mmol)
aqueous sodium hydroxide solution (3 M)	200 mL
<i>tert</i> -butyl methyl ether (Sdp 55 °C)	150 mL
sodium chloride	about 100 g
potassium carbonate, anhydrous, for drying	

## Reaction

The reaction is performed in a dry 500 mL three-neck flask, equipped with an 50 mL addition funnel, internal thermometer, magnetic stir bar and a drying tube. 1.77 g (46.8 mmol) of finely powdered sodium borohydride are filled into the flask, then 80 mL of dry tetrahydrofuran are added and the mixture is stirred until a fine suspension has formed. The mixture is cooled with an ice/sodium chloride cooling bath to a temperature of  $-5$  to  $0$  °C. To the cooled mixture a solution of 4.72 g (18.6 mmol) iodine dissolved in 50 mL dry tetrahydrofuran is added dropwise with an addition funnel. The speed of addition is controlled so that a new drop of iodine solution is added, when the iodine colour of the former drop has disappeared (about 30 minutes). Afterwards a solution of 11.2 g (15.6 mL, 100 mmol) 1-octene dissolved in 50 mL dry tetrahydrofuran is added dropwise with an addition funnel within 10 minutes, the temperature should not rise above  $30$  °C during the addition. The mixture is further stirred for 2 hours at about  $25$  °C. Then the mixture is cooled with an ice bath to a temperature between  $0$  and  $5$  °C and 14 mL of water are added carefully under stirring. Further 80 mL of tetrahydrofuran are added, then the volume of 200 mL of 3 M sodium hydroxide solution is added at once. Finally 20.4 mL (22.6 g, 200 mmol) of hydrogen peroxide (30%) are added dropwise with the addition funnel so that the temperature remains below  $30$  °C. Afterwards the mixture is stirred for additional 20 minutes.

## Work up

The reaction mixture is transferred into a separating funnel and the aqueous phase is saturated with sodium chloride. After separation of the phases the aqueous phase is extracted three times with 50 mL *tert*-butyl methyl ether each. The combined organic phases are washed twice with 50 mL saturated sodium chloride solution each and dried over a small amount of potassium carbonate. The drying agent is filtered off and the solvent is evaporated at a rotary evaporator under reduced pressure. Yield of the crude product: 13.3 g

The crude product is fractional distilled under reduced pressure.

Yield : 11.6 g (89.1 mmol, 89%); bp  $88$  °C (12 hPa); colourless liquid

## Comments

Diborane ( $B_2H_6$ ) is very toxic. Here it is generated *in-situ* and it reacts instantaneously with the alkene.

Side products: 2-octanol, 2-octanone, 2-ethyl-1-hexanol (see analytics)

## Waste management

### Waste disposal

Waste	Disposal
aqueous phases from shaking out	solvent water mixtures, containing halogen
evaporated solvent mixtures (tetrahydrofuran, <i>tert</i> -butyl methyl ether)	organic solvents, halogen free
residue of distillation	organic solvents, containing halogen
potassium carbonate	solid waste, free from mercury

**Time**

4 to 5 hours

**Break**

Before extraction

**Degree of difficulty**

Medium

**Instruction (batch scale 10 mmol)****Equipment**

50 mL three neck flask, drying tube, heatable magnetic stirrer, magnetic stir bar, internal thermometer, addition funnel with pressure balance, separating funnel, rotary evaporator, distillation apparatus, vacuum pump, ice bath, ice/sodium chloride cooling bath, oil bath

**Chemicals**

1-octene (bp 121 °C)	1.12 g (1.56 mL, 10.0 mmol)
sodium borohydrid (NaBH <sub>4</sub> )	177 mg (4.68 mmol)
tetrahydrofuran (dry) (Sdp 66 °C)	26 mL
iodine	472 mg (1.86 mmol)
hydrogen peroxide (30%) (bp 107 °C)	2.1 mL (2.3 g, 20 mmol)
aqueous sodium hydroxide solution (3 M)	20 mL
<i>tert</i> -butyl methyl ether (bp 55 °C)	18 mL
sodium chloride	about 10 g
potassium carbonate, for drying	

**Reaction**

The reaction is performed in a dry 50 mL three-neck flask, equipped with an 50 mL addition funnel, internal thermometer, magnetic stir bar and a drying tube. 177 mg (4.68 mmol) of finely powdered sodium borohydride are filled into the flask, then 8 mL of dry tetrahydrofuran are added and the mixture is stirred until a fine suspension has formed. The mixture is cooled with an ice/sodium chloride cooling bath to a temperature of -5 to 0 °C. To the cooled mixture a solution of 472 mg (1.86 mmol) iodine dissolved in 5 mL dry tetrahydrofuran is added dropwise with an addition funnel. The speed of addition is controlled so that a new drop of iodine solution is added, when the iodine colour of the former drop has disappeared. Afterwards a solution of 1.12 g (1.56 mL, 10.0 mmol) 1-octene dissolved in 5 mL dry tetrahydrofuran is added dropwise with an addition funnel within 10 minutes, the temperature should not rise above 30 °C during the addition. The mixture is further stirred for 2 hours at about 25 °C. Then the mixture is cooled with an ice bath to a temperature between 0 and 5 °C and 1.5 mL of water are added carefully under stirring. Further 8 mL of tetrahydrofuran are added, then the volume of 20 mL of 3 M sodium hydroxide solution is added at once. Finally 2.1 mL (2.3 g, 20 mmol) of hydrogen peroxide (30%) are added

dropwise with the addition funnel so that the temperature remains below 30 °C. Afterwards the mixture is stirred for additional 20 minutes.

### Work up

The reaction mixture is transferred into a separating funnel and the aqueous phase is saturated with sodium chloride. After separation of the phases the aqueous phase is extracted three times with 6 mL *tert*-butyl methyl ether each. The combined organic phases are washed twice with 5 mL saturated sodium chloride solution each and dried over a small amount of potassium carbonate. The drying agent is filtered off and the solvent is evaporated at a rotary evaporator under reduced pressure. Yield of the crude product: 1.40 g

The crude product is fractional distilled under reduced pressure.

Yield: 1.21 g (9.29 mmol, 93%); bp 88 °C (12 hPa); colourless liquid

### Comments

Diborane (B<sub>2</sub>H<sub>6</sub>) is very toxic. Here it is generated *in-situ* and it reacts instantaneously with the alkene.

Side products: 2-octanol, 2-octanone, 2-ethyl-1-hexanol (see analytics)

### Waste management

#### Waste disposal

Waste	Disposal
aqueous phases from shaking out	solvent water mixtures, containing halogen
evaporated solvent mixtures (tetrahydrofuran, <i>tert</i> -butyl methyl ether)	organic solvents, halogen free
residue of distillation	organic solvents, containing halogen
potassium carbonate	solid waste, free from mercury

### Time

4 to 5 hours

### Break

Before extraction

### Degree of difficulty

Medium

## Analytics

### GC

Sample preparation:

A drop of the substance is dissolved in 1 mL of *tert*-butyl methyl ether, 1  $\mu$ L of this solution is injected.

GC-conditions:

column: Macherey und Nagel, SE-54, 326-MN-30705-9, 25 m, ID 0.32 mm, DF 0.25  $\mu$ m

inlet: Gerstel KAS, injector 270  $^{\circ}$ C;

split injection 1:20, injected volume 1  $\mu$ L

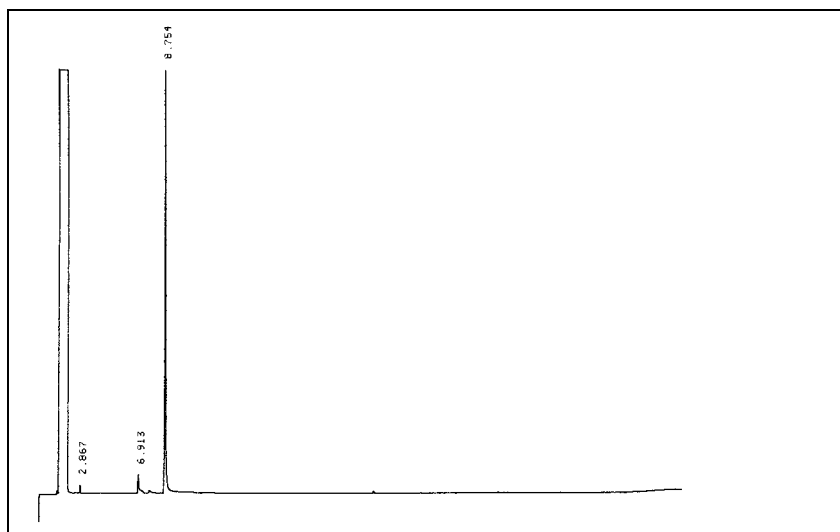
carrier gas: nitrogen, pre-column pressure 62 kPa, flow rate 1.04 mL/min

oven: 80  $^{\circ}$ C (1 min), 5  $^{\circ}$ C/min, 250  $^{\circ}$ C (30 min)

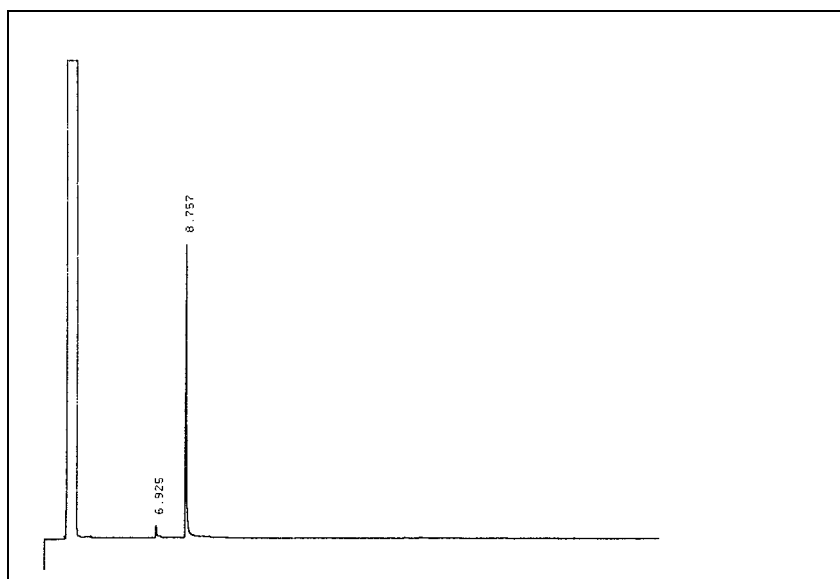
detector: FID, 275  $^{\circ}$ C

Percent concentration was calculated from peak areas.

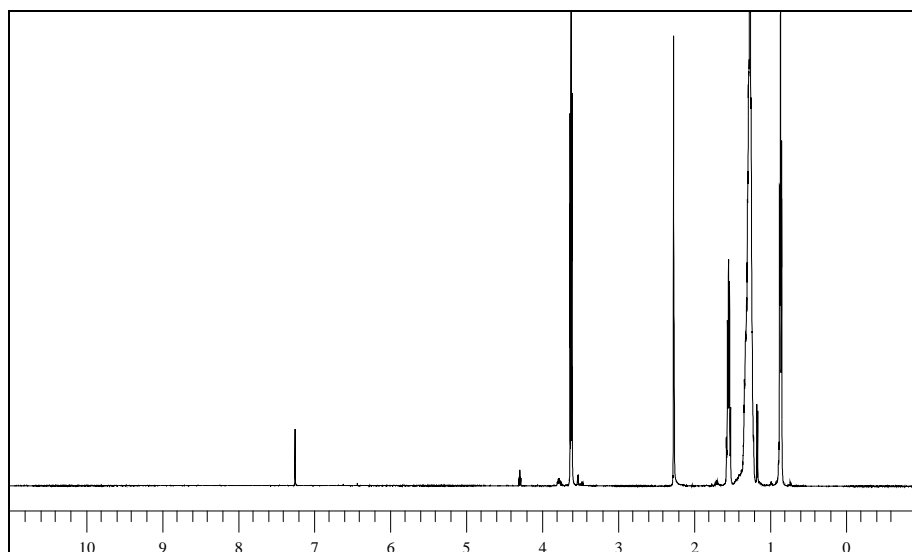
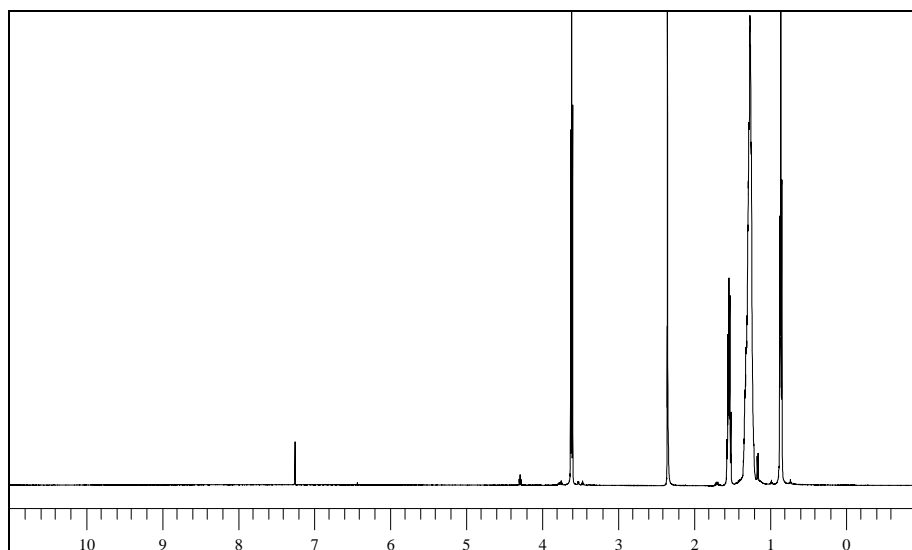
### GC of the crude product



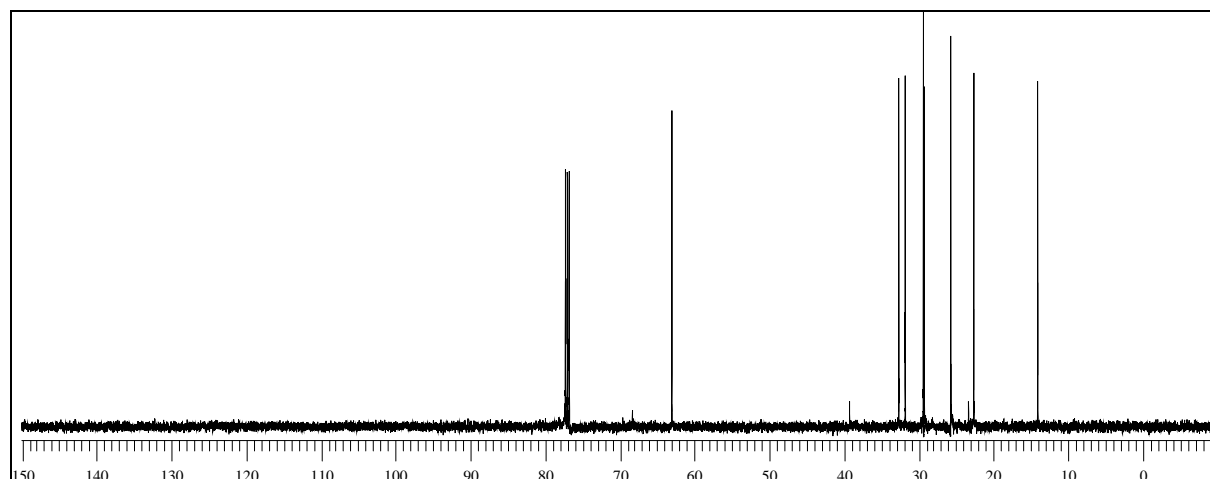
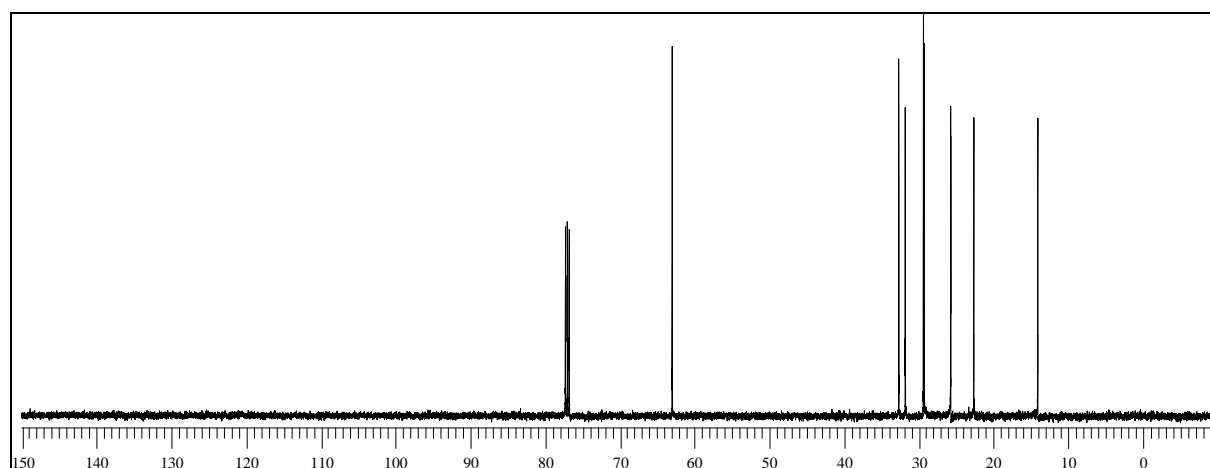
Retention time (min)	Substance	Peak area %
8.7	product (1-octanol)	95
6.9	side products (2-octanol and 2-octanone, identified by GC/MS)	4
2.9	not identified	1

**GC of the pure product**

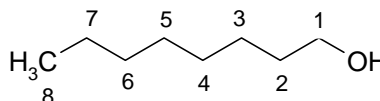
Retention time (min)	Substance	Peak area %
8.87	product (1-octanol)	96
6.9	side products (2-octanol and 2-octanone, identified by GC/MS)	4

**$^1\text{H}$  NMR spectrum of the crude product (500 MHz,  $\text{CDCl}_3$ )** **$^1\text{H}$  NMR spectrum of the pure product (500 MHz,  $\text{CDCl}_3$ )**

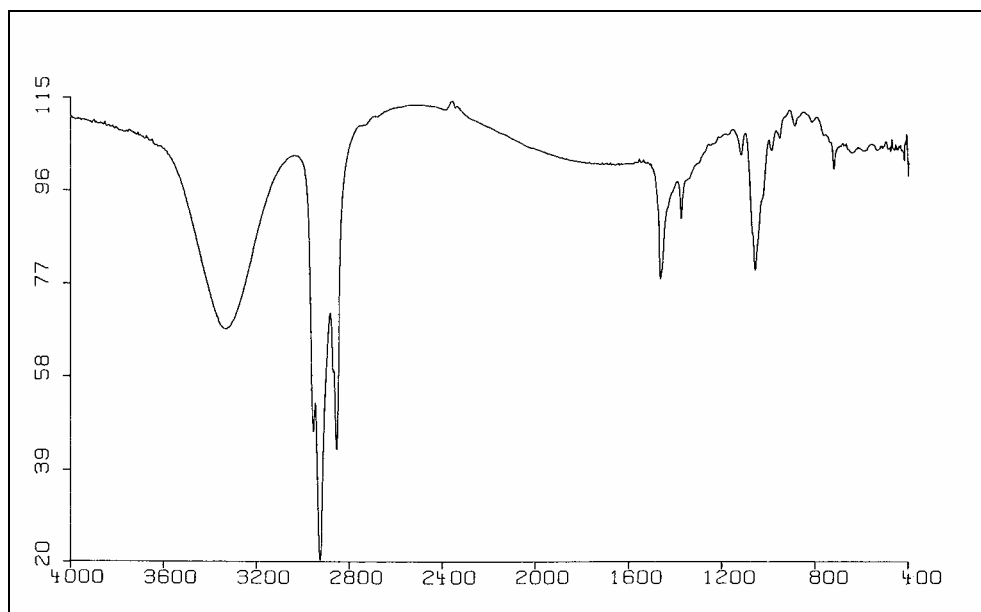
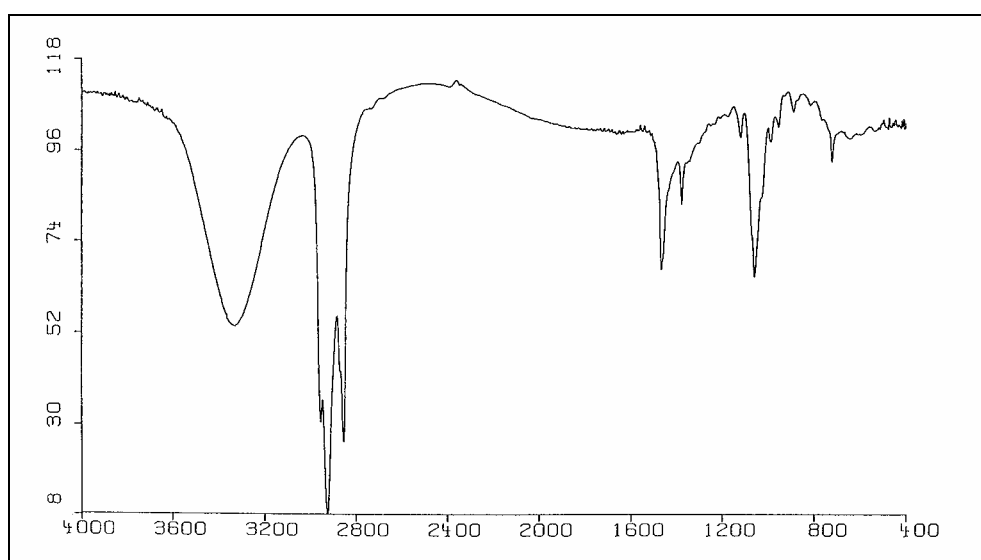
$\delta$ (ppm)	Multiplicity	Number of H	Assignment
0.85	t, $^3J = 6.7$ Hz	3	$\text{CH}_3$
1.19 - 1.34	m	10	$\text{CH}_2$
1.49 - 1.57	m	2	$\text{CH}_2$
2.34	bs	1	OH
3.60	t, $^3J = 6.7$ Hz	2	$\text{CH}_2\text{-OH}$
7.26			solvent

**$^{13}\text{C}$  NMR spectrum of the crude product (125 MHz,  $\text{CDCl}_3$ )** **$^{13}\text{C}$  NMR spectrum of the pure product (125 MHz,  $\text{CDCl}_3$ )**

$\delta$ (ppm)	Assignment
14.0	C-8
22.6	C-7
25.7	C-6
29.2	C-5
29.4	C-4
31.8	C-3
32.6	C-2
63.0	C-1
76.5-77.5	solvent





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

(cm <sup>-1</sup> )	Assignment
3332	O-H-valence
2927	C-H-valence, alkane
2856	C-H-valence, alkane
1379	O-H-deformation
1058	C-O-valence