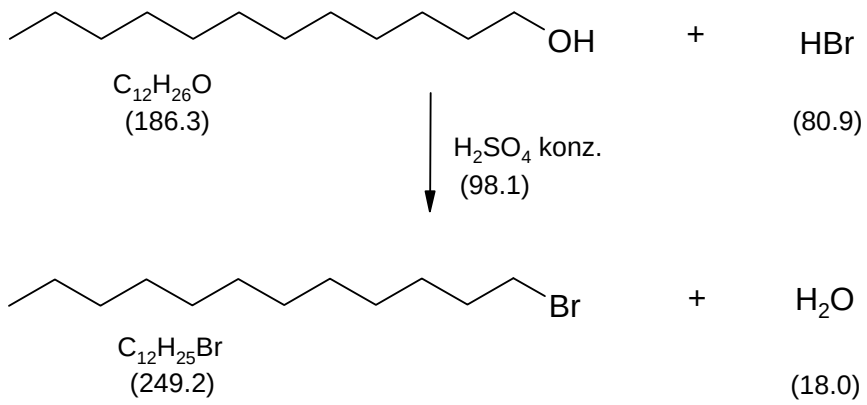
4028 Synthesis of 1-bromododecane from 1-dodecanol



Classification

Reaction types and substance classes
nucleophilic substitution
alcohol, bromoalkane, acid catalyst

Work methods
heating under reflux, stirring with magnetic stir bar, shaking out, extracting, rectifying, evaporating with rotary evaporator, filtering, distilling under reduced pressure, column distillation, heating with oil bath

Instruction (batch scale 10 mmol)

Equipment
10 mL two-neck flask or 10 mL round bottom flask with Claisen adapter, reflux condenser, heatable magnetic stirrer, magnetic stir bar, separating funnel, rotary evaporator, micro distillation apparatus, 10 cm Vigreux column, vacuum pump, oil bath

Substances

1-dodecanol (mp 22-24 °C, bp 258-265 °C)	1.86 g (10 mmol)
hydrobromic acid (48%) (bp 126 °C)	3.4 g (2.3 mL, 20 mmol)
conc. sulfuric acid	0.59 g (0.32 mL, 6.0 mmol)
cyclohexane (bp 81 °C)	20 mL
sodium hydrogen carbonate	about 2 g (for 20 mL saturated aqueous solution)
sodium sulfate for drying	about 1 g

Reaction
1.86 g (10 mmol) 1-dodecanol are filled in a 10 mL two-neck flask with magnetic stir bar and reflux condenser. Under stirring 0.59 g (0.32 mL, 6.0 mmol) conc. H_2SO_4 and 3.4 g (2.3 mL,

20 mmol) hydrobromic acid (48%) are added one after another. Then the reaction mixture is heated under stirring at an oil bath temperature of 140 °C for 5 hours under reflux. The reflux condenser is filled with water once, then the water flow is turned off to avoid a separation of dodecanol at the reflux condenser. The course of the reaction is controlled by means of thin layer chromatography (see analytics).

Work up

The reaction solution is cooled down to room temperature, 6 mL ice water are added and the mixture is shaken out in a separating funnel with 10 mL cyclohexane. The phases are separated, the organic phase is stored, the aqueous phase is shaken out again with 10 mL cyclohexane. The combined organic phases are shaken out with 20 mL saturated $NaHCO_3$-solution. In case of a bad separation of the phases, the mixture can be stored over night. The organic phase is separated and dried over Na_2SO_4. Afterwards the drying agent is filtered off and the solvent is evaporated at a rotary evaporator. A liquid remains as residue.
Crude yield: 2.20 g

The crude product is fractional distilled in a micro distillation apparatus over a 10 cm Vigreux column at about 0.1 hPa.
Yield: 1.60 g (6.42 mmol, 64%); bp 72 °C ($2.3 \cdot 10^{-1}$ hPa, oil bath temperature 118 °C), colourless liquid; $n_D^{20} = 1.4581$

Comments

The product is used in NOP 4029 as educt.

Waste management

Recycling

The evaporated cyclohexane is collected and redistilled.

Waste disposal

Waste	Disposal
aqueous phase	solvent water mixtures, containing halogen
fore-run and residue of distillation	dissolve in a small amount of acetone, then: organic solvents, containing halogen
sodium sulfate	solid waste, free from mercury

Time

8-9 hours

Break

After heating under reflux (5 hours)
After shaking out
Before distillation

Degree of difficulty

Medium

Instruction (batch scale 100 mmol)

Equipment

100 mL two- or three-neck flask, reflux condenser, heatable magnetic stirrer, magnetic stir bar, separating funnel, rotary evaporator, distillation apparatus, "pig type" receiving adapter, 10 cm Vigreux column, vacuum pump, oil bath

Substances

1-dodecanol (mp 22-24 °C, bp 258-265 °C)	18.6 g (100 mmol)
hydrobromic acid (48%) (bp 126 °C)	34 g (23 mL, 200 mmol)
conc. sulfuric acid	7.4 g (4.0 mL, 75 mmol)
cyclohexane (bp 81 °C)	90 mL
sodium hydrogen carbonate	about 6 g (for 60 mL saturated aqueous solution)
sodium sulfate for drying	about 5 g

Reaction

18.6 g (100 mmol) 1-dodecanol are filled in a 100 mL two-neck flask with magnetic stir bar and reflux condenser. Under stirring 7.4 g (4.0 mL, 75 mmol) conc. H_2SO_4 and 34 g (23 mL, 200 mmol) hydrobromic acid (48%) are added one after another. Then the reaction mixture is heated under stirring at an oil bath temperature of 140 °C for 5 hours under reflux. The reflux condenser is filled with water once, then the water flow is turned off to avoid a separation of dodecanol at the reflux condenser. The course of the reaction is controlled by means of thin layer chromatography (see analytics).

Work up

The reaction solution is cooled down to room temperature, 60 mL ice water are added and the mixture is shaken out in a separating funnel with 50 mL cyclohexane. The phases are separated, the organic phase is stored, the aqueous phase is shaken out again with 40 mL cyclohexane. The combined organic phases are shaken out with 60 mL saturated $NaHCO_3$-solution. In case of a bad separation of the phases, the mixture can be stored over night. The organic phase is separated and dried over Na_2SO_4. Afterwards the drying agent is filtered off and the solvent is evaporated at a rotary evaporator. A liquid remains as residue.
Crude yield: 23.1 g

The crude product is fractional distilled over a 10 cm Vigreux column at about 0.1 hPa.
Yield: 20.7g (82.7 mmol, 83%); bp 72 °C ($2.3 \cdot 10^{-1}$ hPa, oil bath temperature 120 °C), colourless liquid; $n_D^{20} = 1.4581$

Comments

The product is used in NOP 4029 as educt.

Waste management

Recycling
The evaporated cyclohexane is collected and redistilled.

Waste disposal

Waste	Disposal
aqueous phase	solvent water mixtures, containing halogen
fore run and residue of distillation	dissolve in a small amount of acetone, then: organic solvents, containing halogen
sodium sulfate	solid waste, free from mercury

Time
8-9 hours

Break
After heating under reflux (5 hours)
After shaking out
Before distillation

Degree of difficulty
Medium

Instruction (batch scale 1 mol)

Equipment
1 L two- or three-neck flask, reflux condenser, heatable magnetic stirrer, magnetic stir bar, separating funnel, rotary evaporator, distillation bridge, "pig type" receiving adapter, 30 cm Vigreux column, vacuum pump, oil bath

Substances

1-dodecanol (mp 22-24 °C, bp 258-265 °C)	186 g (1.00 mol)
hydrobromic acid (48%) (bp 126 °C)	340 g (230 mL, 2.0 mol)
conc. sulfuric acid	74 g (40 mL, 750 mmol)
cyclohexane (bp 81 °C)	400 mL
sodium hydrogen carbonate	about 25 g (for 250 mL saturated aqueous solution)
sodium sulfate for drying	about 50 g

Reaction
186 g (1.00 mol) 1-dodecanol are filled in a 1 L two-neck flask with magnetic stir bar and reflux condenser. Under stirring 74 g (40 mL, 750 mmol) conc. H_2SO_4 and 340 g (230 mL, 2.0 mol) hydrobromic acid (48%) are added one after another. Then the reaction mixture is heated under stirring at an oil bath temperature of 140 °C for 6 hours under reflux. The reflux condenser is filled with water once, then the water flow is turned off to avoid a separation of

dodecanol at the reflux condenser. The course of the reaction is controlled by means of thin layer chromatography (see analytics).

Work up

The reaction solution is cooled down to room temperature, 300 mL ice water are added and the mixture is shaken out in a separating funnel with 240 mL cyclohexane. The phases are separated, the organic phase is stored, the aqueous phase is shaken out again with 160 mL cyclohexane. The combined organic phases are shaken out with 250 mL saturated $NaHCO_3$-solution. In case of a bad separation of the phases, the mixture can be stored over night. The organic phase is separated and dried over Na_2SO_4. Afterwards the drying agent is filtered off and the solvent is evaporated at a rotary evaporator. A liquid remains as residue.
Crude yield: 235 g

The crude product is fractional distilled over a 30 cm Vigreux column at about 0.1 hPa.
Yield: 210 g (0.843 mol, 84%); bp 65°C ($1.6 \cdot 10^{-1}$ hPa, oil bath temperature 115 °C), colourless liquid; $n_D^{20} = 1.4581$

Comments

The product is used in NOP 4029 as educt.

Waste management

Recycling

The evaporated cyclohexane is collected and redistilled.

Waste disposal

Waste	Disposal
aqueous phase	solvent water mixtures, containing halogen
fore-run and residue of distillation	dilute in a small amount of acetone, then: organic solvents, containing halogen
sodium sulfate	solid waste, free from mercury

Time

11-12 hours

Break

After heating under reflux (5 hours)
After shaking out
Before distillation

Degree of difficulty

Medium

Analytics

Reaction monitoring with TLC

Sample preparation:

Using a Pasteur pipette, 2 drops from the upper phase are taken from the reaction mixture and diluted with 0.5 mL diethyl ether.

DC-conditions:

adsorbant:	TLC-aluminium foil (silica gel 60)
eluent:	petroleumether : acetic acid ethyl ester 6 : 4
visualizing:	The TLC-aluminium foil is dipped in 2N H_2SO_4 and then dried with a hot-air dryer.
R_f (dodecanol)	0.44
R_f (bromododecan)	0.72

Reaction monitoring with GC

Sample preparation:

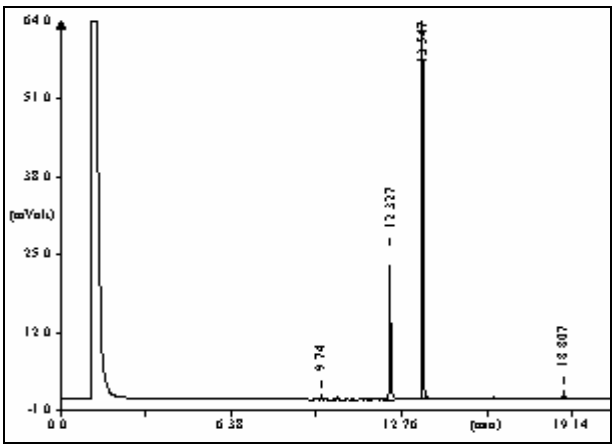
Using a Pasteur pipette, 1 drop from the reaction mixture is taken and diluted with 10 mL dichloromethane, from this solution 0.2 µL are injected.

GC-conditions:

column:	DB-1, 28 m, internal diameter 0.32 mm, film 0.25 µm
inlet:	on-column-injection
carrier gas:	hydrogen (40 cm/sec)
oven:	90 °C (5 min), 10 °C/min to 240 °C (30 min)
detector:	FID, 270 °C

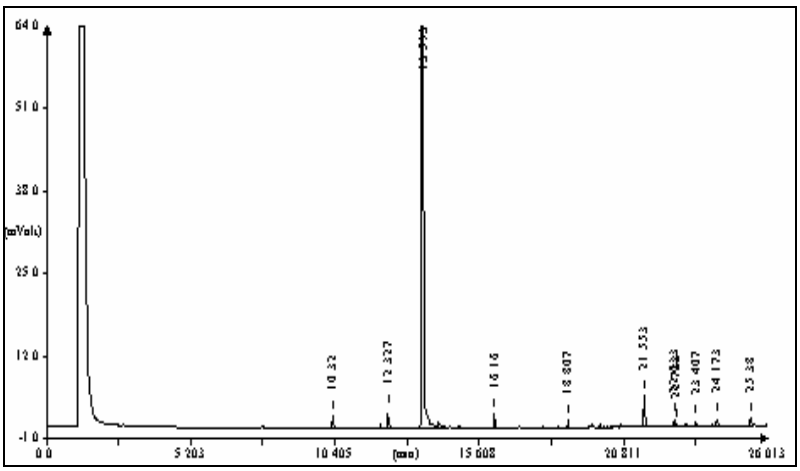
Percent concentration was calculated from peak areas.

GC of the crude product (1 mol batch scale)



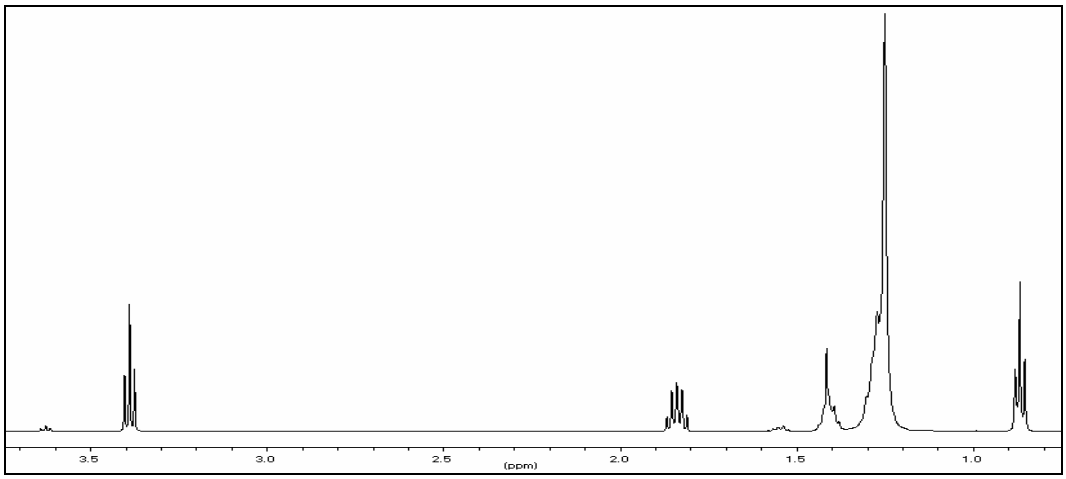
Retention time (min)	Substance	Peak area %
12.33	educt (dodecanol)	9.1
13.55	product (1-bromododecane)	89.5
others	unknown	< 1

GC of the pure product (1 mol batch scale)

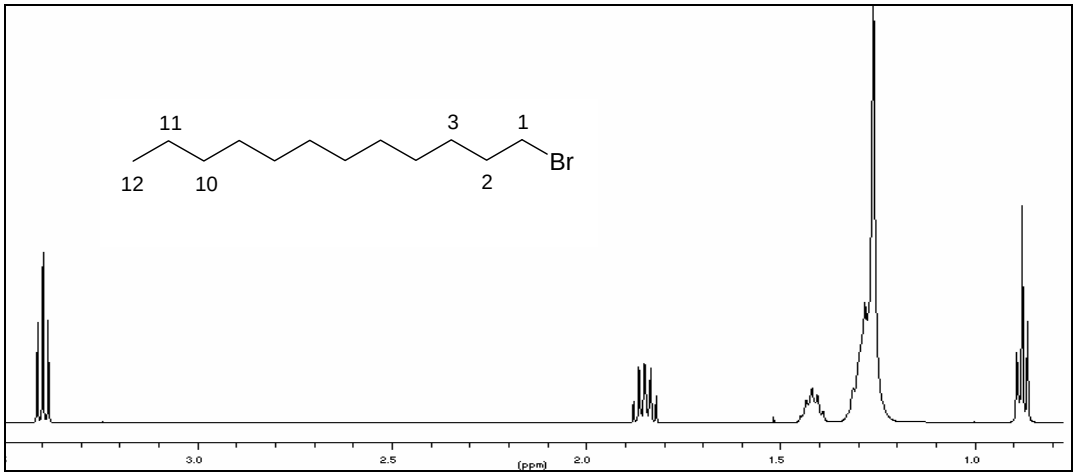


Retention time (min)	Substance	Peak area %
13.59	product (1-bromododecane)	97.8
others		< 1 per peak

^{1}H NMR spectrum of the crude product (500 MHz,$CDCl_3$)

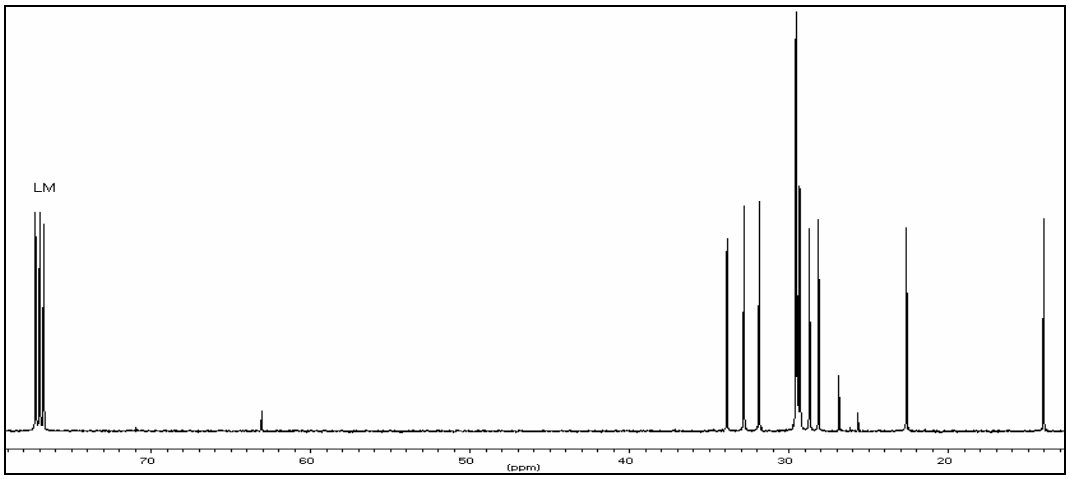


^{1}H NMR spectrum of the pure product (500 MHz,$CDCl_3$)

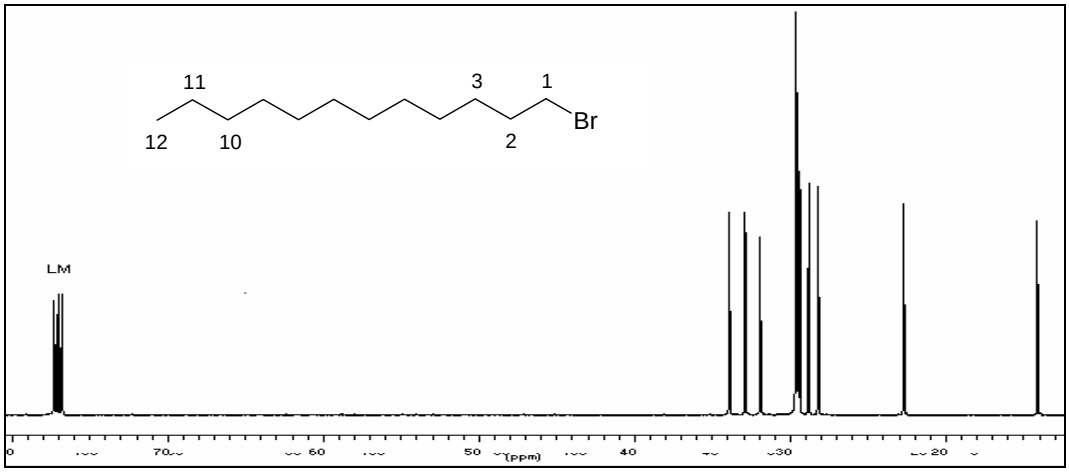


δ (ppm)	Multiplicity	Number of H	Assignment
0.88	t	3	12-H
1.26	m	16	remaining CH_2
1.42	m	2	3-H
1.85	m	2	2-H
3.39	t	2	1-H

^{13}CNMR spectrum of the crude product (125.7 MHz, $CDCl_3$)

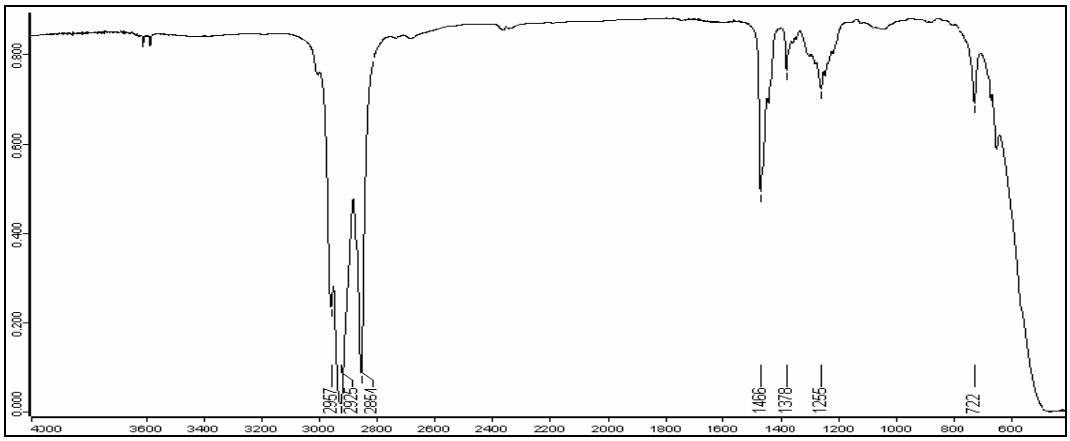


^{13}C NMR spectrum of the pure product (125.7 MHz, $CDCl_3$)



δ (ppm)	Assignment
14.1	C-12
22.7	C-11
31.9	C-10
32.9	C-2
33.8	C-1
76.5-77.5	solvent

IR spectrum of the pure product (film)



(cm^{-1})	**Assignment**
2925, 2851	C-H-valence, alkane
1466	C-H-deformation, alkane
722	C-Br-valence