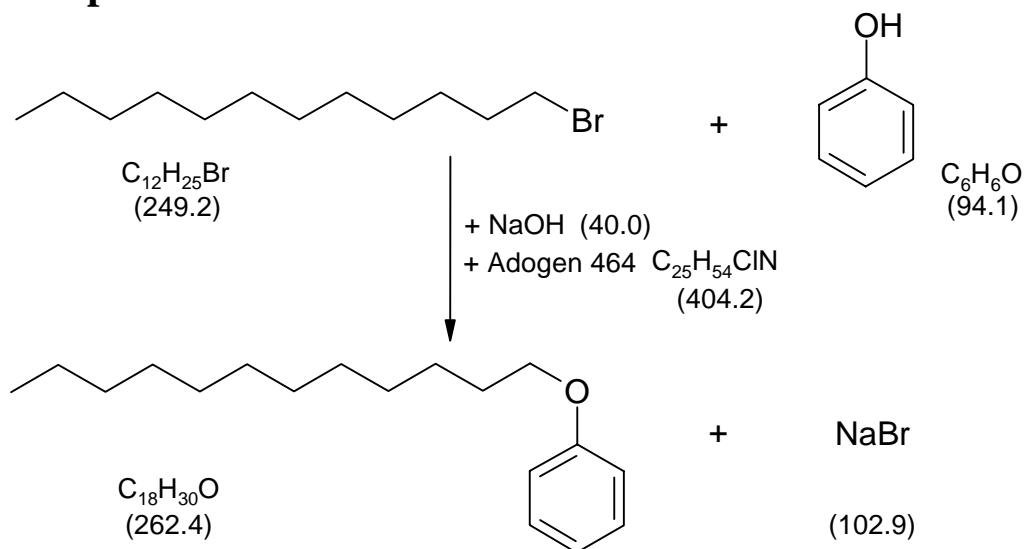


## 4029 Synthesis of dodecyl phenyl ether from bromododecane and phenol



### Classification

#### Reaction types and substance classes

Williamson's ether synthesis, nucleophilic substitution, phase transfer catalysis  
 bromoalkane, phenol, ether

#### Work methods

heating under reflux, stirring with magnetic stir bar, extracting, shaking out, filtering, evaporating with rotary evaporator, 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, separating funnel, Kugelrohr distillation apparatus or micro distillation apparatus, heatable magnetic stirrer, magnetic stir bar, rotary evaporator, vacuum pump, oil bath

#### Substances

bromododecane (bp 139 °C/13 hPa; product from NOP 4028)	2.49 g (2.39 mL, 10.0 mmol)
sodium hydroxide	0.480 g (12.0 mmol)
phenol (mp 41 °C, bp 182 °C)	1.13 g (12.0 mmol)
methyltrioctylammonium chloride (Adogen 464or Aliquat 336)	0.05 g (0.1 mmol)
water	2.5 mL (139 mmol)

<i>tert</i> -butyl methyl ether (bp 55 °C)	40 mL
aqueous sodium hydroxide solution (2 M)	10 mL
sodium sulfate for drying	about 1 g

**Reaction**

0.480 g (12.0 mmol) sodium hydroxide, 1.13 g (2.39 mL, 12.0 mmol) phenol, 2.49 g (10 mmol) bromododecane and 0.05 g Adogen 464 in 2.5 mL water are filled in a 10 mL two-neck round bottom flask with magnetic stir bar and reflux condenser and are heated under strong stirring for 6 hours in an oil bath to 115°C, until the bromododecane has completely reacted. The course of the reaction is followed by means of thin layer or gas chromatography (see analytics).

**Work up**

After cooling down, the reaction mixture is shaken out with 10 mL *tert*-butyl methyl ether. The aqueous phase is again shaken out three times with 10 mL *tert*-butyl methyl ether each, then the combined organic phases are washed with 10 mL 2 M sodium hydroxide solution and then with 10 mL water. The organic phase is dried over Na<sub>2</sub>SO<sub>4</sub>. After the drying agent is filtered off, the solvent is evaporated at a rotary evaporator. Crude yield: 2.49 g

The crude product is distilled in a Kugelrohr distillation apparatus at  $5.5 \cdot 10^{-2}$  hPa and 152 °C. Yield: 2.28 g (8.69 mmol, 87%); colourless liquid, which solidifies after standing for some time.

**Waste management****Recycling**

The evaporated *tert*-butyl methyl ether is collected and redistilled.

**Waste disposal**

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

**Time**

Reaction 4.5 hours

Distillation 2-3 hours

**Break**

After heating under reflux

After shaking out

Before distillation

**Degree of difficulty**

Medium

## Instruction (batch scale 100 mmol)

### Equipment

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

### Substances

bromododecane (bp 139 °C/13 hPa; product from NOP 4028)	24.9 g (23.9 mL, 100 mmol)
sodium hydroxide	4.80 g (120 mmol)
phenol (mp 41 °C, bp 182 °C)	11.3 g (120 mmol)
methyltrioctylammonium chloride (Adogen 464 or Aliquat 336)	0.5 g (1.2 mmol)
water	25 mL (1.4 mol)
<i>tert</i> -butyl methyl ether (bp 55 °C)	100 mL
aqueous sodium hydroxide solution (2 M)	25 mL
sodium sulfate for drying	about 5 g

### Reaction

4.80 g (120 mmol) sodium hydroxide, 11.3 g (120 mmol) phenol, 24.9 g (23.9 mL, 100 mmol) bromododecane and 0.5 g Adogen 464 in 25 mL water are filled in a 100 mL two-or three-neck flask with magnetic stir bar and reflux condenser and are heated under strong stirring for 6 hours in an oil bath to 115°C, until the bromododecane has completely reacted. The course of the reaction is followed by means of a thin layer or gas chromatography (see analytics).

### Work up

After cooling down, the reaction mixture is shaken out with 25 mL *tert*-butyl methyl ether. The aqueous phase is again shaken out three times with 25 mL *tert*-butyl methyl ether each, then the combined organic phases are washed with 25 mL 2 M aqueous sodium hydroxide solution and then with 25 mL water. The organic phase is dried over Na<sub>2</sub>SO<sub>4</sub>. After the drying agent is filtered off, the solvent is evaporated at a rotary evaporator. Crude yield: 24.2 g

The crude product is fractional distilled over a 10 cm Vigreux column. To avoid a solidifying of the distillate in the distillation bridge it is cooled with air instead of water.

Yield: 21.8 g (83.1 mmol, 83%); head temperature 131 °C, colourless liquid, which solidifies after standing for some time.

### Waste management

### Recycling

The evaporated *tert*-butyl methyl ether is collected and redistilled.

**Waste disposal**

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

**Time**

Reaction 5 hours

Distillation 2-3 hours

**Break**

After heating under reflux

After shaking out

Before distillation

**Degree of difficulty**

Medium

**Instruction (batch scale 1 mol)****Equipment**

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

**Substances**

bromododecane (bp 139 °C/13 hPa; product from NOP 4028)	249 g (239 mL, 1.00 mol)
sodium hydroxide	48.0 g (1.20 mol)
phenol (mp 41 °C, bp 182 °C)	113 g (1.20 mol)
methyltrioctylammonium chloride (Adogen 464 or Aliquat 336)	5 g (0.012 mol)
water	200 mL (11.1 mol)
<i>tert</i> -butyl methyl ether (bp 55 °C)	1.00 L
aqueous sodium hydroxide solution (2 M)	200 mL
sodium sulfate for drying	

**Reaction**

48.0 g (1.20 mol) sodium hydroxide, 113 g (1.20 mol) phenol, 249 g (239 mL, 1.00 mol) bromododecane and 5 g Adogen 464 in 2.5 mL water are filled in a 1 L two- or three-neck flask with magnetic stir bar and reflux condenser and are heated under strong stirring for 6 hours in an oil bath to 115°C, until the bromododecane has completely reacted. The course of the reaction is followed by means of thin layer or gas chromatography (see analytics).

**Work up**

After cooling down, the reaction mixture is shaken out with 250 mL *tert*-butyl methyl ether. The aqueous phase is again shaken out three times with 250 mL *tert*-butyl methyl ether each, then the combined organic phases are washed with 200 mL 2 N NaOH and then with 200 mL water. The organic phase is dried over Na<sub>2</sub>SO<sub>4</sub>. After the drying agent is filtered off, the solvent is evaporated. Crude yield: 246 g

The crude product is fractional distilled over a 30 cm Vigreux column. To avoid a solidifying of the distillate, the distillation bridge is cooled with air instead of water.

Yield: 221 g (0.842 mol, 84%); head temperature 145 °C, colourless liquid, which solidifies after standing for some time.

**Waste management****Recycling**

The evaporated *tert*-butyl methyl ether is collected and redistilled.

**Waste disposal**

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

**Time**

Reaction 12 hours

Distillation 6 hours

**Break**

After heating under reflux

After shaking out

Before distillation

**Degree of difficulty**

Medium

## Analytics

### Reaction monitoring with TLC

Sample preparation:

Using a Pasteur pipette, one drop from the reaction mixture is taken and diluted with 0.5 mL diethyl ether.

TLC-conditions:

adsorbant: TLC-aluminium foil (silica gel 60)  
 eluent: petroleum ether (60-80 °C)  
 visualizing agent: The TLC-aluminium foil is dipped in 2 M H<sub>2</sub>SO<sub>4</sub> and then dried with a hot-air dryer.

R<sub>f</sub> (dodecylphenyl ether) 0.22

R<sub>f</sub> (bromododecane) 0.53

### Reaction monitoring with GC

Sample preparation:

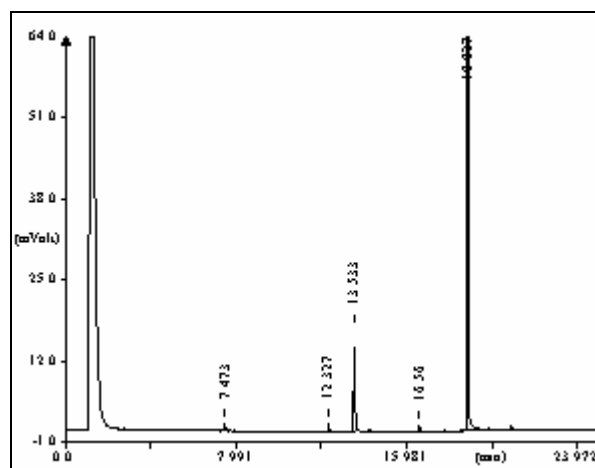
Using a Pasteur pipette, one drop of the crude or pure product is taken and diluted with 10 mL dichloromethane. 0.2 µL from this solution are injected.

GC-conditions:

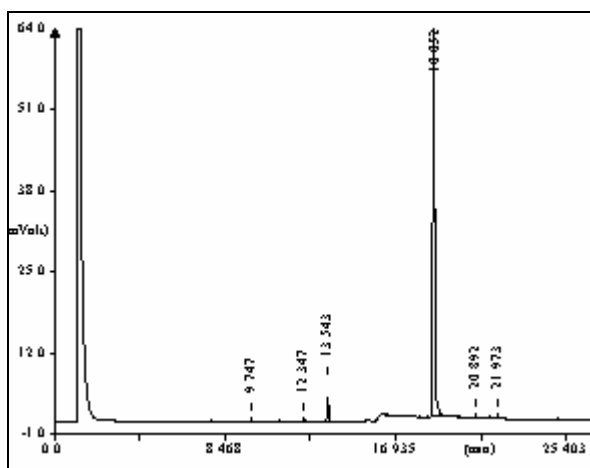
column: DB-1, 28 m, internal diameter 0.32 mm, film 0.25 µm  
 inlet: on-column-injection  
 carriergas: hydrogen(40 cm/sec)  
 oven: 90 °C (5 min), 10 °C/min on 240 °C (30 min)  
 detector: FID, 270 °C

Percent concentration was calculated from peak areas.

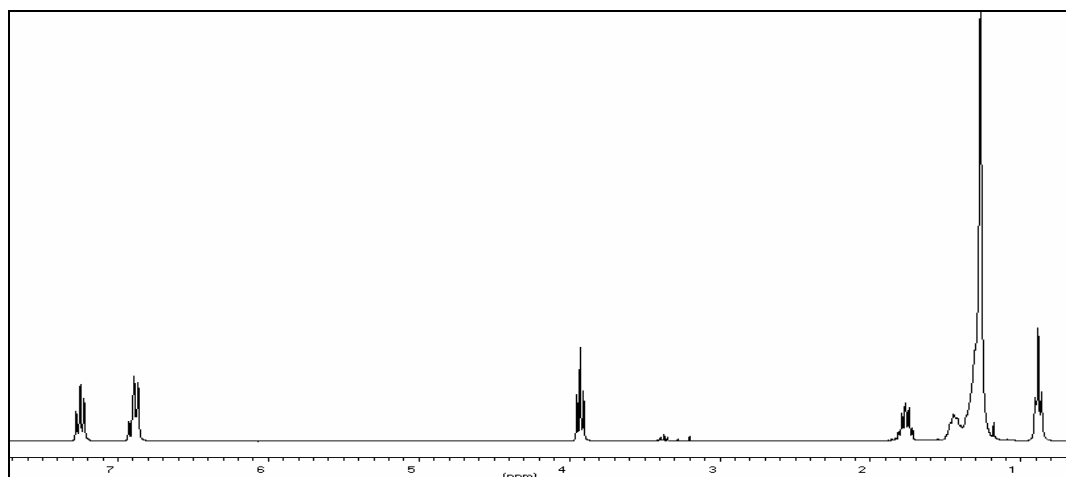
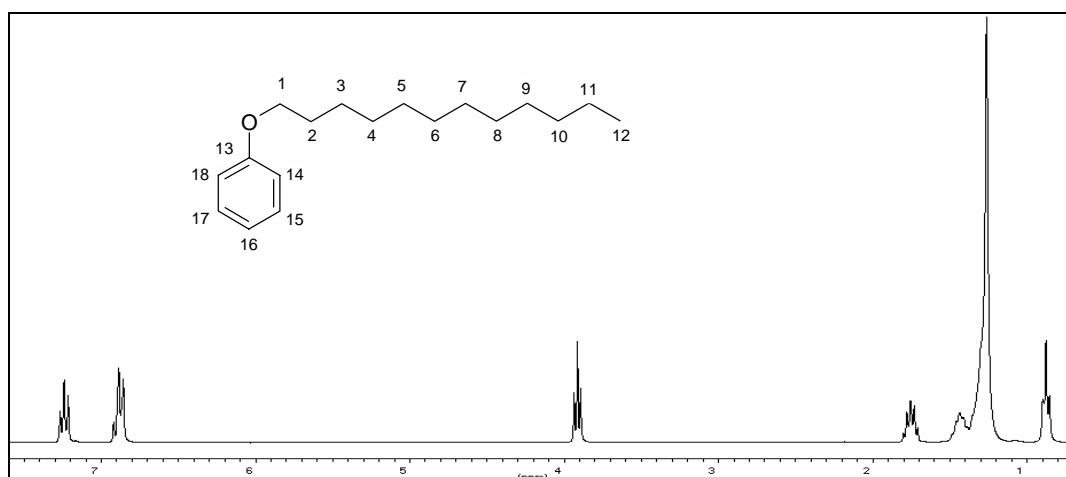
#### GC of the crude product (1 mol batch scale)



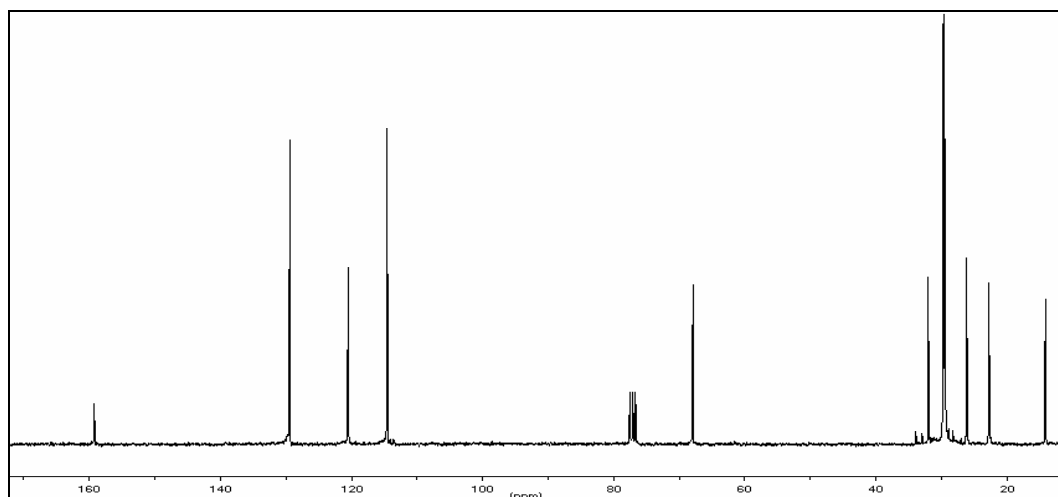
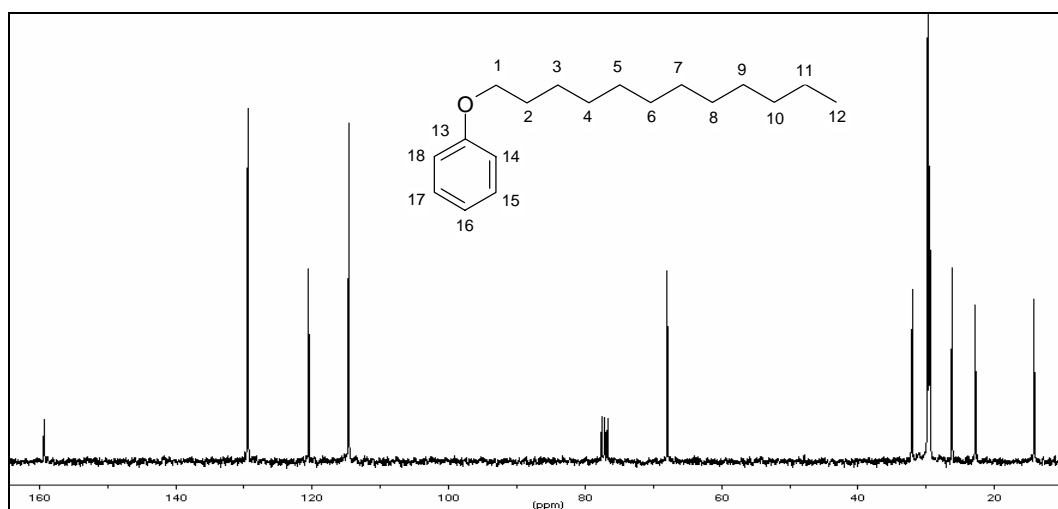
#### GC of the pure product (1 mol batch scale)



Retention time (min)	Substance	Peak area %	
		crude product	pure product
18.85	product (dodecyl phenyl ether)	94.4	98.3
13.54	educt (bromododecane)	4.4	1.1
Others	unknown impurities	< 0.5 per peak	< 0.5 per peak

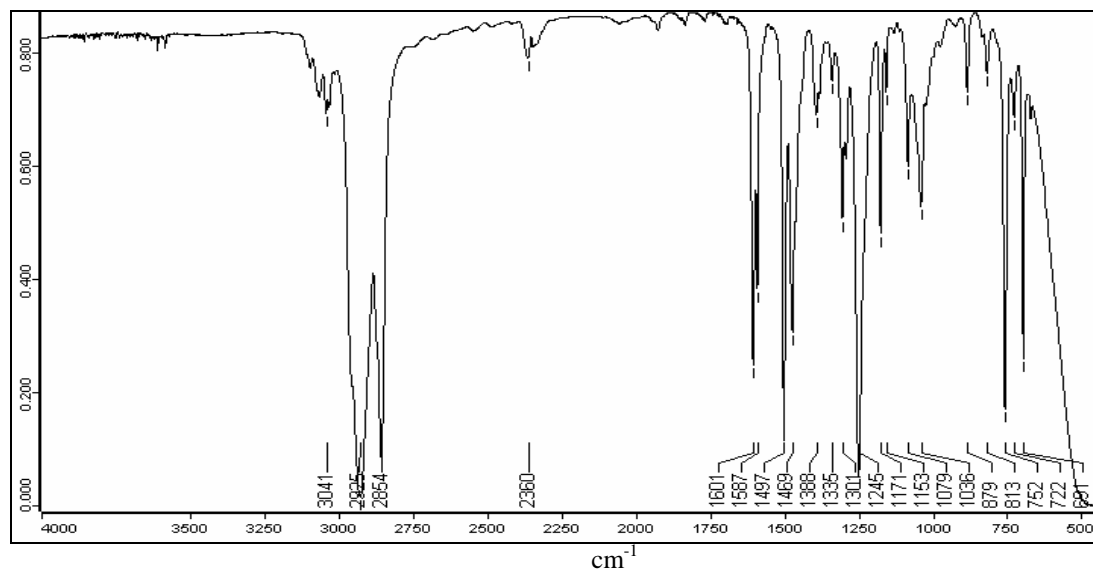
**$^1\text{H}$  NMR spectrum of the crude product (300 MHz,  $\text{CDCl}_3$ )** **$^1\text{H}$  NMR spectrum of the pure product (300 MHz,  $\text{CDCl}_3$ )**

$\delta$ (ppm)	Multiplicity	Number of H	Assignment
0.88	t	3	12-H
1.27	m	16	remaining $\text{CH}_2$
1.44	m	2	3-H
1.75	m	2	2-H
3.91	t	2	1-H
6.88	m	3	14-H, 16-H, 18-H
7.25	dd	2	15-H, 17-H

**$^{13}\text{C}$  NMR spectrum of the crude product (75.5 MHz,  $\text{CDCl}_3$ )** **$^{13}\text{C}$  NMR spectrum of the pure product (75.5 MHz,  $\text{CDCl}_3$ )**

$\delta$ (ppm)	Assignment
14.0	C-12
22.7	C-11
67.9	C-1
114.5	C-14, C-18
120.4	C-16
129.4	C-15, C-17
159.2	C-13
76.5-77.5	solvent



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

( $\text{cm}^{-1}$ )	Assignment
3070, 3041	C-H-valence, arene
2995	C-H-valence, alkane
2854	C-H-valence, alkane, ether
1601, 1587, 1497	C=C-valence, arene