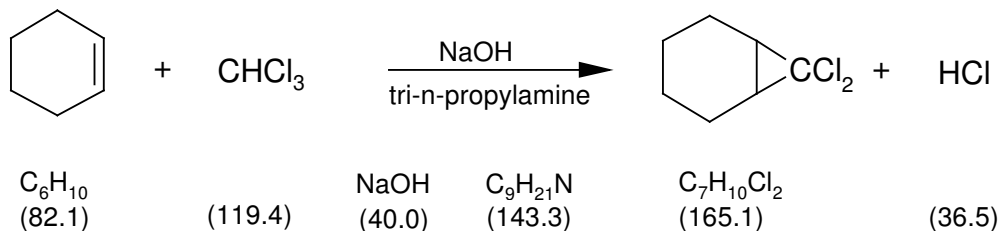


3005 Synthesis of 7,7-dichlorobicyclo[4.1.0]heptane (7,7-dichlornorcarane) from cyclohexene



Classification

Reaction types and substance classes

addition to alkenes, elimination, cycloaddition

alkene, carben, chloroalkane

Work methods

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

Instruction (batch scale 100 mmol)

Equipment

100 mL three neck round bottom flask, reflux condenser, addition funnel with pressure balance, heatable magnetic stirrer, magnetic stir bar, thermometer for inside of the flask, separating funnel, distillation apparatus, rotary evaporator, oil bath, ice bath, vacuum pump

Substances

cyclohexene (bp 83 °C)	8.21 g (10.1 mL, 100 mmol)
chloroform (bp 61 °C)	48.0 g (32.7 mL, 400 mmol)
sodium hydroxide	16.0 g (400 mmol)
tri- <i>n</i> -propylamine (bp 156 °C)	0.14 g (0.19 mL, 1.0 mmol)
water	16 mL
ethanol (bp 78 °C)	1 mL
<i>n</i> -pentane (bp 36 °C)	120 mL
sodium sulfate for drying	about 5 g
sodium chloride	about 18 g

Reaction

Into a 100 mL three neck round bottom flask equipped with a reflux condenser addition funnel, thermometer for measuring the inside temperature and magnetic stir bar, 8.21 g

(10.1 mL, 100 mmol) cyclohexene 0.14 g (0.19 mL, 1.0 mmol) tri-*n*-propylamine, 48.0 g (32.7 mL, 400 mmol) chloroform and 1 mL ethanol is added. The mixture is cooled to 0 °C with an ice bath, then under stirring and further cooling in the ice bath a solution of 16.0 g (400 mmol) sodium hydroxide in 16 mL water is added through an addition funnel. The mixture should be stirred vigorously during the next 20 minutes at 0 °C. After this time the mixture is further stirred during 1 hour at room temperature and 3 hours at 50 °C.

Work up

Chloroform is evaporated with a rotary evaporator, then the residue is transferred with about 50 mL water and 30 mL *n*-pentane into a separating funnel. The organic phase is separated, the aqueous phase is further extracted three times with 30 mL pentane. If an emulsion is formed the aqueous phase is saturated with NaCl. The combined organic phases are dried over sodium sulfate. The solution is filtered from sodium sulfate and the solvent is evaporated with a rotary evaporator, yielding a nearly colourless liquid as crude product. The crude yield is 14.6 g. The crude product is distilled under reduced pressure.

Yield: 13.6 g (82.3 mmol, 82%), colourless liquid; bp 77 °C (11 hPa)

Waste management

Waste disposal

Waste	Disposal
evaporated chloroform (may contain some cyclohexene)	organic solvents, containing halogen
evaporated <i>n</i> -pentane (may contain some chloroform)	organic solvents, containing halogen
aqueous phase, after extraction	solvent water mixtures, containing halogen
distillation residue	organic solvents, containing halogen
sodium sulfate	solid waste, free from mercury

Time

6 hours

Break

Before work up

Degree of difficulty

Easy

Instruction (batch scale 10 mmol)

Equipment

100 mL three neck round bottom flask, reflux condenser, addition funnel with pressure balance, heatable magnetic stirrer, magnetic stir bar, thermometer for inside of the flask, separating funnel, distillation apparatus, rotary evaporator, oil bath, ice bath, vacuum pump

Substances

cyclohexene (bp 83 °C)	0.821 g (1.01 mL, 10.0 mmol)
chloroform (bp 61 °C)	7.5 g (5.0 mL, 62 mmol)
sodium hydroxide	1.60 g (40.0 mmol)
tri- <i>n</i> -propylamine (bp 156 °C)	0.014 g (0.02 mL, 0.10 mmol)
water	1.6 mL
ethanol (bp 78 °C)	0.1 mL
<i>n</i> -pentane (bp 36 °C)	65 mL
sodium sulfate for drying	about 1 g
sodium chloride	about 2 g

Reaction

Into a 10 mL three neck round bottom flask equipped with a reflux condenser addition funnel, thermometer for measuring the inside temperature and magnetic stirring bar, 0.82 g (1.01 mL, 10.0 mmol) cyclohexene 0.014 g (0.019 mL, 0.1 mmol) tri-*n*-propylamine, 4.8 g (0.5 mL, 62 mmol) chloroform and 0.1 mL ethanol is added. The mixture is cooled to 0 °C with an ice bath, then under stirring and further cooling of the ice bath a solution of 1.6 g (40.0 mmol) sodium hydroxide in 1.6 mL water is added by a addition funnel. The mixture should be stirred vigorously during the next 20 minutes at 0 °C. After this time the mixture is further stirred during 1 hour at room temperature and 3 hours at 50 °C.

Work up

Chloroform is evaporated with a rotary evaporator, then the residue is transferred with about 5 mL water and 5 mL *n*-pentane into a separating funnel. The organic phase is separated, the aqueous phase is further extracted three times with 20 mL pentane. If an emulsion is formed the aqueous phase is saturated with NaCl. The combined organic phases are dried over sodium sulfate. The solution is filtered from sodium sulfate and the solvent is evaporated with a rotary evaporator, yielding a nearly colourless liquid as crude product. The crude yield is 1.4 g. The crude product is distilled under reduced pressure.

Yield 1.3 g (8.2 mmol, 82%), colourless liquid; bp 77 °C (11 hPa)

Waste management**Waste disposal**

Waste	Disposal
evaporated chloroform (may contain some cyclohexene)	organic solvents, containing halogen
evaporated <i>n</i> -pentane (may contain some chloroform)	organic solvents, containing halogen
aqueous phase, after extraction	solvent water mixtures, containing halogen
distillation residue	organic solvents, containing halogen
sodium sulfate	solid waste, free from mercury

Time

6 hours

Break

Before work up

Degree of difficulty

Easy

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

100 mL three neck round bottom flask, reflux condenser, addition funnel with pressure balance, heatable magnetic stirrer, magnetic stir bar, thermometer for inside of the flask, separating funnel, distillation apparatus, rotary evaporator, oil bath, ice bath, vacuum pump

Substances

cyclohexene (bp 83 °C)	82.1 g (101 mL, 1.00 mol)
chloroform (bp 61 °C)	480 g (327 mL, 4.00mol)
sodium hydroxide	160 g (4.00 mol)
tri- <i>n</i> -propylamine (bp 156 °C)	1.4 g (1.9 mL, 10 mmol)
water	160 mL
ethanol (bp 78 °C)	10 mL
<i>n</i> -pentane (bp 36 °C)	600 mL
sodium sulfate for drying	about 5 g
sodium chloride	about 35g

Reaction

Into a 1000 mL three neck round bottom flask equipped with a reflux condenser addition funnel, thermometer for measuring the inside temperature and magnetic stir bar, 82.1 g (10.1 mL, 4 mol) cyclohexene 1.4 g (1.9 mL, 10 mmol) tri-*n*-propylamine, 480 g (327 mL, 400 mmol) chloroform and 10 mL ethanol is added. The mixture is cooled to 0 °C with an ice bath, then under stirring and further cooling of the ice bath a solution of 160 g (4mol) sodium hydroxide dissolved in 160 mL water is added by a addition funnel. The mixture should be stirred vigorously during the next 20 minutes at 0 °C. After this time the mixture is further stirred during 1 hour at room temperature and 3 hours at 50 °C.

Work up

Chloroform is evaporated with a rotary evaporator, then the residue is transferred with about 100 mL water and 150 mL *n*-pentane into a separating funnel. The organic phase is separated, the aqueous phase is further extracted three times with 150 mL pentane. If an emulsion is formed the aqueous phase is saturated with sodium chloride. The combined organic phases are dried over sodium sulfate. The solution is filtered from sodium sulfate and the solvent is

evaporated with a rotary evaporator, yielding a nearly colourless liquid as crude product. The crude yield is 151.0 g. The crude product is distilled under reduced pressure.

Yield: 139 g (0.842 mol, 84%), colourless liquid; bp 77 °C (11 hPa)

Waste management

Waste disposal

Waste	Disposal
evaporated chloroform (may contain some cyclohexene)	organic solvents, containing halogen
evaporated <i>n</i> -pentane (may contain some chloroform)	organic solvents, containing halogen
aqueous phase, after extraction	solvent water mixtures, containing halogen
distillation residue	organic solvents, containing halogen
sodium sulfate	solid waste, free from mercury

Time

6 hours

Break

Before work up

Degree of difficulty

Easy

Analytics

GC

Sample preparation:

One drop of the compound is dissolved in 1 mL *tert*-butyl methyl ether, 1 µL is injected.

GC conditions:

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

inlet: Gerstel KAS, injector 250 °C;

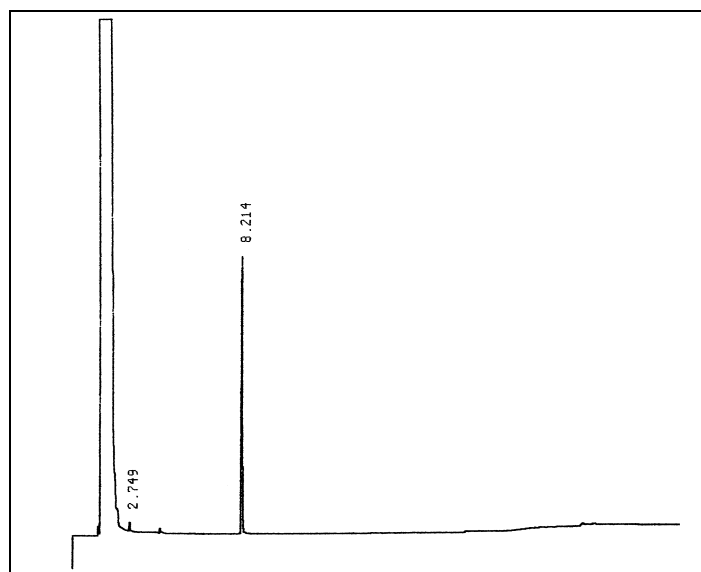
split injection: 1:20, injected volume 1 µL

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

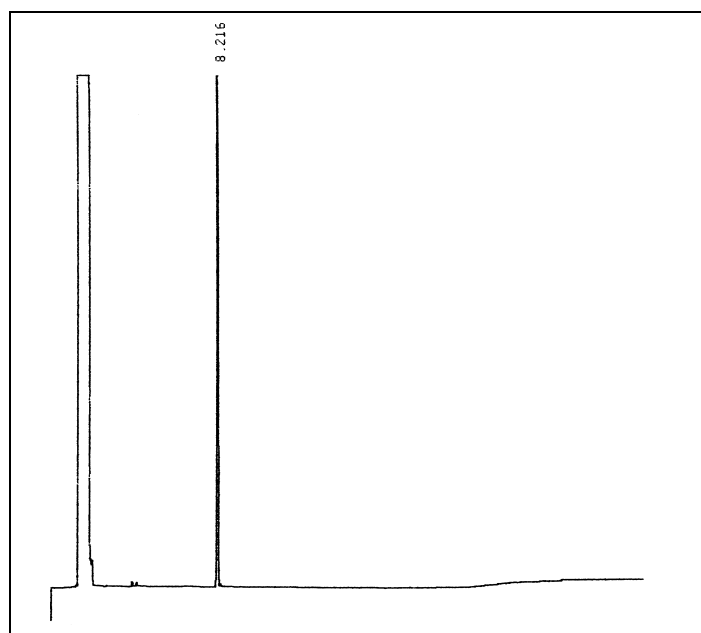
oven: 80 °C (1 min), 10 °C/min (250 °C) (30 min)

detector: FID, 275 °C

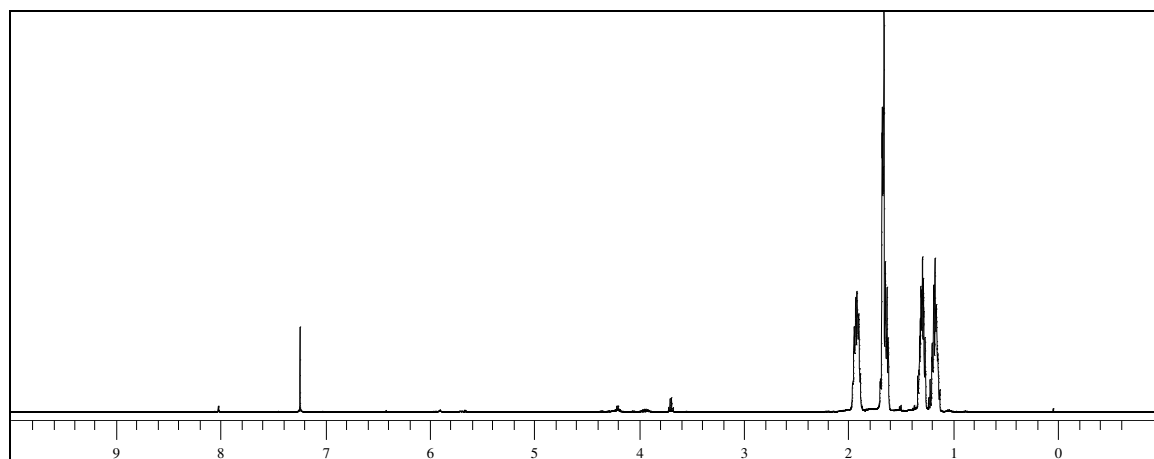
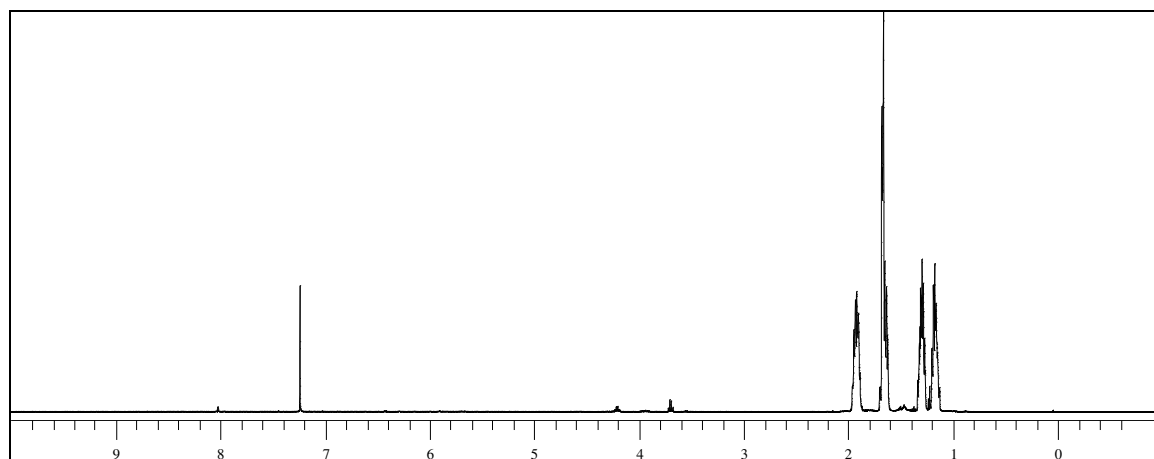
Percent concentration was calculated from peak areas.

GC of the crude product

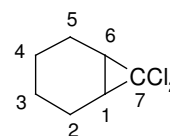
Retention time (min)	Substance	Peak area %
8.2	7,7-dichloronorcarane	98
2.7	not identified	2

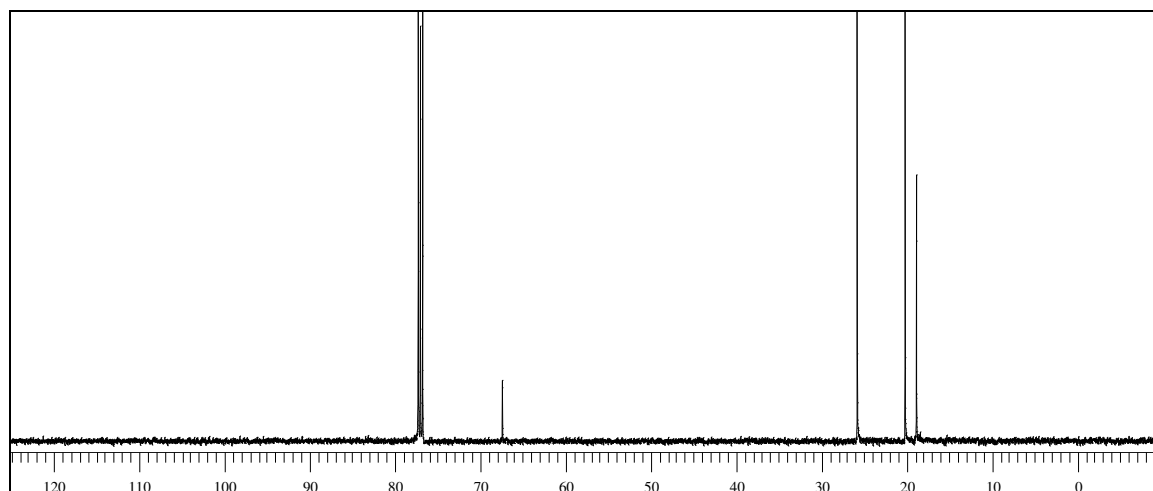
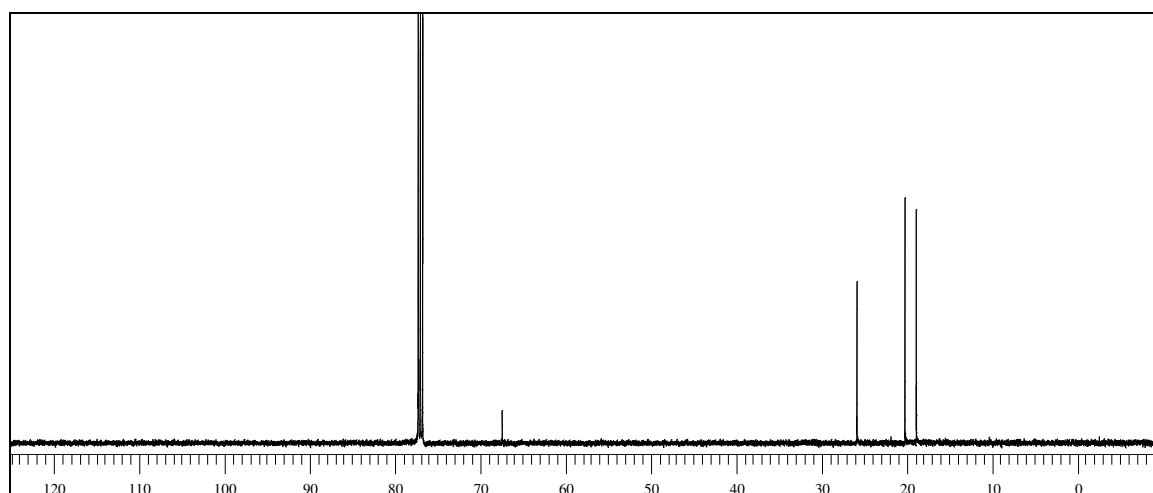
GC of the pure product

Retention time (min)	Substance	Peak area %
8.2	7,7-dichloronorcarane	> 99

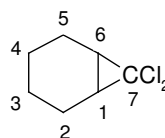
^1H NMR spectrum of the crude product (500 MHz, CDCl_3) **^1H NMR spectrum of the pure product (500 MHz, CDCl_3)**

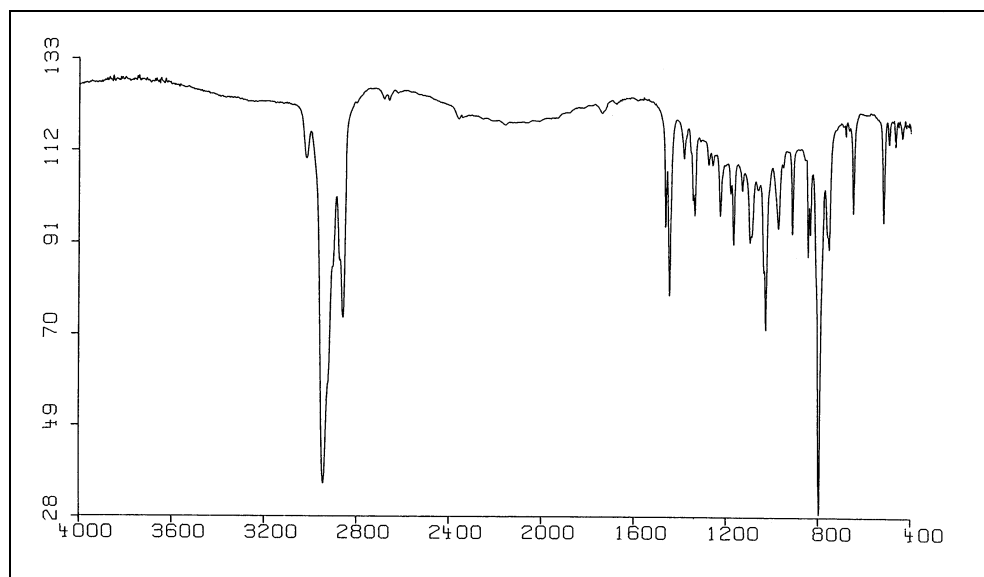
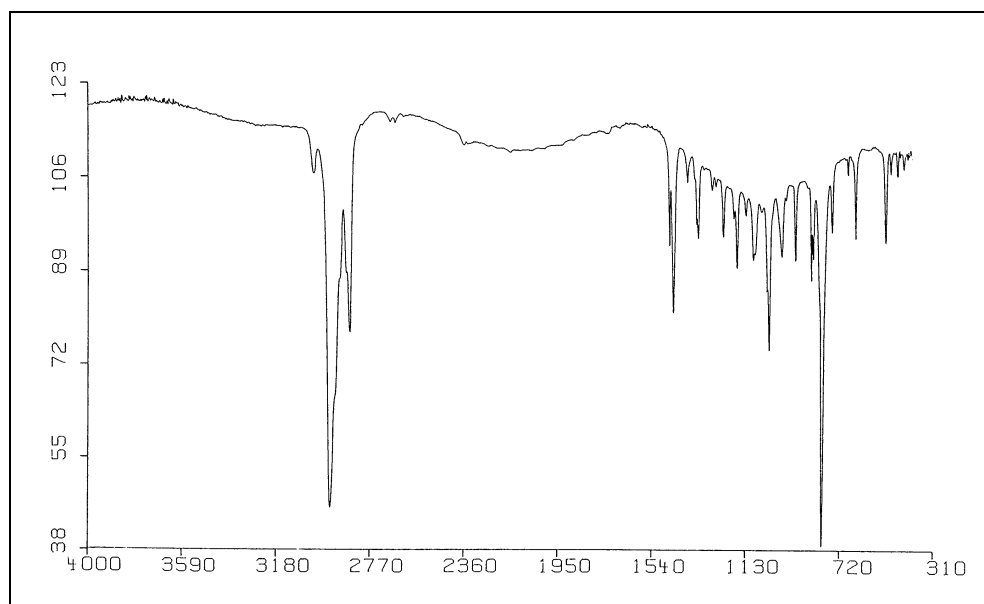
δ (ppm)	Multiplicity	Number of H	Assignment
1.12 - 1.36	m	4	3-H, 4-H
1.61 - 1.71	m	4	2-H, 5-H
1.88 - 1.98	m	2	1-H, 6-H
7.26			solvent



^{13}C NMR spectrum of the crude product (125 MHz, CDCl_3) **^{13}C NMR spectrum of the purified product (125 MHz, CDCl_3)**

δ (ppm)	Assignment
18.9	C-3, C-4
20.2	C-2, C-5
25.8	C-1, C-6
67.4	C-7
76.5-77.5	solvent



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

(cm⁻¹)	Assignment
2944, 2859	C-H-valence, alkane
796	C-Cl-valence