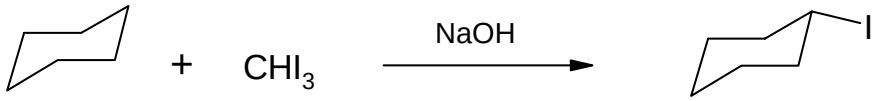
# 3015 Synthesis of iodocyclohexane from cyclohexane and iodoform




| $C_6H_{12}$ | $CHI_3$ | | $C_6H_{11}I$ |
|---|---|---|---|
| (84.2) | (393.7) | (40.0) | (210.1) |

**Literature**

P. R. Schreiner, O. Lauenstein, E. D. Butova, and A. A. Fokin, *Angew. Chem.* **1999**, *111*, 2956-2958; *Angew. Chem. Int. Ed. Engl*. **1999**, *38*, 2786-2788

P. R. Schreiner, O. Lauenstein, E. D. Butova, P. A. Cunchenko, I. V. Kolomistin, A. Wittkopp, G. Feder, A. A. Fokin, *Chem. Eur. J*., **2001**, *7*, 4997

## Classification

**Reaction types and substance classes:**

iodination, radical reaction
alkane, iodoalkane

**Work methods:**

working with light exclusion, stirring with magnetic stir bar, shaking out, extracting, filtering, evaporating with rotary evaporator, distilling under reduced pressure

## Instruction (batch scale 50 mmol)

**Equipment**

250 mL round bottom flask, magnetic stirrer, magnetic stir bar, distillation apparatus, vacuum pump, rotary evaporator, oil bath

**Substances**

| | |
|---|---|
| cyclohexane (bp 81 °C) | 180 mL, 140 g, 1.66 mol, |
| iodoform (triiodomethane) (mp 123 °C) | 19.7 g (50.0 mmol) |
| sodium hydroxide | 28.2 g (706 mmol) |
| cyclohexane (bp 81 °C) | 150 mL |

**Reaction**

180 mL (140 g, 1.66 mol) cyclohexane, 28.2 g (706 mmol) finely powdered NaOH and 19.7 g (50.0 mmol) iodoform are filled into a 250 mL round bottom flask equipped with an efficient magnetic stir bar. The flask is locked with a glass stopper and is wrapped with tin foil in order

to protect the content from light effect. The mixture is stirred for 48 hours at topmost-possible stirring speed at room temperature.

**Work up**
The mixture is filtered and the solid residue five times extracted with 30 mL cyclohexane each. From the organic phases the solvent is removed with a rotary evaporator under slightly reduced pressure (300 hPa). A greasy liquid remains as crude product.
Crude yield: 8.90 g

The crude product is distilled at reduced pressure.
Yield: 5.80 g; (27.6 mmol, 55%); bp 72 °C (13 hPa), clear, easily yellow, viscous liquid.

**Waste management**

**Waste disposal**

| Waste | Disposal |
|---|---|
| filter residue | solid waste, free from mercury |
| evaporated cyclohexane | organic solvents, halogen free |
| distillation residue | dissolve in a small amount of acetone, then: organic solvents, containing halogen |

**Comments**
Since the reaction mixture is heterogeneous, the reaction speed depends strongly on the stirring speed.

**Time**
50 hours, with 48 hours of stirring

**Break**
Before the work up

**Degree of difficulty**
Easy

## Instruction (batch scale 10 mmol)

**Equipment**
100 mL round bottom flask, magnetic stirrer, magnetic stir bar, microdistillation apparatus, vacuum pump, rotary evaporator, oil bath

**Substances**

| | |
|---|---|
| cyclohexane (bp 81 °C) | 60 mL, (46.8 g, 556 mmol) |
| iodoform (triiodomethane) (mp. 123 °C) | 3.94 g (10.0 mmol) |
| sodium hydroxide | 5.65 g (142 mmol) |
| cyclohexane (bp 81 °C) | 50 mL |

**Reaction**
80 mL (46.8 g, 556 mmol) cyclohexane, 5.65 g (142 mmol) finely powdered NaOH and 3.94g (10.0 mmol) iodoform are filled into a 100 mL round bottom flask equipped with an efficient magnetic stir bar. The flask is locked with a glass stopper and is wrapped with tin foil in order to protect the content from light effect. The mixture is stirred for 48 hours with topmost-possible stirring speed at room temperature.

**Work up**
The mixture is filtered and the solid residue three times extracted with 10 mL cyclohexane each. From the organic phases the solvent is removed with a rotary evaporator under slightly reduced pressure (300 hPa). A greasy liquid remains as crude product.
Crude yield: 1.90 g

The crude product is distilled in a microdistillation apparatus at reduced pressure.
Yield: 1.20 g (5.71 mmol, 57%, bp 72 °C (13 hPa),
clear, easily yellow, viscous liquid.

**Waste management**

**Waste disposal**

| Waste | Disposal |
|---|---|
| filter residue | solid waste, free from mercury |
| abrotiertes cyclohexane | organic solvents, halogen free |
| distillation residue | dissolve in a small amount of acetone, then: organic solvents, containing halogen |

**Comments**
Since the reaction mixture is heterogeneous, the reaction speed depends strongly on the Rührgeschwindigkeit.

**Time**
50 hours, with 48 hours of stirring

**Break**
Before the work up

**Degree of difficulty**
Easy

# Analytics

## GC

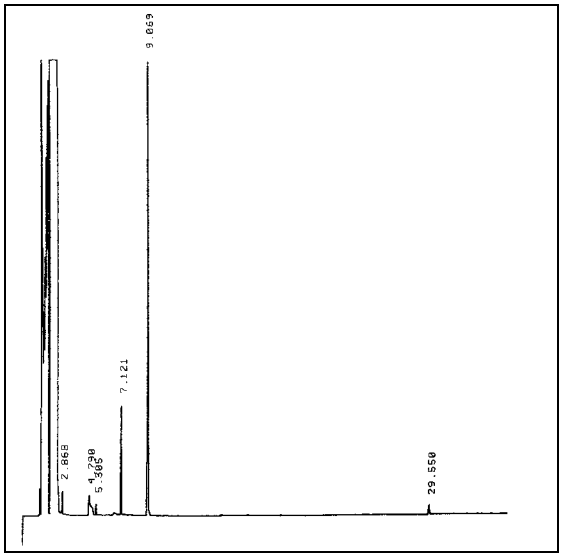
Sample preparation:
One drop of the compound is dissolved in 1 mL *tert*-butyl methyl ether, 1 µL is injected.

GC conditions:

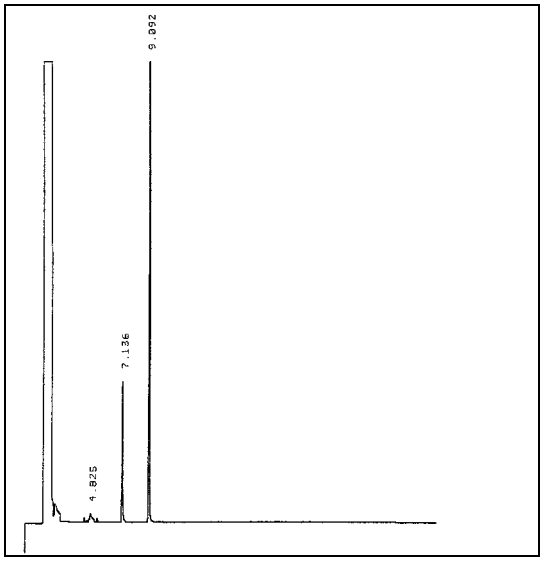
| | |
|---|---|
| column: | Macherey und Nagel, SE-54, 326-MN-30705-9, 25 m, ID 0.32 mm, DF 0.25 µm |
| inlet: | Gerstel KAS, injector 250 °C; |
| | split injection: 1:20, injected volume 1 µL |
| carrier gas: | nitrogen, pre-column pressure 62 kPa, flow rate 1.04 mL/min |
| oven: | 80 °C (1 min), 5 °C/min, 250 °C (30 min) |
| detector: | FID, 275 °C |

Percent concentration was calculated from peak areas.

### GC of the crude product

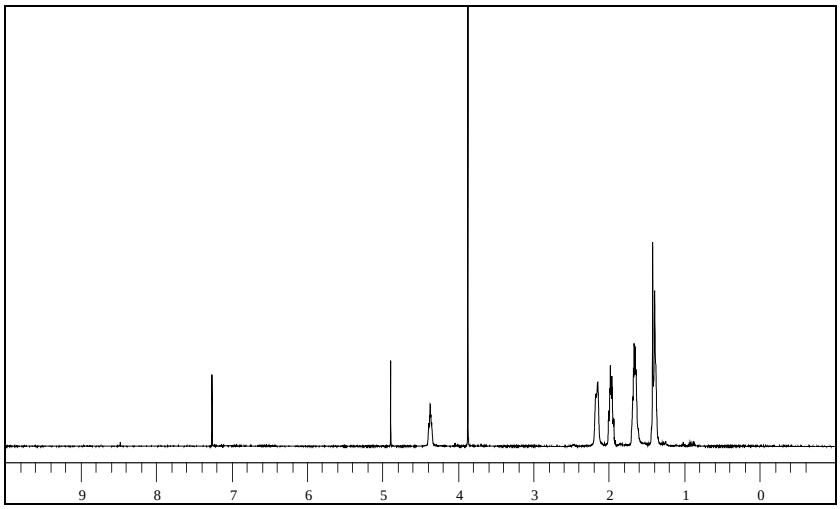



### GC of the pure product

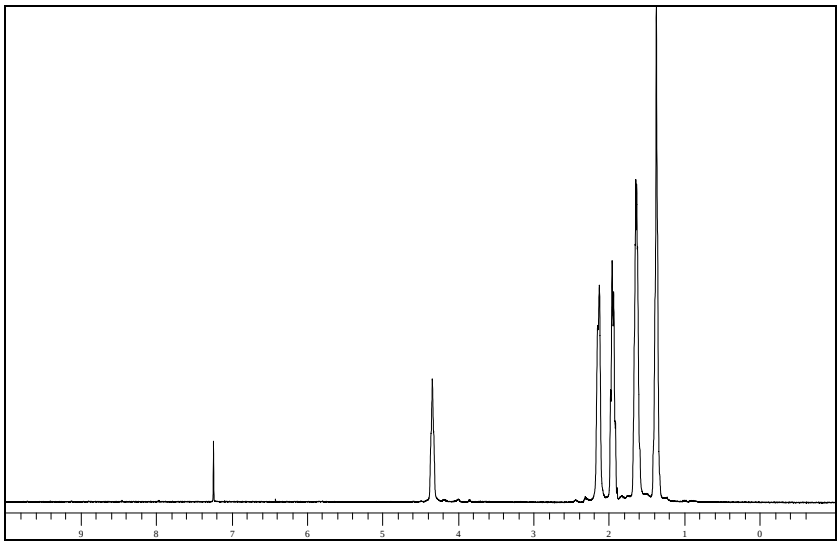



| Retention time (min) | Substance | | Peak area % | |
|---|---|---|---|---|
| | | | Crude product | Pure product |
| 9.1 | product (iodocyclohexane) | | 72 | 81 |
| 7.1 | unidentified | (probably thermic | 15 | 16 |
| others | unidentified | decomposition products) | 13 | 3.5 |

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



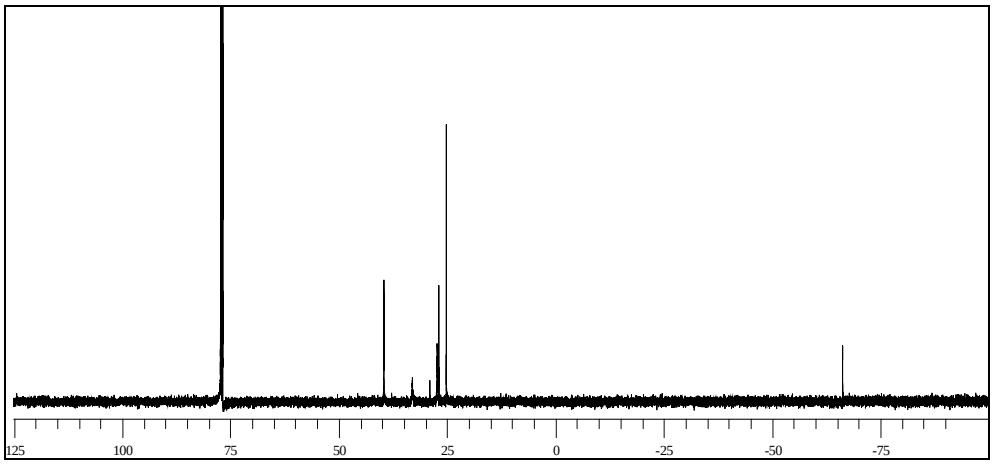

**$^1$H NMR spectrum of the pure product** (500 MHz, $CDCl_3$)



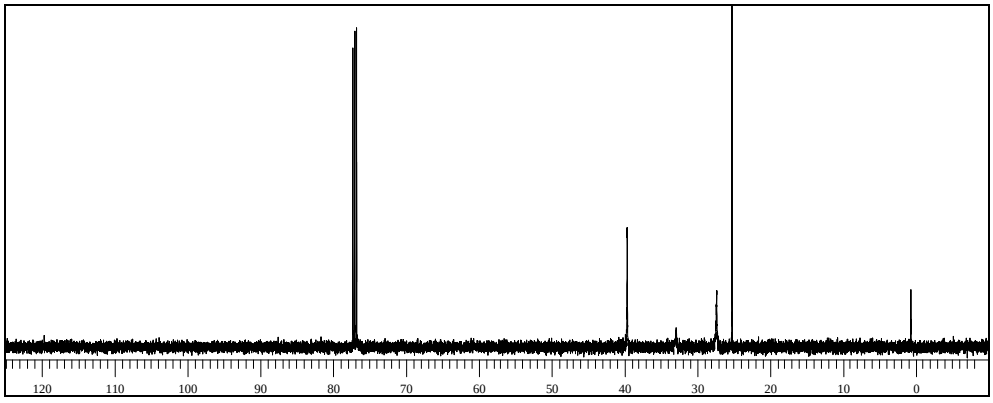

| δ (ppm) | Multiplicity | Number of H | Assignment |
|---|---|---|---|
| 1.32 – 1.42 | M | 3 | C**H$_2$** |
| 1.58 - 1.69 | M | 3 | C**H$_2$** |
| 1.89 - 2.00 | M | 2 | C**H$_2$** |
| 2.10 - 2.18 | M | 2 | C**H$_2$** |
| 4.30 - 4.38 | M | 1 | C**H**I |
| 7.26 | | | solvent |

The signal at 3.87 ppm in the spectrum of the crude product originates from the diiodmethane.

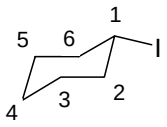
**$^{13}$C NMR spectrum of the crude product** (125 MHz, $CDCl_3$)




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

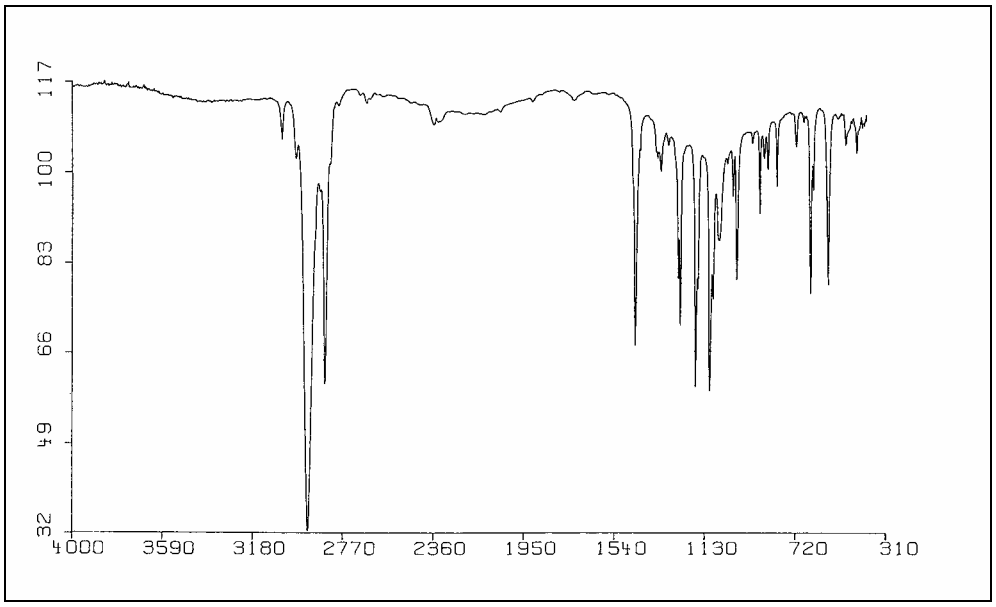



| δ (ppm) | Assignment |
|---|---|
| 25.2 | C-4 |
| 27.3 | C-3, C-5 |
| 32.9 | C-1 |
| 39.6 | C-2, C-6 |
| 76.5-77.5 | solvent |

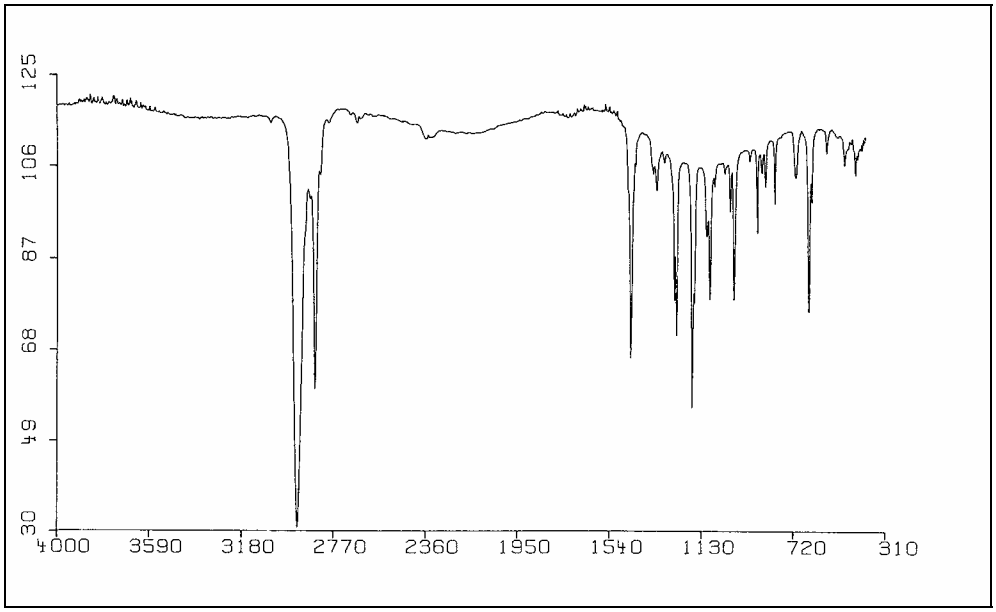



The signal at - 66.3 ppm in the spectrum of the crude product originates from the diiodmethane.

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




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




| **($cm^{-1}$)** | **Assignment** |
|---|---|
| 2931, 2875, 2853, 2829 | C-H-valence, alkane |
| 574 | C-I-valence |