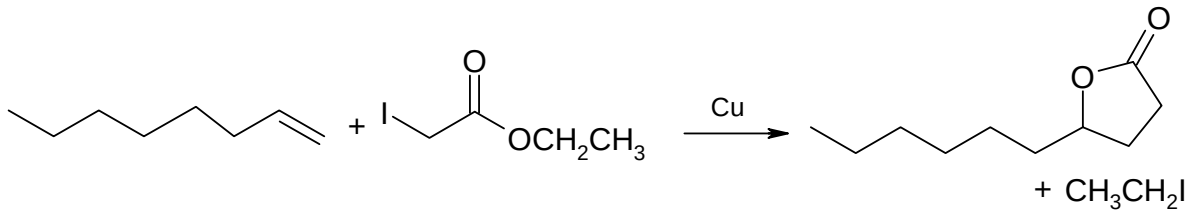
4004 Synthesis of gamma-decalactone from 1-octene and iodoacetic acid ethyl ester



C_8H_{16}	$C_4H_7IO_2$		$C_{10}H_{18}O_2$	C_2H_5I
(112.2)	(214.0)	(63.6)	(170.3)	(156.0)

Classification

Reaction types and substance classes

addition to alkenes, radical reaction, ring closure reaction
alkene, halogencarboxylic acid ester, lactone

Work methods

working with protective gas, stirring with magnetic stir bar, heating under reflux, evaporating with rotary evaporator, filtering, distilling under reduced pressure, heating with oil bath

Instruction (batch scale 10 mmol)

Equipment

50 mL two-neck flask, protective gas supply, reflux condenser, heatable magnetic stirrer, magnetic stir bar, rotatory evaporator, vacuum pump, half-micro distillation apparatus, oil bath

Substances

1-octen (bp 121 °C)	1.12 g (1.56 mL, 10.0 mmol)
iodoacetic acid ethyl ester (bp 73-74 °C/ 21 hPa)	2.78 g (1.54 mL, 13.0 mmol)
copper powder (finely powdered, > 230 mesh ASTM)	1.53 g (24.0 mmol)
tert-butyl methyl ether (bp 55 °C)	35 mL

Reaction

In a 50 mL two-neck flask with magnetic stir bar and a reflux condenser connected with a protective gas piping 1.12 g (1.56 mL, 10.0 mmol) 1-octen are mixed with 2.78 g (1.54 mL, 13.0 mmol) iodoacetic acid ethyl ester and 1.53 g (24.0 mmol) copper powder under a protective gas atmosphere. Afterwards the reaction mixture is stirred at 130 °C oil bath temperature under protective gas for 2 hours under reflux.

Work up

The reaction mixture is cooled down to room temperature, diluted with 20 mL *tert*-butyl methyl ether, stirred for 5 minutes and filtered off. The copper powder on the filter is washed three times with 5 mL *tert*-butyl methyl ether each. Filtrate and wash solutions are combined, the solvent is evaporated at the rotary evaporator. A liquid residue remains as crude product.
Crude yield: 1.5 g

The crude product is fractional distilled in a half-micro distillation apparatus under reduced pressure.
Yield: 1.30 g (7.63 mmol, 77%); head temperature 85 °C ($4.8 \cdot 10^{-2}$ hPa, oil bath temperature 120 °C), colourless liquid; $n_D^{20} = 1.4508$

Waste management

Waste disposal

Waste	Disposal
evaporated *tert*-butyl methyl ether (might contain iodoethane)	organic solvents, containing halogen
distillation residue	organic solvents, containing halogen
copper powder	solid waste, free from mercury, containing heavy metals

Time

6 hours

Break

After heating and before distillation

Degree of difficulty

Easy

Instruction (batch scale 100 mmol)

Equipment

100 mL two-neck flask, protective gas supply, reflux condenser, heatable magnetic stirrer, magnetic stir bar, rotatory evaporator, high vacuum pump, distillation apparatus, oil bath

Substances

1-octen (bp 121 °C)	11.2 g (15.6 mL, 100 mmol)
iodoacetic acid ethyl ester (bp 73-74 °C/ 21 hPa)	27.8 g (15.4 mL, 130 mmol)
copper powder (finely powdered, > 230 mesh ASTM)	15.3 g (240 mmol)
tert-butyl methyl ether (bp 55 °C)	130 mL

Reaction

In a 100 mL two-neck flask with magnetic stir bar and a reflux condenser connected with a protective gas piping 11.2 g (15.6 mL, 100 mmol) 1-octen are mixed with 27.8 g (15.4 mL, 130 mmol) iodoacetic acid ethyl ester and 15.1 g (240 mmol) copper powder under a protectiv gas atmosphere. Afterwards the reaction mixture is stirred at 130 °C oil bath temperature under protective gas for 6 hours under reflux.

Work up

The reaction mixture is cooled down to room temperature, diluted with 30 mL *tert*-butyl methyl ether, stirred for 5 minutes and filtered off. The copper powder on the filter is washed 4 times with 25 mL *tert*-butyl methyl ether each. Filtrate and wash solutions are combined, the solvent is evaporated at the rotary evaporator. A liquid residue remains as crude product.
Crude yield: 15.9 g

The crude product is fractional distilled under reduced pressure.
Yield: 13.5 g (79.3 mmol, 79%); head temperature 70 °C ($1.7 \cdot 10^{-2}$ hPa, oil bath temperature 120 °C), colourless liquid; $n_D^{20} = 1.4508$

Comments

If during work up one distilles directly from the reaction mixture over a 10 cm column without using *tert*-butyl methyl ether, the yield is only 49%.

Waste management

Waste disposal

Waste	Disposal
evaporated *tert*-butyl methyl ether (might contain iodoethane)	organic solvents, containing halogen
distillation residue	organic solvents, containing halogen
copper powder	solid waste, free from mercury, containing heavy metals

Time

11 hours

Break

After heating and before distillation

Degree of difficulty

Easy

Analytics

Reaction monitoring with GC

Sample preparation:

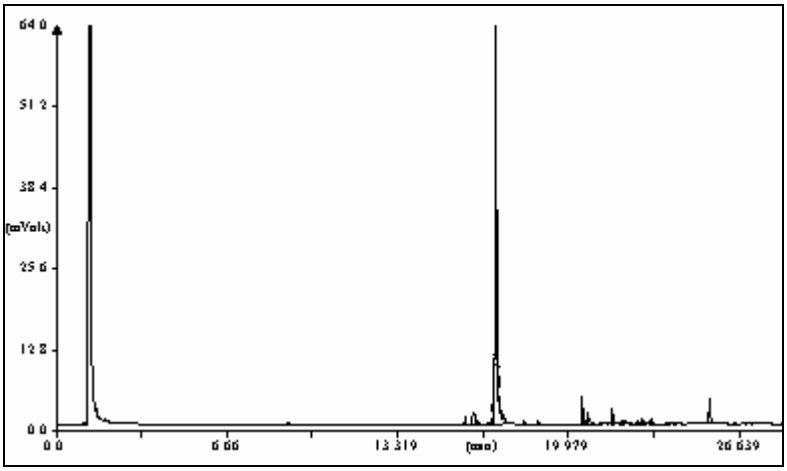
Using a Pasteur pipette, one drop of the reaction mixture is taken, dissolved in 10 mL dichloromethane, from this solution 0.2 µL are injected.

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/s)
oven:	40 °C (5 min), 10 °C/min on 240 °C (40 min)
detector:	FID, 270 °C

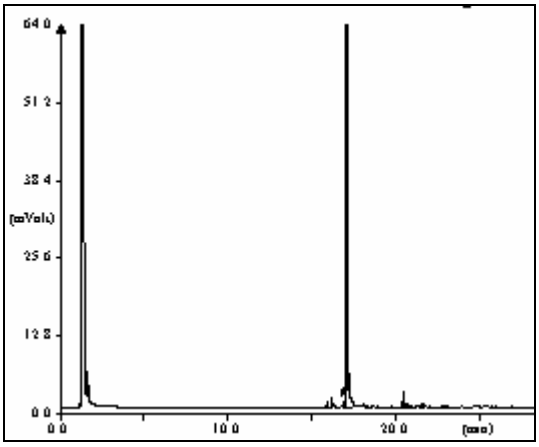
Percent concentration was calculated from peak areas.

GC of the crude product



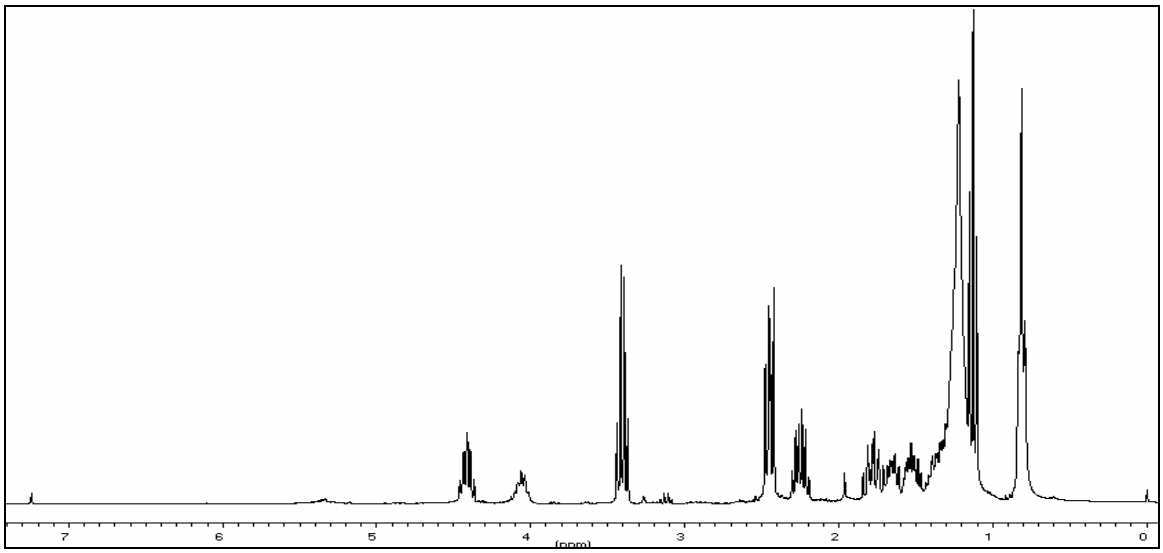
Retention time (min)	Substance	Peak area %
17.15	product	86.4
16.29	side product	2.2
	other impurities	each < 1.6

GC of the pure product

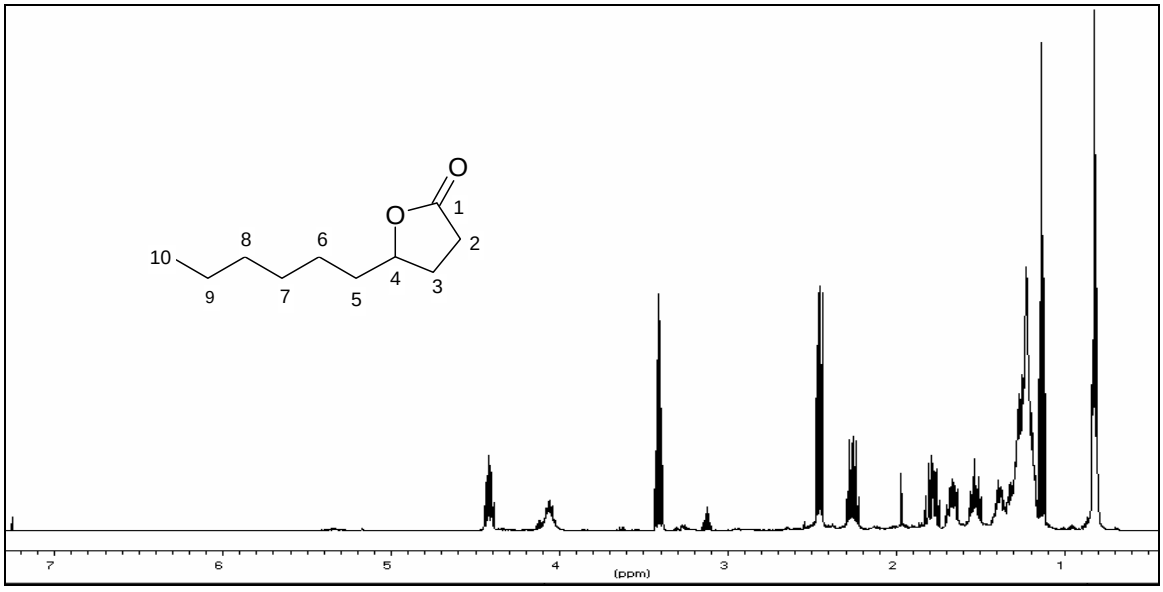


Retention time (min)	Substance	Peak area %
17.09	product	93.4
	impurities	each < 2

^{1}H NMR spectrum of the crude product (300 MHz, $CDCl_3$)

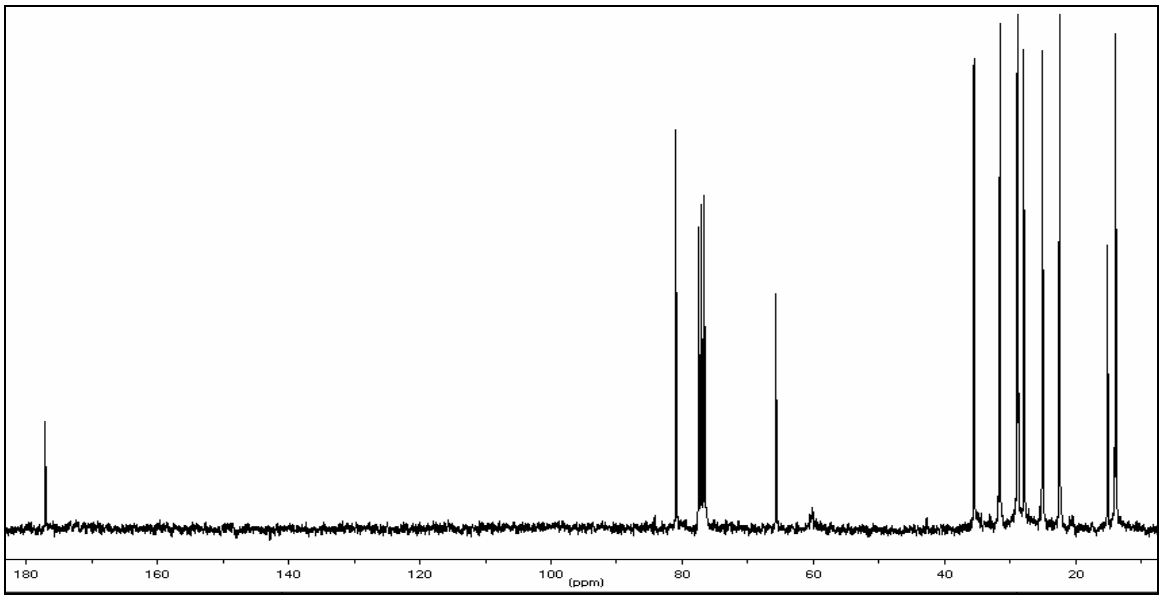


^{1}H NMR spectrum of the pure product (500 MHz, $CDCl_3$)

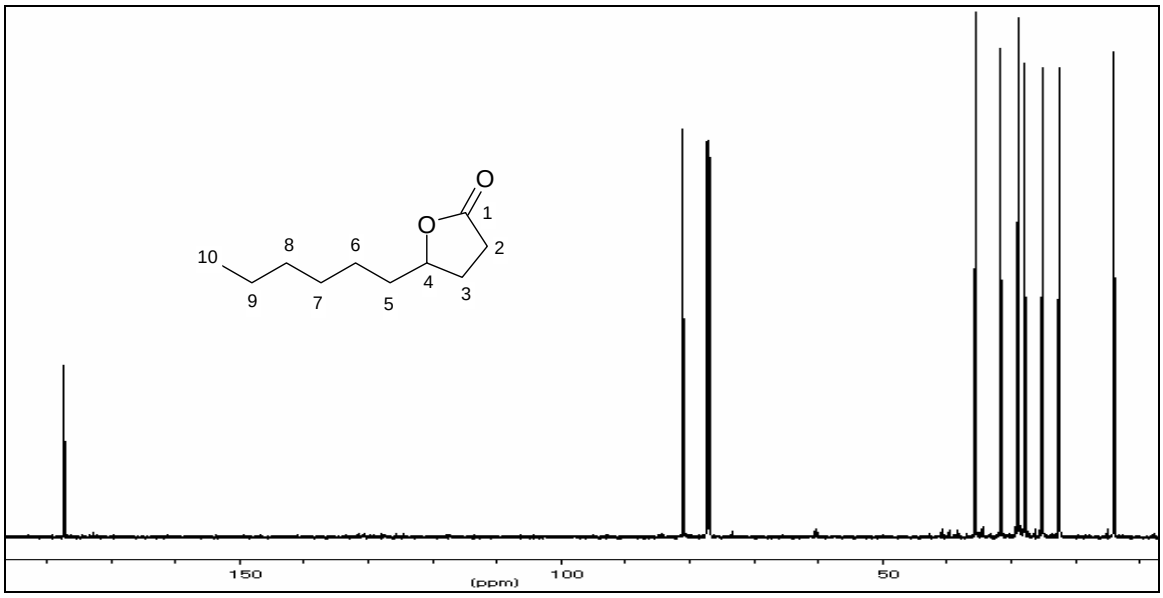


δ (ppm)	Multiplicity	Number of H	Assignment
4.33	tt	1	4-H
2.36	dd	2	2-H
2.18	m	1	5-H_a
1.77-1.39	m	3	3-H, 5-H_b
1.20-1.12	m	8	6-H to 9-H
0.74	t	3	10-H

^{13}C NMR spectrum of the crude product (75.5 MHz, $CDCl_3$)

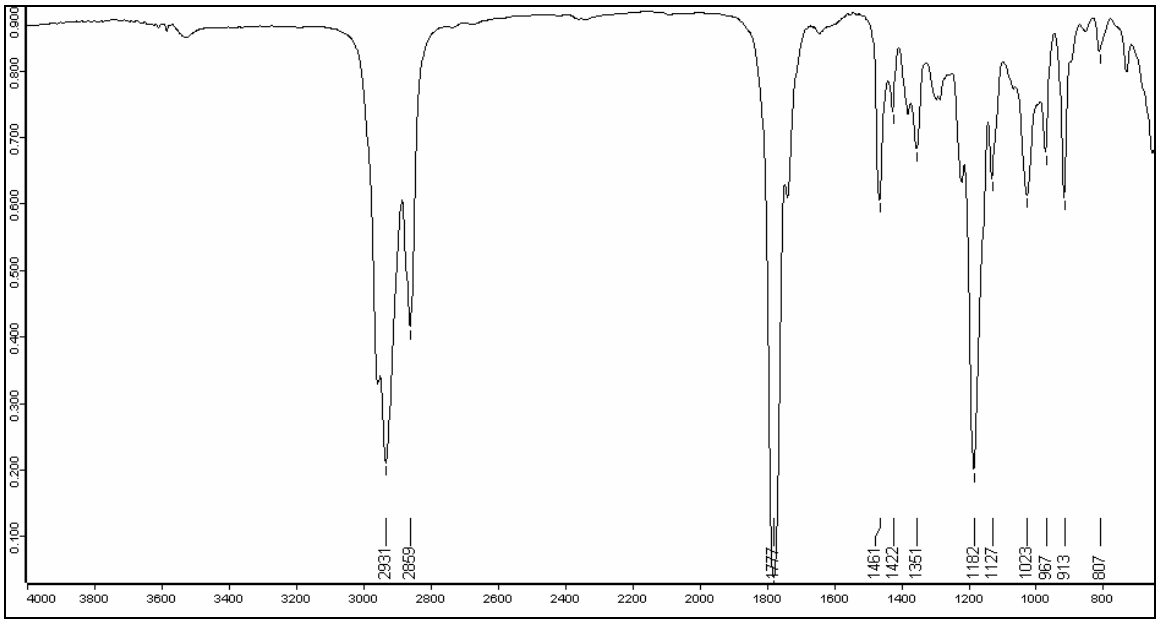


^{13}C NMR spectrum of the pure product (125.7 MHz, $CDCl_3$)



δ (ppm)	Assignment
177.1	C-1
80.9	C-4
35.4	C-2
31.5	C-3
29.0-27.9	C-6 to C-8
25.0	C-5
22.4	C-9
13.9	C-10
76.5-77.5	solvent

IR spectrum of the pure product (film)



(cm^{-1})	**Assignment**
2931, 2859	C-H-valence, alkane
1777	C=O-valence, ester, lactone