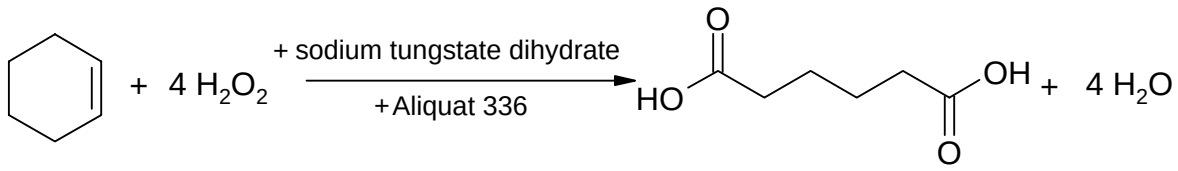
4009 Synthesis of adipic acid from cyclohexene



C_6H_{10}		$Na_2WO_4 \cdot 2\ H_2O$ (329.9)	$C_6H_{10}O_4$
(82.2)	(34.0)	$C_{25}H_{54}ClN$ (404.2)	(146.1)

Classification

Reaction types and substance classes
oxidation, phase transfer catalysis
peroxide, alkene, carboxylic acid

Work methods
stirring with magnetic stir bar, heating under reflux, recrystallizing, filtering, evaporating with rotary evaporator, heating with oil bath

Instruction (batch scale 10 mmol)

Equipment
25 mL two-neck flask, heatable magnetic stirrer, magnetic stir bar, reflux condenser, Buechner funnel, suction flask, desiccator, oil bath

Substances

cyclohexene (bp 83 °C)	0.82 g (1.0 mL, 10 mmol)
hydrogen peroxide 30% (bp 107 °C)	4.4 mL (43 mmol)
sodium tungstate dihydrate	44 mg (0.13 mmol)
methyltrioctylammonium chloride (Aliquat 336 or Adogen 464)	0.03 g (0.07 mmol)
sulphuric acid (0.5 M)	0.30 mL (0.15 mmol)

Reaction
0.03 g (0.07 mmol) methyltrioctylammonium chloride and 0.30 mL (0.15 mmol) 0.5 M sulphuric acid are filled in a 25 mL two-neck flask equipped with a magnetic stir bar and a reflux condenser and stirred for 5 minutes at room temperature. 44 mg (0.13 mmol) sodium tungstate dihydrate and 4.4 mL (43 mmol) hydrogen peroxide are added and the mixture is stirred for further 10 minutes at room temperature. Afterwards 1.0 mL (10 mmol) cyclohexene is added. The reaction mixture is heated under stirring and under reflux at about 110 °C oil bath temperature for 4 hours.

Work up
The reaction mixture is cooled down and stored over night in the refrigerator (4°C) to crystallize the adipic acid. The solid is sucked off over a Buechner funnel, washed with little water (1 mL) and dried in the desiccator over night

Yield: 920 mg (6.30 mmol, 63%); mp 154 °C, white crystals

Waste management

Waste disposal

Waste	Disposal
aqueous filtrate	solvent water mixtures, containing halogen, containing heavy metals

Time
4-5 hours, crystallization over night

Break
After heating of the reaction mixture

Degree of difficulty
Easy

Instruction (batch scale 100 mmol)

Equipment
100 mL two- or three-neck flask, heatable magnetic stirrer, magnetic stir bar, reflux condenser, Buechner funnel, suction flask, rotary evaporator, desiccator, oil bath

Substances

cyclohexene (bp 83 °C)	8.22 g (10.1 mL, 100 mmol)
hydrogen peroxide 30% (bp 107 °C)	44.0 mL (430 mmol)
sodium tungstate dihydrate	0.44 g (1.3 mmol)
methyltrioctylammonium chloride (Aliquat 336, or Adogen 464)	0.61 g (1.5 mmol)
sulphuric acid (0.5 M)	3.0 mL (1.5 mmol)
acetone (bp 56.2 °C) for recrystallization	about 100 mL

Reaction
0.61 g (1.5 mmol) methyltrioctylammonium chloride and 3.0 mL (1.5 mmol) 0.5 M sulphuric acid are filled in a 100 mL three-neck flask equipped with a magnetic stir bar and a reflux condenser and stirred for 5 minutes at room temperature. Then 0.44 g (1.3 mmol) sodium tungstate dihydrate and 44.0 mL (430 mmol) hydrogen peroxide are added and the mixture is stirred for further 10 minutes at room temperature. Afterwards 8.22 g (10.1 mL, 100 mmol) cyclohexene are added. The reaction mixture is heated under reflux and under stirring at about 110 °C oil bath temperature for 5 hours.

Work up

The reaction mixture is cooled down and stored over night in the refrigerator (4 °C) to crystallize the adipic acid. The solid is sucked off over a Buechner funnel and washed with 10 mL water. The mother liquor is concentrated at the rotary evaporator to 50% of the volume and also stored in the refrigerator. If crystals precipitate from the concentrated mother liquor, they are sucked off and combined with the main fraction. The combined crystal fractions are dried in the desiccator.
Crude yield: 12.2 g

The crude product is recrystallized from 100 mL acetone. The mother liquor is concentrated at the rotary evaporator; possibly a further crystal fraction precipitates, whose purity (for example mp) must be examined separately.
Crude yield: 10.5 g (71.9 mmol, 72%,); mp 152 °C, white crystals

Waste management

Recycling

The acetone from the mother liquor is evaporated, collected and redistilled.

Waste disposal

Waste	Disposal
aqueous filtrate	solvent water mixtures, containing halogen, containing heavy metals
residue from the mother liquor of the recrystallization	dissolve in little acetone, then: organic solvents, halogen free

Time

6-7 hours, crystallization over night

Break

After heating of the reaction mixture

Degree of difficulty

Easy

Instruction (batch scale 1 mol)

Equipment

1 L two- or three-neck flask, heatable magnetic stirrer, magnetic stir bar, reflux condenser, Büchner funnel, suction flask, rotary evaporator, desiccator, oil bath

Substances

cyclohexene (bp 83 °C)	82.2 g (101 mL, 1.00 mol)
hydrogen peroxide 30% (bp 107 °C)	440 mL (4.30 mol)
sodium tungstate dihydrate	4.4 g (13 mmol)
methyltrioctylammonium chloride (Aliquat 336, or Adogen 464)	6.1 g (15 mmol)

sulphuric acid (0.5 M)	30 mL (15 mmol)
acetone (bp 56.2 °C) for recrystallization	about 1.0 L

Reaction

6.1 g (15 mmol) methyltrioctylammoniumchlorid and 30 mL (15 mmol) 0.5 M sulphuric acid are filled in a 1 L three-neck flask equipped with a magnetic stir bar and a reflux condenser and stirred for 5 minutes at room temperature. Then 4.4 g (13.2 mmol) sodium tungstate dihydrate and 440 mL (4.30 mol) hydrogen peroxide are added and stirred for further 10 minutes at room temperature. Afterwards 82.2 g (101 mL, 1.00 mol) cyclohexene are added. The reaction mixture is heated under stirring and under reflux at about 110 °C oil bath temperature for 5 hours.

Work up

The reaction mixture is cooled down and stored over night in the refrigerator (4° C) to crystallize the adipic acid. The residue is sucked off over a Buechner funnel and washed with 50 mL water. The mother liquor is concentrated at the rotary evaporator to 50% of the volume and also stored in the refrigerator. If crystals precipitate from the concentrated mother liquor, they are sucked off and combined with the main fraction. The combined crystal fractions are dried in the desiccator.

Crude yield: 123 g, mp 146 °C

The crude product is recrystallized from 1000 mL acetone. The mother liquor is concentrated at the rotary evaporator; possibly a further crystal fraction precipitates, whose purity (for example mp) must be examined separately.

Yield: 105 g (0.719 mol, 72%); white crystals, mp 154 °C

Waste management

Recycling

The acetone of the mother liquor is evaporated at the rotary evaporator, collected and redistilled.

Waste disposal

Waste	Disposal
aqueous filtrate	solvent water mixtures, containing halogen, containing heavy metals
Residue from the mother liquor of recrystallization	dissolve in little acetone, then: organic solvents, halogen free

Time

6-7 hours, crystallization over night

Break

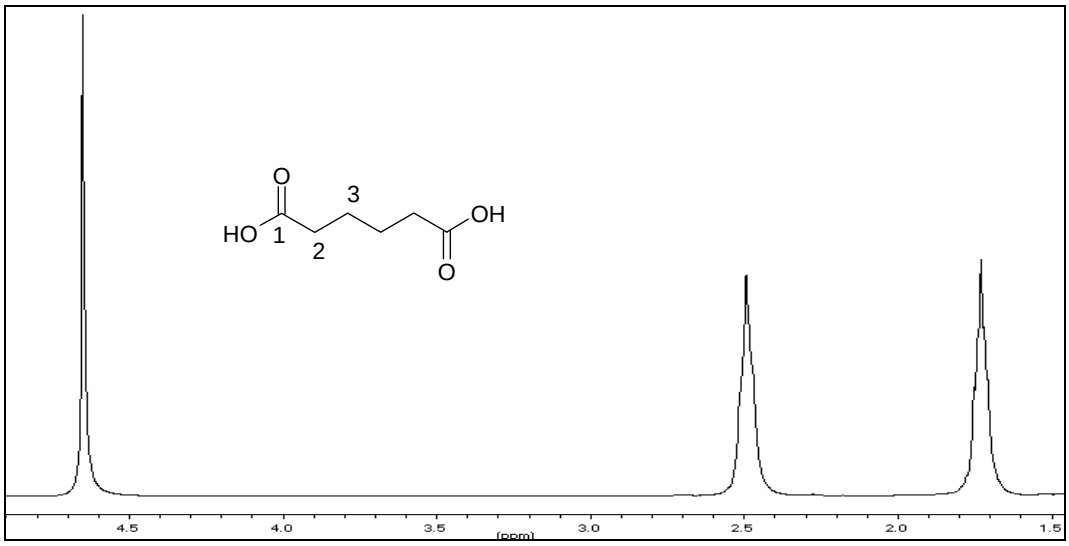
After heating of the reaction mixture

Degree of difficulty

Easy

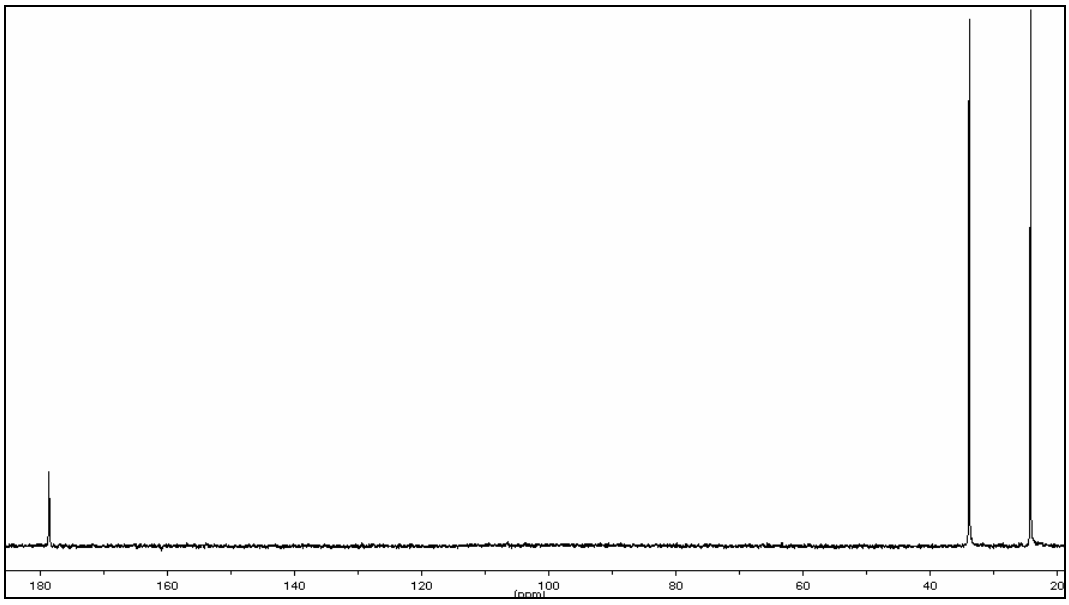
Analytics

^{1}H NMR spectrum of the pure product (300 MHz, D_2O, 60 °C)



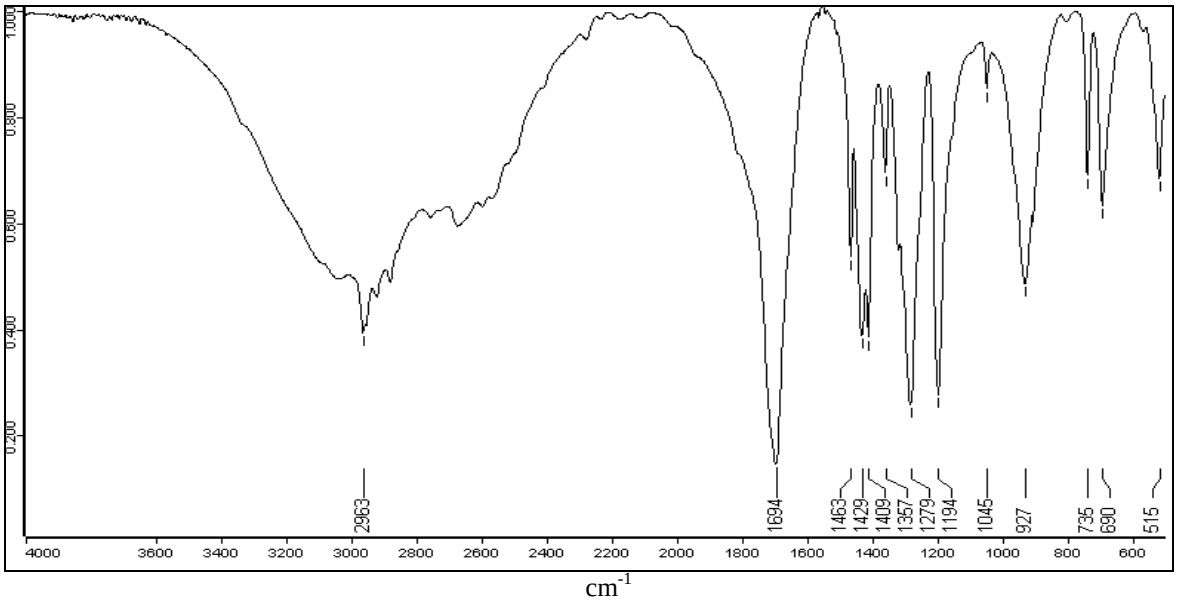
δ (ppm)	Multiplicity	Number of H	Assignment
1.71	m	4	3-H
2.48	m	4	2-H

^{13}C NMR spectrum of the pure product (75.5 MHz, D_2O, 60 °C)



δ (ppm)	Assignment
178.6	C-1
33.8	C-2
24.2	C-3

IR spectrum of the pure product (KBr)



cm^{-1}

(cm^{-1})	**Assignment**
3500-2500	O-H-valence, carboxylic acid, C-H-valence, alkane
1694	C=O-valence, carboxylic acid