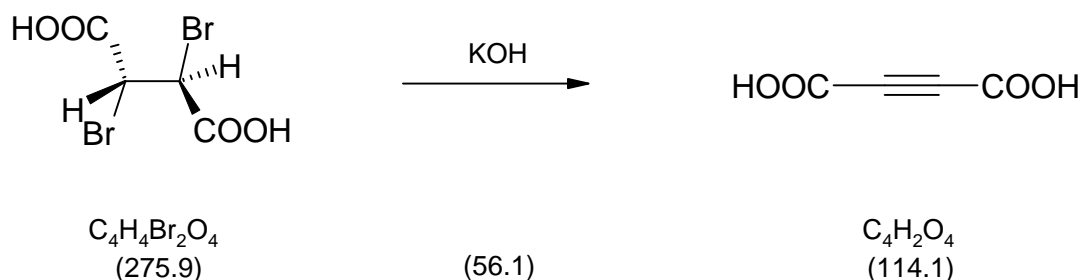


### 3033 Synthesis of acetylenedicarboxylic acid from meso-dibromosuccinic acid



#### Classification

##### Reaction types and substance classes

elimination

bromoalkane, alkyne, carboxylic acid

##### Work methods

heating under reflux, stirring with magnetic stir bar, shaking out, extracting, filtering, evaporating with rotary evaporator, heating with oil bath

#### Instruction (batch scale 100 mmol)

##### Equipment

500 mL round bottom flask, reflux condenser, heatable magnetic stirrer, magnetic stir bar, suction flask, Buechner funnel, separating funnel, possibly liquid liquid extractor, desiccator, rotary evaporator, oil bath

##### Substances

<i>meso</i> -dibromosuccinic acid (mp 255-256 °C; product from experiment number 3002)	27.6 g (100 mmol)
potassium hydroxide	31 g (550 mmol)
ethanol (95%), (bp 78 °C)	200 mL
sulphuric acid (conc.)	17 mL
<i>tert</i> -butyl methyl ether (bp 55 °C)	250 mL
sodium sulfate for drying	

##### Reaction

27.6 g (100 mmol) *meso*-dibromosuccinic acid are filled in a 500 mL round bottom flask with magnetic stir bar and reflux condenser containing the solution of 31 g (550 mmol) potassium hydroxide in 180 mL ethanol. The reaction mixture is heated under stirring for 45 minutes under reflux.

**Work up**

After cooling down the solid is sucked off, and washed with 20 mL ethanol in small portions and dried in the desiccator. Yield: about 40 g

The solid is dissolved in 65 mL water and diluted with a solution of 2 mL concentrated sulphuric acid in 7.5 mL water. It is important to use these exact volumes, since that results in a pH-value of the solution so that the hardly soluble mono-potassium salt of the acetylene carboxylic acid precipitates. For a complete crystallization it is stored for a minimum of 3 hours or over night. The precipitation is sucked off and dissolved in a mixture from 15 mL conc. sulphuric acid and 60 mL water. The solution is shaken out in a separating funnel five times with 50 mL *tert*-butyl methyl ether each. The ether phase is dried with sodium sulfate. After filtering of the drying agent the solvent is evaporated at a rotary evaporator. The product remains as colourless solid, which is dried in the desiccator.

Yield: 7.89 g (69.2 mmol, 69%); colourless solid; mp 179-181 °C (decomposition)

**Comments**

The precipitation of the mono-potassium salt is a purifying operation, impurities remain in the solution.

Alternatively to shaking out of the product it can also be extracted from the acidic aqueous solution in a liquid liquid extractor for about 7 hours.

**Waste management****Recycling**

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

**Waste disposal**

Waste	Disposal
alkaline ethanolic filtrate	neutralize, then: solvent water mixtures, containing halogen
acidic aqueous filtrate acidic aqueous phase	neutralize, then: solvent water mixtures, containing halogen
sodium sulfate	solid waste, free from mercury

**Time**

2–3 hours

(10 hours by using an extractor)

**Break**

After heating under reflux

After precipitation of the mono-potassium salt

**Degree of difficulty**

Easy

## Instruction (batch scale 10 mmol)

### Equipment

50 mL round-bottom flask, reflux condenser, heatable magnetic stirrer, magnetic stir bar, suction flask, Buechner funnel, separating funnel, possibly liquid liquid extractor, desiccator, rotary evaporator, oil bath

### Substances

<i>meso</i> -dibromosuccinic acid (mp 255-256 °C; product from experiment number 3002)	2.76 g (10.0 mmol)
potassium hydroxide	3.1 g (55 mmol)
ethanol (95%), (bp 78 °C)	23 mL
sulphuric acid (conc.)	1.7 mL
<i>tert</i> -butyl methyl ether (bp 55 °C)	25 mL
sodium sulfate for drying	

### Reaction

2.76 g (10.0 mmol) *meso*-dibromosuccinic acid are filled in a 50 mL round bottom flask with magnetic stir bar and reflux condenser containing the solution of 3.1 g (55 mmol) potassium hydroxide in 18 mL ethanol. The reaction mixture is heated under stirring for 45 minutes under reflux.

### Work up

After cooling down the solid is sucked off, washed with 5 mL ethanol in small portions and dried in the desiccator. Yield: about 4 g

The solid is dissolved in 6.5 mL water and then diluted with a solution of 0.2 mL conc. sulphuric acid in 0.75 mL water. It is important to use these exact volumes, since that results in a pH-value of the solution so that the hardly soluble mono-potassium salt of the acetylenecarboxylic acid precipitates. For a complete crystallization it is stored for a minimum of 3 hours or over night. The precipitation is sucked off and dissolved in a mixture of 1.5 mL conc. sulphuric acid and 6 mL water. The solution is shaken out in a separating funnel five times with 5 mL *tert*-butyl methyl ether each. The ether phase is dried with sodium sulfate. After filtering of the drying agent the solvent is evaporated at a rotary evaporator. A colourless solid remains as product, which is dried in the desiccator.

Yield: 619 mg (5.43 mmol, 54%); colourless residue, mp 179-181 °C (decomposition)

### Comments

The precipitation of the mono potassium salt is a purifying operation, impurities remain in the solution.

Alternatively to shaking out of the product it can also be extracted from the acidic aqueous solution in a liquid liquid extractor for about 7 hours.

**Waste management****Recycling**

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

**Waste disposal**

Waste	Disposal
alkaline ethanolic filtrate	neutralize, then: solvent water mixtures, containing halogen
acidic aqueous filtrate acidic aqueous phase	neutralize, then: solvent water mixtures, containing halogen
sodium sulfate	solid waste, free from mercury

**Time**

2–3 hours

**Break**

After heating under reflux

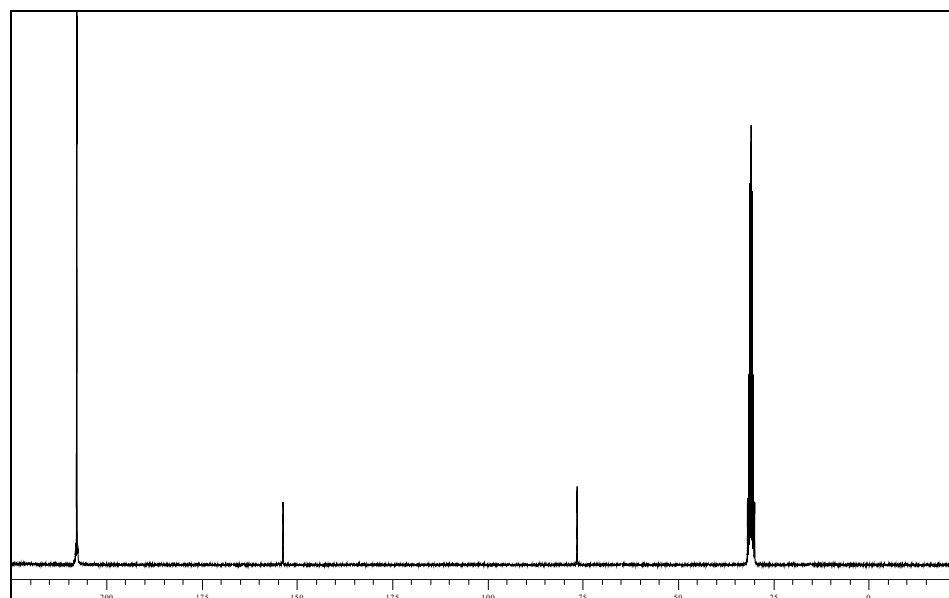
After precipitation of the mono potassium salt

**Degree of difficulty**

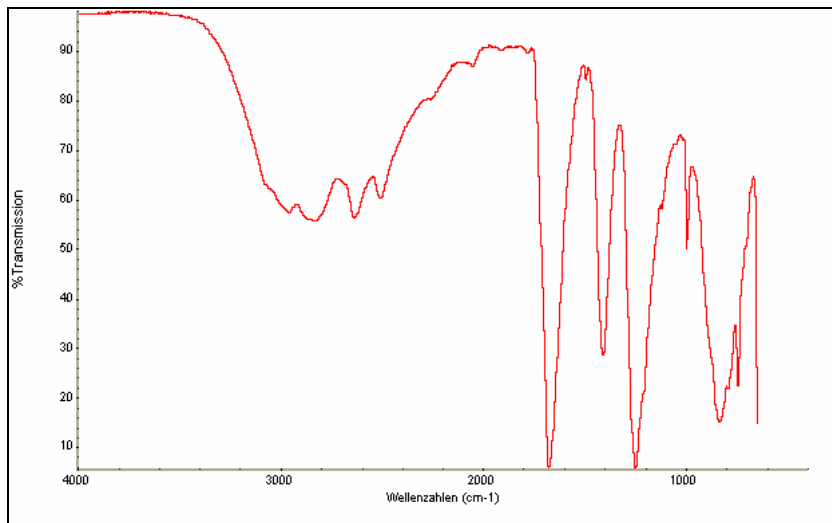
Easy

**Analytcs**

$^{13}\text{C}$  NMR spectrum of the product (62.5 MHz, acetone- $\text{D}_6$ )



$\delta$ (ppm)	Assignment
76.5	$\text{C}\equiv\text{C}$
153.8	$\text{COOH}$
30.8	$\text{CH}_3$ (acetone- $\text{D}_6$ )
207.5	$\text{C}=\text{O}$ (acetone- $\text{D}_6$ )

**IR spectrum of the product (ATR)**

(cm <sup>-1</sup> )	Assignment
3300-2400	O-H-valence, carboxylic acid
1677	C=O-valence, carboxylic acid