3033 Synthesis of acetylenedicarboxylic acid from meso-dibromosuccinic acid

\[
\begin{align*}
\text{HOOC} & \quad \text{Br} & \quad \text{Br} & \quad \text{COOH} \\
\text{H} & \quad \text{H} & \quad & \\
\text{KOH} & \quad & & \\
\text{HOOC} & \quad \equiv & \quad \text{COOH}
\end{align*}
\]

\[
\begin{align*}
\text{C}_4\text{H}_2\text{O}_4 & \quad \text{(275.9)} \\
\text{KOH} & \quad \text{(56.1)} \\
\text{C}_4\text{H}_2\text{O}_4 & \quad \text{(114.1)}
\end{align*}
\]

**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**
- *meso*-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
- tert-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**

<table>
<thead>
<tr>
<th>Waste</th>
<th>Disposal</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkaline ethanolic filtrate</td>
<td>neutralize, then: solvent water mixtures, containing halogen</td>
</tr>
<tr>
<td>acidic aqueous filtrate</td>
<td>neutralize, then: solvent water mixtures, containing halogen</td>
</tr>
<tr>
<td>acidic aqueous phase</td>
<td></td>
</tr>
<tr>
<td>sodium sulfate</td>
<td>solid waste, free from mercury</td>
</tr>
</tbody>
</table>

**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**
- *meso*-dibromosuccinic acid (mp 255-256 °C; 2.76 g (10.0 mmol) product from experiment number 3002)
- potassium hydroxide 3.1 g (55 mmol)
- ethanol (95%), (bp 78 °C) 23 mL
- sulphuric acid (conc.) 1.7 mL
- *tert*-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 overnight. 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

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Time
2–3 hours

Break
After heating under reflux
After precipitation of the mono potassium salt

Degree of difficulty
Easy

Analytics

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

<table>
<thead>
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<th>δ (ppm)</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>76.5</td>
<td>C≡C</td>
</tr>
<tr>
<td>153.8</td>
<td>COOH</td>
</tr>
<tr>
<td>30.8</td>
<td>CH$_3$ (acetone-D$_6$)</td>
</tr>
<tr>
<td>207.5</td>
<td>C=O (acetone-D$_6$)</td>
</tr>
</tbody>
</table>
IR spectrum of the product (ATR)

<table>
<thead>
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<th>(cm(^{-1}))</th>
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<tbody>
<tr>
<td>3300-2400</td>
<td>O-H-valence, carboxylic acid</td>
</tr>
<tr>
<td>1677</td>
<td>C=O-valence, carboxylic acid</td>
</tr>
</tbody>
</table>