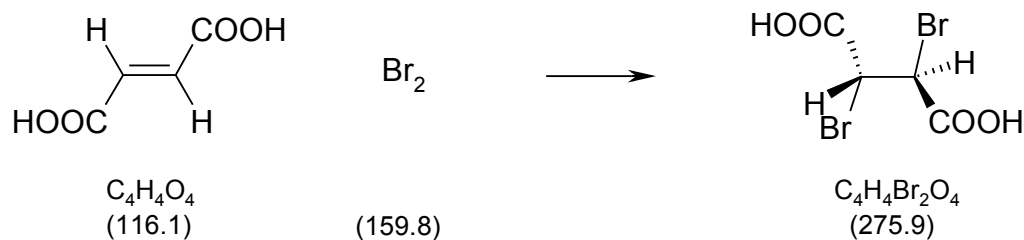


3002 Addition of bromine to fumaric acid to *meso*-dibromosuccinic acid



Literature

A. M. McKenzie, *J. Chem. Soc.*, **1912**, 101, 1196.

M. Eissen, D. Lenoir, *Chem. Eur. J.*, **2008**, 14, 9830-9841

Classification

Reaction types and substance classes

additions to alkenes, stereoselective addition, bromination
alkene, carboxylic acid, bromoalkane

Work methods

heating under reflux, stirring with magnetic stir bar, adding dropwise with an addition funnel, filtering, evaporating with rotary evaporator, recrystallizing, use of cooling bath, heating with oil bath

Instruction (batch scale 100 mmol)

Equipment

100 mL two neck round bottom flask, heatable magnetic stirrer, magnetic stir bar, addition funnel with pressure balance, reflux condenser, graduated pipette, suction flask, Buechner funnel, rotary evaporator, desiccator, ice bath, oil bath

Substances

fumaric acid (mp 287 °C)	11.6 g (100 mmol)
bromine (bp 59 °C)	18 g (5.7 mL, 110 mmol)
2 N hydrochloric acid for recrystallization	

Reaction

The reaction must be performed in a hood. (vapour of bromine!).

In a 100 mL two neck round bottom flask equipped with a reflux condenser, dropping funnel and magnetic stirring bar 11.6 g (100 mmol) of fumaric acid in 40 mL water is heated to boiling of water while stirring the solution. Under boiling and stirring of the solution 5.7 mL (18 g, 110 mmol) of bromine is added dropwise to the solution with such a speed, that before

each drop the brown colour of the mixture has been ceased away. At the end of addition there should be a slight excess of bromine.

Work up

The reaction mixture is cooled to room temperature and further cooled in an ice bath to 10 °C, during cooling crystallization does occur. The crystallized crude material is filtered by a suction funnel and washed several times with 20 mL of ice water. The crude product is dried to a constant weight in a desiccator. Yield of the crude product: 23.7 g

The mother liquor is evaporated with a rotary evaporator yielding a crystalline precipitate, consisting of a mixture of bromomaleic acid and bromofumaric acid as side products.

The crude product is crystallized from 2 N hydrochloric acid. (Crystallization using boiling water leads to elimination of HBr !)

Yield: 17.4 g (63.1 mmol, 63%); mp 255 °C; colourless crystals; *meso*-dibromosuccinic acid.

Comments

The product can be used in experiment Nr. 3033 as starting material.

Caution by handling of bromine! It should be used by measuring it by a graduated pipette.

Extended heating of the reaction mixture increases the percentage of the side products, bromomaleic acid and bromofumaric acid.

Waste management

Waste disposal

Waste	Disposal
mother liquor from recrystallization	solvent water mixtures, containing halogen
evaporated water	when yellow, treatment with aqueous sodium sulfite solution, then: aqueous waste, alkaline
residues of bromine	treatment with aqueous sodium sulfite solution, then: aqueous waste, alkaline
side products, bromomaleic acid, bromofumaric acid	dissolve in water, then: aqueous waste, containing halogen

Time

2 to 3 hours

Break

Before recrystallization

Degree of difficulty

Medium

Instruction (batch scale 10 mmol)

Equipment

100 mL two neck round bottom flask, heatable magnetic stirrer, magnetic stir bar, addition funnel with pressure balance, reflux condenser, graduated pipette, suction flask, Buechner funnel, rotary evaporator, desiccator, ice bath, oil bath

Chemicals

fumaric acid (mp 287 °C)	1.16 g (10.0 mmol)
bromine (bp 59 °C)	1.8 g (0.6 mL, 11.0 mmol)
2 N hydrochloric acid for recrystallization	

Reaction

The reaction must be performed in a hood (vapour of bromine!).

In a 100 mL two neck round bottom flask equipped with a reflux condenser, dropping funnel and magnetic stir bar 1.16 g (10.0 mmol) of fumaric acid in 5 mL of water is heated to boiling of water while stirring the solution. Under boiling and stirring of the solution 0.6 mL (1.8 g, 11.0 mmol) of bromine is added dropwise to the solution with such a speed, that before each drop the brown colour of the mixture has been ceased away. At the end of addition there should be a slight excess of bromine.

Work up

The reaction mixture is cooled to room temperature and further cooled in an ice bath to 10 °C, during cooling crystallization does occur. The crystallized crude material is filtered by a suction funnel and washed several times with 10 mL of ice water. The crude product is dried to a constant weight in a desiccator. Yield of the crude product: 2.2 g

The mother liquor is evaporated with a rotary evaporator yielding a crystalline precipitate, consisting of a mixture of bromomaleic acid and bromofumaric acid as side products.

The crude product is crystallized from 2 N hydrochloric acid. (Crystallization using boiling water leads to elimination of HBr !)

Yield: 1.77 g (6.31 mmol, 64%); mp 255 °C; colourless crystals; *meso*-dibromosuccinic acid.

Comments

The product can be used in experiment Nr. 3033 as starting material.

Caution by handling of bromine! It should be used by measuring it by a graduated pipette.

Extended heating of the reaction mixture increases the percentage of the side products, bromomaleic acid and bromofumaric acid.

Waste management**Waste disposal**

Waste	Disposal
mother liquor from crystallization	solvent water mixtures, containing halogen
evaporated water	when yellow, treatment with aqueous sodium sulfite solution, then: aqueous waste, alkaline
residues of bromine	treatment with aqueous sodium sulfite solution, then: aqueous waste, alkaline
side products, bromomaleic acid, bromofumaric acid	dissolve in water, then: aqueous waste, containing halogen

Time

2 to 3 hours

Break

Before recrystallization

Degree of difficulty

Medium

Analytics**TLC**

TLC conditions:

adsorbant:

TLC-aluminium foil, Merck silica gel 60 F₂₅₄, 5 x 10 cm

eluent

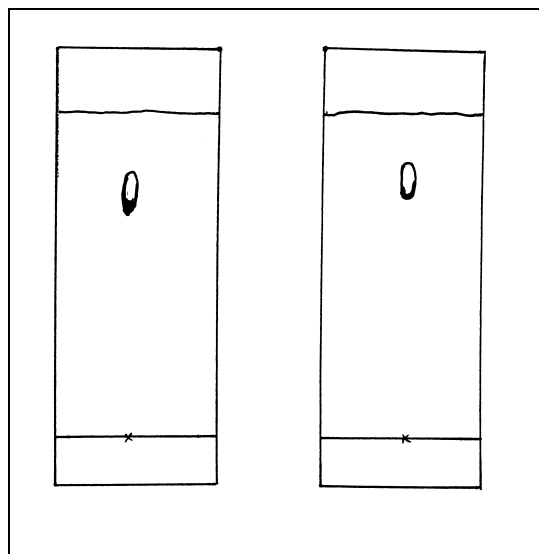
methanol

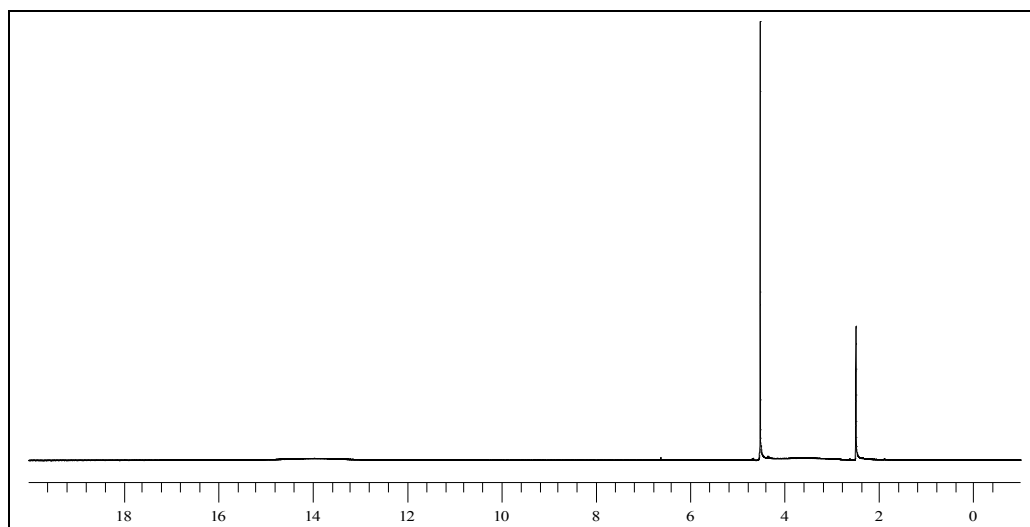
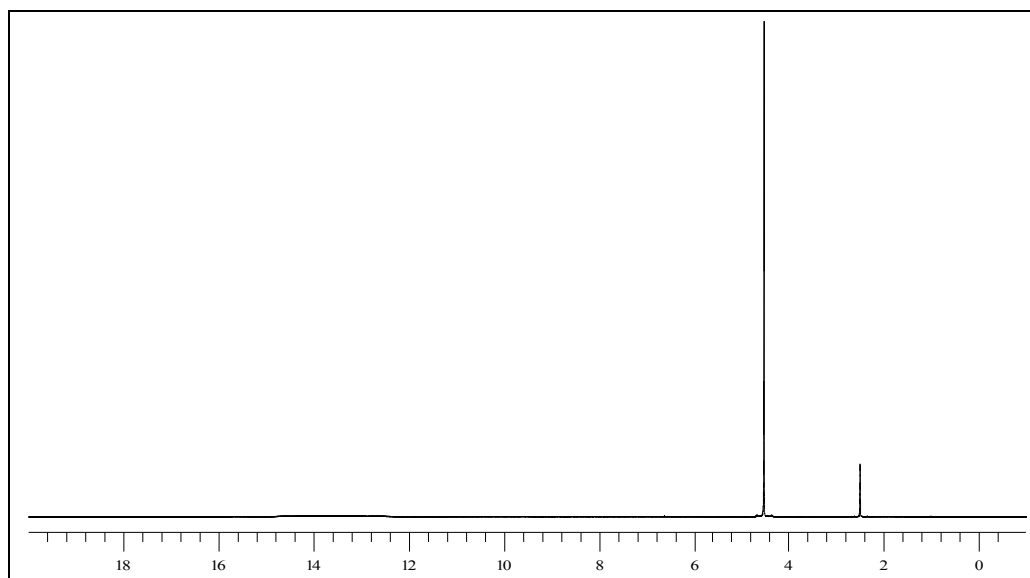
R_f (*meso*-dibromosuccinic acid)

0.71

crude product

pure product

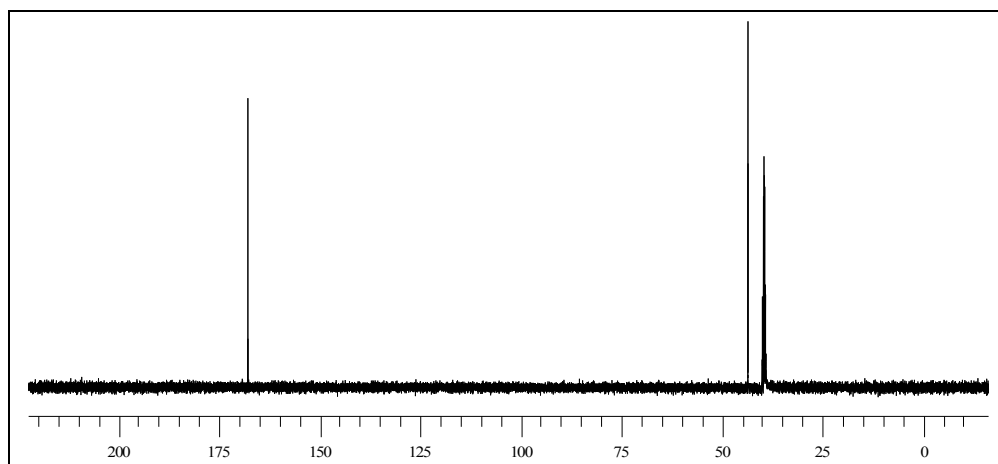
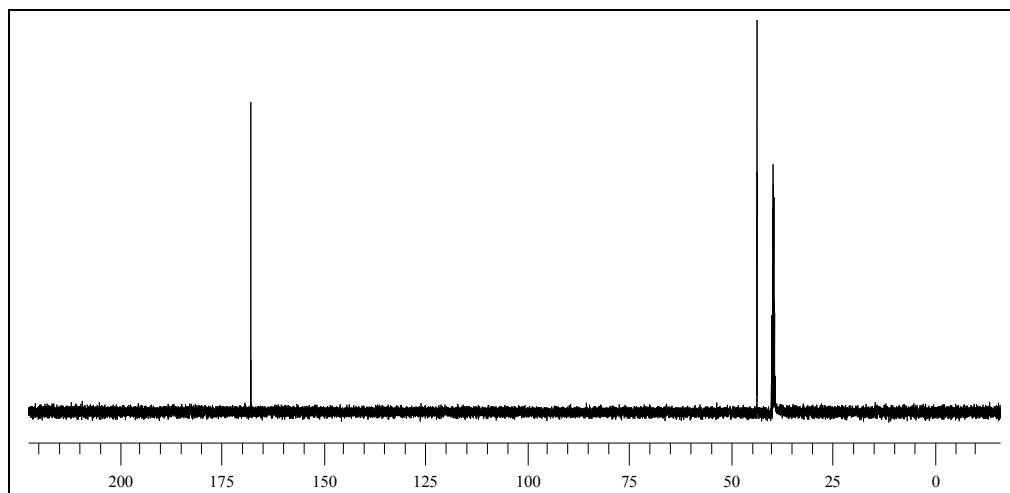


¹H NMR spectrum of the crude product (500 MHz, DMSO-D₆)**¹H NMR spectrum of the pure product (500 MHz, DMSO-D₆)**

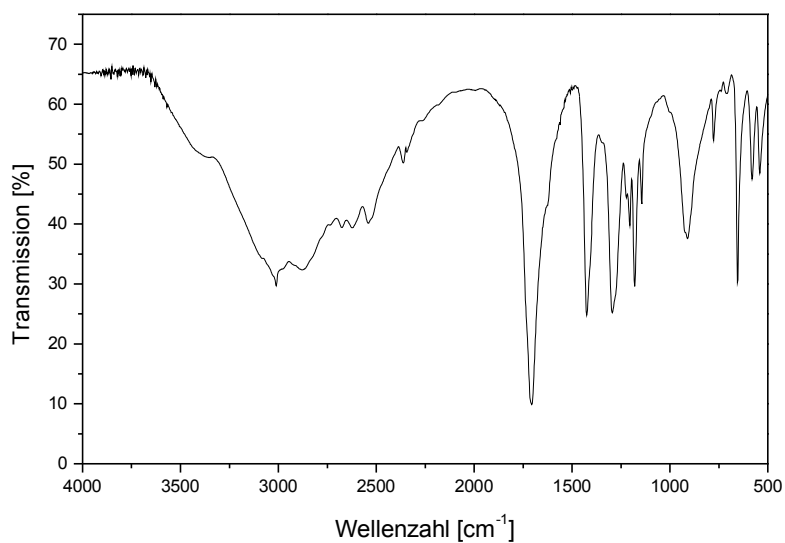
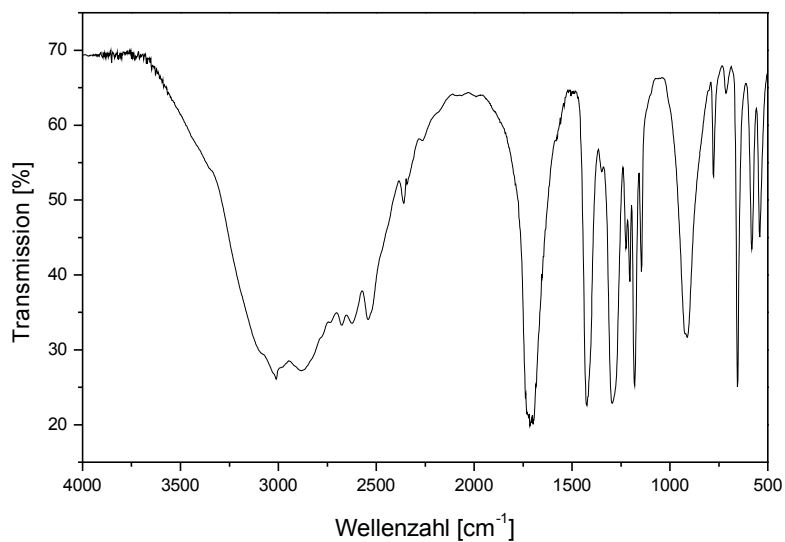
δ (ppm)	Multiplicity	Number of H	Assignment
4.52	s	2	CHBr
~13.75 ¹	bs	2	COOH
2.45			Lsgm.

¹very broad signal at 13.75 ppm, observed only with strong enlargement of the signals of the spectrum.

For either side products, bromofumaric acid and bromomaleic acid, there should be a signal for the proton at the double bond, a singlet at about 7.5 ppm. Apparently neither the crude nor the purified product contains the side products, within the NMR detection limit.

^{13}C NMR spectrum of the crude product (125 MHz, DMSO- D_6) **^{13}C NMR spectrum of the pure product (125 MHz, DMSO- D_6)**

δ (ppm)	Assignment
43.5	CHBr
167.7	COOH
39.5	solvent

IR spectrum of the crude product (KBr)**IR spectrum of the pure product (KBr)**

(cm ⁻¹)	Assignment
3500 – 2200	O-H-valence (COOH), superimposed on C-H-valence
1722	C=O-valence
655	C-Br-valence