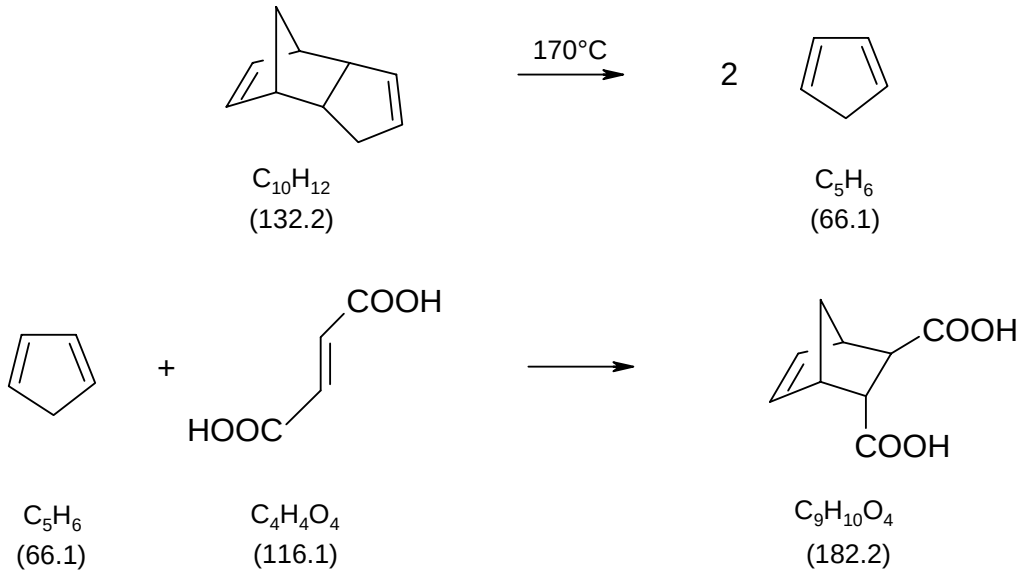
3009 Synthesis of *trans*-5-norbornene-2,3-dicarboxylic acid from fumaric acid and cyclopentadiene



$C_{10}H_{12}$ (132.2) — C_5H_6 (66.1)

C_5H_6 (66.1) + $C_4H_4O_4$ (116.1) → $C_9H_{10}O_4$ (182.2)

Classification

Reaction types and substance classes
cycloelimination, cycloaddition, Diels-Alder reaction
alkene, carboxylic acid, diene, dienophile

Work methods
column distillation, stirring with magnetic stir bar, heating under reflux, adding dropwise with an addition funnel, filtering, recrystallizing, use of a cooling bath, heating with oil bath

Instruction (batch scale 100 mmol)

Equipment
250 mL round bottom flask, 30 cm Vigreux or packed column, distillation apparatus, drying tube, 250 mL three-neck flask, heatable magnetic stirrer, magnetic stir bar, internal thermometer, addition funnel with pressure balance, Buechner funnel, suction flask, desiccator, ice / sodium chloride cooling bath, oil bath

Substances

dicyclopentadiene (bp 166 °C)	66.1 g (67.5 mL, 500 mmol)
or cyclopentadiene (bp 40 °C)	7.27 g (9.1 mL, 110 mmol)
fumaric acid (mp 287 °C, bp 290 °C)	11.6 g (100 mmol)
water	100 mL

Reaction

Preparation of cyclopentadiene:

The reaction apparatus consists of a 250 mL round-bottom flask equipped with a 30 cm Vigreux or packed column with a distillation bridge. The distillation bridge is connected with a drying tube, the receiving flask is cooled in an ice / sodium chloride cooling bath. No smaller distillation flask should be used, because strong foaming can occur during the reaction.

66.1 g (67.5 mL, 500 mmol) dicyclopentadiene is slowly heated in the reaction flask under stirring until it is strongly boiling at an oil bath temperature of 170-200 °C. After a short time the monomer cyclopentadiene starts to distill over. The oil bath temperature is adjusted, so that the distillation temperature does not exceed 45 °C. The reaction is finished, when under these conditions no more distillate passes over. The cyclopentadiene should be used immediately, since it dimerises again at room temperature. If necessary, it can be stored in the freezer over night.

Cycloaddition:

11.6 g (100 mmol) fumaric acid and 100 mL water are filled in a 250 mL three-neck flask with magnetic stir bar, addition funnel, reflux condenser and internal thermometer. Under stirring 7.27 g (9.1 mL, 110 mmol) cyclopentadiene are added dropwise with an addition funnel. Afterwards the mixture is carefully heated to an internal temperature of about 70 °C under reflux. When the main part of the cyclopentadiene has reacted, what means that the upper phase has disappeared, the mixture is heated for one further hour until the reflux temperature of the water is reached. Then the reaction solution is cooled down to 0 °C.

Work up

The precipitated product is sucked off, washed with a small amount of ice-cold water and dried in the desiccator over silica gel under reduced pressure.

Yield: 16.2 g (88.9 mmol, 89%), colourless crystals, mp 88 °C. With TLC and NMR no impurities can be detected.

The product can be recrystallized from water.

Waste management

Waste disposal

Waste	Disposal
distillation residue	organic solvents, halogen free
filtrate	solvent water mixtures, halogen free

Time

3-4 hours

Break

Before sucking off the product

Degree of difficulty

Medium

Instruction (batch scale 10 mmol)

Equipment

50 mL round-bottom flask, 30 cm Vigreux or packed column, distillation apparatus, drying tube, 25 mL two-neck flask, heatable magnetic stirrer, magnetic stir bar, internal thermometer, graduated pipette, Buechner funnel, suction flask, desiccator, ice / sodium chloride cooling bath, oil bath

Substances

dicyclopentadiene (bp 166 °C)	6.61 g (6.8 mL, 50 mmol)
or cyclopentadiene (bp 40 °C)	727 mg (0.91 mL, 11.0 mmol)
fumaric acid (mp 287 °C, bp 290 °C)	1.16 g (10.0 mmol)
water	10 mL

Reaction

Preparation of cyclopentadiene:

The reaction apparatus consists of a 50 mL round-bottom flask equipped with a 30 cm Vigreux or packed column with a distillation bridge. The distillation bridge is connected with a drying tube, the receiving flask is cooled in an ice / sodium chloride cooling bath. No smaller distillation flask should be used, because strong foaming can occur during the reaction.

6.61 g (6.85 mL, 50 mmol) dicyclopentadiene is slowly heated in the reaction flask under stirring until it is strongly boiling at an oil bath temperature of 170-200 °C. After a short time the monomer cyclopentadiene starts to distill over. The oil bath temperature is adjusted, so that the distillation temperature does not exceed 45 °C. The reaction is finished, when under these conditions no more distillate passes over. The cyclopentadiene should be used immediately, since it dimerises again at room temperature. If necessary, it can be stored in the freezer over night.

Cycloaddition:

1.16 g (10.0 mmol) fumaric acid and 10 mL water are filled in a 25 mL three-neck flask with magnetic stir bar, addition funnel, reflux condenser and internal thermometer. Under stirring 727 mg (0.91 mL, 11.0 mmol) cyclopentadiene are added with a graduated pipette. Afterwards the mixture is carefully heated to an internal temperature of about 70 °C under reflux. When the main part of the cyclopentadiene has reacted, what means that the upper phase has disappeared, the mixture is heated for one further hour until the reflux temperature of the water is reached. Then the reaction solution is cooled down to 0 °C.

Work up

The precipitated product is sucked off, washed with little ice-cold water and dried in the desiccator over silica gel under reduced pressure.

Yield: 1.50 g (8.20 mmol, 82%), colourless crystals, mp 88 °C. With TLC and NMR no impurities can be detected.

The product can be recrystallized from water.

Waste management

Waste disposal

Waste	Disposal
distillation residue	organic solvents, halogen free
filtrate	solvent water mixtures, halogen free

Time
3-4 hours

Break
Before sucking off the product

Difficulty
Medium

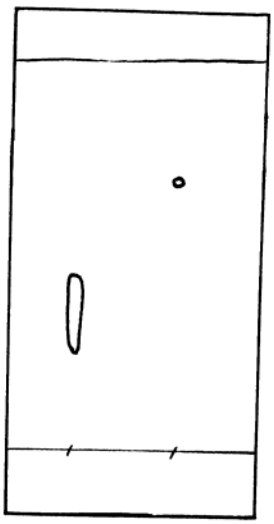
Analytics

TLC

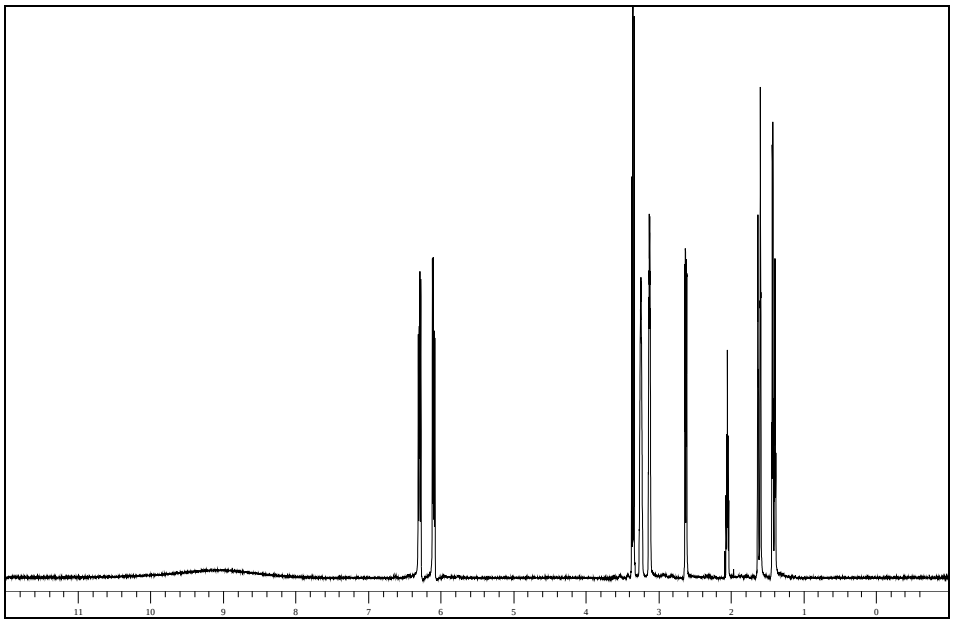
TLC-conditions:

adsorbant:	Merck silica gel 60 F_{254}, 5 x 10 cm
eluent:	ethanol
visualizing reagent:	iodine-vapor in the iodine chamber
R_f (product)	0.69

fumaric acid product

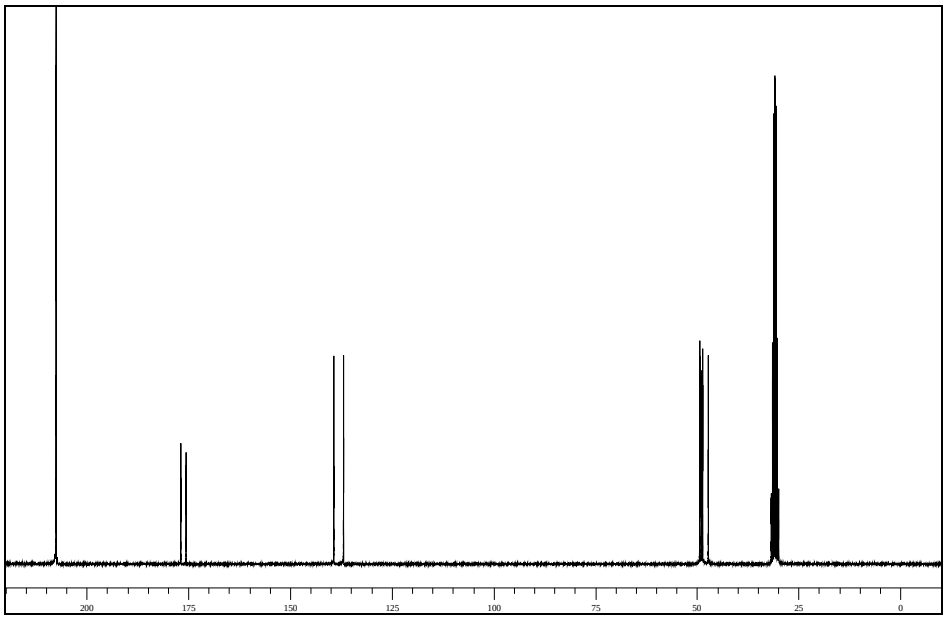


^{1}H NMR spectrum of the pure product (250 MHz, acetone-D_6)



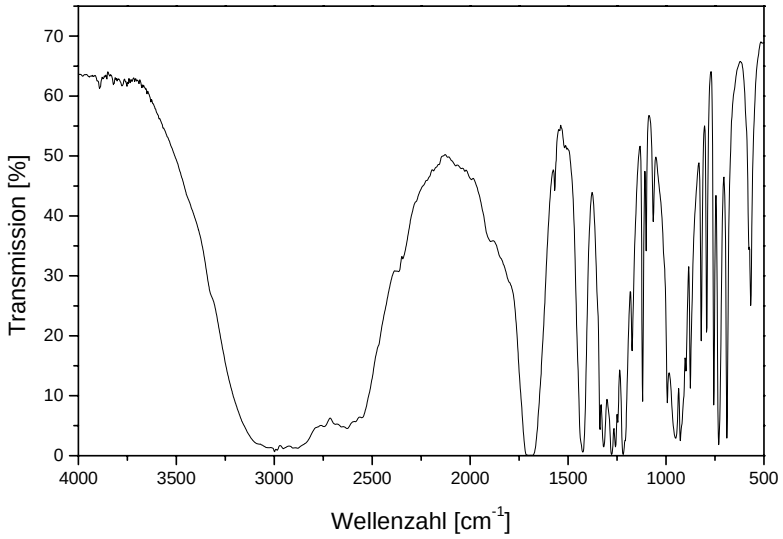
δ (ppm)	Multiplicity	Number of H	Assignment
1.41	Ddd, ^{2}J = 8.5, ^{3}J = 4.0, J = 1.8	1	C**H$_2$**
1.61	m, ^{2}J = 8.5	1	C**H$_2$**
2.62	dd, ^{3}J = 4.6, J = 1.8	1	C**H**-COOH
3.12	M	1	C**H**
3.24	M	1	C**H**
3.35	dd, ^{3}J = 4.6; ^{3}J = 4.1	1	C**H**-COOH
6.09	dd, ^{3}J = 5.8, J = 2.7	1	C**H**=C**H**
6.29	dd, ^{3}J = 5.8, J = 3.0	1	C**H**=C**H**
9	Bs	2	COO**H**
2.09			solvent

^{13}C NMR spectrum of the pure product (62.5 MHz, acetone-D_6)



δ (ppm)	Assignment
47.2	**C**H_2
48.6	**C**H
48.9	**C**H
49.3	**C**H-COOH
49.4	**C**H-COOH
136.8	**C**H=**C**H
139.2	**C**H=**C**H
175.7	**C**OOH
176.9	**C**OOH
30.6, 206.6	solvent

IR spectrum of the pure product (KBr)



(cm^{-1})	**Assignment**
2300-3300	O-H-valence, carboxylic acid C-H-valence, superimposed by O-H
1725	C=O-valence, carboxylic acid