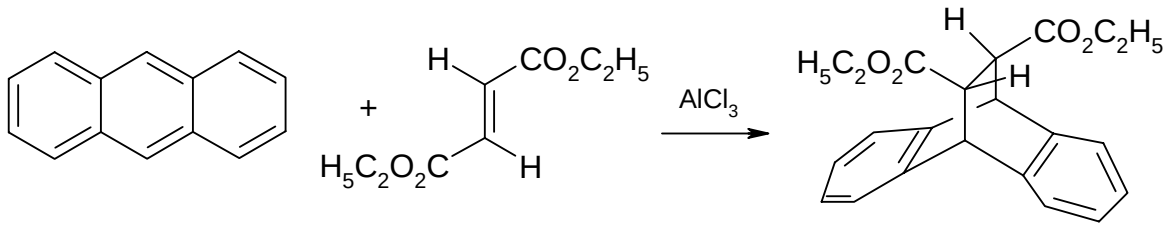
3010 Synthesis of 9,10-dihydro-9,10-ethanoanthracene-11,12-trans-dicarboxylic acid diethyl ester



$C_{14}H_{10}$	$C_8H_{12}O_4$		$C_{22}H_{22}O_4$
(178.2)	(172.2)	(133.3)	(350.4)

Literature

P. Yates, P. Eaton, *J. Am. Chem. Soc.* **1960**, *82*, 4436

Classification

Reaction types and substance classes

cycloaddition, Diels-Alder reaction

alkene, aromatics, carboxylic acid ester, diene, dienophile, acid catalyst

Work methods

working with moisture exclusion, heating under reflux, stirring with magnetic stir bar, filtering, evaporating with rotary evaporator, recrystallizing, use of an ice cooling bath, heating with oil bath

Instruction (batch scale 100 mmol)

Equipment

1000 mL three-neck flask, adapter with ground glass joint and hose coupling, protective gas supply, reflux condenser, drying tube, bubble counter, powder funnel, heatable magnetic stirrer, magnetic stir bar, rotary evaporator , ice bath, desiccator, oil bath

Substances

anthracene (mp 215-217 °C9	17.8 g (100 mmol)
fumaric acid diethyl ester (bp 219 °C)	17.2 g (16.4 mL, 100 mmol)
aluminium chloride (water free)	13.3 g (100 mmol)
cyclohexane (water free) (bp 81 °C)	500 mL
cyclohexane (bp 81 °C)	200 mL
sodium carbonate decahydrate	24.9 g (150 mmol)
sodium carbonate (water free)	25.0 g (236 mmol)
ethanol (bp 78 °C)	150 mL

Reaction

The reaction apparatus consists of a thoroughly dried 1000 mL three-neck flask with reflux condenser, drying tube and magnetic stir bar. On one opening of the flask is placed an adapter with ground glass joint and hose coupling as inlet for nitrogen. This adapter is replaced through a glass stopper after the addition of aluminium chloride to the flask. The reaction apparatus is flushed with nitrogen. Then under stirring 17.8 g (100 mmol) anthracene and 17.2 g (16.4 mL, 100 mmol) fumaric acid diethyl ester are dissolved in the flask in 500 mL absolute cyclohexane. After cooling down in the ice bath 13.3 g (100 mmol) water-free aluminium chloride are added in one portion over a powder funnel under nitrogen counter flow. The reaction mixture is heated under stirring for four hours under reflux.

Work up

The reaction mixture is cooled down to room temperature, then 24.9 g (150 mmol) sodium carbonate decahydrate are added. The drying tube is replaced through a bubble counter filled with paraffin oil and the mixture is stirred until no more gas is formed. Then 25 g (236 mmol) sodium carbonate (water free) are added. The mixture is stirred for 10 minutes. The solid is filtered off and washed in portions with a total of 200 mL cyclohexane. The solvent is evaporated from the filtrate at a rotary evaporator. A solid residue remains as crude product, which is dried in the desiccator. Crude yield: 32.6 g

The crude product is recrystallized from about 150 mL ethanol.

Yield: 30.8 g (87.9 mmol, 88%); colourless crystals, mp 103 °C

Comments

The yield strongly depends on the quality of the aluminium chloride. Aluminium chloride is very hygroscopic, therefore the storage flask should be closed immediately after the chloride has been taken out. The addition to the reaction flask should be as fast as possible, and under nitrogen atmosphere.

Waste management

Recycling

The evaporated cyclohexane is collected and redistilled.

The ethanol from the mother liquor can be evaporated, collected and redistilled.

Waste disposal

Waste	Disposal
filtered solid	solid waste, free from mercury
mother liquor, if not worked up	organic solvents, halogen free

Time

7 hours

Break

After filtration of the solid

Degree of difficulty
Medium

Instruction (batch scale 10 mmol)

Equipment

100 mL three-neck flask, adapter with ground glass joint and hose coupling, protective gas supply, reflux condenser, drying tube, bubble counter, powder funnel, heatable magnetic stirrer, magnetic stir bar, rotary evaporator, ice bath, desiccator, oil bath

Substances

anthracene (mp 215-217 °C)	1.78 g (10.0 mmol)
fumarsäurediethylester (bp 219 °C)	1.72 g (1.64 mL, 10.0 mmol)
aluminium chloride (water free)	1.33 g (10.0 mmol)
cyclohexane (water free) (bp 81 °C)	50 mL
cyclohexane (bp 81 °C)	20 mL
sodium carbonate-decahydrate	2.49 g (15.0 mmol)
sodium carbonate (water free)	2.5 g (23.6 mmol)
ethanol (bp 78 °C)	15 mL

Reaction

The reaction apparatus consists of a thoroughly dried 100 mL three-neck flask with reflux condenser, drying tube and magnetic stir bar. On one opening of the flask is placed an adapter with ground glass joint and hose coupling as inlet for nitrogen. This adapter is replaced through a glass stopper after the addition of aluminium chloride to the flask. The reaction apparatus is flushed with nitrogen. Then under stirring 1.78 g (10.0 mmol) anthracene and 1.72 g (1.64 mL, 10.0 mmol) fumaric acid diethyl ester are dissolved in the flask in 50 mL absolute cyclohexane. After cooling down in an ice bath 1.33 g (10.0 mmol) water-free aluminium chloride are added in one portion over a powder funnel under nitrogen counter flow. The reaction mixture is stirred for 4 hours under reflux.

Work up

The reaction mixture is cooled down to room temperature, then 2.49 g (15.0 mmol) sodium carbonate decahydrate are added. The drying tube is replaced through a bubble counter, filled with paraffin oil and the mixture is stirred until no more gas is formed. Then 2.5 g (23.6 mmol) sodium carbonate (water free) is added. The mixture is stirred for 10 minutes. The solid is filtered off and washed in portions with a total of 20 mL cyclohexane. The solvent is evaporated from the filtrate at a rotary evaporator. A solid residue remains as crude product, which is dried in the desiccator. Crude yield: 3.18 g

The crude product is recrystallized from about 15 mL ethanol.
Yield: 3.00 g (8.56 mmol, 86%); colourless crystals, mp 103 °C

Comments
The yield strongly depends on the quality of the aluminium chloride. Aluminium chloride is very hygroscopic, therefore the storage flask should be closed immediately after the chloride has been taken out. The addition to the reaction flask should be as fast as possible and under nitrogen atmosphere.

Waste management

Recycling
The evaporated cyclohexane is collected and redistilled.

Waste disposal

Waste	Disposal
filtered solid	solid waste, free from mercury
mother liquor	organic solvents, halogen free

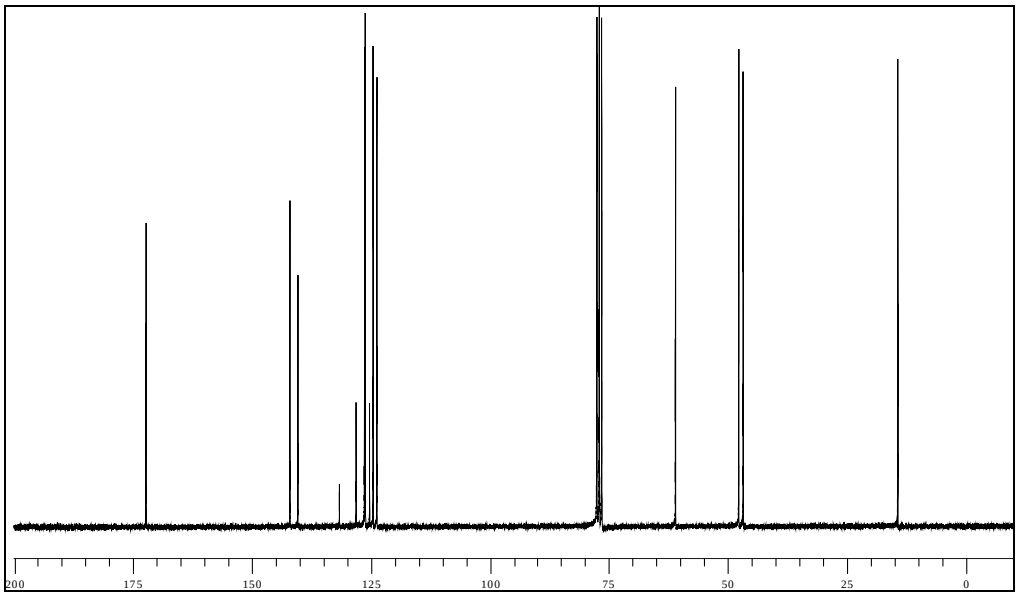
Time
6 hours

Break
After filtration of the solid

Degree ofDifficulty
Medium

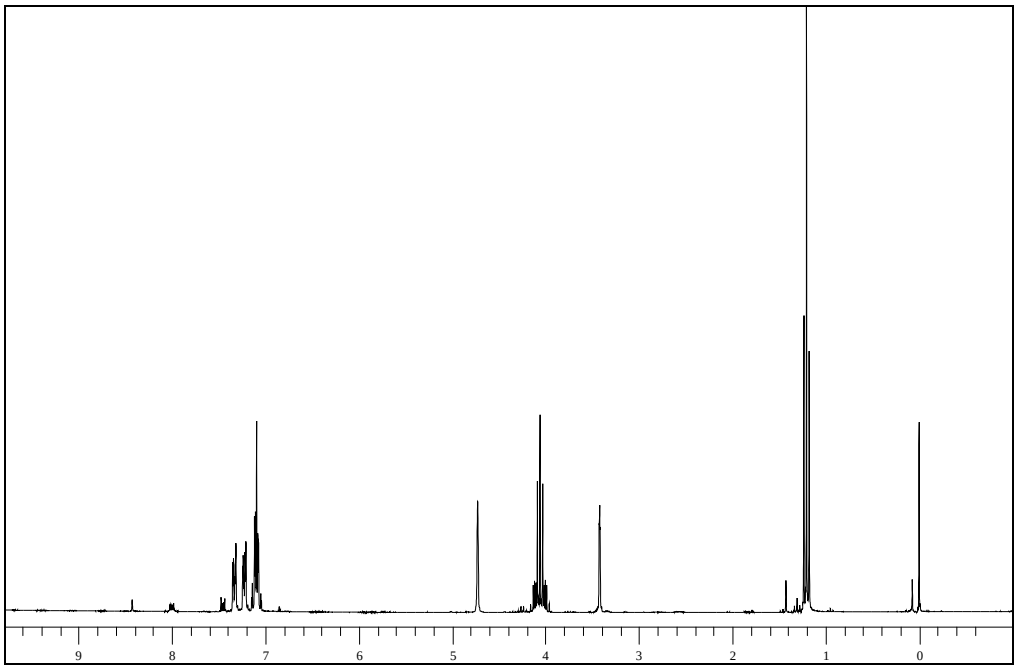
Analytics

^{13}C NMR spectrum of the pure product (62.5 MHz, $CDCl_3$)

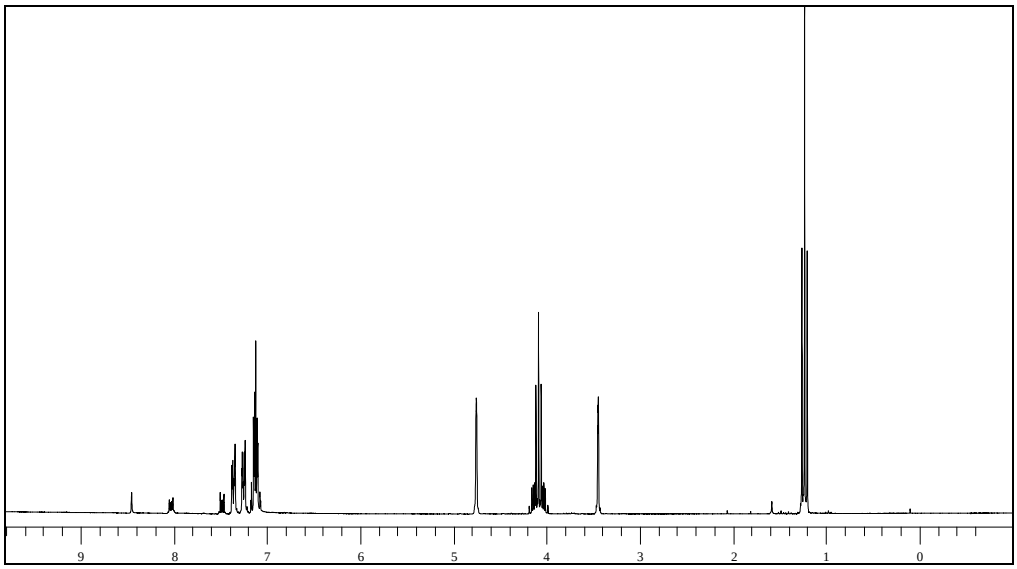


δ (ppm)	Assignment
14.2	**C**H_3
46.7	**C**H-CH arene
47.7	**C**H-COO
60.9	O-**C**H_2-CH_3
123.8, 124.5, 126.2, 126.3, 140.3, 142.0	**C**H arene
172.3	**C**OO
76.5-77.5	solvent

^{1}H NMR spectrum of the crude product (250 MHz, $CDCl_3$)



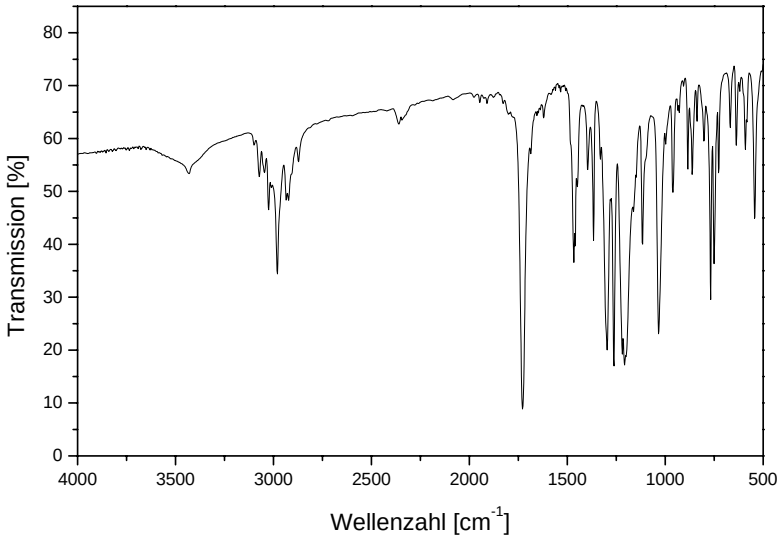
^{1}H NMR spectrum of the pure product (250 MHz, $CDCl_3$)



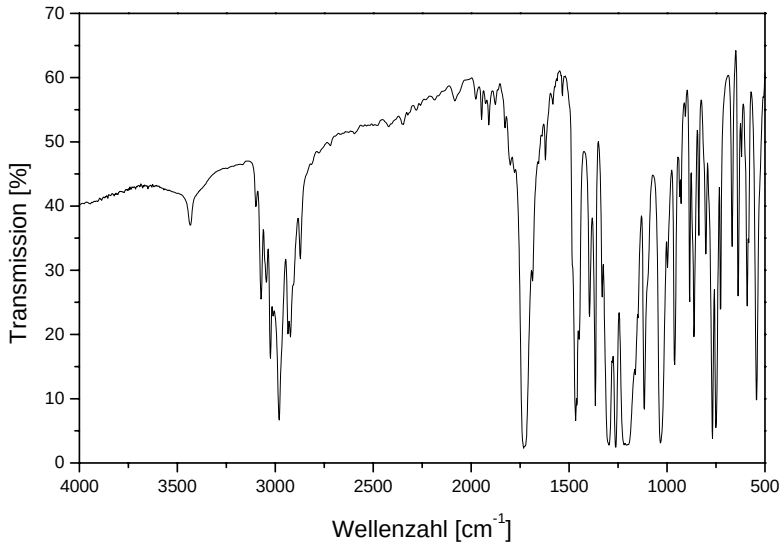
δ (ppm)	Multiplicity	Number of H	Assignment
1.23	t, ^{3}J=7.2 Hz	6	C**H$_3$**
3.45	M	2	C**H**-COO
4.08	M	4	C**H$_2$**
4.75	M	2	C**H**-C arene
7.09-7.38	m	8	C**H** arene

The signals at δ > 7.4 refer to remaining anthracene.

IR spectrum of the crude product (KBr)



IR spectrum of the pure product (KBr)



(cm^{-1})	**Assignment**
3074, 3026	C-H-valence, arene
2981, 2935, 2897	C-H-valence, alkane
1739	C=O-valence, ester
1467	C=C-valence, arene