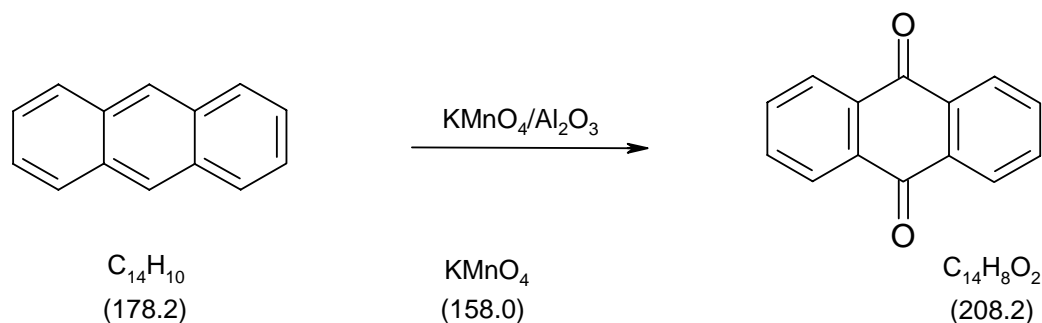


5026 Oxidation of anthracene to anthraquinone



Literature

Nüchter, M., Ondruschka, B., Trotzki, R., *J. Prakt. Chem.* **2000**, 342, No. 7

Classification

Reaction types and substance classes

oxidation
aromatics, quinone

Work methods

mechanochemical reaction, grinding with a planet ball mill, filtering, evaporating with rotary evaporator

Instruction (batch scale 2 mmol)

Equipment

planet ball mill (Pulverisette 7) with two grinding cups (20 mL) and seven grinding balls from agate for each cup (10 mm), Schlenk tube with frit G3 (diameter 2 cm, height 15 cm) with ground glass joint (NS 14), adapter with ground glass joint and hose coupling, 100 mL round-bottom flask, powder funnel, rotary evaporator

Substances

anthracene (mp 215-217 °C)	360 mg (2.02 mmol)
potassium permanganate	3.80 g (24.1 mmol)
aluminumoxid (Merck Al ₂ O ₃ 90 activ / neutral)	3.8 g
water	380 mg (21.1 mmol)
dichloromethane (bp 40 °C)	about 50 mL
magnesium sulfate (anhydrous)	about 5 g

Reaction

In each of the grinding cups a mixture of 3.8 g aluminum oxide and 3.80 g (24.1 mmol) potassium permanganate is placed. 360 mg (2.02 mmol) anthracene and 380 mg (21.1 mmol) water are added to each cup and the reaction mixture is ground at 800 rpm for 10 minutes.

Work up

The product is isolated by flash chromatography of the reaction mixture. A frit G3 with ground joints is used as the separation column, magnesium sulfate as the stationary phase and dichloromethane as eluting solvent. The frit is filled with a 2 cm layer of magnesium sulfate and then to the upper edge of the magnesium sulfate layer with dichloromethane. A 100 mL round-bottom flask serves as collecting flask.

The red-brown solid from the grinding cups is transferred onto the magnesium sulfate layer using a powder funnel. One grinding cup with the grinding balls is washed thoroughly with 10 mL dichloromethane which is also then used to wash the second grinding cup. The liquid is then poured onto the packed column. The ground glass adaptor which can be connected via tubing to the air or nitrogen line is placed onto the frit and the liquid phase under slight pressure (1.1 – 1.2 bar) is passed over the column until no further liquid is present above the solid phase. One refills the frit with 10 mL dichloromethane and elutes, again under slight pressure, a further two times. Thereafter the column is allowed to run dry. The solvent is evaporated completely from the eluted solution using the rotary evaporator. Anthrachinone remains as a yellow solid.

Yield: 420 mg (2.02 mmol, 100%); mp 284-287 °C; purity according to GC > 99%

Comments

The presence of water in equimolar amounts to the used permanganate is critical for the successful oxidation on a solid substrate.

Dichloromethane as a elution solvent is not easily replacable, because the product has a very poor solubility in non-polar solvents and protic solvents also dissolve excess permanganate partially.

Magnesium sulfate impedes the carrying over of permanganate by water from the elution solvent or from the ground material.

If the filtration is performed at atmospheric pressure, the time for work up of the product is increased by at least one hour.

The mechanochemical reaction does not necessarily need a planet ball mill: The reaction mixture is ground intensively in a mortar with a pestle for half an hour, until the light violet color has changed into a pale brown color.

The batch size can be increased up to 10 mmol.

Waste management**Recycling**

The evaporated dichloromethane is collected and redistilled.

Waste disposal

Waste	Disposal
solid residue from frit	solid waste, free from mercury, containing heavy metals

Time

1 hour

Break

The ground mixture is stable at room temperature.

Degree of difficulty

Easy

Analytics**Reaction monitoring by GC**

Sample preparation: For each sample 5 mg are dissolved in 0.5 mL dichloromethane and analyzed

GC conditions:

column: HP-5; L=30 m,d=0.32 mm, film=0.25 µm (Phenomenex)

inlet: split injection 150:1

carrier gas: He, precolumn pressure 41 kPa

oven: 120 °C, 10 °C/min 280 °C

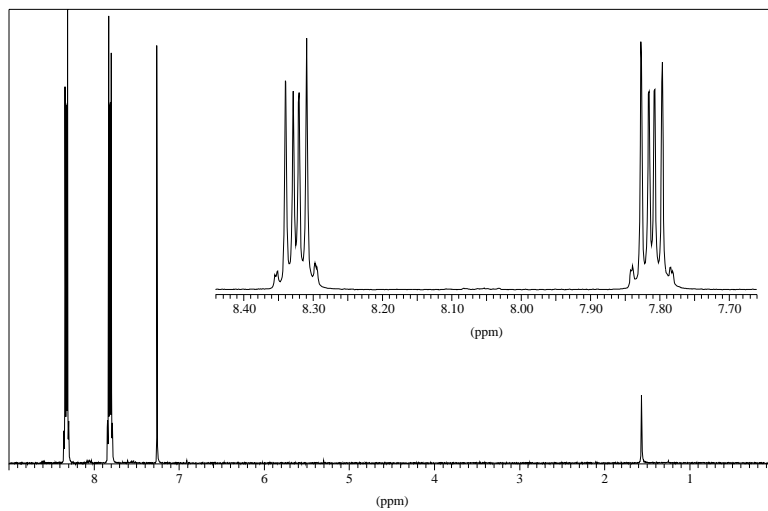
detector: 300 °C

Percent concentration was calculated from peak areas

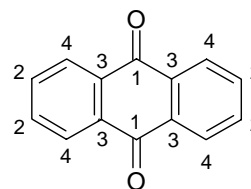
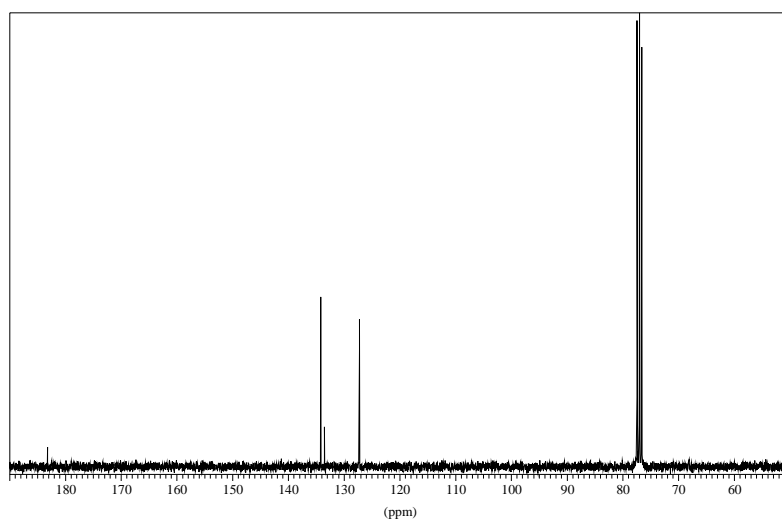
GC of the product

Retentiontime (min)	Substance	peak area %
7.89	(educt) anthracene	0.15
9.72	(product) anthrachinone	99.85

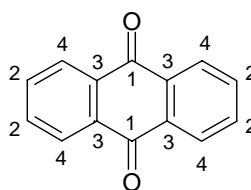
The characterization of the compounds and the assignment of the retention times was done by GC-MS.

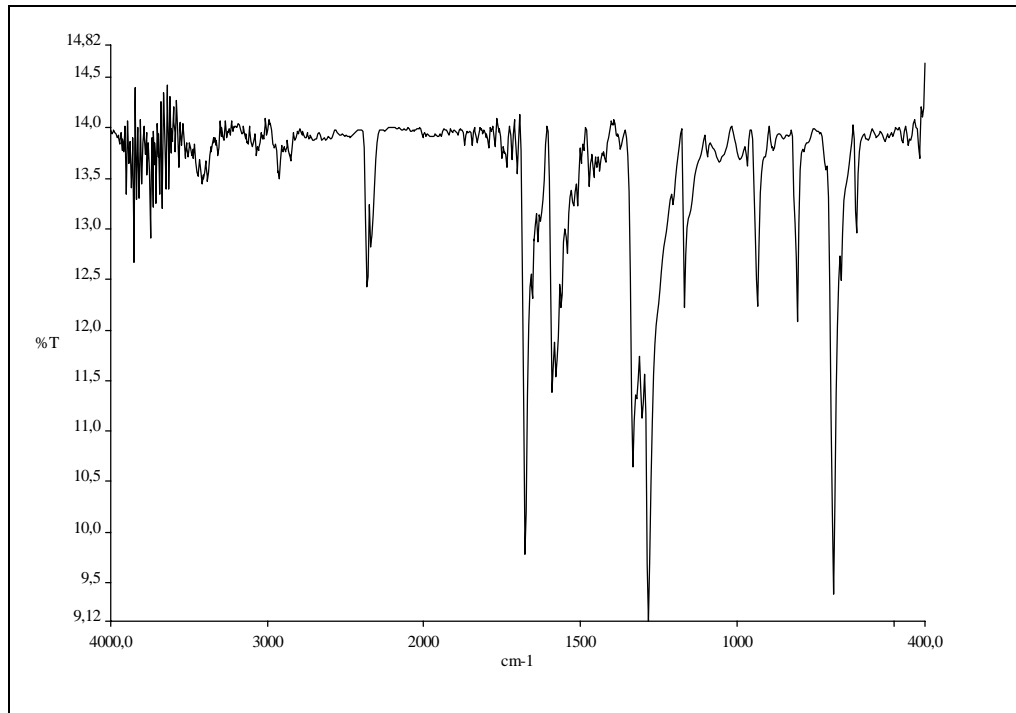
^1H NMR spectrum of the product (300 MHz, CDCl_3)

δ (ppm)	Multiplicity	Number of H	Assignment
7.81	m (AA')	4	2-H
8.32	m (BB')	4	4-H
1.57			water
7.26			solvent

 **^{13}C NMR spectrum of the product (300 MHz, CDCl_3)**

δ (ppm)	Assignment
127.2	C-4
133.5	C-3
134.1	C-2
183.1	C-1
76.5-77.5	solvent



IR spectrum of the product (KBr)

(cm ⁻¹)	Assignment
1680	C = O – valence
1590	C = C – valence, arene