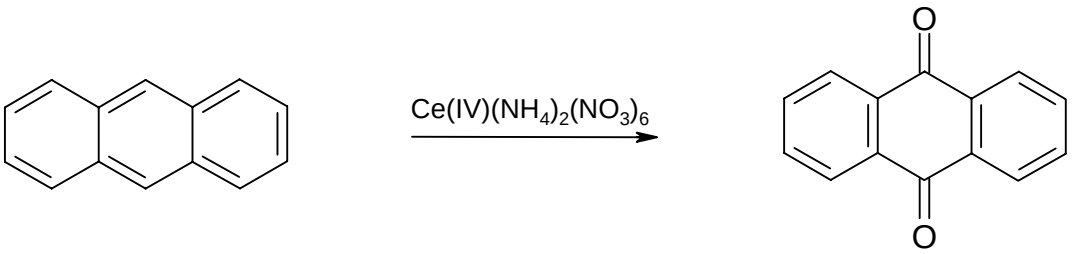
3021 Oxidation of anthracene to anthraquinone



$C_{14}H_{10}$ (178.2) | $CeH_8N_8O_{18}$ (548.2) | $C_{14}H_8O_2$ (208.2)

Literature
Tse-Lok Ho et al., *Synthesis* **1973**, 206.

Classification

Reaction types and substance classes
oxidation
aromatics, quinone

Work methods
stirring with magnetic stir bar, evaporating with rotary evaporator, filtering, recrystallizing

Instruction (batch scale 10 mmol)

Equipment
250 mL round-bottom flask, magnetic stirrer with magnetic stir bar, rotary evaporator, suction flask, suction filter, desiccator

Substances

anthracene (mp 215-217 °C)	1.78 g (10.0 mmol)
ammonium cerium(IV)-nitrate	21.9 g (40.0 mmol)
tetrahydrofuran (bp 66 °C)	65 mL
water	170 mL
acetic acid (99-100%) (bp 118 °C)	150 mL

Reaction
1.78 g (10.0 mmol) Anthracene and 65 mL tetrahydrofuran are placed in a 250 mL round-bottom flask and whilst stirring 20 mL water are added. A white suspension forms to which 21.9 g (40.0 mmol) ammonium cerium(IV) nitrate are added and the mixture is allowed to stir for a further 5 minutes.

Work up

The solvent is evaporated to 15 mL on the rotary evaporator at 25 hPa. The residue in the flask consists of an aqueous phase and a solid. The aqueous phase is decanted or the solid is filtered off. In order to remove any water soluble components, the solid is placed in an Erlenmeyer flask or round-bottom flask and washed thoroughly with 150 mL water before being filtered. The solid is dried either in a round-bottom flask on the rotary evaporator at 20 hPa and a water bath temperature of 50 °C, or in a vacuum desiccator. Crude yield: 2.07 g; purity according to GC 96%

The crude product is recrystallized from 100 mL acetic acid (99-100%).
Yield: 1.69 g (8.12 mmol, 81%); yellow needles; mp 284 °C; purity according to GC 100%

After evaporation of the solvent from the mother liquor, the residue can be recrystallized from 50 mL acetic acid.
Yielde: 179 mg (0.86 mmol, 8.6%); purity according to GC 100%

Total yield: 1.86 g (8.98 mmol, 90%)

Comments

It is unneccessary to dry the crude product before recrystallization, if the yield of crude product does not need to be determined.

Waste management

Waste disposal

Waste	Disposal
evaporated tetrahydrofuran water mixture	solvent water mixtures, halogen free
aqueous filtrate of crude product isolation	solvent water mixtures, halogen free, containing heavy metals
mother liquor from recrystallization	neutralize with NaOH, then: solvent water mixtures, halogen free

Time

1 hour

Break

After evaporation of the solvent on the rotary evaporator

Degree of Difficulty

Easy

Instruction (batch scale 2 mmol)

Equipment

50 mL round-bottom flask, magnetic stirrer with magnetic stir bar, rotary evaporator, suction flask, suction filter, desiccator

Substances

anthracene (mp 215-217 °C)	356 mg (2.00 mmol)
ammonium cerium(IV)-nitrate	4.39 g (8.00 mmol)
tetrahydrofuran (bp 66 °C)	13 mL
water	34 mL
acetic acid (99-100%) (bp 118 °C)	30 mL

Reaction

356 mg (2.00 mmol) Anthracene and 13 mL tetrahydrofuran are placed in a 50 mL round-bottom flask and whilst stirring 4 mL water are added. A white suspension forms to which 4.39 g (8.00 mmol) ammonium cerium(IV) nitrate are added and the mixture is allowed to stir for a further 5 minutes.

Work up

The solvent is evaporated to about 3 mL on the rotary evaporator at 25 hPa. The residue in the flask consists of an aqueous phase and a solid. The aqueous phase is decanted or the solid is filtered off. In order to remove any water soluble components, the solid is placed in a small Erlenmeyer flask or round-bottom flask and washed thoroughly with 30 mL water before being filtered. The solid is dried either in a round-bottom flask on the rotary evaporator at 20 hPa and a water bath temperature of 50 °C, or in a vacuum desiccator. Crude yield: 414 mg; purity according to GC 96%

The crude product is recrystallized from 20 mL acetic acid (99-100%).
Yield: 339 mg (1.63 mmol, 81%); yellow needles; mp. 284 °C; purity according to GC 100%

After evaporation of the solvent from the mother liquor, the residue can be recrystallized from 10 mL acetic acid.
Yielde: 30 mg (0.14 mmol, 7%); purity according to GC 100%

Total yield: 369 mg (1.77 mmol, 88%)

Comments

It is unneccessary to dry the crude product before recrystallization, if the yield of crude product does not need to be determined.

Waste management

Waste disposal

Waste	Disposal
evaporated tetrahydrofuran water mixture	solvent water mixtures, halogen free
aqueous filtrate of crude product isolation	solvent water mixtures, halogen free, containing heavy metals
mother liquor from recrystallization	neutralize with NaOH, then: solvent water mixtures, halogen free

Time
1 hour

Break
After evaporation of the solvent on the rotary evaporator

Degree of Difficulty
Easy

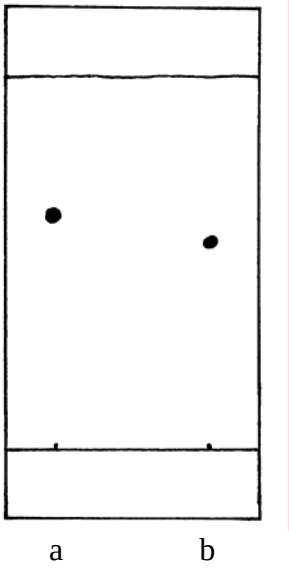
Analytics

Reaktion monitoring with TLC

Sample preparation:
Reaction mixture: Four drops of the reaction mixture are diluted with 1 mL *tert*-butylmethylether and extracted with 0.5 mL water. The organic phase is spotted.
Solid: A few crystals of the solid are dissolved in 1 mL *tert*-butylmethylether and the solution is spotted.

TLC conditions:

adsorbent:	Merck TLC Alu plates silica gel 60 F_{254}, 5 x 10 cm
elution solvent:	ethyl acetate/cyclohexane 50:50
R_f (anthracene **a**)	0.62
R_f (anthraquinone **b**)	0.55



Reaction monitoring with GC

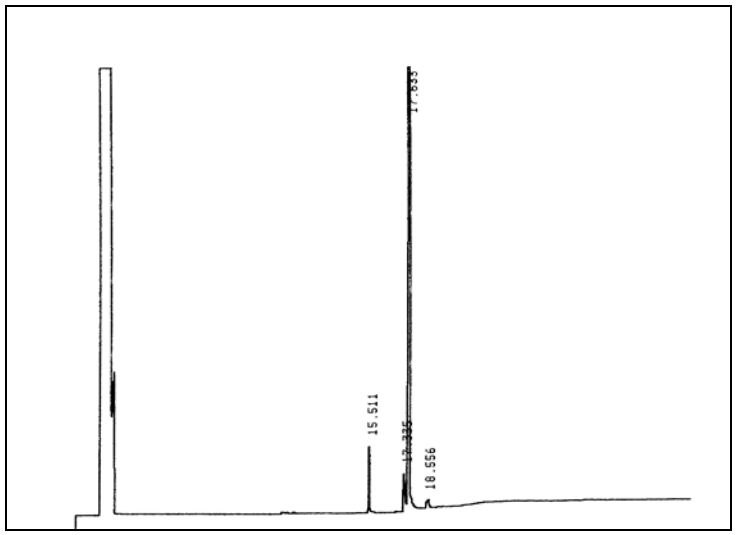
Sample preparation:
Four drops of the reaction mixture are diluted with 1 mL *tert*-butylmethylether and extracted with 0.5 mL water. Of the organic phase, 2 µL are injected.
A few crystals of the solid are dissolved in 1 mL *tert*-butylmethylether and 2 µL of the solution is injected.

GC conditions:

column:	Macherey and Nagel, SE-54, L=25 m, d=0.32 mm, film=0.25 µm
inlet:	injector 250 °C, split injection 1:20, injected volume 2 µL
carrier gas:	N_2, precolumn pressure 62 kPa
oven:	100 °C (1 min), 10 °C/min 250 °C (30 min)
detector:	FID, 275 °C

Percent concentration was calculated from peak areas

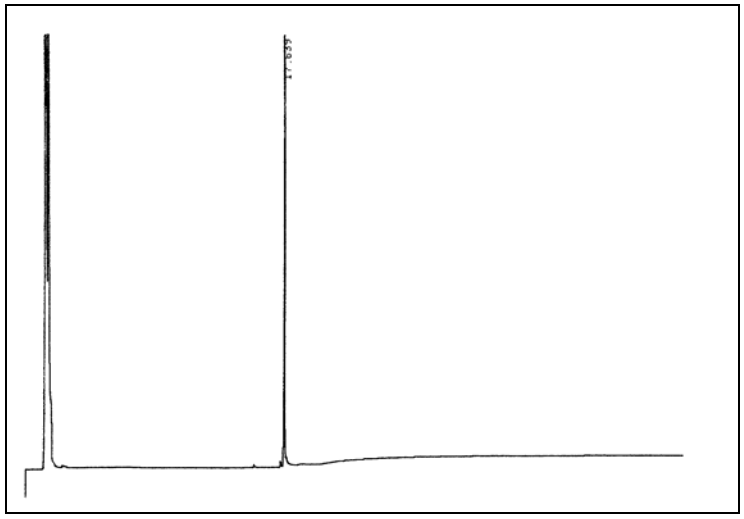
GC of the crude product



Retention time (min)	Substance	Peak area %
17.6	product (anthraquinone)	96.4
15.5	educt (anthracene) (GC/MS)	2.1
17.3	side product (anthrone) (GC/MS)[3]	1.1
18.6	side product (2-hydroxyanthraquinone) (GC/MS)[4]	0.4

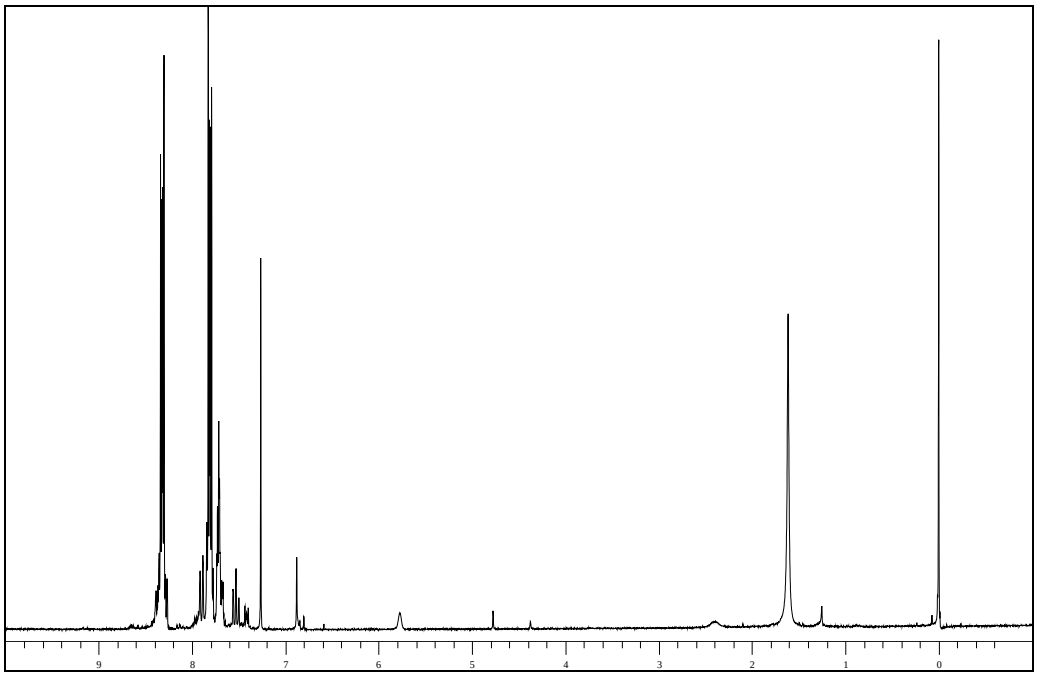
[3] m/e: 195, 194 (100, M^+), 193, 166, 164, 163, 82.
[4] m/e: 224 (M^+), 223, 196, 168, 139, 84, 76.

GC of the pure product

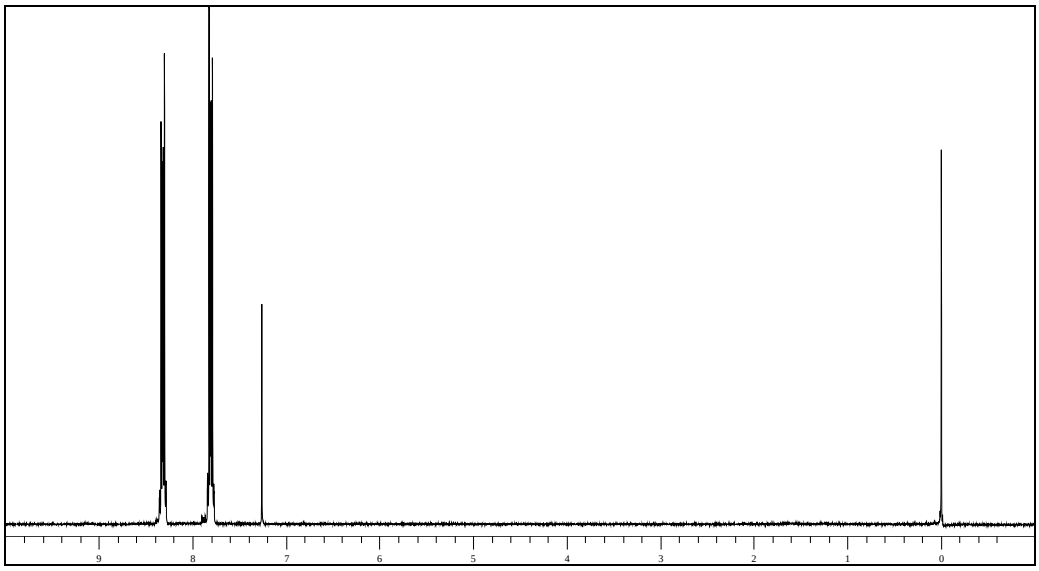


Retention time (min)	Substance	Peak area %
17.6	product (anthraquinone)	100

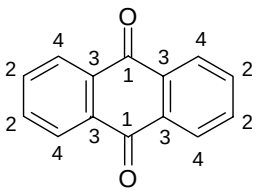
^{1}H NMR spektrum of the crude product (250 MHz, $CDCl_3$)



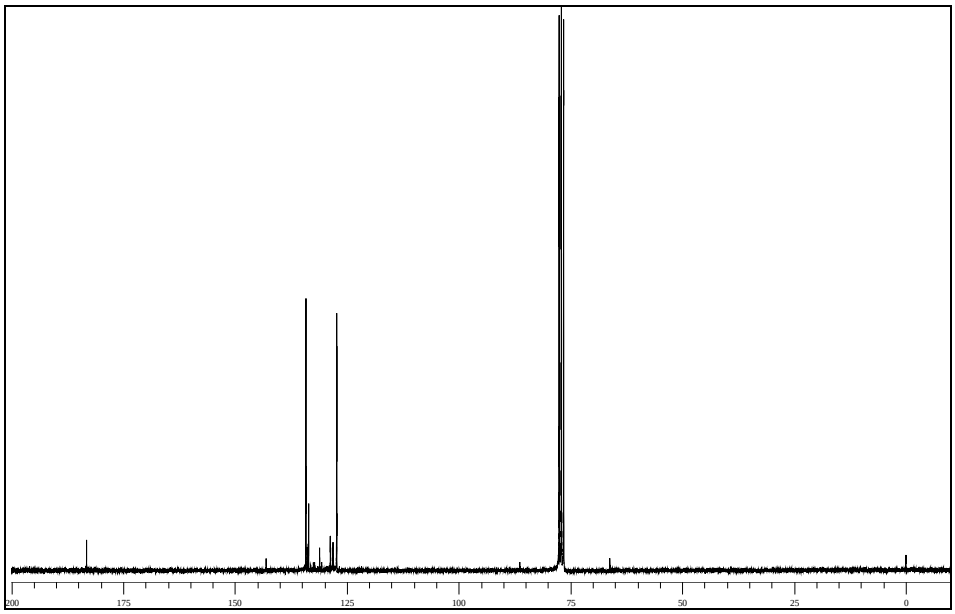
^{1}H NMR spectrum of the pure product (250 MHz, $CDCl_3$)



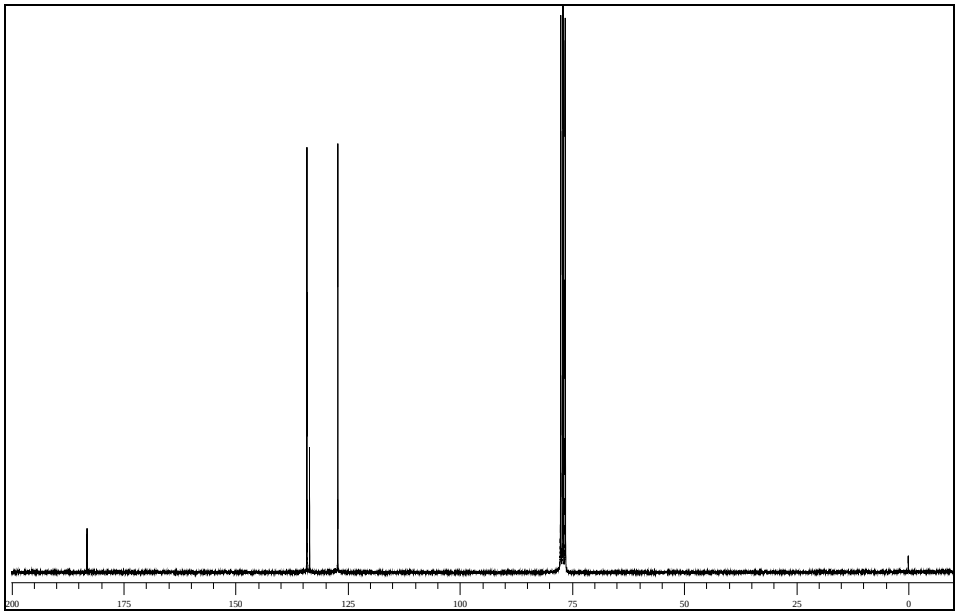
δ (ppm)	Multiplicity	Number of H	Assignment
7.81	m (AA')	4	2-H
8.32	m (BB')	4	4-H
7.26			solvent



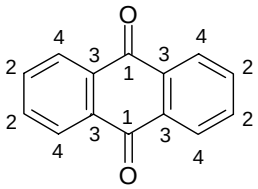
^{13}C NMR spectrum of the crude product (62.5 MHz, $CDCl_3$)



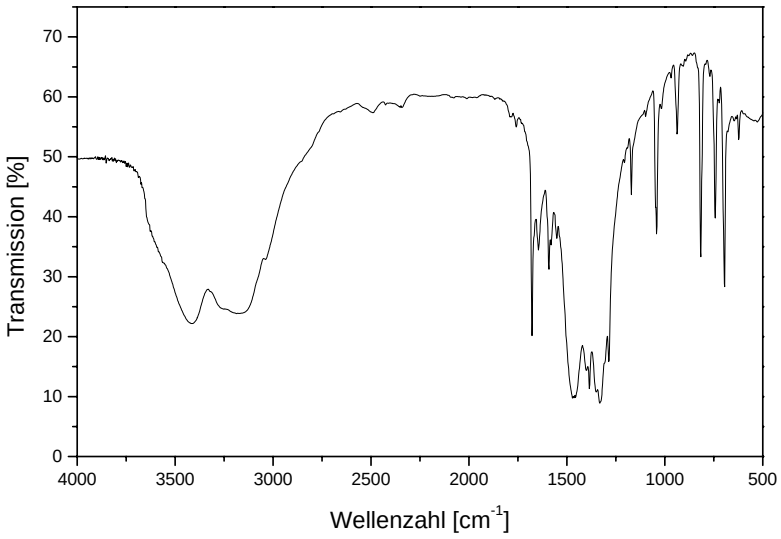
^{13}C NMR spectrum of the pure product (62.5 MHz, $CDCl_3$)



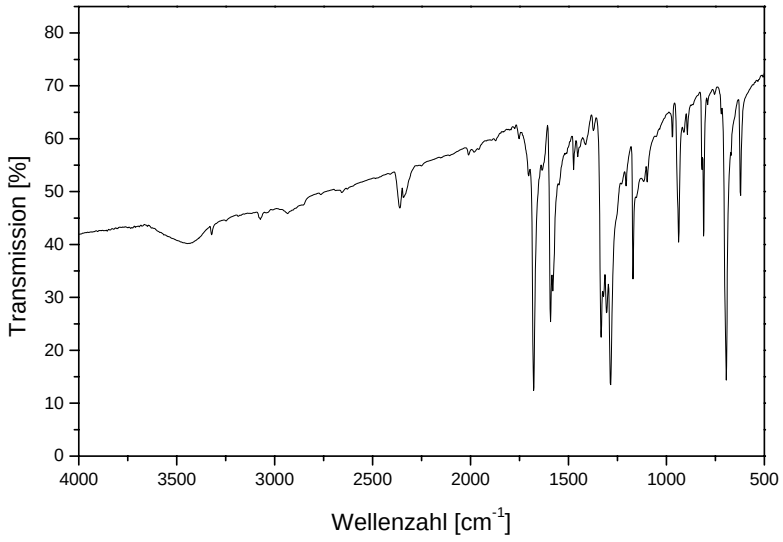
δ (ppm)	Assignment
127.2	C-4
133.5	C-3
134.1	C-2
183.1	C-1
76.5-77.5	solvent



IR spectrum of the crude product (KBr)



IR spectrum of the pure product (KBr)



(cm^{-1})	**Assignment**
1680	C = O – valence
1590	C = C – valence, arene