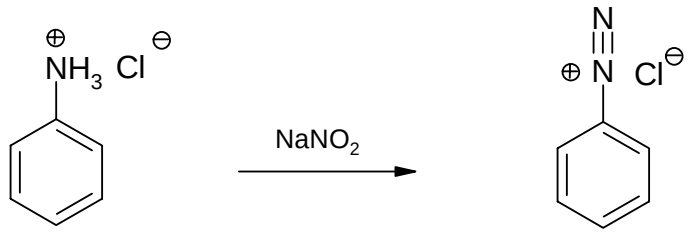
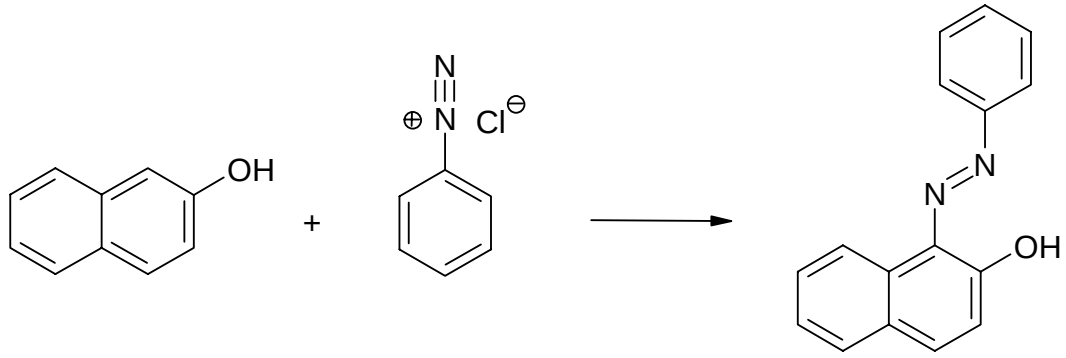
1017 Azocoupling of benzenediazonium chloride with 2-naphthol to 1-phenylazo-2-naphthol



C_6H_8ClN (129.6) — (69.0) — $C_6H_5ClN_2$ (140.6)



$C_{10}H_8O$ (144.2) + $C_6H_5ClN_2$ (140.6) → $C_{16}H_{12}N_2O$ (248.3)

Classification

Reaction types and substance classes

electrophilic substitution of aromatics, azocoupling
aromatics, diazonium salt, naphthol, dye

Work methods

stirring with magnetic stir bar, filtering, recrystallizing, use of an ice cooling bath, heating with oil bath

batch scale 100 mmol, additional:
stirring with KPG-stirrer, adding dropwise with an addition funnel

Instruction (batch scale 10 mmol)

Equipment

250 mL Erlenmeyer flask, 100 mL Erlenmeyer flask, internal thermometer, pipette, heatable magnetic stirrer, magnetic stir bar, suction flask, Büchner funnel, desiccator, ice bath, oil bath

Substances

aniline hydrochloride (mp 199-202 °C)	1.43 g (11.0 mmol)
2-naphthol (mp 122-123 °C)	1.44 g (10.0 mmol)
sodium nitrite	759 mg (11.0 mmol)
conc. hydrochloric acid (35%)	2.5 mL
aqueous sodium hydroxide solution (1 M)	40 mL
ethanol for recrystallizing	about 50 mL
urea	small amount
potassium iodide starch test strips	
ice	

Reaction

Preparation of the diazonium salt solution:

13 g ice, 5 mL water and 2.5 mL conc. hydrochloric acid are filled in a 100 mL Erlenmeyer flask with magnetic stir bar and internal thermometer. To this mixture 1.43 g (11.0 mmol) aniline hydrochloride are added. Under ice cooling and stirring and at an internal temperature of 0-5 °C so much from a solution of 759 mg (11.0 mmol) sodium nitrite in 3 mL water (about 2.5 mL) is added slowly by using a pipette, that an excess of nitric acid is avoided. The test for HNO_2 is carried out with potassium iodide starch test strips by dropping a sample of the reaction solution with a pipette on a test strip. A blue coloured paper shows HNO_2. So much sodium nitrite solution is added, that a proof is positive still 5 minutes after the last addition of nitrite. Excessive nitric acid is removed by addition of a small amount of urea.

Azocoupling:

1.44 g (10.0 mmol) 2-naphthol are dissolved in 40 mL 1 M sodium hydroxide solution in a 250 mL Erlenmeyer flask. The solution is cooled. Under strong stirring and ice cooling the ice cooled benzenediazonium salt solution is added in portions. Towards the end of addition the pH value of the solution is controlled. To keep the solution in the alkaline range, a 1 M sodium hydroxide solution is added dropwise by means of a pipette, if necessary. After the addition is finished, the mixture is stirred for 30 minutes at 0-5 °C.

Work up

The orange precipitated product is sucked off over a Buechner funnel and repeatedly washed with water. The product is dried in the vacuum desiccator until weight constancy. According to the vacuum and drying agent, the drying procedure can last up to a few days.

Crude yield (humid): 6.5 g

Crude yield (dry): 2.20 g; mp 129 °C

The crude product is recrystallized from about 50 mL ethanol and then dried in the vacuum desiccator.

Yield: 1.97 g (7.93 mmol, 79%); mp 134 °C

Waste management

Recycling
The ethanol from the mother liquor is evaporated, collected and redistilled.

Waste disposal

Waste	Disposal
aqueous filtrate	solvent water mixtures,containing halogen
residue from the mother liquor	dissolve in a small amount of acetone, then: organic solvents, halogen free

Time
4 hours, without time for drying

Break
Before recrystallization

Degree of difficulty
Medium

Instruction (batch scale 100 mmol)

Equipment
250 mL Erlenmeyer flask, 1 L beaker, internal thermometer, addition funnel, heatable magnetic stirrer, magnetic stir bar, KPG-stirrer, suction flask, Buechner funnel, desiccator, ice bath, oil bath

Substances

aniline hydrochloride (mp 199-202 °C)	14.3 g (110 mmol)
2-naphthol (mp 122-123 °C)	14.4 g (100 mmol)
sodium nitrite	7.59 g (110 mmol)
conc. hydrochloric acid (35%)	25 mL
aqueous sodium hydroxide solution (1 M)	400 mL
ethanol for recrystallizing	about 500 mL
urea	small amount
potassium iodide starch test strips	
ice	

Reaction

<u>Preparation of the diazonium salt solution:</u>
130 g ice, 50 mL water and 25 mL conc. hydrochloric acid are filled in a 100 mL Erlenmeyer flask with magnetic stir bar and internal thermometer. To this mixture 14.3 g (110 mmol) aniline hydrochloride are added. Under ice cooling and stirring and at an internal temperature of 0-5 °C so much from a solution of 7.59 g (110 mmol) sodium nitrite in 3 mL water (about 25 mL) is added slowly dropwise with an addition funnel, that an excess of nitric acid is

avoided. The test for HNO_2 is carried out with potassium iodide starch test strips by dropping a sample of the reaction solution with a pipette on a test strip. A blue coloured paper shows HNO_2. So much sodium nitrite solution is added, that a proof is positive still 5 minutes after the last addition of nitrite. Excessive nitric acid is removed by addition of a small amount of urea.

Azocoupling:

14.4 g (100 mmol) 2-naphthol are dissolved in 400 mL 1 M sodium hydroxide solution in a 1 L beaker. The solution is cooled. Under strong stirring with a KPG-stirrer and ice cooling the ice cooled benzenediazonium salt solution is added slowly in portions. Towards the end of the addition the pH-value is checked. To keep the solution in the alkaline range, a 1 M sodium hydroxide solution is added dropwise by means of a pipette, if necessary. After the addition was finished, the mixture is stirred for 30 minutes at 0-5 °C.

Work up

The orange precipitated product is sucked off over a Buechner funnel and then washed with 500 mL water in a 1 L beaker. The product is again sucked off strongly and then dried in a vacuum desiccator until weight constancy. According to the vacuum and drying agent, the drying procedure can last up to a few days.

Crude yield (humid):160 g

Crude yield (dry): 21.5 g; mp 129 °C

The crude product is recrystallized from 500 mL ethanol and dried in the vacuum desiccator.

Yield: 19.5 g (78.5 mmol, 79%); mp 134 °C

Waste management

Recycling

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

Waste disposal

Waste	Disposal
aqueous filtrate	solvent water mixtures, containing halogen
residue from the mother liquor	dissolve in a small amount of acetone, then: organic solvents, halogen free

Time

5-6 hours, without time for drying

Break

Before recrystallization

Degree of difficulty

Medium

Analytics

TLC

TLC-conditions:

adsorbant:	Macherey and Nagel Polygram SilG/UV foil, 0.2 mm
eluent:	cyclohexane/acetic acid ethyl ester 8:2
R_f (1-phenylazo-2-naphthol)	0.65
R_f (2-naphthol)	0.39

Traces of not reacted 2-naphthol can be detected in the crude product, and also in the mother liquor from the recrystallization.

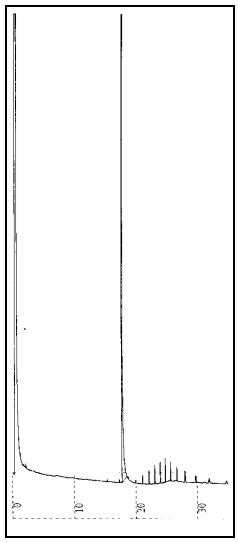
GC

GC-conditions:

column:	ZB–1, 7 HM–G001-11, length 30 m, internal diameter 0.32 mm, film 0.25 µm
inlet:	injector temperature 210 °C, split injection, injected volume 1 µL
carrier gas:	H_2, pre-column pressure 50 kPa
oven:	70 °C (2 min), heating rate 10 °C/min, isotherme 300 °C (10 min)
detector:	FID, 310 °C
integrator:	Shimadzu

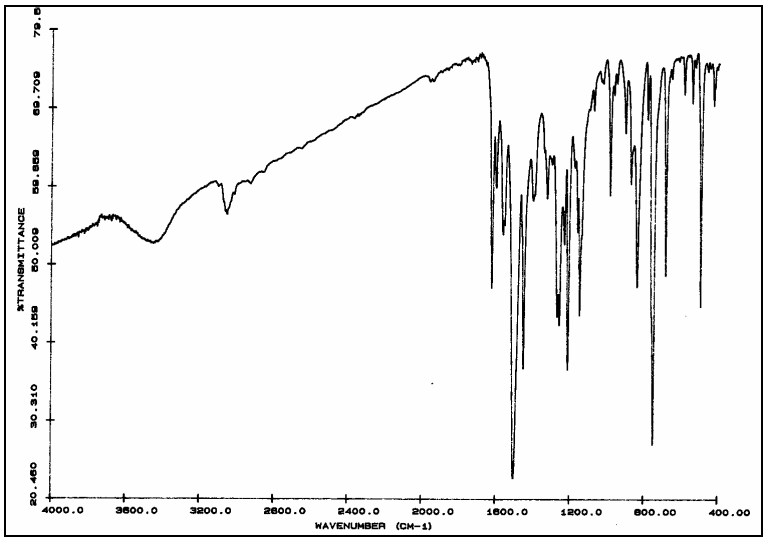
Percent concentration was calculated from peak areas.

GC of the product (not recrystallized)



Retention time (min)	Substance	Peak area %
17.9	product (1-phenylazo-2-naphthol)	> 99
from 20	impurities	

IR spectrum of the pure product (KBr)



(cm^{-1})	**Assignment**
3400	O-H-valence
3040	C-H-valence, arene
1620	C=C-valence, arene

UV Spectrum (ethanol)

λ_{max} = 422 nm, log ε = 4.05
λ_{max} = 478 nm, log ε = 4.17