
Application Bulletin

Of interest to: Organic chemistry
 Textiles, paper, ceramics
 Paints, lacquers, solvents

K 3, 13, 14

Synthesis of phenyl azonaphthol

Summary

The important class of azo dyes comprises more compounds than all other classes of dyes together. The azo compounds form the basis of many dyestuffs and pigments used in the textile, paper and wood industry today.

This bulletin describes the automated synthesis of phenyl azonaphthol by diazotisation of aniline and subsequent azo coupling with 2-naphthol. The 711 Liquino is used to control and monitor the whole process.

Instruments and accessories

- 2.711.0010 Liquino
 - 6.1111.030 Pt 100 temperature sensor
 - 2.700.0020 4 x Dosino
 - 6.1570.250 4 x 50 mL Dosing Unit (with glass cylinder)
 - 6.1805.130 4 x FEP extension tubing (length 2 m)
 - 6.1829.010 4 x FEP aspiration tubing (length 250 mm)
 - 6.1808.000 4 x Coupling bush for extension tubing
 - 6.2709.020 SGJ stopper
 - 6.2134.040 Cable 711 – PC (9 pin)
 - 2 L round flask with thermostatic jacket
 - Cooling bath
 - Precision glass stirrer
 - Condenser
 - PC
-

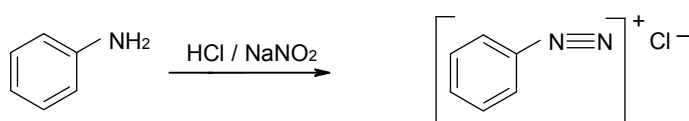
Reagents

- Aniline, $\rho(\text{C}_6\text{H}_5\text{NH}_2) = 1.021 \text{ g/mL}$
- Hydrochloric acid, half-concentrated, $c(\text{HCl}) \approx 5 \text{ mol/L}$
- Sodium nitrite solution, $c(\text{NaNO}_2) = 2.5 \text{ mol/L}$

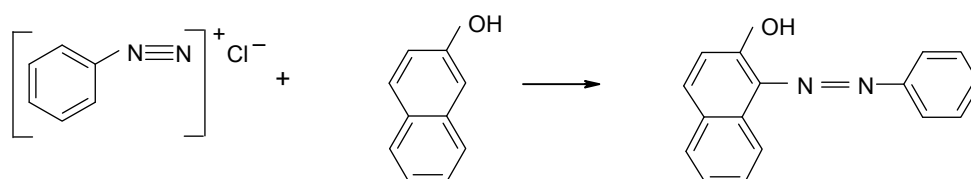
- 2-Naphthol solution, $\sigma(\text{C}_{10}\text{H}_7\text{OH}) = 8\%$ in $c(\text{NaOH}) = 2 \text{ mol/L}$
- Sodium hydroxide solution, $c(\text{NaOH}) = 2 \text{ mol/L}$
- Sodium chloride solution, saturated

Synthesis procedure

To 0.3 mol aniline in a 2 L round flask 1 mol hydrochloric acid [this corresponds to 200 mL $c(\text{HCl}) = 5 \text{ mol/L}$] is added. After the addition of 190 mL $c(\text{HCl}) = 5 \text{ mol/L}$ (method 1) the mixture is cooled down with vigorous stirring to $0 \text{ }^\circ\text{C}$ using a cooling bath at $-2 \text{ }^\circ\text{C}$ and the last 10 mL of half-concentrated hydrochloric acid are added (method 2). Afterwards 0.3 mol sodium nitrite [this corresponds to 120 mL $c(\text{NaNO}_2) = 2.5 \text{ mol/L}$] are added at a very low rate and with thorough stirring (method 3). During the whole process the temperature has to be kept below $5 \text{ }^\circ\text{C}$.



To the freshly prepared diazonium salt 300 mL of the 2-naphthol solution are added using a low dosing rate (method 4). During the addition the temperature has to be kept between 5 and $10 \text{ }^\circ\text{C}$ and thorough stirring is essential. The azo coupling of the benzene diazonium chloride with 2-naphthol results in phenyl azonaphthol, which forms red crystals:



The precipitation of the azo dye is completed by adding saturated NaCl solution to the mixture.

Useful hints

- Towards the end of the NaNO_2 addition it has to be checked if there is any free nitrous acid present in the bulk solution, which could interfere with the subsequent reactions. Iodide starch paper can be used for this assay. If the assay is positive, i.e. the indicator paper turns blue, add a small amount of urea or sulphamic acid, which removes the excess of free nitrous acid.
- Having added most of the 2-naphthol, check the pH of the bulk solution. If necessary add more sodium hydroxide solution [$c(\text{NaOH}) = 2 \text{ mol/L}$] to make sure that the mixture remains alkaline during the whole addition process.
- The red crystals of the synthesised phenyl azonaphthol can be purified by washing them with iced water.

Method sequence for the synthesis of phenyl azonaphthol

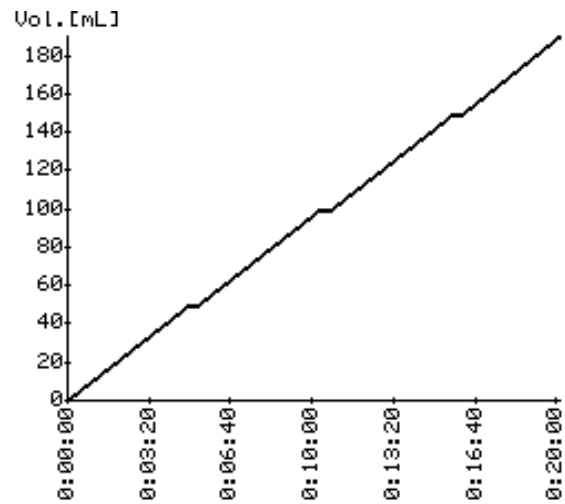
```
'pa
711 Liquino          01129  711.A011
date 1998-01-21    time 08:29
mode: SEQ          user method: DYES
parameters
>SEQ sequence
  auto start              1
step 1
  command:             METHOD
  method:              HCl add
step 2
  command:             METHOD
  method:              HCl add2
step 3
  command:             METHOD
  method:              NaNO2
step 4
  command:             PAUSE
  pause                00:01:00
step 5
  command:             METHOD
  method:              Naphthol
step 6
  command:             ENDSEQ
step 7
  command:             NO OPERATION
>SEQ preselections
  req.ident:           off
  >>SEQ prompts
    id1                Id1
    id2                Id2
    id3                Id3
>SEQ reports
  report1:             parameter
  report2:             off
  -----
```

**Parameters of method 1: addition of HCl
(190 mL) without temperature monitoring**

```
'sr
711 Liquino          01129 711.A011
date 1998-01-21    time 08:56
mode: XDOS          user method: HCl add

total dosing time   = 000:20:09
total volume        = 190.000 mL
dosing rate         = 10.000 mL/min
=====
```

```
'pa
711 Liquino          01129 711.A011
date 1998-01-21    time 08:56
mode: XDOS          user method: HCl add
parameters
>XDOS parameter
  XDOS type:        volume&rate
  volume            190.0 mL
  feed rate         10.0 mL/min
  temp. measuring:  off
  fill rate         max mL/min
  auto fill:        on
>XDOS dosing units
  setup:            single
  dosing drive:     DOS1
  dos.unit:         HCl halfconc
  port use:         custom
  dosing port       3
  filling port      2
  waste port        4
>XDOS monitoring
  temperature:      off
  volume:           off
>XDOS preselections
  req.ident:        off
  >>XDOS prompts
    id1             Id1
    id2             Id2
    id3             Id3
  start delay       00:00:00
>XDOS reports
  temp. auto scale: on
  temp. scale low   -70 °C
  temp. scale high  200 °C
  report1:          result
  report2:          parameter
  report3:          curve
  report4:          comb. list
  report5:          off
  report6:          off
  report7:          off
  report8:          off
=====
```

Volume vs. time curve for method 1


Parameters of method 2: addition of HCl (10 mL) with temperature monitoring

```
'sr
711 Liquino          01129 711.A011
date 1998-01-21    time 09:26
mode: XDOS          user method: HCl add2

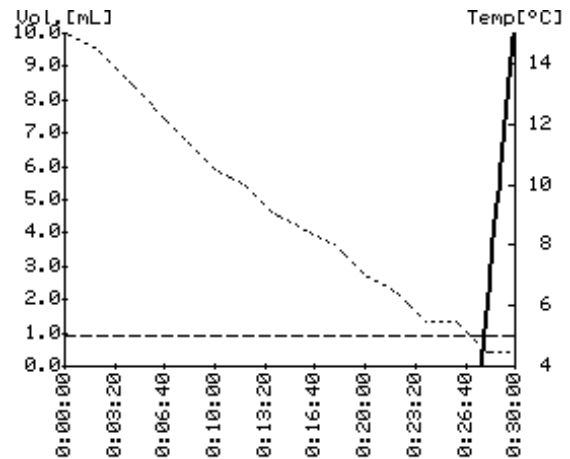
total dosing time   = 000:29:58
total volume        = 10.000 mL
dosing rate         = 5.000 mL/min
=====

'pa
711 Liquino          01129 711.A011
date 1998-01-21    time 09:26
mode: XDOS          user method: HCl add2
parameters
>XDOS parameter
  XDOS type:        volume&rate
  volume            10.0 mL
  feed rate         5.0 mL/min
  temp. measuring:  on
  rec. interval     00:02:00
  fill rate         max mL/min
  auto fill:        on
>XDOS dosing units
  setup:            single
  dosing drive:     DOS1
  dos.unit:         HCl halfconc
  port use:         custom
  dosing port       3
  filling port      2
  waste port        4
>XDOS monitoring
  temperature:      on
  low limit         -5.0 °C
  upper limit       5.0 °C
  action:           wait
  alarm pins:       none
  volume:           off
>XDOS preselections
  req.ident:        off
>>XDOS prompts
  id1               Id1
  id2               Id2
  id3               Id3
  start delay       00:00:00
>XDOS reports
  temp. auto scale: on
  temp. scale low   -70 °C
  temp. scale high  200 °C
  report1:          result
  report2:          parameter
  report3:          curve
  report4:          comb. list
  report5:          off
  report6:          off
  report7:          off
  report8:          off
=====
```

Measuring point list for method 2; volume and temperature vs. time curves

```
'cb
711 Liquino          01129 711.A011
date 1998-01-21    time 09:27
mode: XDOS          user method: HCl add2

time    vol.(mL)  temp(°C)  event
-----
000:00:00  0.000      15.0
000:00:00  0.000      *** START ***
000:00:00  0.000      T-limit,Wait
000:02:00  0.000      14.5 upper T-limit
000:04:00  0.000      13.5 upper T-limit
000:06:00  0.000      12.5 upper T-limit
000:08:00  0.000      11.5 upper T-limit
000:10:00  0.000      10.5 upper T-limit
000:12:00  0.000      10.0 upper T-limit
000:14:00  0.000      9.0 upper T-limit
000:16:00  0.000      8.5 upper T-limit
000:18:00  0.000      8.0 upper T-limit
000:20:00  0.000      7.0 upper T-limit
000:22:00  0.000      6.5 upper T-limit
000:24:00  0.000      5.5 upper T-limit
000:26:00  0.000      5.5 upper T-limit
000:27:49  0.000      Continue
000:27:56  0.630      T-limit,Wait
000:27:57  0.630      Continue
000:28:00  0.847      4.5
000:28:18  2.305      T-limit,Wait
000:28:19  2.305      Continue
000:28:39  3.980      T-limit,Wait
000:28:40  3.980      Continue
000:28:53  5.025      T-limit,Wait
000:28:54  5.025      Continue
000:28:58  5.340      T-limit,Wait
000:28:59  5.340      Continue
000:29:01  5.550      T-limit,Wait
000:29:02  5.550      Continue
000:29:56  10.000
000:29:57  10.000      T-limit,Wait
000:29:58  10.000      *** END ***
000:30:00  4.5
=====
```



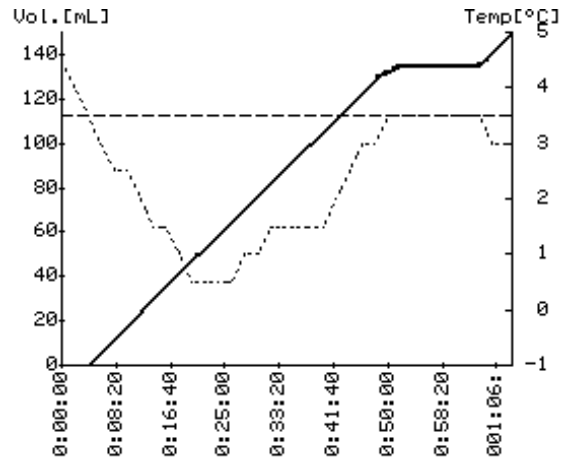
Parameters of method 3: diazotisation of aniline

Volume and temperature vs. time curves for method 3

```
'sr
711 Liquino          01129 711.A011
date 1998-01-21    time 10:36
mode: XDOS          user method: NaNO2

total dosing time   = 001:09:01
total volume        = 150.000 mL
dosing rate         = 3.000 mL/min
=====
```

```
'pa
711 Liquino          01129 711.A011
date 1998-01-21    time 10:36
mode: XDOS          user method: NaNO2
parameters
>XDOS parameter
  XDOS type:        volume&rate
  volume            150.0 mL
  feed rate         3.0 mL/min
  temp. measuring:  on
  rec. interval     00:02:00
  fill rate         max mL/min
  auto fill:        on
>XDOS dosing units
  setup:            single
  dosing drive:     DOS2
  dos.unit:         DIAZO
  port use:         custom
  dosing port       1
  filling port      2
  waste port        4
>XDOS monitoring
  temperature:      on
  low limit         -15.0 °C
  upper limit       3.5 °C
  action:           wait
  alarm pins:       none
  volume:           off
>XDOS preselections
  req.ident:        off
  >>XDOS prompts
    id1              Id1
    id2              Id2
    id3              Id3
  start delay       00:00:00
>XDOS reports
  temp. auto scale: on
  temp. scale low   -70 °C
  temp. scale high  200 °C
  report1:          result
  report2:          parameter
  report3:          curve
  report4:          comb. list
  report5:          off
  report6:          off
  report7:          off
  report8:          off
=====
```



Parameters of method 4: azo coupling with 2-naphthol

```
'sr
711 Liquino          01129  711.A011
date 1998-01-21    time 11:38
mode: XDOS          user method: Naphthol

total dosing time   = 001:00:01
total volume        = 300.000 mL
dosing rate         = 5.000 mL/min
=====
```

```
'pa
711 Liquino          01129  711.A011
date 1998-01-21    time 11:38
mode: XDOS          user method: Naphthol
parameters
>XDOS parameter
  XDOS type:        volume&rate
  volume            300.0 mL
  feed rate         5.0 mL/min
  temp. measuring:  on
  rec. interval     00:02:00
  fill rate         max mL/min
  auto fill:        on
>XDOS dosing units
  setup:            tandem
  dosing drive:     DOS3
  dos.unit1:        AZOCOUPPING
  port use1:        custom
  dosing port1      3
  filling port1     2
  waste port1       4
  dosing drive:     DOS4
  dos.unit2:        AZO TANDEM
  port use2:        custom
  dosing port2      3
  filling port2     2
  waste port2       4
>XDOS monitoring
  temperature:      on
  low limit         -10.0 °C
  upper limit       10.0 °C
  action:           wait
  alarm pins:       none
  volume:           off
>XDOS preselections
  req.ident:        off
  >>XDOS prompts
    id1             Id1
    id2             Id2
    id3             Id3
  start delay       00:00:00
>XDOS reports
  temp. auto scale: on
  temp. scale low   -70 °C
  temp. scale high  200 °C
  report1:          result
  report2:          parameter
  report3:          curve
  report4:          comb. list
  report5:          off
  report6:          off
  report7:          off
  report8:          off
=====
```

Volume and temperature vs. time curves for method 4

