Lab 9 - Synthesis of Nerolin

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1 Introduction

This experiment uses a replacement reaction to synthesis nerolin (2-methoxynapthalene) from 2-napthol. The nerolin is used as a fixative in perfumes to reduce evaporation of more volatile compounds in a mixture so that the perfume maintains it fragrance over time.

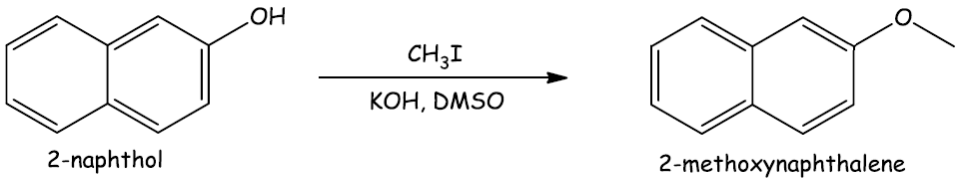

Figure 1: Summary of the conversion of 2-napthol to nerolin (2-methoxynapthalene) by replacement

2 Materials

2.88g 2-napthol	heat plate	ice bath
1.50g KOH	magnetic stir bar	filter funnel
220mL methanol: water (9:1)	50mL graduated cylinder	capillary tube
2.5mL methyliodide	1 ring stand & clamps	IR spectrometer
20mL DMSO	watch glass	melting point apparatus
(500mL) Erlenmeyer flask	filter paper	

3 Procedure

20mL DMSO, 2.88g 2-naphthol, and 1.50g KOH was added to a 500mL Erlenmeyer flask along with a magnetic stir stick. The mixture was stired at 50°C until KOH was dissolved 2.5mL methyliodide was added and stired for 20 minutes. After 20 minutes the contents of the flask were left to cool to room temperature $\approx$ 25°C. A solution 200mL ice cold methanol: water (9:1) was added to the flask. The solution was then cooled in an ice bath for ten minutes. The solid product was then collected by vacuum filtration rinsing twice with 10mL ice cold methanol: water (9:1). The collected crystals were then placed on a pre-weighed watch glass and stored in a locker to dry. Once dried, the watch glass was weighed with the product, the IR spectrum was obtained, and the melting range was determined.

4 Calculations/Results

Experimental Data

Mass 2-naphthol:

$2.8800g$

Mass watch glass:

Initial (empty) weight = $53.2047g$
Final weight (with nerolin) = $55.4286g$
Actual yield nerolin = $M_f - M_i = 2.2239g$

Overall reaction:

$$C_{10}H_8O_{(s)} \underset{DMSO,\ KOH}{\overset{CH_3I}{\rightleftharpoons}} C_{11}H_{10}O_{(s)}$$

Theoretical yield:

$$2.88g \text{ 2-naphthol} * \frac{\text{1mol 2-naphthol}}{144.17g \text{ 2-naphthol}} * \frac{\text{1mol nerolin}}{\text{1mol 2-naphthol}} * \frac{\text{158.20g nerolin}}{\text{1mol nerolin}} = 3.16g \text{ nerolin}$$

Theoretical yield 2-methoxynaphthalene (nerolin). $= 3.16g$

Percent yield:

$$\text{Percent yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} * 100 = 70.37\%$$

Boiling Point:

Initial melt= $69.9\ ^\circ C$
Final melt= $71.9\ ^\circ C$

$$\text{Midrange=} \frac{B.P._{initial} + B.P._{final}}{2} = 70.2\ ^\circ C$$

IR Spectrum

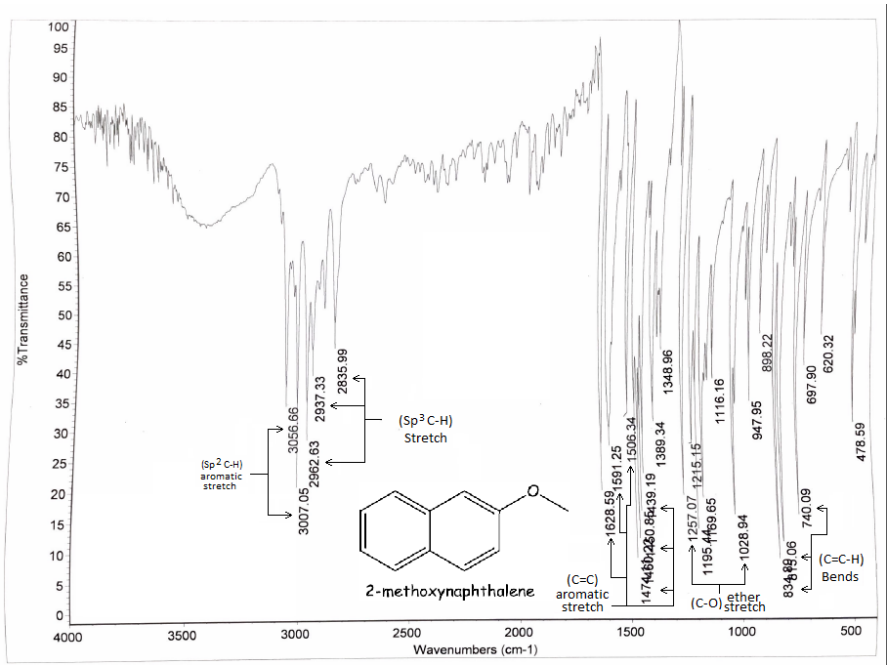

Figure 2: IR spectrum of 2-methoxynaphthalene (nerolin), taken in lab.

Figure 3 displays the IR spectra of the nerolin product that was taken in lab. The molecule exhibited strong (C-O) ether stretches at $1028.94cm^{-1}$ and $1257.07cm^{-1}$. There were also strong (=C-H) bends at $740.09cm^{-1}$, $815.06cm^{-1}$, and $834.89cm^{-1}$. There were medium-weak aromatic (C=C) stretches between $1400 - 1600cm^{-1}$ most evident at $1439.19cm^{-1}$,$1460.22cm^{-1}$,$1506.34cm^{-1}$, $1591.25cm^{-1}$, and $1628.59cm^{-1}$. There were 3 medium (Sp^3 C-H) stretches at $2835.99cm^{-1}$, $2937.33cm^{-1}$, $2962.63cm^{-1}$. There were also medium aromatic (Sp^2 C-H) stretches between $3000-3100cm^{-1}$ most notable at $3007.05cm^{-1}$and $3056.66cm^{-1}$. A large copy of the original IR spectrum with the most significant peaks labeled is attached at the end of the report.

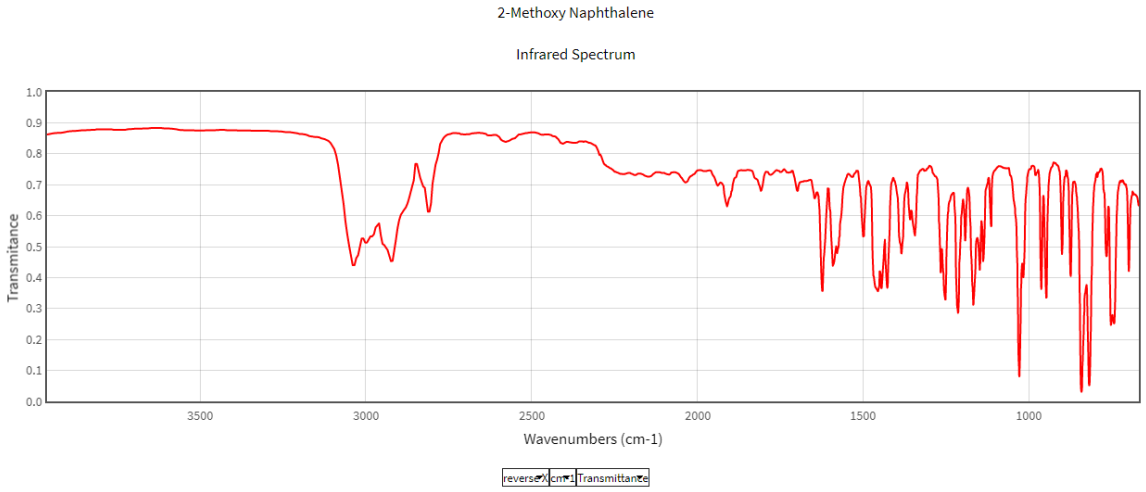

Figure 3: Standard IR spectrum of pure 2-methoxynaphthalene (nerolin) from *NIST Chemistry WebBook, SRD* 69

http://webbook.nist.gov/cgi/cbook.cgi?ID=C93185&Mask=80#IR-Spec

5 Conclusion

The sythesis of 2-Methoxynaphthalene (nerolin) from 2-naphthol was a success. Sample purity was verified by comparison to the standard IR spectrum of pure nerolin from the literature. The major peaks of both the IR spectrum of the product formed in lab and the Standard IR spectrum of pure nerolin agreed. The comparison can be observed between $figure$ 2 and $figure$ 3 on page 3. The nerolin molecule was characterized by strong (C-O) stretches at $1028.94cm^{-1}$ and $1257.07cm^{-1}$. There was no strong broad hydroxyl stretch present on the product confirming the deprotonation of the hydroxyl group of the original 2-naphthol molecule. There was however, a weak broad stretch withing the $3200 - 3500cm^{-1}$ range which does not appear in the standard IR spectrum of pure nerolin. This raises question as to how pure the product actually was and what potential contaminates may be present. The melting range of the sample was between 69.9 $°C$-71.9 $°C$ which gave a midrange of 70.2 $°C$ and was slightly lower than the predicted $\approx$ 72 $°C$ m.p. of pure nerolin noted in the literature. The conversion produced 70% of the expected yield. The actual yield was $2.2239g$ nerolin.

- Phenols are acidic because once deprotonated the phenoxide ion delocalizes the negative charge from the oxygen atom around the ring. Because of the stability of the phenoxide anion the phenol molecule can readily react with a base by donating a hydrogen proton.
- The reaction begins when the acidic hydrogen proton is removed from the oxygen atom on the 2-naphtol molecule and protonates the KOH molecule which results in a K^+ion and an H_2O molecule. Then an $Sn2$ reaction proceeds, the oxygen, with a negative charge is a good nucleophile and attacks the carbon center of the $(CH_3 - I)$ molecule and the iodine atom leaves simultaneously. The final product is the nerolin molecule with the CH_3 molecule having replaced the hydrogen atom of the original 2-naphthol molecule.

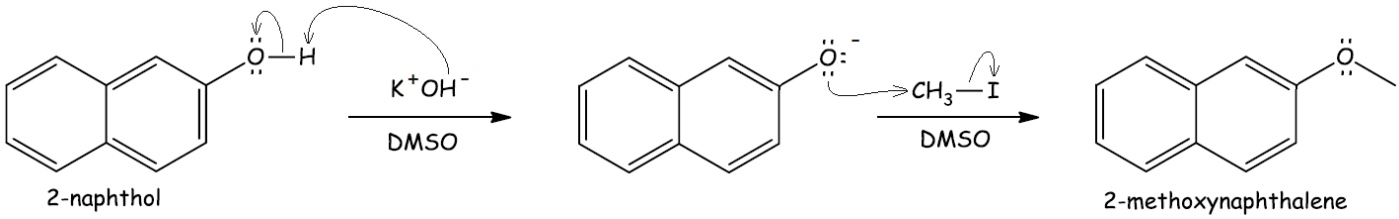

Figure 4: Mechinism of the conversion of 2-naphthol to 2-methoxynaphthalene (nerolin)

- The Sn^2 reaction would still work if we used sodium methoxide and β naphthyl iodide because the iodine is a good leaving group and there is a Na^+ cation attached to a good nucleophile OCH_3^-.

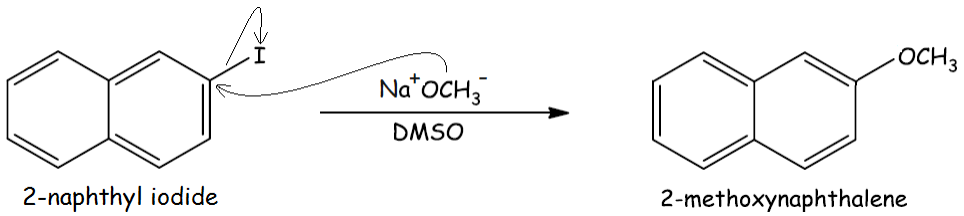

Figure 5: Mechinism of the conversion of 2-naphthyl iodide to 2-methoxynaphthalene (nerolin)