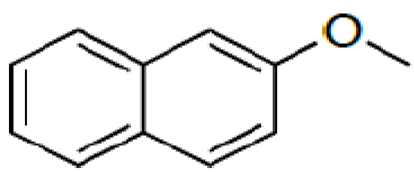
Experiment -5- Perfumes

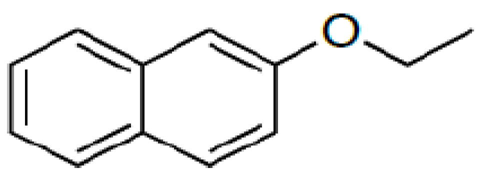
The Synthesis of Nerolin

BACKGROUND

- In the seventeenth century, Anna Maria de la Tremoille, the Italian princess of Nerolin, introduced a perfume containing oil distilled from orange blossoms.
- A major constituent of her *Nerolin oil is* the aromatic ether Nerolin (2-methoxynaphthalene).
- 2-Ethoxynaphthalene, which has the same aromatic qualities as its methyl homolog, is sometimes called "new Nerolin" because of its more recent discovery and use by the perfume industry.



2-methoxynaphthalene
Nerolin



2-ethoxynaphthalene
New Nerolin

- The fragrances of perfumes have found their way into many products and used directly as perfumes, colognes, and lotions; perfumes are also found in soaps, shampoos, bath oils, deodorants, cosmetics, oils, creams, powders, etc.

BACKGROUND

- Most perfumes came from plant or animal sources.
- Demand for perfumes led to synthetically derived perfumes from coal tar or petroleum products.
- The most expensive perfumes contain oils from fresh flowers (low yield).
- Perfumes consist of a blend of ingredients diluted in alcohol and water to a certain concentration.

INTRODUCTION

Major Constituents of Perfumes

1. Odorous Substances:

- The delightful aroma of any perfume is due to the presence of odorous substances. These come from:
  Volatile perfume oils or any other isolates

2. Vehicles:

- solvent for blending and holding the perfume materials.
- highly refined Ethanol.
- volatile, helps in projecting the scent it carries.
- inert, Not irritating to human skin.

3. Fixatives:

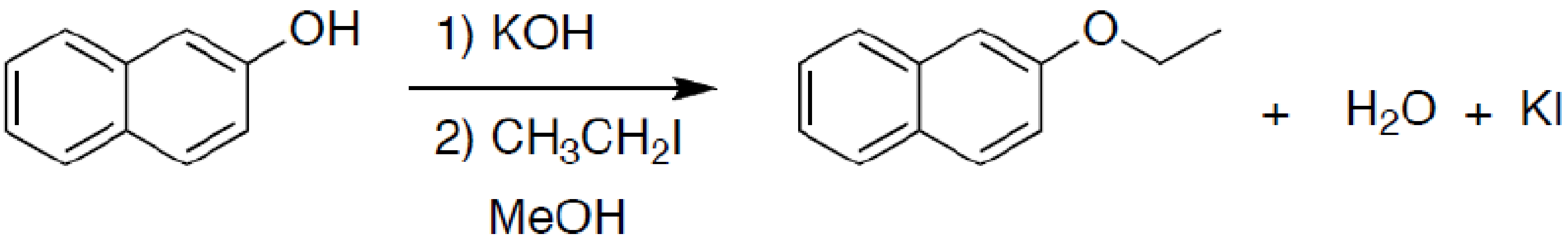
- binds the other ingredients
- less volatile than perfume oils.
- diminishes the rate of evaporation of the more volatile components.
- if not present, the fragrance of a complex perfume would change with time as the more volatile oils evaporated and left behind the less volatile substances.

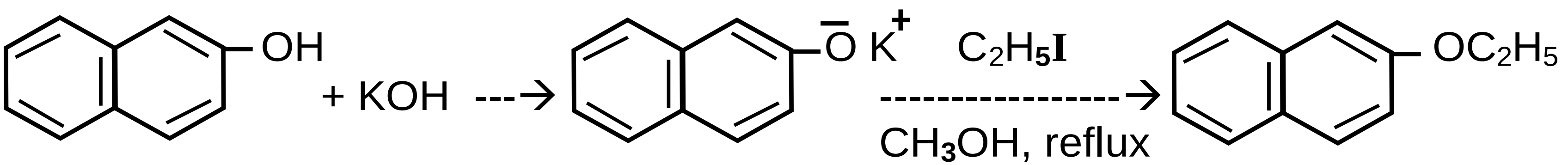
DESCRIPTION

- Nerolin (2-ethoxynaphthalene or β-naphthyl ethyl ether)is prepared using a Williamson ether synthesis.(Symmetrical or unsymmetrical ethers)
- This reaction utilizes an SN2 mechanism:
- ***The reaction occurs between a nucleophillic alcohol and an electrophillic alkyl halide.***
- ***The nucleophile, β-naphthol, is deprotonated by a methanolic solution of potassium hydroxide.***
- ***The more nucleophillic β-naphthoate anion substitutes for the excellent leaving group iodide, on the ethyl iodide.***

- Potassium hydroxide is used rather than sodium hydroxide because of its greater solubility in the alcohol solvent.
- After completion of the reaction to form Nerolin the reaction is cooled and the product is isolated by addition of ice-cold water. The crude product precipitates from solution.
- Purified through recrystallization.(Mixed solvent technique, water-methanol)

REACTION


OH
1) KOH
2) CH3CH2I
MeOH
O
+ H2O + KI


OH
+ KOH
O K+
C2H5I
CH3OH, reflux
OC2H5

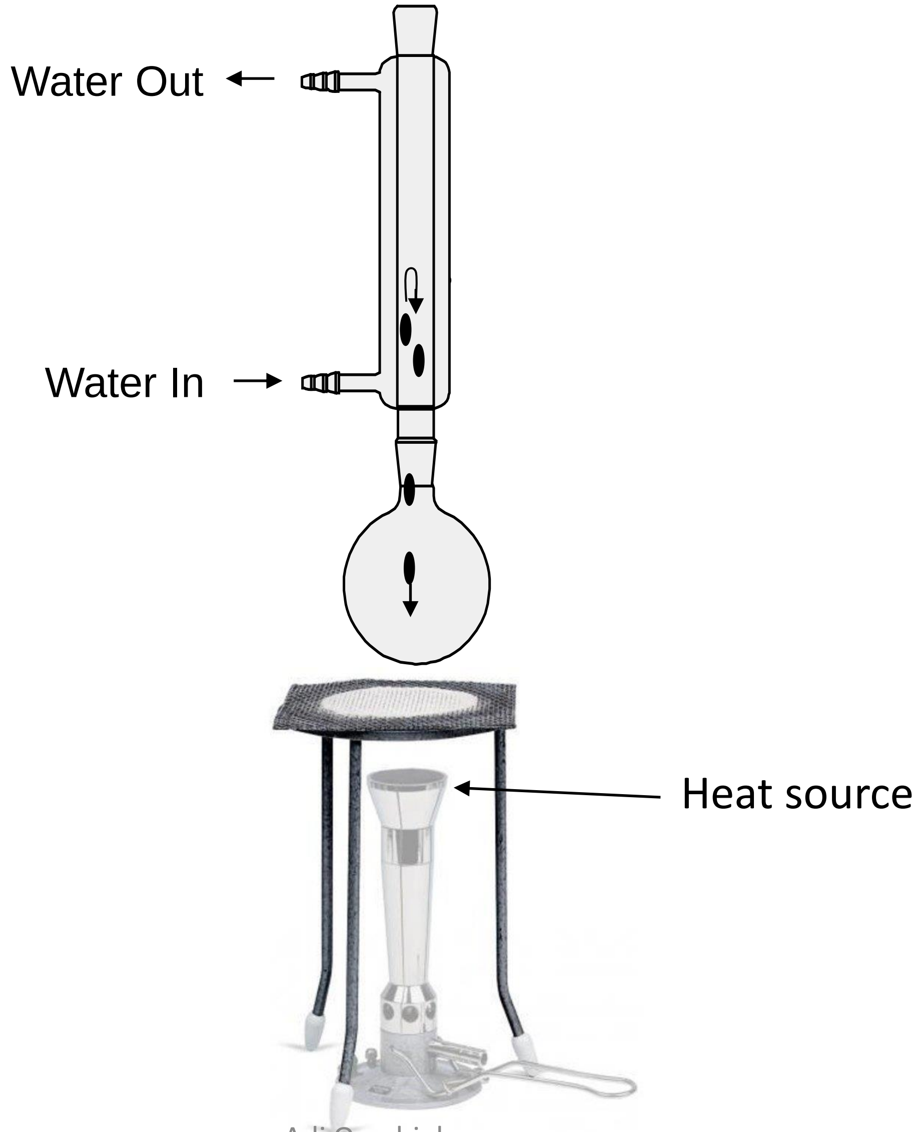
REFLUX TECHNIQUE

- This technique is useful for performing chemical reactions under controlled conditions that require substantial time for completion.
- This technique involves placing a liquid reaction mixture in a round bottomed flask connected to a condenser.
- The condenser is open from the top. Any vapors given off are cooled back to liquid, and fall back into the reaction flask(see fig. next slide).
- The round bottomed flask is heated vigorously for the course of the reaction.
- Thermally accelerate the reaction by conducting it at an elevated temperature (the solvent`s boiling point).
- The advantage of this technique:

➢ is that it can be left for a long period of time without the need to add more solvent or fear of the reaction vessel boiling dry as any vapor is immediately condensed in the condenser.

➢ the reaction will proceed at a constant temperature. The constant boiling action also serves to continuously mix the solution.

Reflux setup



EXPERIMENTAL PROCEDURE

Preparation of 2-Ethoxynaphthalene(Nerolin)

1. Place 40 ml of methanol, 5.8 g (0.040 mol) of β-naphthol, and 3.3 g (0.05 mol) of KOH into a 100 ml to round bottom flask (**Caution**: **KOH is corrosive/caustic-Avoid skin contact)**.

2. Stir the mixture well. Allow a few minutes for the acid-base reaction to occur, do not go further in the procedure before complete dissolution of all KOH.

3. Add 3.6 ml ethyl iodide in 10% excess (0.045 mol).

4. Add a couple of boiling chips.

5. Attach a condenser(See the previous fig.) and reflux the mixture for 1.5 hours.

6. Allow the hot reaction mixture to cool to room temperature.

7. Pour it into a 250 ml beaker containing 100 ml of ice cold water.

EXPERIMENTAL PROCEDURE

8. Cool the mixture in an ice bath to effect crystallization of Nerolin.

9. The Nerolin may at this point appear as an oil, due to its low melting point and the impurities present, but eventually it will crystallize upon cooling (use a glass rod to scratch the beaker during cooling.

10. Collect the crystallized Nerolin by suction filtration.

11. Recrystallize the product using decolorizing carbon from methanol and water(mixed solvent technique –Next slide).

12. Weigh the dry sample; determine the percent yield and the melting point .

RECRYSTALLIZATI0N
Mixed solvent technique

1. Place the solid sample in a 100 ml beaker and add enough **hot methanol** to just dissolve the solid (remember the solution needs to be kept hot also, why?).

2. To encourage crystallization add a small amount of **hot** water until the solution turns turbid.

3. Add a few drops of **hot** methanol to clear the solution.

4. Allow the solution to cool undisturbed to room temperature, then place the solution in an ice-bath.

5. Collect the crystals by suction filtration, allowing air to be drawn through the sample by the vacuum to aid in drying of the sample.