

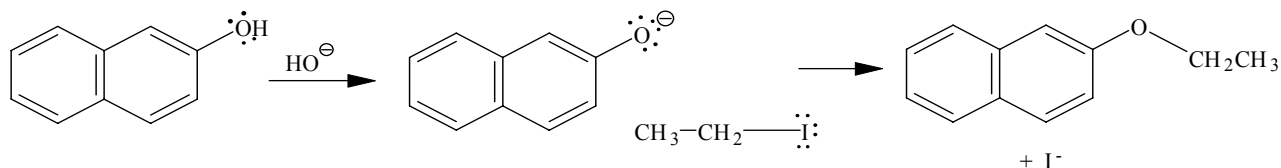
CHEM 321: An S_N2 Reaction: Synthesis of 2-ethoxynaphthalene

From J.A. Miller and E.F. Neuzil, Modern Experimental Organic Chemistry, D. C. Heath, Lexington, MA, 1980, pp. 228-231

Most of organic chemistry is concerned with converting one functional group into another. Nucleophilic substitution is a frequently used method. An electron-rich entity (nucleophile) is physically mixed with another molecule that has an electron-poor atom called the electrophile (carbon in most cases). The electrophilic atom is made electron deficient by its link to an electron-withdrawing leaving group. In a successful encounter that follows the S_N2 path, the incoming nucleophile "reaches out" electronically toward the electrophilic atom. As it does so, the leaving group "slurps up" the pair of electrons that links it to the electrophilic atom and departs with them. A new bond forms between the electrophile and the nucleophile. Almost endless variations are possible in the identities of the nucleophile, electrophile and leaving group.

The purposes of this experiment are to demonstrate a typical S_N2 reaction, to show one way to convert a weak nucleophile into a strong one (ROH to RO⁻), to show how a reactant can be added slowly to a reaction mixture, to learn mixed solvent recrystallization as a method for purifying a solid, and to make a KBr pellet to analyze the IR spectrum of a compound.

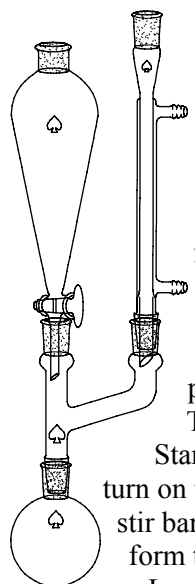
In this experiment, the weak nucleophile 2-naphthol is converted into a strong one, and carbon-1 of iodoethane serves as the electrophile. The mechanism of the reaction is shown below (you need to add curved arrows). This reaction is an example of the *Williamson synthesis*.



What type of functional group transformation happened between the starting material and the product (i.e. what is the functional group that changed from the starting material to the product)? What is the new functional group formed in the product? {Note: these should be answered in the introduction section (or under the reaction mechanism figure) of your report.}

It may be of interest that the product is used as a fragrance in some soaps, and as a fixative agent in perfumes. In the latter case it attracts (in fact, dissolves) fragrance elements that would otherwise evaporate too rapidly, helping the perfume to last a long time by releasing the fragrances very slowly.

Experimental Protocol



CAUTION: avoid skin contact with any of the chemicals used; wash with soap and water in case of contamination. Do not breathe vapors of iodoethane.

If you spill any KOH pellets, clean them up immediately. They draw water from the air and make very corrosive puddles.

SYNTHESIS: To a 100 mL round bottom flask, add a medium stir bar, use a micropipettor to add 1.5 mL of iodoethane, and use a dispensette to add approx. 5 mL of methanol. Clamp the reaction flask near the face of your hood. Bury the reaction flask in a shallow sand bath that is on top of a stirring hot plate, and start stirring the mixture. Mount a Claisen adapter and a condenser on the side joint of the Claisen adaptor (as seen in the picture to the left). Make sure the top of the condenser is open. Mount a 125 mL separatory funnel on the vertical joint of the Claisen adaptor (as seen in the picture to the left).

To a 100 mL beaker, add 1.2 g of 85 % KOH and 2.61 g of 2-naphthol (also known as β -naphthol). Start vigorously stirring the solution of iodoethane and methanol, turn on the water to the condenser, and turn on the heat to start your reflux. Using a dispensette, add 13 mL of methanol to the 100 mL beaker, add a stir bar, cover the beaker with a watch glass, and use a stirring hot plate to slightly warm the mixture and form the alkoxide ion (RO⁻) of 2-naphthol. Once all the solids are in solution, transfer the solution to the 125 mL separatory funnel, and cap the separatory funnel with a glass stopper (paper!). Slowly add the solution of the alkoxide ion of 2-naphthol to your reaction flask. When nearly all the alkoxide solution is mixed into the

reaction mixture, use a dispensette to add approx. 7 mL of methanol into the 100 mL beaker used to make the alkoxide solution.

When all the solution containing the alkoxide ion of 2-naphthol has been added to the reaction flask, add the 7 mL of methanol to the separatory funnel, and slowly add this to the reaction mixture to chase any remaining alkoxide ion into the reaction flask. Reflux gently for 1 hour while stirring vigorously. Turn off the heat, cool briefly, and pour the reaction mixture over about 70 mL of ice chips in a 250 mL beaker. Stir until all the ice chips have completely melted, vacuum filter the solid on a Büchner funnel, and wash the solid with 150 mL of tap water.

PURIFICATION: The product dissolves readily in methanol but not in water. Recrystallize from a methanol/water solvent as follows. **Keep the beaker covered at all times unless you need to access its contents!** In a 100 mL beaker, dissolve the crude product in approx. 10 mL of methanol. Heat the mixture until it begins to just barely boil. Check to be sure that all the solids are dissolved, if not, quickly add more methanol until the solids dissolve. Once all of the solids have dissolved, remove the beaker from the hot plate. With good mixing, slowly add DI water from your squirt bottle to the warm solution until just persistently cloudy. Then, put the beaker back on the hot plate, and warm until clear. Cool the mixture **slowly** to room temperature, stirring vigorously and watching carefully for evidence of oil droplets coming out of solution. If this happens, add a little methanol, warm until everything redissolves, then cool slowly again. *The product will come out as an oil if the solution temperature is above the product's melting range.* Scratching with a glass rod can help induce crystals to form if temperature is below the melting range. Eventually cool to ice temperature, vacuum filter on a Hirsch funnel, and let dry for a day. Measure yield and melting range, and record your impression of its odor. Obtain an IR spectrum of your product by making a KBr pellet of your product.

Report for this experiment The Report Section Focus changes to Results and Discussion sections. However, you still need to include Introduction and Experimental Sections.

For results, report the yield (g, %), melting range (published melting range with source in footnote), fragrance, and important peaks from the IR spectra of 2-ethoxynaphthalene and 2-naphthol. Attach your IR spectrum of 2-ethoxynaphthalene, authentic 2-ethoxynaphthalene, and authentic 2-naphthol using the format listed below. Conclude with a short paragraph in which you (a) restate the objectives, (b) compare the three spectra to decide whether there is significant contamination with unreacted starting material, (c) state reasons why the yield was low, and (d) estimate the success of the experiment in light of its objectives.

Enrichment questions (include answers in Appendix):

1. The stockroom is out of ethyl iodide. What could be used in place of ethyl iodide to still make 2-ethoxynaphthalene? Explain your reasoning. Hint: Review the introduction of this experiment before answering this question.
2. Based on the known properties of 2-ethoxynaphthalene (outlined in the above protocol), could 2-ethoxynaphthalene be purified using a single solvent recrystallization method? Why or why not?

PLEASE NOTE AND REMEMBER: For all future reports: whenever IR spectra are attached to a report, they should always be annotated with:

- a) Name of compound responsible for the spectrum
- b) Structure of compound
- c) Assignments for enough significant peaks to allow the reader to see that the product is what it is claimed to be and is pure (or contaminated) as claimed in the report. *Label each chosen peak explicitly with the name of the responsible molecular vibration. Examples: O-H stretch, sp^2 C-H stretch, C=O stretch. These assignments should be chosen to confirm that the molecule is of the class you claim it to be. You should not use the sp^3 C-H stretch unless it is a main significant signature peak.*
- d) Complete bibliographic (or web) citation of source used to assign peaks

Do not forget that these are figures. Because of this, you should follow the figure guidelines listed which can be found here: <http://www.linfield.edu/chem/assets/files/Courses/CHEM%20321/Figures%20Guidelines.pdf>. In your discussion of the IR spectra, you should always compare and contrast the product spectrum with those of the starting materials and any plausible side products. To decide whether contamination from specific compounds is significant, evaluate the relative intensities of pertinent peaks in the product spectrum along with intensities of those peaks in the spectra of the starting materials and/or plausible side products.