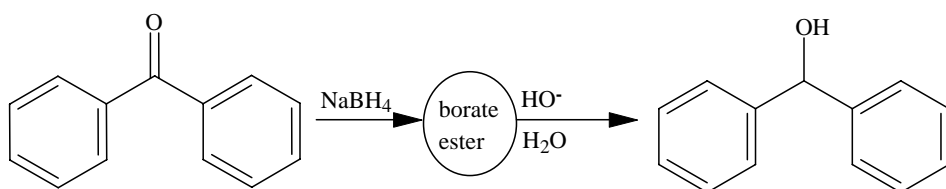


CHEM 321: REDUCTION OF A KETONE

Reduction and oxidation are complementary processes that dramatically change the behavior of certain susceptible functional groups. For example, nitro groups (-NO₂) can be reduced to amino groups (-NH₂). Nitro groups are potent electron withdrawing groups that can oxidize other molecules. On the other hand, amino groups are good nucleophiles, and compounds with amino groups tend to be easily oxidized.

This experiment illustrates a mild way to carry out reduction of a carbonyl group to an alcohol. The reducing agent is sodium borohydride, NaBH₄. This reagent is particularly convenient because: 1) All four hydrogens are active; 2) It is not excessively reactive with inexpensive solvents, like water or alcohols; and 3) The reduction is selective. Functional groups other than aldehydes and ketones will remain unchanged.

Reduction of benzophenone to benzhydrol:



Another reducing agent that could be considered is LiAlH₄. The Al-H bond has more ionic character than the B-H bond. Therefore, the H atoms in AlH₄⁻ are far more electron-rich than those of BH₄⁻. This makes AlH₄⁻ far more reactive and less selective than BH₄⁻. For example, LiAlH₄ reacts violently with most protic solvents to generate H₂ gas (which can lead to fire or explosion), but in suitable aprotic solvents, LiAlH₄ can successfully reduce functional groups that NaBH₄ cannot.

Experimental Protocol

CAUTION: *NaBH₄ is corrosive to skin and membranes. Avoid its dust, and wash with lots of water if you get any on your skin or clothing. Clean up any spilled material immediately with a wet sponge, and rinse the sponge out thoroughly.*

SYNTHESIS: In a 100 mL boiling flask, prepare a slurry of NaBH₄ (0.3 g) in 15 mL of 2-propanol. Add benzophenone (2.75 g) and a medium sized stir bar. Bury the reaction flask in a shallow sand bath that is on top of a stirring hot plate and reflux gently for 45 minutes. Allow the reaction mixture to cool, and add 15 mL of 10% NaOH (same as 3 M). Swirl the mixture vigorously until all the solid has dissolved (lumps can be broken up with a glass rod, but be careful that you don't crack your flask!).

RECOVERY: Add 80 mL of DI water into a 250 mL beaker. While constantly stirring, slowly add the entire reaction mixture to the 80 mL of DI water. Keep stirring until there is no evidence of oily material. The product should start to become a solid. Place the beaker into an ice-water slush and cool to approx. 5 °C to allow as much solid as possible to form. Vacuum filter the mixture on a medium size Büchner funnel. While the crude product is on the funnel, wash it with 50 mL of ice cold water to rid it of as much 2-propanol as possible.

RECRYSTALLIZATION: There is no single good recrystallization solvent for this product, but a combination of methanol and water can be used to purify it.

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. 20 mL of methanol. Heat the mixture until it begins to just barely boil. You will probably need to do a hot filtration to remove insoluble particles. A link which describes the process of hot filtration is found here:

http://www.linfield.edu/chem/assets/files/Courses/CHEM%20321/USEFUL_PROCEDURAL_GOODIES.pdf } 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 temp, 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. After no further crystals form at room temperature, cool to ice temperature (approx. 5 °C). Vacuum filter on a Hirsch funnel. Fold the crystals into a paper towel to air dry in your desk drawer for at least one day.

ANALYSIS: The next day (or later) obtain the weight of the product, the melting range of the product, and the IR spectrum (ATR) of the product; get the IR spectra of authentic benzhydrol and benzophenone from the web.

REPORT: The following information should appear at appropriate places:

1. **Balanced reaction:** This is a redox reaction. It occurs in alkaline solution, and the inorganic product is BO_3^{3-} . Consult a Gen. Chem. text if you have forgotten how to balance redox reactions.
Hint: the balanced reaction does include HO^- ions, but not 4.
2. **Yield:** Report in usual manner; suggest where major losses may have occurred or other reasons for low yield.
3. **Melting ranges of your product and of benzophenone:** Compare with published values, and comment on the significance of this comparison. Don't forget to cite the source of your m.p. data.
4. **IR:** Compare the annotated spectra of benzhydrol and benzophenone with respect to the presence/absence of O–H, C=O, C–O, aromatic C=C and aromatic =C–H peaks.
5. Why was it important to let the crystals dry before obtaining their melting range?
6. Could you have used LiAlH_4 instead of NaBH_4 under the conditions of this experiment? Why?