

SELECTIVITY USING SODIUM BOROHYDRIDE

EXPERIMENTAL PROCEDURE



- Ethanol is highly flammable and is toxic.
- Ethyl acetate is flammable and is toxic.
- Hexanes are highly flammable and toxic.
- Benzophenone is an irritant.
- Benzaldehyde is a combustible liquid and an irritant.
- Methyl benzoate is a combustible liquid and an irritant.
- Sodium borohydride is a flammable solid and is corrosive.

Each individual student is required to perform the reaction of benzophenone with sodium borohydride and isolate the product and record the melting point. In addition, each student will carry out a small scale investigation of the reaction of either benzaldehyde or methyl benzoate with sodium borohydride, so by working in pairs they get data for the reaction of sodium borohydride with three different functional groups. The TA will provide each pair of students with a sample of sodium borohydride to use.

Preparing to run Thin Layer Chromatography (TLC)

For complete information on TLC see the [chromatography techniques pages](#).

You will need to prepare **TLC applicators**, a **TLC developing jar** and two **TLC plates each**. Remember to handle the TLC plates with care: don't touch the coating with your fingers, don't chip the coating and use pencil to mark the plates.

TLC developing jar

Use a small clear jar lined with a piece of filter paper cut to fit as a developing jar. The filter paper helps to provide a solvent saturated environment. The solvent depth should be less than 5mm. There is a picture of a developing jar on the [chromatography techniques pages](#). (alternatively a 50ml beaker covered with a watch glass as a lid).

TLC plates

You will be provided with two silica on aluminum foil TLC plates each (5cm by 2.5cm). Each plate should be marked (in pencil) with the origin line and four crosses to mark the lanes at 5mm intervals.

Reaction of sodium borohydride with benzophenone:

Weigh out approximately (but accurately) 0.364g of powdered benzophenone into a 15ml reaction vial and dissolve the solid in 5ml of ethanol. Once the solid has dissolved, use a TLC applicator to spot a sample of the solution onto the first (left) cross on the pencil line on the lower end of your first TLC plate.

Weigh out approximately (but accurately) 0.084g of sodium borohydride. Using a spatula, slowly transfer the sodium borohydride to the benzophenone solution in the vial in 4 portions over about 5 minutes,

recording the time when you make the first addition ($t=0$). Make sure to swirl the solution after each portion is added (note the sodium borohydride might not all dissolve, but that is not important). When 10 minutes have elapsed (*i.e.* $t=10$ mins) use a clean TLC applicator to spot a sample of the reaction solution on to the second cross on the TLC plate. Repeat the spotting procedure with another clean TLC applicator at $t=30$ minutes and then again at $t=60$ minutes. Once the spots have dried (the volatile solvent will evaporate) develop the TLC plate as described below.

Obtain 10ml of 10% aq. hydrochloric acid. Using a Pasteur pipette, slowly and carefully add the hydrochloric acid **dropwise** to the reaction mixture, swirling to ensure mixing after each addition. **CAUTION** : Vigorous evolution of hydrogen occurs initially as excess sodium borohydride reacts with the acid during this acid work-up.

Once the addition of 10% hydrochloric acid is complete, cool the reaction flask in an ice bath and wait until precipitation is complete (approximately 15 minutes). Collect the product by vacuum filtration using a Buchner funnel, wash the product with 2 x 5ml of ice cold water. Allow the solid product to dry in the Buchner funnel under vacuum for 5 minutes. Record your crude yield. If required, recrystallise a small, but known weight of crude product (approx. 50-100mg) using a minimum volume of hot hexanes.

CAUTION : since hexanes is highly flammable, use a beaker of hot water to heat hexanes in a test tube, make sure there are **NO FLAMES** in the vicinity.

Collect the recrystallised product by vacuum filtration, determine the yield and the melting point of the purified product. Submit a labeled sample of your product to your TA.

Developing the TLC plate

Develop the TLC plate using a 10 : 90 (v/v) ethyl acetate : hexanes solvent system. Remember to handle the TLC plate carefully using tweezers to lower it carefully in to place making sure the sample spots (the crosses on the line) lie above the initial solvent level. Allow the TLC plate to develop (approx. 2 minutes) until the solvent front is almost at the top of the plate. Remove the plate (tweezers) and immediately mark the solvent front with a pencil. Allow the plate to dry by allowing the solvent to evaporate from the plate then examine the plate under a UV lamp. Record the position of the spots on the plate by using a pencil to mark the position of each spot (circle the outline of the spot). Calculate the R_f values for each spot.

Reaction of sodium borohydride with benzaldehyde or methyl benzoate**(Work in pairs, one student use benzaldehyde, the other methyl benzoate).**

In a 15ml reaction vial, prepare a solution of 5 drops of either the aldehyde or the ester in 3ml of ethanol. Using a clean TLC applicator, spot a sample of this solution onto the first (left) cross on the pencil line on the lower end of the second TLC plate.

Weigh out approximately (but accurately) 0.04g of sodium borohydride. Using a spatula, slowly transfer the sodium borohydride to the solution in the vial in 2 portions over about 5 minutes, recording the time when you make the first addition ($t=0$). Make sure to swirl the solution after each portion is added (note the sodium borohydride might not all dissolve, but that is not important). When 10 minutes have elapsed (*i.e.* $t=10$ mins) use a clean TLC applicator to spot a sample of the reaction solution on to the second cross on the TLC plate. Repeat the spotting procedure with another clean TLC applicator at $t=30$ minutes. Develop the TLC plate as described previously.

Make sure you and your partner exchange and discuss your findings on these two reactions.

CLEAN UP

- Return the vials of sodium borohydride to your TA.
- All organic solutions from the ketone experiment should be placed in the organic waste container.
- All aqueous solutions should be placed in the aqueous waste container.
- The reaction solution from the reaction of sodium borohydride with either the aldehyde or the ester should be poured into a container of ice in the fumehood as directed by your TA.

REPORT

The report for this experiment is a formal report (**maximum 4 pages**). **More details on writing formal reports can be found in the introduction to this manual.** Remember that more is not necessarily better. It is important to be accurate and concise rather than verbose and vague. Proper English should be used and it should be written in your own words. A **guide** to the sections you should include is shown below.

1. Title and Date
2. Introduction: Describe the purpose of the experiment, include equations of the reactions (show the starting materials and their potential reduction products)
3. Procedure
4. Results - yield, % yield, melting points, TLC results (include a full size sketch or image of the three TLC plates) *etc.*
5. Discussion (*e.g.* selectivity of sodium borohydride, functional group reactivity, sources of error *etc.*)
6. Conclusions - summarise your results and discussion
7. References – provide citations of any references used, see section 9 in the introduction to this manual for appropriate styles.
8. Questions:
 - (a) Give the mechanism for the reaction of a hydride ion, H^- (assume it's from LiAlH_4) with benzaldehyde through the acidic work-up to give the products.
 - (b) Give the mechanism for the reaction of a hydride ion, H^- (assume it's from LiAlH_4), with methyl benzoate through the acidic work-up to give the products.
 - (c) Analysis of [spectra](#). The IR spectra (A and B) and ^1H NMR spectra (C and D) of benzaldehyde and its reduction product are provided, but they are not labeled. Match each of the spectra to drawn structures and briefly rationalise your choices.