12AL Experiment 9: Markovnikov's Rule

Safety: Proper lab goggles/glasses must be worn (even over prescription glasses). WEAR GLOVES – this lab utilizes hydrogen peroxide which can burn your skin and multiple organic solvents. As always, ask where organic waste containers are located in the lab.

Background: There are many different ways to view Markovnikov's Rule – however, the most important aspect in performing Markovnikov's Rule is to learn which organic reactions actually follow it and which do not. These reactions are learned in your organic chemistry 12A course and you will be performing some of these reactions this year in a lab setting.

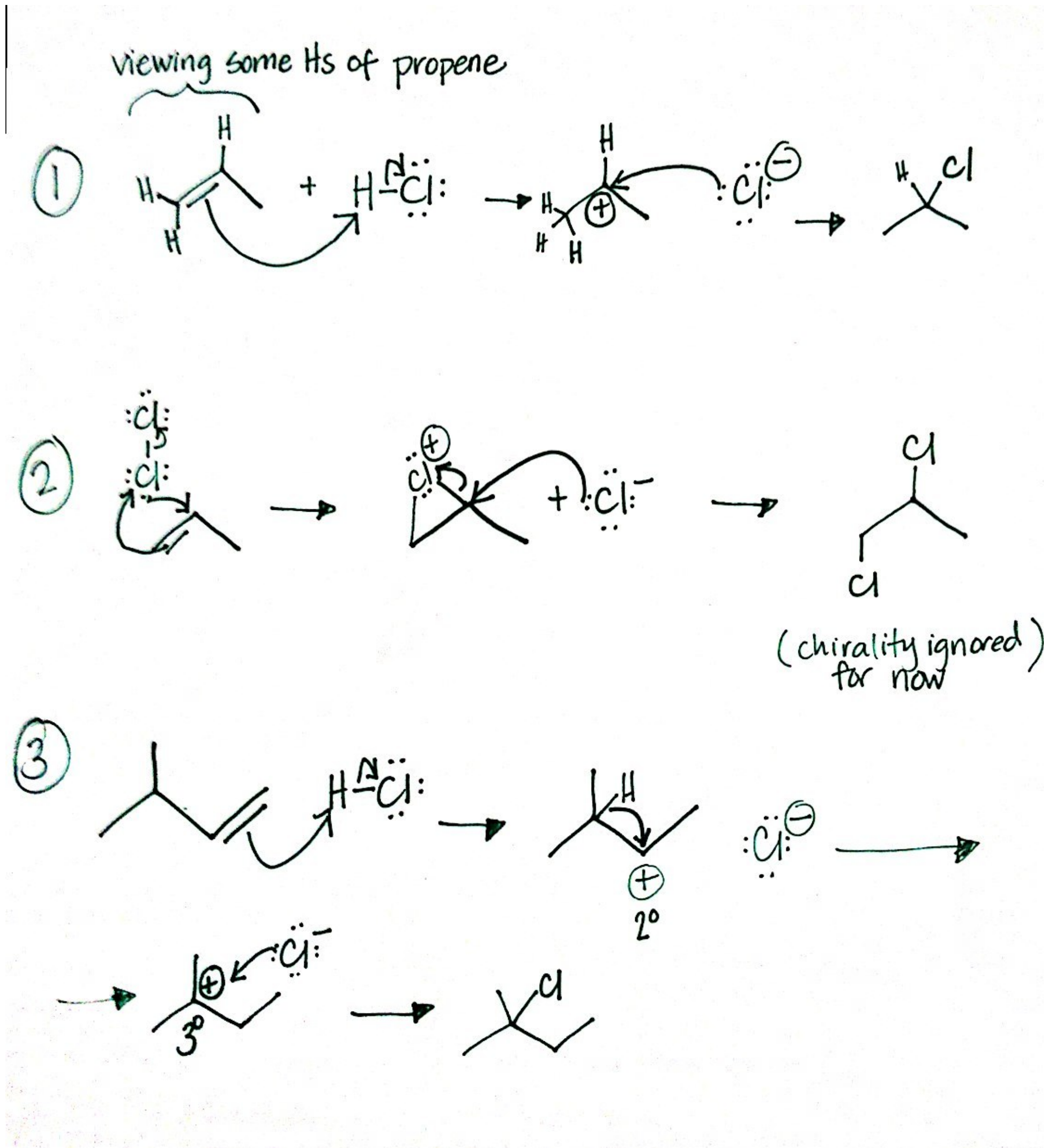
In general, when you first learned about "Addition of HX to Alkenes," you saw that the hydrogen atom of HX added to the sp^2 carbon with the most hydrogen atoms. And eventually in the mechanism, the halogen atom added to the sp^2 carbon with the least hydrogen atoms. This became known as Markovnikov's rule.

Another viewpoint of Markovnikov's rule which still supports the above lesson, is that the Carbocation that forms in the reaction should always be on the most substituted sp^2 carbon (with the H still going to the sp^2 carbon with the most hydrogen atoms). When the nucleophilic pi bond attacks an electrophile which causes the pi bond to break and a carbocation to form in many organic reactions, a very unstable high energy state is observed. Afterall, carbon does not want to have a + charge on it; it wants to have a full octet. Stability of a carbocation increases with the more alkyl groups that are attached to the sp^2 carbon – they donate their electron density to help make "carbon happy." It is this stable carbocation that is attacked by a nucleophile in a reaction.

In some reactions that do not form carbocations, but instead form cyclic intermediates, Markovnikov's rule can also be seen. The original alkene sp2 carbon atoms that become part of a cyclic intermediate (like in halogenation X2), may not be carbocations, but they are "very partially positive." Thus, the more stable of the two carbon atoms is the one that is more substituted, and it is this carbon atom that is attacked by a nucleophile.

In addition to understanding Markovnikov's Rule, it is imperative that you have a thorough understanding of all mechanisms involved in each organic reaction that you learn. Sometimes it is difficult to predict the major product of a reaction if you do not draw out the mechanism…. You have to always be on the lookout for Carbocation Shifting (aka carbocation rearrangement) in reactions that form carbocations. If an adjacent atom to the sp2 carbocation is more substituted, the molecule will do a hydride or methyl shift to the sp2 carbocation, creating a new more stable, lower energy, carbocation.

View examples below:



You will be performing the Hydroboration-Oxidation of an Alkene today. The BH_3 reagent needed will be generated in solution from sodium borohydride, iodine, sodium hydroxide, and hydrogen peroxide because BH_3 is very unstable. You are to understand the classic reaction mechanism of Hydroboration-Oxidation learned in lecture using the following reagents: Alkene + 1. BH_3, THF 2. H_2O_2, OH^-, H_2O.

Objective: 1. To review reactions of alkenes from lecture. 2. To review Markovnikov's Rule & those reactions that are Anti-Markovnikov. 3. To perform an organic alkene reaction and prove whether or not it follows Markovnikov's Rule.

Procedure:

1. Obtain a screw-cap vial from your instructor. It is very important that the solution you put in this is immediately capped to prevent inhalation and the evaporation of the solution you are to prepare.

2. Into the vial put the following: 0.20304 grams of solid Iodine (0.0412 mL if liquid Iodine) AND 0.80 mL of THF. Use your micro syringe to measure out small volumes. (Make sure to always clean your syringe with acetone after each use. Iodine will stain your syringe, but that is OK; just make sure to clean with acetone!)

3. To your micro 10mL round bottom flask with long neck, add 0.497 mL of 1-hexene, 4.0 mL of THF, and a micro stir bar (Check out stir bar from instructor, make sure you do not lose! They are very tiny!).

4. Under the hood, clamp your round bottom flask in a small ice-water bath on your magnetic stir plate and begin to stir. (Two students can be on the same plate).

5. Under the hood, add 0.0605 grams of sodium borohydride to your solution in step 3. (please make sure you are careful with the powered sodium borohydride – it is a small amount AND make sure to cap the jar after each student measures out their mass).

6. Using your syringe, slowly add the iodine solution from the capped vial in 0.2 mL portions. Add each portion to the round bottom flask when the solution inside becomes colorless/light yellow OR after 5 minutes. DO NOT DUMP THE IODINE SOLUTION IN ALL AT ONCE – your entire reaction may foam over! (Remember to IMMEDIATELY clean syringe with acetone).

7. After all the iodine solution has been added, remove the ice water bath and continue stirring for **at least 1 hour.**

8. Put your round bottom flask back in an ice-water bath and continue to stir. Slowly add 2.0 mL of distilled water to decompose any unreacted sodium borohydride. The decomposition is complete when no more gas evolves – this may take awhile (10-20 minutes)!

9. Prepare a 35˚C warm water bath and heat your reaction mixture for 5 min. Add 0.5 mL of 3M sodium hydroxide and continue to stir.

10. Then SLOWLY add 0.80 mL of 30% hydrogen peroxide DROP by DROP! Your solution may darken.

11. Continue to stir in warm water bath for **30 minutes.**

12. Transfer the reaction mixture to a large test-tube. Rinse the reaction flask with 3.0 mL of hexane (note: hexane NOT hexene). Pour into the large test-tube as well.

13. Add 1.0 gram of potassium carbonate to the test-tube, stopper with a cork, and shake vigorously.

14. Using a plastic pipette separate the organic layer from the aqueous layer. As encountered before, what piece of information do you need to look up to determine which layer is the top and which is the bottom? Your organic product is in the organic layer! (If you are encountering difficulty with separating the layers in the large test-tube with a plastic pipette, you can always pour it into another container and proceed from there).

*If after looking up the information needed above, you are still unsure about your layers you can always do the water test: add a few drops – 1mL of water to your layers – the added water should mix with the water layer, but not with the organic.

*Remember, NEVER DISCARD ANY LAYERS UNTIL YOU HAVE ISOLATED & PURIFIED YOUR PRODUCT AT THE END OF THE EXPERIMENT!

15. Now it is time to "wash" your organic layer: add 2-3 mL or more of aqueous sodium thiosulfate solution to remove most of the color; a remaining pale yellow color is fine. Make sure to thoroughly mix the solutions before you separate. Again, separate the organic layer from the aqueous layer.

16. Now wash your organic layer with 2.0 mL of saturated aqueous sodium chloride. Repeat this step. Separate the organic layer from the aqueous layer.

17. Dry your organic layer by adding a tiny amount of anhydrous powder. Decant the organic layer into a clean container and GENTLY evaporate the solvent in a warm water bath leaving behind your product **– you should have 0.5 mL of product.** DO NOT EVAPORATE TO DRYNESS and lose your product.

18. Use ONE DROP of your product to obtain an IR to prove you synthesized an alcohol (even though this does not prove Markovnikov's Rule). Remember, you can put a glove on to smear the drop of product in the IR trough plate. Attach analyzed IR to postlab.

*If your IR does not show an alcohol product, you need to repeat the experiment.

19. Carefully set up your boiling point determination set-up. USE AN OIL BATH in this experiment. Be careful and pay attention. You only have 0.5mL of product to work with!

Boiling Point ___________˚C Instructor viewed set-up Signature______________________

12AL Prelab Experiment 9: Markovnikov's Rule

Alkene Reactions:

You have covered most, if not all, reactions in organic lecture. Take the time to review and if new, make sure you use your textbook to look it up! Remember, research is a big part of this course!

Give the name of the reaction and describe what type of product the following reactions synthesize. Also, state whether the resulting product follows Markovnikov's rule, for some if it is syn or anti addition, and whether or not a carbocation is formed during the reaction (which could lead to rearrangement).

1. Alkene + H-X (X = Cl, Br, I)

Name of Rxn:

Description of Product:

Markovnikov / Anti-Markovnikov:

Carbocation formed?

2. Alkene + HBr/ROOR (peroxide)

Name of Rxn:

Description of Product:

Markovnikov / Anti-Markovnikov:

Carbocation formed?

3. Alkene + X_2/CCl_4

Name of Rxn:

Description of Product:

Markovnikov / Anti-Markovnikov:

Syn / Anti-Addition:

Carbocation formed?

4. Alkene + X_2/H_2O

Name of Rxn:

Description of Product:

Markovnikov / Anti-Markovnikov:

Syn / Anti-Addition:

Carbocation formed?

5. Alkene + H_2/Pd

Name of Rxn:

Description of Product:

Syn / Anti-Addition:

Carbocation formed?

6. Alkene + H_3O^+, H_2O

Name of Rxn:

Description of Product:

Markovnikov / Anti-Markovnikov:

Carbocation formed?

7. Alkene + H_3O^+, ROH

Name of Rxn:

Description of Product:

Markovnikov / Anti-Markovnikov:

Carbocation formed?

8. Alkene + 1. BH_3, THF, 2. $H_2O_2/OH^-/H_2O$

Name of Rxn:

Description of Product:

Markovnikov / Anti-Markovnikov:

Carbocation formed?

9. Alkene + 1. $Hg(OAc)_2/H_2O$ 2. $NaBH_4$

Name of Rxn:

Description of Product:

Markovnikov / Anti-Markovnikov:

Carbocation formed?

10. Alkene + 1. $Hg(OAc)_2/ROH$ 2. $NaBH_4$

Name of Rxn:

Description of Product:

Markovnikov / Anti-Markovnikov:

Carbocation formed?

11. Alkene + RCOOOH (peroxy acid)

Name of Rxn:

Description of Product:

Markovnikov / Anti-Markovnikov:

Carbocation formed?

12. Read "Boiling Point Determination Procedure" on our organic website.

***Instructor: include questions about procedure on quiz for previous lab.**

12AL Postlab Experiment 9: Markovnikov's Rule

1. What is the major product of the hydroboration-oxidation reaction you performed in lab? (give structure, name, and theoretical boiling point).

1-hexene + 1. BH_3, THF, 2. $H_2O_2/OH^-/H_2O$

2. Does your experimental boiling point indicate a pure product? Explain.

3. Give the major product for the following reactions. Proper stereochemistry (shape, geometry) is required / chirality may be ignored. Watch out for carbocation rearrangement, and proper geometry like cis/trans. (Be sure to check your work by working out reaction mechanisms – practice, practice, practice!)

a. 2-methyl-1-pentene + HBr

b. 2-methyl-1-pentene + HBr/peroxide

c. 3-methyl-1-pentene + H_3O^+

d. 3-methyl-1-pentene + 1. $Hg(OAc)_2/ROH$ 2. $NaBH_4$

e. 2-methyl-1-pentene + 1. BH_3, THF, 2. $H_2O_2/OH^-/H_2O$

f. 3-methyl-1-cyclohexene + Br_2, H_2O

g. 3-methyl-1-cyclohexene + peroxy acid