Roadmaps

As stated in the syllabus, the "point" of organic chemistry is synthesis, the construction of more complex molecules from simpler ones. By the end of the semester, you will have to solve synthesis problems in which you put together a sequence of several reactions to convert a starting molecule into a product molecule or product molecules. How do you study to prepare yourself for these problems? I believe the best way to review/learn organic chemistry reactions is through the creation of a so-called "roadmap".

A roadmap is a large piece of paper, the size of a poster, in which the essential information (i.e. reagents used, stereochemistry, regiochemistry, key mechanistic steps) about each reaction we study is recorded. To make a roadmap:

1) Write the names of the key functional groups we study (alkanes, alkyl halides, vicinal dihalides, alkenes, alkynes, alcohols, ketones/aldehydes, carboxylic acids, carboxylic acid derivatives, amines, thiols, ethers, epoxides, various aromatic compounds we will study this semester) spread out over the paper. I have prepared templates for both 310M/318M and 310N as well as a brief chart summary that lists the important reactions from 310M/318M .

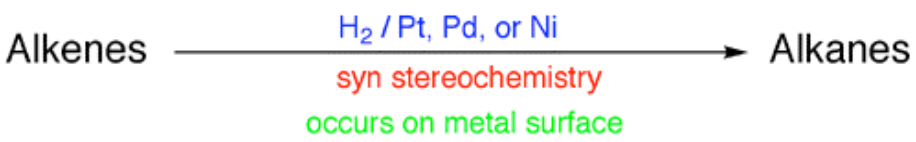
2) List all reactions as arrows that point from a starting functional group to a product functional group.

3) On the top of the arrow is written the reagents required to carry out the reaction. For example, you would write an arrow from "alkenes" to "alkanes" that has "H2 / Pt, Pd, or Ni" written on top of it to describe catalytic hydrogenation.

4) Just under the arrow write the important features of the mechanism of the reaction, listing the stereochemistry (syn or anti), regiochemistry (Markovinikov, non-Markovnikov), and key mechanistic steps (i.e. free radical process, E2 elimination, occurs on metal surface, etc.). Note that not all reactions have stereochemistry or regiochemistry considerations to keep track of, but many do and these issues were discussed at the time the reactions were introduced to you. Recall that knowing the exact stereochemistry or regiochemistry of a reaction, if relevant, will tell you exactly which isomer, either which stereoisomer or regioisomer, of a given product is produced (i.e. cis or trans, R or S configuration, primary or secondary alcohol, etc.)

5) Keep track of those few precious reactions that make or break carbon-carbon bonds. I will make a big deal of these in class.

For example, I would have the following written on an arrow from alkenes to alkanes, describing transition metal catalyzed hydrogenation of alkenes:



See the end of the handout for the suggested arrangement of functional groups for a first semester roadmap (310M/318M), with some representative examples filled in. This arrangement was chosen to minimize the number of arrows that must cross each other, although some will. Write the functional

groups in this arrangement on your large piece of paper, leaving plenty of space between functional groups.

Make sure you use a VERY LARGE sheet of paper, and leave plenty of room between functional groups. Do not use the page at the end of this handout, it is meant as only a guide for your very large version.

I recommend you view the map as being roughly analogous to the state of Texas, with the I-35 corridor represented by alkanes (like San Antonio in the south), followed by alkyl halides (San Marcos), alkenes (Austin), vicinal or geminal dihalides (Waco) and alkynes (Dallas). You will find that as you convert different functional groups in synthesis problems, you will often travel along this path. Even more, you will notice that the alkenes, aka Austin, is the most versatile functional group covered in 310M/318M and it is the center of the "action", as is Austin in real life, of course. Most syntheses involve alkenes in one step or another (just like Texans generally find some reason to go through Austin whenever traveling within the state).

By the time you have completed this task for all the reactions we learn, you should be struck by how alkenes (aka Austin) really is at the center of the chemistry you learned in 310M/318M. That is, alkenes have the most arrows pointing toward them and away from them. You should now be ready to study for synthesis. For example, you should be able to see that if you were asked to synthesize an alkene from a corresponding alkane, you cannot do it directly. Rather, you would break it into two steps (alkane to alkyl halide using X_2 and light or heat, followed by an E2 elimination of the alkyl halide using base such as KOtBu making sure to follow Zaitsev's rule). I call this a roadmap, because synthesis comes down to moving from one “location” (i.e. functional group) on the roadmap, to a different location, and the arrows (i.e. “roads”) tell you how you must travel. For 310M/318M, "I-35" is the most often traveled route in synthesis problems!

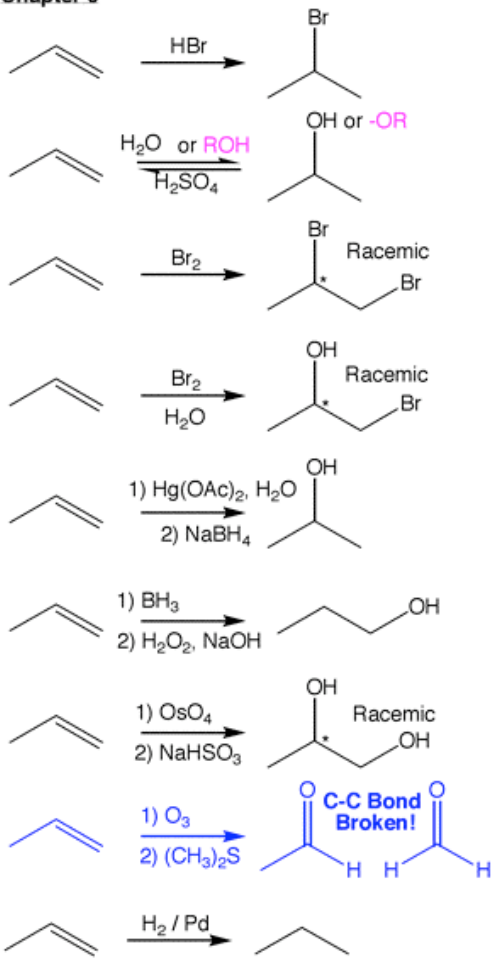
To assist in this process, I have created a brief chart summarizing the important reactions from 310M/318M. The chart is also included at the end of this handout. Note that I have not included the important mechanistic points of each reaction on the chart such as regiochemistry, stereochemistry and the key transition state or intermediate. You must recall those on your own and add them to your roadmap.

For this semester, use the 310N roadmap template. Fill in reactions as we go so you continually see the "big picture" of how each individual reaction relates to the others we have learned. Keep your 310M/318M roadmap handy as you will always be responsible for those reactions as we go through this semester. Notice that this semester the carbonyl chemistry is the center of the map, and we make many, many more carbon-carbon bonds!

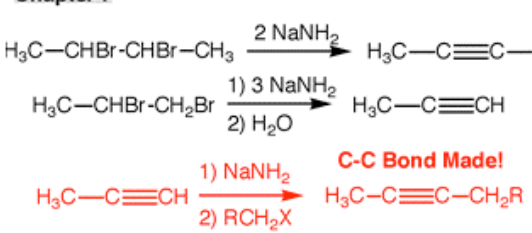
A final comment. Many students find it helpful to keep the large roadmaps posted on their wall. This will not only reinforce the material several times a day as you glance at it, it will also greatly impress your friends, parents, and roommates who do not know organic chemistry. As you go through the semester in 310N, add new reactions to the roadmap after each lecture. It will help provide a big picture understanding of the chemistry you are learning!

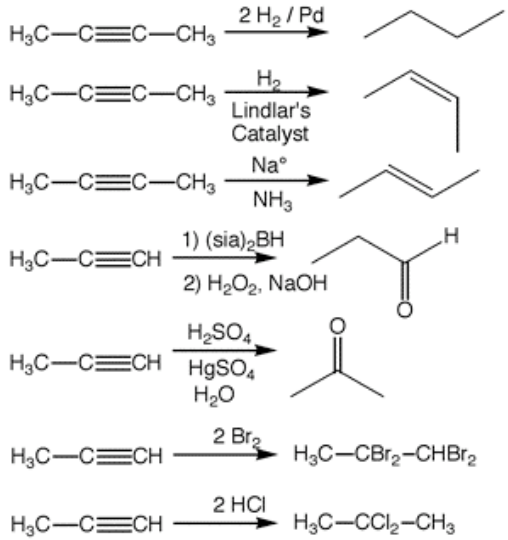
Suggested layout of a 310M Roadmap. Use a very large sheet of paper, like a poster board. For each reaction, draw an arrow between the appropriate functional groups, with the reagents on top of the arrow, and stereochemistry (syn, anti, antiperiplanar), regiochemistry (Markovnikov, non-Markovnikov), and key mechanism steps (free radical, E2, occurs on metal surface, etc.) under the arrow. Keep track of any reactions that make (or break) carbon-carbon bonds! There were not that many of these in 310M. I have filled in four reactions to get you started.

Chapter 6

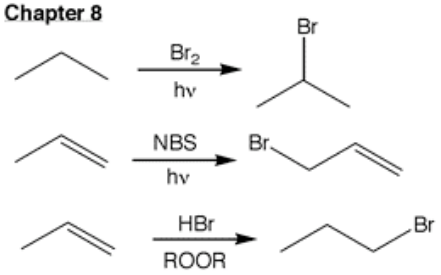


Chapter 7

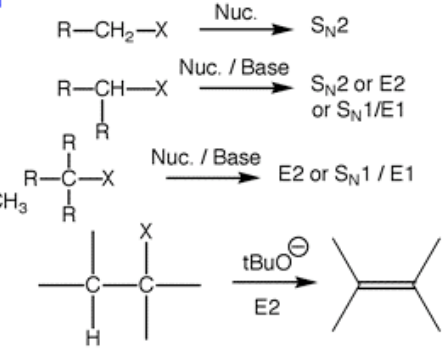




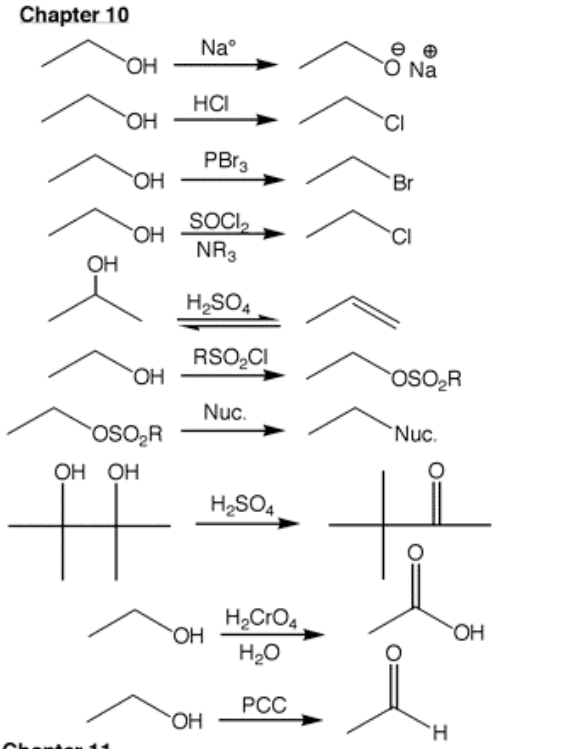
Chapter 8



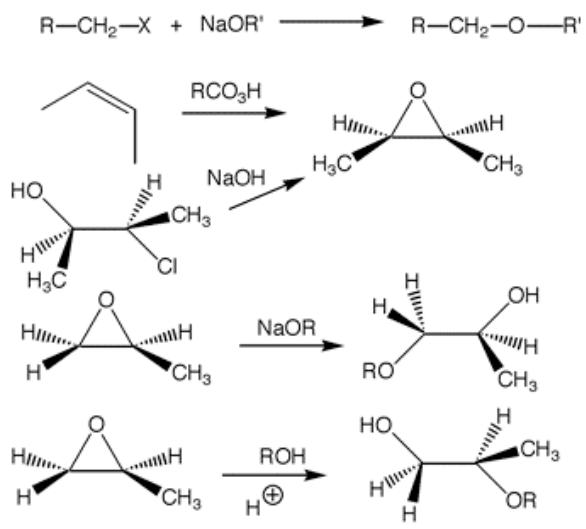
Chapter 9



Chapter 10



Chapter 11



Suggested layout of **310N** Roadmap. This arrangement is intended to minimize the number of arrows that must cross each other, although some crosses are unavoidable. Use a very large sheet of paper, like a poster board. Leave plenty of room between the functional groups. For each reaction, draw an arrow between the appropriate functional groups, with the reagents on top of the arrow, and stereochemistry, regiochemistry, and key mechanism steps under the arrow. Keep track of any reactions that make (or break) carbon-carbon bonds! These are especially valuable for synthesis.

Benzene

(leave plenty of space around this benzene ring as there will be many reactions here late in the semester)

α,β-Unsaturated carbonyl compounds

β-Dicarbonyl compounds

β-Keto esters

β-Hydroxy aldehydes
α,β-Unsaturated aldehydes

Acid anhydrides

Aldehydes

Ketones

Carboxylic esters

Amides

Carboxylic acids

Alcohols

Nitriles

Amines

Alkanes

Alkyl halides

Alkenes

Alkyl dihalide

Alkynes