Chapter 9:

Alkynes and Reactions with Alkynes

- Today (End Chapter 9)
 - ✓ Acetylide Formation
 - ✓ Hydrohalogenation
 - ✓ Anti Markovnikov Hydrohalogenation
 - ✓ Preparation of Alkynes
 - ✓ Addition of Halogens (Dibromination)
 - ✓ Reduction of Alkynes (Hydrogenation)
 - Acid Catalyzed Addition of Water
 - Hydroboration/Oxidation

Hydration Regioselectivity

- Markovnikov hydration leads to a ketone.
- Anti-Markovnikov hydration leads to an aldehyde.



Alkyne Ozonolysis

• When alkynes react under ozonolysis conditions, the pi system is completely broken.



• The molecule is cleaved, and the alkyne carbons are fully oxidized.

Alkyne Ozonolysis

• Predict the product(s) for the following reactions.



Alkylation of Terminal Alkynes

- As acids, terminal alkynes are quite weak.
- With a VERY strong base, a terminal alkyne can be deprotonated and converted into a good nucleophile.

$$R-C\equiv C - H \xrightarrow{\ominus} NH_2 \qquad R-C\equiv C^{\ominus}$$

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The alkynide ion can attack a methyl or 1° alkyl halide electrophile.

Alkylation of Terminal Alkynes

• Acetylene can be used to perform a double alkylation.

 $H-C \equiv C-H \xrightarrow{1) \text{ NaNH}_2} Et-C \equiv C-H \xrightarrow{1) \text{ NaNH}_2} Et-C \equiv C-Me$ $= \frac{2 \text{ eq. NaNH}_2}{2 \text{ eq. Et-Br}} \xrightarrow{1) \text{ NaNH}_2}$

• Complex target molecules can be made by building a carbon skeleton and converting functional groups.

Synthetic Strategies

• Recall the methods for increasing the saturation of alkenes and alkynes.



Synthetic Strategies

 Halogenation of an alkene followed by two dehydrohalogenation reactions can decrease saturation.



- - What conditions would you use in step B?

Designing a Synthesis

Example 1

$CH_3CH_2C \equiv CH \xrightarrow{?} CH_3CH_2CCH_2CH_2CH_2CH_3$

Strategy for a Successful Synthesis

- 1. Know the Reactions.
- 2. Analyze the Carbon Skeletons.
- 3. Analyze the Functional Groups.
- 4. Work Backwards. (Retrosynthesis)
- 5. Check your work.

Retrosynthesis

$CH_{3}CH_{2}C \equiv CH \Longrightarrow CH_{3}CH_{2}C \equiv CCH_{2}CH_{3} \Longrightarrow CH_{3}CH_{2}CCH_{2}CH_{$

synthesis

 $CH_{3}CH_{2}C \Longrightarrow CH \xrightarrow{1. \text{ NaNH}_{2}} CH_{3}CH_{2}C \Longrightarrow CH_{3}CH_{2}C \Longrightarrow CH_{2}CH_{3} \xrightarrow{H_{2}O} CH_{3}CH_{2}C$

For Next Time....

Suggested Homework Problems Chapter 9 # 1,7,9,13,18,20,32-37, 41,44,52,57

MONDAY Chapter 10 (10.1-10.4)