TOPIC 8. ADDITIONS TO ALKENES AND ALKYNES

OBJECTIVES

1. Describe mechanisms for addition reactions of alkenes and alkynes
2. Predict the structure of the product(s) of addition reactions
3. Understand the mechanisms which explain the regiochemical and stereochemical outcome of addition reactions
4. Use combination of substitution, elimination and addition chemistry to propose synthetic routes to useful value-added compounds

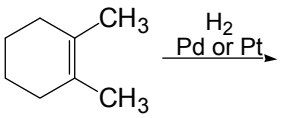
ADDITION REACTIONS

1. Addition of H_2
   - H_2/Pd (alkene, alkyne)
   - H_2/Lindlar catalyst (alkyne → cis alkene)
   - dissolving metal reduction (alkyne → trans alkene)
2. Addition of H-Hal
   - Markovnikov
   - anti-Markovnikov
3. Addition of H_2O
   - H_3O^+ (regiochemistry)
   - Oxymercuration-demercuration (regiochemistry, stereochemistry)
   - Hydroboration-oxidation (regiochemistry, stereochemistry)
   - hydration of alkynes (regiochemistry)
4. Addition of Hal_2
   - Hal_2 (regiochemistry, stereochemistry)
   - Hal_2/H_2O (regiochemistry)
5. Generation and reaction of carbenes
6. Epoxidation
7. Nucleophilic ring opening reactions of epoxides (H_2O, ROH, HCN, nucleophiles)
8. syn-Hydroxylation
9. Oxidative cleavage of alkenes and alkynes
   - $KMnO_4$
   - Ozonolysis

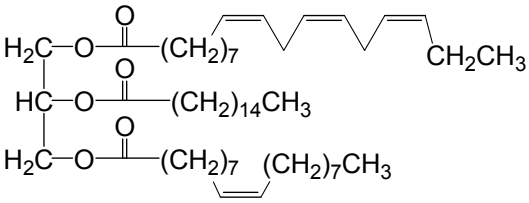
~MAKE FLASHCARDS ~

HYDROGENATION OF ALKENES AND ALKYNES

Hydrogenation of Alkenes

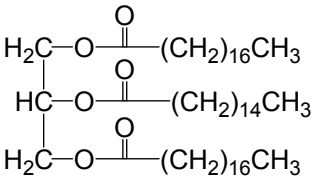


A Practical Application of Hydrogenation – Hydrogenated Oils and Fats

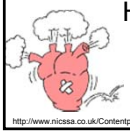


Soybean Oil
Mixture of saturated and various *cis*-unsaturated hydrocarbon chains.
Low melting (-16 °C) because cis C=C impede crystallization.

H_2/Pt



Margarine
Mixture of saturated hydrocarbon chains (some C=C kept to adjust consistency).
Saturated alkyl chains pack together (crystallize).

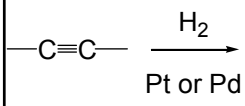


http://www.nicssa.co.uk/Contentpages/Fitness&Exercise/contentweightetc.htm

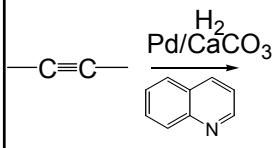
http://www.bassriverchairs.com/new_prodMargarine.html

Hydrogenation of Alkynes

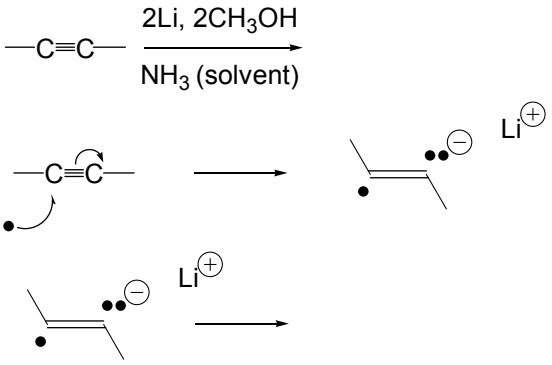
Complete Hydrogenation



cis-Semihydrogenation

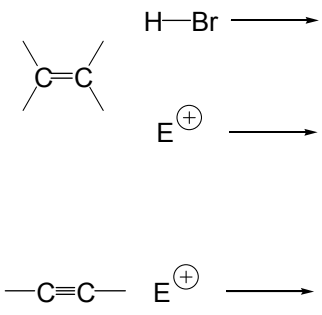


Dissolving Metal Reduction



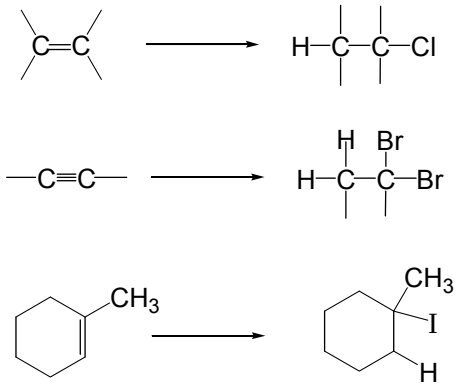
PREVIEW OF REACTIVITY

Alkenes and Alkynes are Weakly _____ and Weakly _____



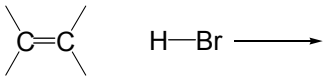
ADDITION OF HYDROGEN HALIDES TO ALKENES AND ALKYNES

Overview

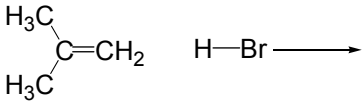


Addition of H-Hal to Alkenes

Mechanism



Regiochemistry



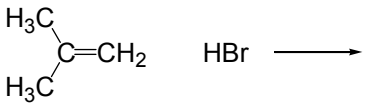
Markovnikov's Rule

In the addition of HX to an unsymmetrical alkene, the hydrogen adds to the

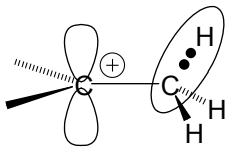
_____ substituted carbon and the X groups adds to the

_____ substituted carbon.

The Basis of Markovnikov's Rule: Stability of Carbocations

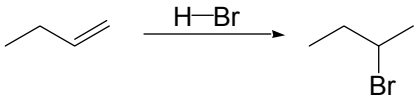


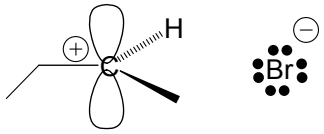
The more substituted carbocation is formed. Remember hyperconjugation!



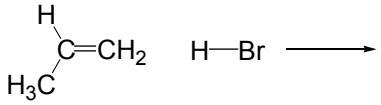
Mechanistic Restatement of Markovnikov's Rule
In the ionic addition of HX to an unsymmetrical alkene, protonation gives the more stable carbocation as an intermediate.

Stereochemistry of H–Hal Addition to Alkenes



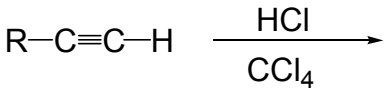


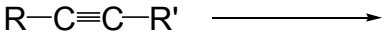
Anti-Markovnikov Addition of H-Hal to Alkenes



Mechanistic Rationale for Anti-Markovnikov Addition

Addition of H-Hal to Alkynes





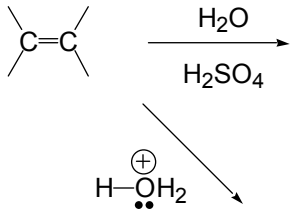
~ MAKE FLASHCARDS ~

Hydrogenation
Dissolving metal reduction
Hydrogenation over Lindlar catalyst
Markovnikov addition of H-Hal
Anti-Markovnikov addition of H-Hal

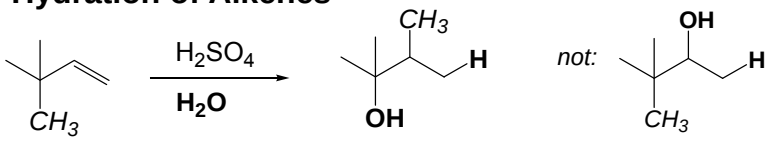
…..more next lecture

SYNTHESIS OF ALCOHOLS BY HYDRATION OF ALKENES

Addition of Water to Alkenes



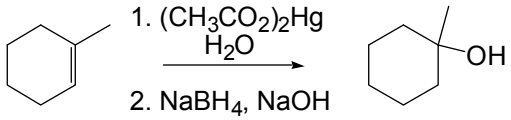
Rearrangements During Acid Catalyzed Hydration of Alkenes



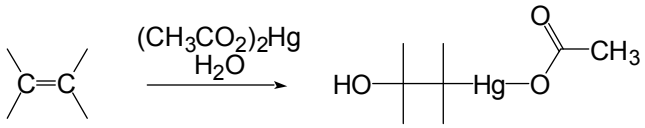
Intermediate carbocations can rearrange.

Oxymercuration-Demercuration of Alkenes

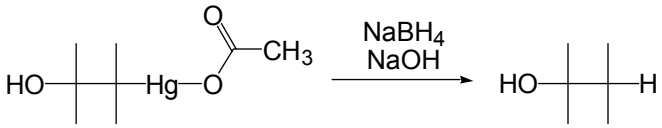
e.g.,



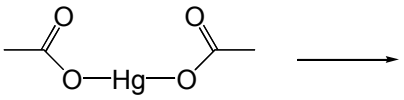
Step 1: Oxymercuration



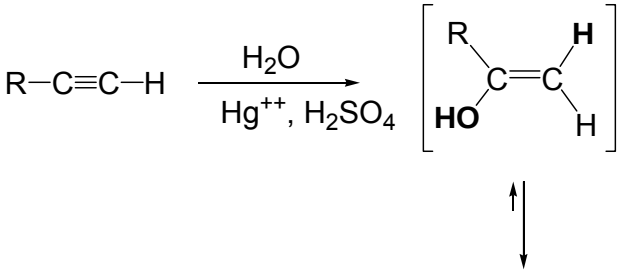
Step 2: Demercuration



Mechanism

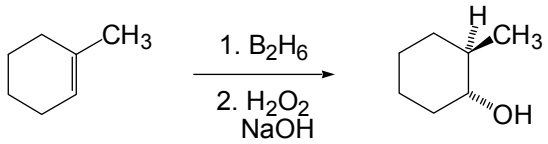


Hydration of Alkynes (keto-enol tautomerization)

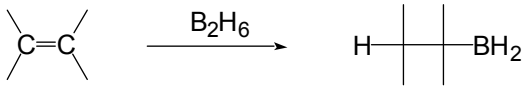


Hydroboration-Oxidation: Anti-Markovnikov Hydration of Alkenes

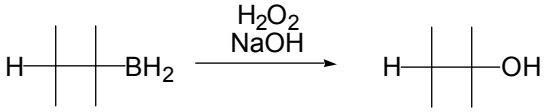
e.g.,



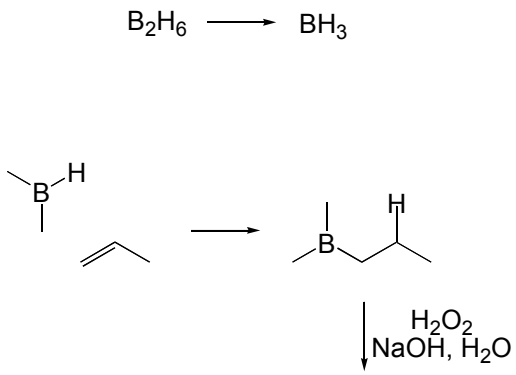
Step 1: Hydroboration



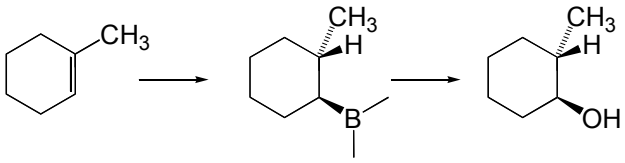
Step 2: Oxidation



Mechanism: Regiochemistry

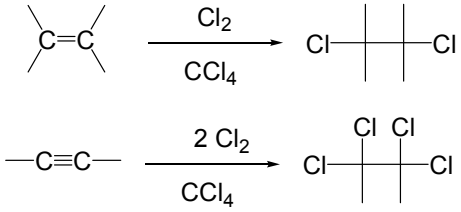


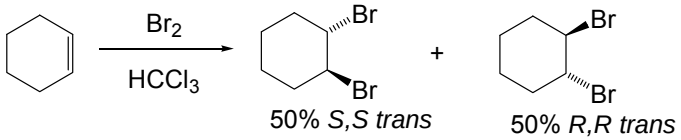
Stereochemistry



ADDITION OF BROMINE AND CHLORINE TO ALKENES AND ALKYNES

Overview

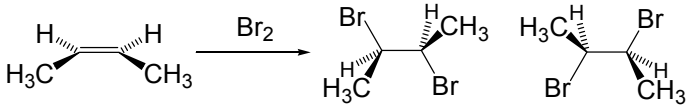


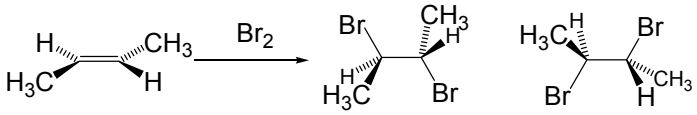


50% *S,S trans* 50% *R,R trans*

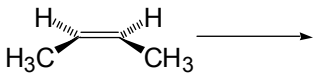
Addition of Hal_2 to Alkenes

Stereochemistry



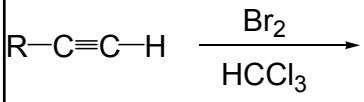


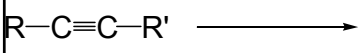
Mechanism



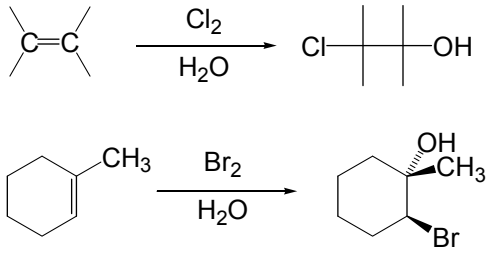
Br—Br

Addition of Hal_2 to Alkynes

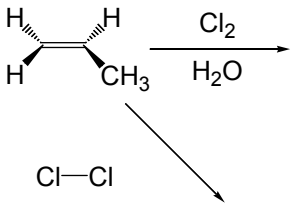




Formation of Halohydrins



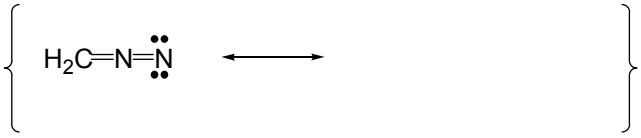
Mechanism

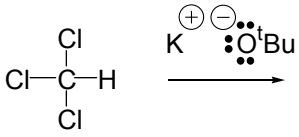


ADDITION OF CARBENES TO ALKENES

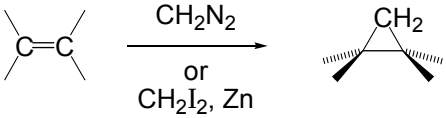
What is a Carbene? $:CH_2$

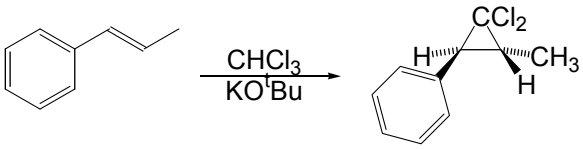
What is a Carbenoid? $I{-}CH_2{-}I \longrightarrow I{-}CH_2{-}Zn{-}I$



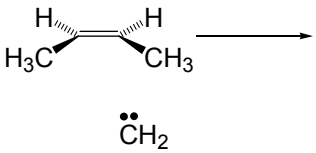


Additions to Alkenes



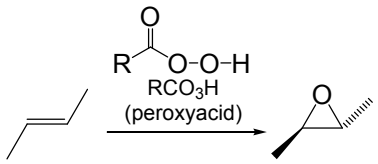


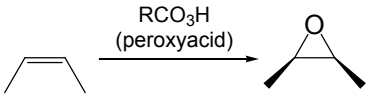
Mechanism

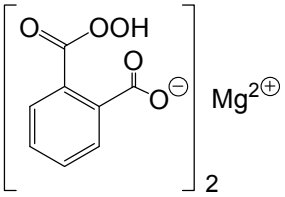


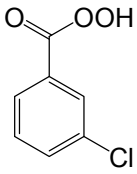
EPOXIDES

Synthesis

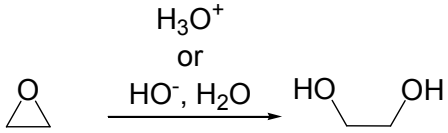




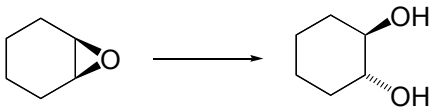
MMPP 

*m*CPBA 

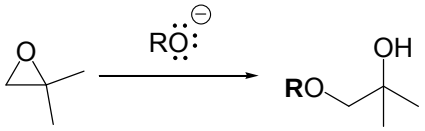
Nucleophilic Ring-opening

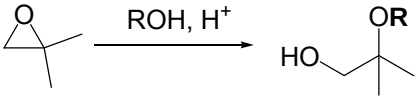


Stereochemistry

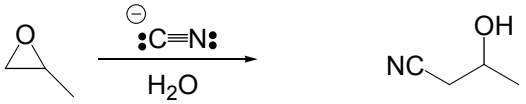


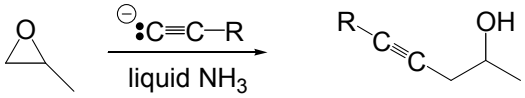
Regiochemistry

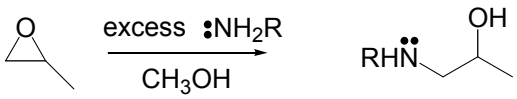




Addition of Other Nucleophiles

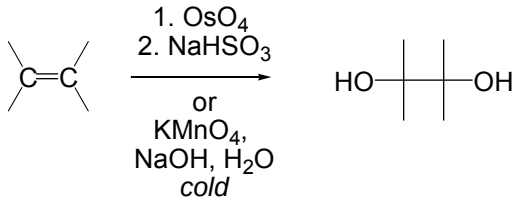


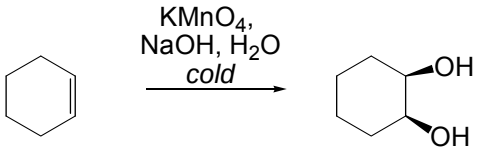




OXIDATION OF ALKENES AND ALKYNES

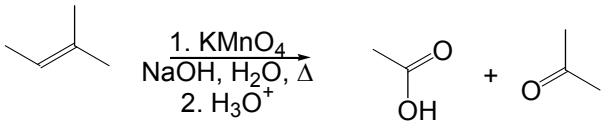
Syn-Hydroxylation of Alkenes

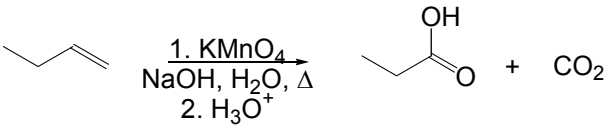




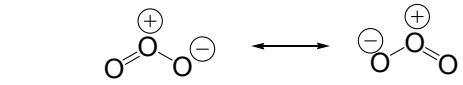
Oxidative Cleavage of Alkenes

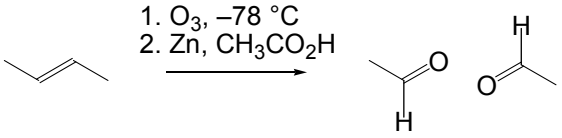
Permanganate Oxidation



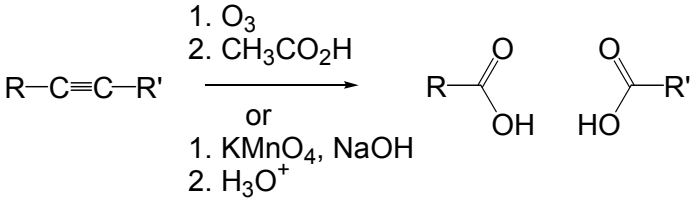


Ozonolysis



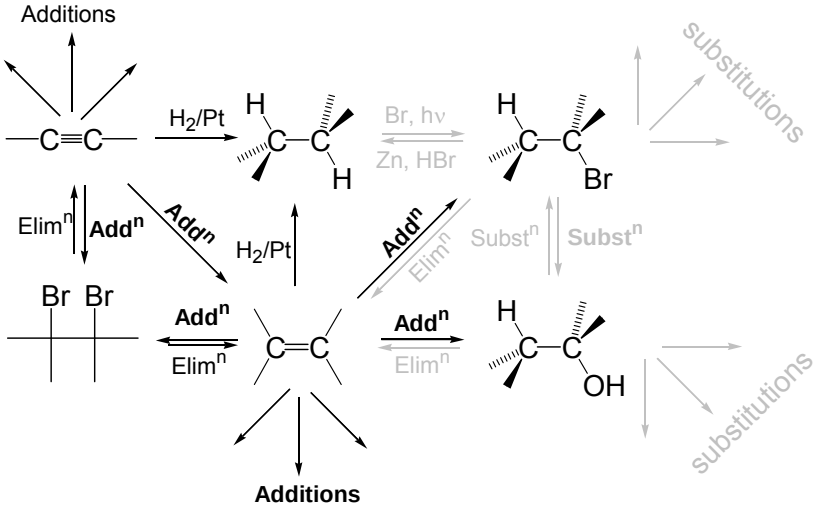


Oxidative Cleavage of Alkynes



SYNTHETIC STRATEGIES

Add to your chart of organic reactions



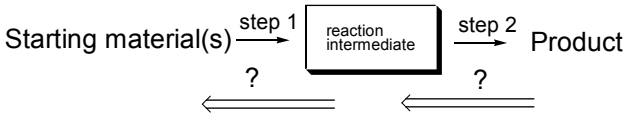
DESIGNING SYNTHESES

One Step Syntheses

This is just the opposite of learning reactions - just think backwards. Although one step syntheses are *relatively easy, they are harder than learning reactions.*

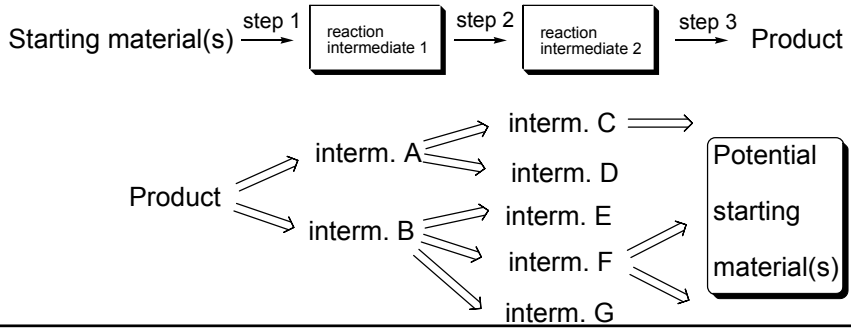
Two Step Syntheses

This is involves considerable imagination and is quite different than "just the opposite of learning reactions". You must be able to conceive of the intermediate. However, there is a direct link between the intermediate and both the product and the starting material. Think "retro" (retrosynthesis) - how do you synthesize the product from anything? Can you then synthesize your proposed synthetic intermediate from the starting material?

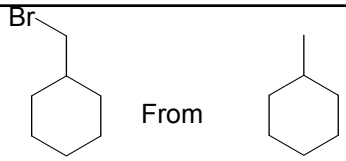


Three Step Syntheses

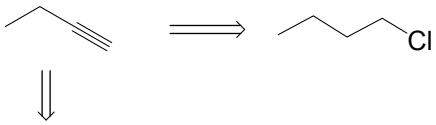
Three design of three-step organic syntheses requires a little more imagination and can be a little more difficult than two-step syntheses. You must be able to conceive of two intermediates. In this case there may not be a clear link between intermediate one and the product or intermediate two and the starting material. Again “think retro”. Can you think of *ANY* compounds that could be converted to the product by chemistry you know? Can you then think of one or more compounds that could be converted to these proposed intermediates by chemistry you know? Can any of these second proposed intermediates be synthesized from the starting material?



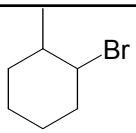
Problem:



Problem: Show how 1-butyne could be synthesized from each of the following1-chlorobutane

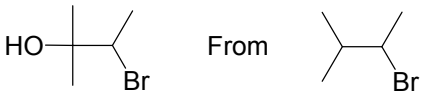


Problem:

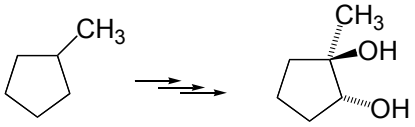


From any alkane

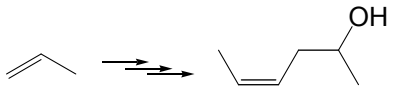
Problem:



Problem: Propose a synthesis of 1-methyl-1,2-cyclopentanediol (with the two hydroxy groups trans to one another) from methylcyclopentane.



Problem: An insect physiologist required 4*Z*-hexen-2-ol for the study of insect pheromones. Propose a synthesis of 4*Z*-hexen-2-ol from propene.



TOPIC 8

Types of Questions

- Describe addition reaction mechanisms
- Predict the products of addition reactions
- Provide a series of synthetic to steps to make a desired product