

Module 3, Lecture 9

Structure and Reactions of Organic Molecules

**Introduction to reaction mechanisms
Addition Reactions to Alkenes**

James Crowley

jcrowley@chemistry.otago.ac.nz

Dr. Bill Hawkins

bhawkins@chemistry.otago.ac.nz

References to Brown *et al* text shown in BLUE

1

Learning Objectives:

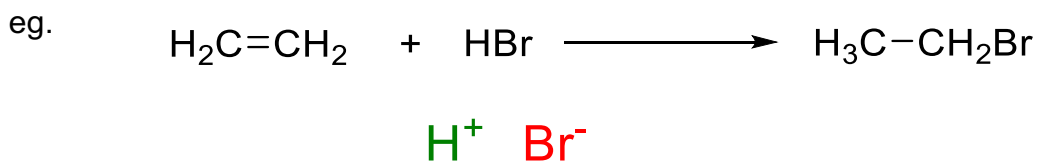
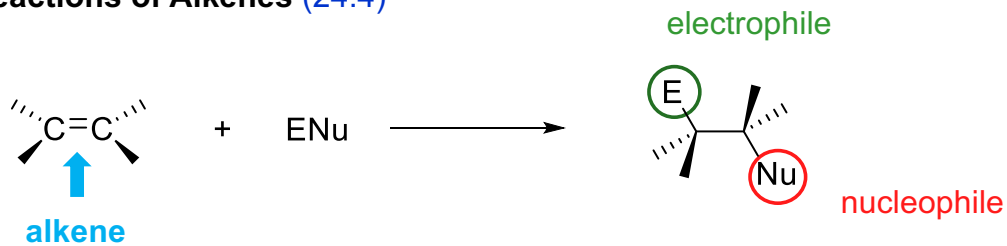
- to have an understanding of addition reactions to alkenes
- to be able to draw the mechanism of an addition to an alkene
- to be able to determine the major and minor products generated from the addition of acids to unsymmetrical alkenes
- to be able to identify a bromonium ion

Textbook: [**Chapter 24, sections 24.4-23.6, Brown**](#)

2

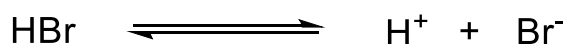
Reactions of multiply bonded functional groups

Addition Reactions of Alkenes (24.4)

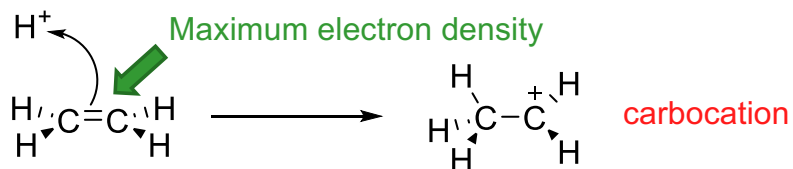


3

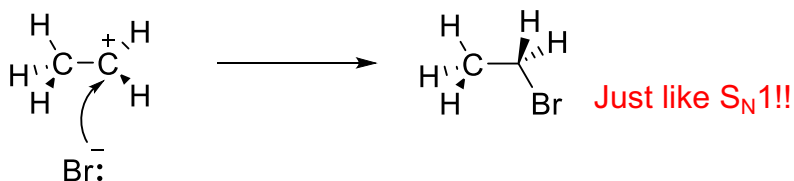
Mechanism



First step: Slow addition of an **electrophile** (H^+) to the electron rich double bond *perpendicular to the atom plane*:



Second step: Fast attack by a nucleophile at the carbocation intermediate:



4

Mechanism

Rate determining step involves the electrophile (*electron seeking*)

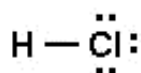
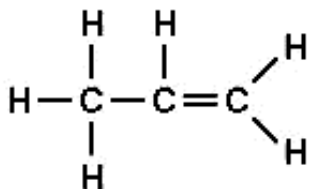
- **electrophilic addition.**

$$\text{rate} = k[\text{H}^+][\text{H}_2\text{C}=\text{CH}_2]$$

The carbocation intermediate will react with the most *abundant* nucleophile.

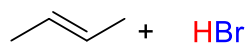
5

Mechanism

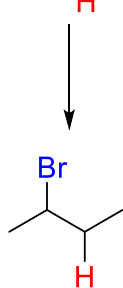
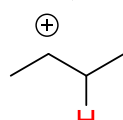


6

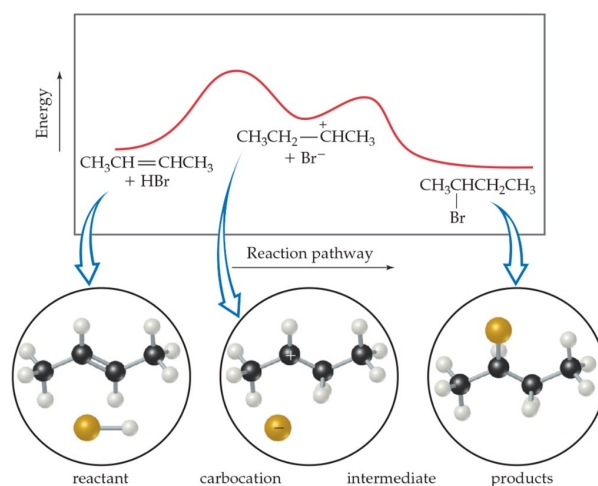
Addition to HBr to a C=C bond



RDS



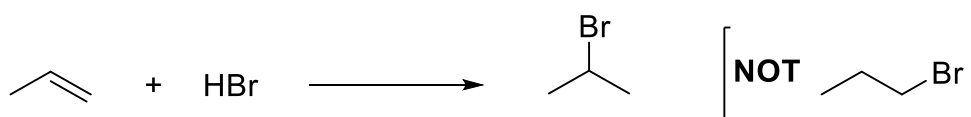
► FIGURE 24.20 Energy profile for addition of HBr to but-2-ene.



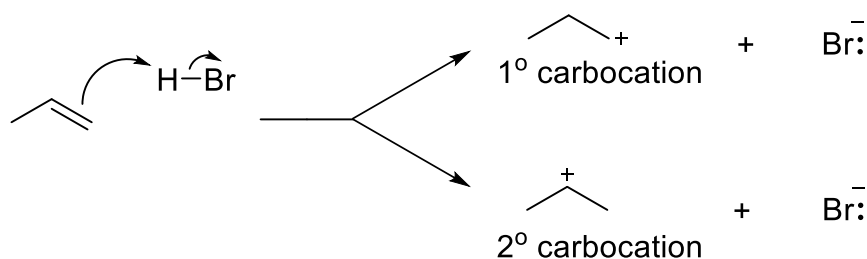
7

Addition to Unsymmetrical C=C

eg.



Two possible pathways:

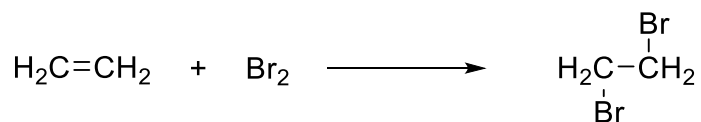


2° carbocation is more stable (alkyl groups are electron donating – stabilise +ve charge, refer to $\text{S}_{\text{N}}1$)

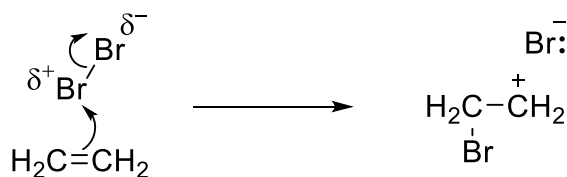
8

Addition of Cl₂ and Br₂

Nonpolar Cl₂ and Br₂ react readily with alkenes:



Approach to electron-rich double bond induces dipole character in Br₂ bond:

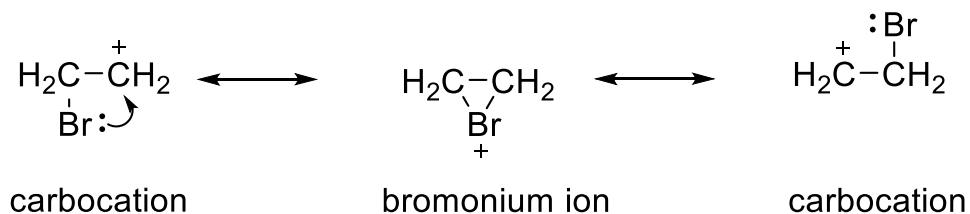


9

Addition of Cl₂ and Br₂

Nature of the carbocation

Bromine can share the positive charge

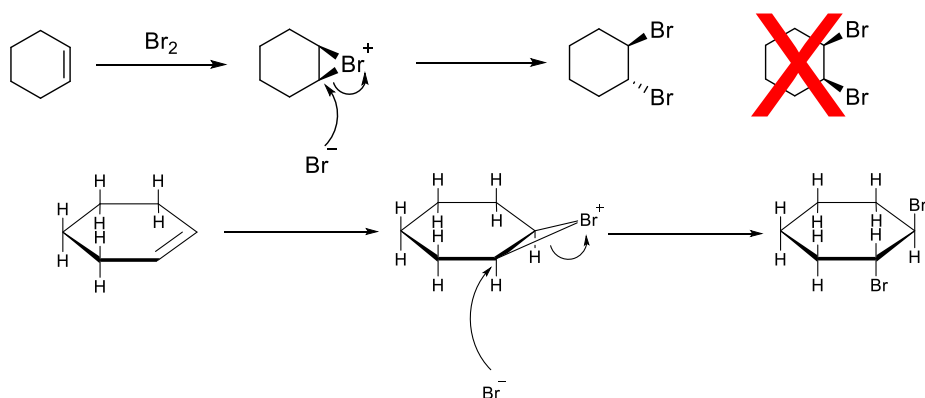


Bromonium ion is significant for symmetrical alkenes

10

Bromination of Cyclohexene

- Evidence for the bromonium ion



- you will learn how to draw cyclohexane in a chair conformation in **Module 4**

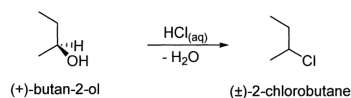
11

Past Exam Q

- Past exam papers are always a good idea!

12

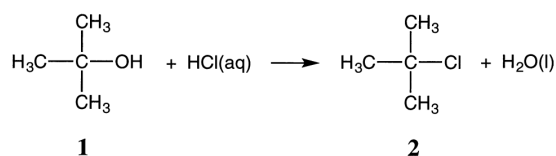
3. (a) For the following nucleophilic substitution reaction:



- (i) Classify (+)-butan-2-ol as primary, secondary or tertiary.
[1 mark]
- (ii) What do the symbols (+) and (±) in the reactant and product names mean?
[1 mark]
- (iii) With consideration of your answer in part (a)(ii) give a mechanism for the reaction. Show all intermediates and identify the rate determining step.
[3 marks]
- (iv) Draw a transition state for the rate determining step and briefly discuss factors that stabilise it.
[2 marks]
- (v) Assign the absolute configuration of (+)-butan-2-ol as (*R*) or (*S*).
[1 mark]

13

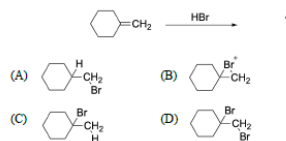
3. (a) For the following nucleophilic substitution reaction:



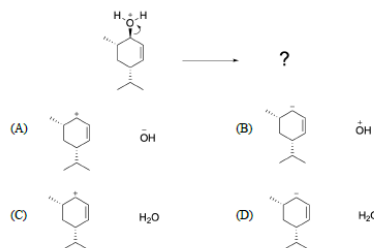
- (i) Classify alcohol (**1**) as primary, secondary or tertiary.
[1 mark]
- (ii) Give a mechanism for the reaction using mechanistic arrows as appropriate. Show all intermediates and identify the rate determining step.
[3 marks]
- (iii) Draw a transition state for the rate determining step and briefly discuss the factors that stabilise it.
[3 marks]
- (iv) What is the alternative mechanism by which nucleophilic substitution can occur? Explain why would this be unlikely to be operating in the reaction of **1**?
[2 marks]

14

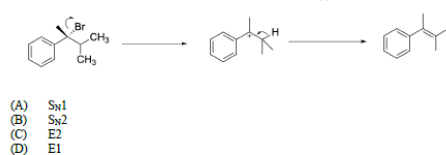
56. Which compound is most likely to be the major product in the following reaction?



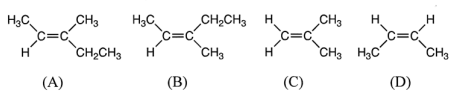
57. The products from the following mechanistic steps are:



58. Consider the reaction mechanism shown below, the reaction type is:



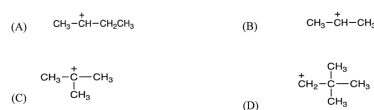
14. Which one of these structures is an *E*-isomer?



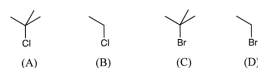
15. Which one of the following statements about nucleophilic substitution reactions is **CORRECT**?

- (A) The rate of nucleophilic substitution reactions is not affected by the solvent.
 (B) An S_N1 reaction proceeds with complete inversion at the reaction centre.
 (C) An S_N2 reaction will be fast at a tertiary carbon due to steric hindrance.
 (D) A good leaving group is required for nucleophilic substitution reactions.

16. Which is the most stable carbocation?



17. Which one of the following will react fastest in an S_N2 reaction?



15

* Homework *

Chemistry – the central science 3rd Ed

Brown et al.

Problems 26.18, 26.19, 26.26

Answers on Blackboard

16