



# Organic chemistry

Lec: \_\_\_\_\_

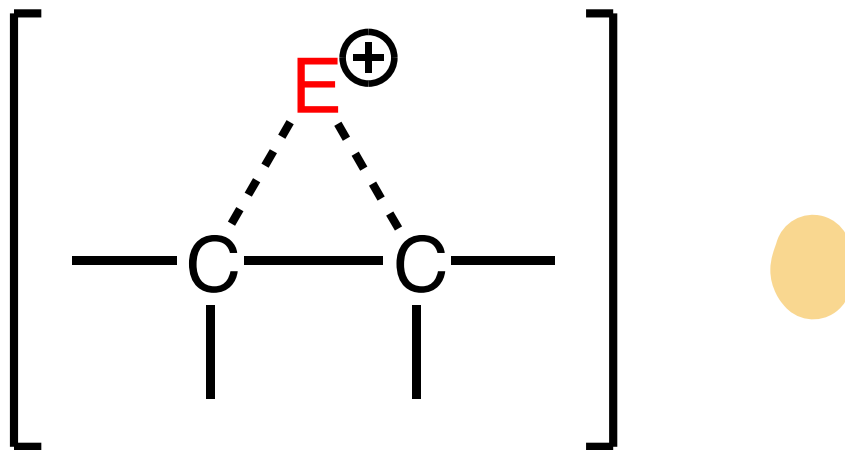
9 "P.2 Chapter 3"

Done by: \_\_\_\_\_

Yasser Yaghi

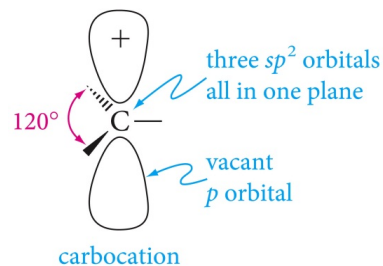
## Mechanism

Sometimes do not go through a “free carbocation”, may go via

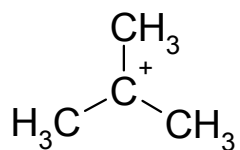


# Carbocations

Are electron deficient and have an empty p orbital ( $sp^2$  hybridized). Not all carbocations are equally stable so there are predictable patterns for which ones will form.

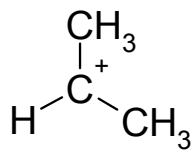


The Most Stable



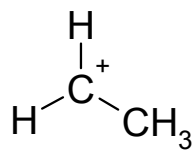
3°

>



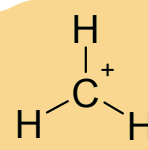
2°

>



1°

>



methyl

The least Stable

The most reactive

Note: this is the same order of stability as carbon radicals.

# Carbocations (cont'd)

(إعطائها إلكترونات) استقرارها.

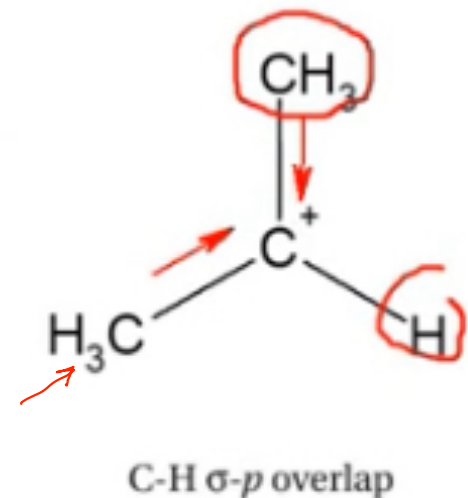
يؤدي إلى زيادة

الاستقرار

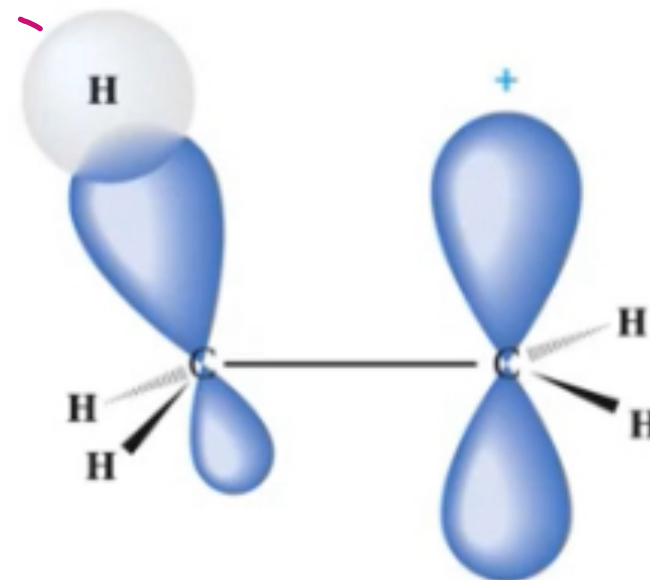
مع: ربي شيء يوزع الشحنة الموجبة ويشتتها أيضا يؤدي إلى زيادة الاستقرار

The order of carbocation stability arise from three sources.

1) **Inductive electron donation:** the electrons in C-C  $\sigma$  bonds will be pulled closer to the  $C^+$  helping to minimize the charge. Note: this does not work for C-H bonds.



2) **Hyperconjugation:** this is an orbital interaction between adjacent C-H bonds that can overlap the empty p orbital of the  $C^+$ , this again helps to minimize the charge on the  $C^+$ .

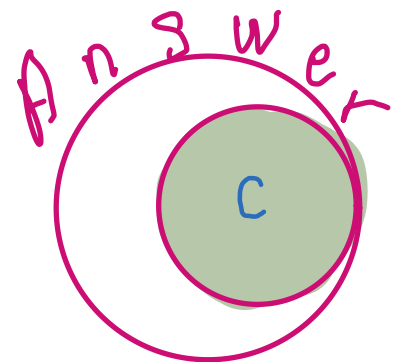




# Test Yourself

\* Inductive electron donation occurs between:

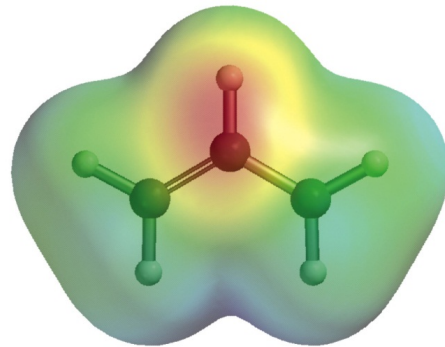
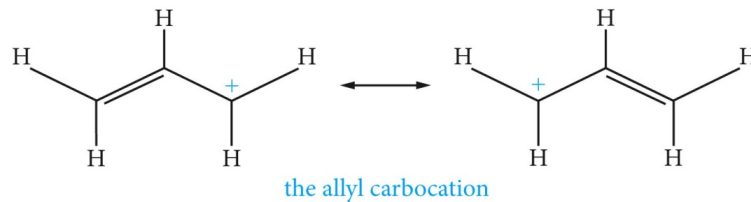
- a- Electrons in C-H  $\sigma$  bonds and  $C^+$ .
- b- Electrons in C-C  $\sigma$  bonds and empty p orbital.
- c- Electrons in C-C  $\pi$  bonds and  $C^+$ .
- d- Electrons in C-H  $\sigma$  bonds and empty p orbital.



# Carbocations (cont'd)

3)

**Resonance:** a carbocation immediately adjacent to a p system (double bond, triple bond or aromatic ring) can be stabilized by resonance. This lowers the energy by spreading the charge over more atoms, i.e.

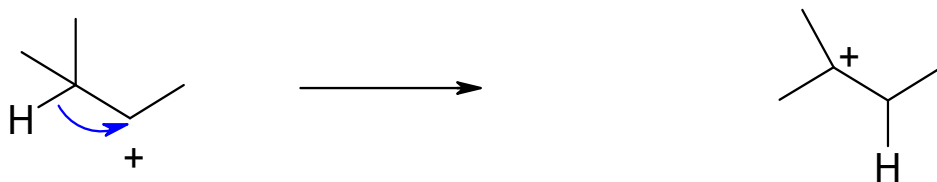


قوة استقرائية  
السحابة الموجبة  
ما يزيد من ادر  
Stability

# Carbocations (cont'd)

One final complexity for carbocations: rearrangement.

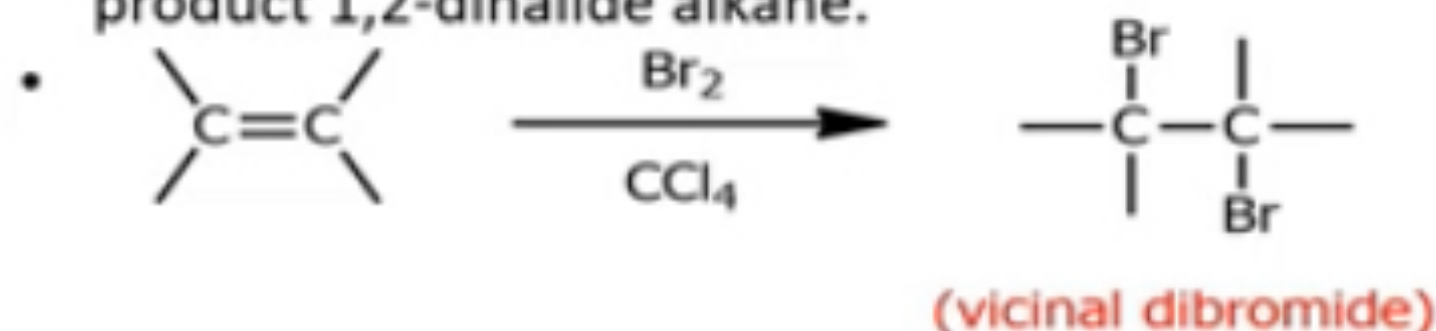
Carbocations are susceptible to 1,2-hydride shifts, where an adjacent H atom (and its bonding electrons) shift to the C<sup>+</sup> to produce a more stable carbocation, i.e.



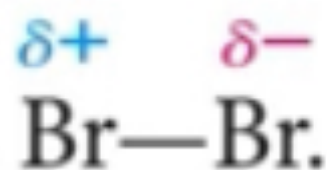
This is also possible for methyl groups. These shifts are common when a tertiary, allylic or benzylic carbocation is produced.

### 3.7.a Addition of Halogens

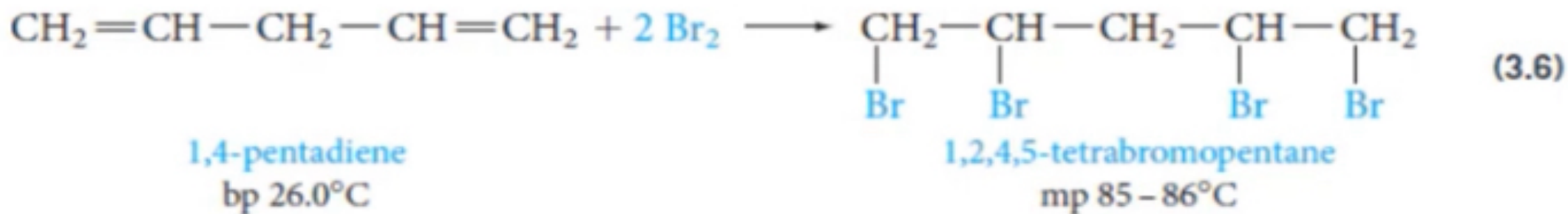
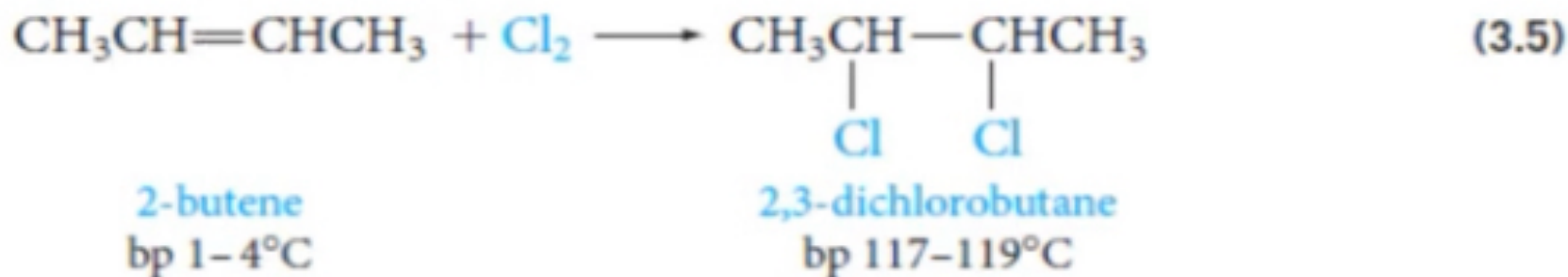
- Addition of  $\text{Cl}_2$  or  $\text{Br}_2$  across the double bond to product 1,2-dihalide alkane.



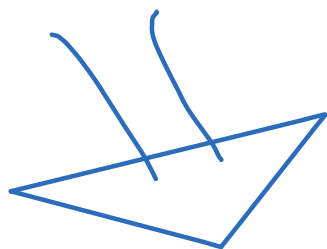
- Halogen is usually dissolved in chloroform or carbon tetrachloride.
- Reaction is rapid at room temperatures
- Addition of bromine is a common chemical test for the presence of double bonds as the red colored bromine solution turns colorless when it reacts with an alkene
- Reaction relies on the polarizability of the halogen bonds



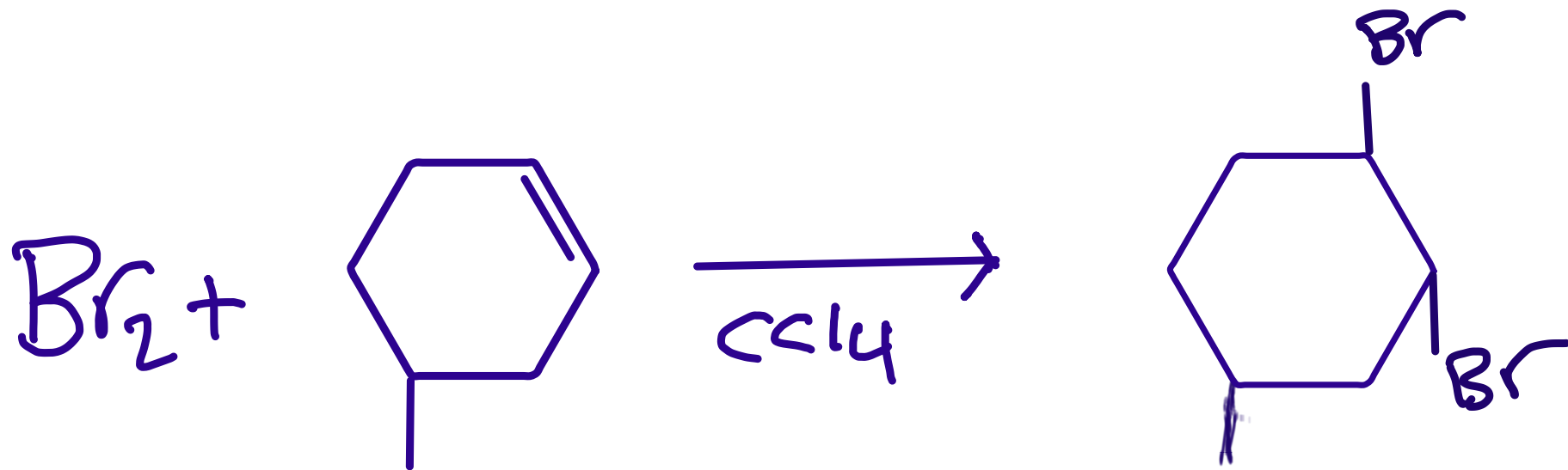
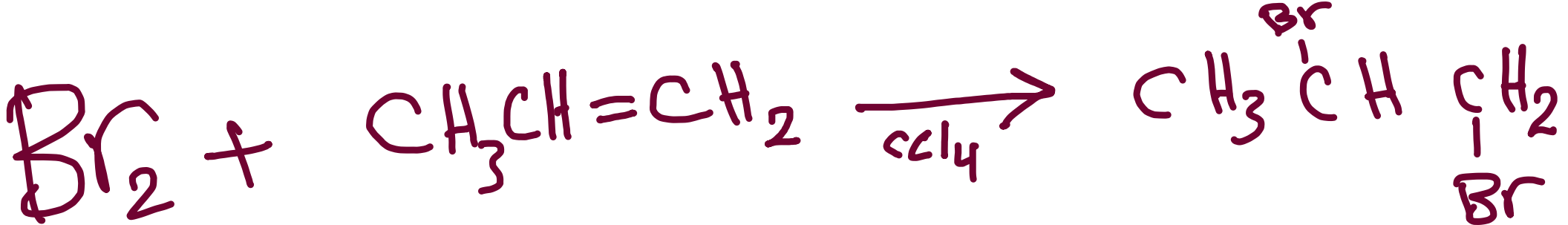
Alkenes readily add chlorine or bromine.



**PROBLEM 3.8** Write an equation for the reaction of bromine at room temperature with a. propene b. 4-methylcyclohexene





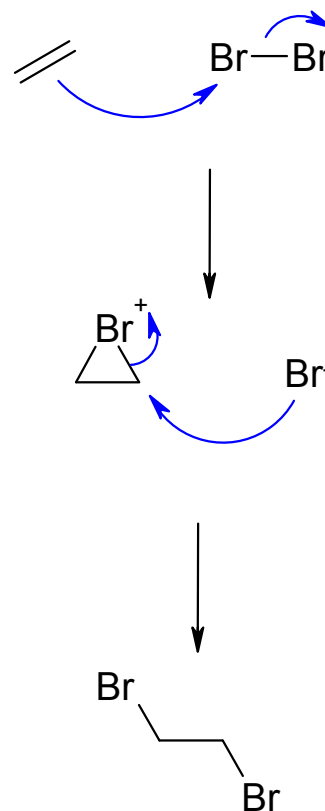


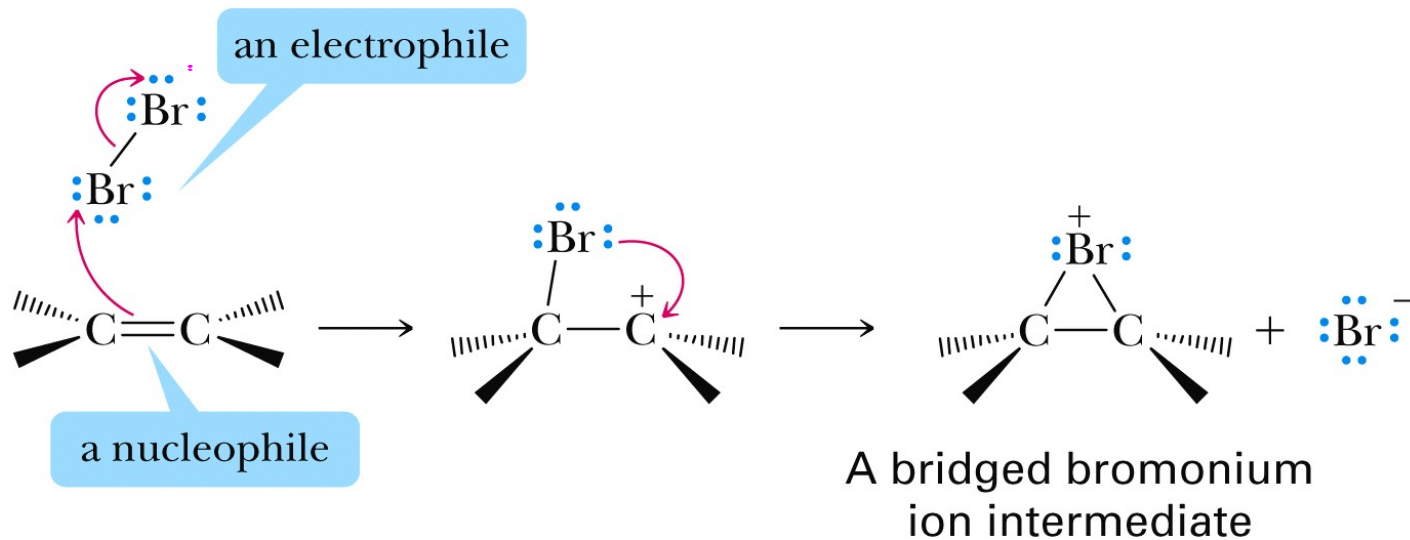
# Halogenation (cont'd)

In the first step the  $\pi$  electrons act as a nucleophile attacking the bromine displacing a bromide ion and forming the cyclic bromonium cation intermediate.

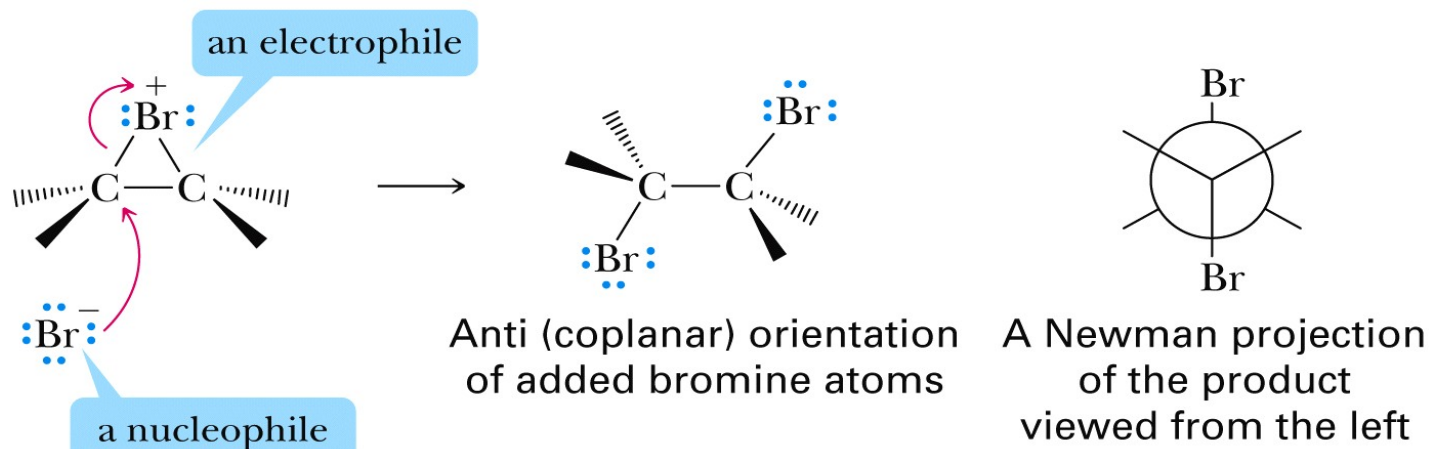
In the second step the nucleophilic bromide ion attacks the side of the bromonium ion away from the bromine atom opening the highly strain cyclic structure and producing the 1,2 dibromo hydrocarbon.

Note this is a **trans addition** since the two Br atoms add to opposite side of the double bond.





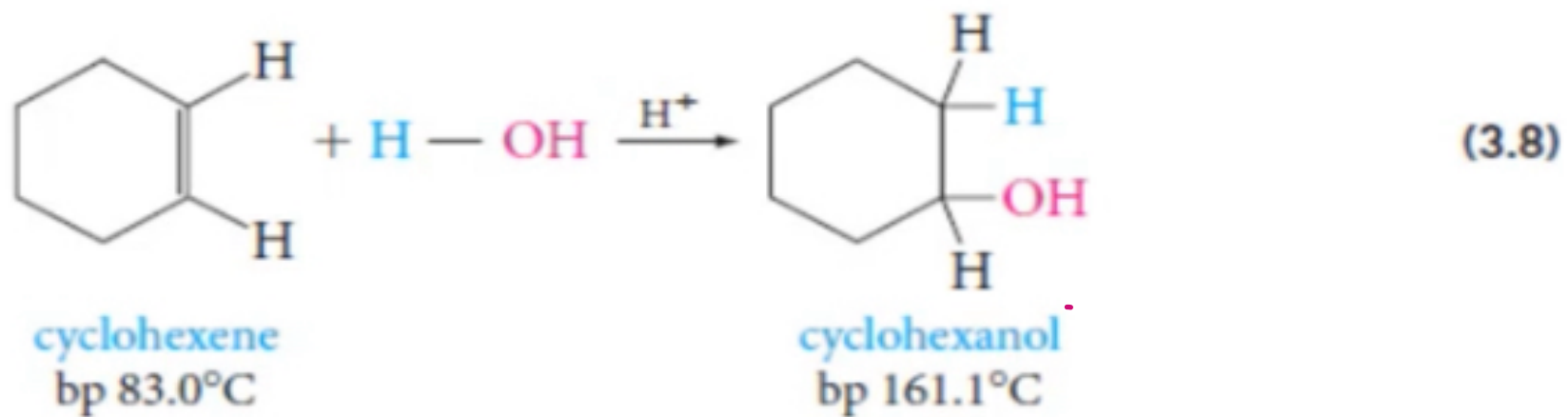
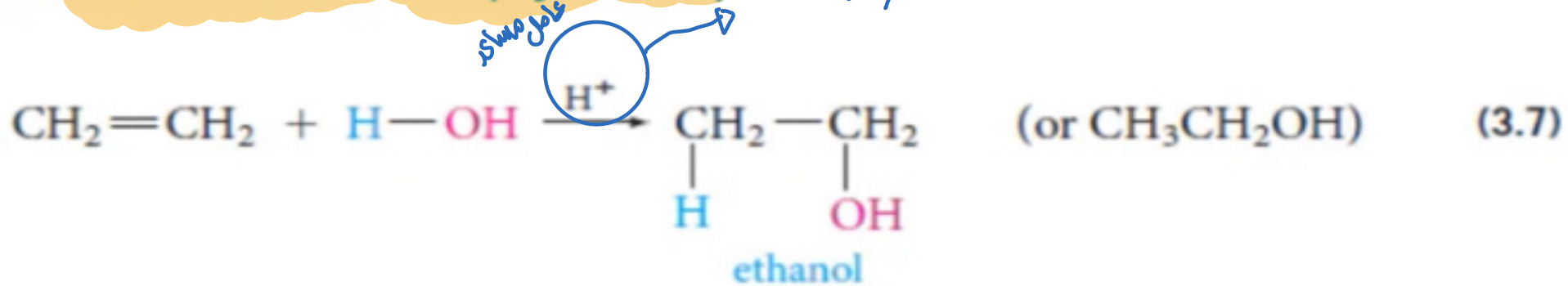
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### 3.7.b Addition of Water (Hydration)

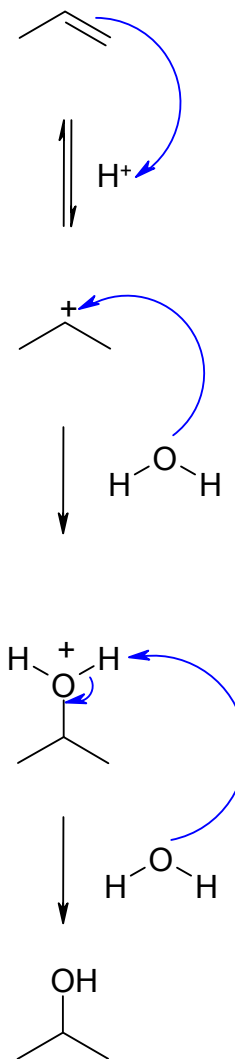
$H_3PO_4 / H_2SO_4$  می



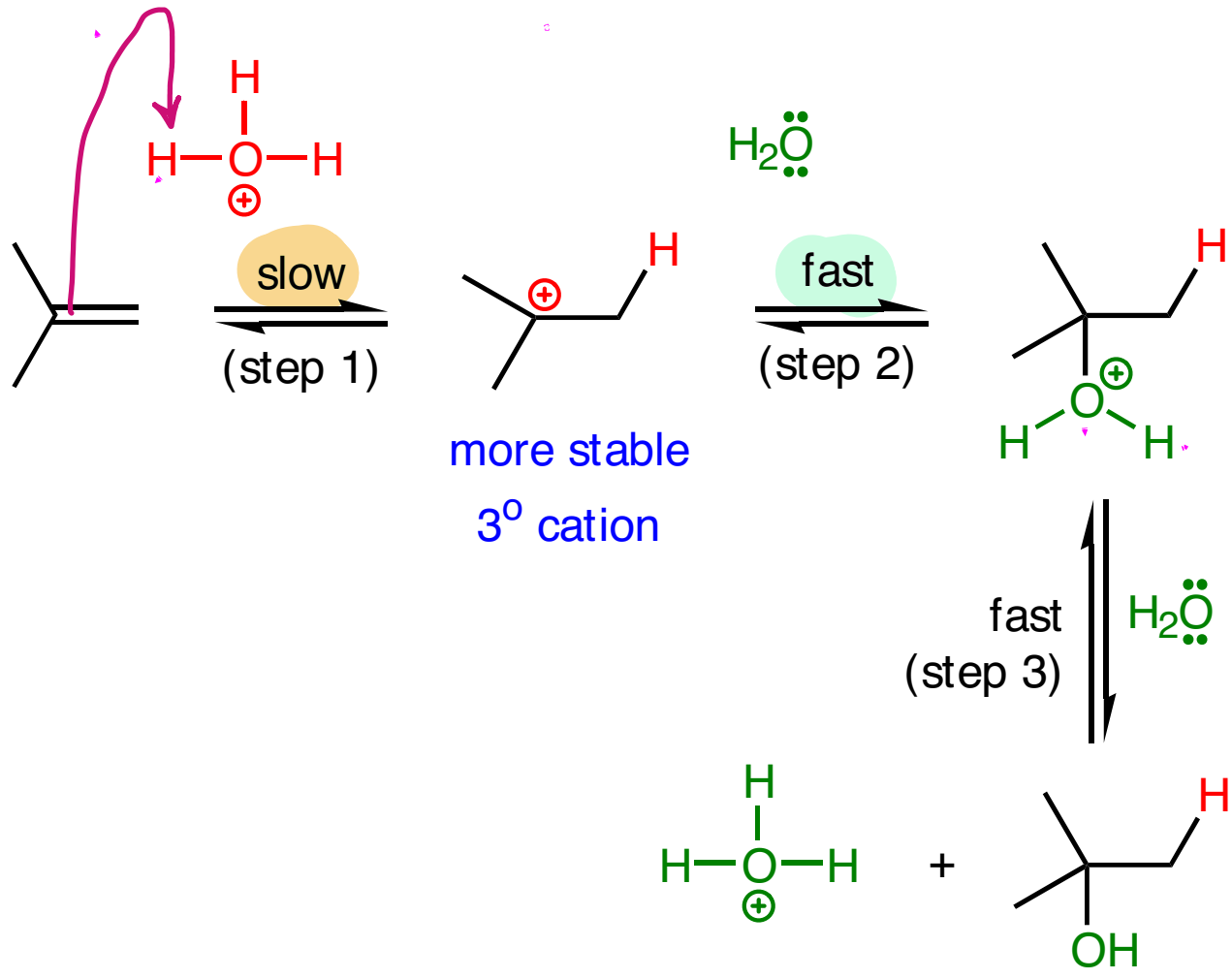
## Hydration (cont'd)

First step is the protonation of the alkene in a Markovnikov orientation to generate the most stable carbocation.

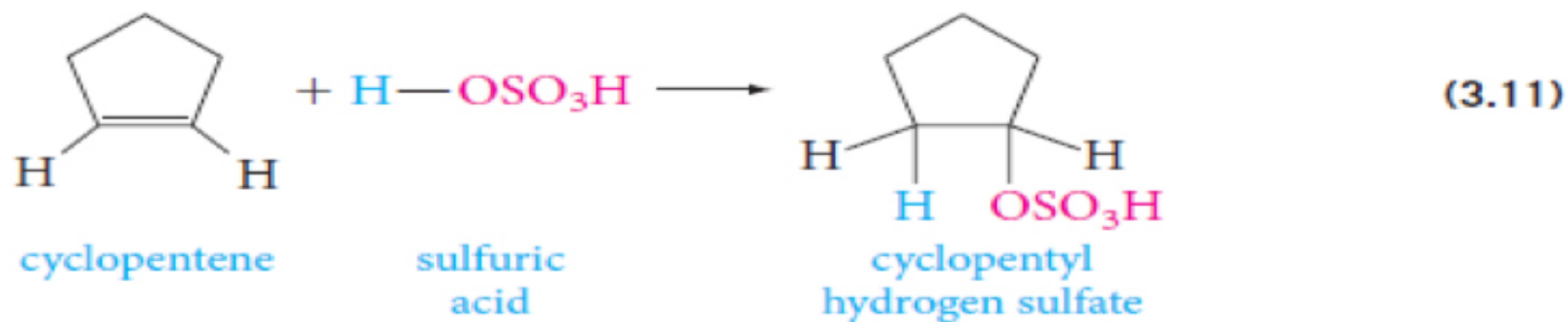
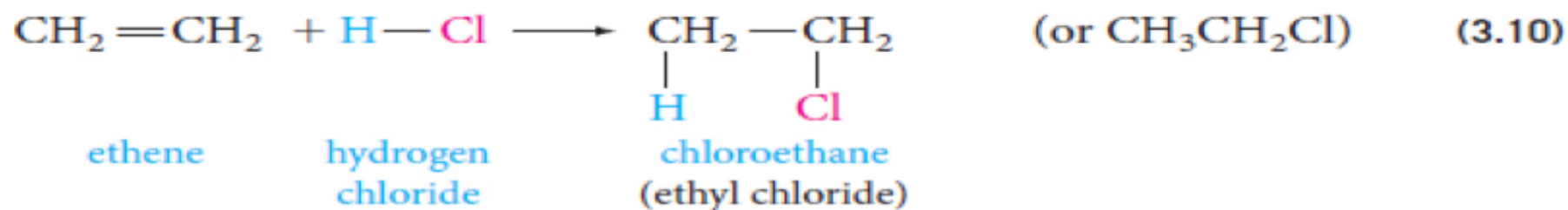
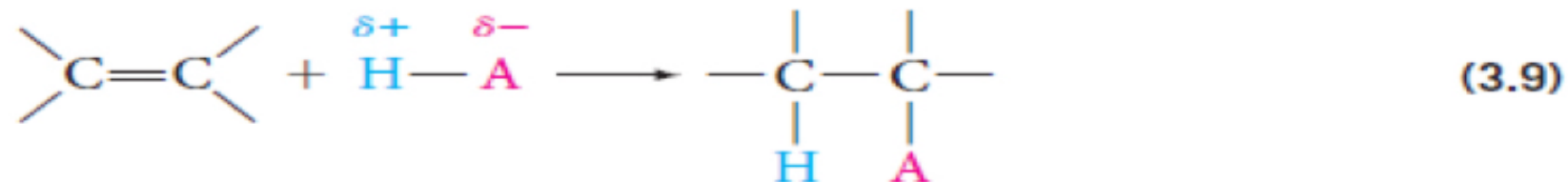
The second step is the attack of the nucleophilic water molecule on the carbocation







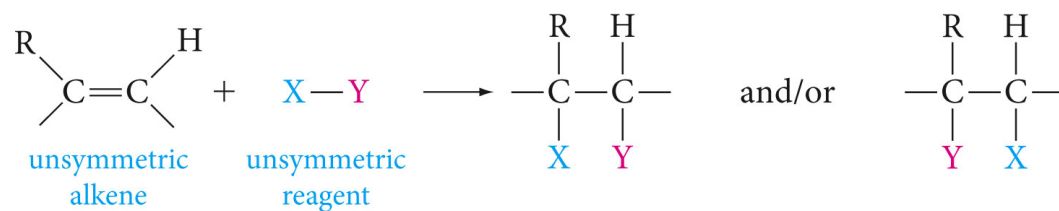
### 3.7.c Addition of Acids



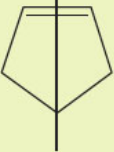
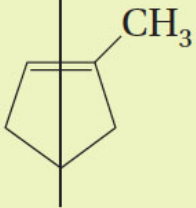
# Symmetry and Addition Reactions

The halogenation of ethene is a very symmetry reaction as both the reagent (Br<sub>2</sub>) and the substrate (ethene) are symmetric. In this situation there can only be a single product. What about asymmetric reactions? Two products are possible now, which *regioisomer* will form?

Table 3.2 — Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions		
	Symmetric	Unsymmetric
Reagents	$\begin{array}{c} \text{Br} - \text{Br} \\   \quad   \\ \text{Cl} - \text{Cl} \\   \quad   \\ \text{H} - \text{H} \end{array}$	$\begin{array}{c} \text{H} - \text{Br} \\   \quad   \\ \text{H} - \text{OH} \\   \quad   \\ \text{H} - \text{OSO}_3\text{H} \end{array}$
Alkenes	$\begin{array}{c} \text{CH}_2 = \text{CH}_2 \\   \\ \text{Cyclopentane} \end{array}$	$\begin{array}{c} \text{CH}_3\text{CH} = \text{CH}_2 \\   \\ \text{Cyclopentane with } \text{CH}_3 \end{array}$
	mirror plane	not a mirror plane



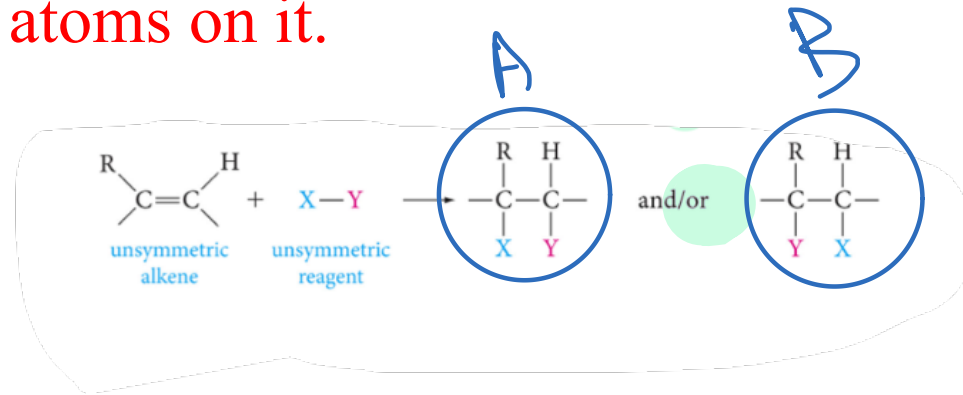
**Table 3.2** ▀ Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

	Symmetric	Unsymmetric
Reagents	$\begin{array}{c} \text{Br} - \text{Br} \\   \\ \text{Cl} - \text{Cl} \\   \\ \text{H} - \text{H} \end{array}$	$\begin{array}{c} \text{H} - \text{Br} \\   \\ \text{H} - \text{OH} \\   \\ \text{H} - \text{OSO}_3\text{H} \end{array}$
Alkenes	$\text{CH}_2 = \text{CH}_2$ 	$\text{CH}_3\text{CH} = \text{CH}_2$ 
	mirror plane	not a mirror plane

# Markovnikov's Rule

\* نصف H ذی خرد  
الکربون المرتبط بتعدد  
اکثر من الهيدروجين.

Fortunately there is a simple rule of thumb to predict which product will form: Markovnikov's rule, which states that when **an unsymmetrical reagent adds to a double bond the electrophilic part of the reagent adds to the carbon with the most hydrogen atoms on it.**

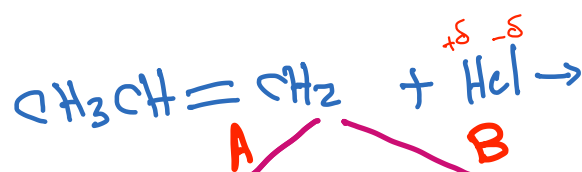
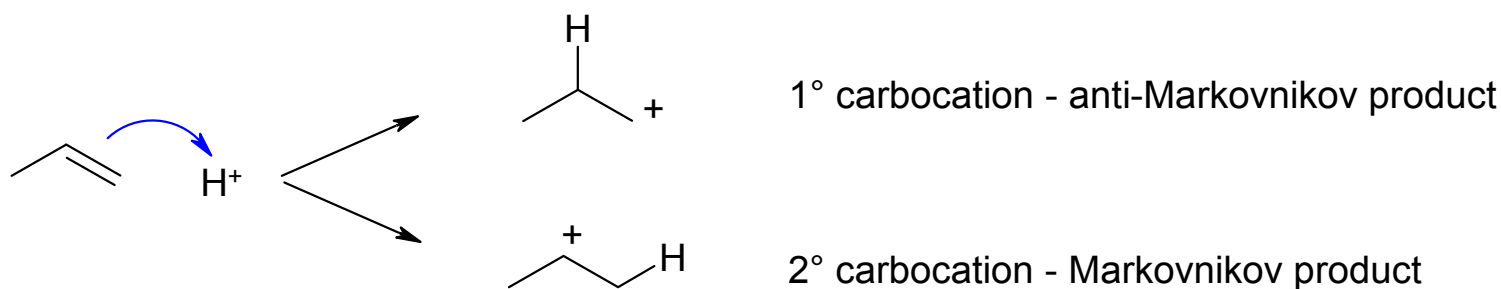


\* لتحديد أي المركبين  
سنتبع نتيج قاعدة  
Markovnikov



# Markovnikov's Rule (cont'd)

Why? This mode of addition will always produce the most stable carbocation intermediate, i.e. consider the addition of H<sup>+</sup> to propene...

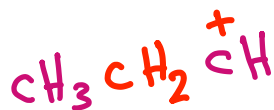


أول خطوة

الخطوة الثانية

منحقة على جميع الحالات  
 $\text{Cl}^-$

في حال تفاعل الألكترونات مع ذرة الكربون الأولى.



1°

less stable



2°

Carbocation more stable

\* المركب الناتج فعلاً هو  
 $\text{CH}_3\text{C}^+\text{HCH}_3$  (A)

# Hydrohalogenation

سرعة تفاعل الألكين مع الهالوجين تعتمد على قوة الرابطة.  
بعضها يكون تفاعل الألكين مع HI الأسرع.  
متفاعل مع HF الأبطأ.

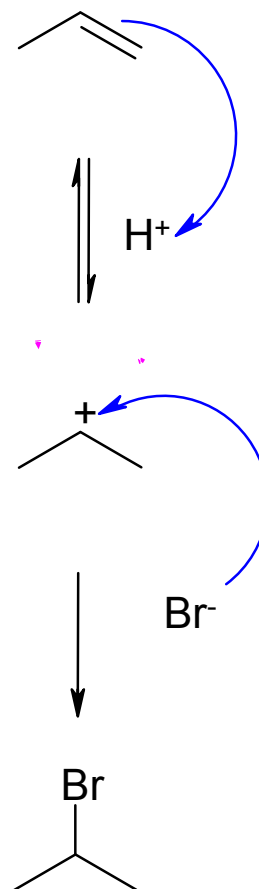
- Addition of HX across a double bond to produce a Markovnikov halide alkane
- Reactivity:  $HI > HBr > HCl > HF$  (parallels acidity)
- HBr needs to be used in the dark and under an inert atmosphere to prevent a free radical addition process that produces the anti-Markovnikov product.
- Note: this same mechanism applies to other acids such as  $H_2SO_4$

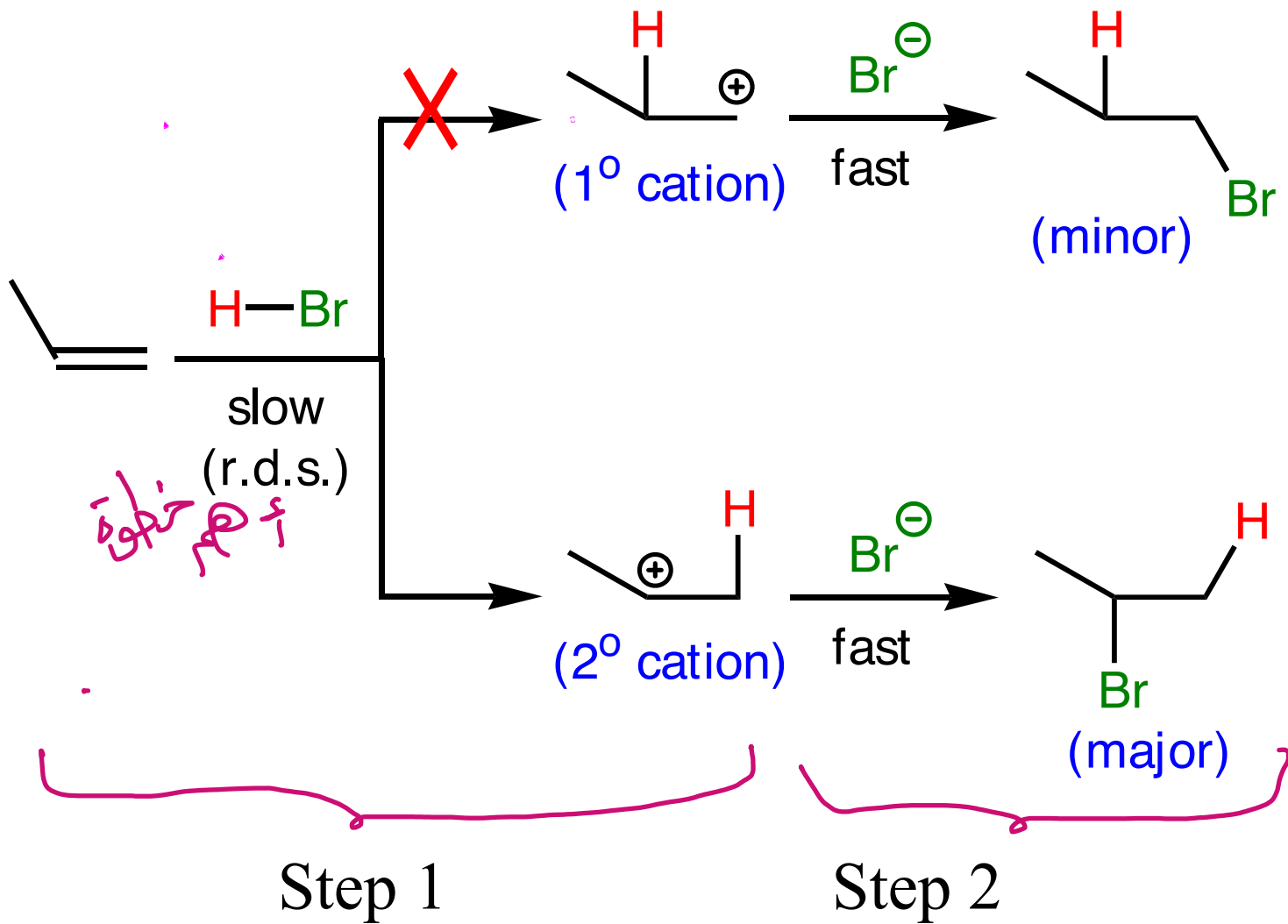
# Hydrohalogenation (cont'd)

تذكر نوع الإضافة والكسور فيلص

First step in the Markovnikov addition of the electrophilic acidic proton to produce the most stable carbocation intermediate.

The second step is the nucleophilic attack of the halide anion on the carbocation intermediate generating the alkyl halide product.





# Hydroboration/Oxidation

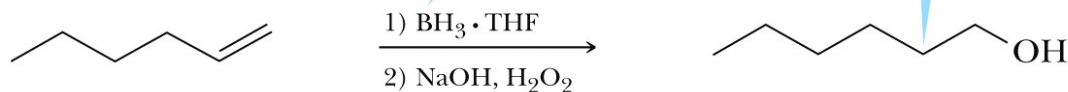
boron

NaOH / H<sub>2</sub>O<sub>2</sub>

- Final product is an anti-Markovnikov alcohol
- Two step reaction, BH<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>/NaOH

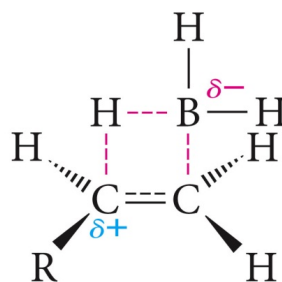
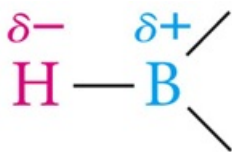
the net result of hydroboration-oxidation is the addition of H and OH across the C—C double bond

contrary to Markovnikov's rule, the hydrogen has added to the former double-bond carbon with the fewer hydrogens

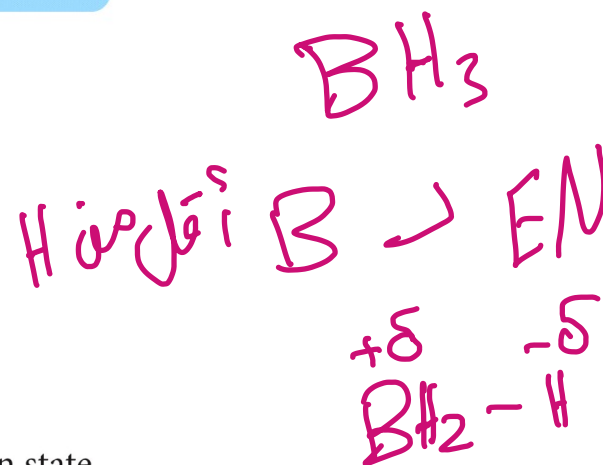


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- Electrophile is the B atom (H is more EN than B!)
- Concerted addition reaction



transition state for hydroboration



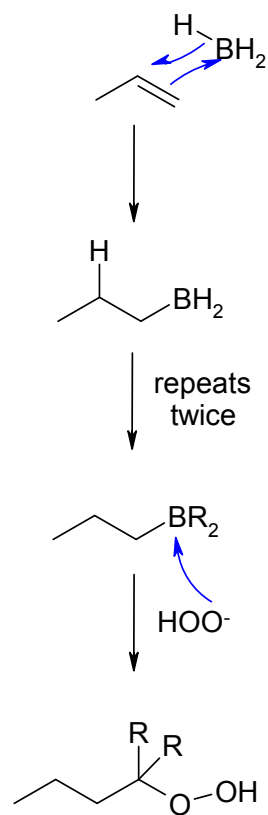
IF we want Markovnikov alcohol we use H<sub>2</sub>O / H<sup>+</sup>  
IF we want Anti-Markovnikov alcohol we use BH<sub>3</sub> + NaOH / H<sub>2</sub>O<sub>2</sub>



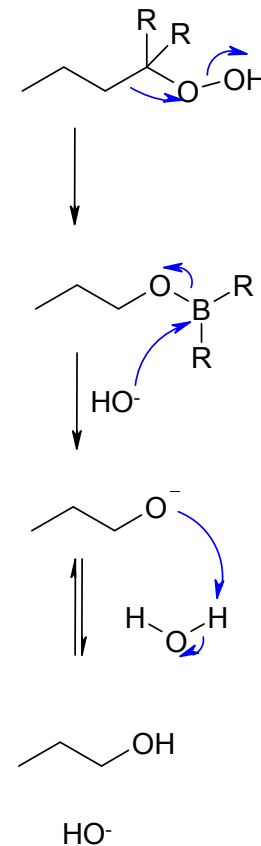
boron

# Hydroboration (cont'd)

Step 1: alkene  $\pi$  electron acts as nucleophile and add to the electrophilic B, at the same time the H is transferred to the C atom.



Step 2: step 1 repeats twice more



Step 3: peroxide ion acts

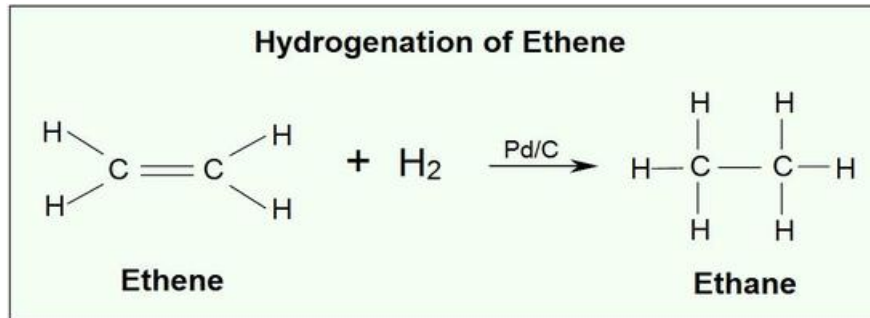
التفاعل ليس  
غير مطلوب

# تفاعل الهدرجة

## Hydrogenation

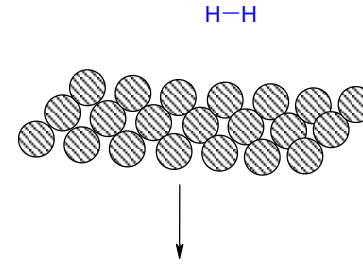
- Addition of H<sub>2</sub> across the double bond to produce an alkane
- Requires a metal catalyst, Pt, Pd, Ni or Rh
- “syn” addition, both atoms add to the same side of the double bond.

إضافة بنفس الاتجاه  
عكس  
Br<sub>2</sub>  
Anti addition

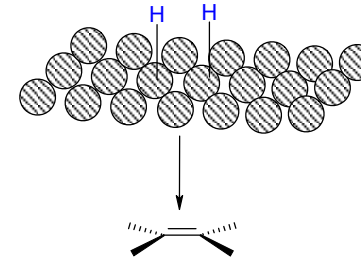


# Hydrogenation

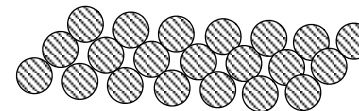
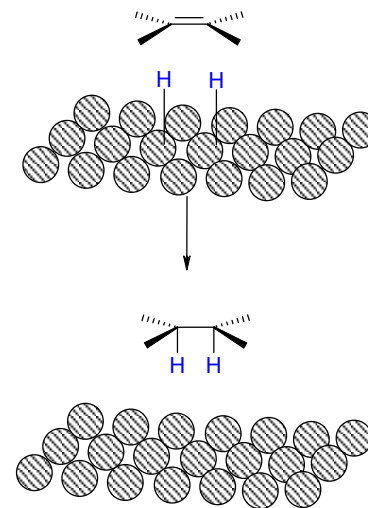
Step 1: hydrogen adsorbs onto the face of the metal



Step 2: alkene approaches H atoms

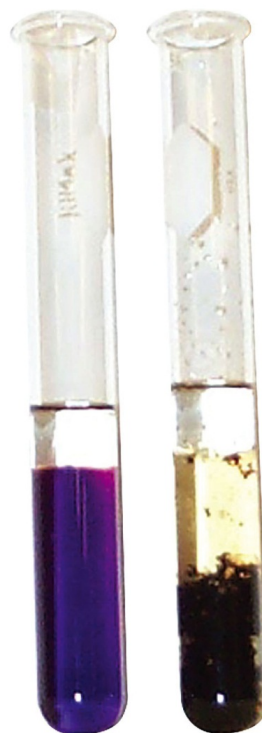


Step 3: H atoms add to the two C atoms producing an alkane



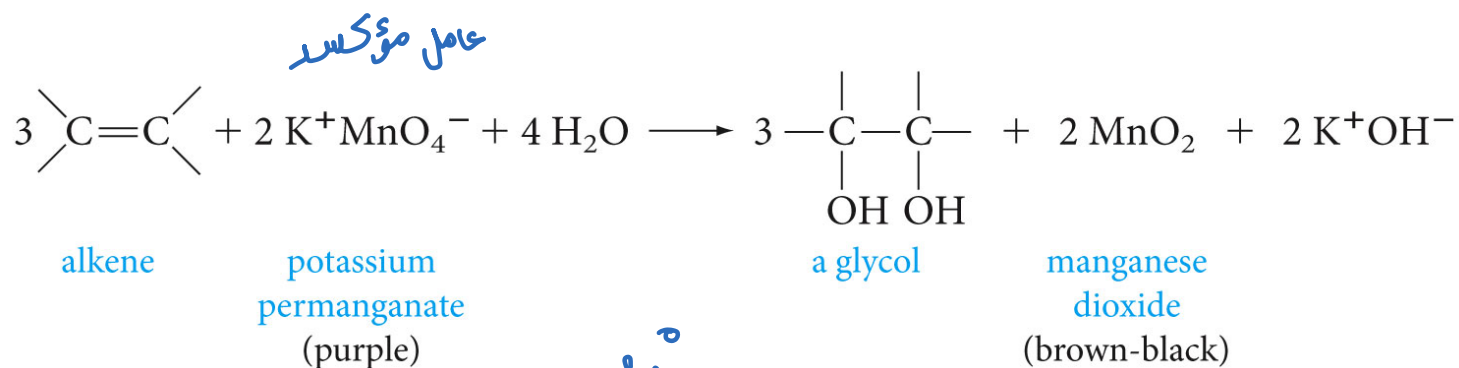
# Oxidation: Permanganate

- Used as a chemical test
- Product is a glycol (1,2-diol) and manganese oxide
- Color change from purple to brown-black  $\text{MnO}_2$  solid
- $\text{OsO}_4$  also used to make 1,2-diols



# Oxidation: Permanganate (cont'd)

- Complex reaction mechanism
- Reactive via a five membered cyclic ester intermediate.
- Both O atoms are transferred from the permanganate ion.



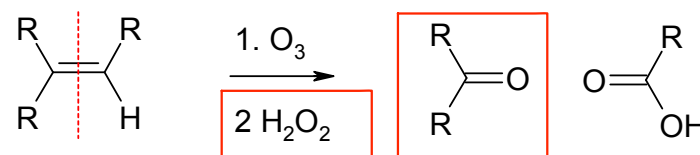
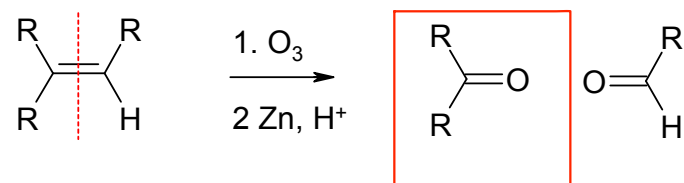
Alkene  
 يعني ان العادة  
 KMnO<sub>4</sub>  
 chemical test

إذا احتزل  
 يعني اعتباره

# Oxidation: Ozonolysis

تحليل  
لتتبع تفاعل تأكسد

- Cleaves the double bonds in half generating two carbonyl groups
- In Zn/H<sup>+</sup> get aldehydes or ketones (reductive products)
- In H<sub>2</sub>O<sub>2</sub> ketones or carboxylic acids (oxidative products)
- Was primarily used for



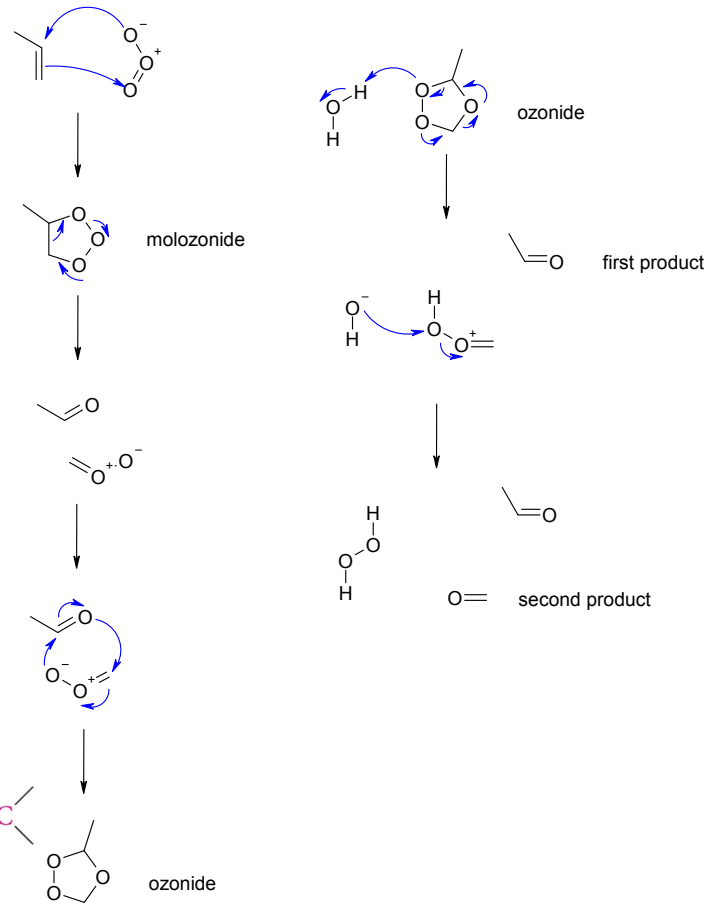
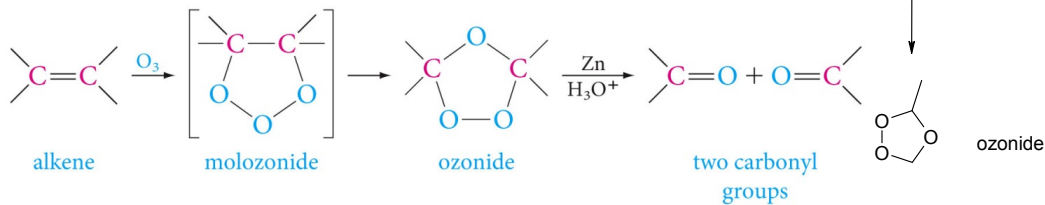
حامل هوكسيد

النتون بيقى كيون  
في الحالين

H<sub>2</sub>O<sub>2</sub> توكسد  
الالهيدروكسي  
Carboxylic acid

# Oxidation: Ozonolysis (cont'd)

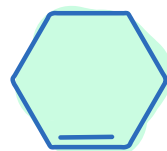
Step 1: p electrons act as nucleophile attacking the ozone at the electrophilic terminal O atom. A second C-O bond is formed by a nucleophilic attack of the other terminal O



تفاعل التفاعل  
غير مطلوبة  
فقط افهم الآلية  
واحفظ نتائجها.

# Cycloadditions: the Diels-Alder Reaction

There is an additional type of reaction for conjugated alkenes, a cycloaddition. This is a very important reaction as it is an easy way to generate cycloalkenes in very high yields. The reaction involves a conjugated diene and an alkene or alkyne. There is a rearrangement of the p electrons that will produce two new  $\sigma$  bonds forming the ring.





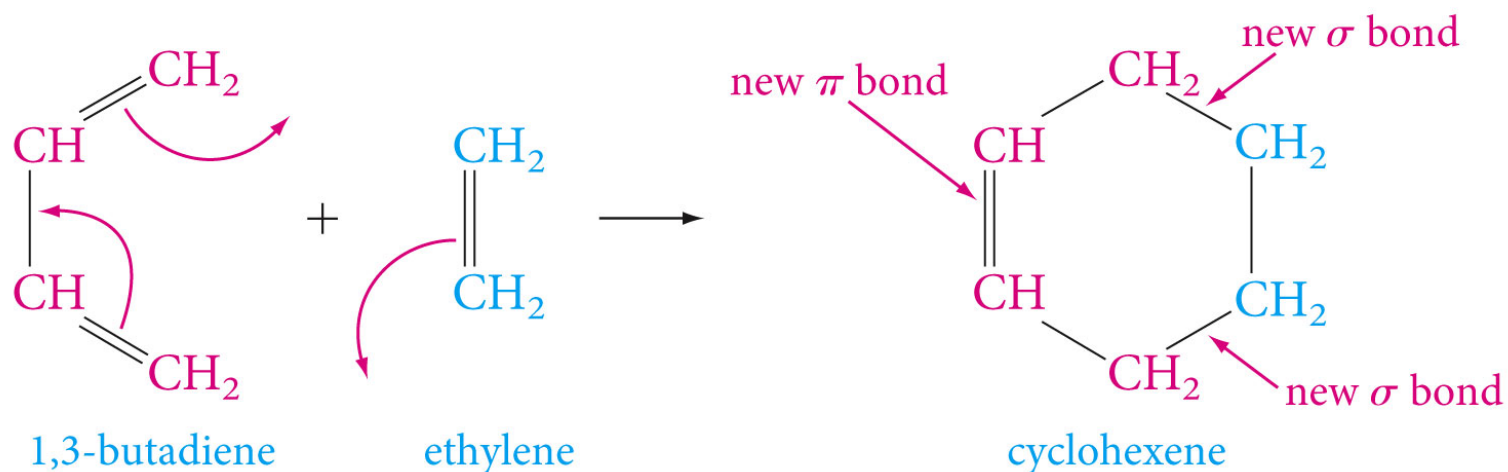
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Reaction between  
Diene and Dienophile

Diene: 1,3-butadiene

Dienophile: ethene

Product: cyclohexene

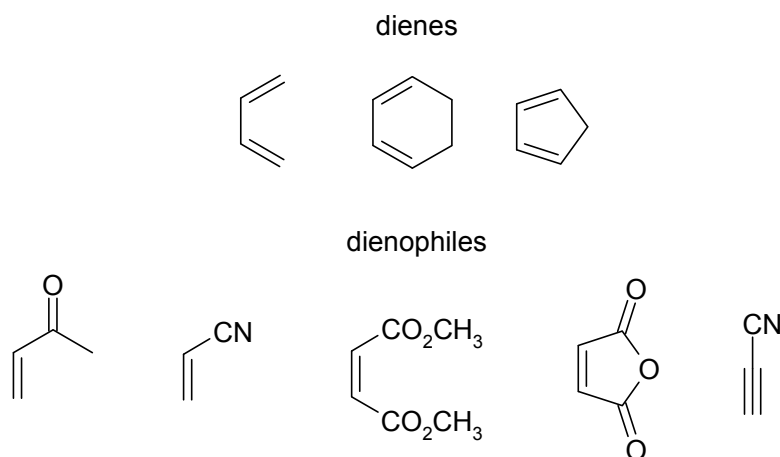


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The reaction proceeds best when an electron withdrawing group is attached to the dienophile.

Electron withdrawing groups are groups of atoms that will withdraw electron density of the dienophile  $\pi$  bond which makes it a better electrophile. Common electron withdrawing groups include: carbonyl ( $-\text{C}(=\text{O})\text{R}$ ), cyano ( $-\text{C}\equiv\text{N}$ ) and esters ( $-\text{CO}_2\text{R}$ ).



Dienophile \* ار  
بجبوا يكون عليهم مجموعان  
لأنها بتسحب الالكترونات  
ما يزيد من سرعة التفاعل.

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The stereochemistry of the reactants is preserved in the product, i.e. a cis-dienophile give cis substituents in the product, a trans-dienophile give trans substituents in the product, i.e.

