



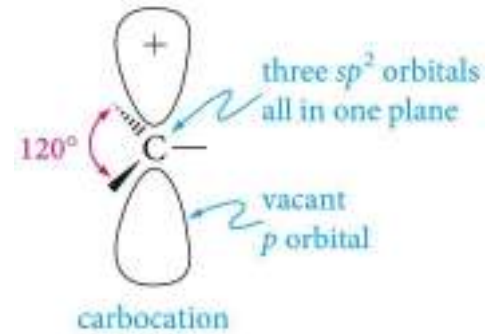
Organic chemistry

Lec: 8

Done by: Dema Alhussine

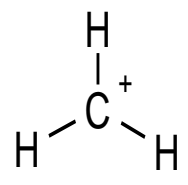
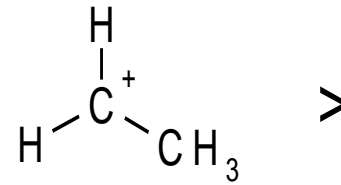
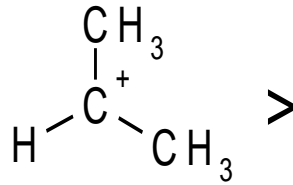
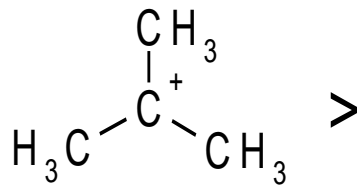
Carbocations

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.



R group ما كان حوالين الكربون R stability أكثر group يعني tertiary carbocations secondary أكثر استقرار مقارنة ب carbocations

The most stable



3°
وإذا كان مثل
الثالثية R

tertiary carbocations

2°
Two R group
يعني اثنين
secondary carbocations

1°
One R group
ما بهمني إذا كانت ميثيل أو إيثيل... (يعني مش مهم نوعها المهم إنها من ضمن R group)
(primary carbocation)

مethyl
حالة رتبة
مethyl

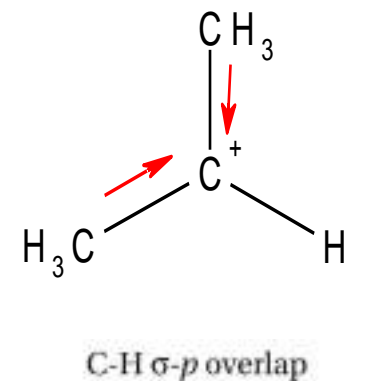
primary و methyl ال stability ال carbocations قليلة فصعب يتكونوا الا في حالات حنحكي عنها

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

Carbocations (cont'd)

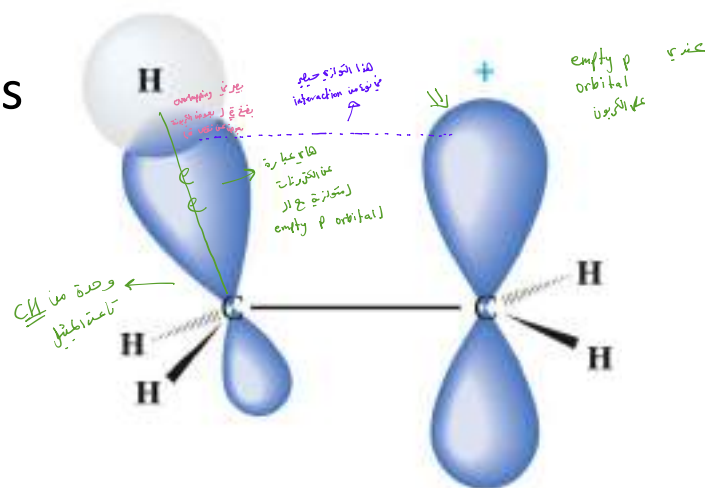
The order of carbocation stability arise from three sources.

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



مختبر الجزيئات
أفضل من المبرورين
في مواد الكيمياء
الكيمياء
Tertiary carbocation
أفضل استقرار من غيرها
(Inductive electron donation)

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^+ .

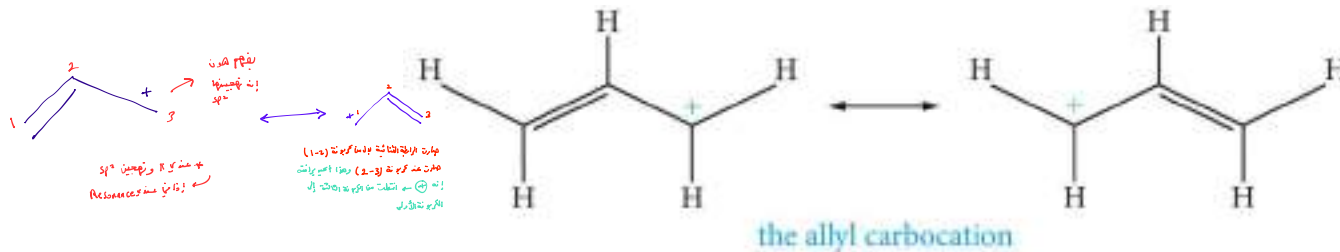


مethyl
H-C-H
overlapping
التركيبات الثلاثة
مفيدة في فهم
energy & stability

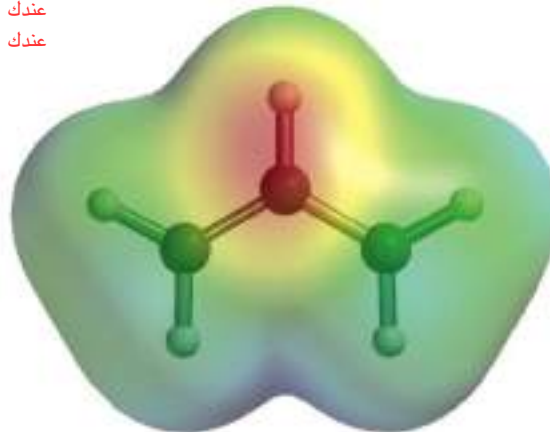
empty p orbital
على الكربون

Carbocations (cont'd)

3) **Resonance**: a carbocation immediately adjacent to a π 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.

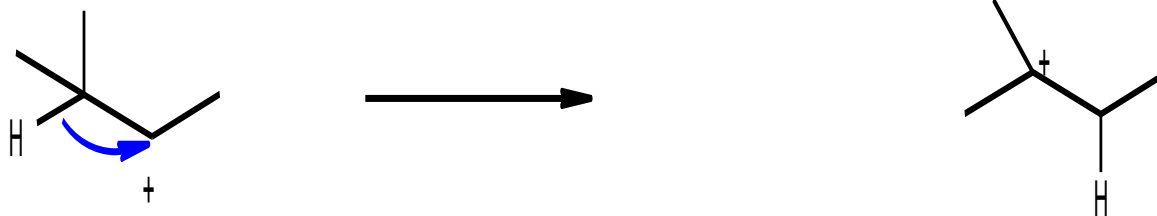


خدها قاعدة: وين ما في
 عندك resonance في
 عندك stabilizaton



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⁺ to produce a more stable carbocation, i.e.

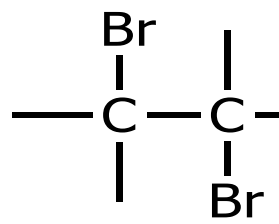
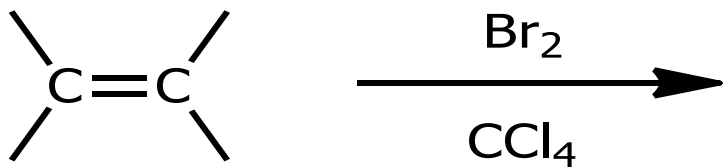


This is also possible for methyl groups. These shifts are common when a tertiary, allylic or benzylic carbocation is produced.

3.7.a Addition of Halogens

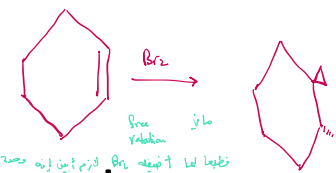
Non Polar Solvents ← مني ← Polarization
 Non Polar ← مني ← Polarization

- Addition of Cl_2 or Br_2 across the double bond to product 1,2-dihalide alkane.



(vicinal dibromide)

- 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



يمكن الموضوع يفرق معاي إذا حكيت عن cyclohexene

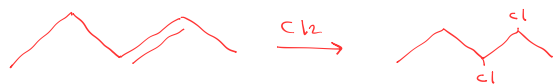
في حالة haloalkane ١،٢ - dibromo ما بتفرق لو كتبتهم هيك أو اذا حطيت ال Br في نفس الاتجاه لانه عندي free rotation مثل ما تعلمنا سابقا لكن هوه عم يحكيلنا إنه عملية إضافة ال Br2 يكونوا عكس بعض (antiaddition)

الفكرة إنه ال Br بتسببوا anti يعني عكس بعض



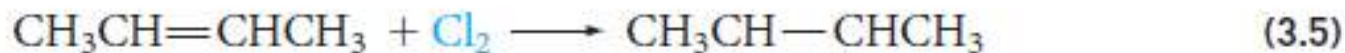
الخطوة تكونها Carbocations





در صورت $C=C$ ≤ 4
 ذرات از X_2

Alkenes readily add chlorine or bromine.



2-butene
 bp 1-4°C

2,3-dichlorobutane
 bp 117-119°C



1,4-pentadiene
 bp 26.0°C

1,2,4,5-tetrabromopentane
 mp 85-86°C

از آنجا که anti است
 از آنجا که anti است
 خرد عملی و لو عملیها زیر همند
 برضه عادی

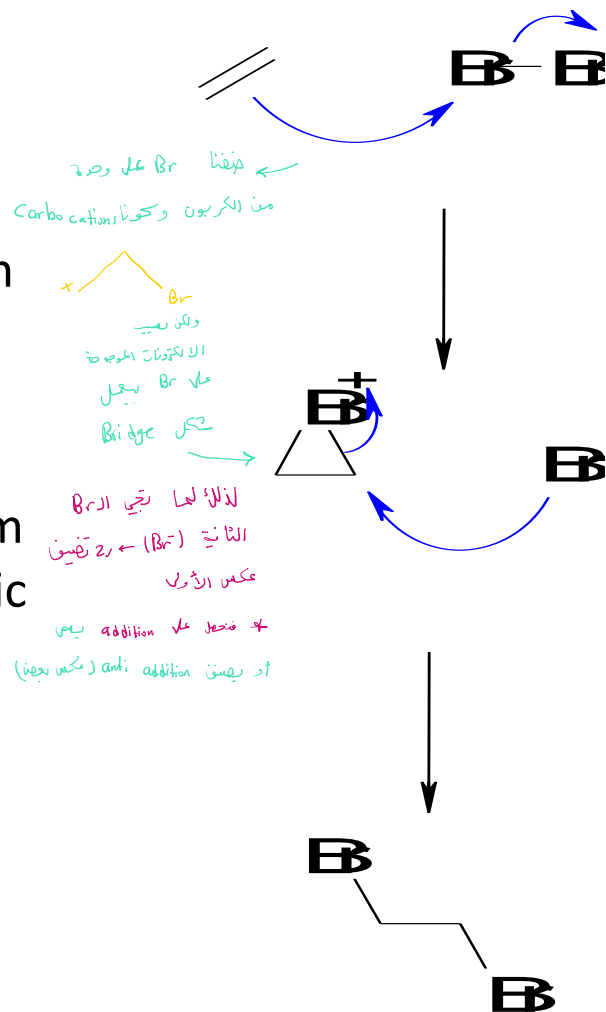
PROBLEM 3.8 Write an equation for the reaction of bromine at room temperature with a. propene b. 4-methylcyclohexene

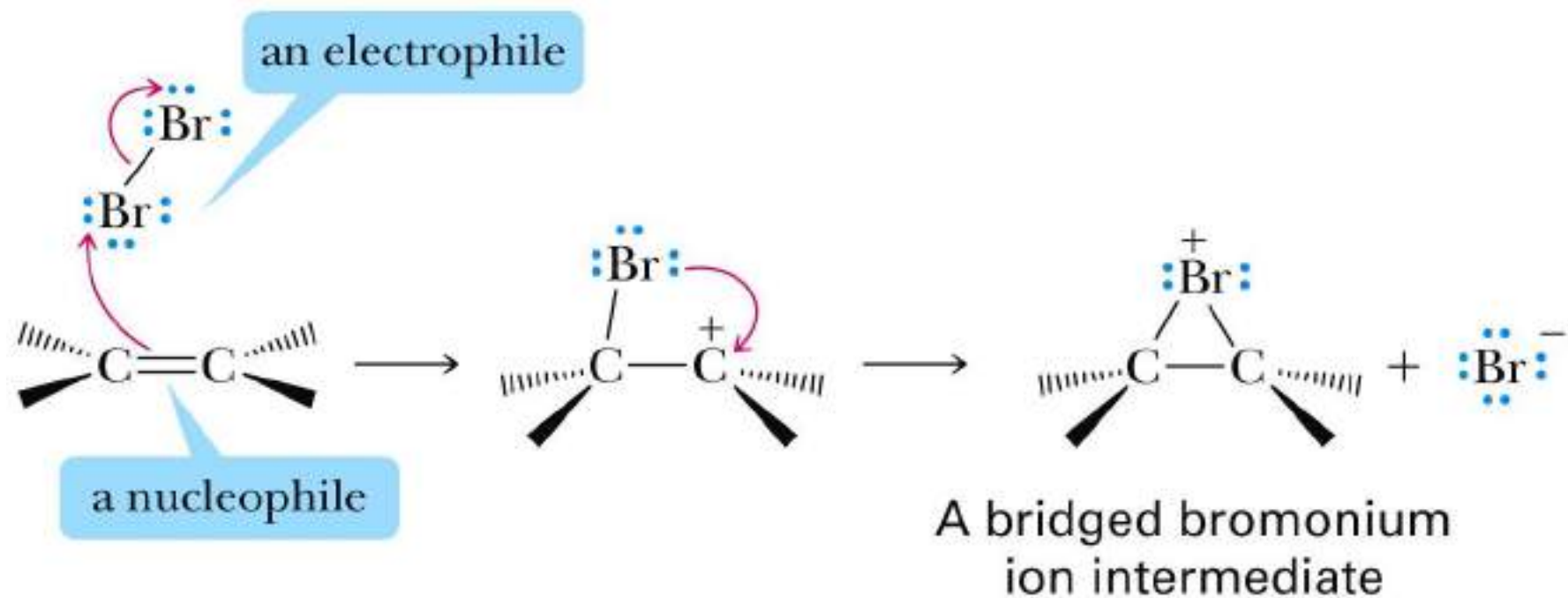
Halogenation (cont'd)

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

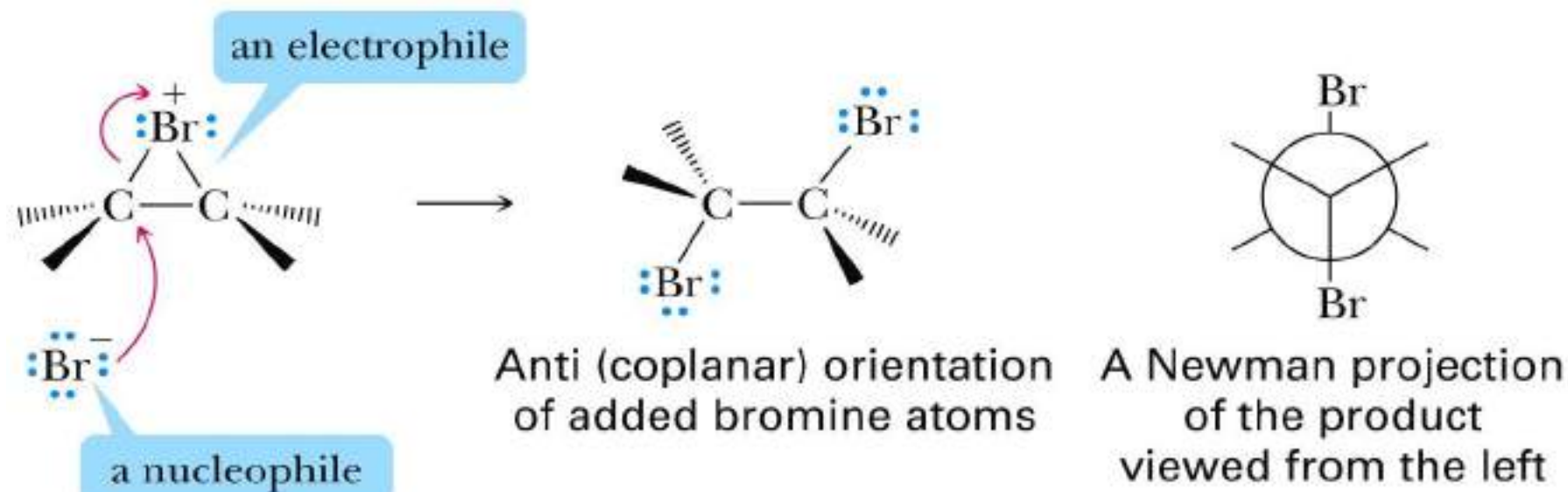
In the second step the nucleophilic bromide ion attacks the side of the bromonium ion away from the bromine atom opening the highly strain cyclic structure and producing the 1,2 dibromo hydrocarbon.

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





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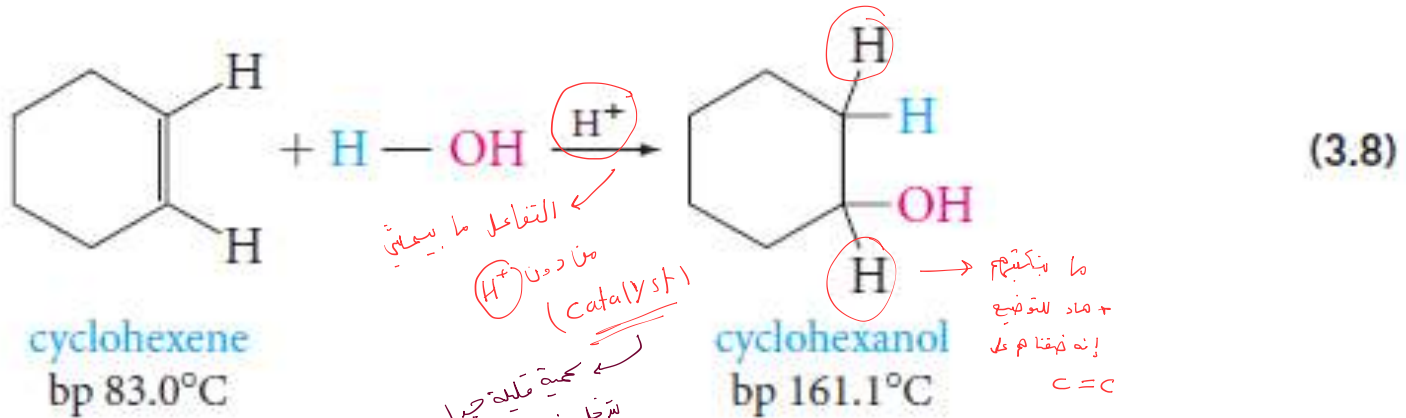
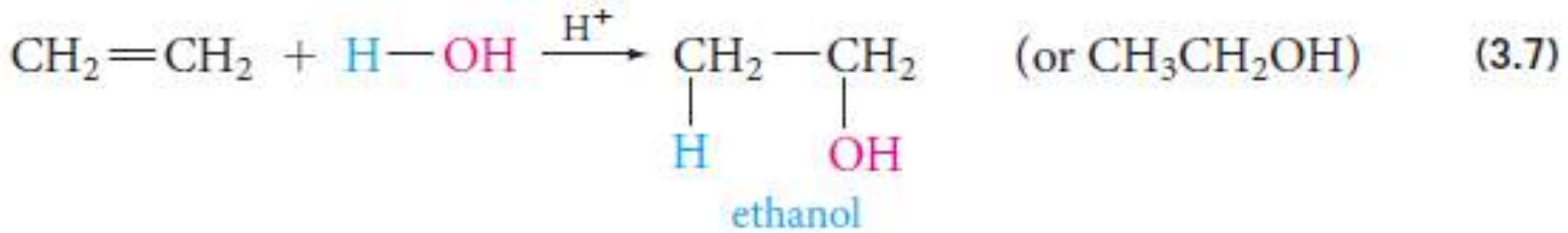


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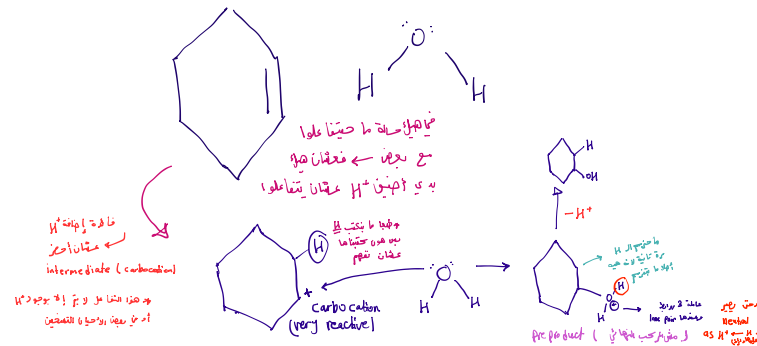
3.7.b Addition of Water (Hydration)

العائنة الناتجة هي الكحول

(بعضها H₂)

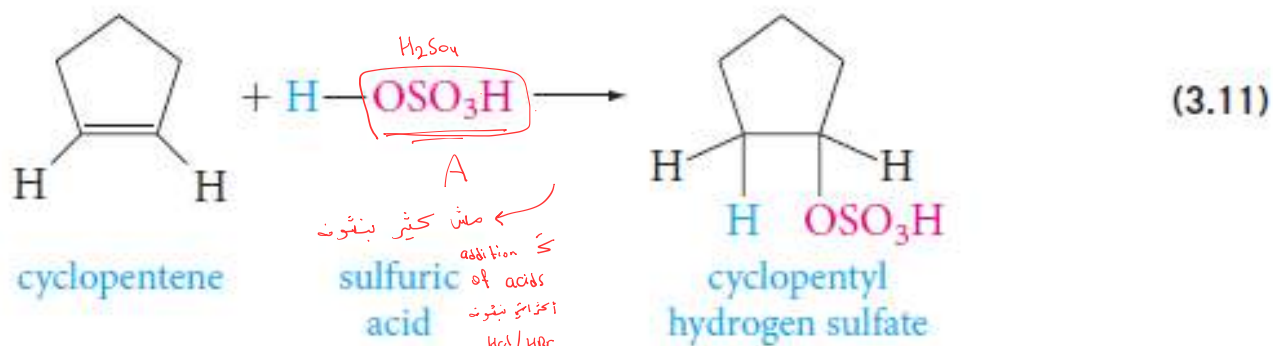
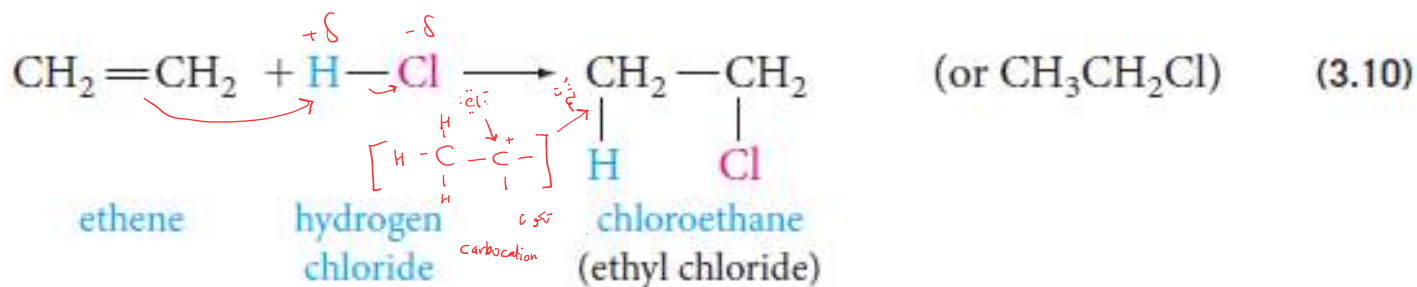
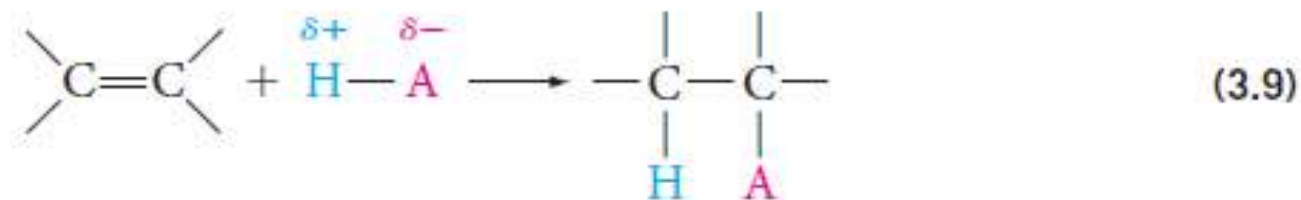


Weak acid
ما بعضه H⁺ بغيره



3.7.c Addition of Acids

HA
ex: HCl



Symmetry and Addition Reactions

The halogenation of ethene is a very symmetry reaction as both the reagent (Br_2) 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	$\begin{array}{c} \text{Br} - \text{Br} \\ \\ \text{Cl} - \text{Cl} \\ \\ \text{H} - \text{H} \end{array}$	$\begin{array}{c} \text{H} - \text{Br} \\ \\ \text{H} - \text{OH} \\ \\ \text{H} - \text{OSO}_3\text{H} \end{array}$
Alkenes	$\begin{array}{c} \text{CH}_2 = \text{CH}_2 \\ \\ \text{Cyclopentene} \end{array}$	$\begin{array}{c} \text{CH}_3\text{CH} = \text{CH}_2 \\ \\ \text{1-Methylcyclopentene} \end{array}$
	mirror plane	not a mirror plane

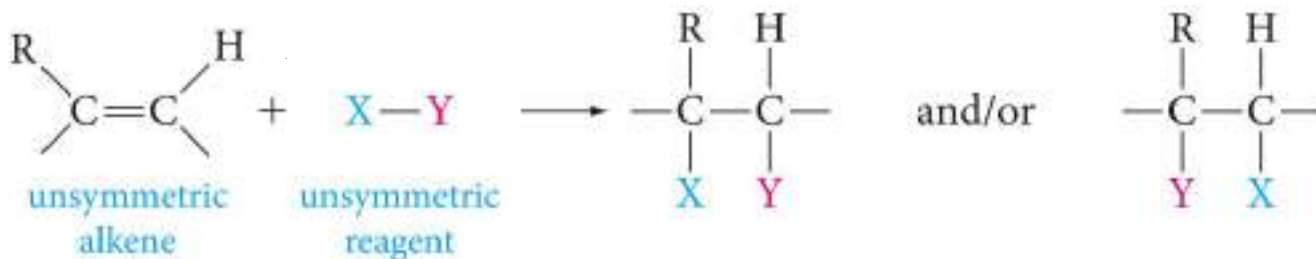
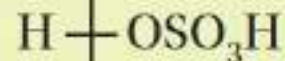
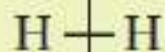
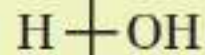
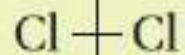


Table 3.2 ▀ **Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions**

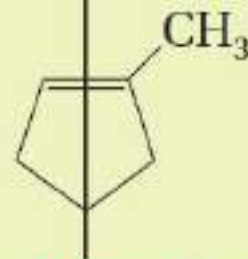
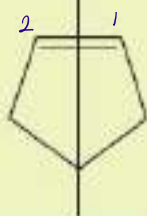
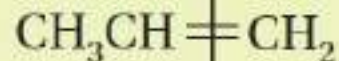
Symmetric

Unsymmetric

Reagents



Alkenes



mirror plane

not a mirror plane

هون ما صيفوق
رينا تظلم

ex 6

Br₁, Br₂
① ②

Br₁ → C₁

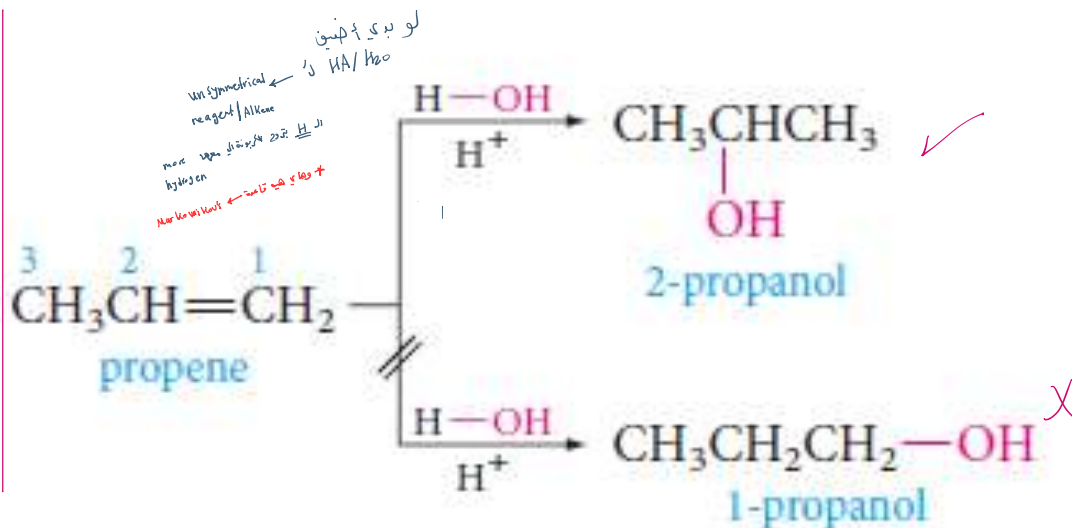
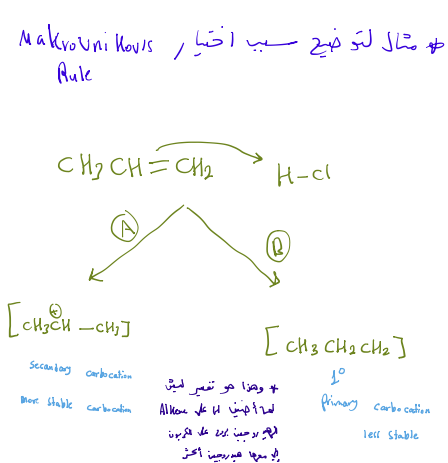
Br₂ → C₂

نفس الازمة ماخترنا

نه symmetric

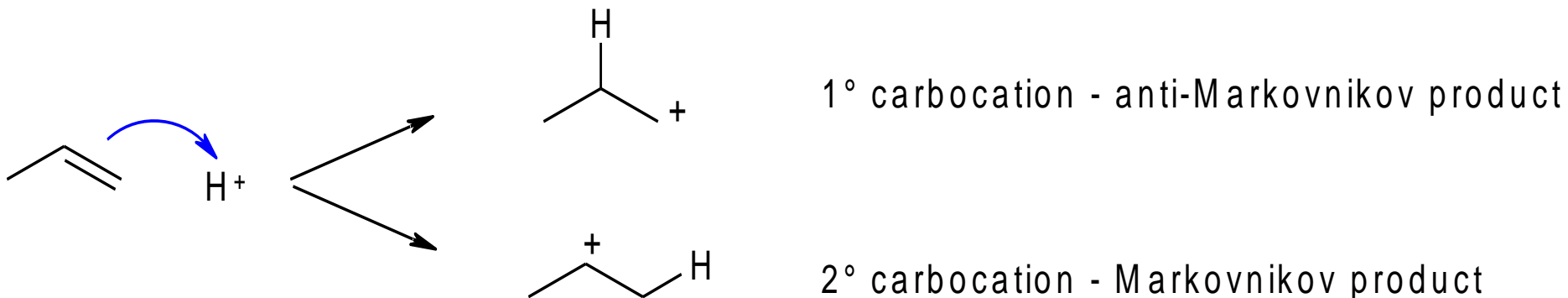
Markovnikov's Rule

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.**



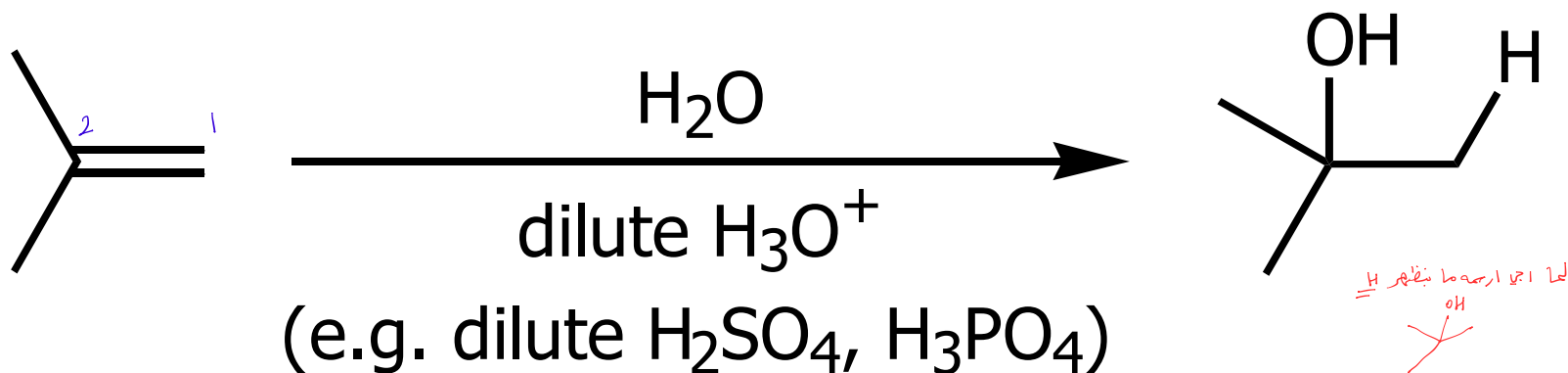
Markovnikov's Rule (cont'd)

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



Hydration

- Addition of water across the double bond
- Product is an alcohol
- Requires an acid as a catalyst as water is not acidic enough to produce the electrophile



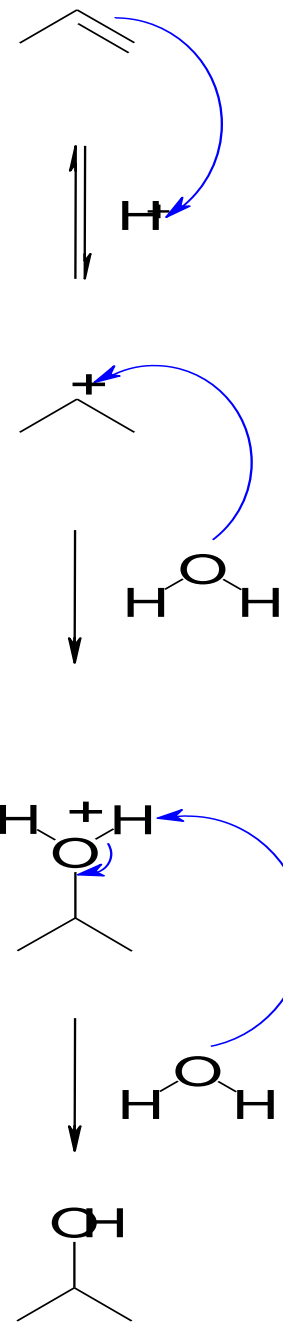
لا حاجة H^+
دكتور السب فوق

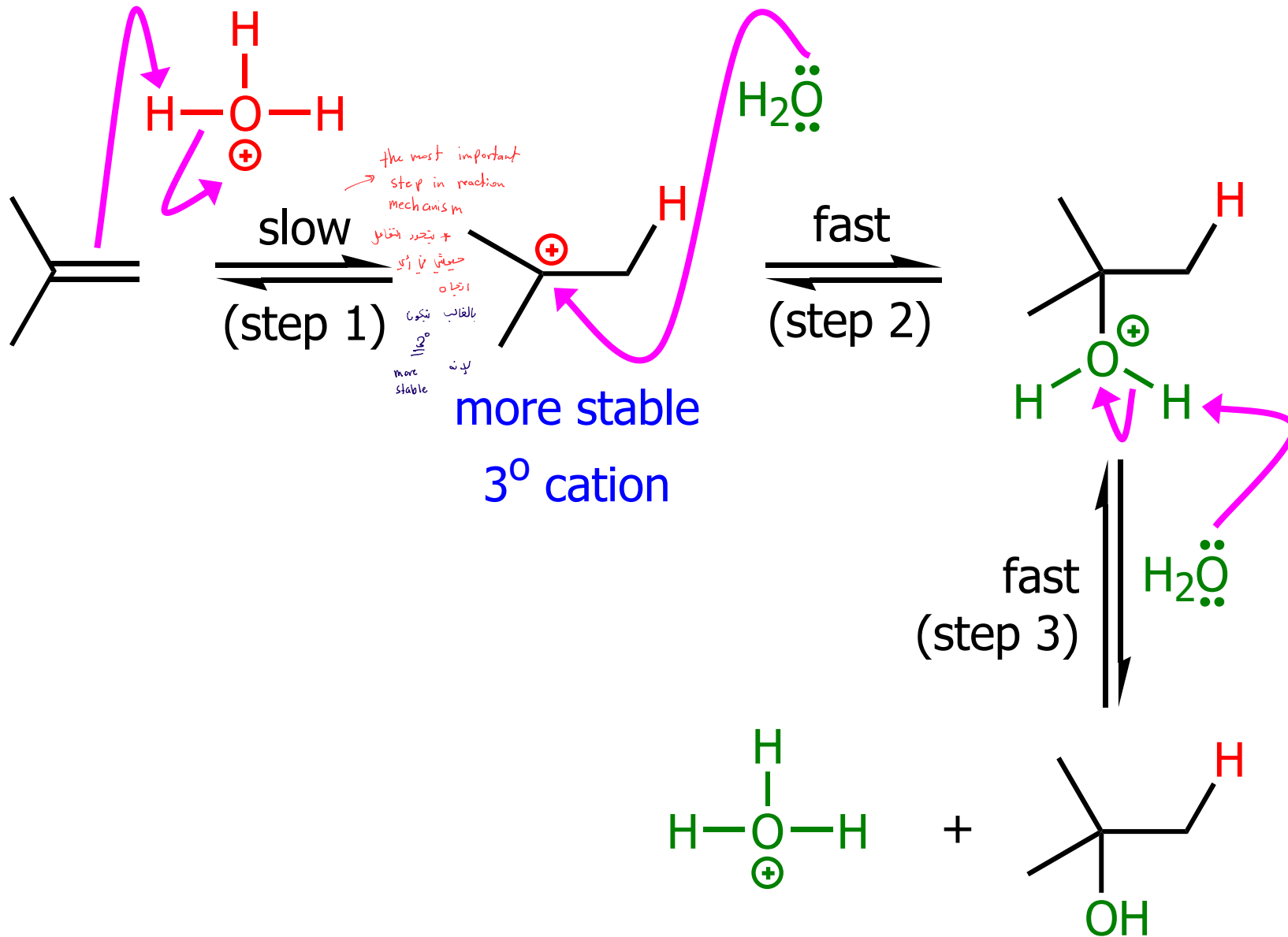
Hydration (cont'd)

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

Finally an acid/base reaction deprotonates the alkyloxonium ion to form the alcohol.



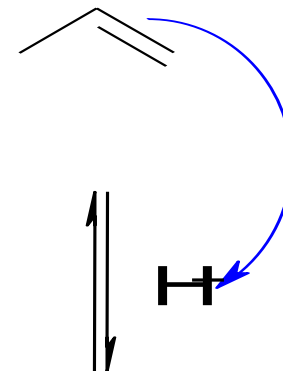


Hydrohalogenation

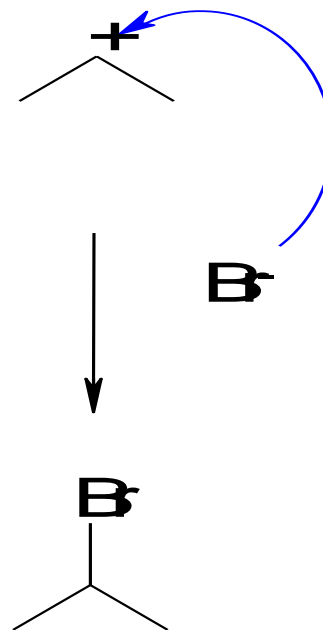
- Addition of HX across a double bond to produce a Markovnikov halide alkane
- more acidic
→ HBr > HCl
Reactivity: $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ (parallels acidity)
- HBr needs to be used in the dark and under an inert atmosphere to prevent a free radical addition process that produces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

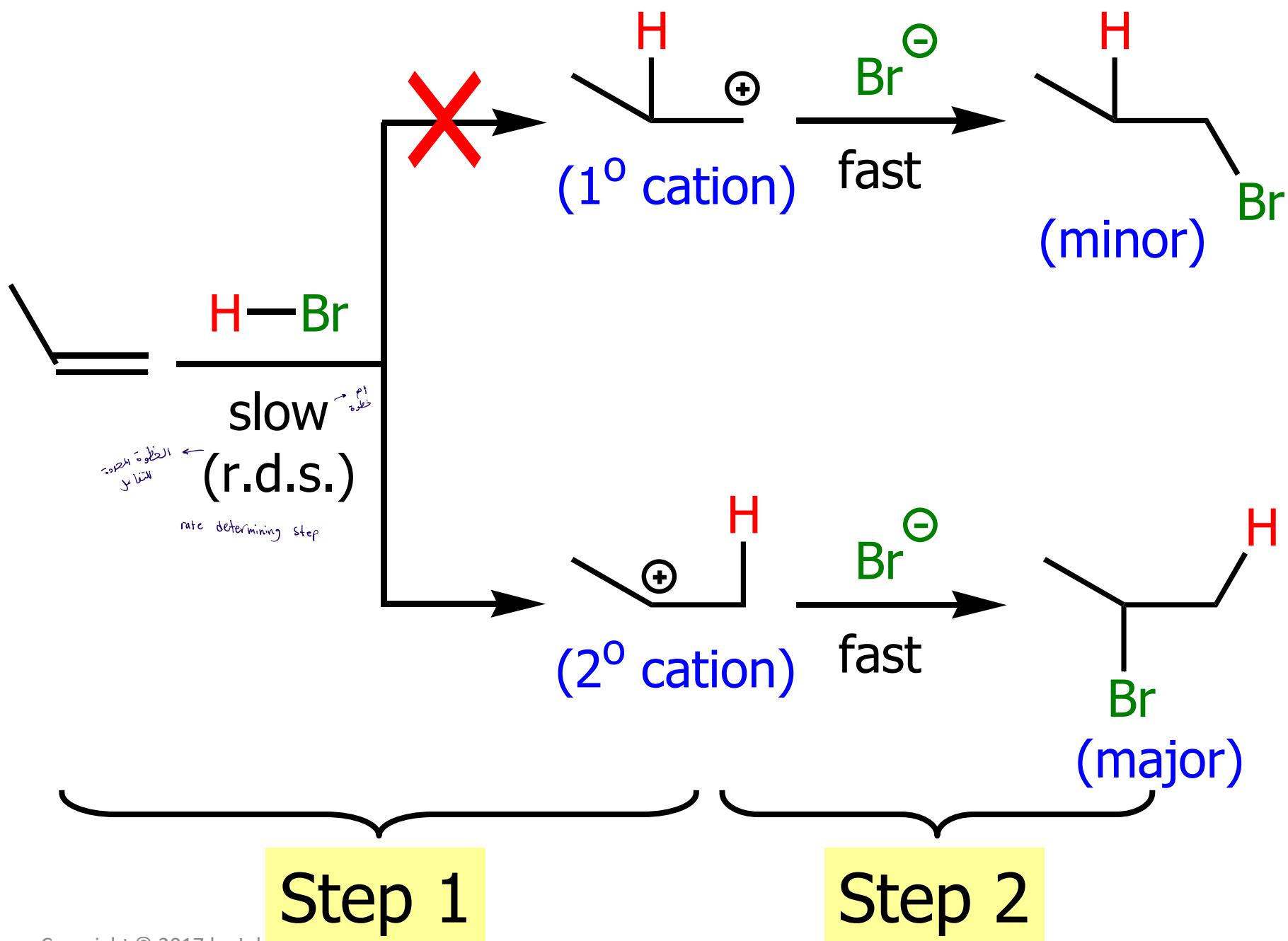
Hydrohalogenation (cont'd)

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.



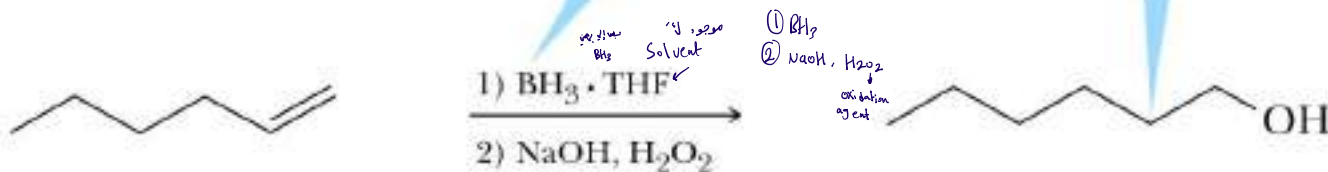


Hydroboration/Oxidation

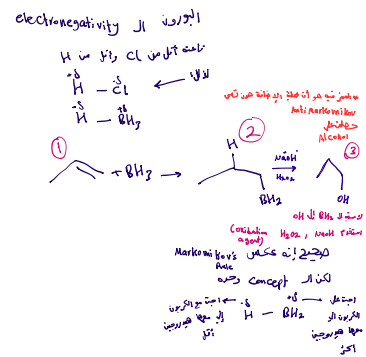
- Final product is an anti-Markovnikov alcohol
- Two step reaction, BH_3 , $H_2O_2/NaOH$

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

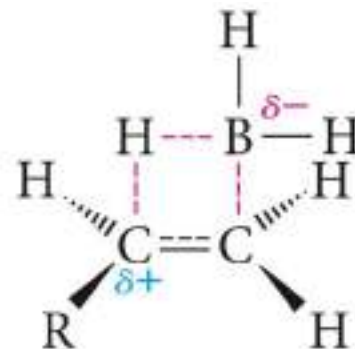
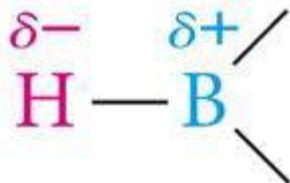
contrary to Markovnikov's rule, the hydrogen has added to the former double-bond carbon with the fewer hydrogens



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



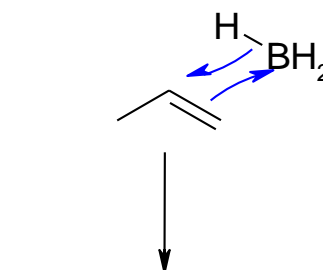
transition state for hydroboration

إذا ال alcohol بإمكانك
 تحضره سواء كانت بطريقة
 markovnikov or
 antimarkovnikov
 إذا كان مع Makrovnikov يكون H مع ايش
 (water) لا تنسوا ال H2O
 انتا هان
 انتا هان

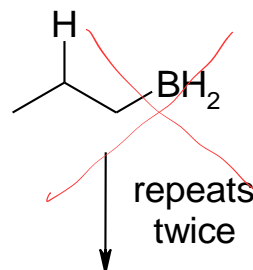
Hydroboration (cont'd)

في شوية details في ال mechanisms... ما بهمنا إنه البورون بيتفاعل أكثر من مرة

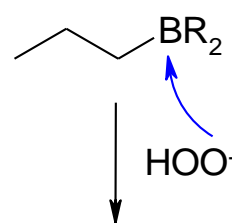
Step 1: alkene π electron acts as nucleophile and add to the electrophilic B, at the same time the H is transferred to the C atom.



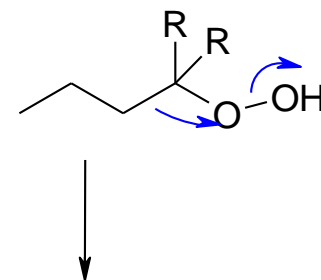
Step 2: step1 repeats twice more



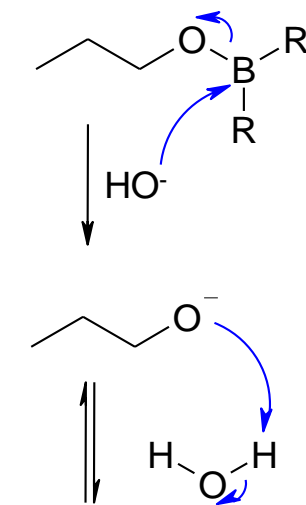
Step 3: peroxide ion acts as nucleophile with the B atom.



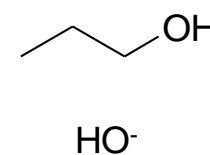
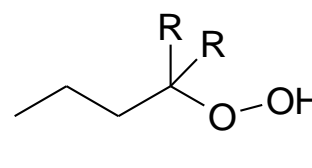
Step 4: migration of the C-B bond to form a C-O bond and displace hydroxide



Step 5: nucleophilic attack by hydroxide on B displacing it as BOH



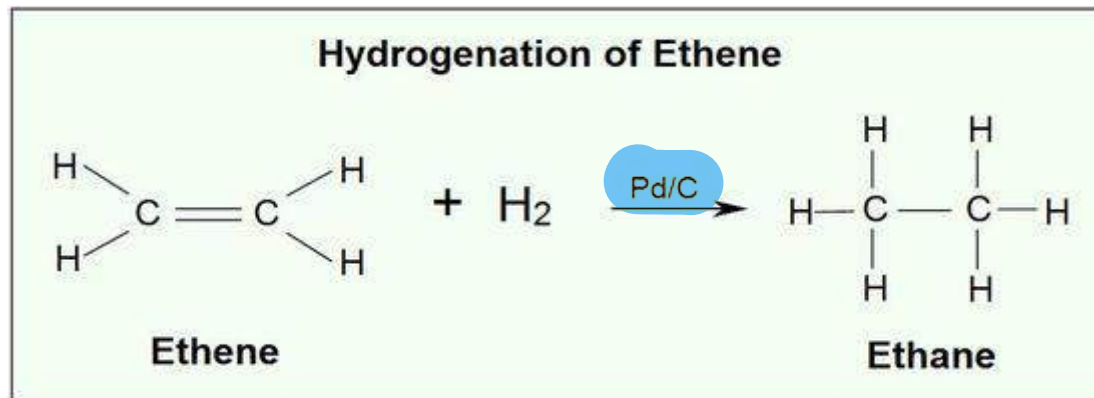
Step 6: acid/base reaction to protonate the alcohol



Hydrogenation

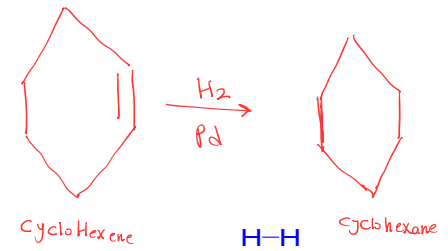
→ Alkene تحويل ال
Alkane إلى

- Addition of H_2 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.

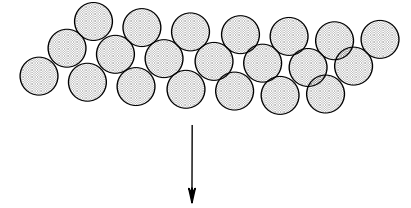


لا شك انه في ال

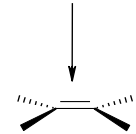
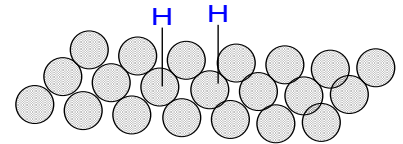
Hydrogenation



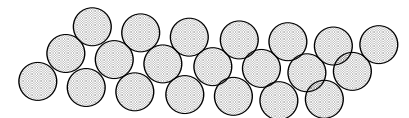
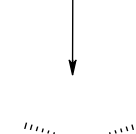
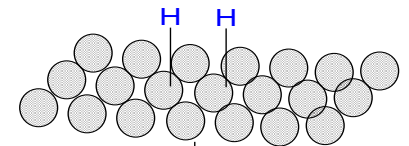
Step 1: hydrogen adsorbs onto the face of the metal



Step 2: alkene approaches H atoms



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



cyn
addition
← الهدروجين يكون في نفس الاتجاه

Oxidation: Permanganate

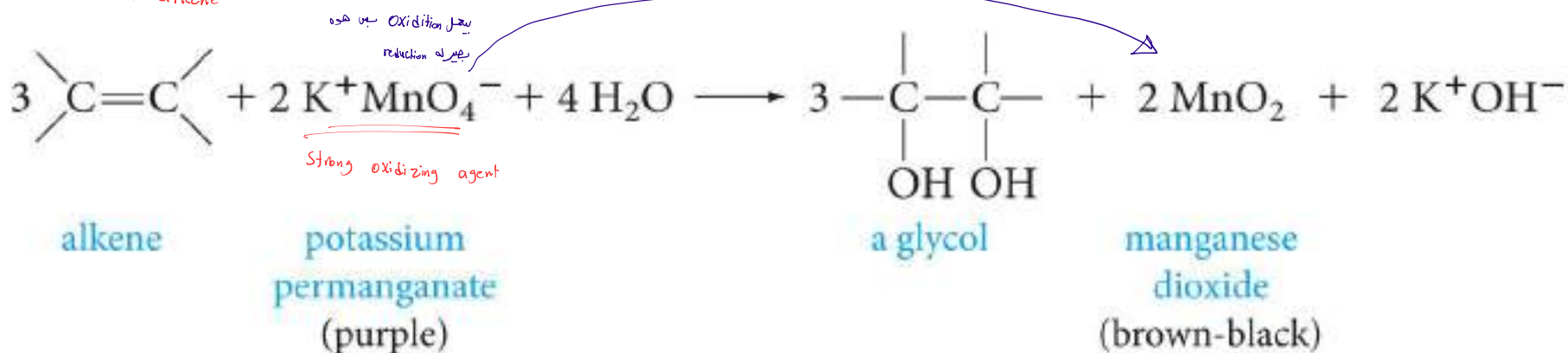
- Used as a chemical test
- Product is a glycol (1,2-diol) and manganese oxide
- Color change from purple to brown-black MnO_2 solid
- OsO_4 also used to make 1,2-diols



Oxidation: Permanganate (cont'd)

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

Oxidation of alkene



يعمل Oxidation على هذه
تغيره reduction

Strong oxidizing agent

يمكن ان يتغير تغير اللون
as chemical test
كحلون ابيض او اصفر او احمر
Potassium Permanganate
تغيره oxidation
تغيره reduction
تغيره oxidation
تغيره reduction

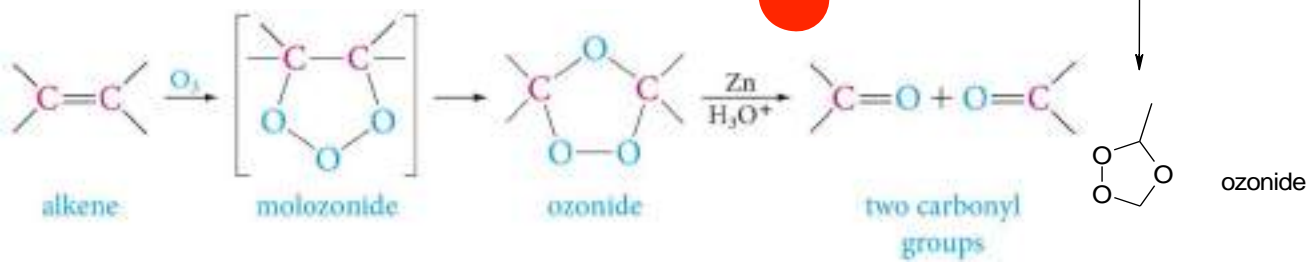
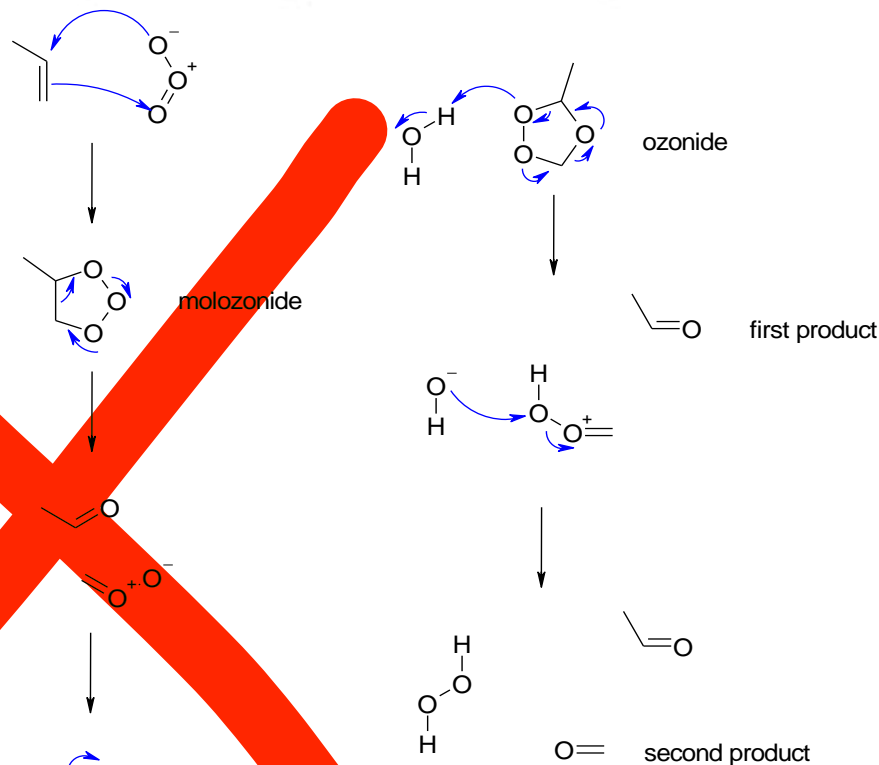
Oxidation: Ozonolysis (cont'd)

Step 1: π 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 atom

Step 2: the molozonide rearranges to an ozonide

Step 3: the ozonide peroxide O acts as a base to a water molecule producing one of the final products.

Step 4: the hydroxide attacks the hydroxy O forming a peroxide and the second carbonyl compound



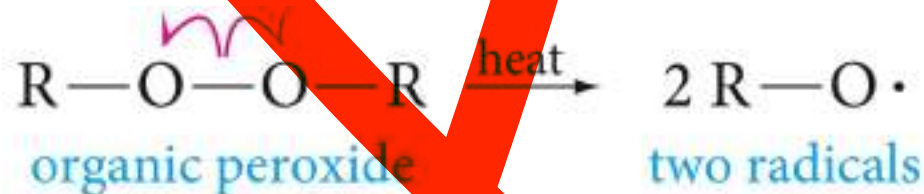
Radical Addition Reactions: Polymers

One of the most useful reactions of small alkenes is a free radical polymerization. Polyethylene, polypropylene and polybutylene are all very common plastics used throughout society.

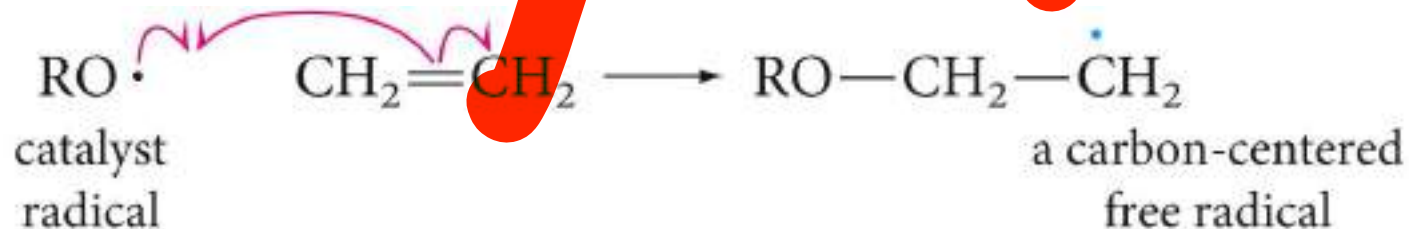
As with the other free radical reaction we have seen, this requires an initiation step, followed by chain growth and finally a termination step.

Radical Addition Reactions: Polymers

Initiation is commonly done using peroxides since they break at moderate temperatures.

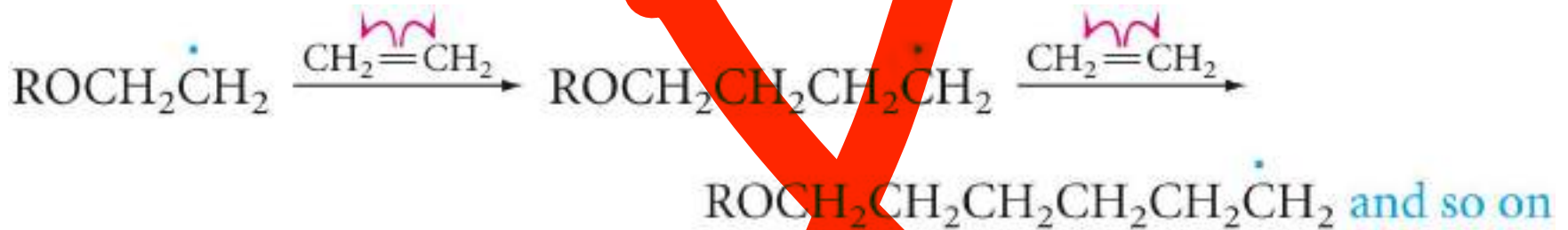


In contrast to the free radical substitution reaction in a free radical addition the initiator adds to the monomer rather than removing a H atom.



Radical Addition Reactions: Polymers

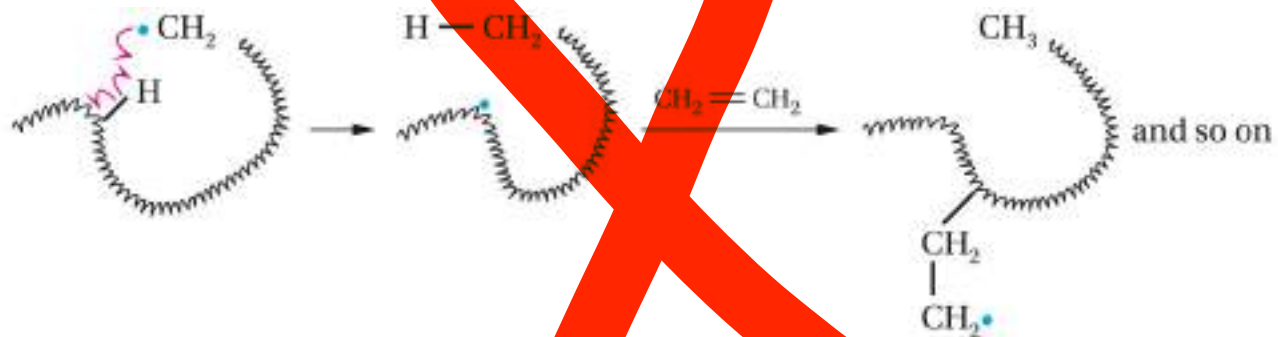
Chain growth occurs as the carbon radical reacts with additional monomers.



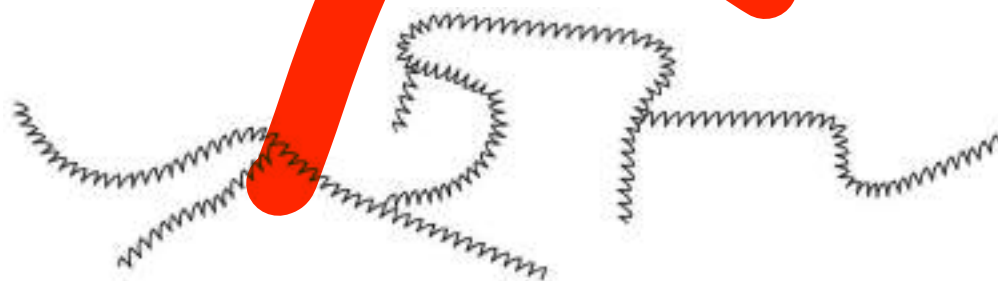
Termination usually occurs when two carbon radical react with each other.

Radical Addition Reactions: Polymers

During chain growth a branch point can be introduced if the chain wraps back on itself and abstracts a H atom from the middle of the chain. Growth will then proceed from this point.



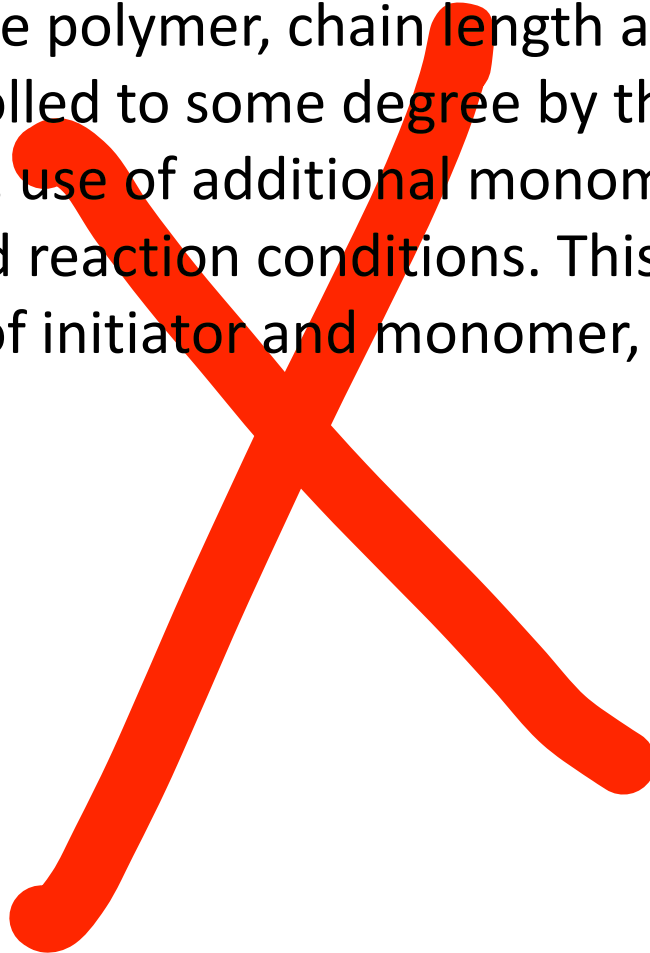
The result is a complex branched polymer.



branched polyethylene

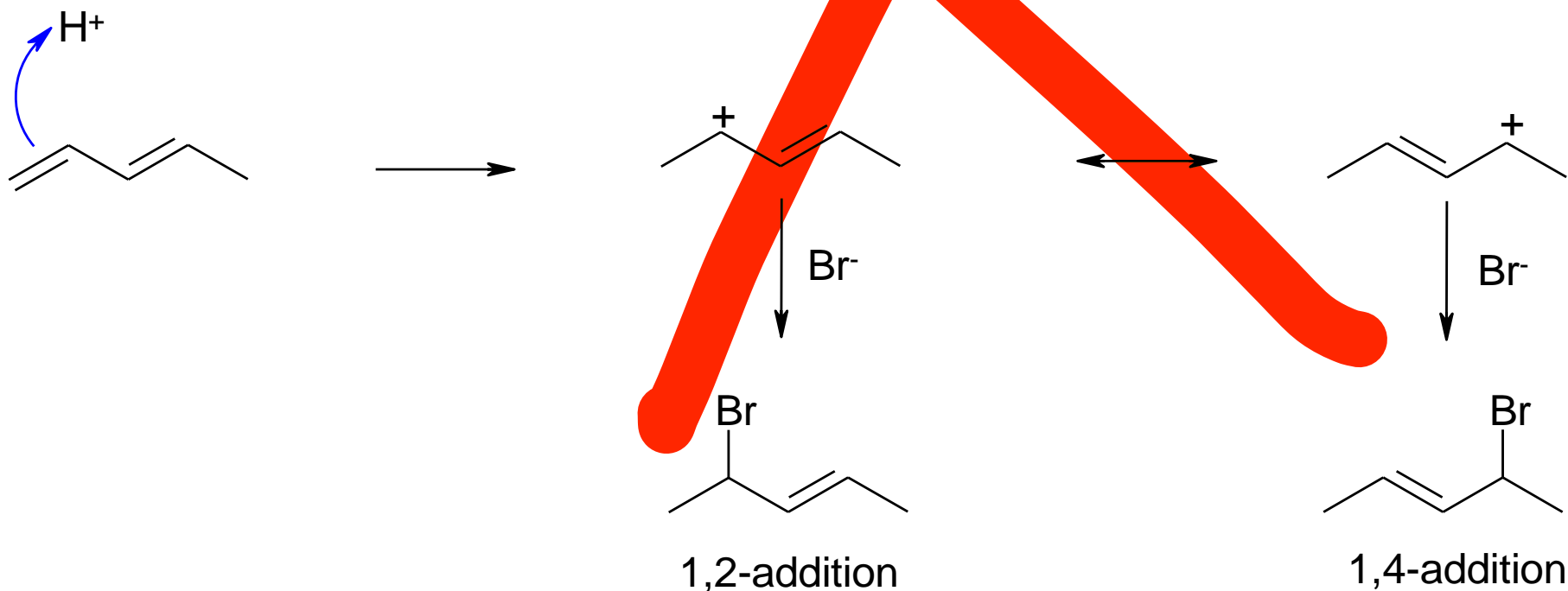
Radical Addition Reactions: Polymers

The exact structure of the polymer, chain length and amount of branching, can be controlled to some degree by the choice of initiator, use of catalysts, use of additional monomer types to introduce branching and reaction conditions. This include the relative concentrations of initiator and monomer, and reaction temperature.



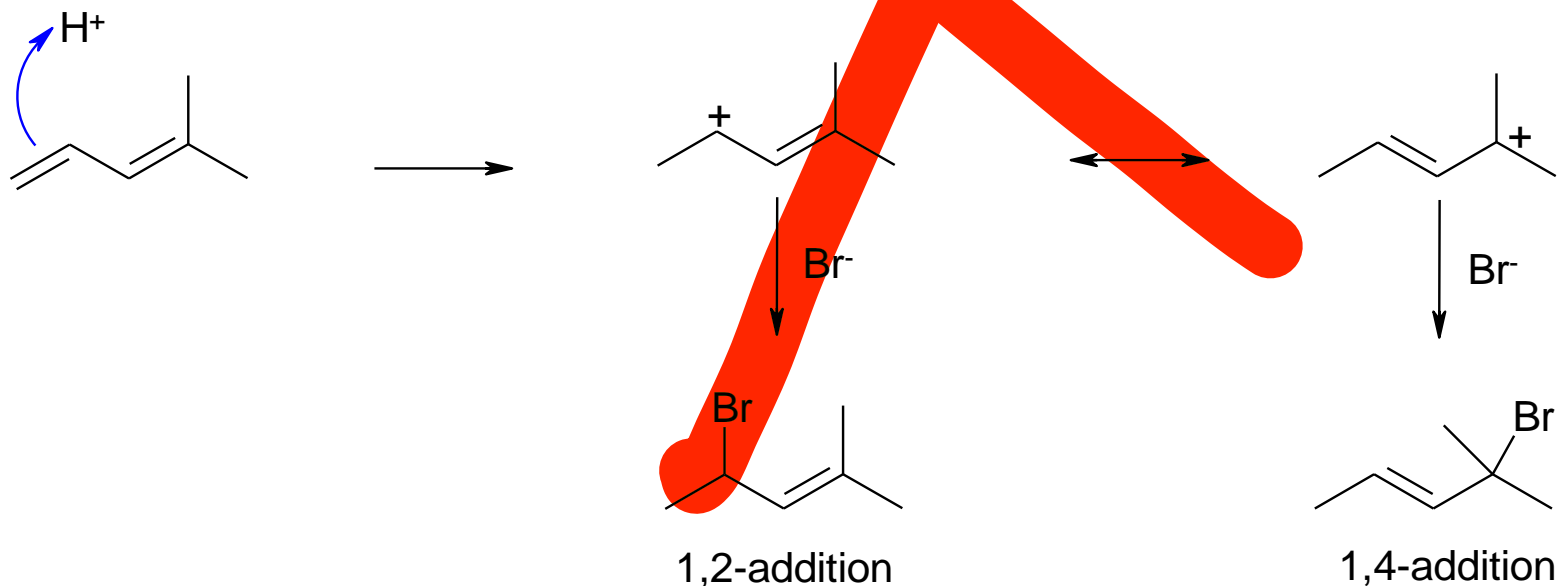
Additions to Conjugated Systems

Conjugated systems provide an extra complication for addition reactions. The first step is an electrophilic addition generating a carbocation. But since the two double bonds are conjugated resonance is possible for the carbocation intermediate, i.e.



Additions to Conjugated Systems

There will usually be both the 1,2 and 1,4 addition products from conjugated alkenes. The only time a single product will dominate is if the carbocations have unequal stability, i.e.



In this case there will be more of the 1,4 addition product as it reacts through a 3° carbocation which is more stable than the 2°.

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 π electrons that will produce two new σ bonds forming the ring.

Cycloadditions: the Diels-Alder Reaction

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 π bond which makes it a better electrophile.

Common electron withdrawing groups include: carbonyl ($-C(=O)R$), cyano ($-C\equiv N$) and esters ($-CO_2R$).

