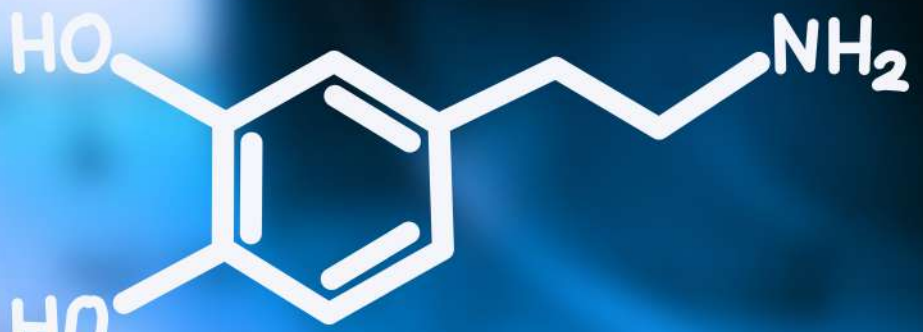
Organic 1

لجان الدُّفعات

DOPAMINE ACADEMY

Subject: Lecture 6

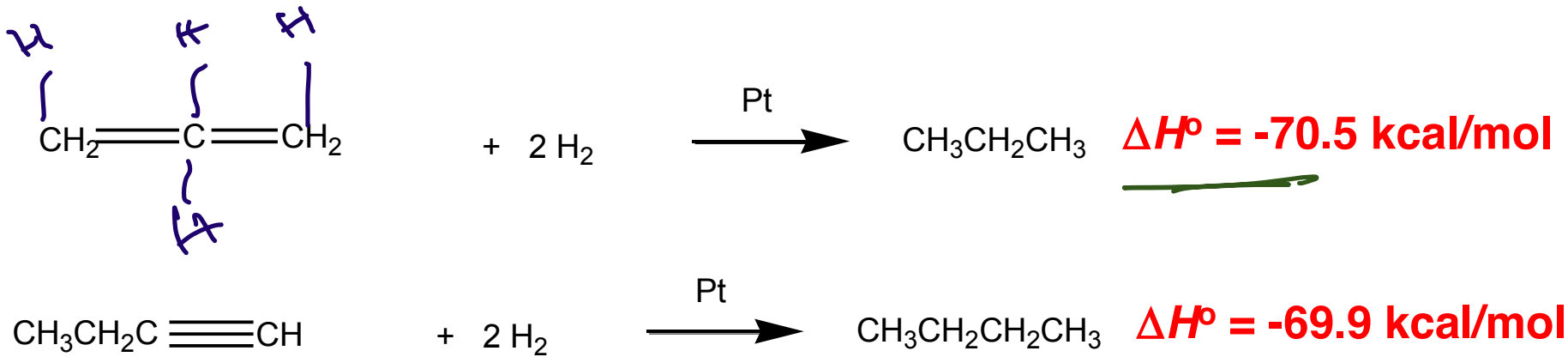


Dopamine

Student Name: Otba Khalid

25-7-2024

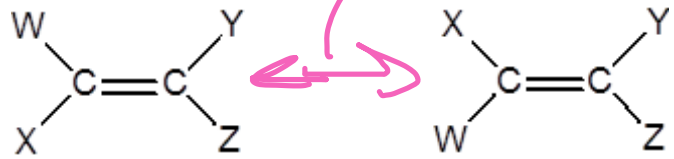
Relative Stabilities of Dienes



- The heat of hydrogenation of allene is similar to that of 1-butyne; both have at least one *sp* carbon
- Additional reactivity of cumulated dienes will not be considered in this course

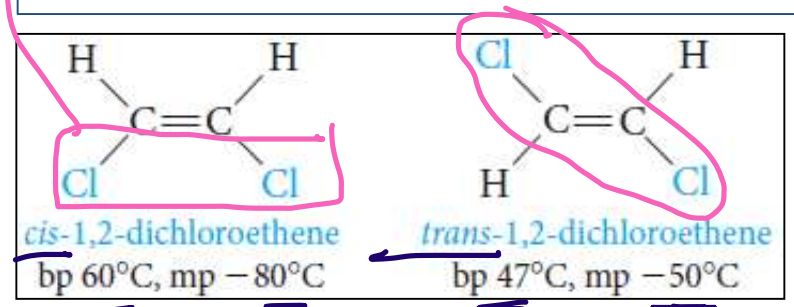
Geometric Isomerism in Alkenes

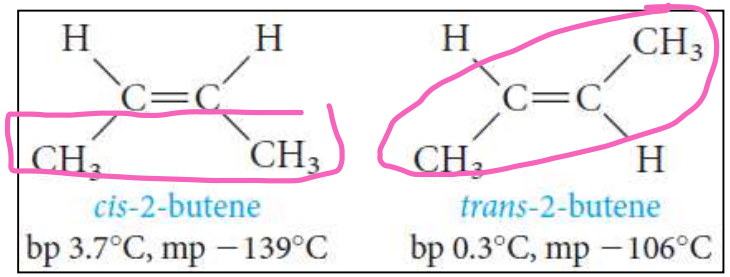
- In alkenes, geometric isomerism is due to restricted rotation about the carbon - carbon double bond.

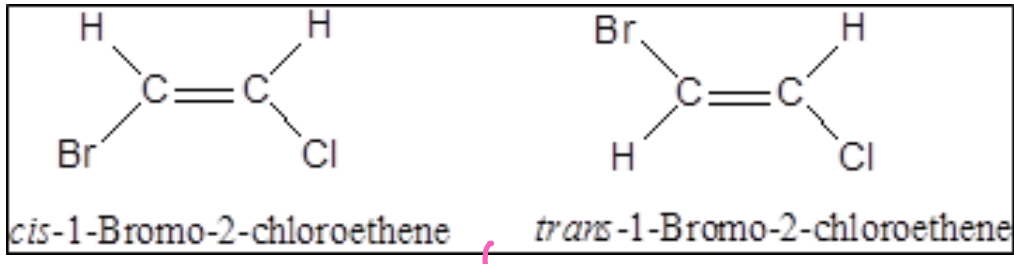


Geometric isomers

A) when W differs from X and Y from Z, Alkenes exist as geometric isomers

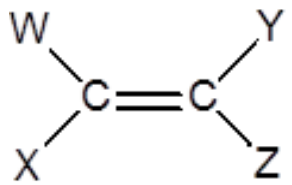


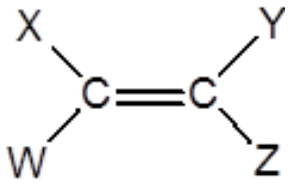




- *cis* isomer; when two similar groups are on the same side of the double bond.
- *trans* isomer; when two similar groups are on the opposite sides of the double bond.
- They have different physical properties and can be separated by fractional crystallization or distillation.

Geometric Isomerism in Alkenes

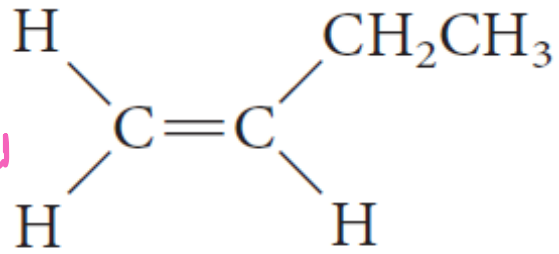




'is not Geometric isomers

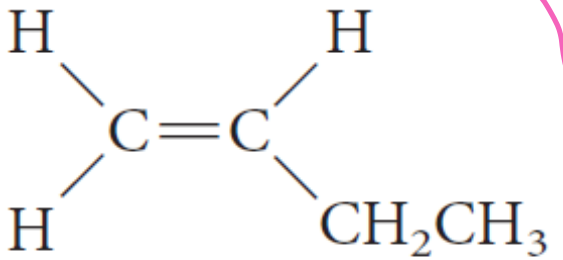
B) If (W = X or Y = Z), geometric isomerism is not possible.

* ممكن يجي سؤال يقول فيه أي من الـ alkenes ليست geometrical isomers ؟

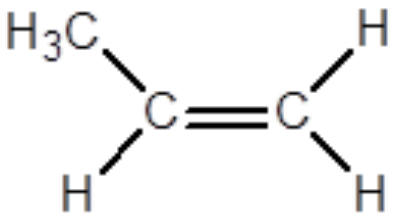


1-butene

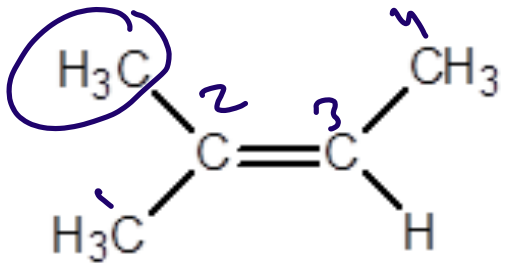
is identical to



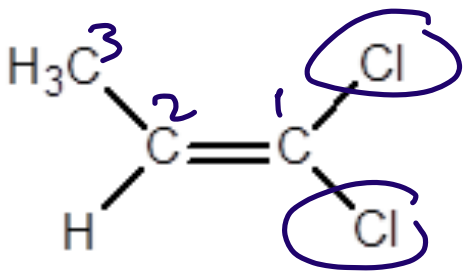
1-butene



Propene



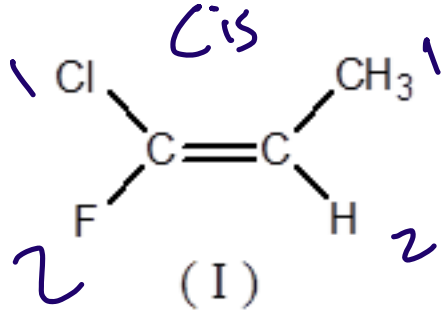
2-Methyl-2-butene



1,1-Dichloropropene

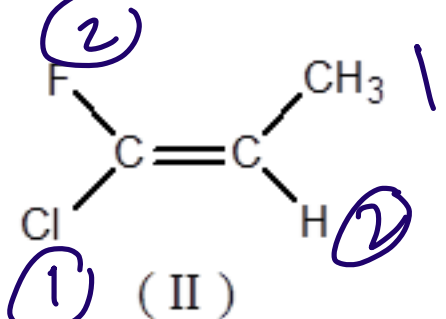
Geometric Isomerism in Alkenes

- For alkenes with four different substituent such as



(I)

or



(II)

Another system, the *E, Z* system,

- Basically, the E,Z system works as follows;

Arrange the groups on each carbon of the C=C bond in order of priority

- The priority depends on atomic number:

The higher the atomic number of the atom directly attached to the double-bonded carbon, the higher the priority.

Thus, in structure (I),

Cl > F, and CH_3 > H.

Geometric Isomerism in Alkenes

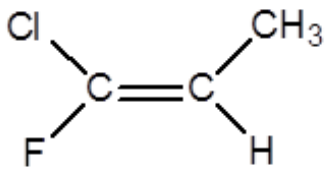
- If the two groups of higher priority are on the same side of the C=C plane,

  The isomer is labeled *Z;* (from the German *zusammen*, together).

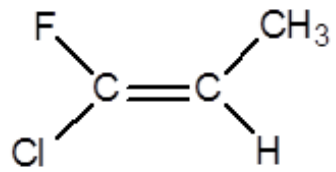
- If the two groups of higher priority are on opposite sides of the C=C plane,

  The isomer is labeled E; (from the German entgegen, opposite).

Priority: Cl > F, CH_3 > H

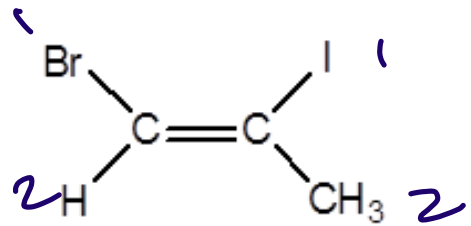


Z-1-Chloro-1-fluoropropene
(Cl and CH_3 on same side)



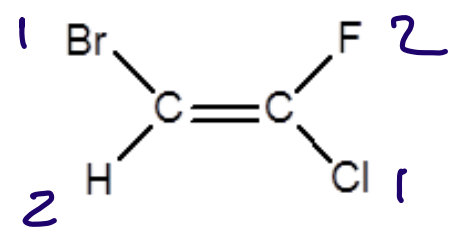
E-1-Chloro-1-fluoropropene
(Cl and CH_3 on opposite side)

Priority: Br > H, I > CH_3



Z-1-Bromo-2-iodopropene

Priority: Br > H, Cl > F



E-1-Brfomo-2-chloro-2-fluoroethene

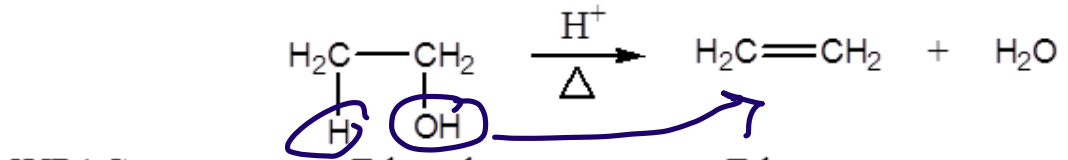
Preparation of Alkenes

- Alkenes are prepared by *Elimination* of an atom or group of atoms from adjacent carbons to form *carbon-carbon double bond*.

(A=H or halogen;
B=OH or halogen)

1) Dehydration of Alcohols

- *When an alcohol is heated in the presence of a mineral acid catalyst, It readily loses a molecule of water to give an alkene.*

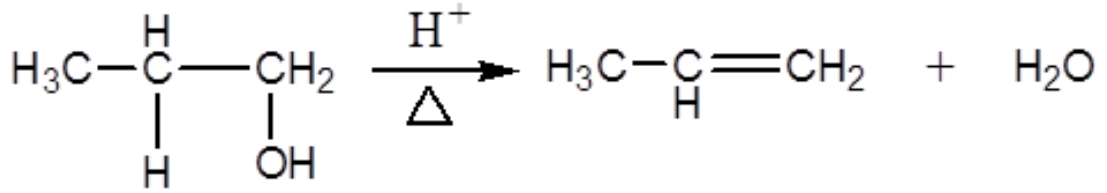


IUPAC name:	Ethanol	Ethene
Common name:	Ethyl alcohol	Ethylene

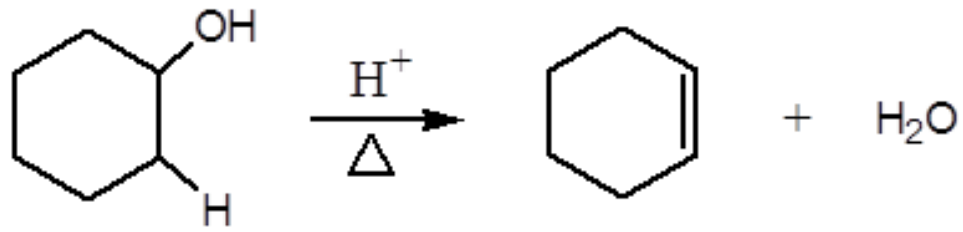
- The acid *catalysts* most commonly used are sulfuric acid, H_2SO_4, and phosphoric acid, H_3PO_4.

1) Dehydration of Alcohols

Removal of OH group and a proton from two adjacent carbon atoms using mineral acids such as H_2SO4 or H_3PO_4



IUPAC name:	1-Propanol	Propene
Common name:	*n*-Propyl alcohol	Propylene



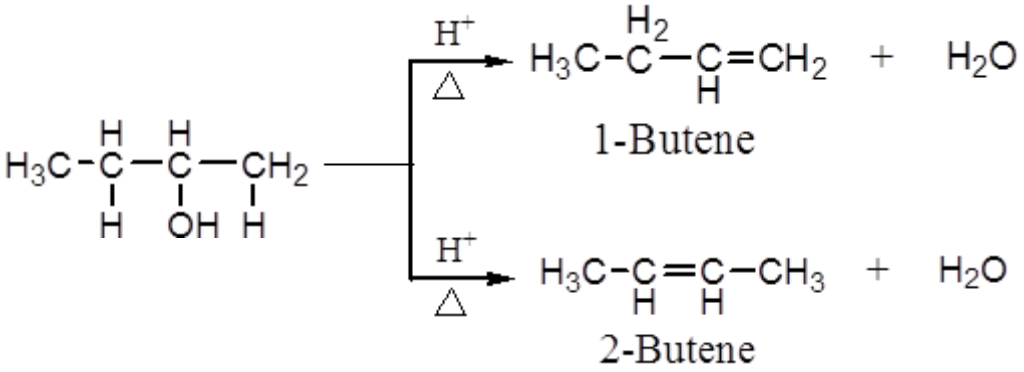
IUPAC name:	Cyclohexanol	Cyclohexene
Common name:	Cyclohexyl alcohol	

1) Dehydration of Alcohols

Which Alkene Predominates?; Saytzeff's Rule

The loss of water from adjacent carbon atoms, can give rise to more than one alkene.

Example: the dehydration of 2-butanol.



2-butene is the major (with two alkyl substituents attached to C=C)

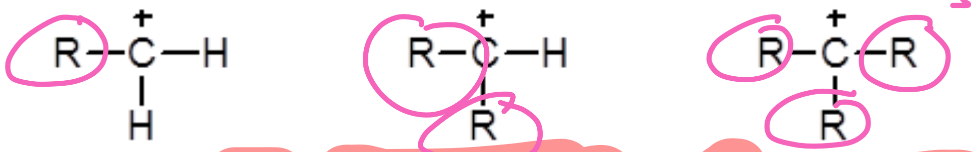
Saytzeff's Rule applies

In every instance in which more than one Alkene can be formed

The major product is always the alkene with the most alkyl substituents attached on the double-bonded carbons.

1) Dehydration of Alcohols

- Classes of Carbocations



1° carbocation   2° carbocation   3° carbocation

according to the number of carbon atoms attached to the positively charged carbon.

The ease of formation and the stabilities of carbocations follow the order

3° > 2° > 1°

←

Ease of formation and stabilities of carbocations

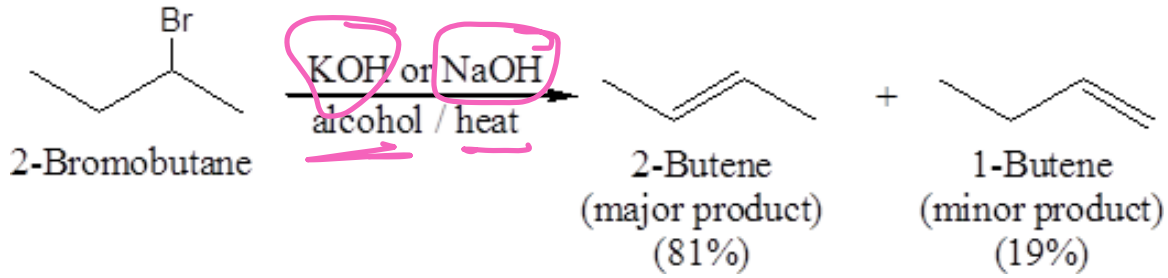
- Generally

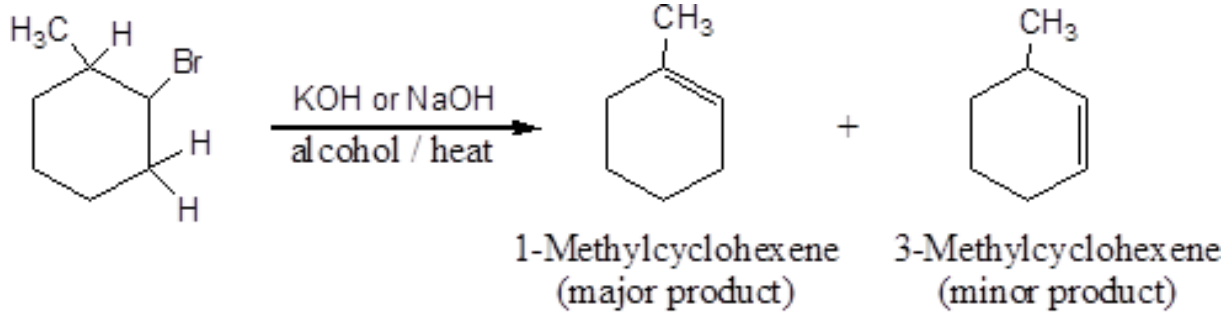
1. The dehydration of alcohols requires an acid catalyst.
2. The predominant alkene formed follows Saytzeffs rule.
3. The reaction proceeds *via* a carbocation intermediate.
4. The stabilities of carbocations and the ease of dehydration of alcohols follows the order 3° > 2° > 1°.

2) Dehydrohalogenation of Alkyl Halides

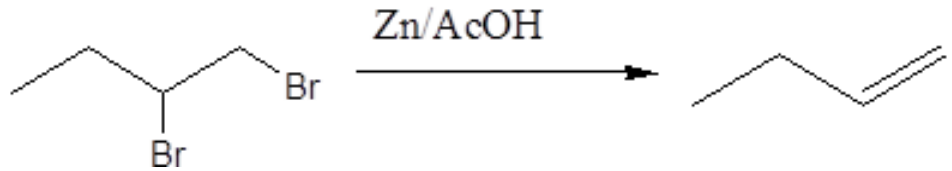
- Alkenes can also be prepared under alkaline conditions.

heating an alkyl halide with a solution of KOH or NaOH in alcohol, yields an alkene.





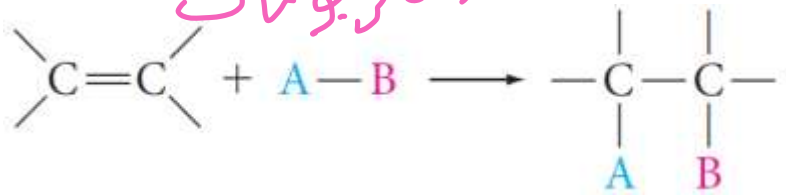
3) Dehalogenation of Vicinal Dibromides



Reactions of Alkenes

- The chemistry of alkenes can be divided into two general types of reactions:

(1) Electrophilic Addition Reactions



Addition of Symmetric and Unsymmetric Reagents to symmetric Alkenes.

1. Addition of Hydrogen: Catalytic Hydrogenation
2. Addition of Halogens: Halogenation

Addition of Unsymmetric Reagents to Unsymmetric Alkenes; Markovnikov's Rule.

1. Addition of Hydrogen Halides
2. Addition of Sulfuric Acid
3. Addition of Water: Hydration
4. Addition of HOX: Halohydrin Formation

(2) Oxidation Reactions

1. Ozonolysis ⇌ (O3) أوزونيد
2. Oxidation Using $KMnO_4$

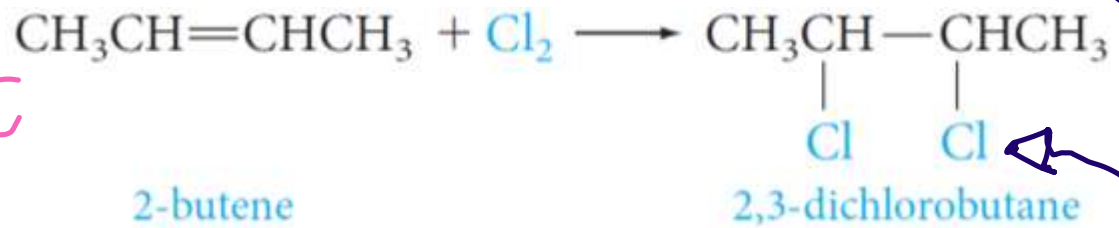
Electrophilic Addition Reactions

2. Addition of Halogen: Halogenation

F / Cl / Br / I

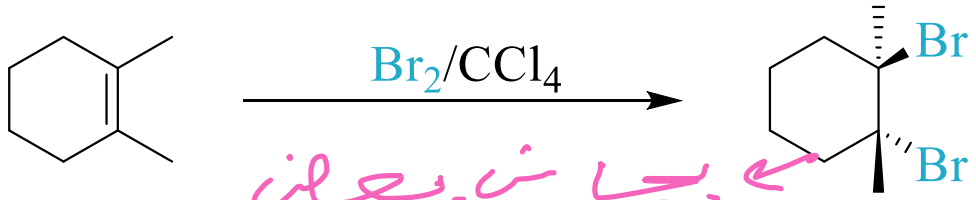
When an alkene is treated at room temperature with a solution of bromine or chlorine in carbon tetrachloride to give the corresponding vicinal dihalide (two halogens attached to adjacent carbons)

the solvent (non Polar)



2-butene — 2,3-dichlorobutane

2 Cl's attached to adjacent carbons.



1,2-Dimethyl-cyclohexene — *trans*-1,2-Dibromo-1,2-dimethyl-cyclohexane

I - Iodine is too unreactive and will not add to the double bond.

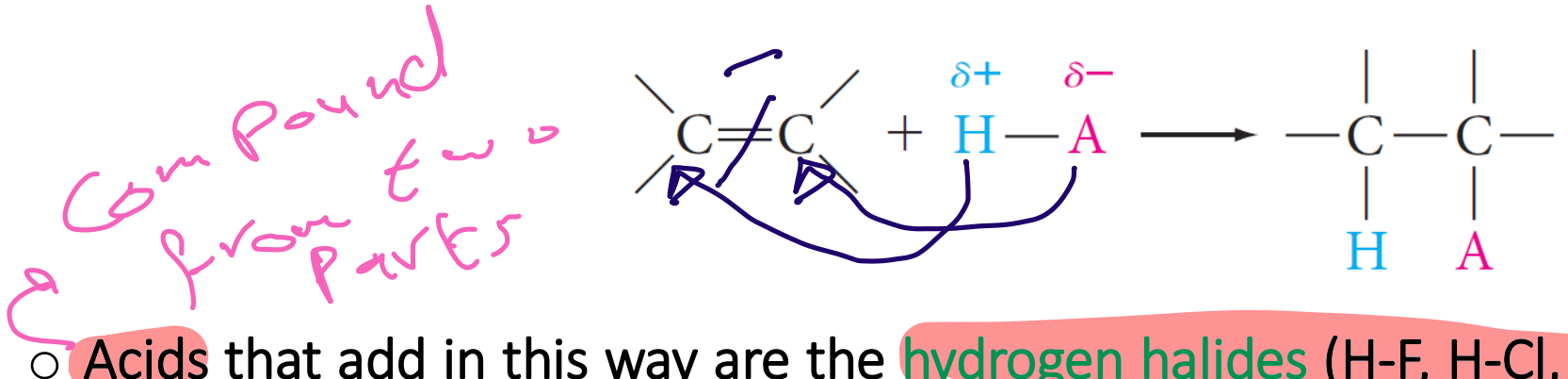
F - Fluorine is too reactive and reacts explosively with an alkene.

Electrophilic Addition Reactions

3. Addition of Acids

- A variety of acids add to the double bond of alkenes.

  The hydrogen ion (or proton) adds to one carbon of the double bond, and the remainder of the acid becomes connected to the other carbon.



- Acids that add in this way are the hydrogen halides (H-F, H-Cl, H-Br, H-I), and water (H-OH).

Note that

- Any electron-deficient species is called an electrophile.
- Any electron-rich species is called a nucleophile.

Electrophilic Addition Reactions

Examples of Electrophile:

i) Positive reagents: protons (H^+), alkyl group R^+ , nitronium ion (NO_2^+), etc....

ii) Neutral reagents having positively polarized centers: HCl, bromine (because it can be polarized so that one end is positive).

iii) Lewis acids: molecules or ions that can accept an electron pair ⇒ BF_3 and $AlCl_3$.

iv) Metal ions that contain vacant orbitals: the silver ion (Ag^+), the mercuric ion (Hg^{2+}), and the platinum ion (Pt^{2+}).

Examples of Nucleophile:

a)Negative ions

e.g. $H\ddot{O}:^-$ Hydroxide ion, $H\ddot{S}:^-$ Hydrosulphide ion, $R\ddot{O}:^-$ Alkoxide ions,

$:N\equiv C:^-$ Cyanide ion, $:\ddot{X}:^-$ Halide ions, ...etc.

b) Neutral molecules

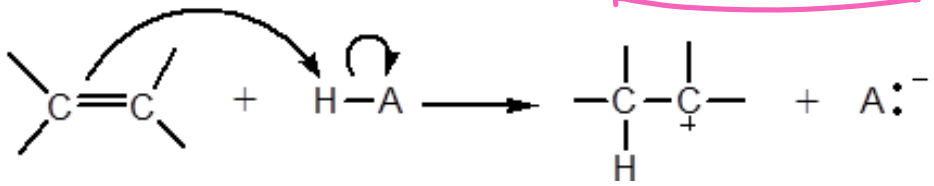
e.g. $H_2\ddot{O}$, $R—\ddot{O}—H$, $R—\ddot{O}—R$, $H_3\ddot{N}$, $R_3\ddot{N}$, ...etc.

Electrophilic Addition Reactions

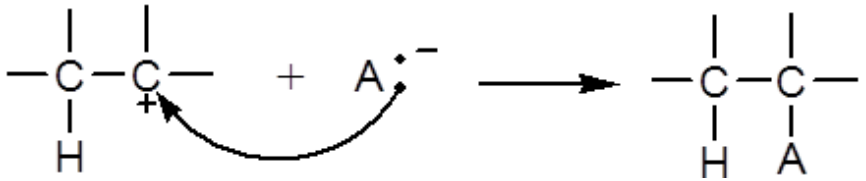
3. Addition of Acids

- The addition of H—A to an alkene is believed to be a two-step process.

Step 1. The hydrogen ion (the electrophile) attacks the ∏-electrons of the alkene, forming a C—H bond and a carbocation.



Step 2. The negatively charged species A:⁻ (a nucleophile) attacks the carbocation and forms a new C—A bond.



- The attack by an electrophilic reagent on the ∏-electrons, falls in a general category called electrophilic addition reactions.

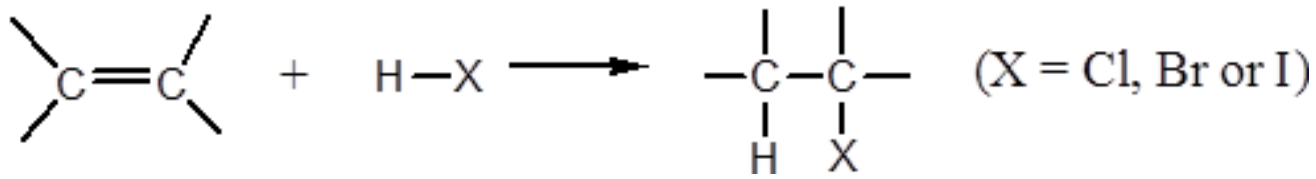
rich in electrons

Electrophilic Addition Reactions

3.1. Addition of Hydrogen Halide

Alkenes react with hydrogen chloride, HC1, hydrogen bromide, HBr and hydrogen iodide, HI, to form alkyl halides, RX.

General equation



Examples;