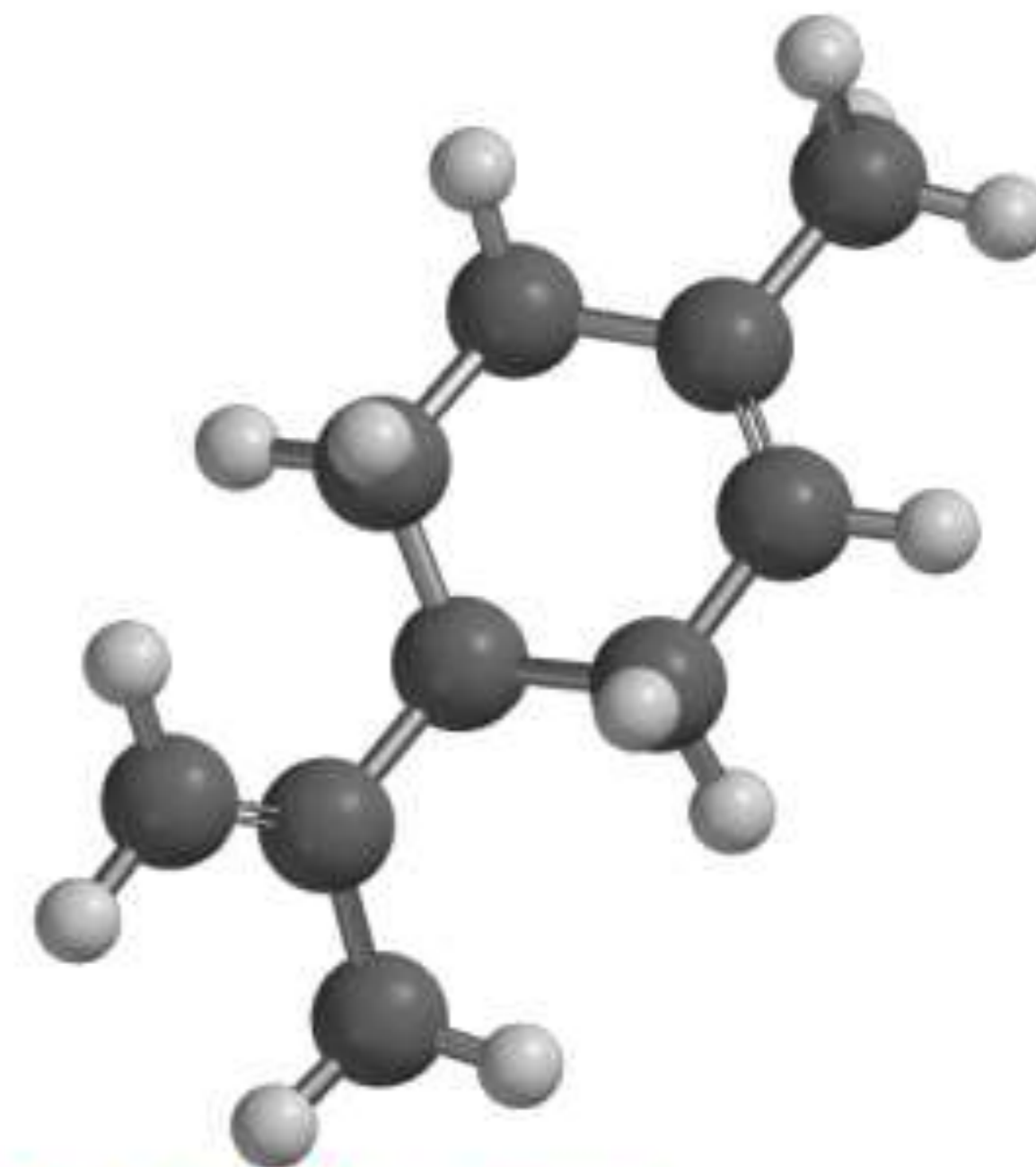
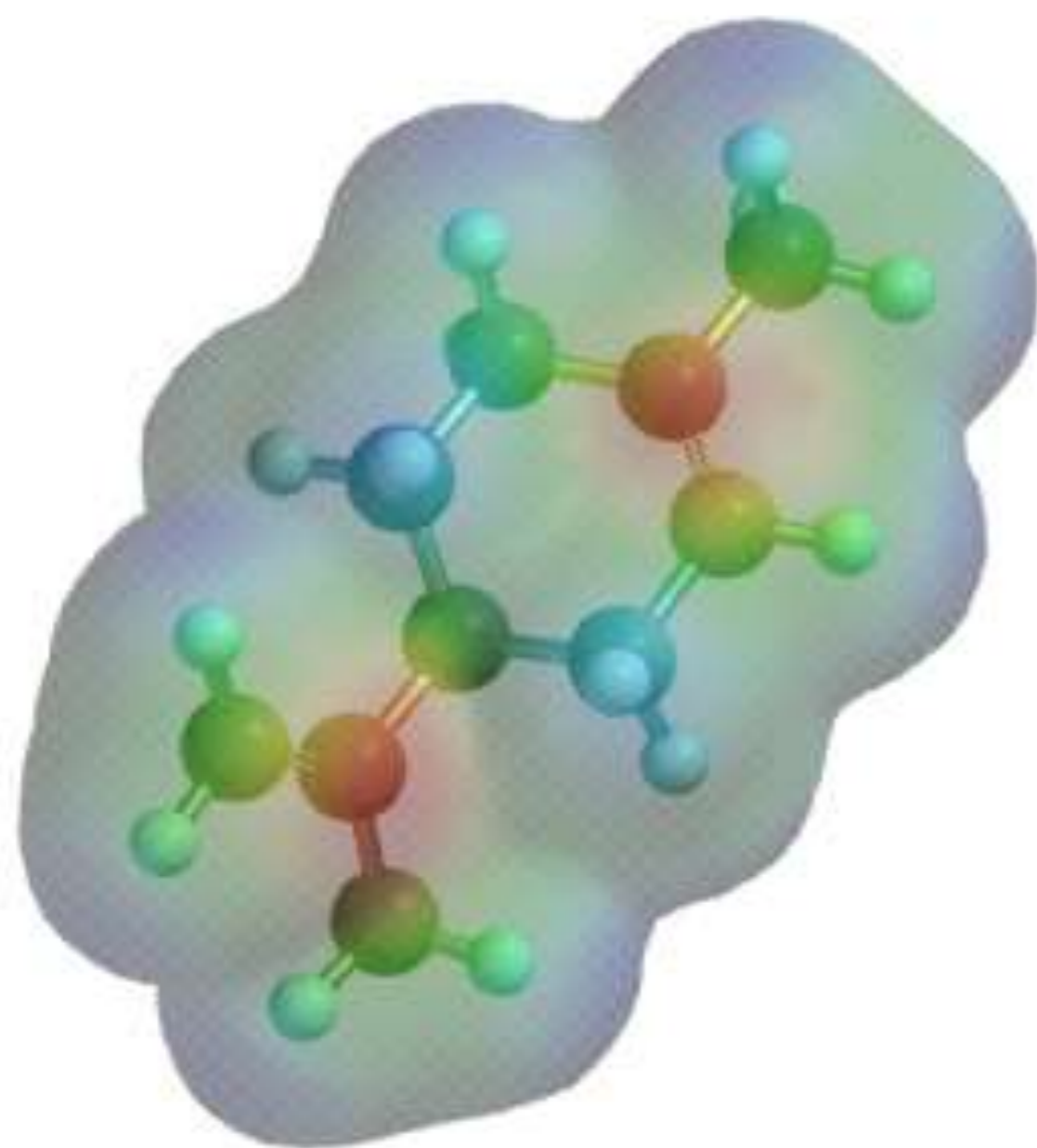




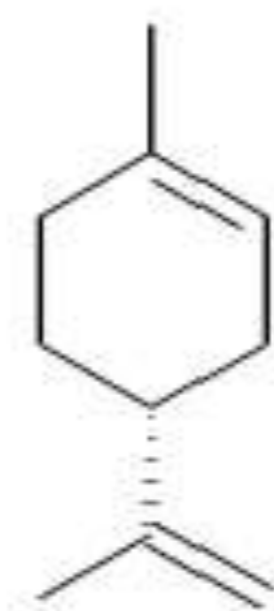
Organic chemistry

Lec: 7

Done by: Shahed Zaytoon



Chapter 3: Alkenes and Alkynes

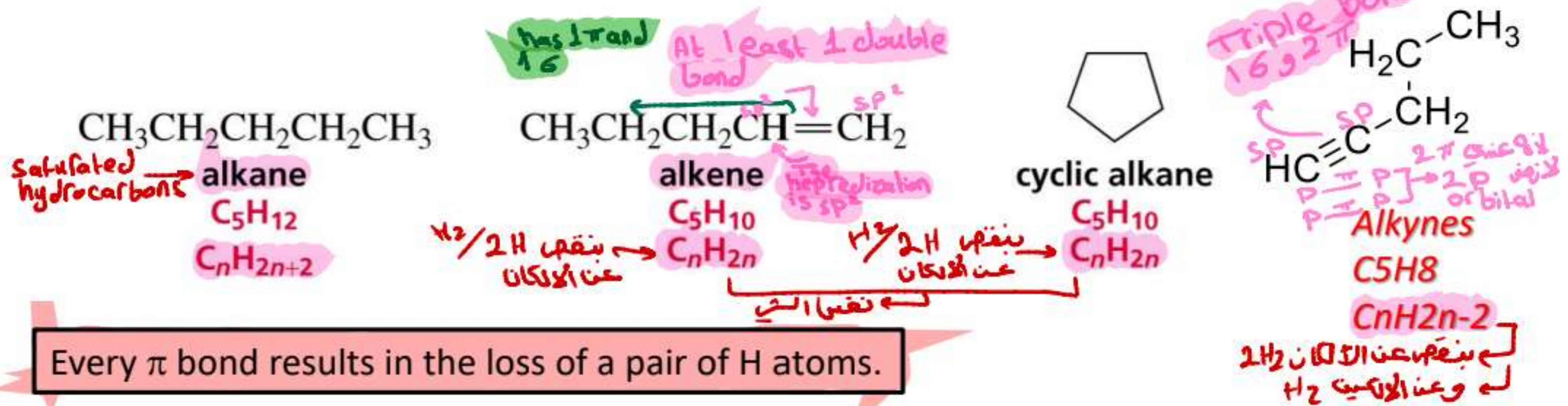


limonene

General Properties

Alkenes contain double bonds and alkynes triple bonds. Both classes of compounds are hydrocarbons, containing only C and H atoms.

- a double bond consists of 1 σ and 1 π bond,
- a triple bond consists of 1 σ and 2 π bonds.

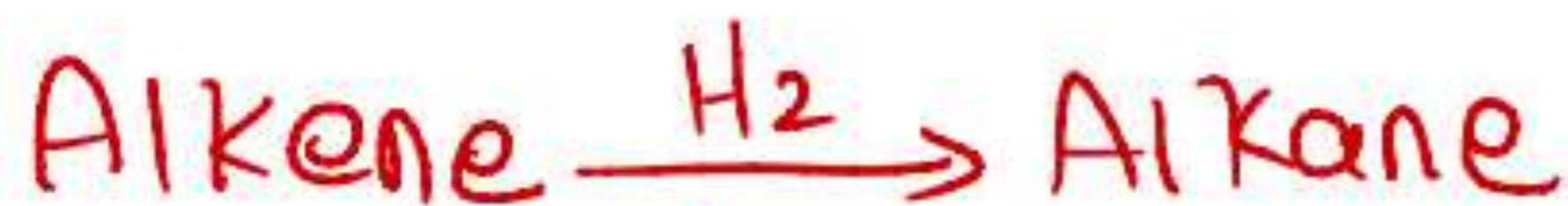


General Properties (cont'd)

الفكرة انه في اربعة المركب يتقده mole of H₂ حتى
يعبر زي زي الاكوان

The **Index of Hydrogen Deficiency (IHD)** can give an idea of possible structures based on the ratio of C to H. This is a count of the number of H₂ molecules needed to obtain the corresponding saturated acyclic structure. The IHD is also equal to the **number of rings** and **π bonds** in the molecule.

IHD for alkyne = 2



we need 1 mole for inverting Alkene to Alkane

تق الفكرة
cyclic

so, the IHD = 1

معناها به 1 مول من H₂ عشان احول الاكوان الى الكان

more than one multiple bond → double bond أكثر من وحدة

With multiple double (or triple) bonds three possible arrangements arise: cumulated, conjugated or isolated (non-conjugated).

multiple bond
المقود فيها
double or triple

Conjugated are especially important as the π bonds can interact.

هنا المركبات تقسم إلى 3 أنواع
لحسب شكل / مكان الرابطة multiple bond

Cumulated	Conjugated	Isolated / non conjugated
$C=C=C$	$C=C-C=C$	$C=C-C-C=C$
$C=C=C=C$	$C\equiv C-C\equiv C$	$C\equiv C-C-C-C\equiv C$

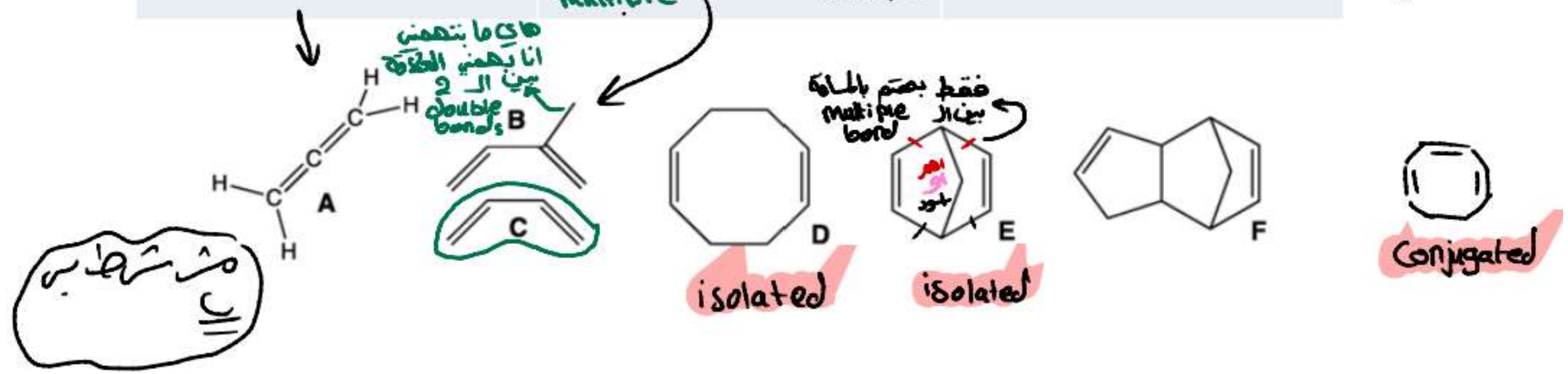
يكون في هذا
أكثر من وحدة multiple bond
والملافة بينهم تكون
more than one single bond

Resonance
هذا النظام الذي فيه resonance

Double bond
فيها
وا يعنى

Conjugated
عبارة عن
multiple - single - multiple

المع
multiple



- Parent \rightsquigarrow The longest chain
- Prefix \rightsquigarrow substituent
- Suffix \rightsquigarrow functional group

alkane نفا ال
 ولكن الفرق انه لما ندر
 على ا طول
 سلسلة لازم تكون بتحتوي على ال double bond
 ال double bond
 هاي هي ال suffix
 الاطية هون لحيك
 لازم نعطيهما الرقم
 الاقل

IUPAC Nomenclature of alkenes

- Use the Suffix **-ene** to show the presence of a carbon-carbon double bond.
- Number the parent chain to give the 1st carbon of the double bond the lower number.
- Follow IUPAC rules for numbering and naming substituents.
- For a cycloalkene, the numbering of the atoms of the ring the must begin with the two carbons of the double bond.

- Some alkenes, particularly low-molecular-weight ones, are known almost exclusively by their common names.

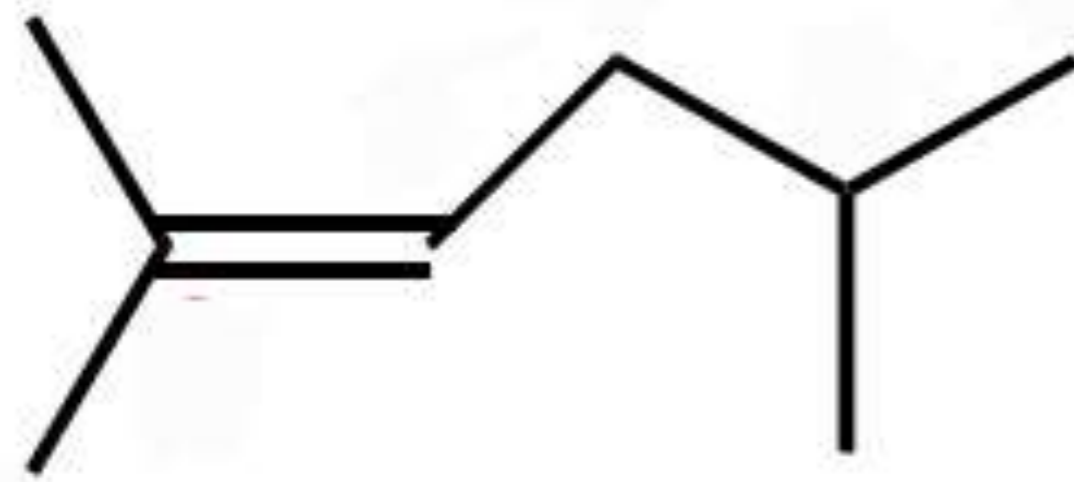
	$\text{CH}_2=\text{CH}_2$	$\text{CH}_3\text{CH}=\text{CH}_2$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C}=\text{CH}_2 \end{array}$
IUPAC name:	Ethene	Propene	2-Methylpropene
Common name:	Ethylene	Propylene	Isobutylene

حفظ

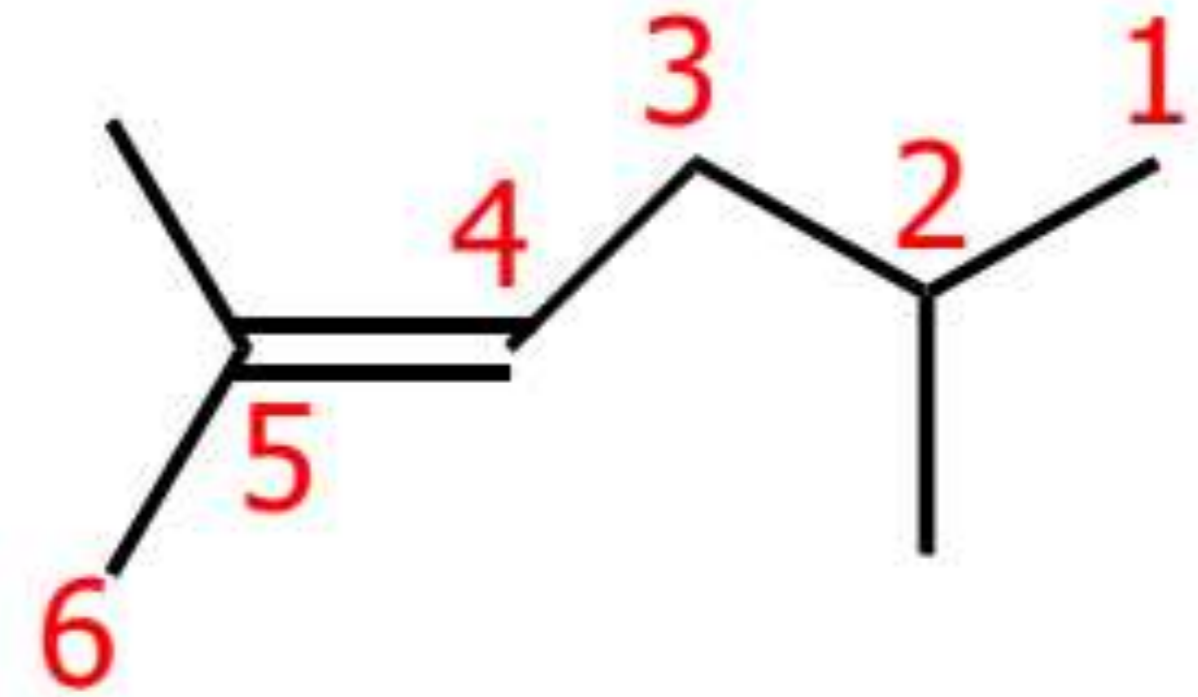
← ما في راعي
 امك وين ار
 double bond
 ما بعطيها رقم
 لانها على كد الاحوال
 هي (1)
 ← بينا لو اطول سلسله
 كانت بنختوي على اكثر
 من 3 حون لازم
 نرقم ار double bond

ممكن
الترقيم عشان
خل براحتنا
اندر جوان

Number the chain in the direction that gives the functional group the lowest number.



NOT

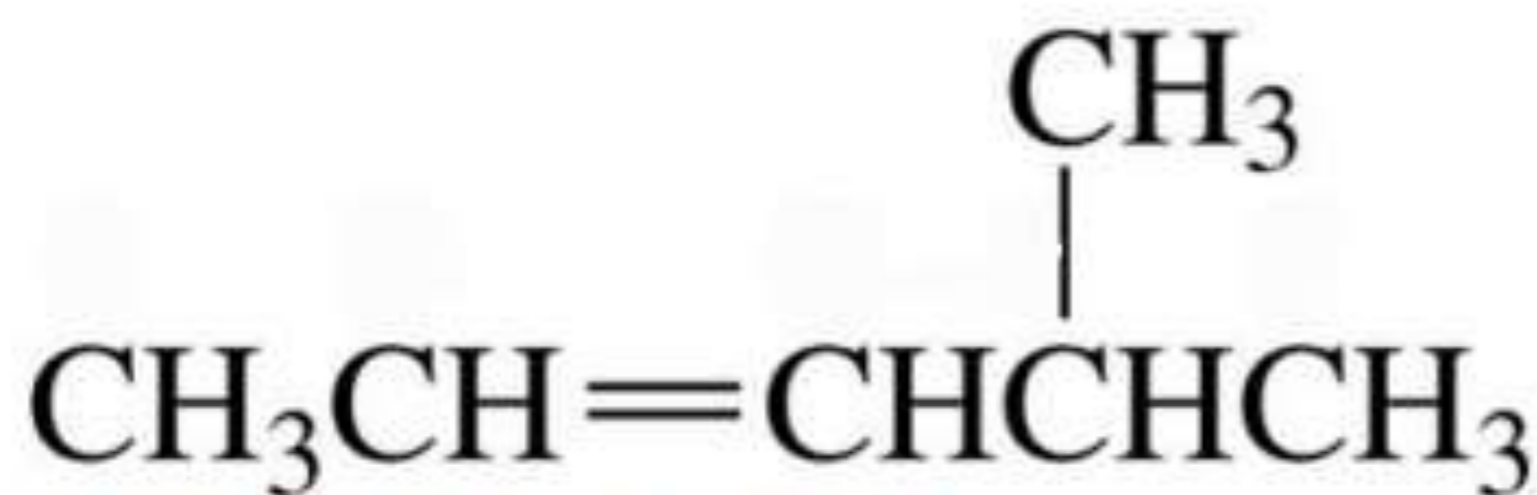


2,5-Dimethyl-2-hexene

2,5-Dimethyl-4-hexene

لأن لازم
اعطيها اقل
رقم لعينك
ما رح امش من
اليمين

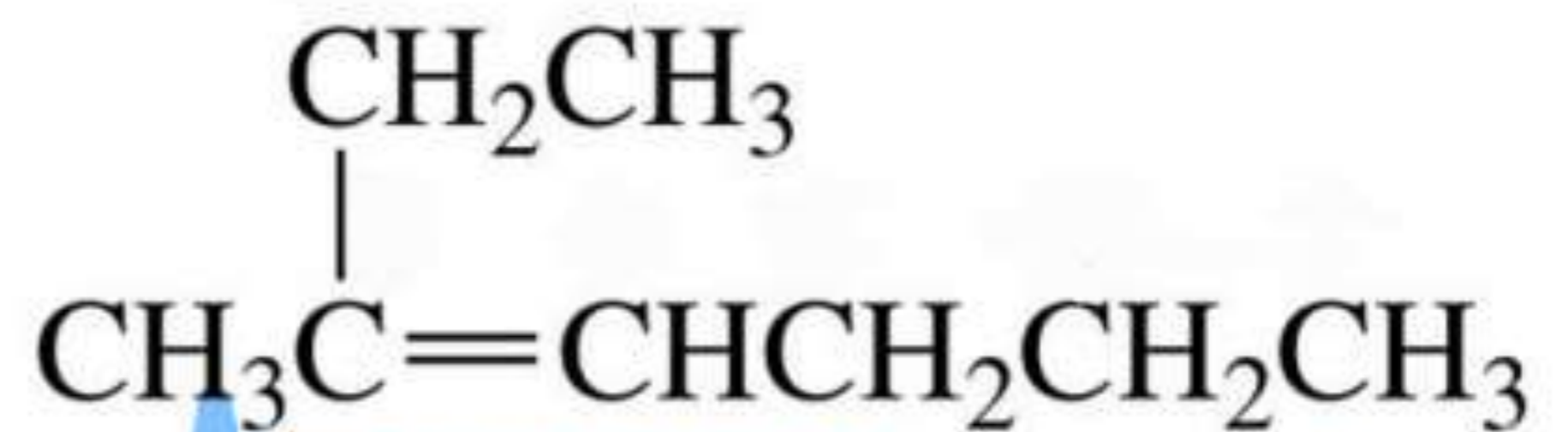
لأن هون هرقمين من اليمين
غلط



4-methyl-2-pentene

المهم عندي هو رقم
ال double bond

*لأنك اول شروح ارقم ال double bond

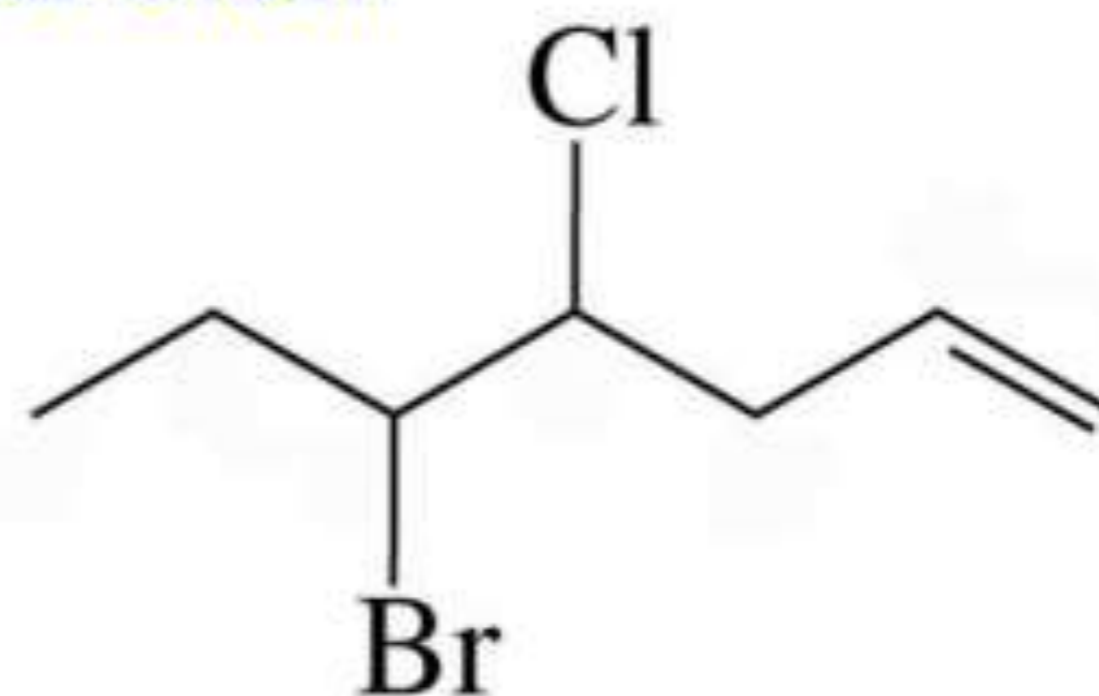


3-methyl-3-heptene

Substituents are stated in alphabetical order.

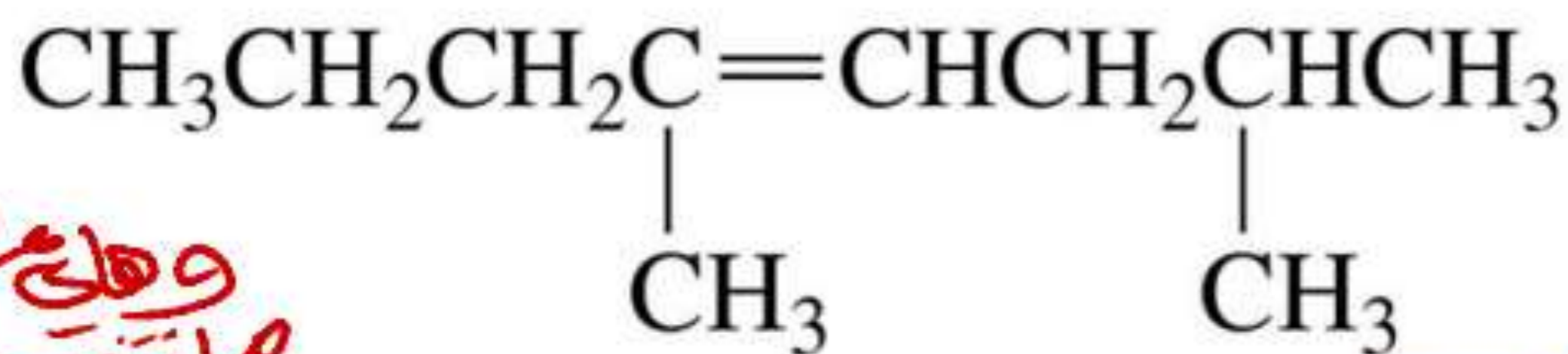


6-ethyl-3-methyl-3-octene



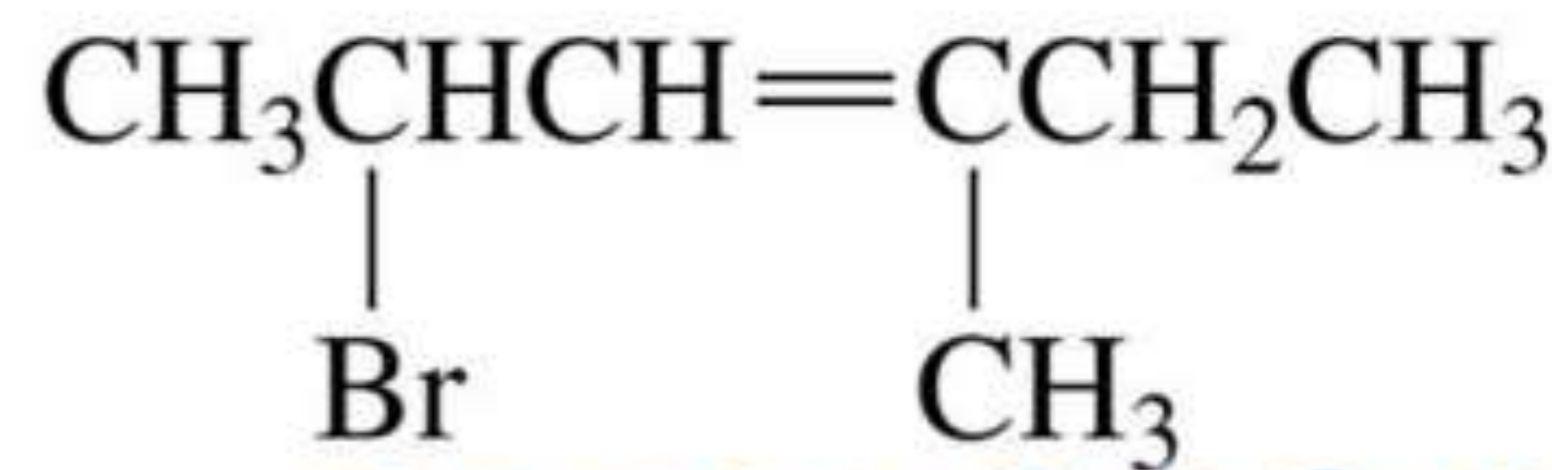
5-bromo-4-chloro-1-heptene

Hw:

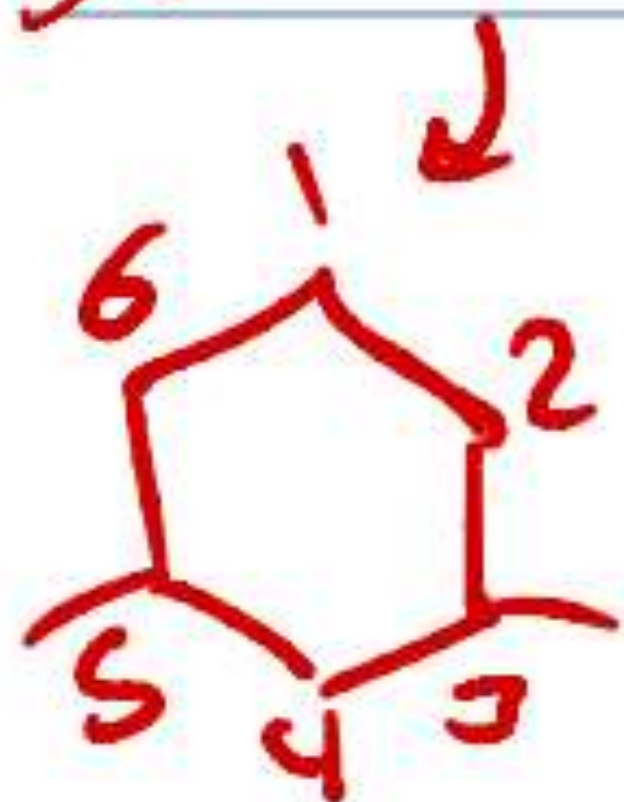


وهي مثال ما نتعجبوا

2,5-dimethyl-4-octene

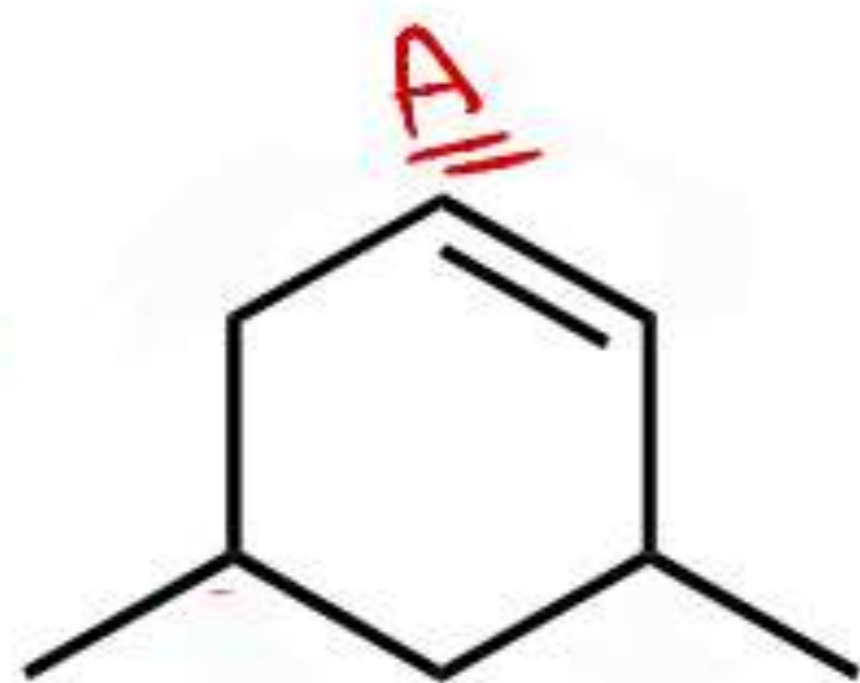


2-bromo-4-methyl-3-hexene



3,5-Dimethylcyclohexene

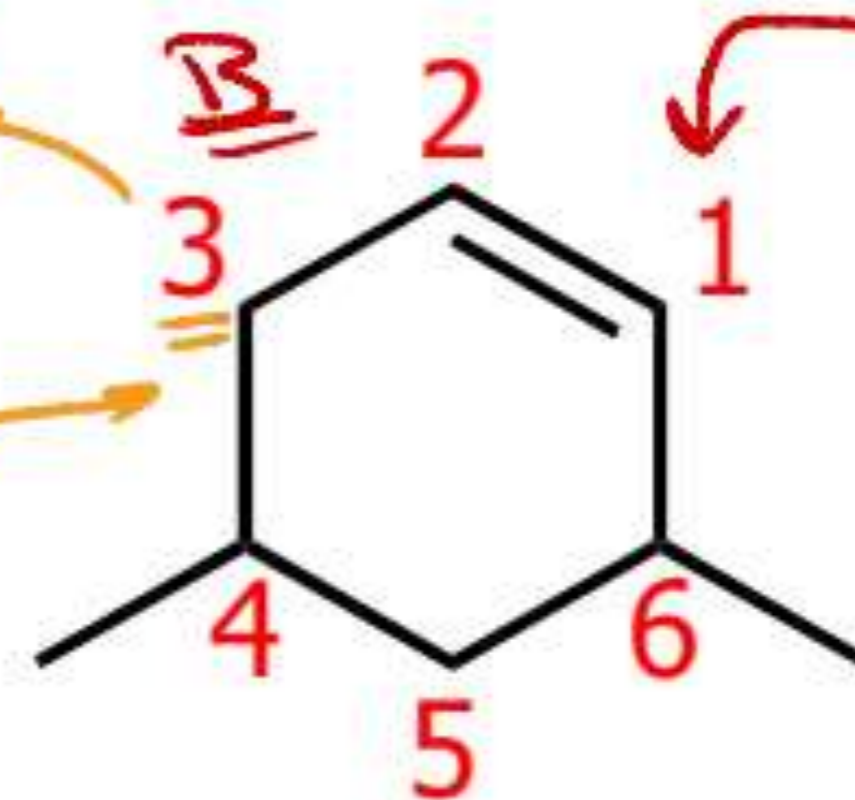
لعمري نساها



* او 2 دائما لازم يكونوا هولين ال double

NOT

ما بقدر انا عن هاي 2 بحاله A



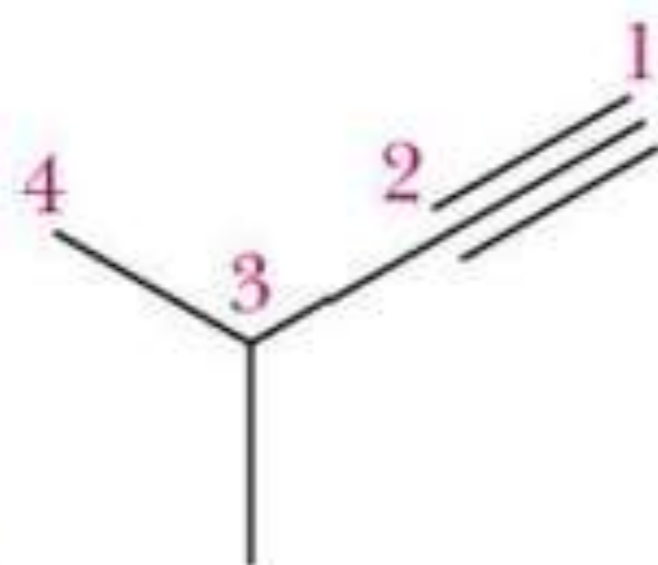
4,6-Dimethylcyclohexene

بال حاله ج تكون ال double bond دائما رقم 1 فعنا هيارين ال double bond... A or B ولكن هون ج يفتق معنا رقم ال Substituent

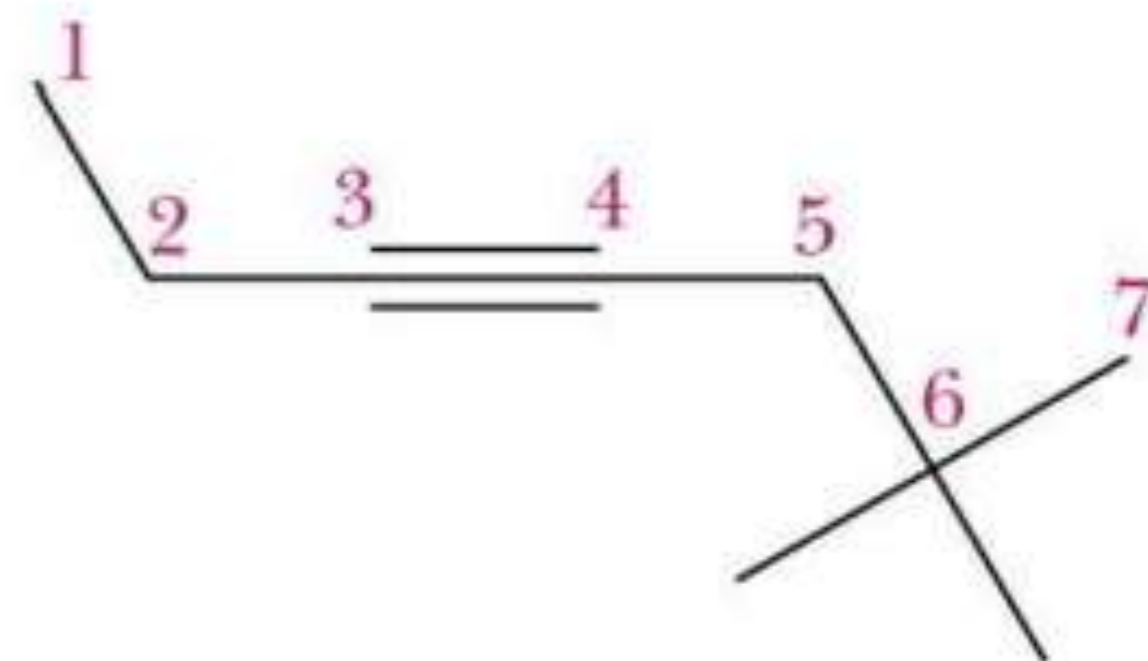
IUPAC nomenclature of alkynes

تسمية الكيرك

- Use the infix **-yne** to show the presence of a carbon-carbon triple bond.
- Number the parent chain to give the 1st carbon of the triple bond the lower number.
- Follow IUPAC rules for numbering and naming substituents.



3-Methyl-1-butyne



6,6-Dimethyl-3-heptyne

- Common Name:

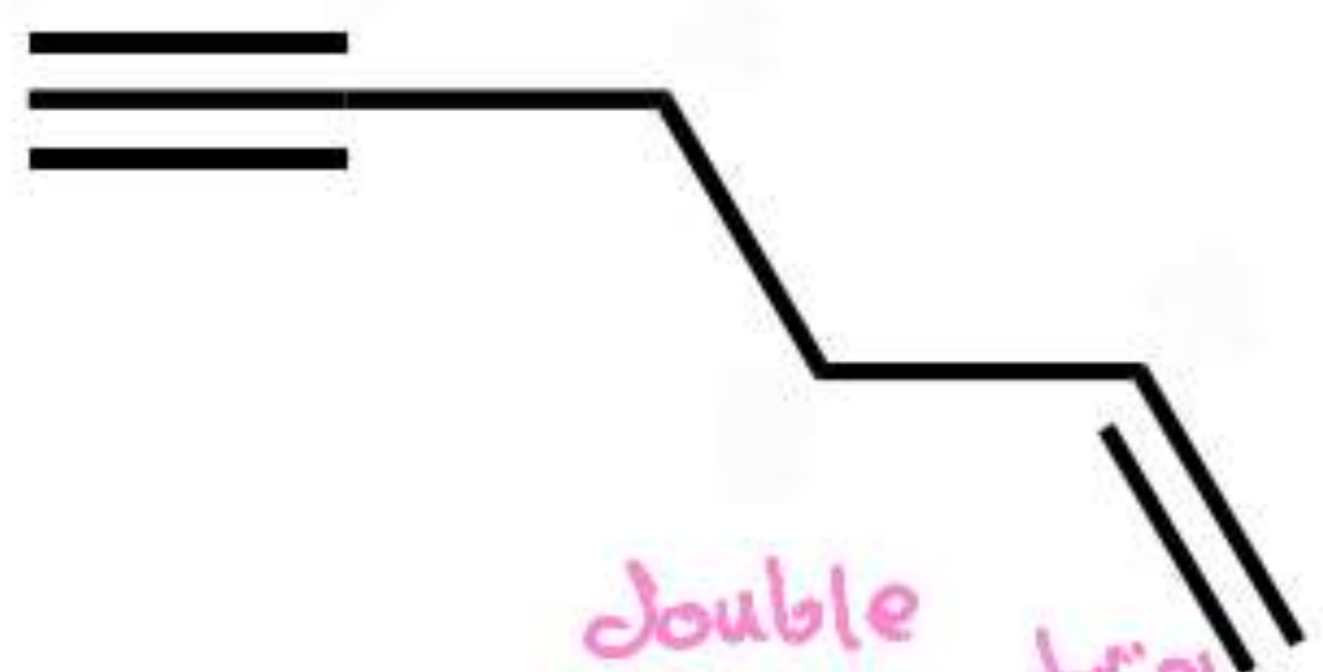


acetylene

(ethyne)

← the simplest alkyne

double + عتا
triple
سقف المركب



الطويلة
Double
triple
Hex-1-en-5-yne

* The same priority
الاهم نفس الأولوية
لو عدنا يميناً ← Double (1)
+ triple (0)
ولو عدنا يساراً ← Double (5)
triple (1)

لأنه في الحالة لازم اعطي ال double bond
أقل رقم

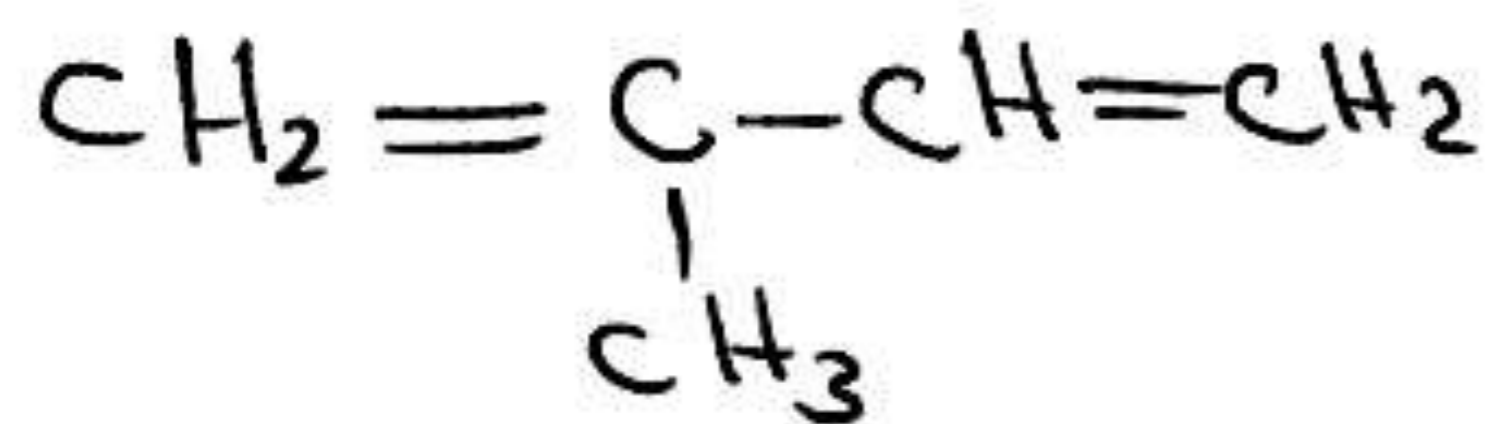
هنا
تكون
الترتيب
* ما ننسى
ارقامهم



(2E)-Oct-2-en-6-yne

لأنه انشوها
صنعتي
عنها بغيرين

* 2 Double bond at the same molecule:-



2-methyl-1,3-butadiene



1,3-cyclohexadiene

* منتظر الطول
سلسلة ومنتظر
ترقيم ومنتظر
اهتمام الفرع

لكن ما رخ غاب ene
رخ تحي diene
لانه عنا 2 ene

Alkene عبارة عن

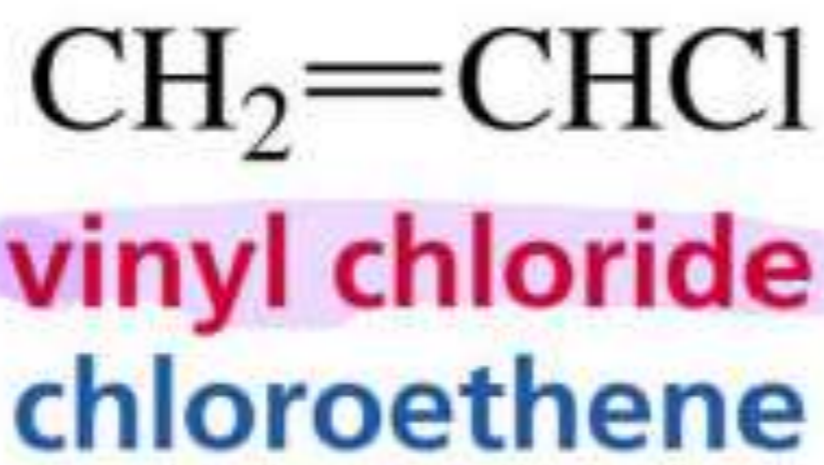
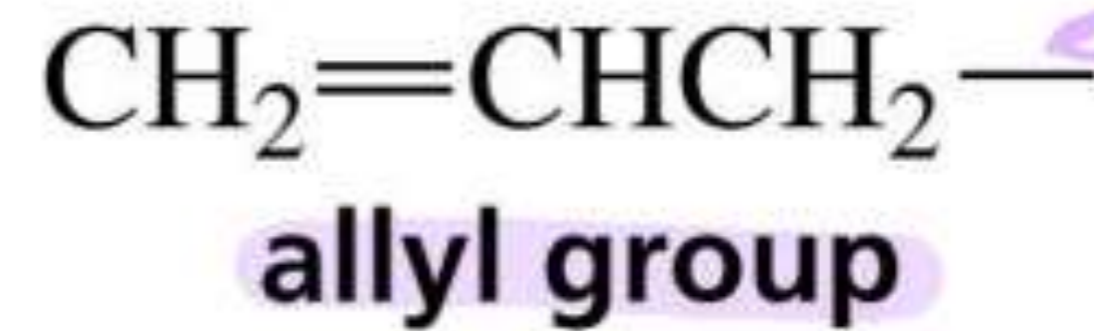
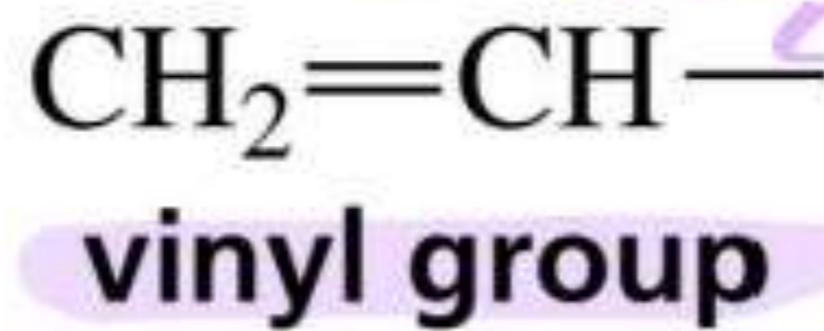
Vinyl and Allyl Groups

تفسر مبدأ الـ isobutyly
الـ tert-butyl والآخره

A vinyl group is the smallest group that contains a vinylic carbon.

An allyl group is the smallest group that contains an allylic carbon.

يمكن استخذه منهم بحاله
اذا كانوا branches
او قتي Common name



common name:
systematic name:

تفسر المبدأ
R-X
Alkyl halide

The substituent is on the vinylic or allylic carbon.

as a substituent



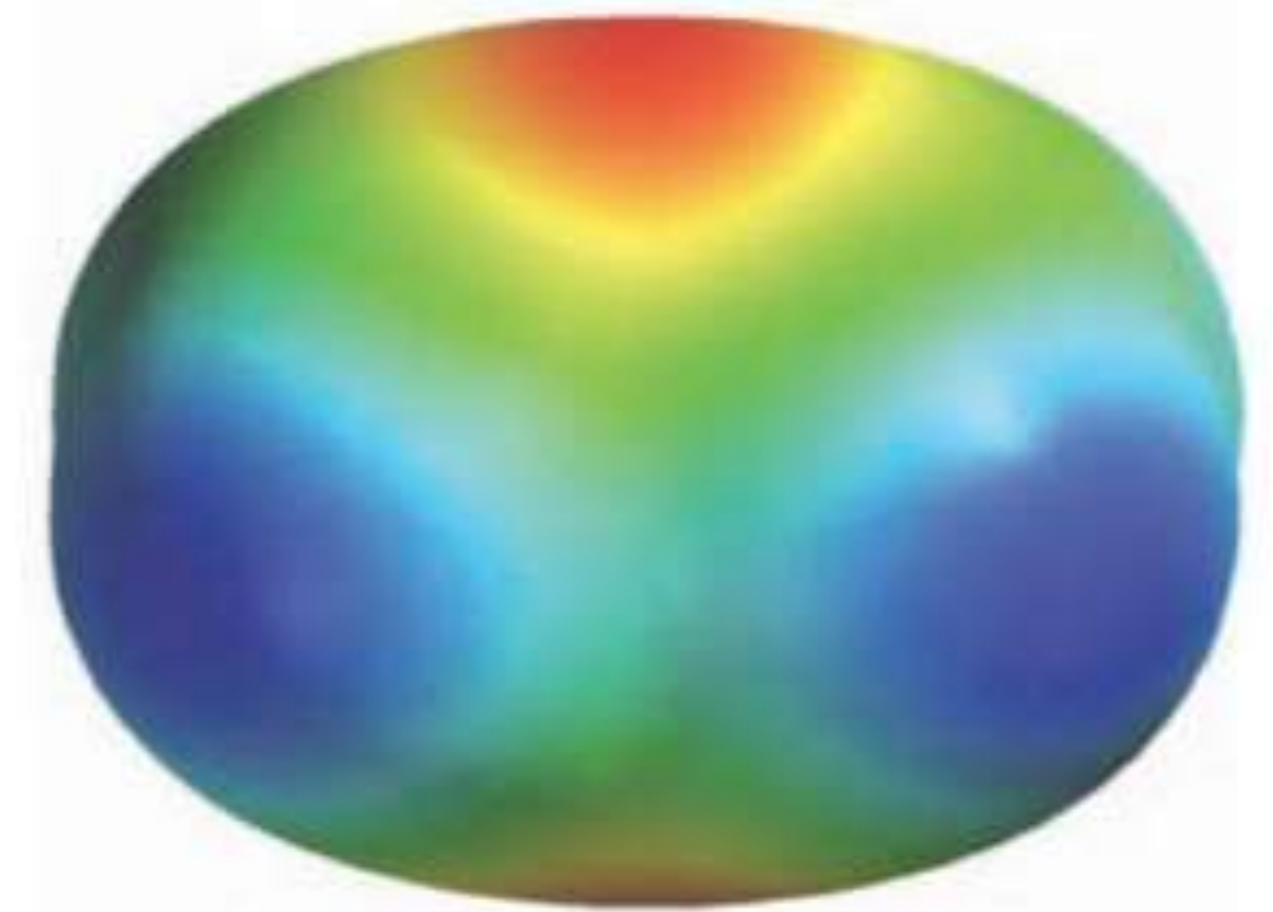
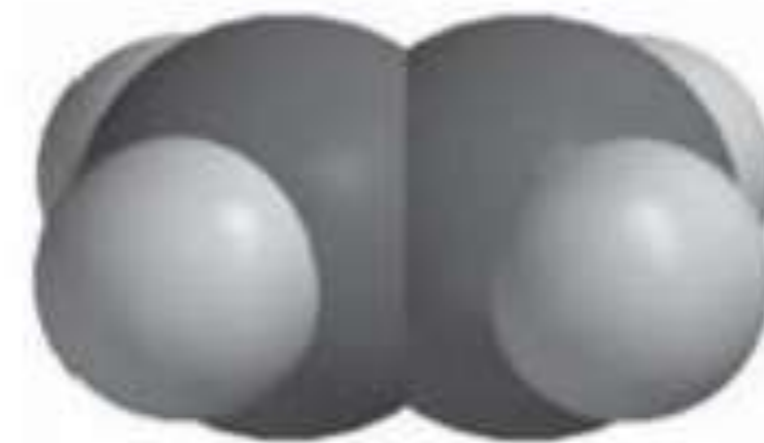
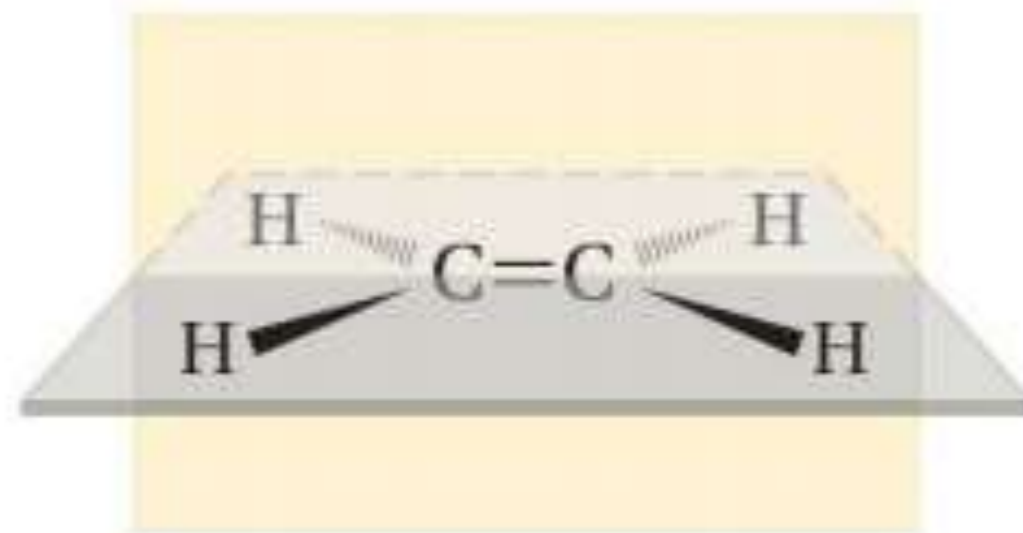
Bonding in Alkenes

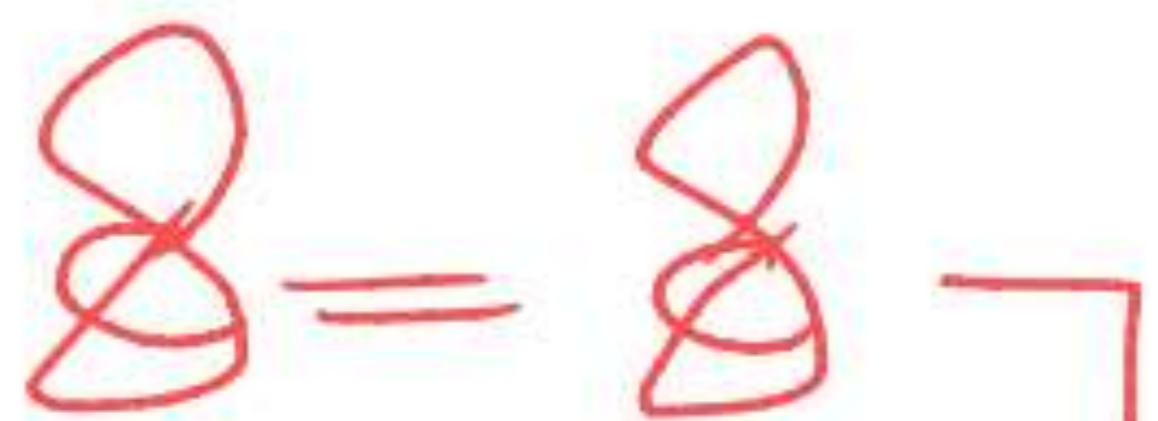
- Alkenes are sp^2 hybridized
- Trigonal planar – bond angle $\sim 120^\circ$
- 3 σ and 1 π bond (or 2 single and 1 double)
- $C=C$ double bond $\sim 1.34 \text{ \AA}$
- The π bond lock the geometry to planar

تخطيطي

الرابطة اقوى واغوى من ار single bond

فيهم $2\sigma + 1\pi$ ولكن ار C الوحدة فيهم يتكامل $3\sigma + 1\pi$





← رابطة π تتكون عن طريق

2 parallel (p) orbitals

لـ يعني إذا P_x
لازم الثانية كمان
تكون P_x

لـ أيام الـ 6 كنا خيانه متقمر
تعمل rotation

ولكن روابط π ممكنة تعمل rotation
ولكن لو عمسها الموضع رح يكافئ
طاقة كثير لانه انا جاية ابي الحمر الـ

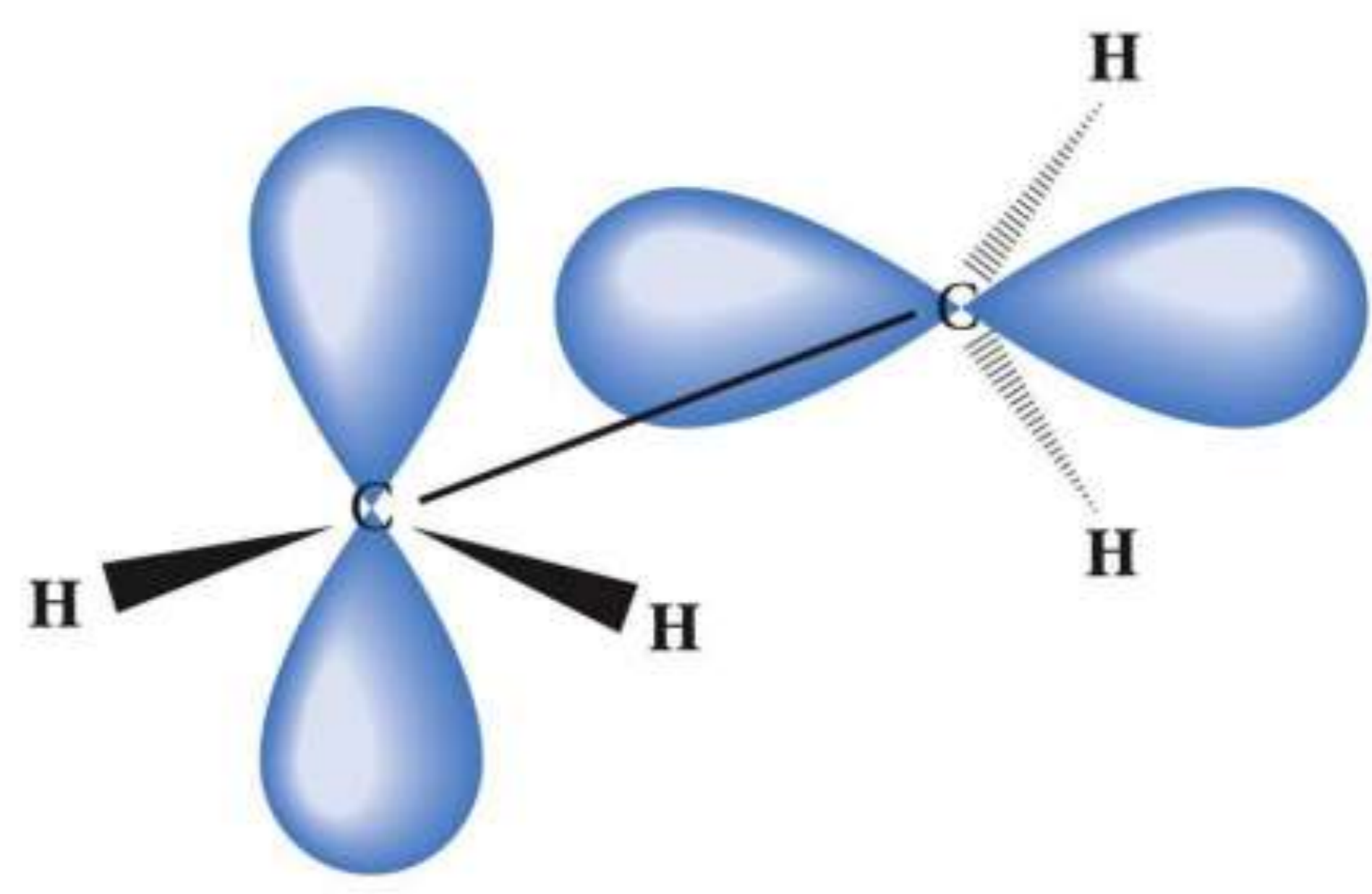
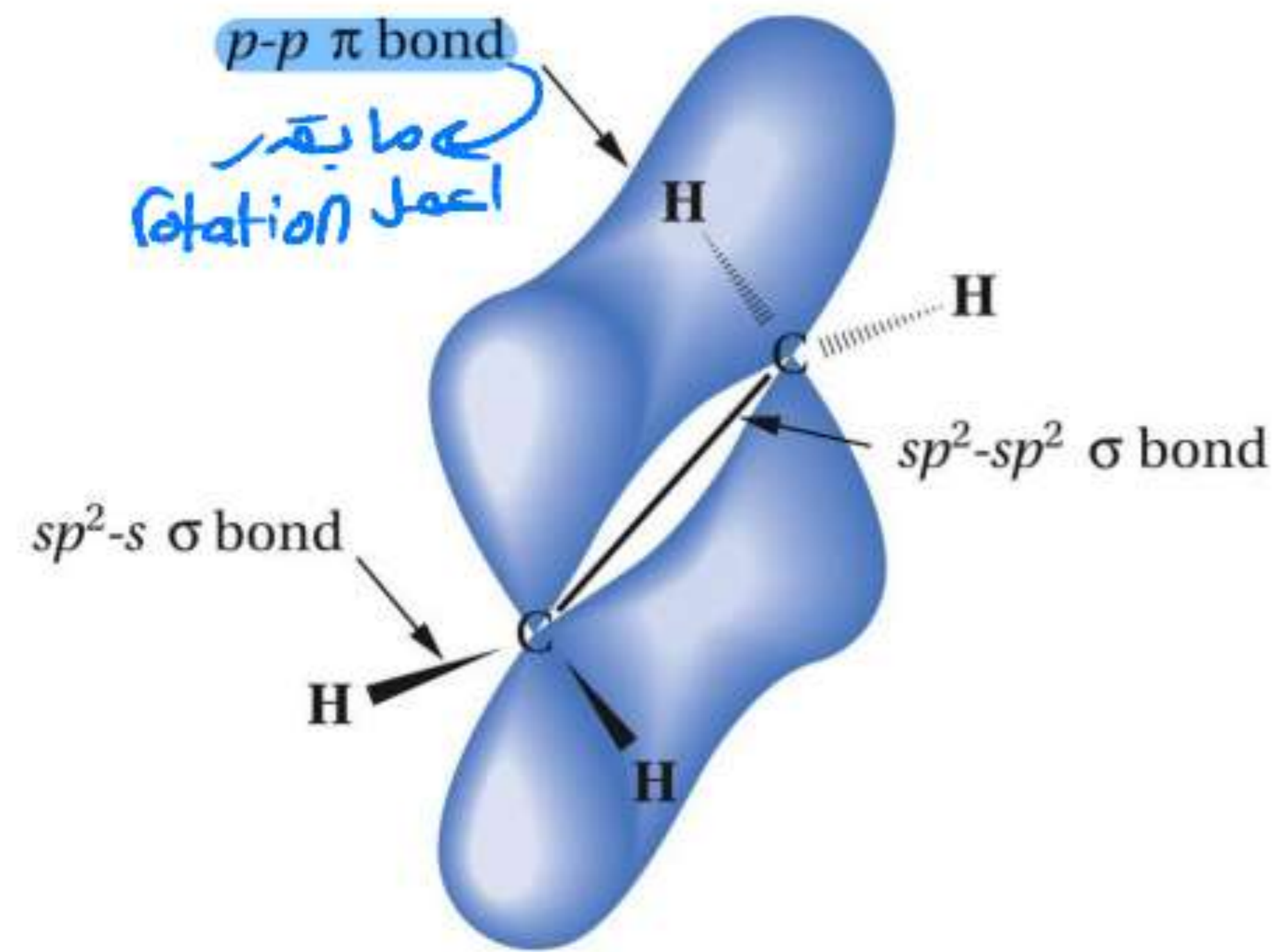
π bond
← لهية

There is no rotation
around π bond

عشان ممنوع ال rotation
هاد الكيمياء بتكوننا لو بود بسج Geometrical isomers

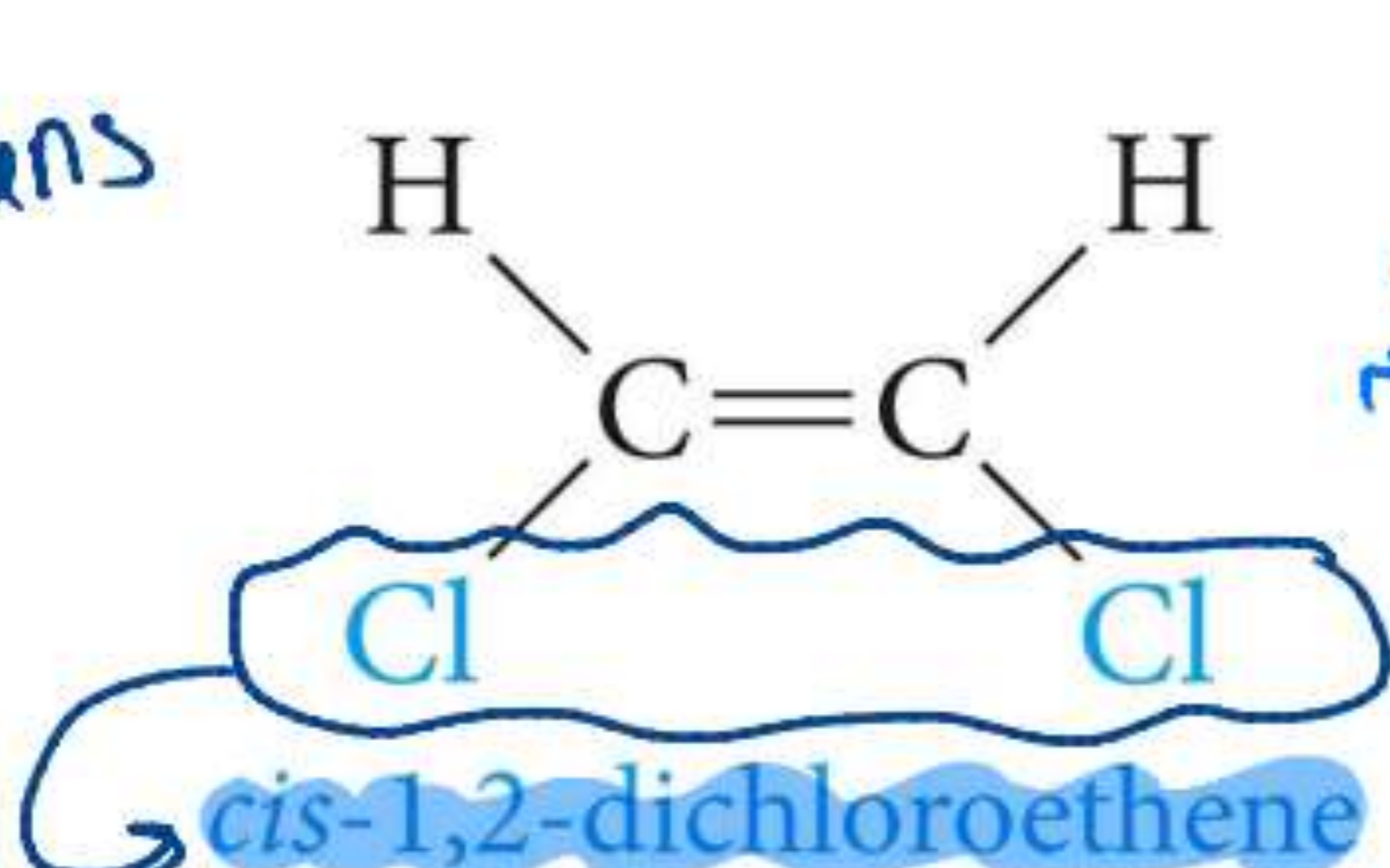
Cis - Trans Isomerism

The double bond in an alkene is rigid, that is it will not rotate freely. Therefore substituents on the carbon atoms will produce geometric isomers the same as on a cycloalkane ring.



If the two non-hydrogen atoms or groups are on the same side of the double bond it is a cis- arrangement, on opposite sides a trans- arrangement, i.e.

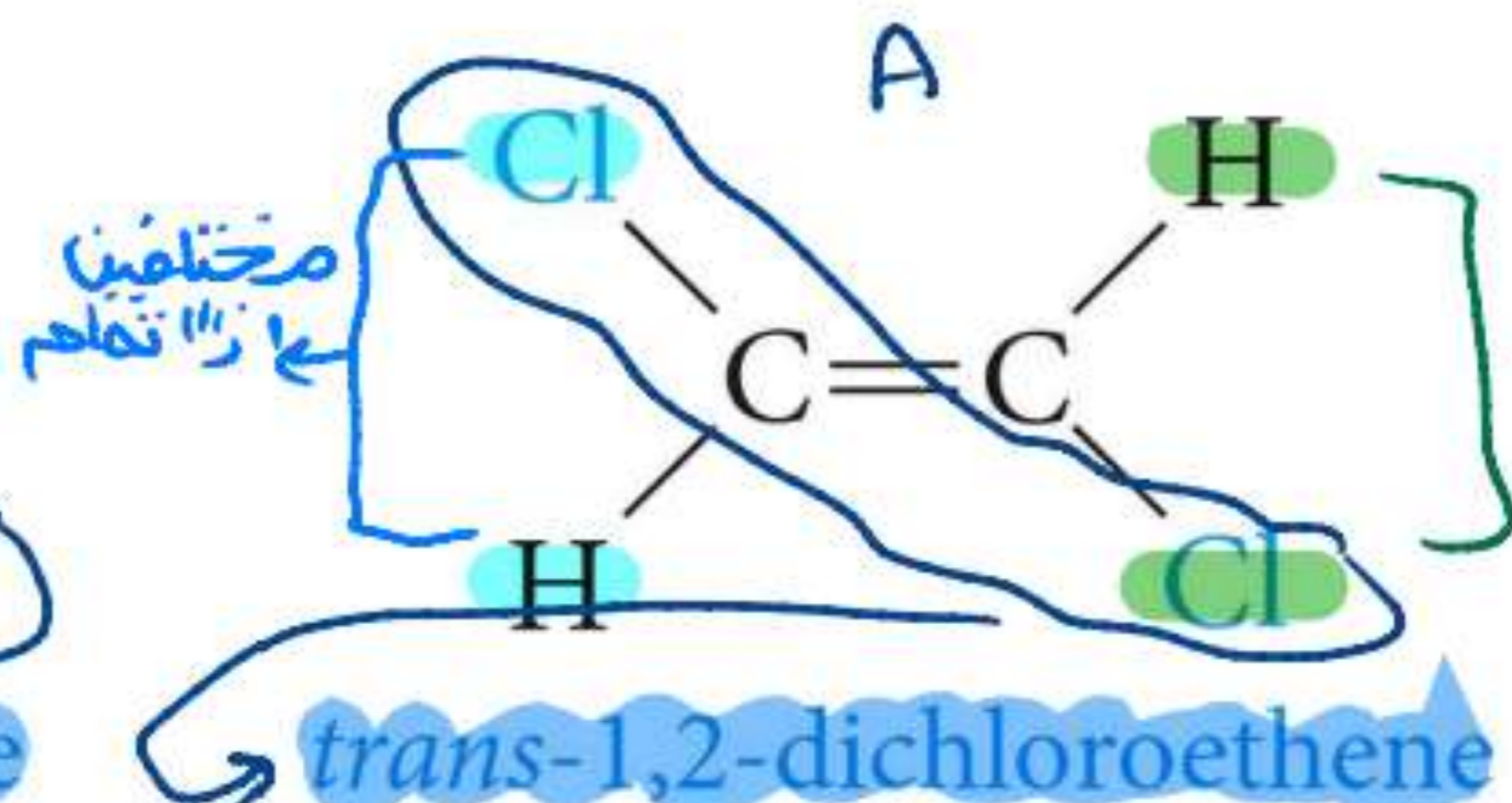
سؤال على
Cis-trans



cis-1,2-dichloroethene

bp 60°C , mp -80°C

cis boiling point



trans-1,2-dichloroethene

bp 47°C , mp -50°C

مختلفين
از زاوية تمام

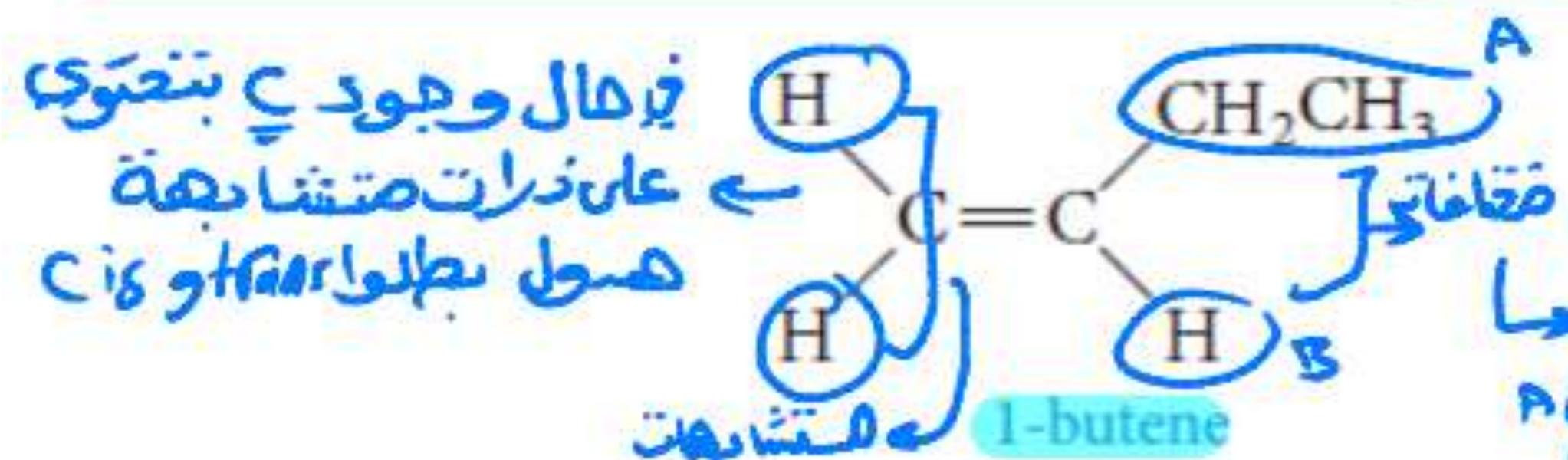
عكس ال conformers
اللي كنا في عندهم
زي بعض

Note that they have different physical properties, this is because their dipole moments are different.

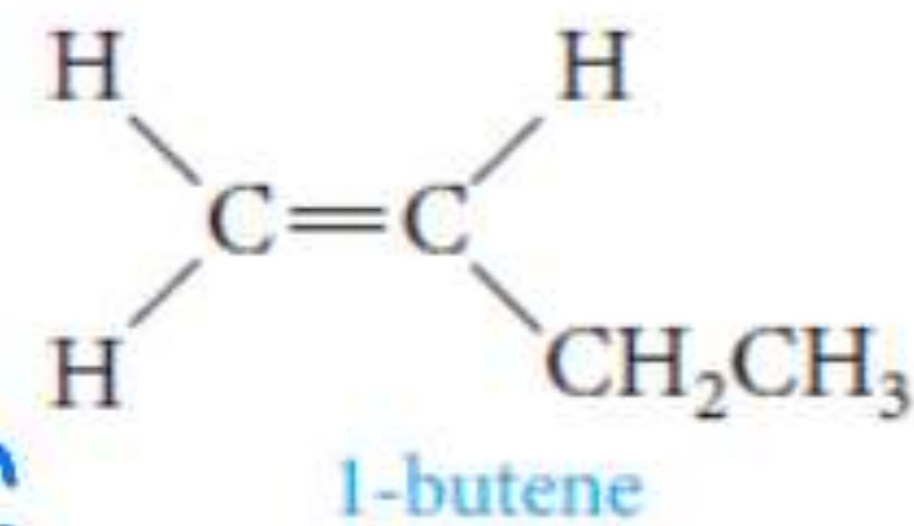
* Trans is more stable than Cis

For *cis-trans* isomerism to occur in alkenes, each carbon of the double bond must have two different atoms or groups attached to it.

منه يكون في عندي *cis-trans* isomer



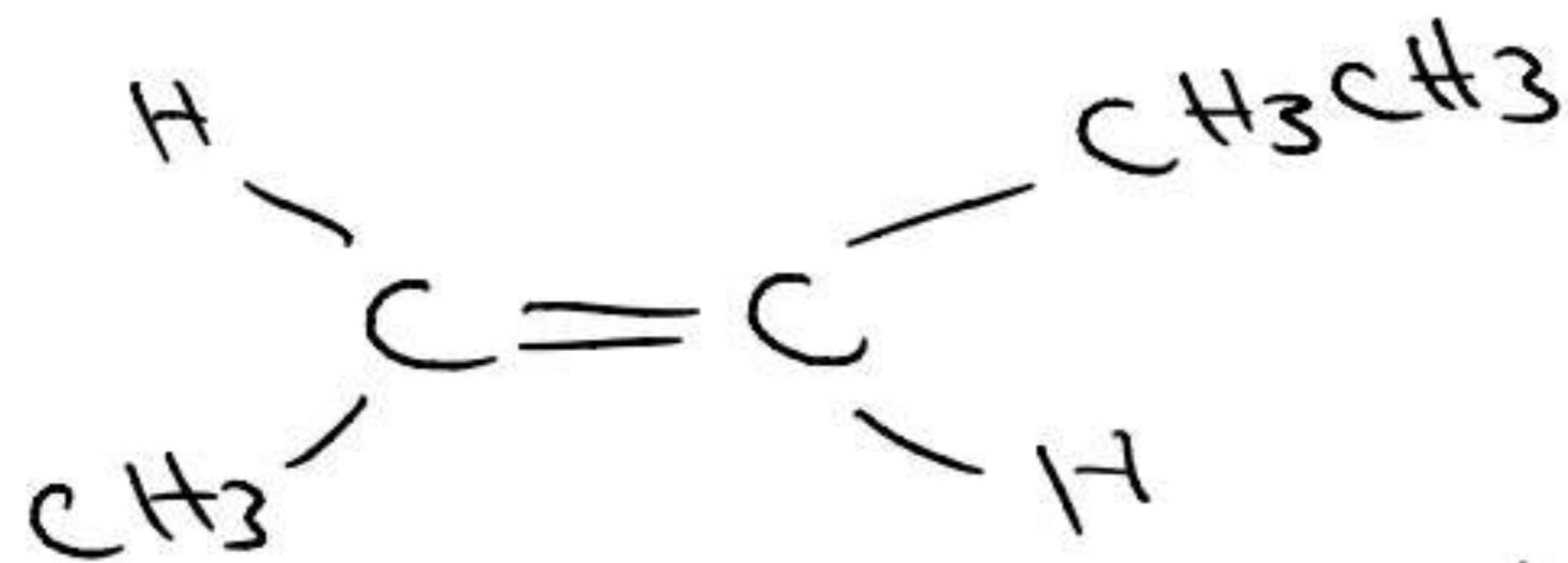
is identical to



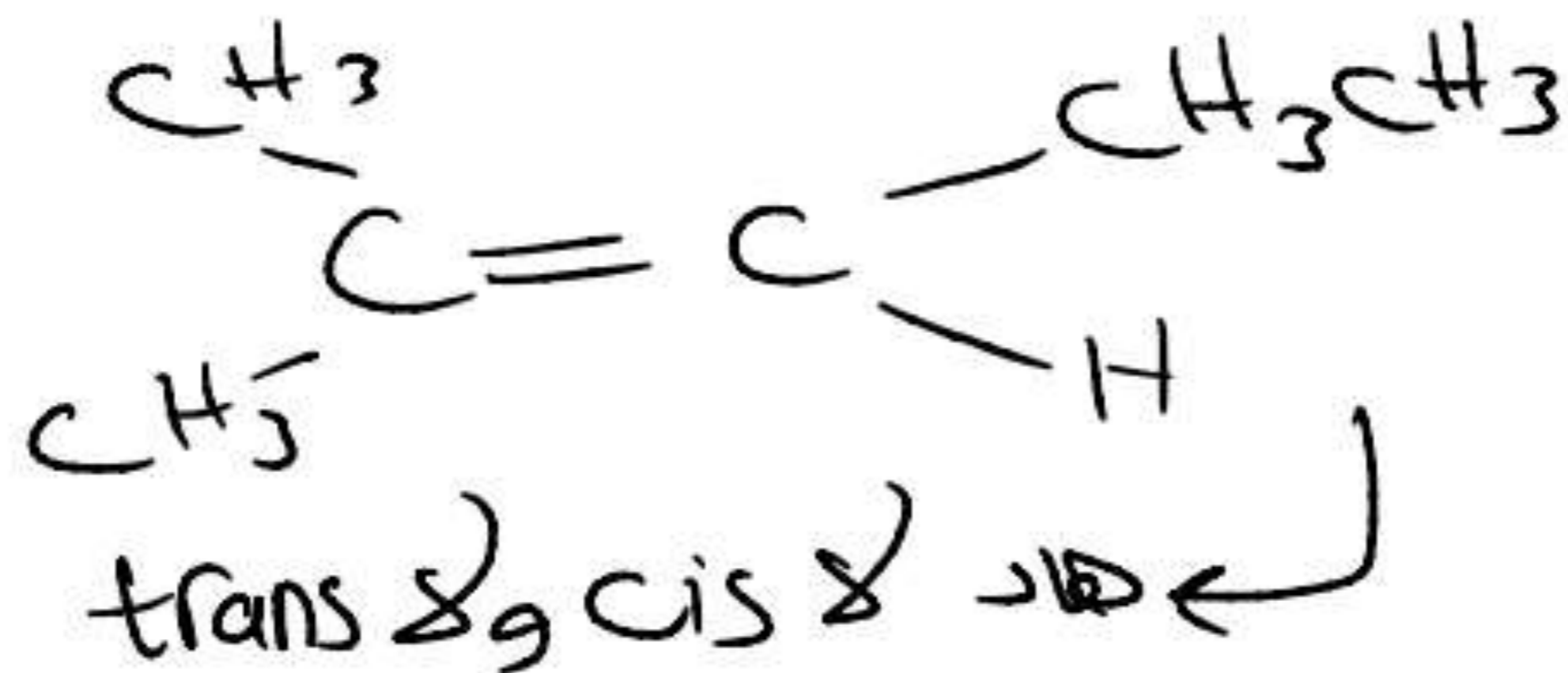
همزمو دنا ولا
trans لانها لو عطينا
rotation وعكست مكان
A و B وكان B - A
رح بطلعوا نفس الشيء

فتي امكنه انه
في عندي Cis
or trans
لكل مجموعة وشوف
الذرات اللي معها
از مو صتا بهين
از زاوية تمام
زي A فوق
له بالازرق والافقر

في حال وجود C بنصوي
عاز ذرات صتتبا به
هلوا *cis* و *trans*



← هل ممكن يكون هون Cis or trans
 ← Yes وهو مطلوب منا هون نعرف
 إنا هي Cis و trans



صمم لفهم التفاعلات

Polar reagents can be divided into :



Polar reagents ممكن يكونوا

(+) Nucleophiles nucleophilic like

A nucleophile has

electron rich وغالبًا يكونوا

a negative charge,

a lone pair,

or a π bond.



these are nucleophiles because they



have a pair of electrons to share

Electrophiles like

electron poor or positively charged

An electrophile has

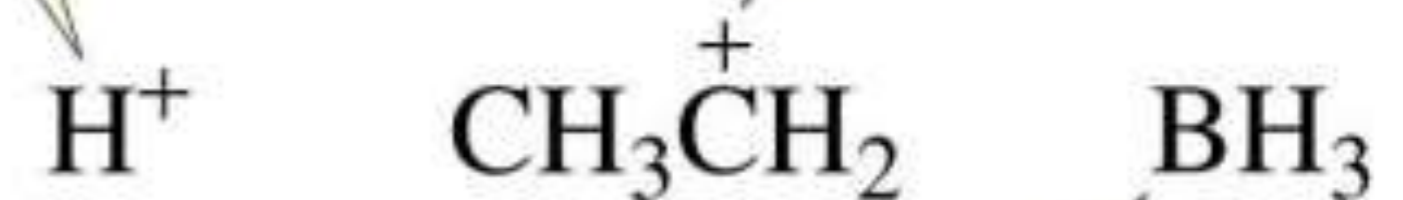
a positive charge,

a partial positive charge,

or an incomplete octet.

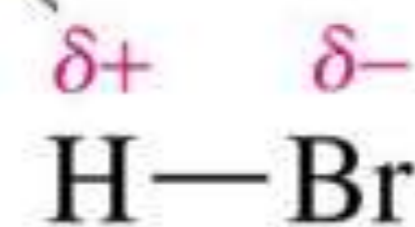


these are electrophiles because they have a positive charge



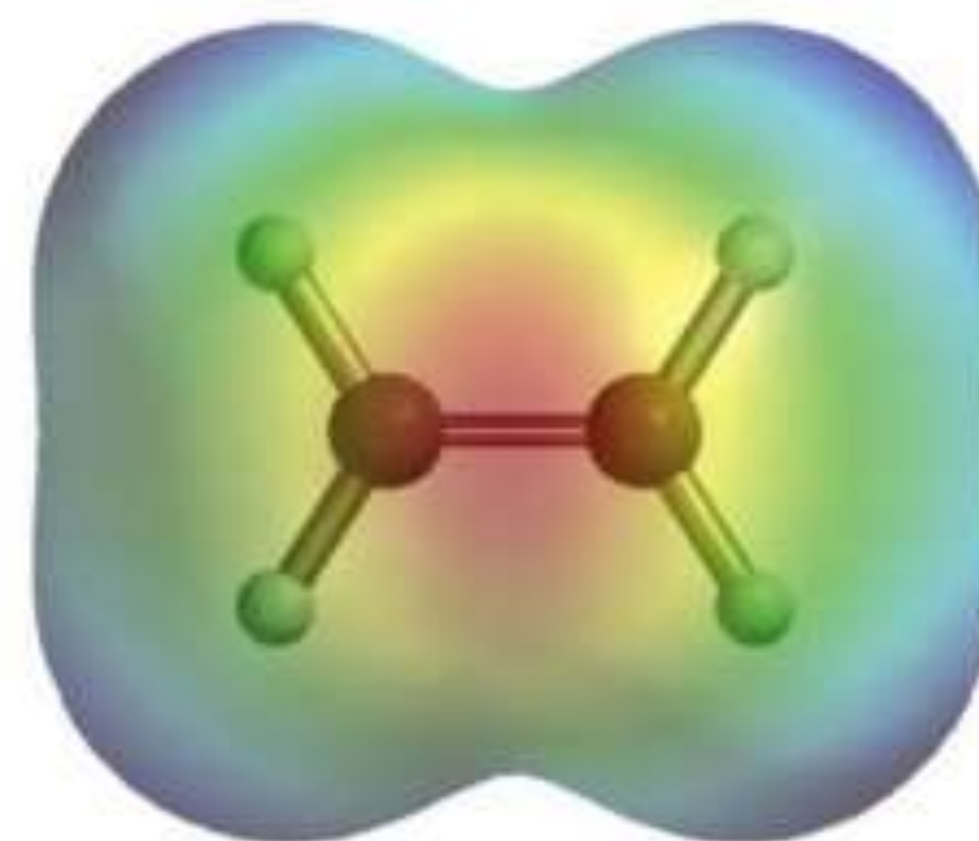
this is an electrophile because it has an incomplete octet

this is an electrophile because it has a partial positive charge



Chemical Reactivity

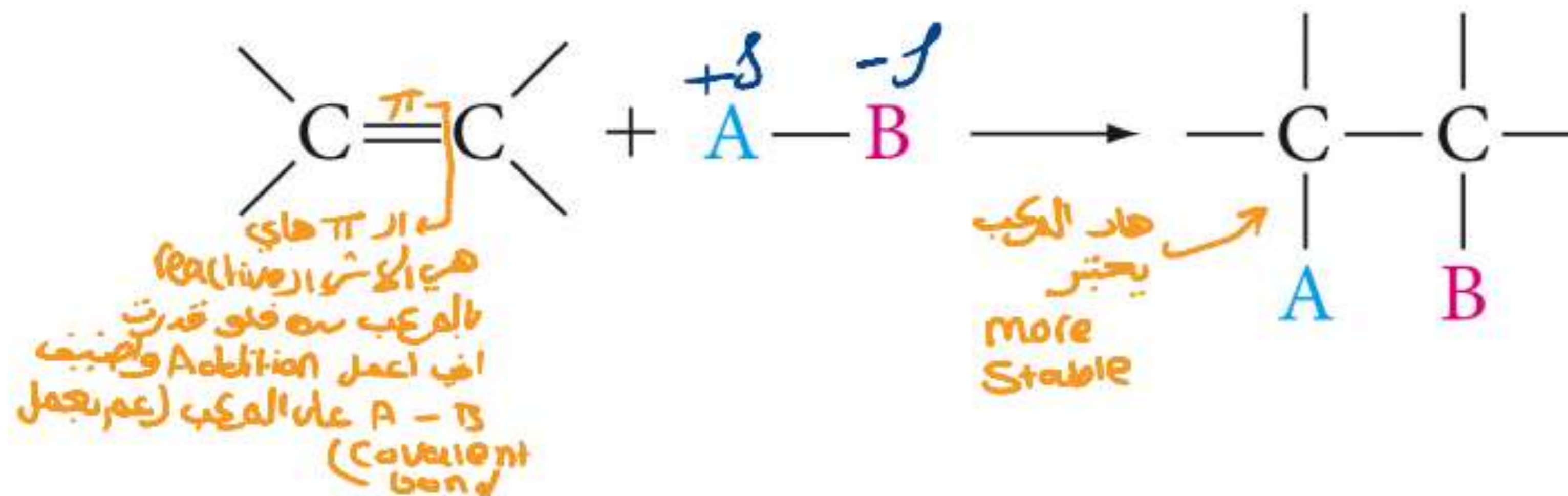
The chemical reactivity of alkenes arise from the π electrons. The π bond is weaker than the σ bond so these electron react first. The reagent will add across the double bond so these are



addition reactions.

الكيميائيات يجمعوا بتفاعلات
ال addition

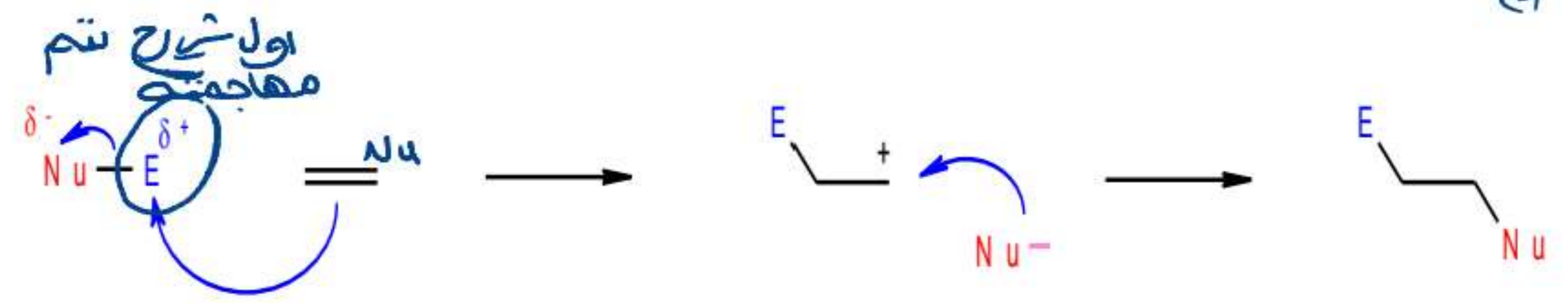
كيث ابي انا بضيف
additional Reagent





Electrophilic Addition Mechanism

The basic mechanism is the same for all reagents, a two step reaction where an electrophile (E) add to the π bond in the first step creating a **carbocation** intermediate. A nucleophile (Nu) then adds to the carbocation in the second step.



وارتبطت بها الحرة
 الاخر، يعني هون Cl
 ح تافده
 وح تفسر Cl⁻



لواحييت خطيت
 double bond
 معها، وقتها ح
 تروح باتجاه H

له وهاد اللي يهيس فعليا

انها ال C=C او π
 (Nucleophile) ح

تروح على الجزء الموجب

ح تحتاجه هي E^x

را = ح تحتاج H

له وقتها تجر ال H
 لو هذ من ال C تتكونها
 وتكون معها رابطة



كيف يتم التفاعل؟

هنا π هي عبارة عن

nucleophiles

شخصتها سالبة ويتجذب

الاشياء الموجبة

له الهيكل ح تفسر

تجذب عن اشياء

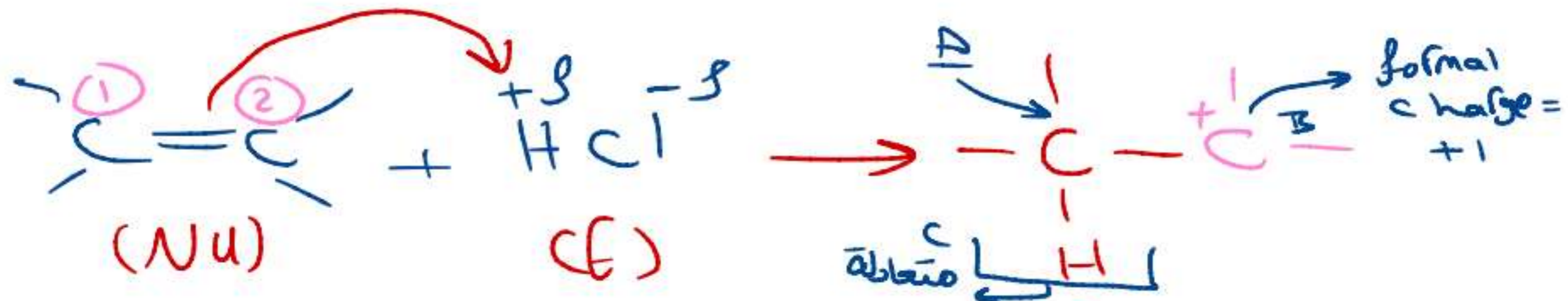
Electrophiles

ح تفاعلها

← والدمان Electrophiles

هون غالباً ما يكونوا

كالهم



له هو ال E هو ال H
 لهي ال = رح تروح على ال H
 ورح تافدها ونعمل معها رابطة
 و Cl + H ال رابطة رح تنكسر

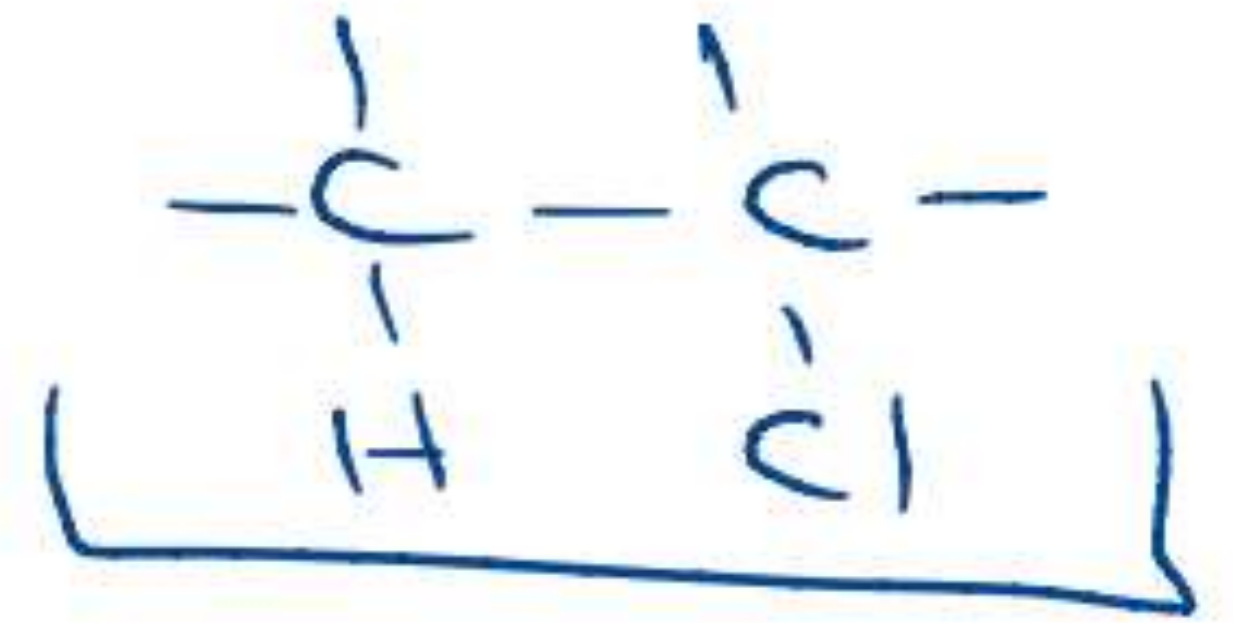
وهذه من ال C
 رح تافدها
 ويجيب من ال C
 ال C
 و ال π راحت لانها
 هي اللي هاجت وافتت
 ال H

المركب اللي نتج اسمه
 → Carbocation
 لانه في عندي (C) (B) عمات
 3 روابط وعليها charge (+)

Formal Charge ← (A) C
 الها هف ← متعاطة
 C (2) هار معها 3 روابط ← B
 و ال formal charge الها ← (+1)

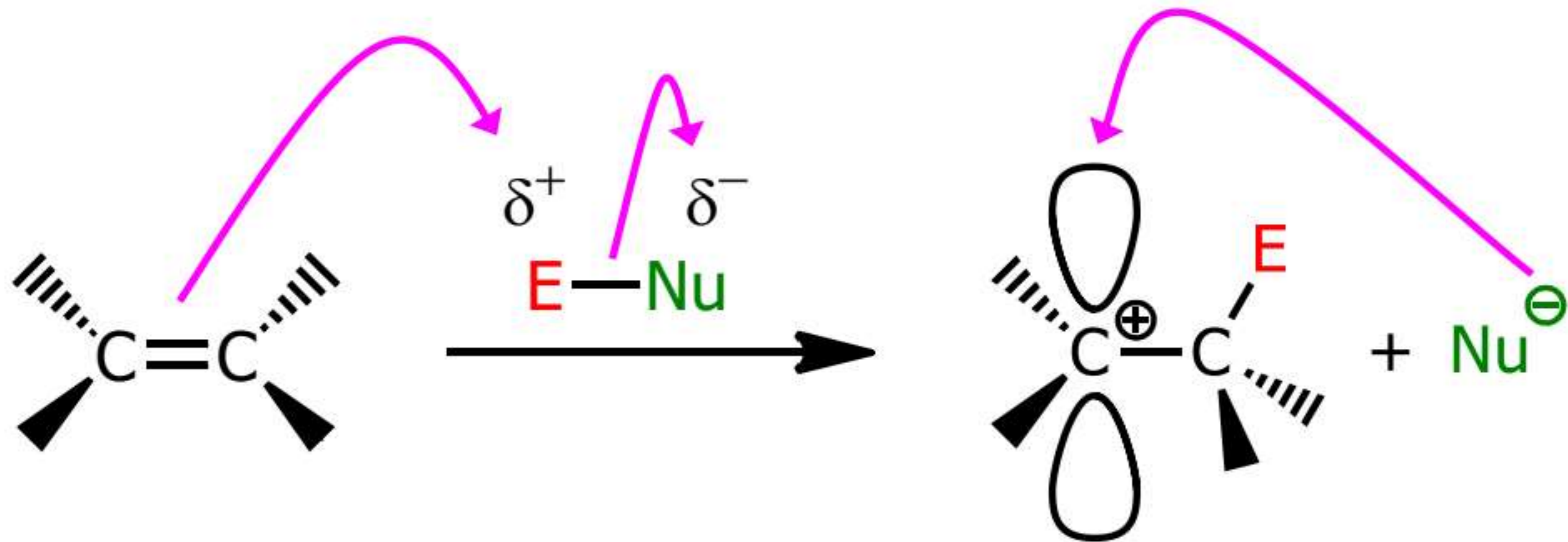


Carbocation
intermediate

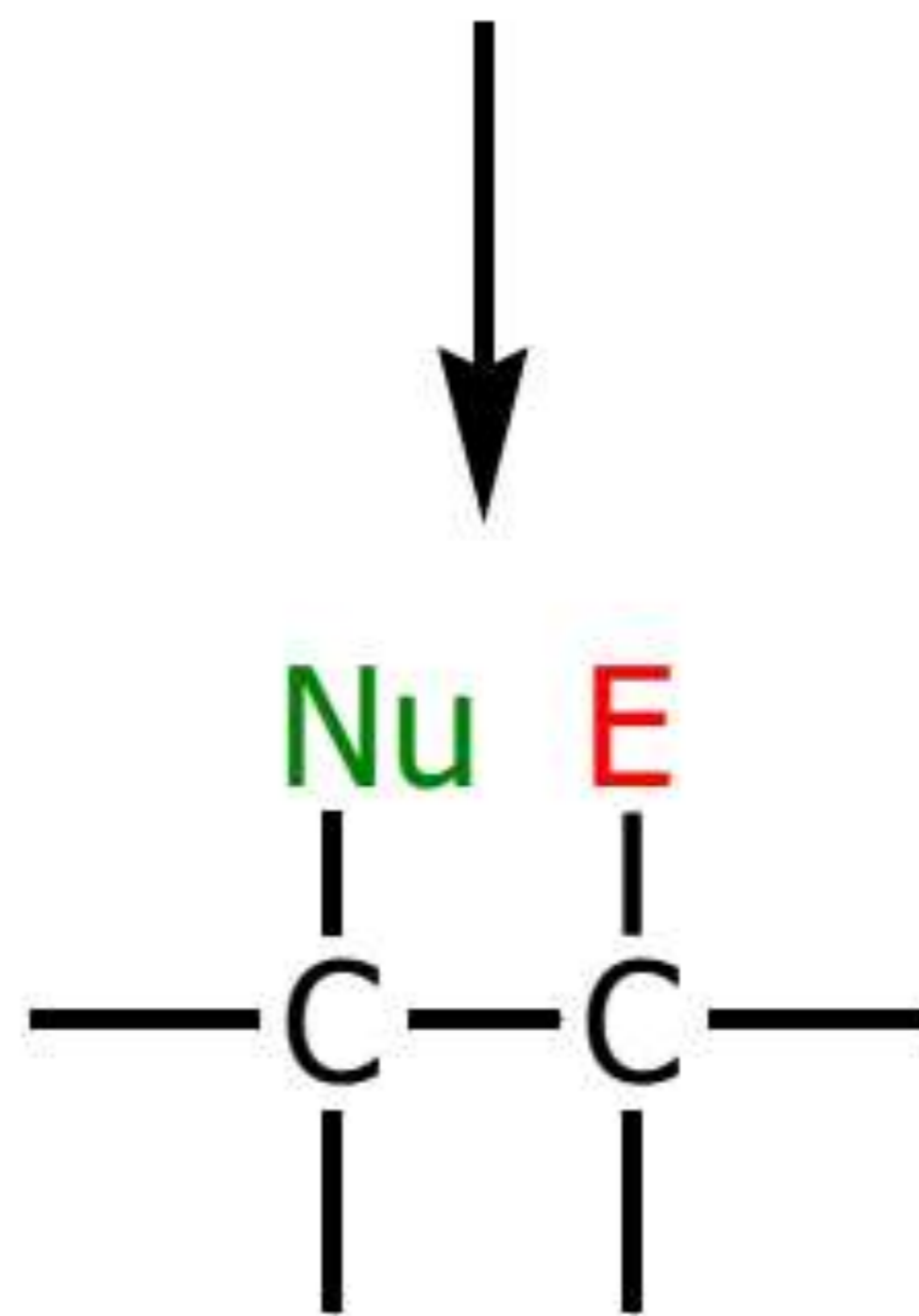


هذا اللي نتج رح يكون Electron poor
 لأنه عنده (+)

لهيك رح يتصرف ك Electrophile
 لهيك ال nucleophile رح تكسرتور
 عليه واللي هي - :C



↪
mechanism
تأثير ال
addition to
alkene
(in general)





Organic chemistry

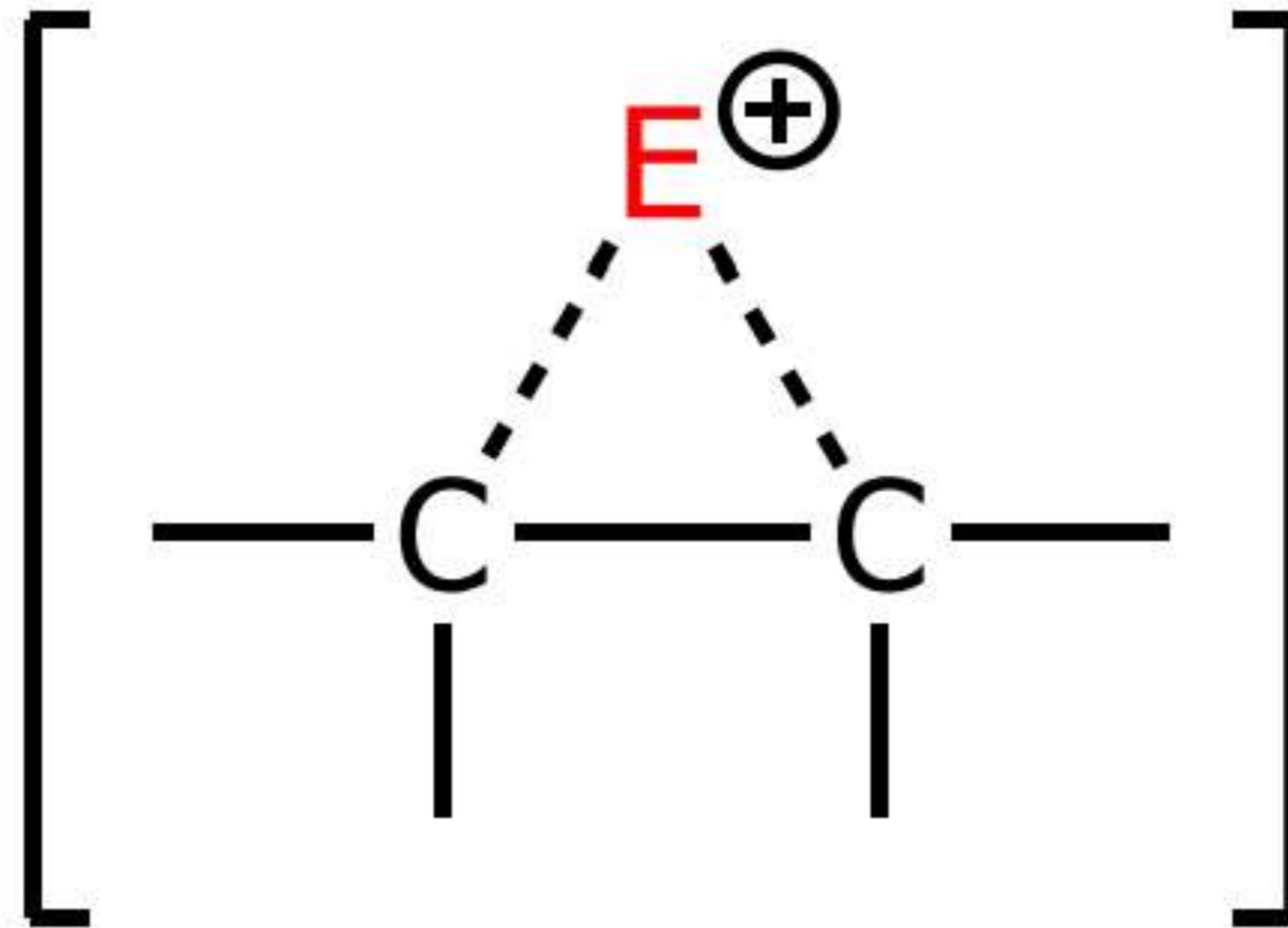
Lec: 8 + 9

Done by: Shahed Zaytoon

Carbocation في بعض الأحيان
يأتي كجدار
bridge

❖ Mechanism

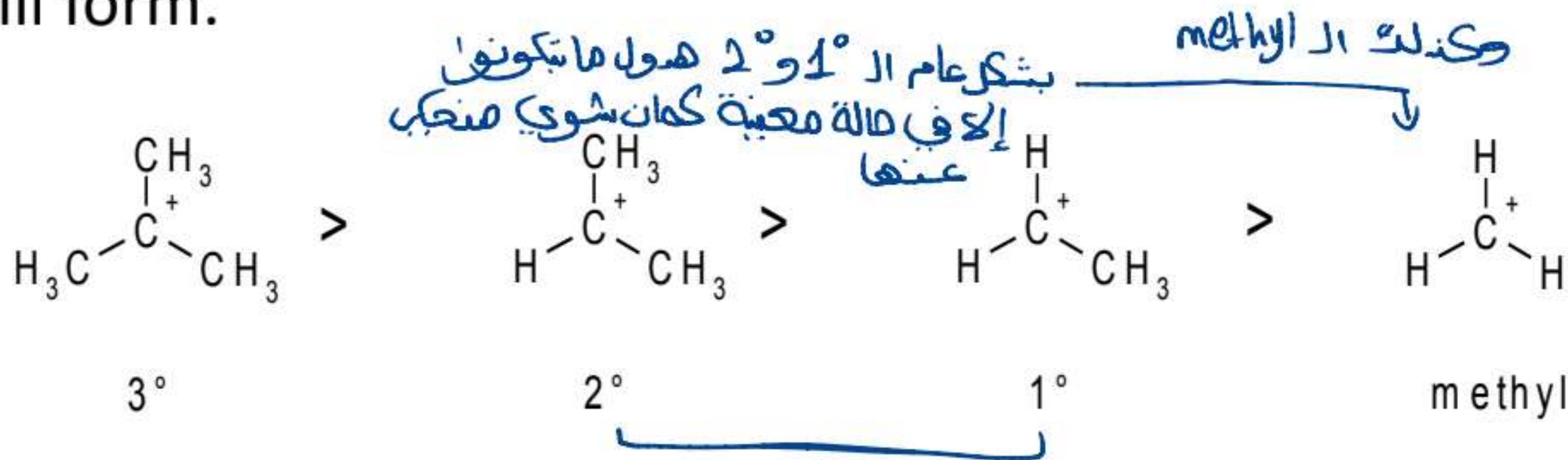
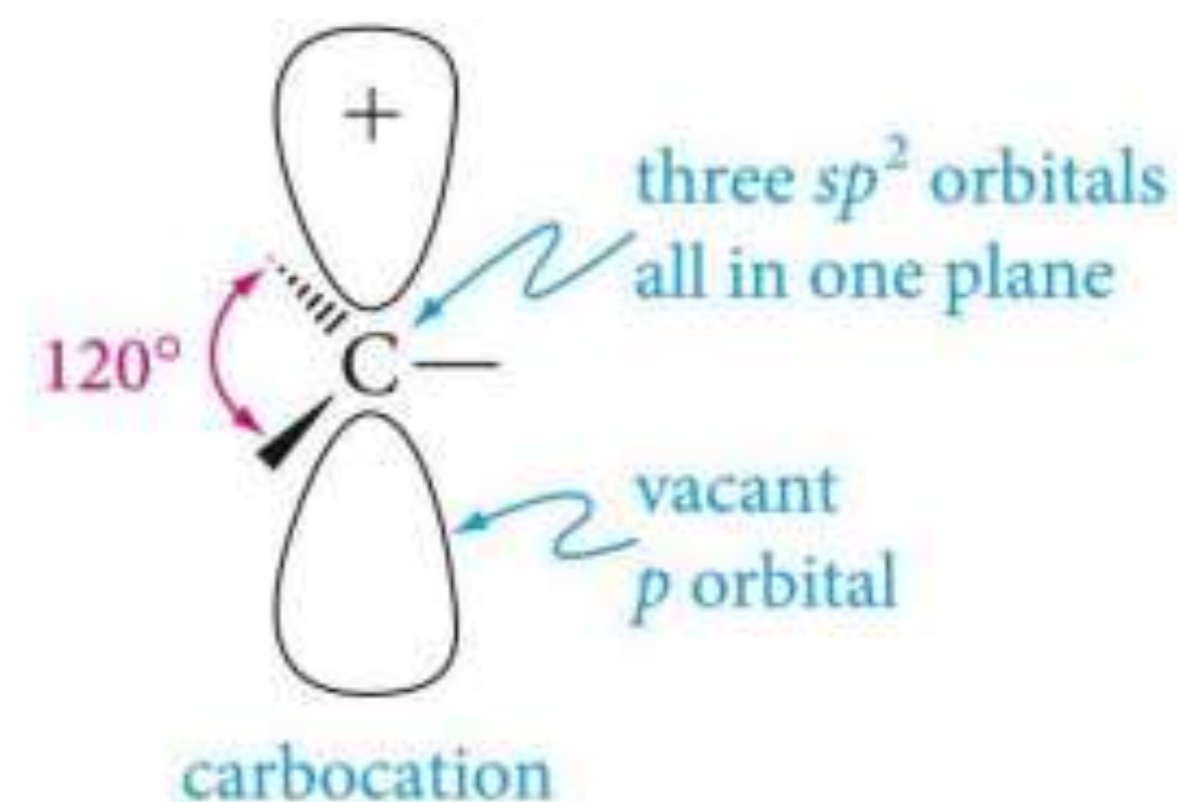
- Sometimes do not go through a "free carbocation", may go via



الخطوة الأولى هي
الخطوة الرئيسية الأخرى
إضافة A-B

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.



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

Carbocations

وفي اعني هالة وحدة اللي هي



ال methyl

ال ان انا رهنين ال (Stability)

مين اكثرهم Stable وشو همن

ال factors اللي باثروا عليه

* Note: وجود ال R groups حوليت ال

بنيد ال Stability

يعني انما كان حولين ال C سه (tertiary) 3R

هار يكون the most stable one مقارنة

بال 2° وال 1° وال methyl

* تقسم ايا ثلاثة انواع :-

1- منتفح على ال C اذا كان حوليها او يعني شايكة مع 3R

لهذا يهينف as tertiary Carbocation

2- ممكن ال C تكون رايكة مع

2R ومعاهم H

لهذا يهينف as secondary

3- وممكن تكون شايكة مع 1R

و 2H

لهذا يهينف as primary

* Note: ماد همن شو هب ال R كانت ميثيل / ايثيل وت ايفر المهم R

Carbocations (cont'd)

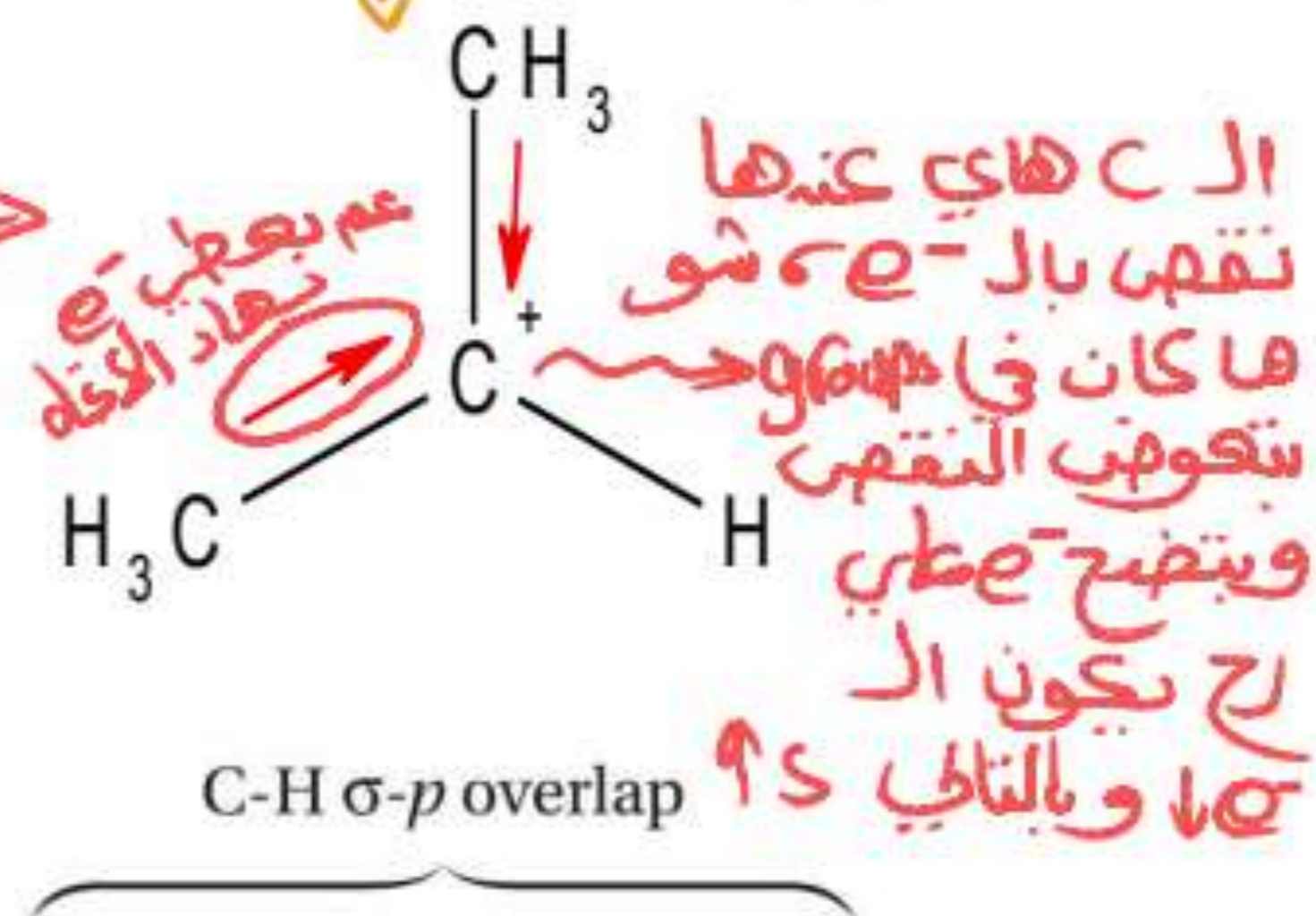
شو السبب؟ ليه ال 3° احسن هن ال 2°؟!
وال 2° احسن من ال 1°

The order of carbocation stability arise from three sources.

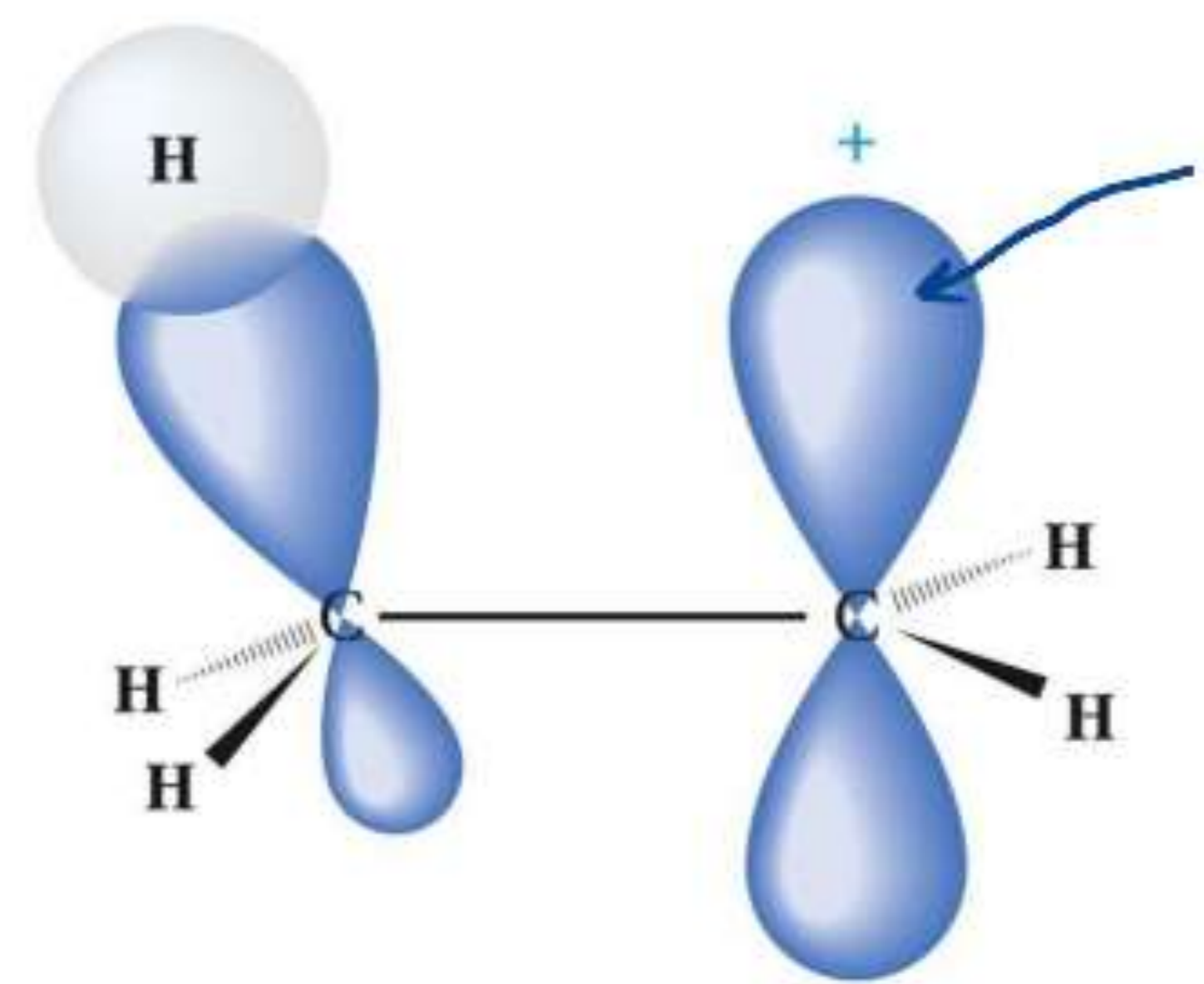
اللي هو انا اعم يعطي ع عبر ال 6

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.

① ال اولي تعتبر
e⁻ rich
من ال H



2) **Hyperconjugation**: this is a 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⁺.



2) Hyper Conjugation

فالقصة وما فيها كأنه أنا عندي 6 باي متوازياً

مع ال empty (P) orbital

له ورج يكون افضل لو كان عندي 6 كما ان

لما يكون عندي 6 كما ان

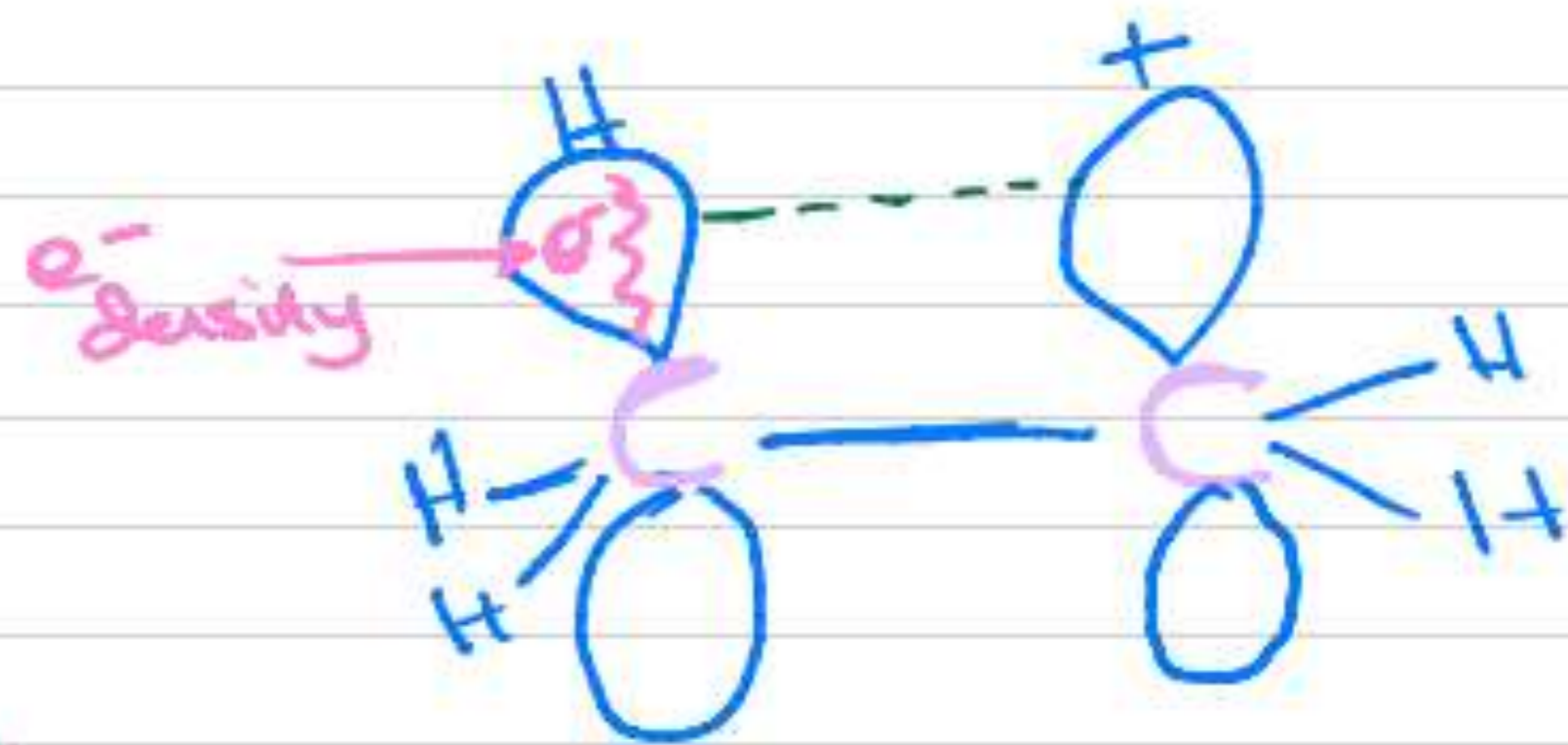
له فمدول عم بنفخوا e-density على ال empty

(P) orbitals به فعم بعملوا minimizing ال E

فيخفوا ال E وهيك أنا عم بزيد ال Stability

Note * ال Carbo cation هو مش Stable لأنه عنده empty p orbital وهو اللي معطيه ال (+)

← فهي حولها 6e⁻ فقط عشان هيك عندها نقص بال e⁻



← أنا عندي ال Carbo cation عندها ال empty p orbital ال C

له فلو عندي جنبها R وحدة من ال CH بالميشل عبارة عن e⁻ (اللي باللون الزهري فوق)

له وهاي ال e⁻ باي متوازياً مع ال empty p orbital

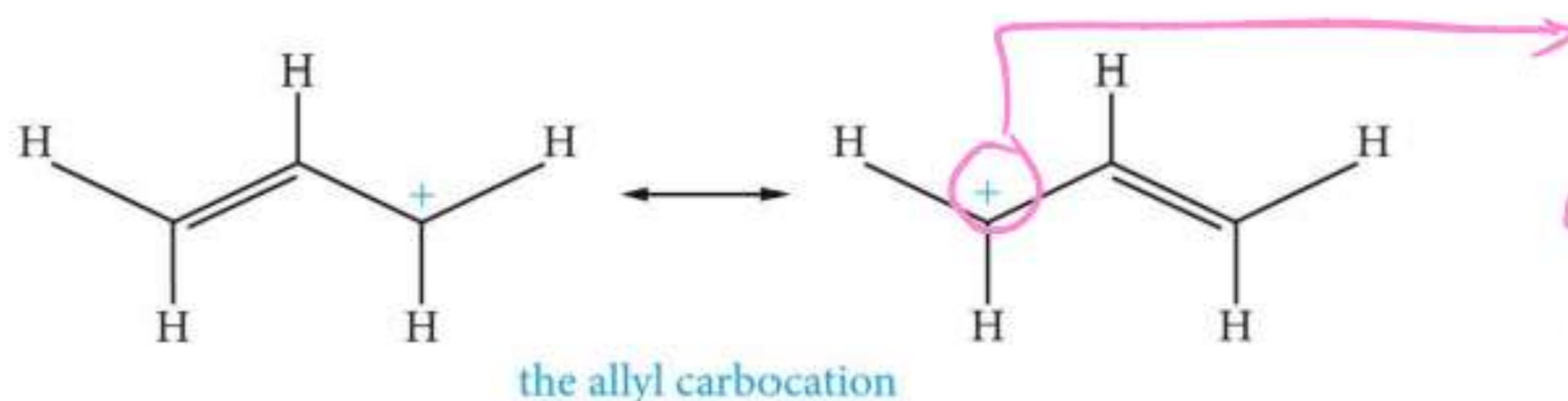
له هاد التوازي رح يهبر فيه نوع من ال (overlapping) interaction

له نفس قصة ال π ← δ-δ P-P

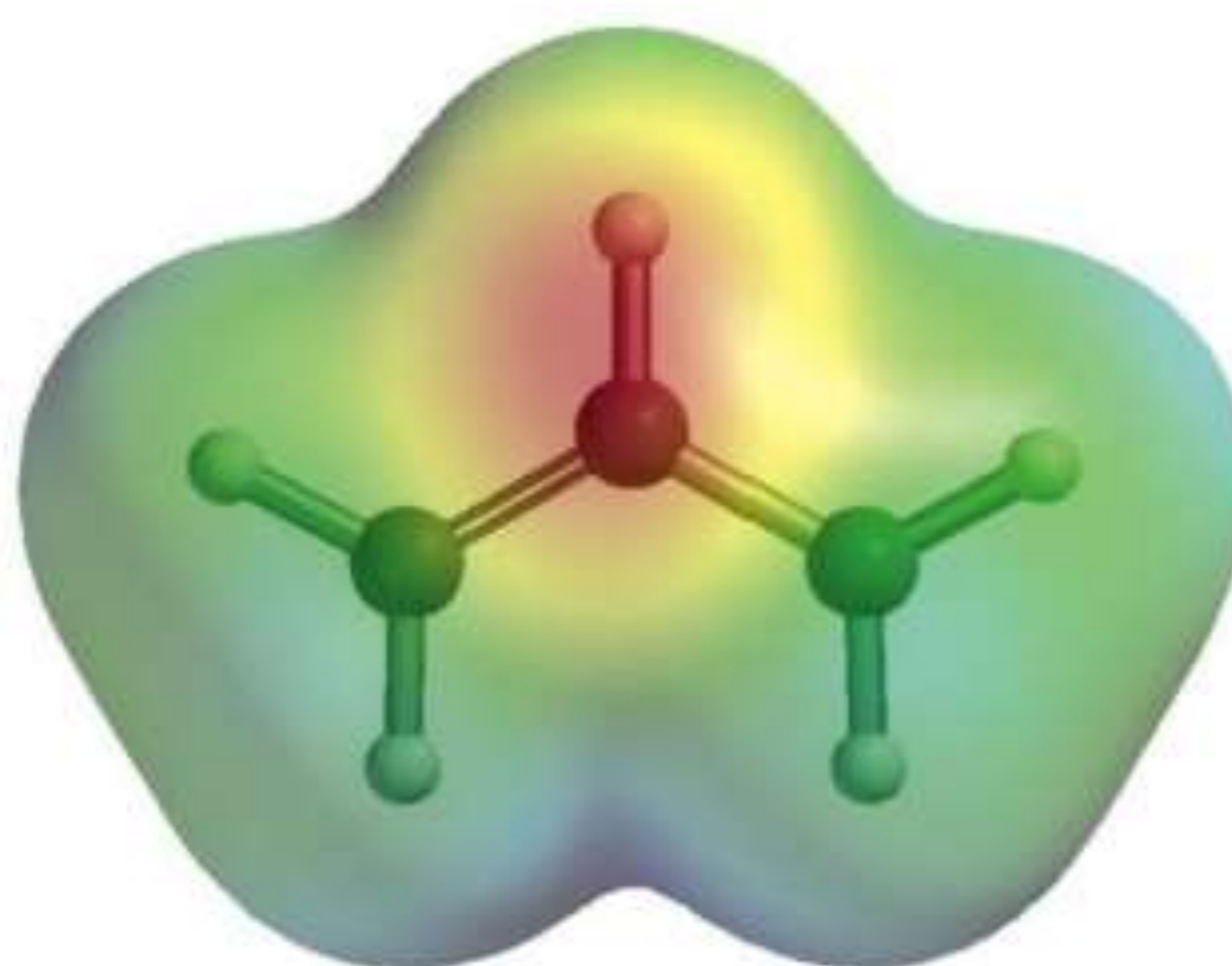
Carbocations (cont'd)

في عني عامل ثالث في بعض الأحيان يكون موجوب

- 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.



ال (+) عم تتوزع
يعني الاشء الثقيل
عم بتوزع، صوف يكون
على 1 و صوف على 3
فهار عم يزيد ال
Stability



3) Resonance:-

Note * - بين ما عندك resonance عندك Stabilization

* ال resonance دائماً يعمل Stability لل intermediate او للمركبات بشكل عام .

* الشكل اللي رسمناه يعتبر 1° لأنه كطيين ال C في R وحدة

لـ ولكن هار ال Stability لاله عالية (اقل بيثوي لهغيره من ال 2°)

لـ والسبب هو انتقال ال π

لو كان في عنا Carbocation بهالشكل :- هار الشكل اللي اجلناه قبل



Carbocation عامله 3 روابط وفي جنبها π bond

لـ اللي رح يخطر ببالنا انه انا عندي π وال (π) نتجت ال Carbocation تهجينها (sp²)

لـ فبالتالي رح احصل عن resonance

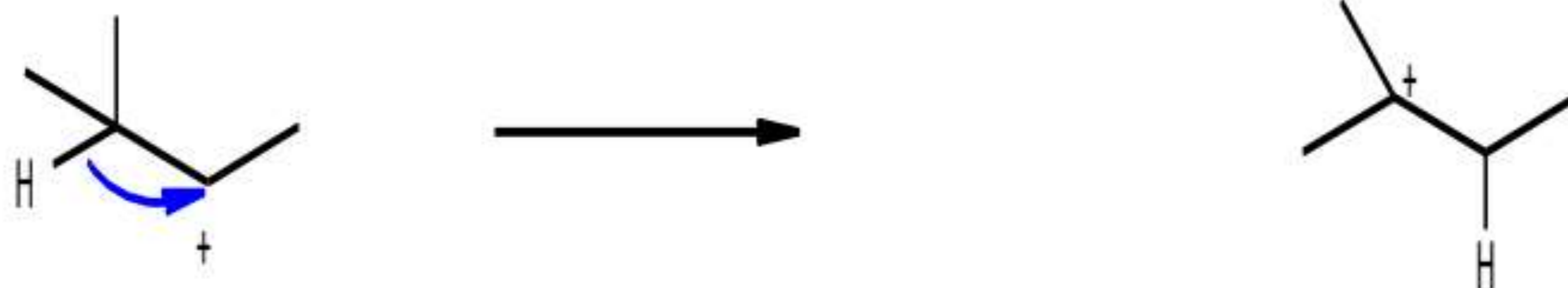


لـ رح تنقل عندي ال double bond من (1 و 2) لـ (2 و 3)

لـ هار برافقه انه ال (+) انتقلت للذ C اى C1

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

هنا يبدأ حتى عن تفاعلات الهالوجين
 واما طبقاً عم حتى عن ال addition

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

انتقل لسليبه 38 بعد ان ارجع ت
 * و لكن هون
 خيال (Halo alkane)
 (vicinal dibromide)
 ما ح يعرف سواء
 كتبهم مع او عك
 بعض
 لانها في
 عنى
 free rotation



* الفكرة دائماً هي A-B ولكن دائماً أول خطوة هي تكوين Carboanion

- 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



* اول خطوة هي رابعا تكوين ال Carbo cation

فلا صبح ال $\times 2$ همن non polar لكننا في Non Polar Solvent عاري ممكن يسهلهم Polarization

له وال Polarization هي ازاوية \ominus فبمير عندي جزء عليه $\delta+$ وجزء عليه $\delta-$

وهي نفس فكرة $A-B$



تتجاهمها وينتس
الرابطه $\text{Br}-\text{Br}$
وح ينتج عندي
ال Carbo cation



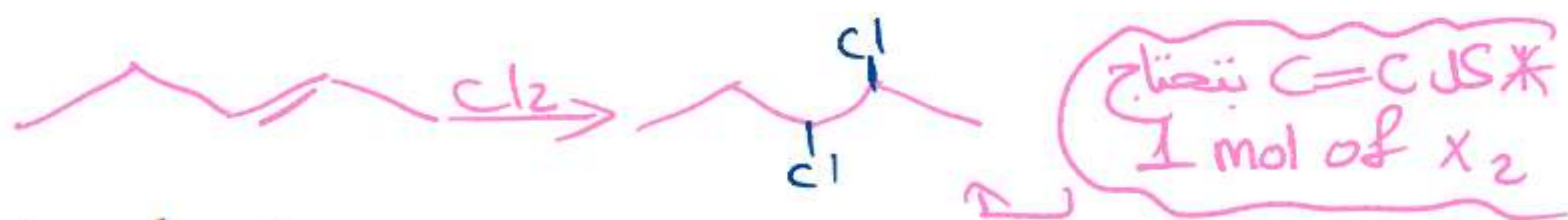
زي ما فكينا هون مارج معنا بالنسبة لمواقع ال Br لانه عننا free rotation

ولكن راج يفرق معي مثلا لو مركبي Cyclohexene

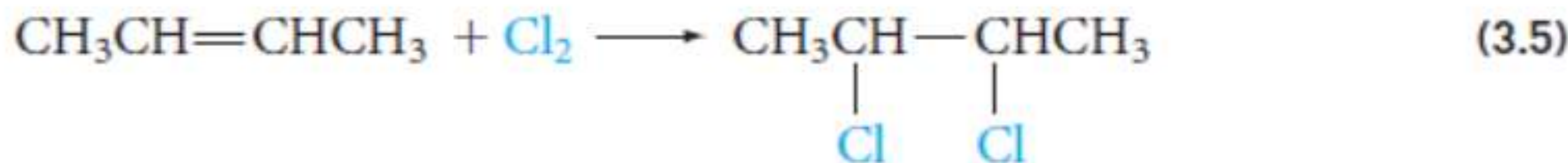


هون لجزء ايبين ال Br همن trans لبعض

* الفكرة انه الـ 2^2 بتضيفوا antiaddition (عكس بعضها)
لـ في حالة الـ Halobakane مت كثير بيهتم فيهم لانه انا اصلاً
عندي free rotation والـ conformers كلهم موجودين
لـ لكن لو كان في restriction على الـ rotation مثل الـ
Cyclohexene الـ الذي انه انا بحاجة اهتم بال isomers
الذي يطلعوا عندي ضلالتا بتضيف antiaddition as



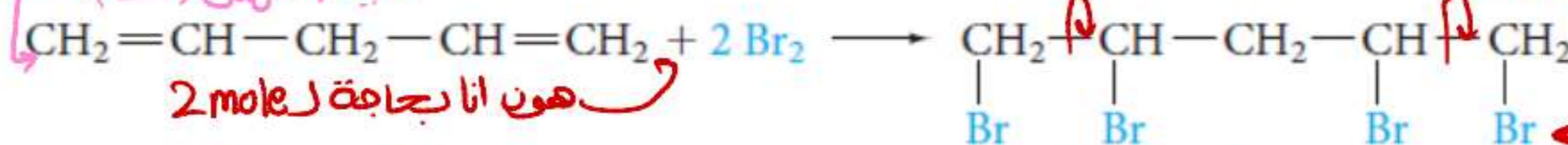
Alkenes readily add chlorine or bromine.



2-butene
bp 1-4°C

2,3-dichlorobutane
bp 117-119°C

لكن صمكت يكون المركب فيه أكثر من (=) جوا



هون انا بحاجة لـ 2 mole

1,4-pentadiene
bp 26.0°C

1,2,4,5-tetrabromopentane
mp 85-86°C

free rotation
لو عطيتناهم بنفس المكان عاين ولوعكس يكون احسن

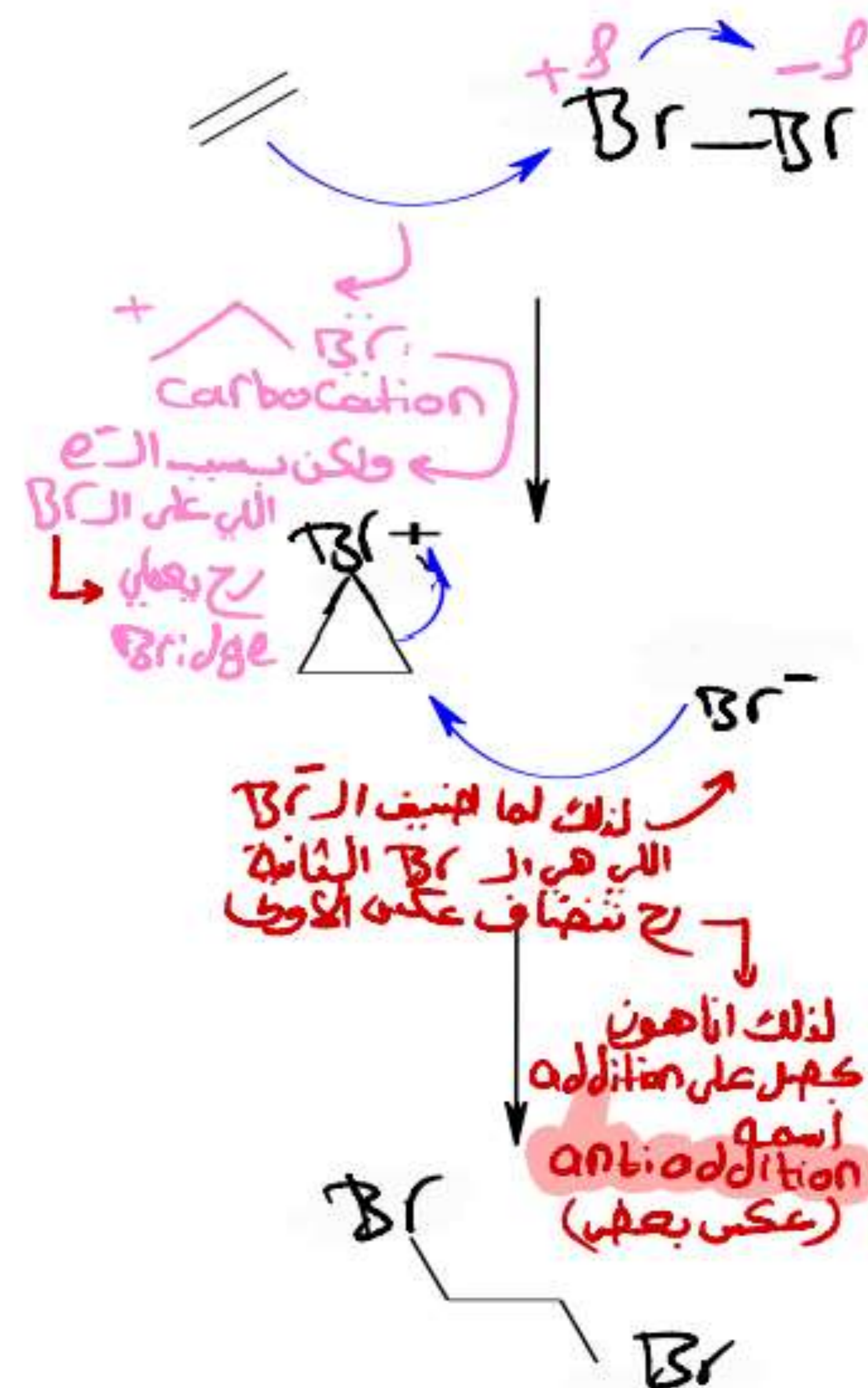
PROBLEM 3.8 Write an equation for the reaction of bromine at room temperature with a. propene b. 4-methylcyclohexene

Halogenation (cont'd)

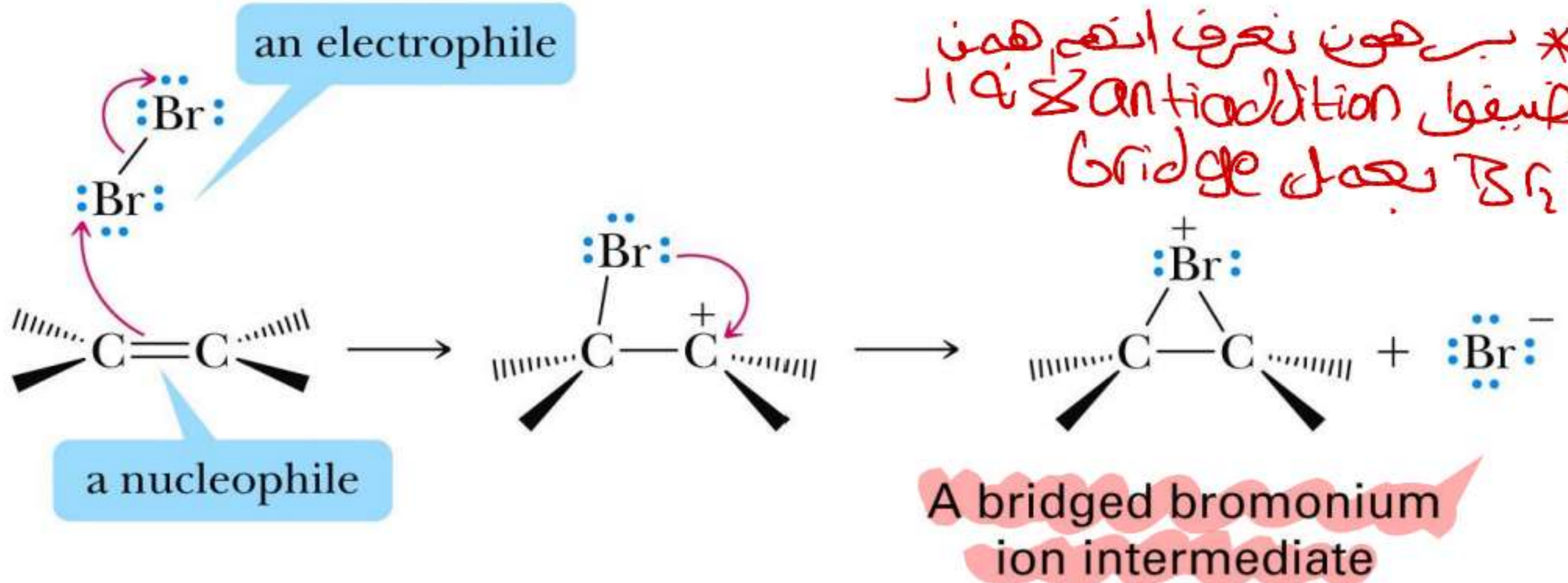
In the first step the π electrons act as a nucleophile attacking the bromine displacing a bromide ion and forming the cyclic bromonium cation intermediate.

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.

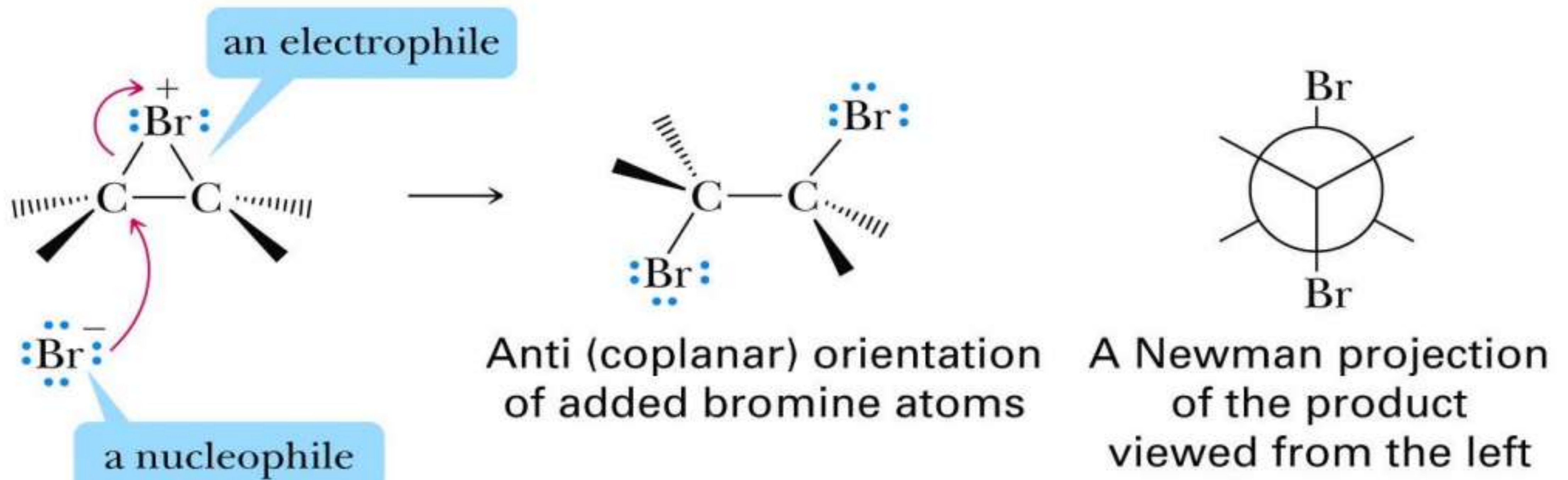
Note this is a trans addition since the two Br atoms add to opposite side of the double bond.



* برهون زعفران انتهم همن
دقیقوا S_N2 addition
جسکے بعد Bridge



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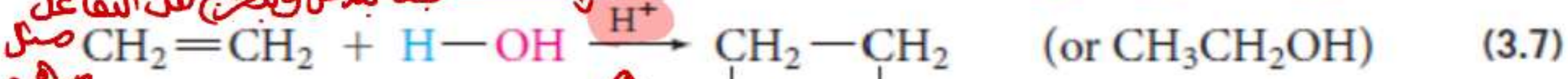


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3.7.b Addition of Water (Hydration)

* Synthesis of Alcohol from Alkene

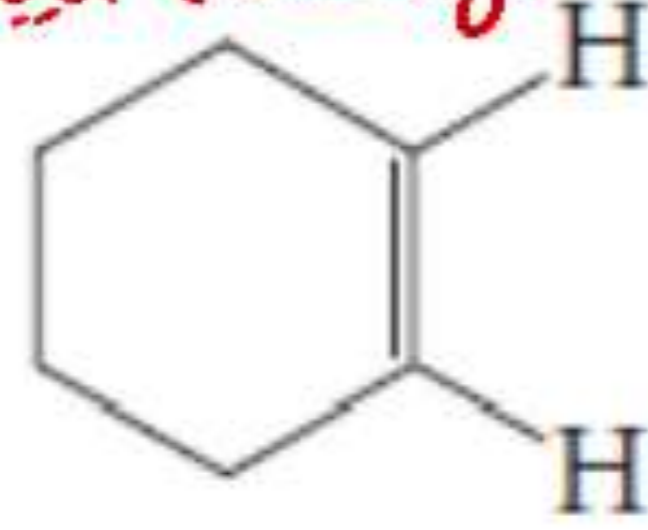
ال Catalyst هي عبارة عن كمية قليلة جدًا تدخل ويتخرج من التفاعل



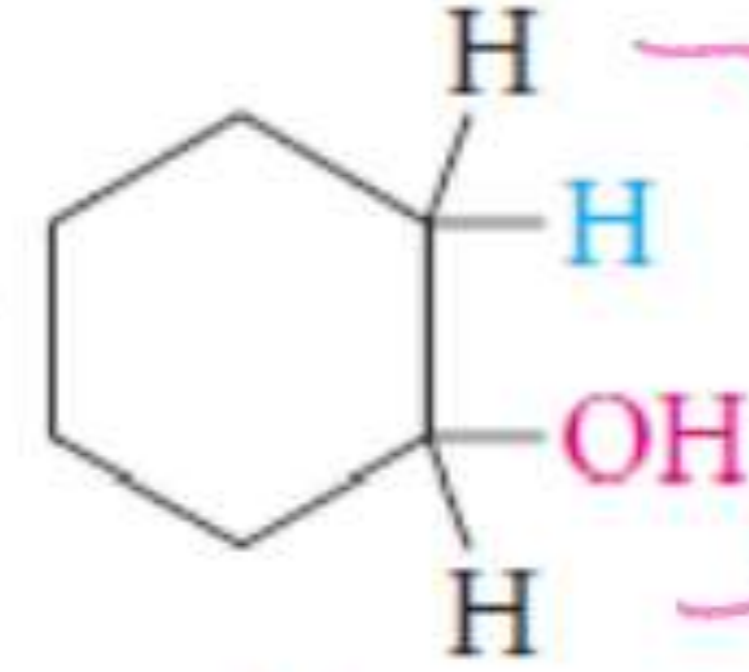
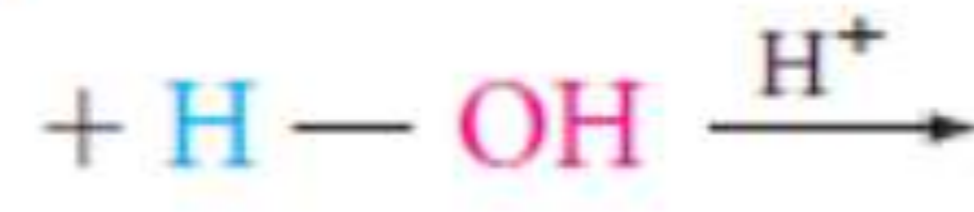
صحيح

الفكرة هون انه

هاد التفاعل مارح
لنك الا لجزا حبيب
Catalyst اللي هو (H⁺)



cyclohexene
bp 83.0°C



cyclohexanol
bp 161.1°C

(3.8)
ار H (الفتحات)
احنا ما
منكتبهم



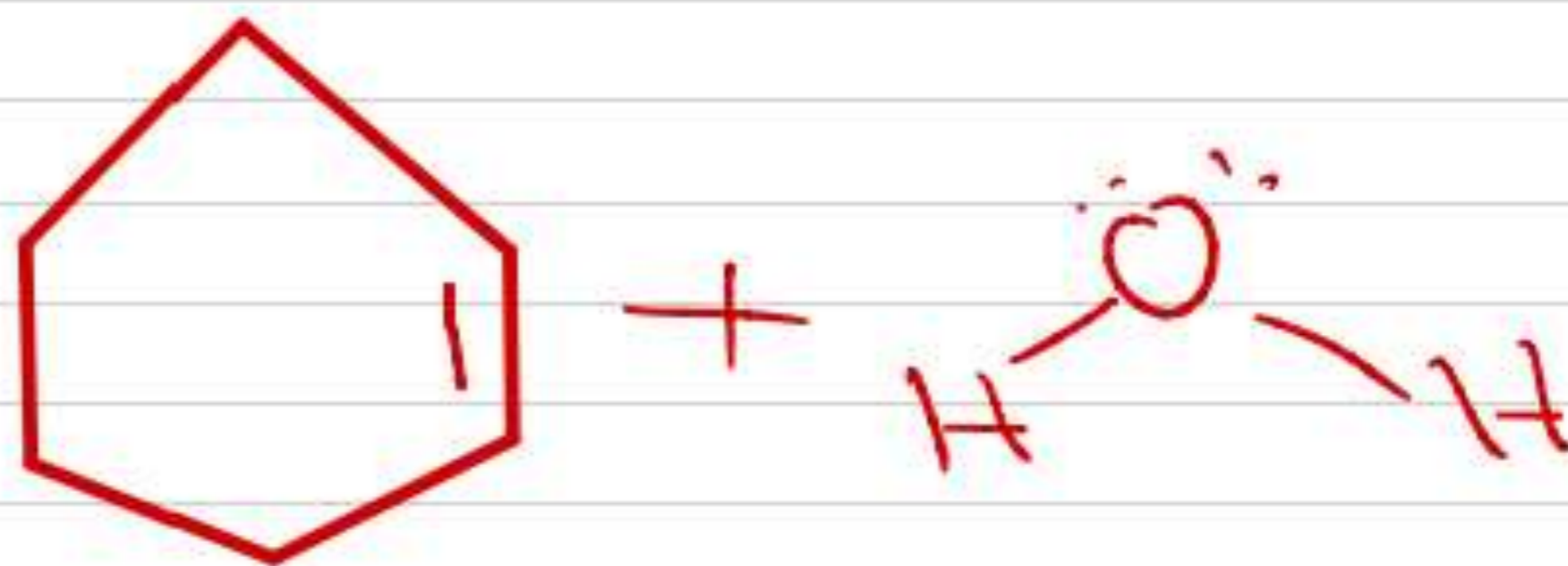
* الفكرة هون انه انا بدري اهنيف مي H₂O



ل هون ار function group اللي رح يطلع معي هو كحول

* لست انا جاية Catalyst ؟

قلينا نسوف هاد المثال :-



اما منعرف انه الميه مارح تعطيني ال H بكل سهولة لانه هسو (weak acid)

منقدر نعمل خطة كيت انه نتغلب على المشكله هاي

* Note :- H2SO4 / H3PO4
The Common reagents
كعسر ال H+

الميه والاكسين هسول مارح يتفاعلوا مع بعض

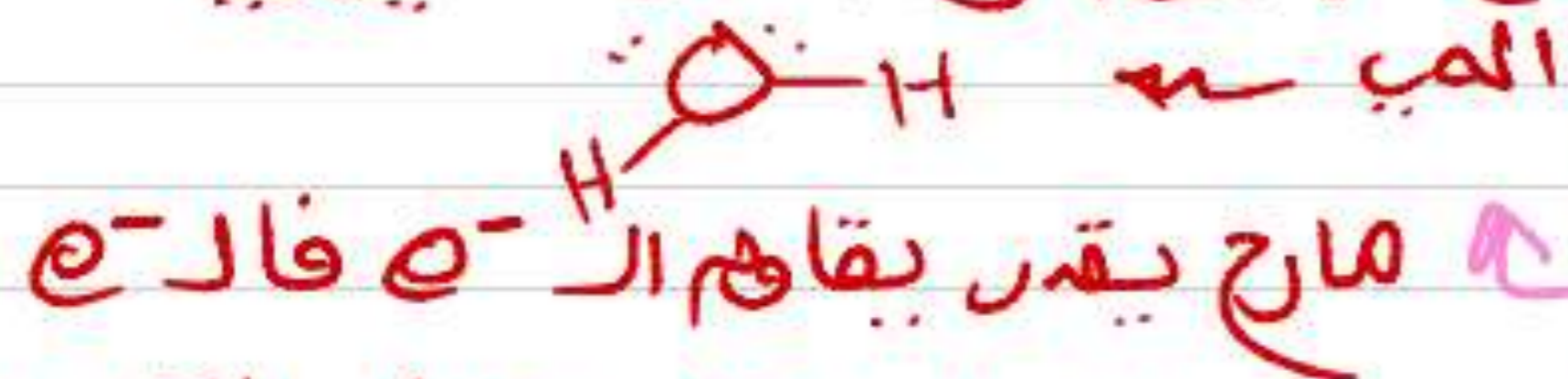
لولاكن لو حطيت H+ امام الاكسين

الفكرة انا ال = مارح تقدر تقاوم ال H+ فرح تتهاجمها

فازا صنعنا H+ وعملنا معها رابطة رح يهيب عندي :-

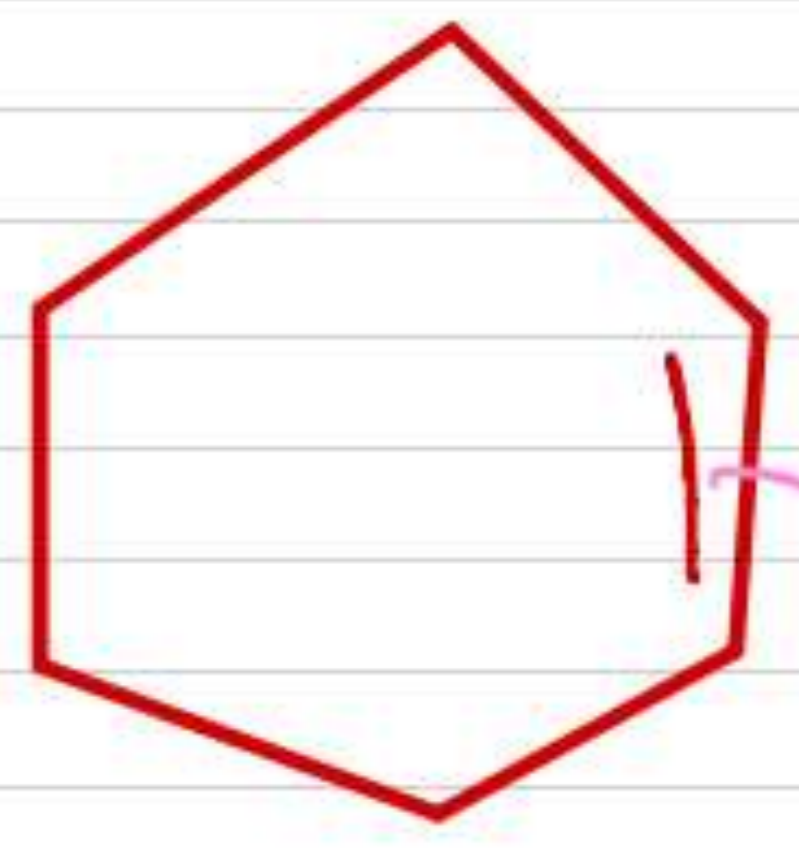


له هلا هاد ال Carbocation هو Very reactive ، فلما يلاقي قدامه



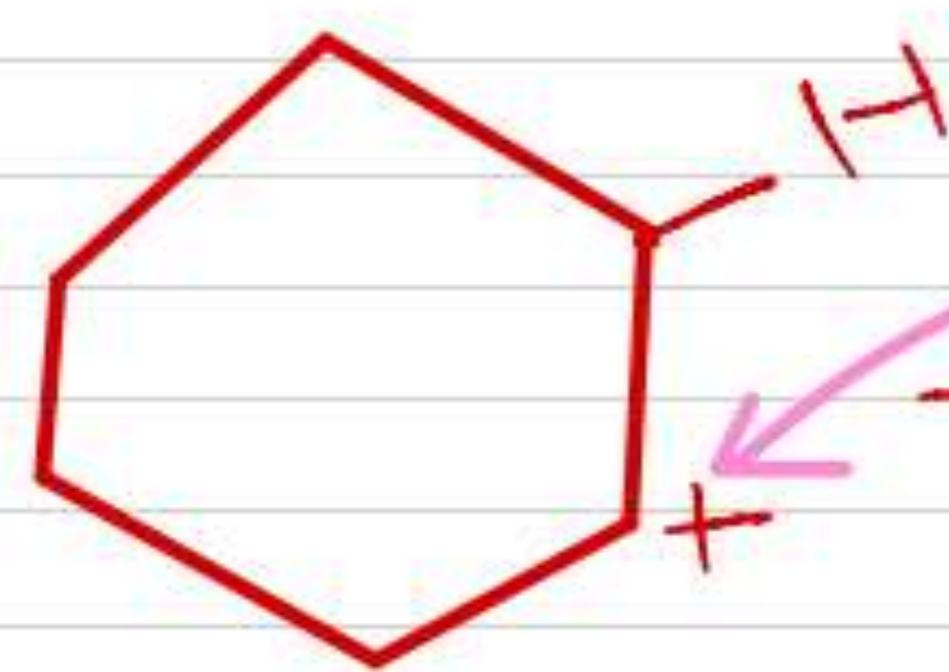
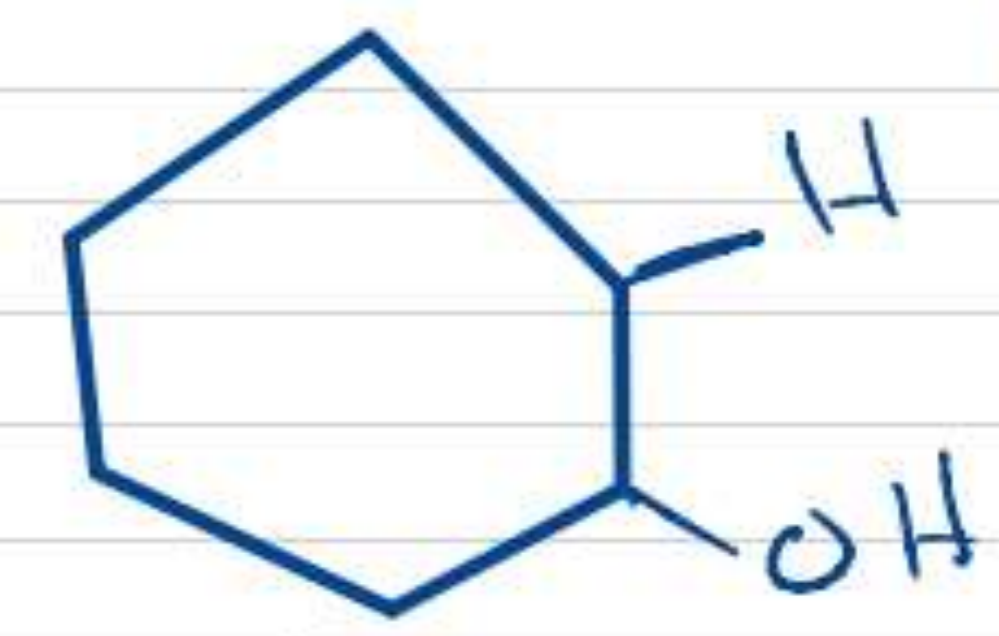
يتزوج بنعمل مع ال C اللي ناقصها bond

الفتح النهائي

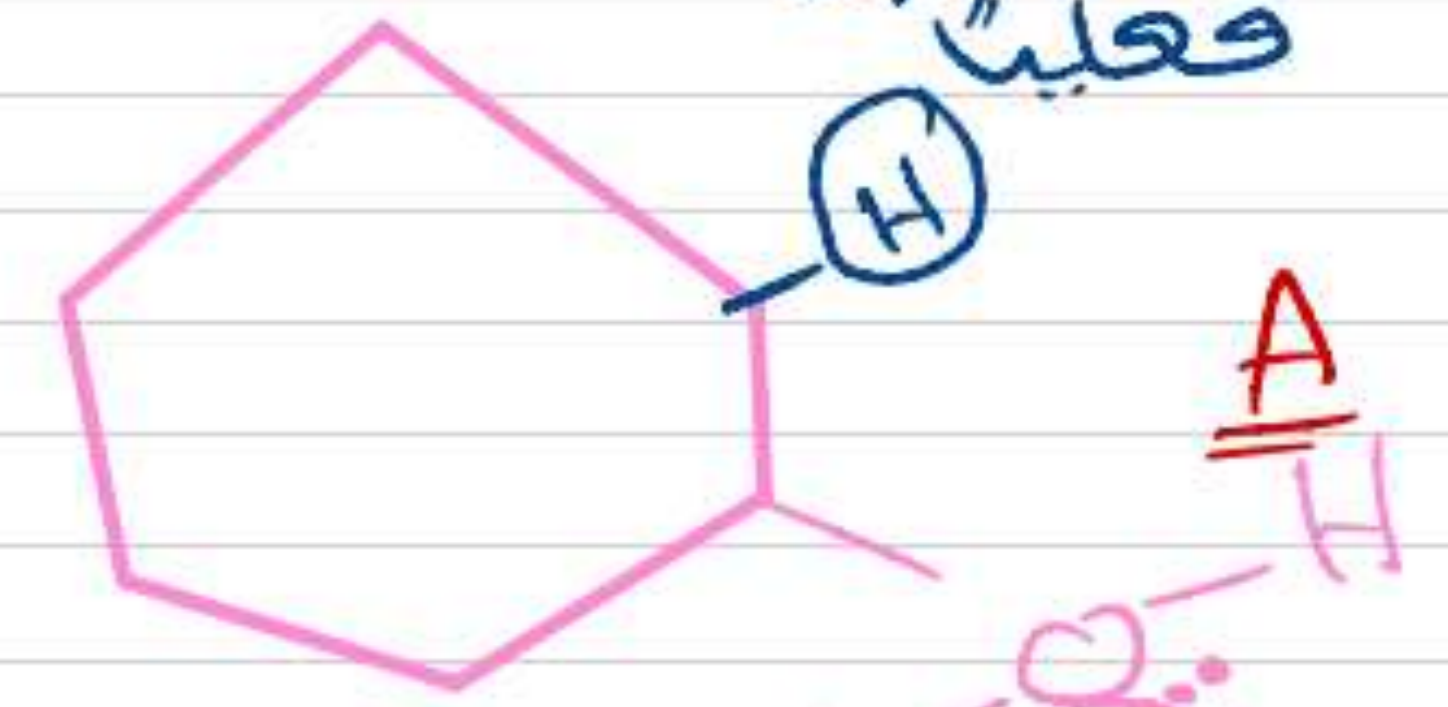


تتطلبنا Carbo-cation
ووظيفتها انها

هو يحتاج Catalyst
لانه البرد قد
بالنهاية طلع
لهون



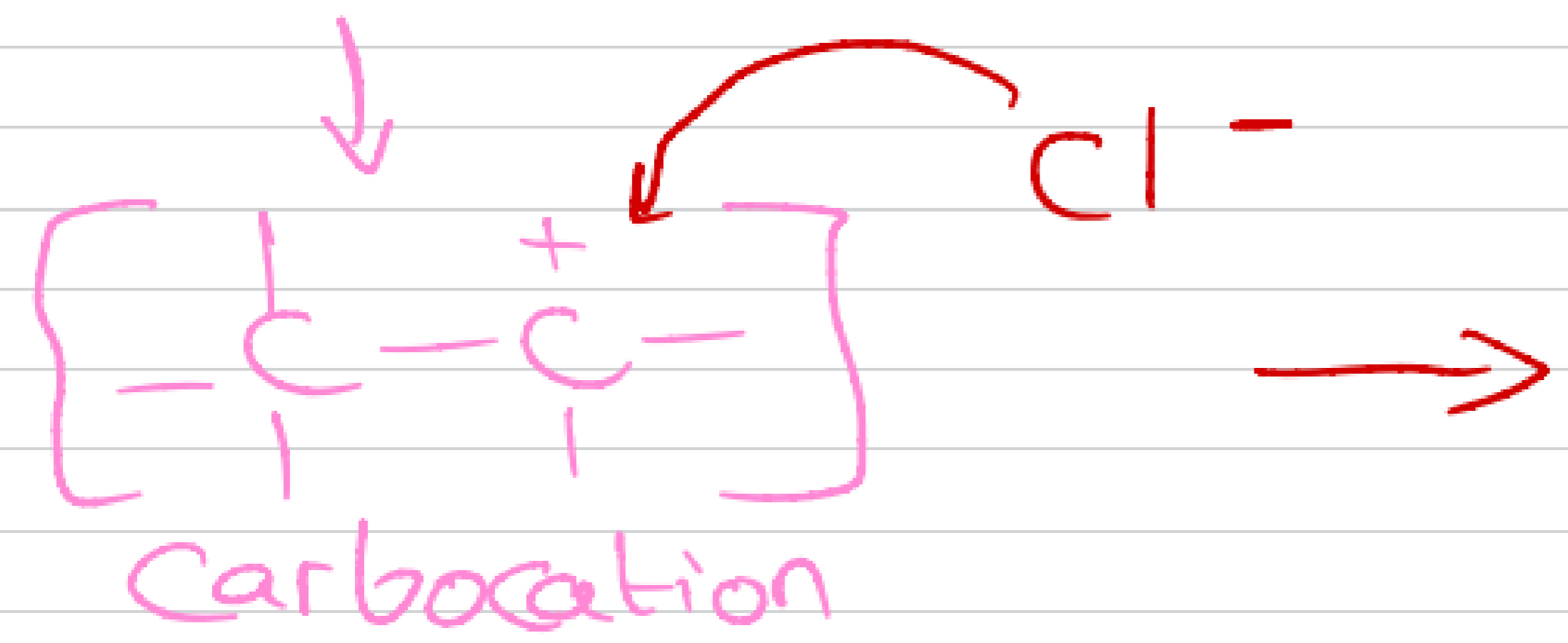
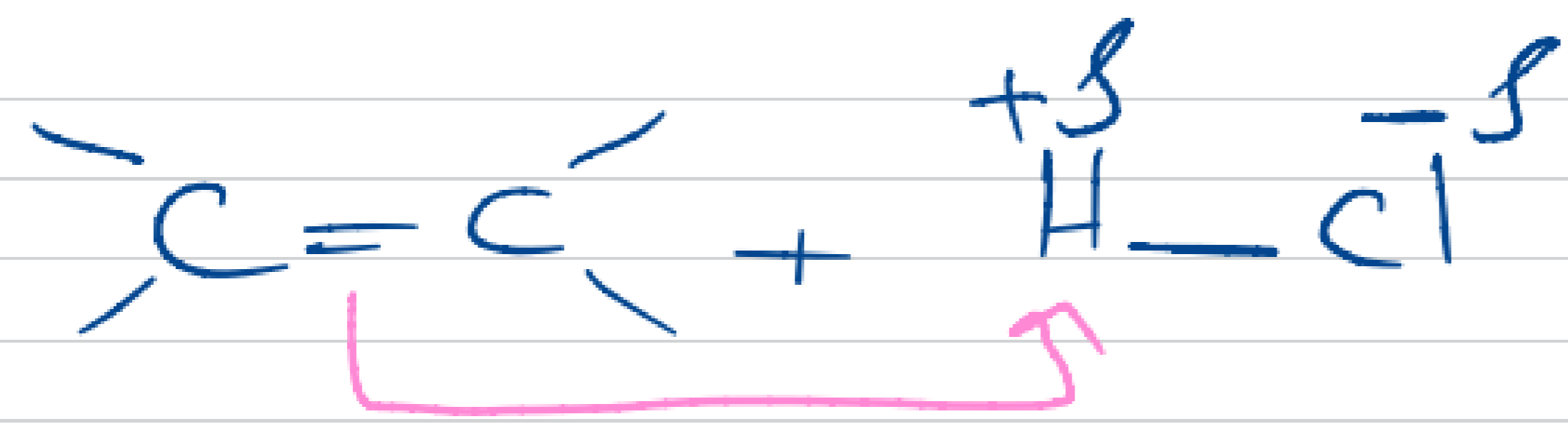
هاي ال H
صانعتها
فعليا



له عليها (positive)

له عتات يغير neutral يفتح ال H (A) بفتحها (H^+) ds مدها

الفكرة انه :-



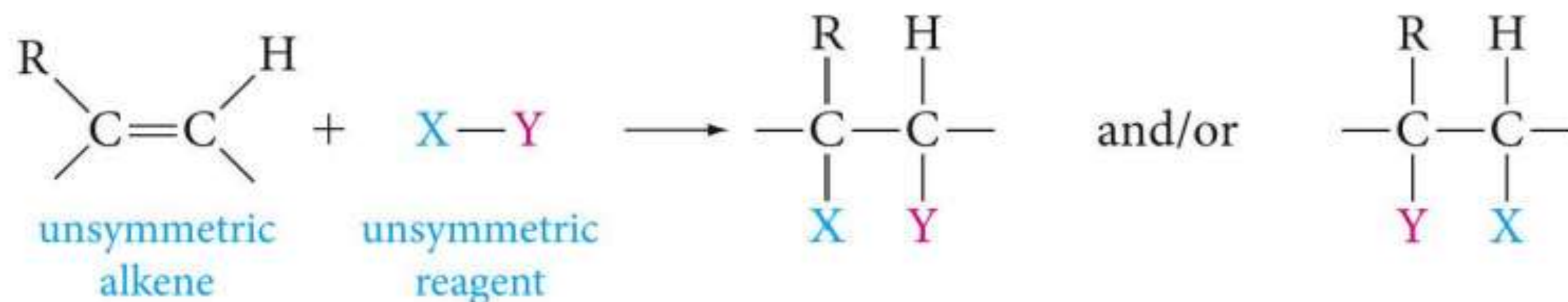
* الفكرة انه بنفت H على C
وال C على ال C الثانية

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

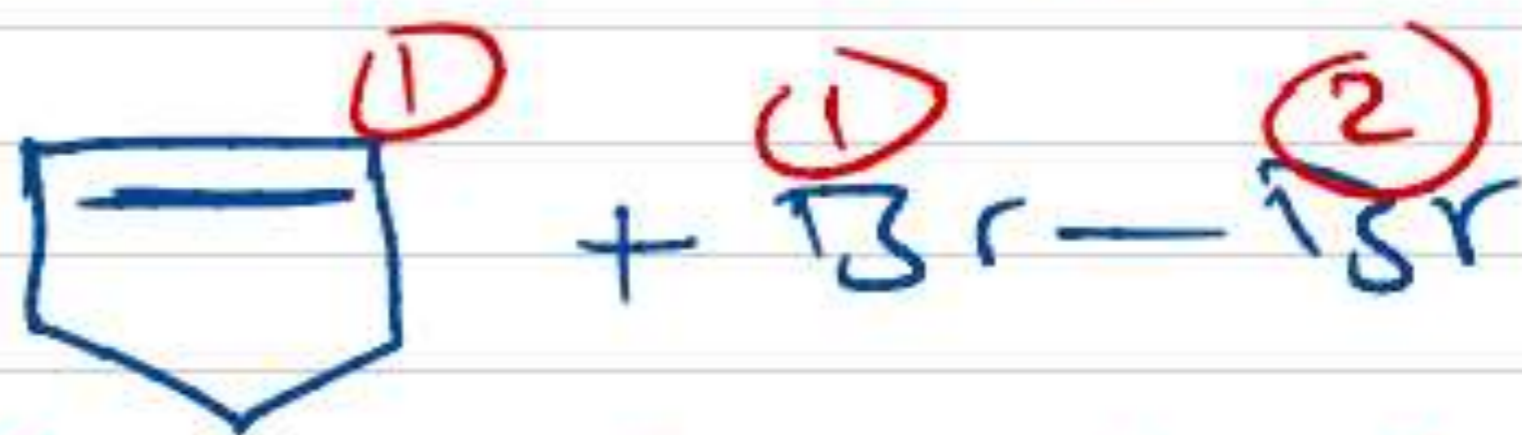
	Symmetric	Unsymmetric
Reagents	$\begin{array}{c} \text{Br} - \text{Br} \\ \quad \\ \text{Cl} - \text{Cl} \\ \quad \\ \text{H} - \text{H} \end{array}$	$\begin{array}{c} \text{H} - \text{Br} \\ \quad \\ \text{H} - \text{OH} \\ \quad \\ \text{H} - \text{OSO}_3\text{H} \end{array}$
Alkenes	$\begin{array}{c} \text{CH}_2 = \text{CH}_2 \\ \\ \text{Cyclopentene} \end{array}$ <p style="text-align: center;">mirror plane</p>	$\begin{array}{c} \text{CH}_3\text{CH} = \text{CH}_2 \\ \\ \text{1-Methylcyclopentene} \end{array}$ <p style="text-align: center;">not a mirror plane</p>



كل التفاعلات التي درينا عنهم سابقاً
همن symmetry سواء الألكين
أو ال reagents

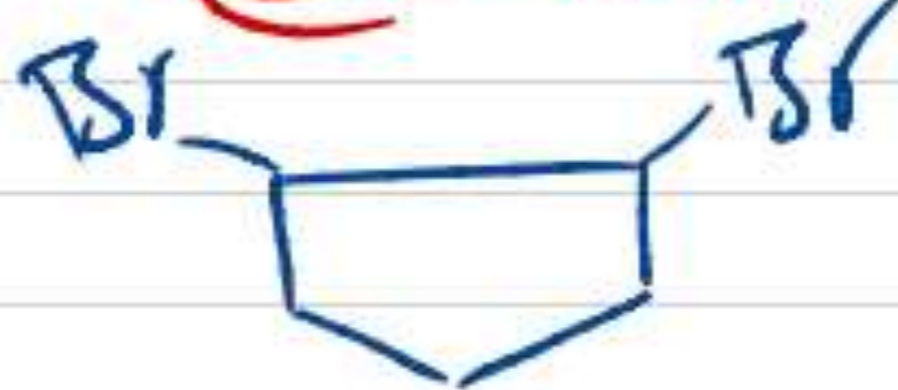


لما صنعت ال Br_2 على الألكين



هل نرج بفرق لو صنعت ال Br_2 ← رقة (1) على
على كربونة (1) أو صنعت Br_2 ← 2
على كربونة (1) ؟!

ما نرج تفرق ، لأنه بكل الحالات
يطلع معي (1 product)



* إذا كان عن ال reagent
أو الألكين أو كلاهما فيه
symmetry

له فهو بطلع معنا فقط

1 isomer or 1 product

ما في احتمال ل isomer ثاني

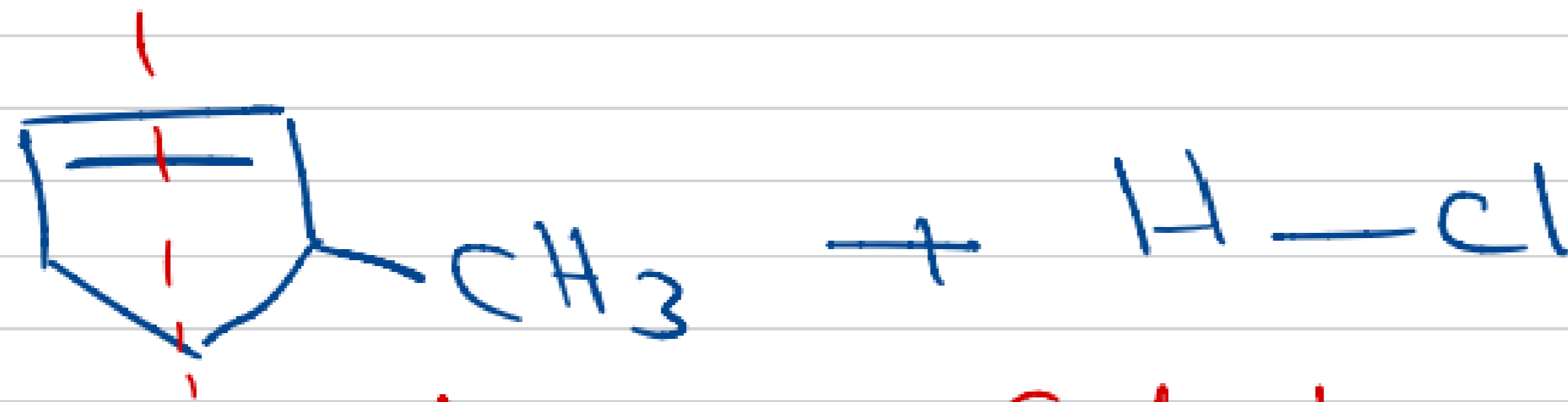
* ولكن رج يطلع عنا اختلاف

ويطلع عنا 2 isomers

إذا كان عن asymmetric

بالألكين وبال reagent

يتبع



لأنه غير متماثل
 unsymmetry

هذه بداية عملية تكوين Carbocation
 (عملية الـ Protonation)

لأنه لدينا هنا اضعف H^+ هذان يفرق
 لوضفقتها بمين او يساين ؟
 في يفرق ح يطلع معنا

2 products

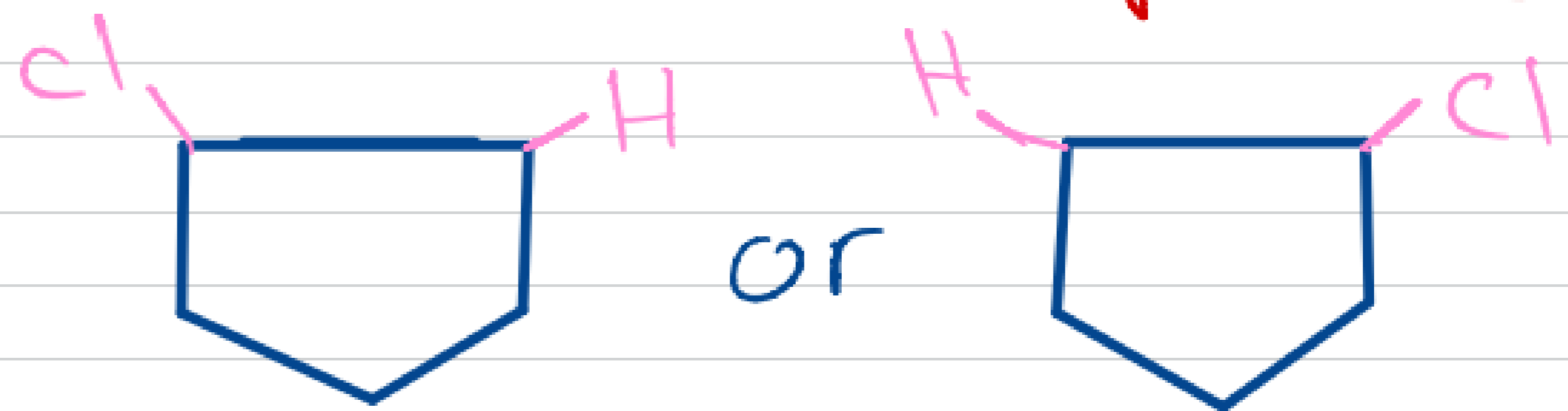
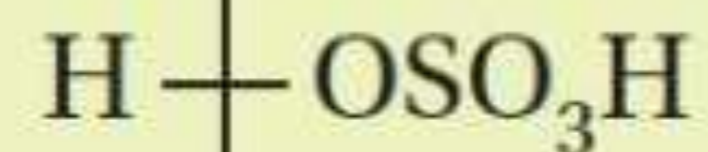
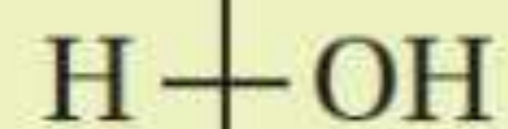
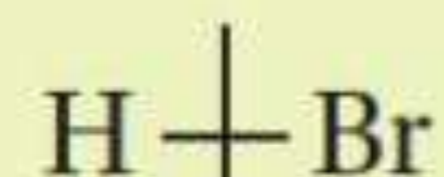
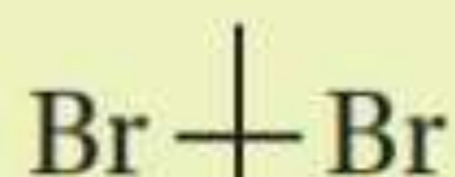


Table 3.2 ■ Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

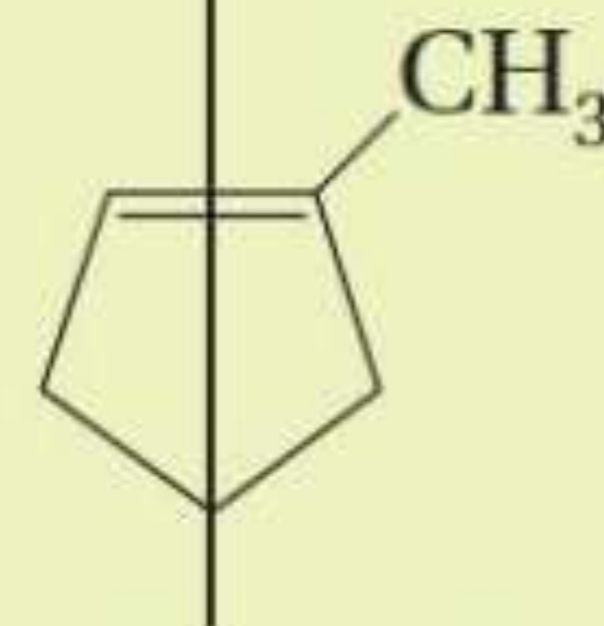
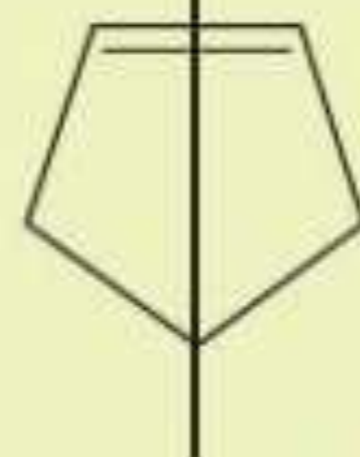
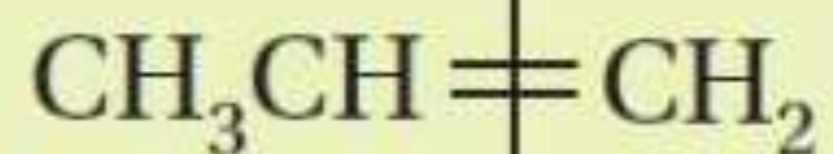
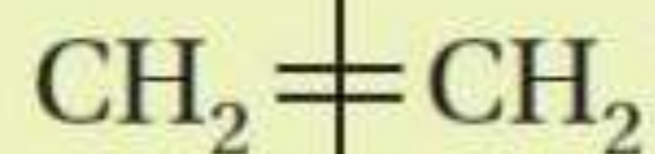
Symmetric

Unsymmetric

Reagents



Alkenes



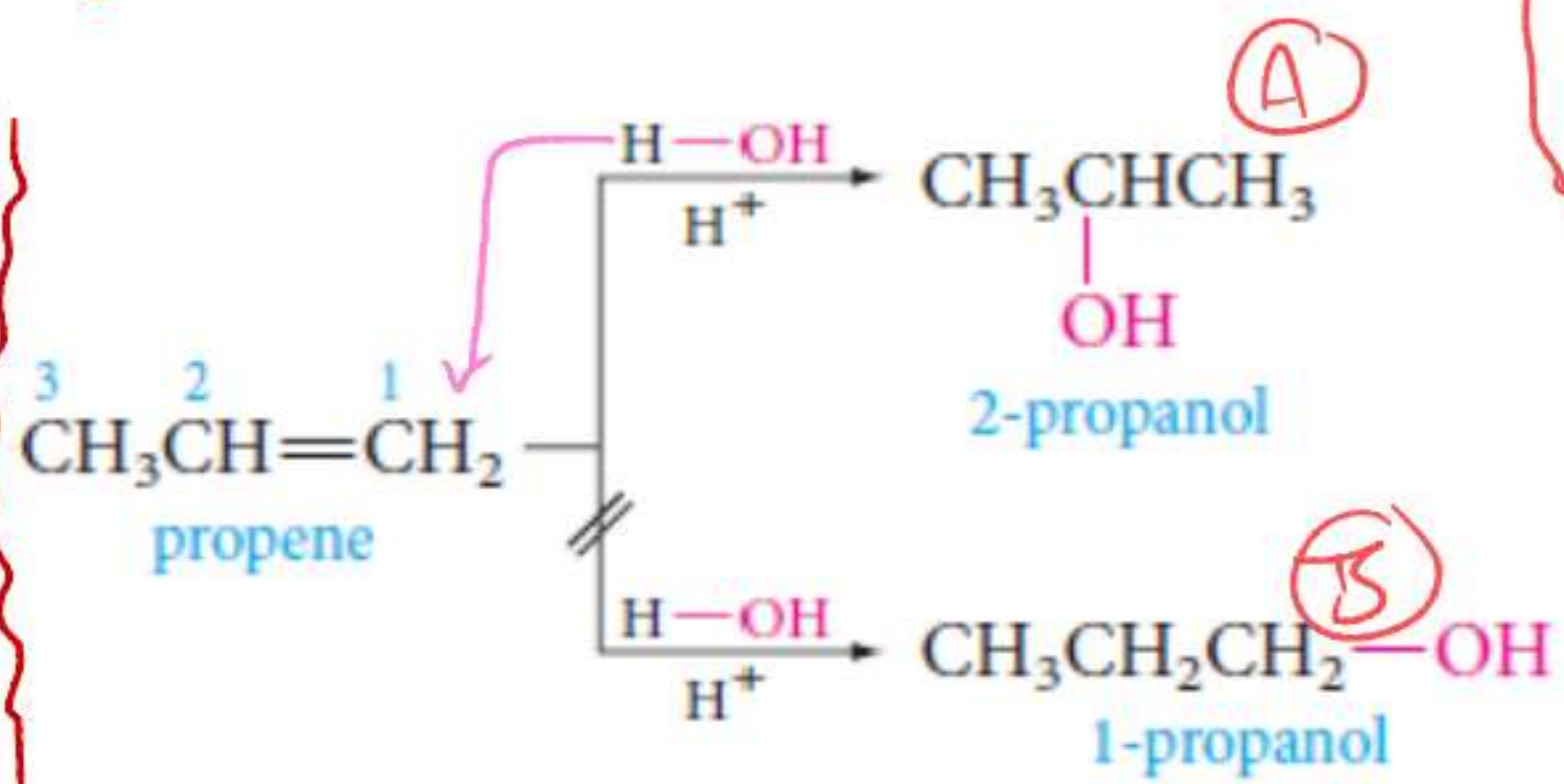
mirror plane

not a mirror plane

H^+ يتزوج للـ C التي معها H أكثر
Markovnikov's Rule

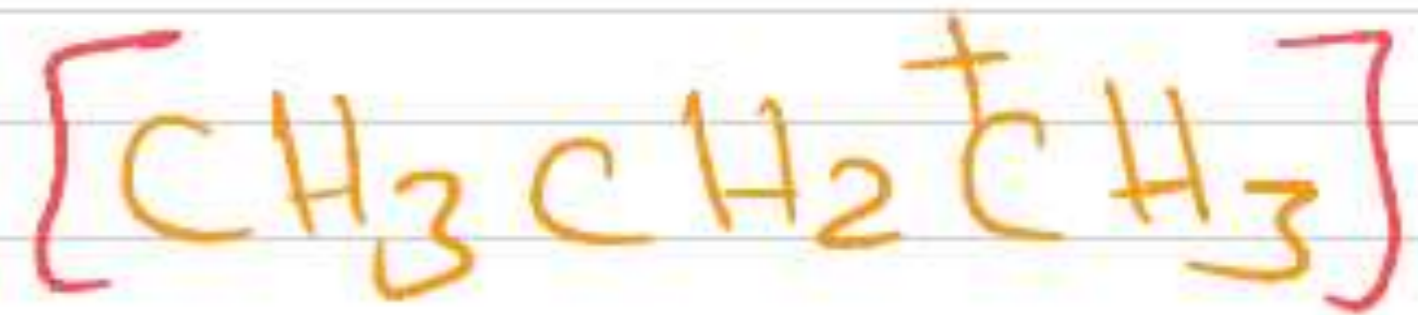
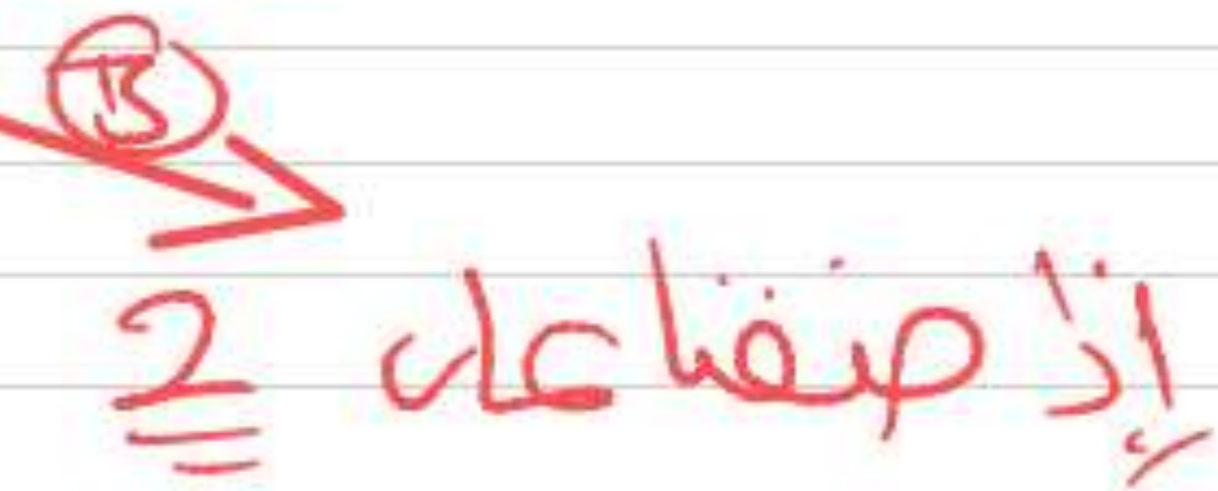
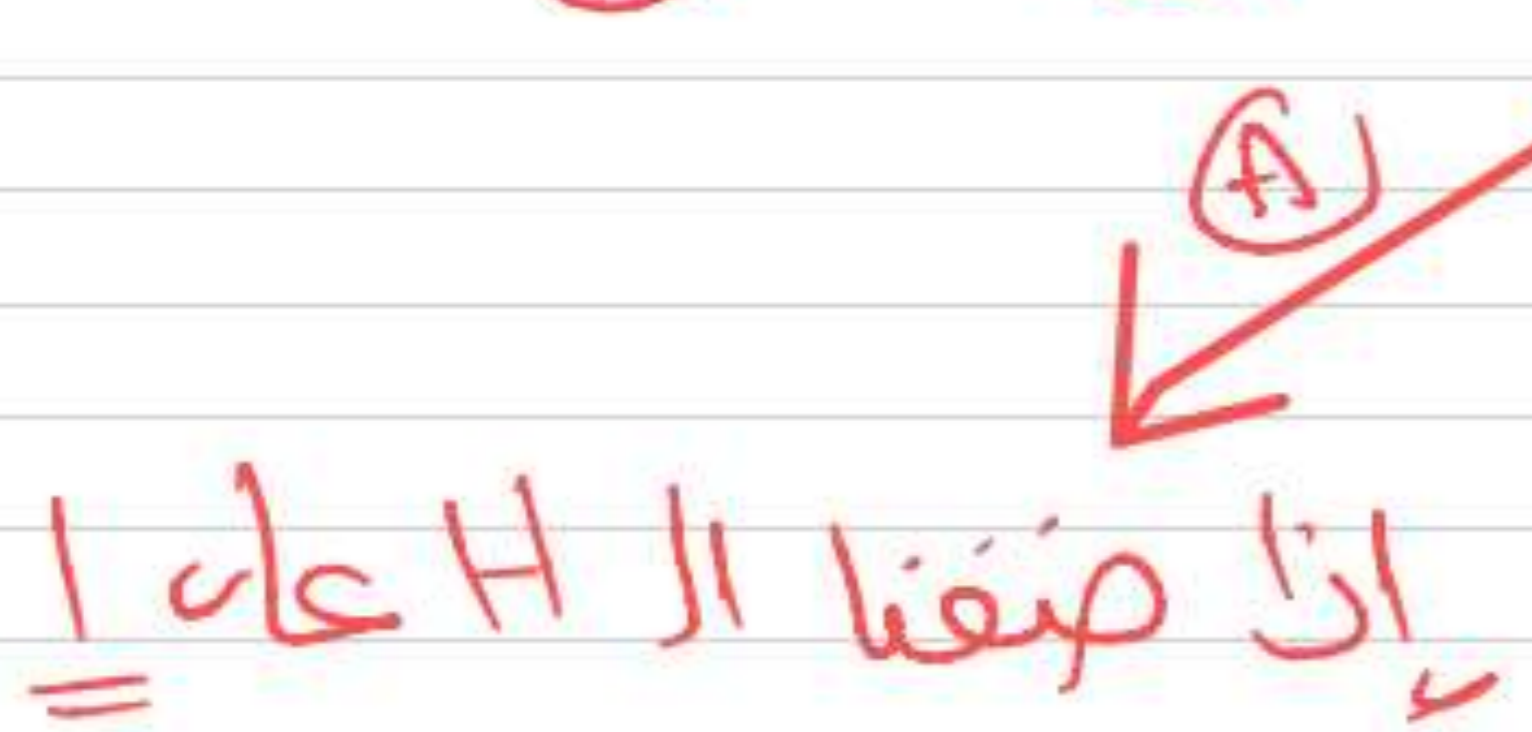
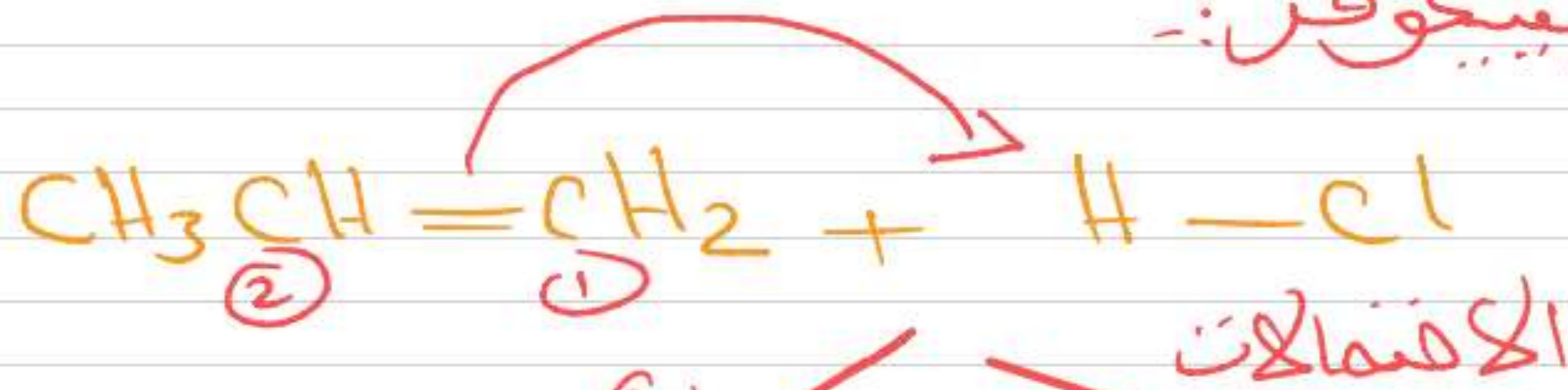
Fortunately there is a simple rule of thumb to predict which product will form: Markovnikov's rule, which states that when **an unsymmetrical reagent adds to a double bond the electrophilic part of the reagent adds to the carbon with the most hydrogen atoms on it.**

* وجدوا اننا اذا
 لدينا H مثل
 H_2O or HA
 على Asymmetrical
 Alkene
 وقتها ار H ياتوا
 الاوكسجين تزوج على
 C التي معها اكثر H



حسب القاعدة
 المركب الذي يح
 يتبع عننا هو
 A

تفسير قاعدة ماركوفاييف:-



هنا هـ دول عبارة عن (intermediate)

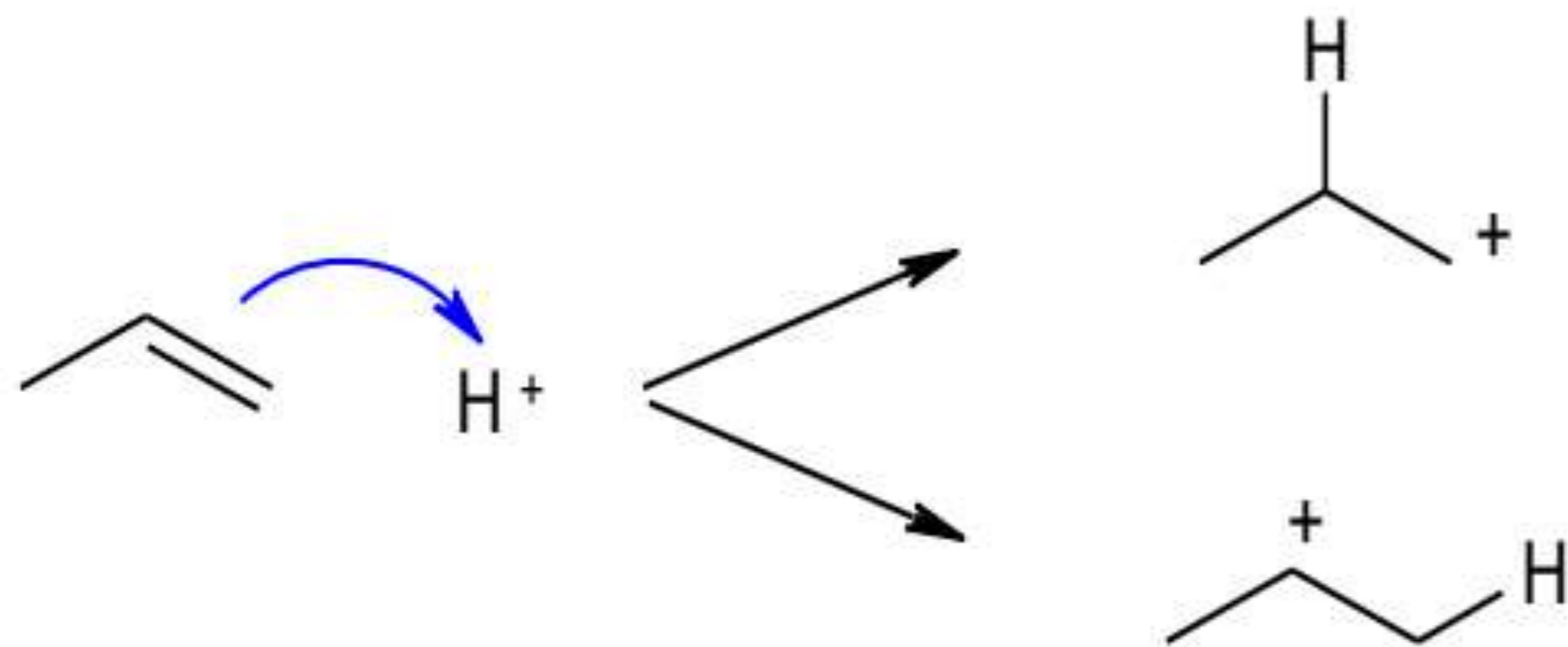
ولكن A هو الصحيح مو B لانه
عبارة عن 2° بينما B هو 1°
فال stability لـ A هي افضل

* لما اصنف ال H على
الكيف رح تروح على ال C
الابامعها ال اكثر لانها
more stable ال
Carbocation

Markovnikov's Rule (cont'd)

تكوين کاربocation
های متفاوت است
و ثابت است

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

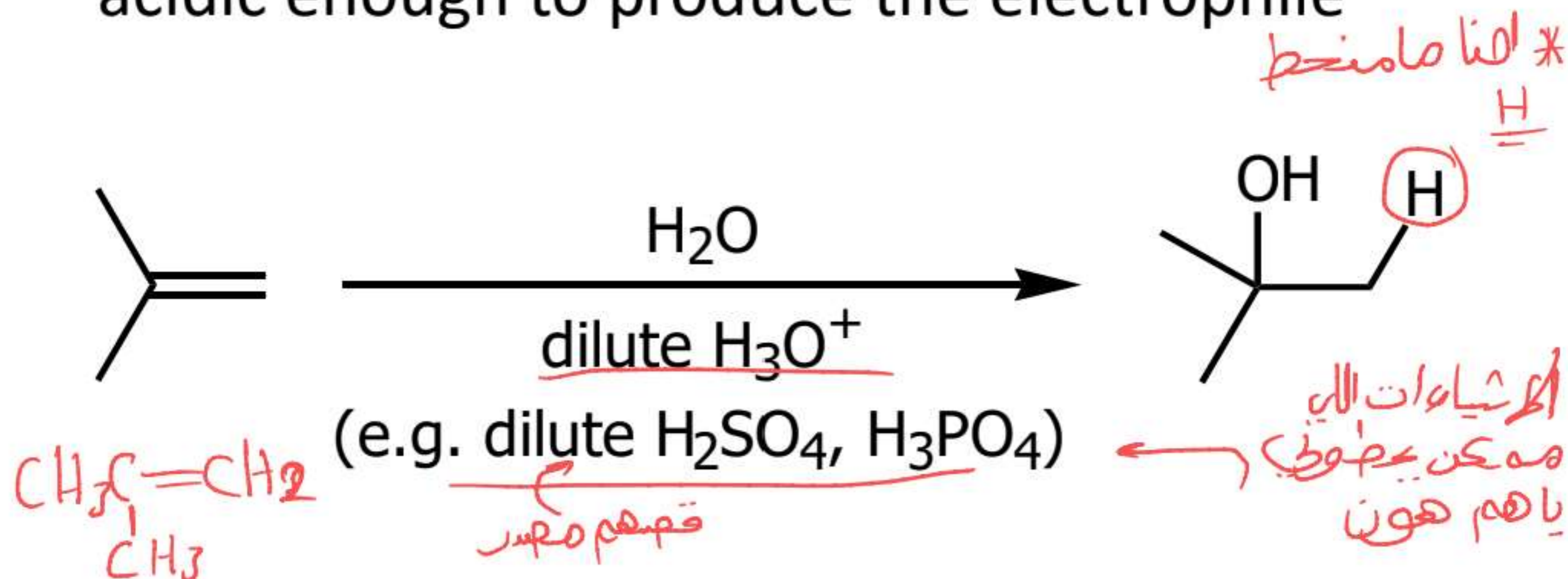


1° carbocation - anti-Markovnikov product

2° carbocation - Markovnikov product

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

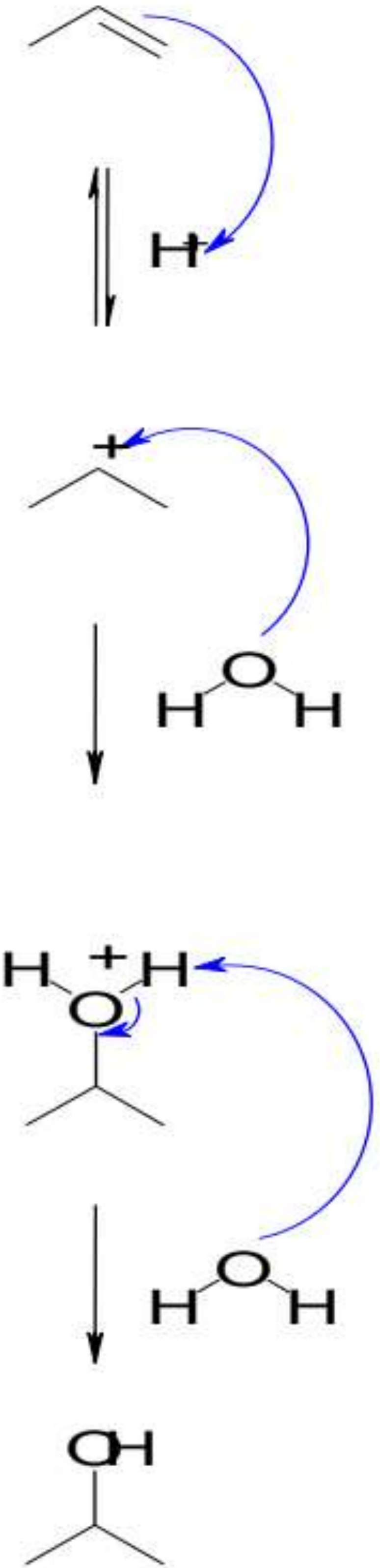


Hydration (cont'd)

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.



Adding of acids Hydrohalogenation

- Addition of HX across a double bond to produce a Markovnikov halide alkane

حفظ

- Reactivity: $HI > HBr > HCl > HF$ (parallels acidity)

* هون لو صهينا الكينا مع HI رح نلحقا تفاعله اسرع من الباقي وهكذا

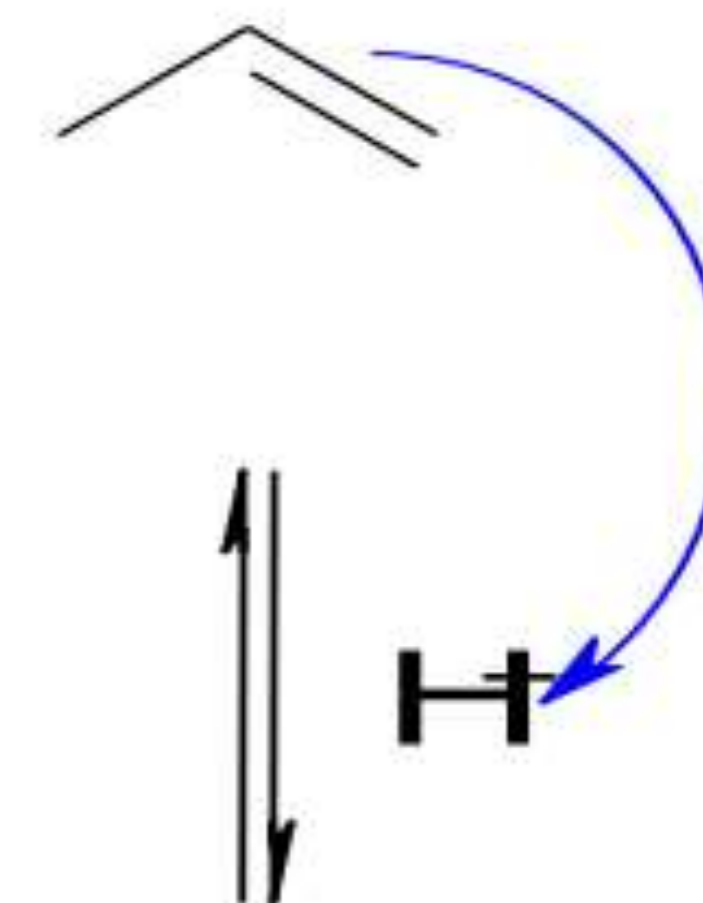
- HBr needs to be used in the dark and under an inert atmosphere to prevent a free radical addition process that produces the anti-Markovnikov product.

- Note: this same mechanism applies to other acids such as H_2SO_4

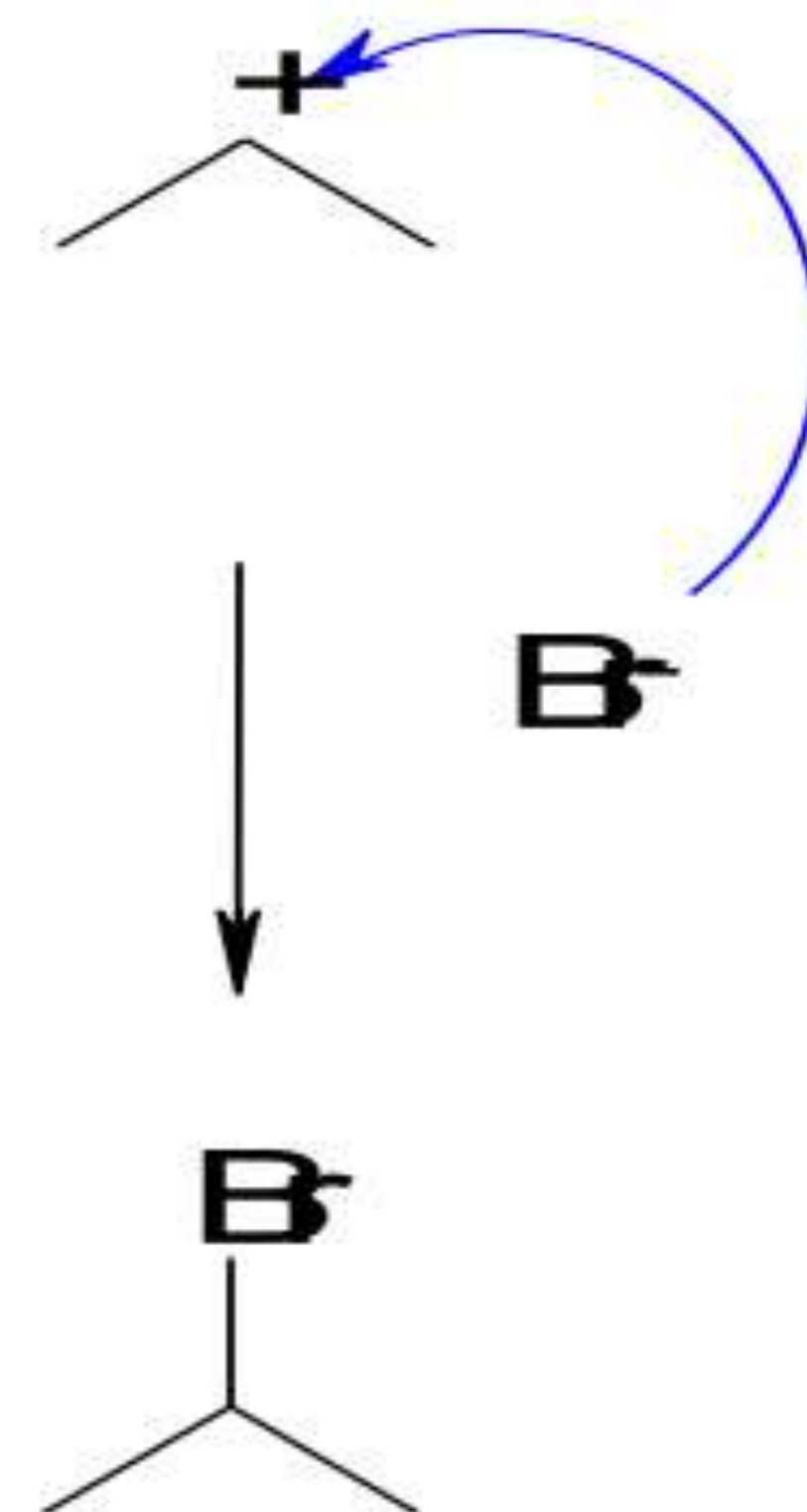
HI هو الاكثرب لانو
هو اكثرب acidity فيجبنا
الـ H^+ اسرع

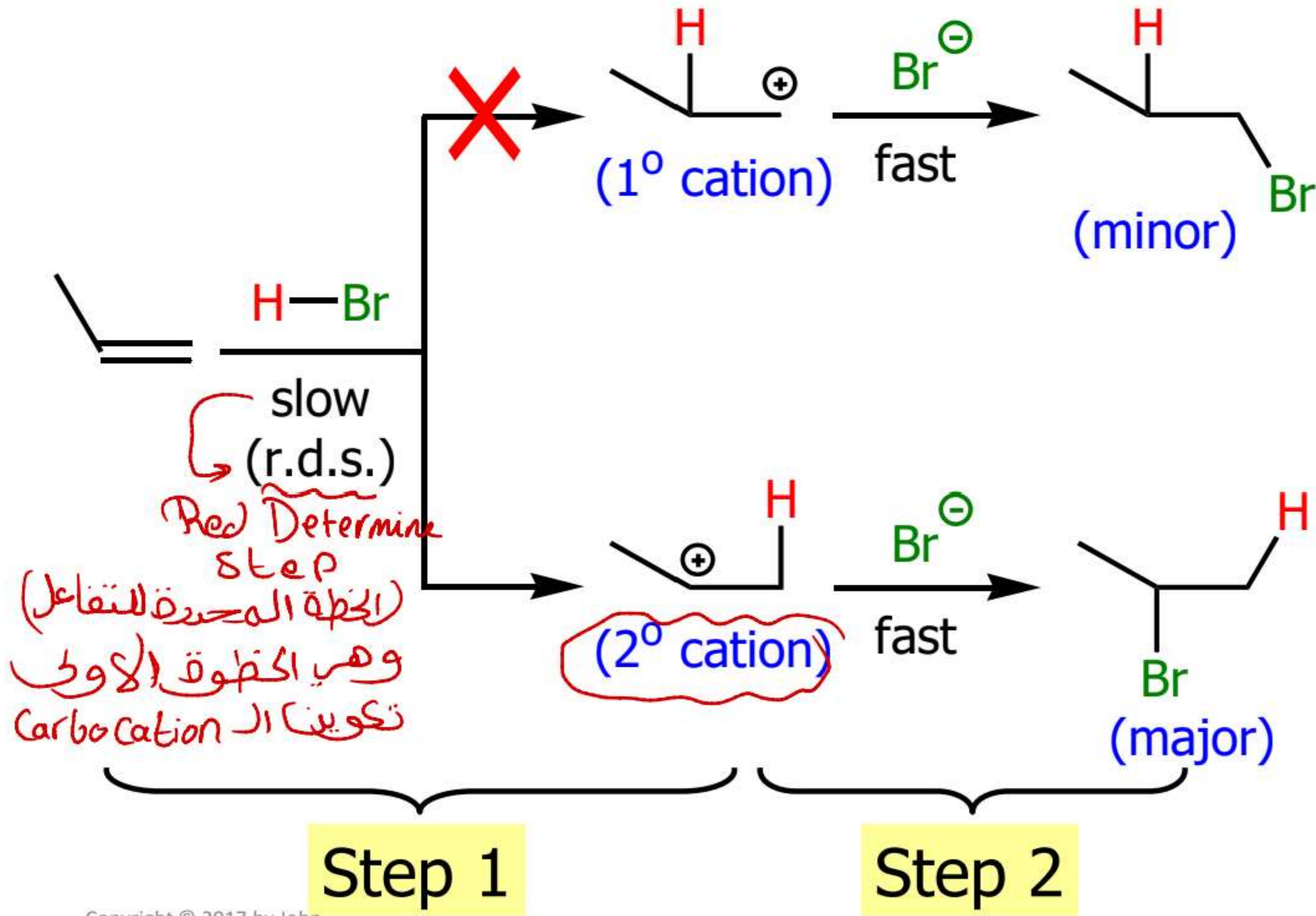
Hydrohalogenation (cont'd)

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.





slow
 (r.d.s.)
 Red Determine
 Step
 الخطوة المحددة للتفاعل
 وهي الخطوة الأولى
 تكوين ال Carbo cation

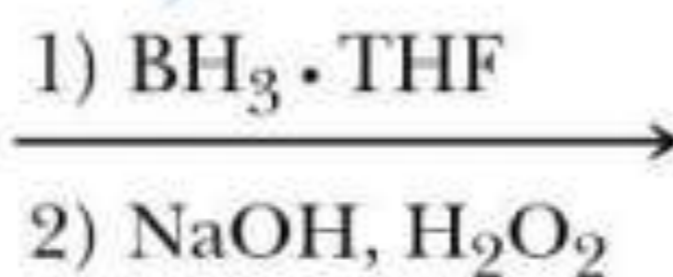
Step 1

Step 2

Hydroboration/Oxidation

- Final product is an anti-Markovnikov alcohol
- Two step reaction, BH_3 , $\text{H}_2\text{O}_2/\text{NaOH}$

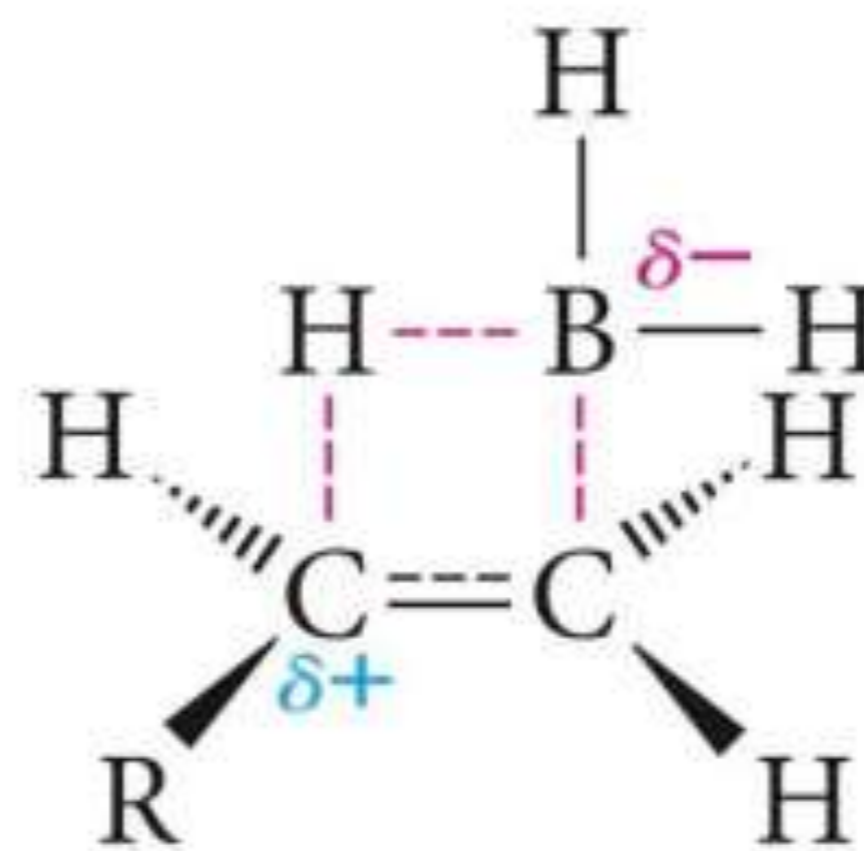
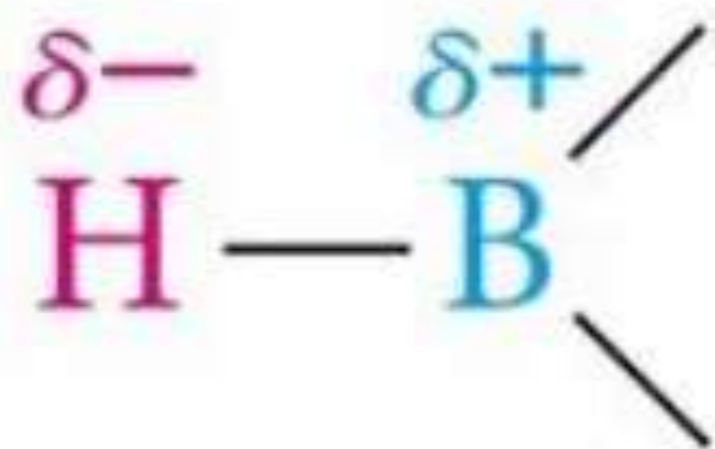
the net result of hydroboration-oxidation is the addition of H and OH across the C—C double bond



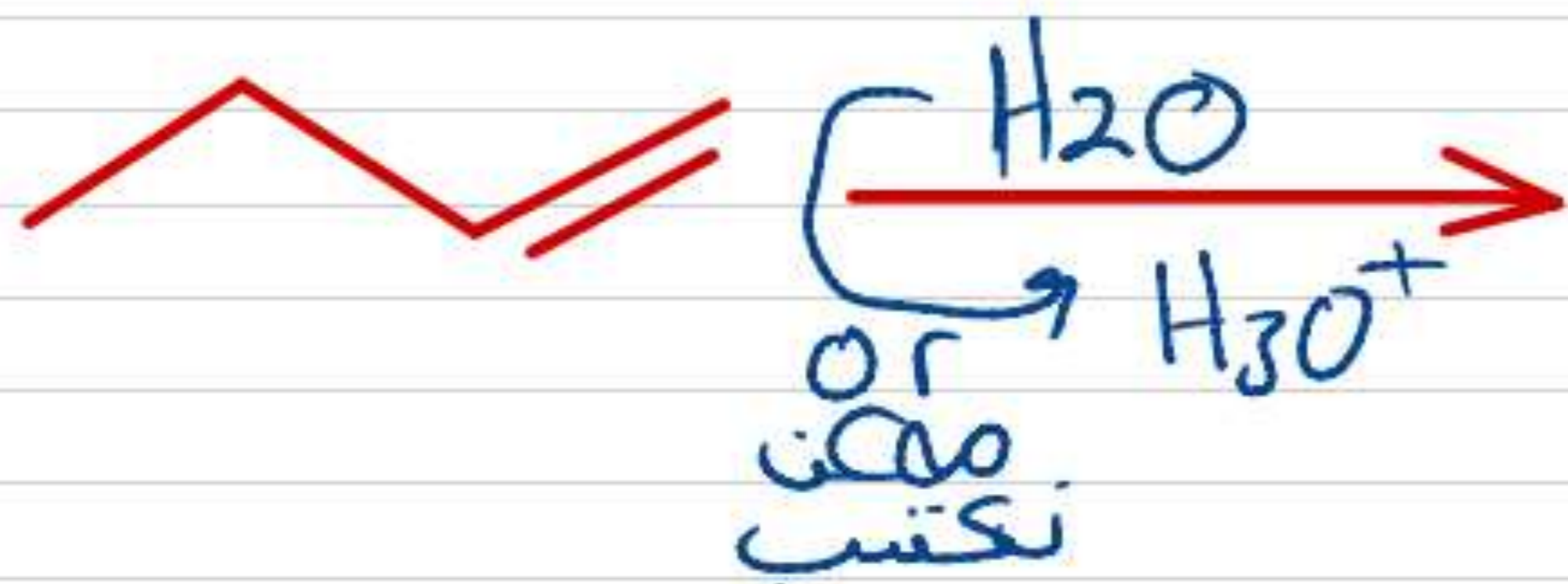
contrary to Markovnikov's rule, the hydrogen has added to the former double-bond carbon with the fewer hydrogens

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



transition state
for hydroboration



طيب انا مايدي احقر ↑ هاد
 انا بيدي احقر هاد

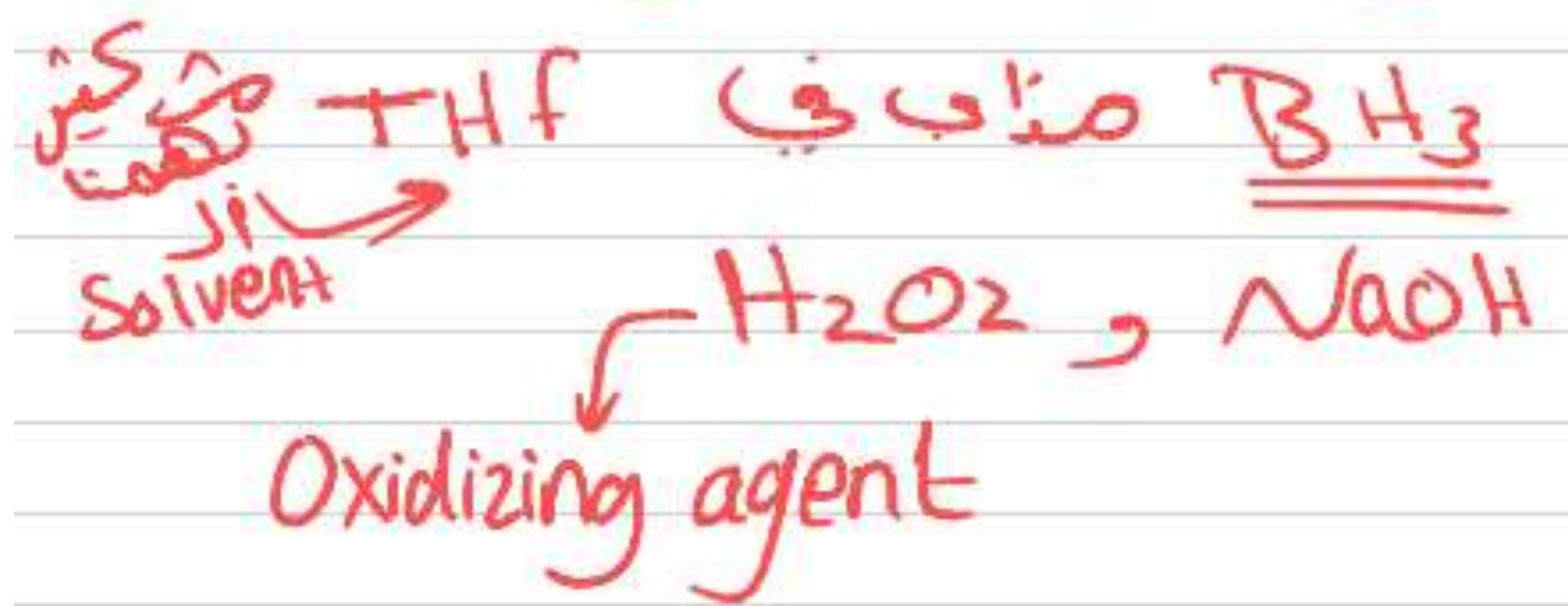


* الفكرة هون انه انا صنت

ال H وال OH مع **antimarkovnikov**

ل هاد في reagents ممكن يعطوني
 هاد ال product؟ يه في reagents هون
 عبارة عن 2 steps reaction

وهول ال reagents :-



الآن ال double bond يحتاجنها
ال BH_2

امنا كنا فعي عن ال HCl
انها $\delta^- C - \delta^+ H$
وانه يتجى ال double bond
ويتهاجم ال H

So we can prepare

Alcohol either with
or anti Markovnikov

لكن هون بيحى دورنا فى اختيار
ال reagent

لما بنا يان مع Markovnikov لازم نختار
 H^+ مع H_2O

طيب فيجى لـ BH_3



هنا البورون ال EN لها
هي اقل من ال C لترانها

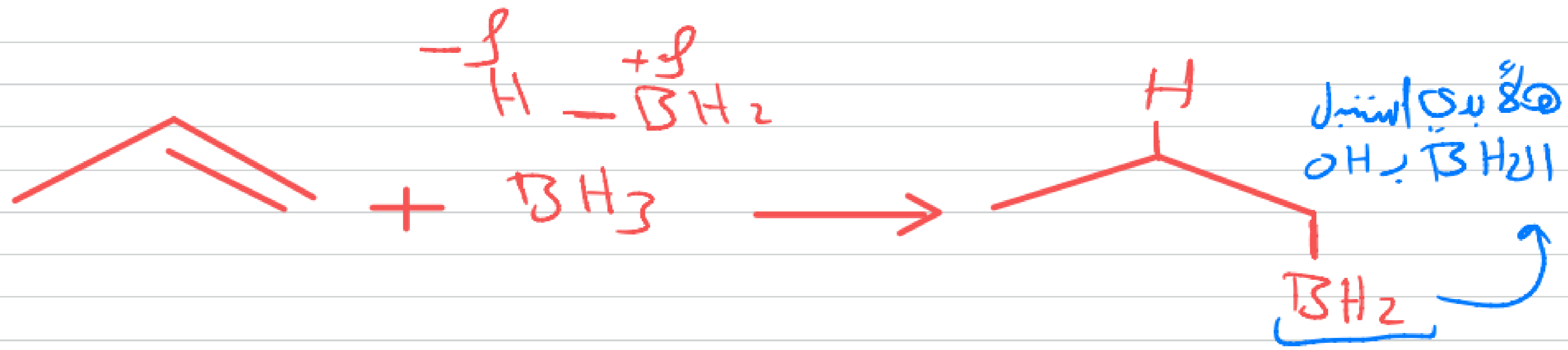
اقل من H ، لذلك هون ح

تنعكس قصة ال Polarization



لكن اذا نختار ال anti ح نختار BH_3 و THF 1)

2) $NaOH$ و H_2O_2



إضافة BH_2 إلى الكربون الأقل استبدالاً

BH_2

NaOH
 H_2O_2



Alcohol

هون تسمي antimarkovnikov وليكن عملية الإضافة

* Note: الفرق بين الـ EN قلت عملية الإضافة: لـ الـ H^+ يتروح على C الأقل H

صابتهم

Hydroboration (cont'd)

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.

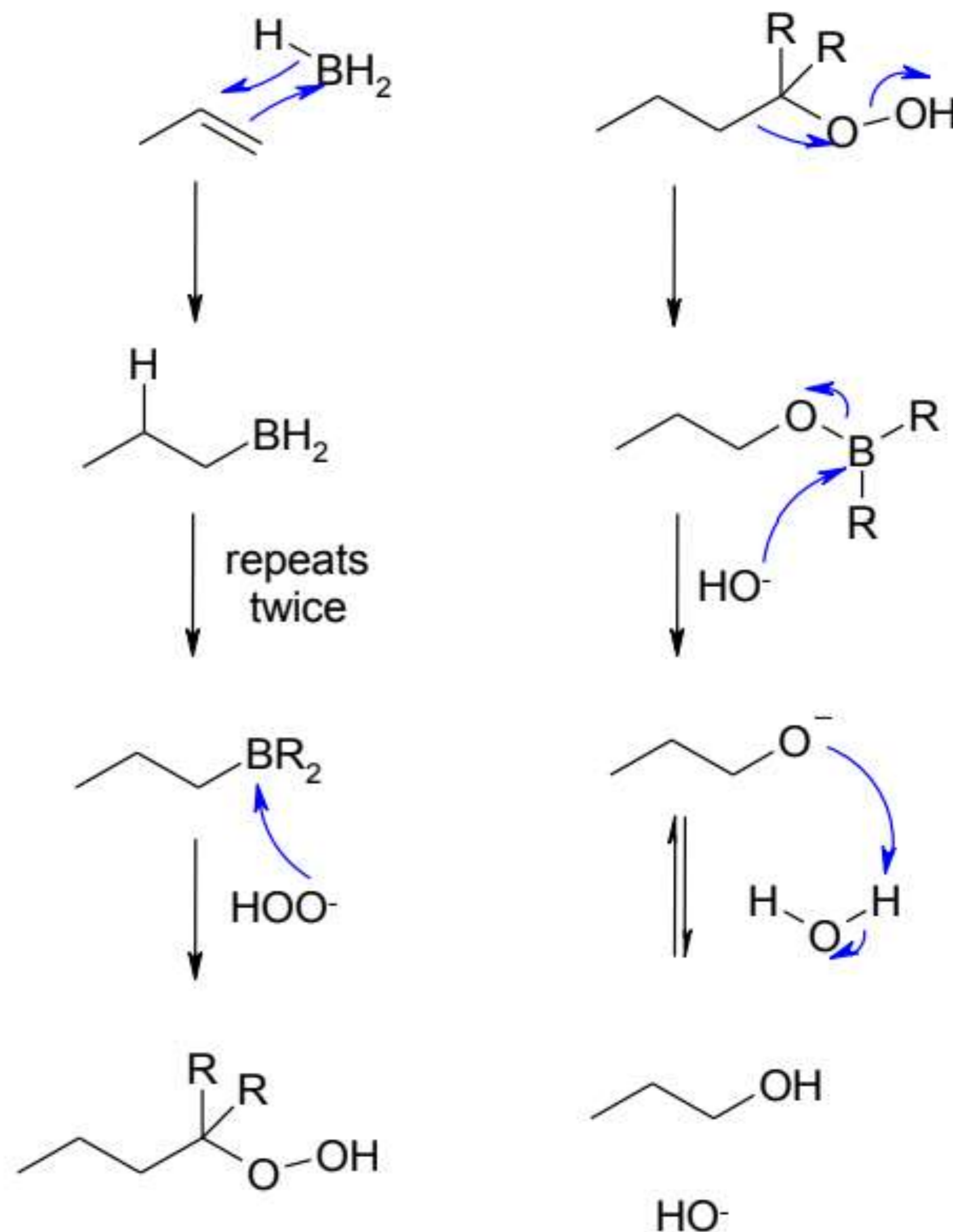
Step 2: step1 repeats twice more

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

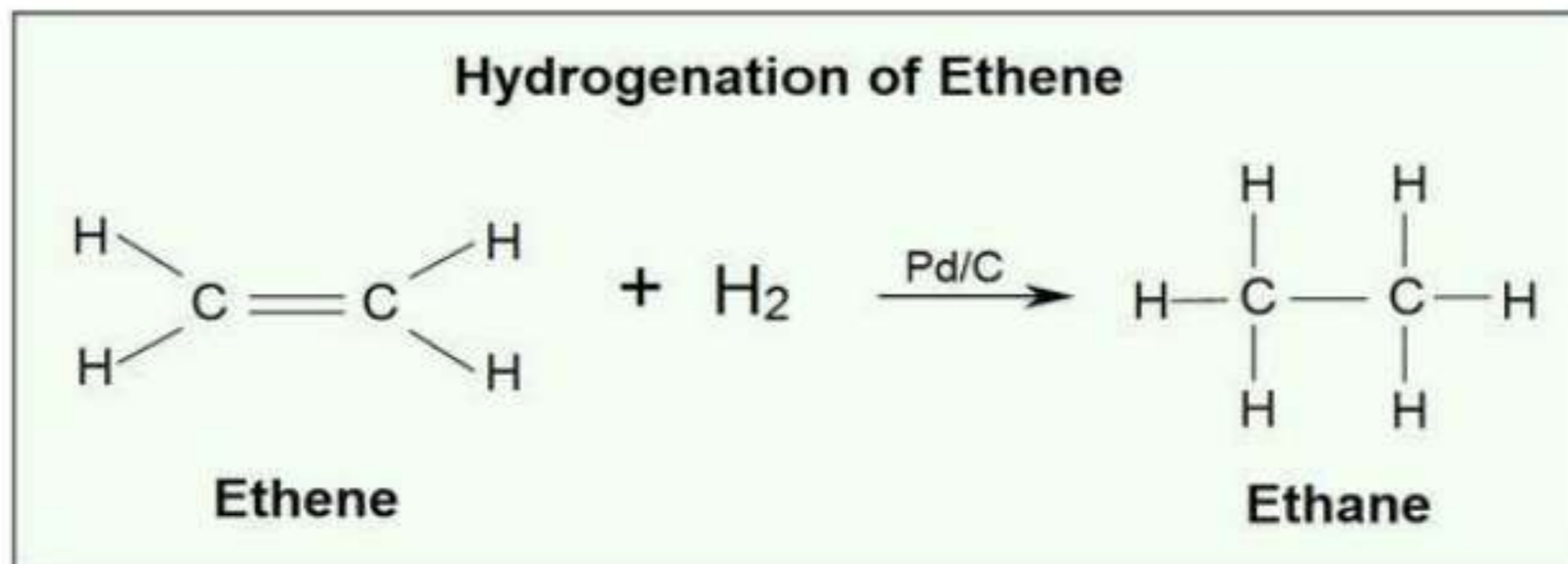
Step 6: acid/base reaction to protonate the alcohol



الفكرة اف بي احوال الالكين لان كان

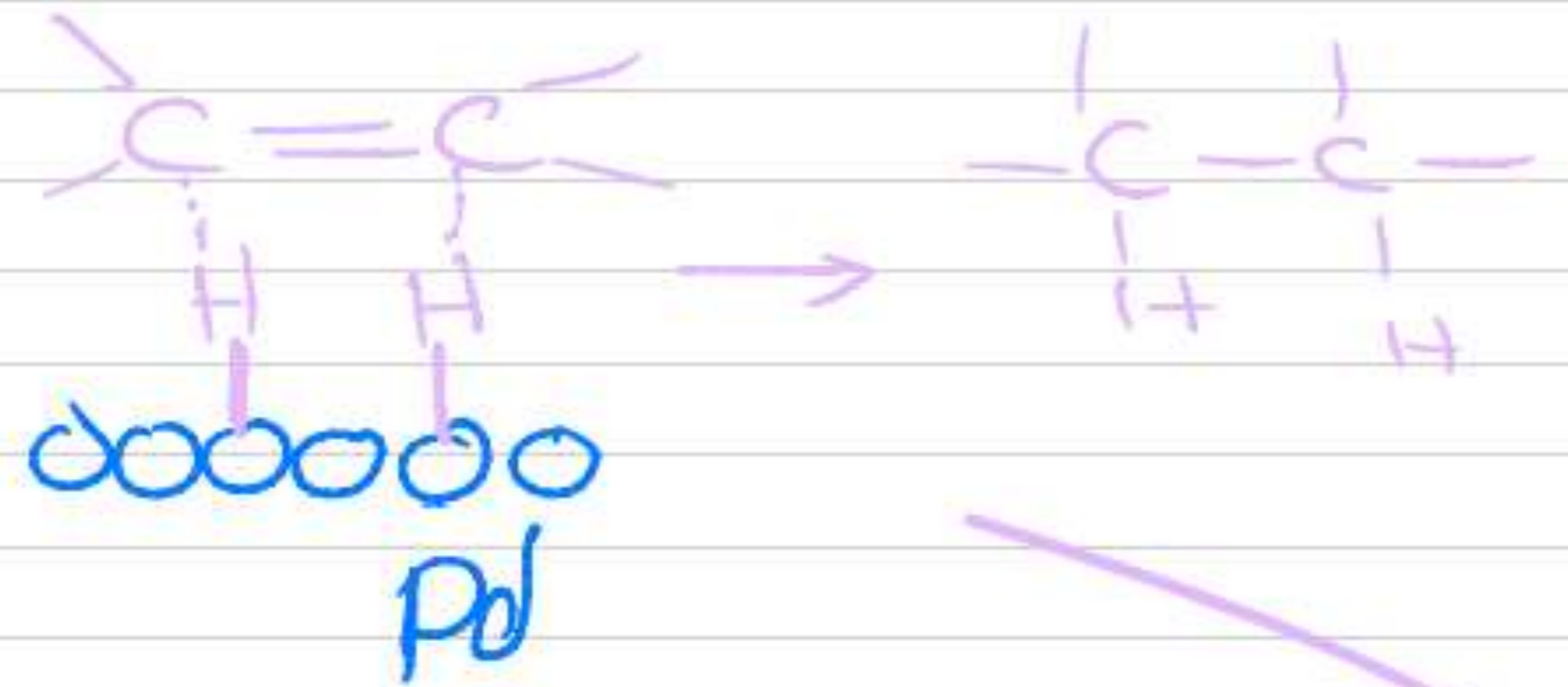
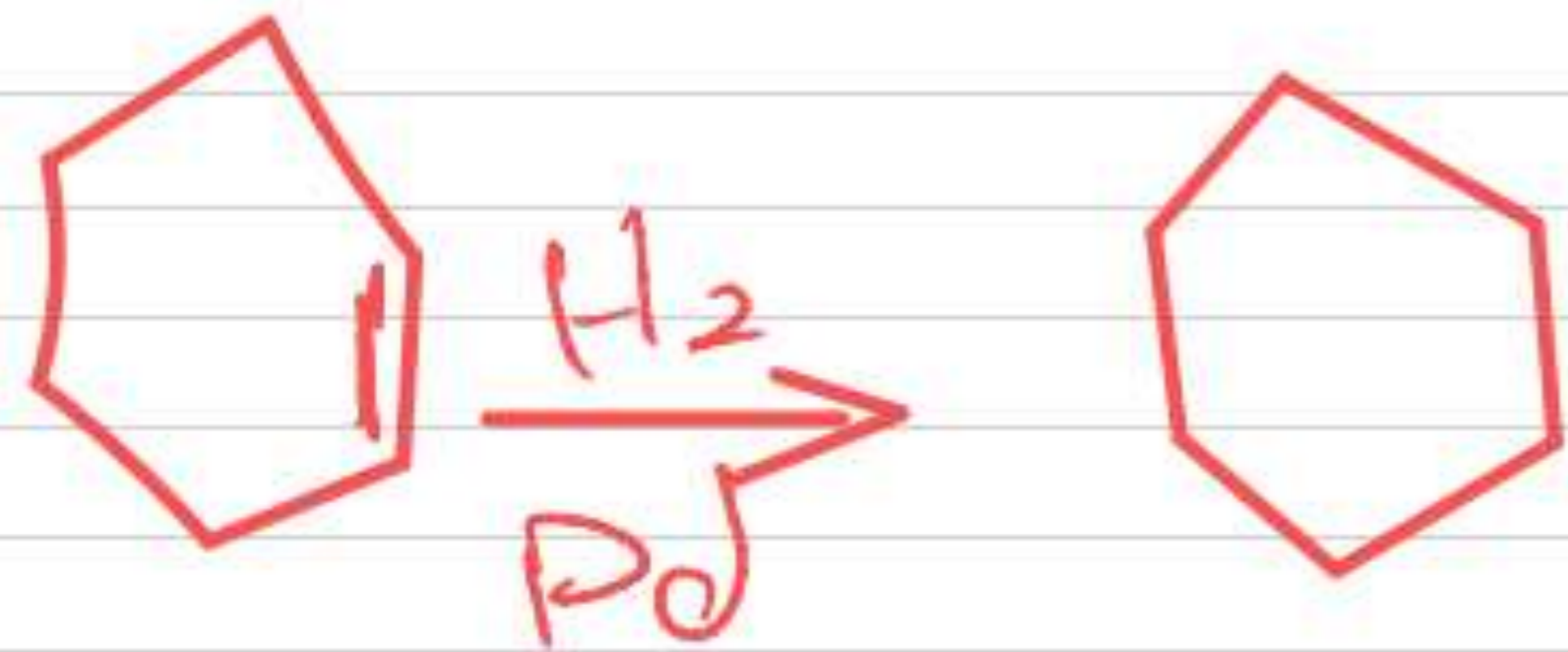
Hydrogenation

- Addition of H₂ 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.



فكرق هاد التفاعل :-

انا عندي catalyst
له مثلا Pd



ال catalyst يتفاعل
ال surface كانه مع ال H₂
ولكن بيس عن interaction
مع ال H₂ و ينتج الكان

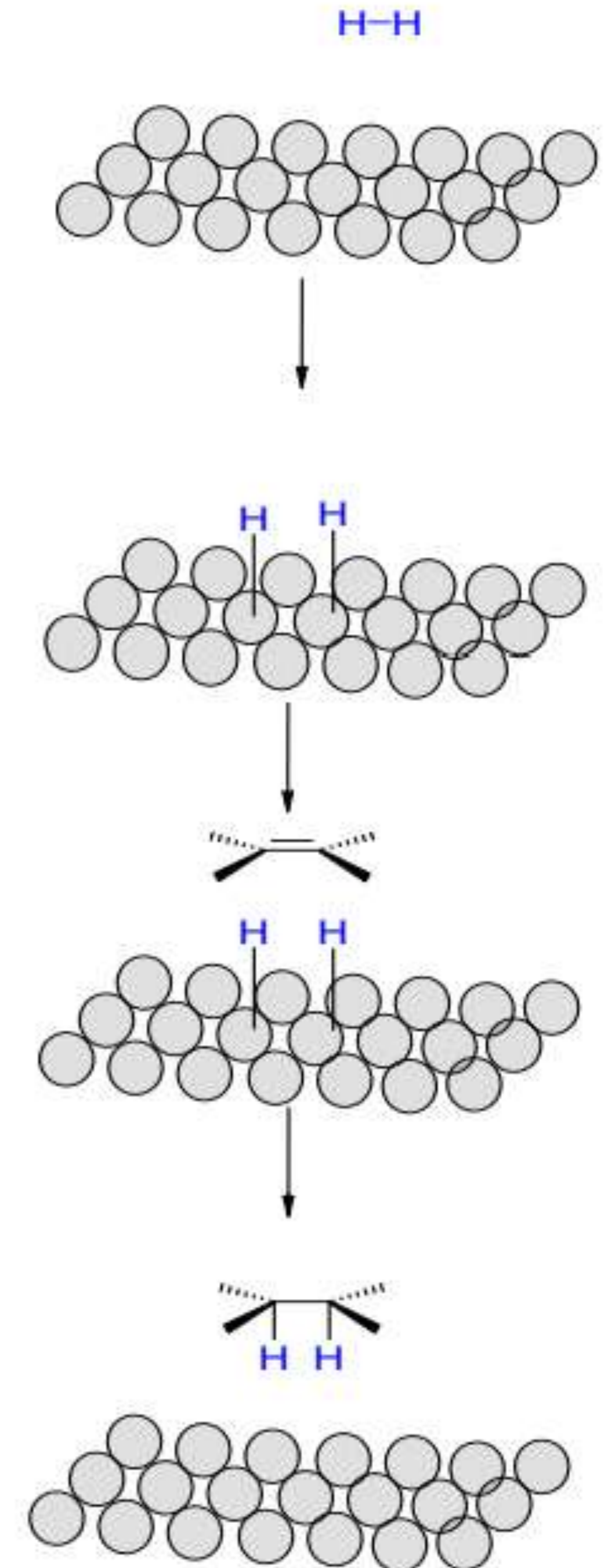
* عملية الاضافة ال H₂ تقوا بنفس
الطرق مع وهاد ما يسمى بال
syn addition

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 MnO_2 solid
- OsO_4 also used to make 1,2-diols



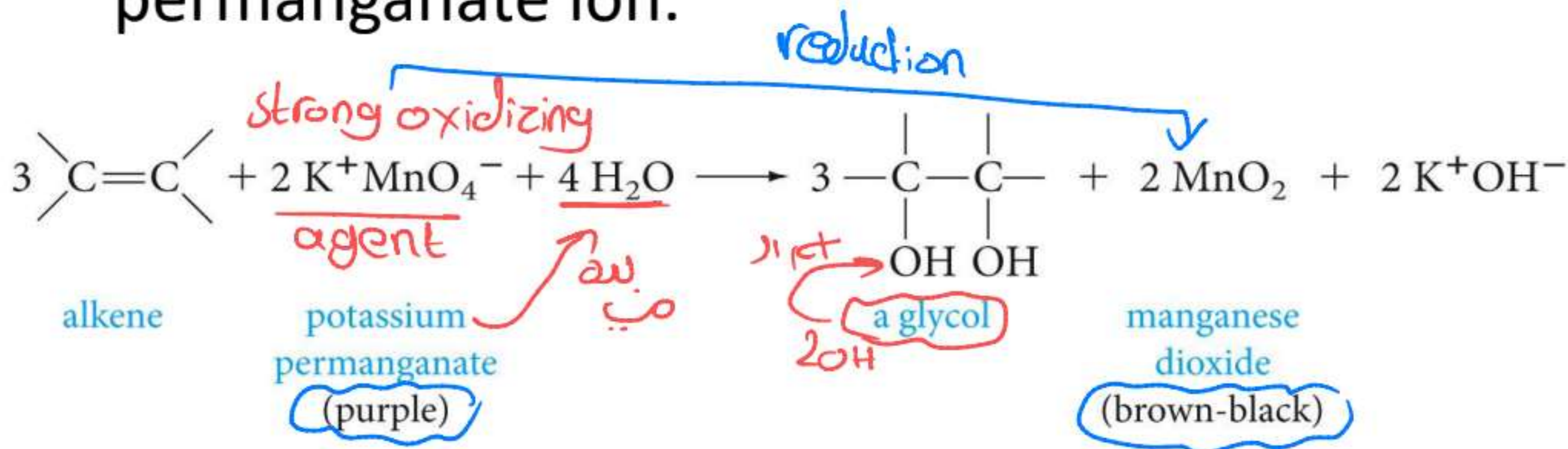
عملية التغير في اللون
had indication انه
مبار في oxidation

Purple

brown -
black

Oxidation: Permanganate (cont'd)

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



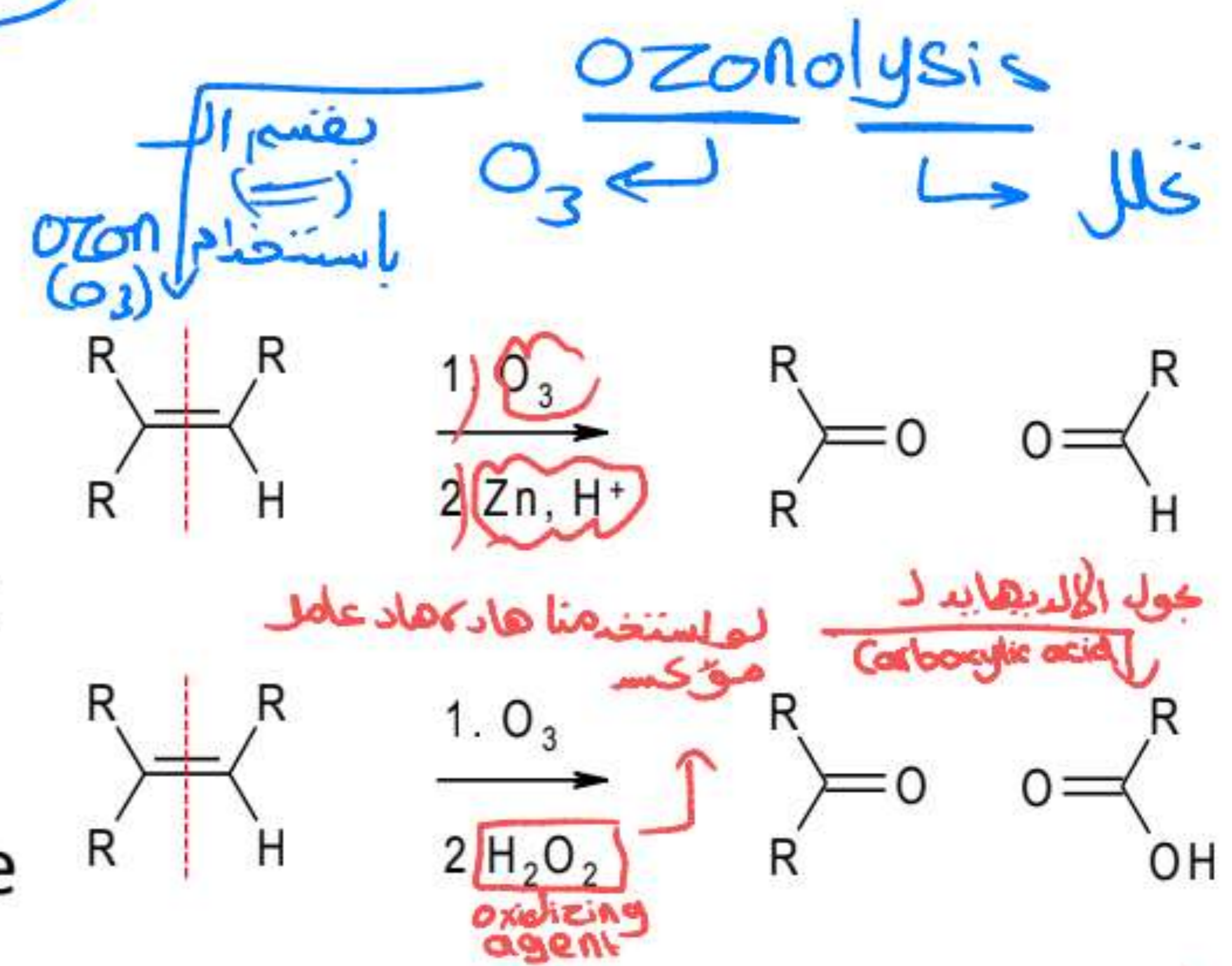
Ph يعنى حلقة البنزين (فينيل)

فقط بدنا نعرف التفاعل

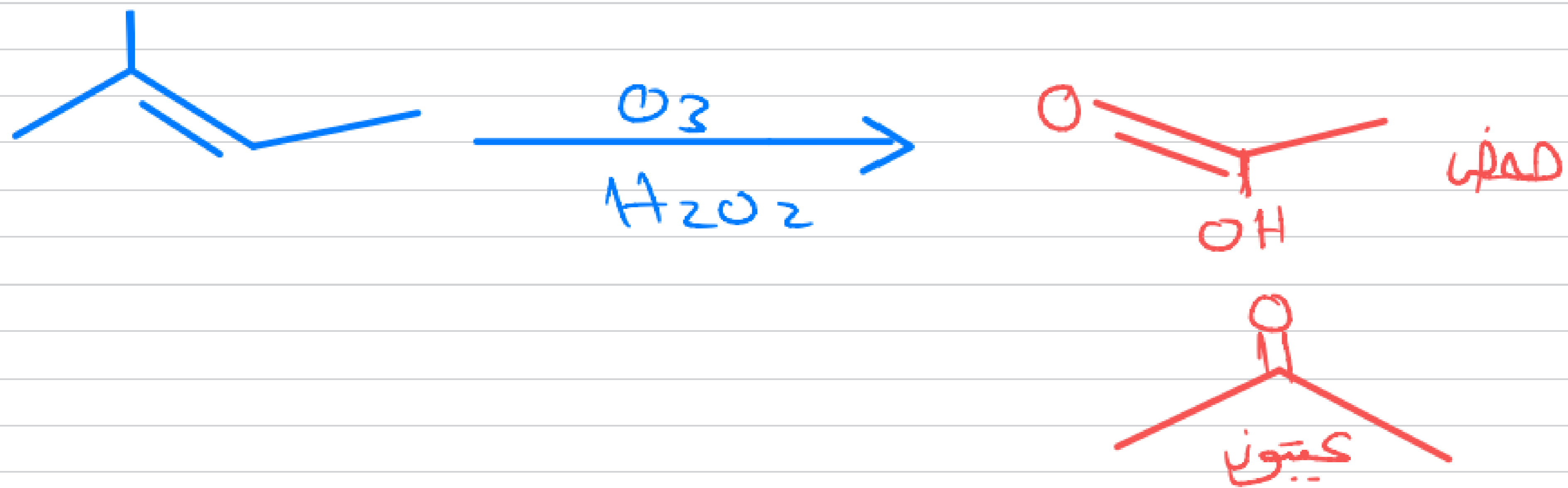
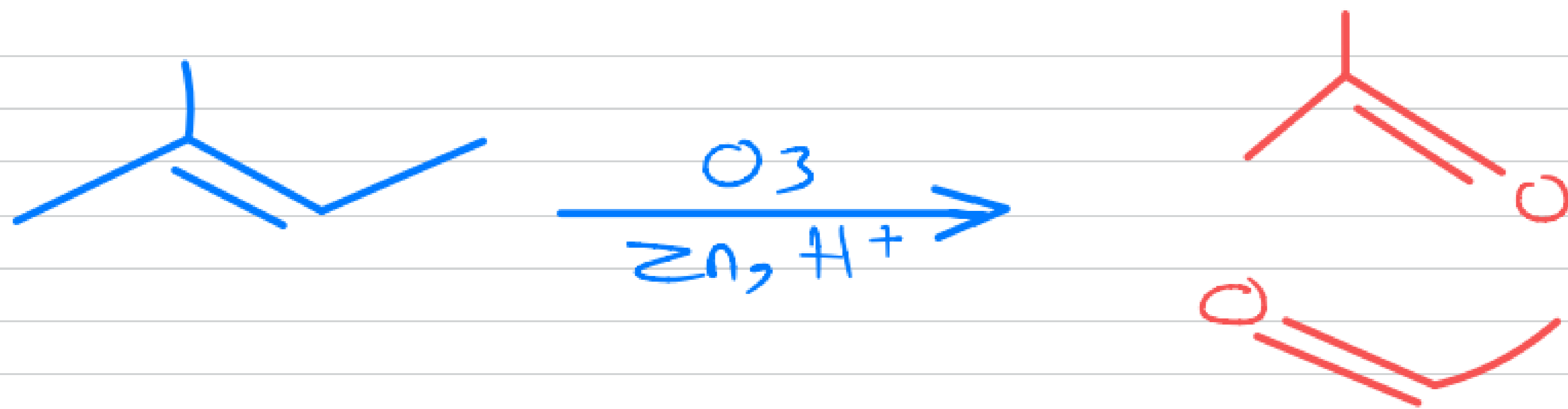
Oxidation: Ozonolysis

بعضه يعتبر Oxidation

- Cleaves the double bonds in half generating two carbonyl groups
- In Zn/H⁺ get aldehydes or ketones (reductive products)
- In H₂O₂ ketones or carboxylic acids (oxidative products)
- Was primarily used for structure determination since ozone only reacts with C-C multiple bonds.
- Generates smaller molecules that are easier to identify.



* عننا C=C ح تنقسم زئين ٥ الجزء اليمين
 ح يافد (O) والجزء الاخر (O) ويطلع product ثاني
 ← ال products المحتملين :-
 - الديهايڊ
 - كيتون



Oxidation: Ozonolysis (cont'd)

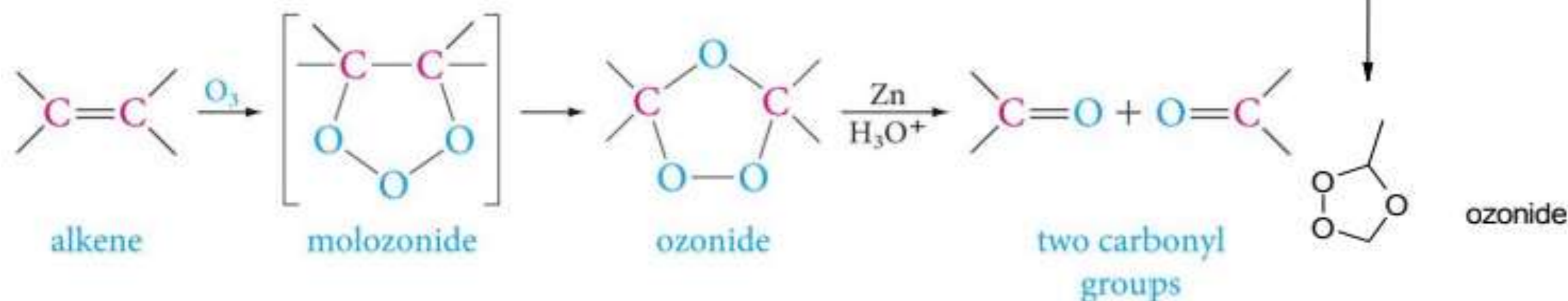
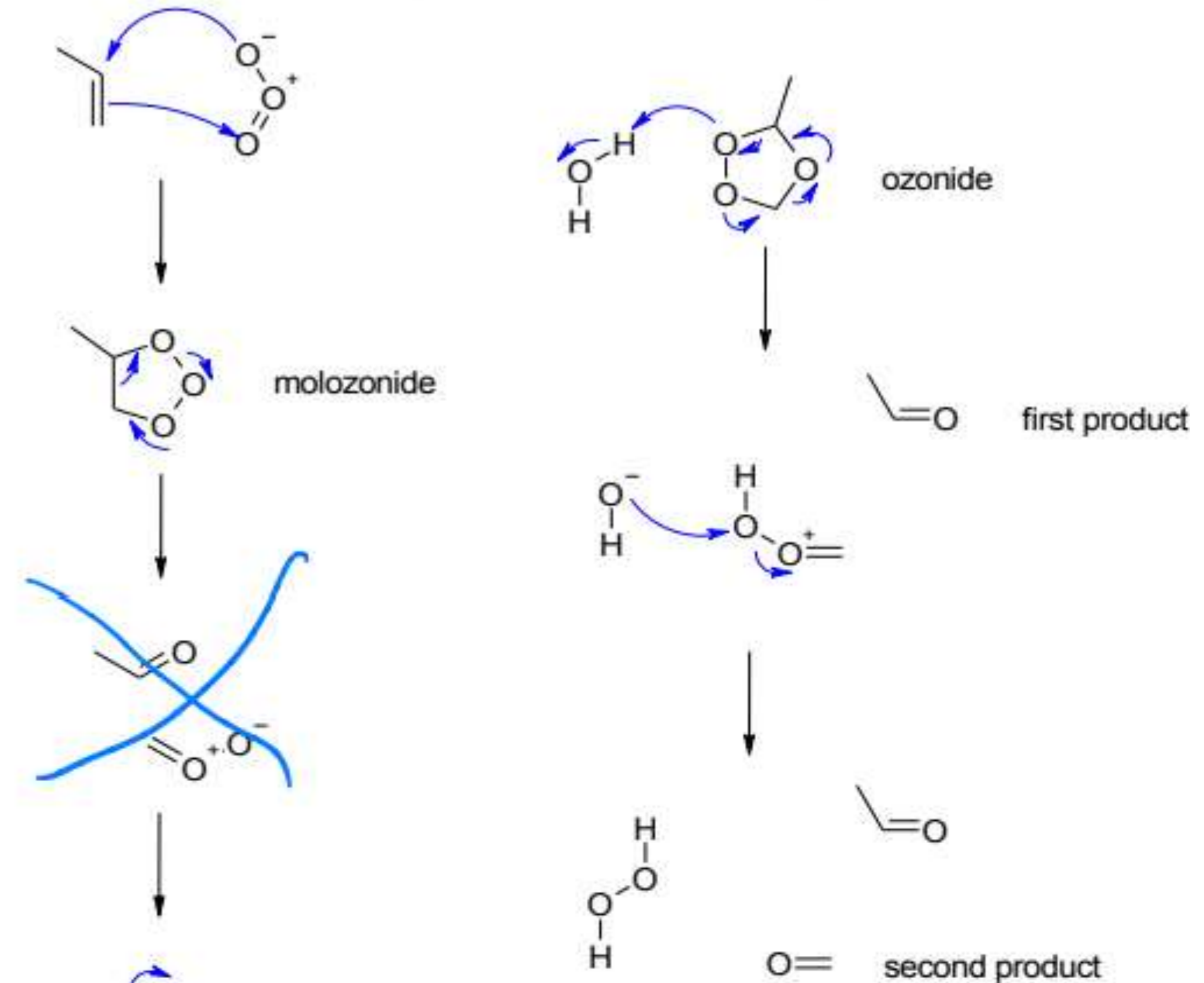
Handwritten signature

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



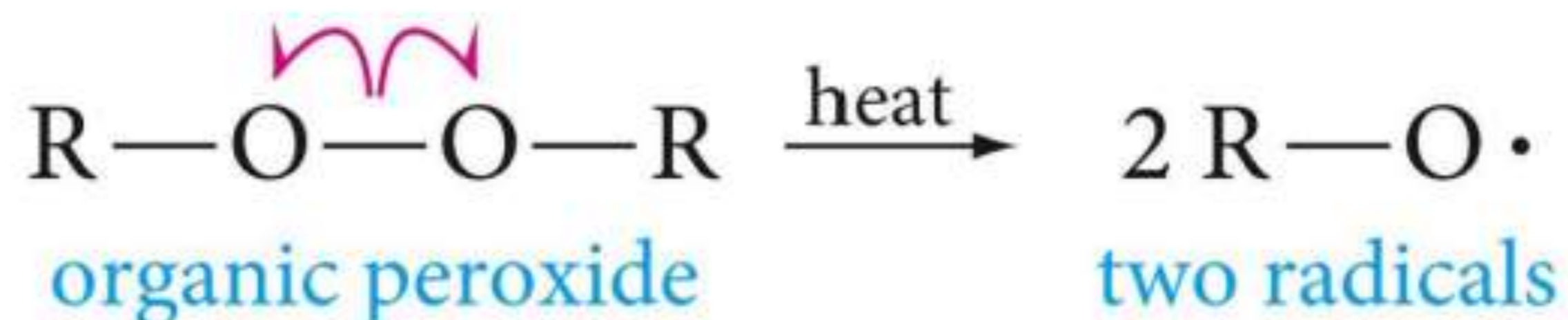
Radical Addition Reactions: Polymers

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.

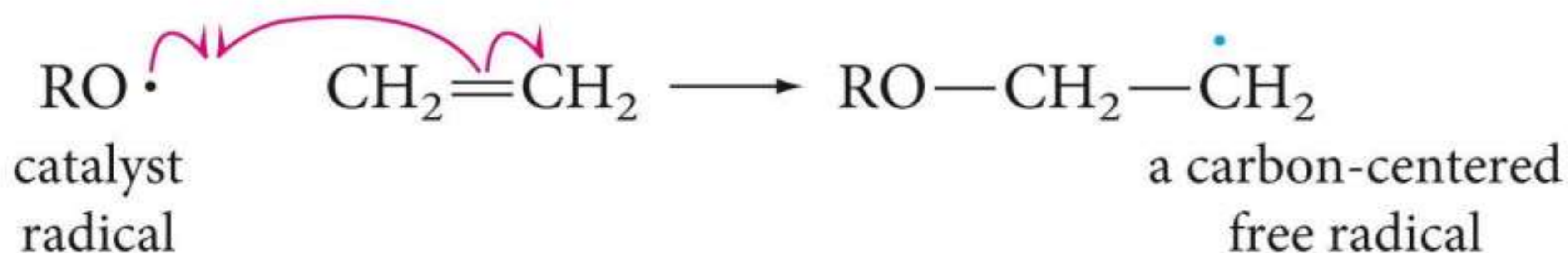
As with the other free radical reaction we have seen, this requires an initiation step, followed by chain growth and finally a termination step.

Radical Addition Reactions: Polymers

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

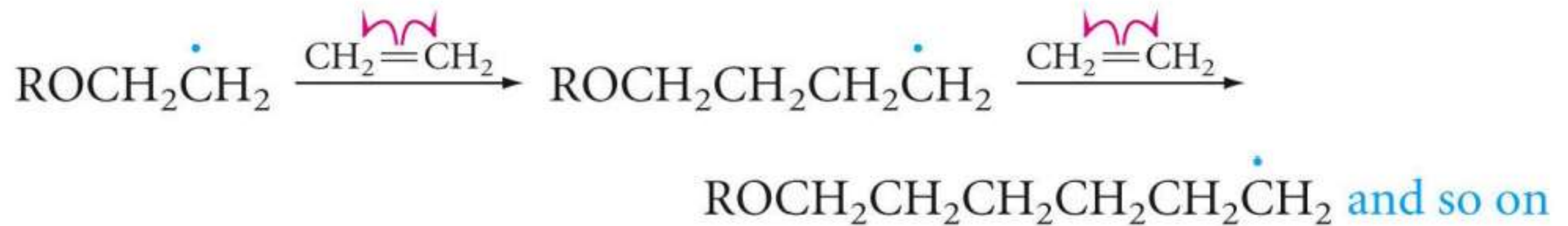


In contrast to the free radical substitution reaction in a free radical addition the initiator adds to the monomer rather than removing a H atom.



Radical Addition Reactions: Polymers

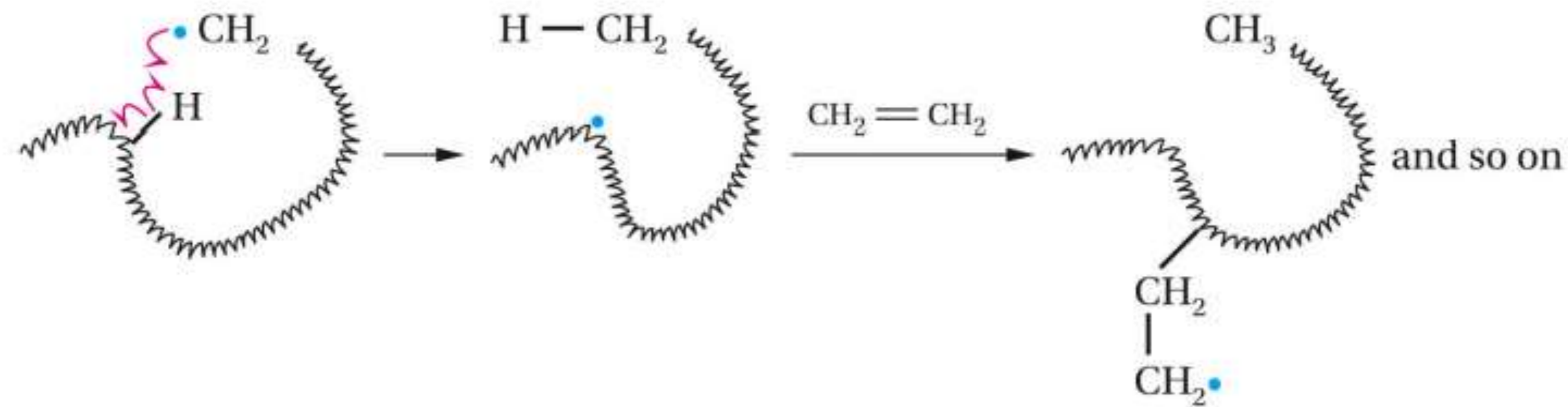
Chain growth occurs as the carbon radical reacts with additional monomers.



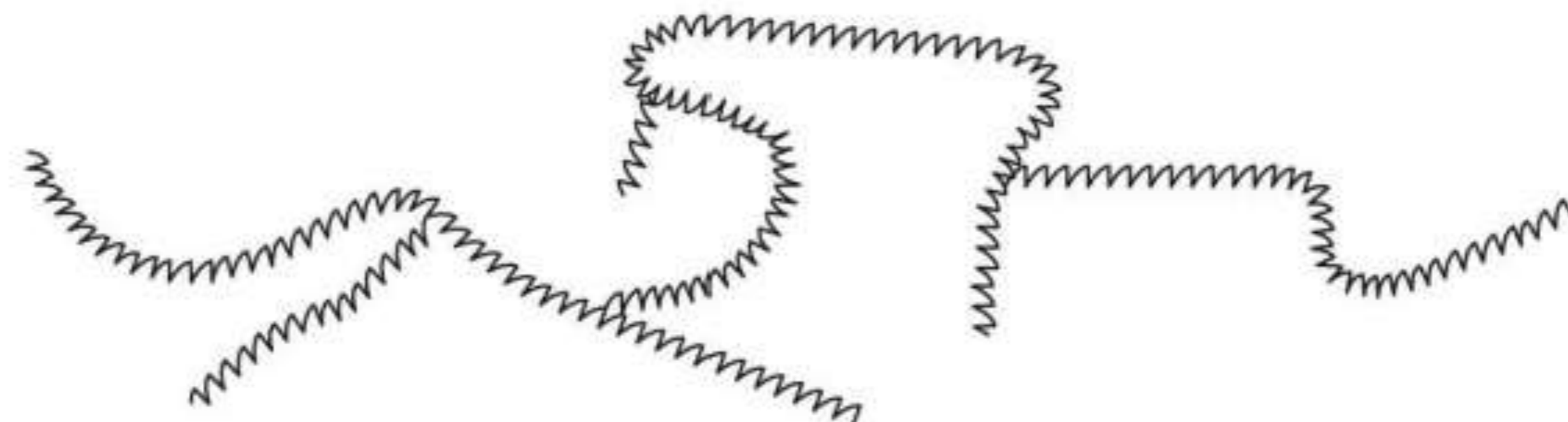
Termination usually occurs when two carbon radical react with each other.

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.



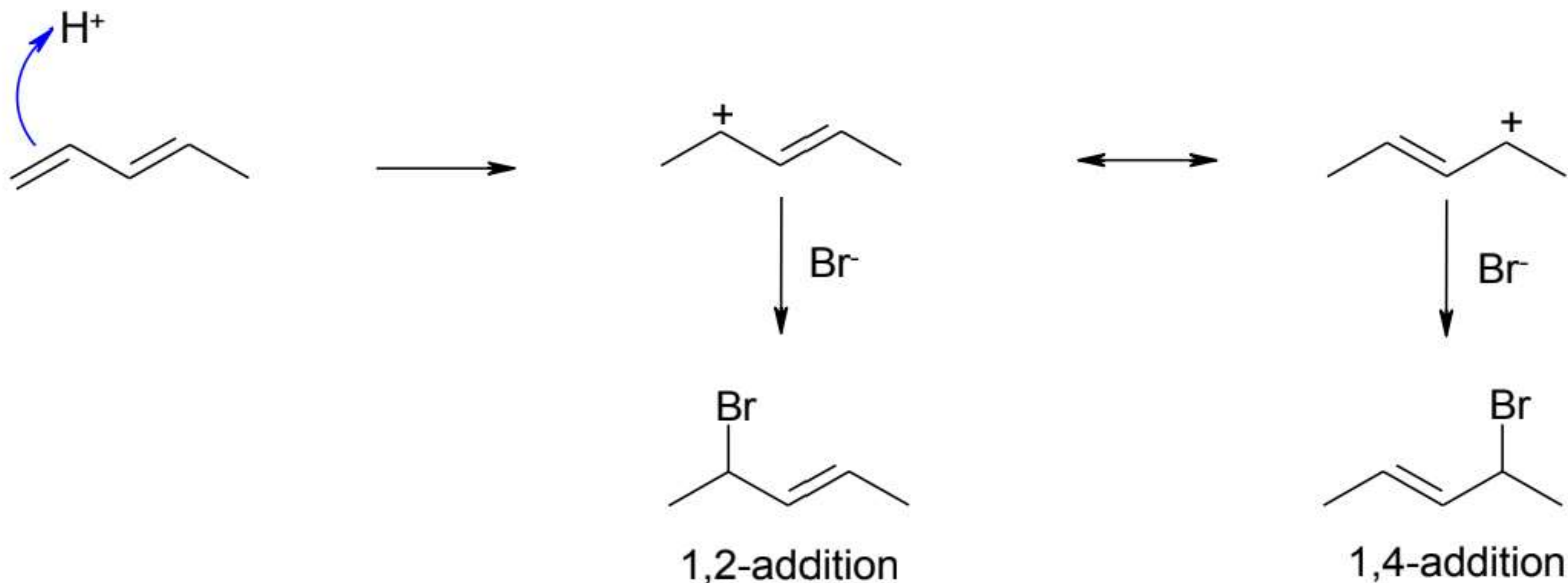
branched polyethylene

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.

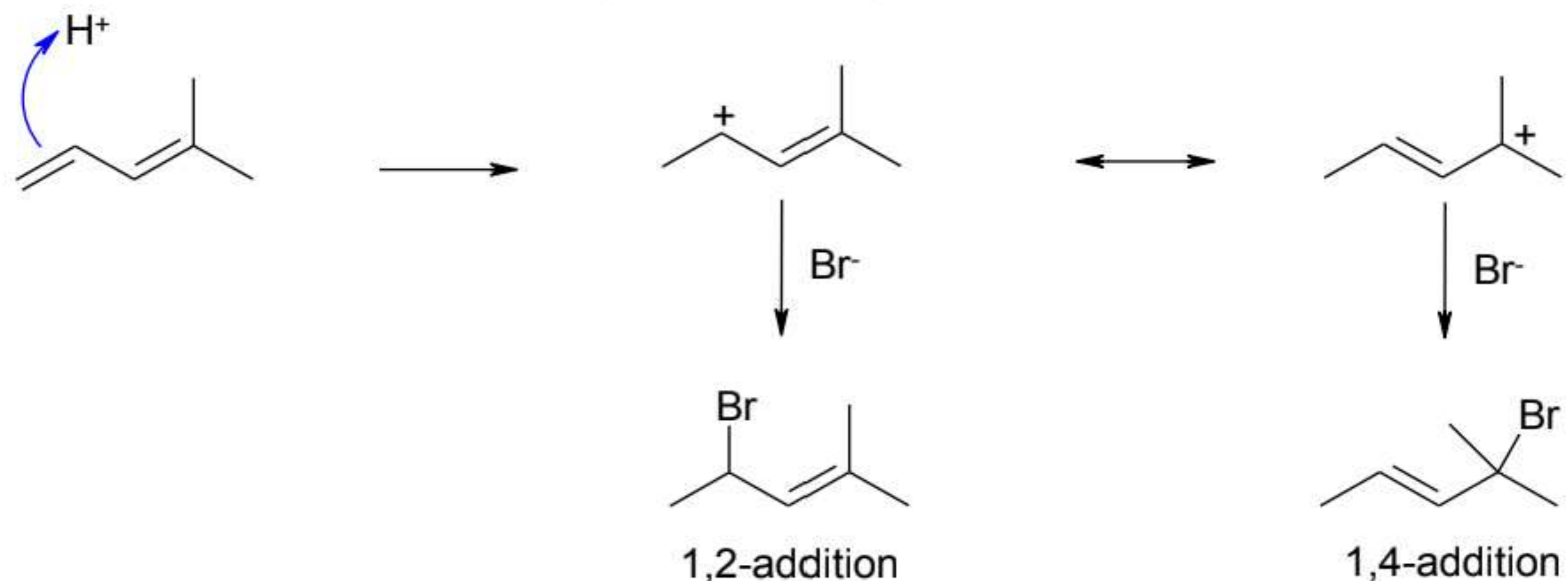
Additions to Conjugated Systems

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°.

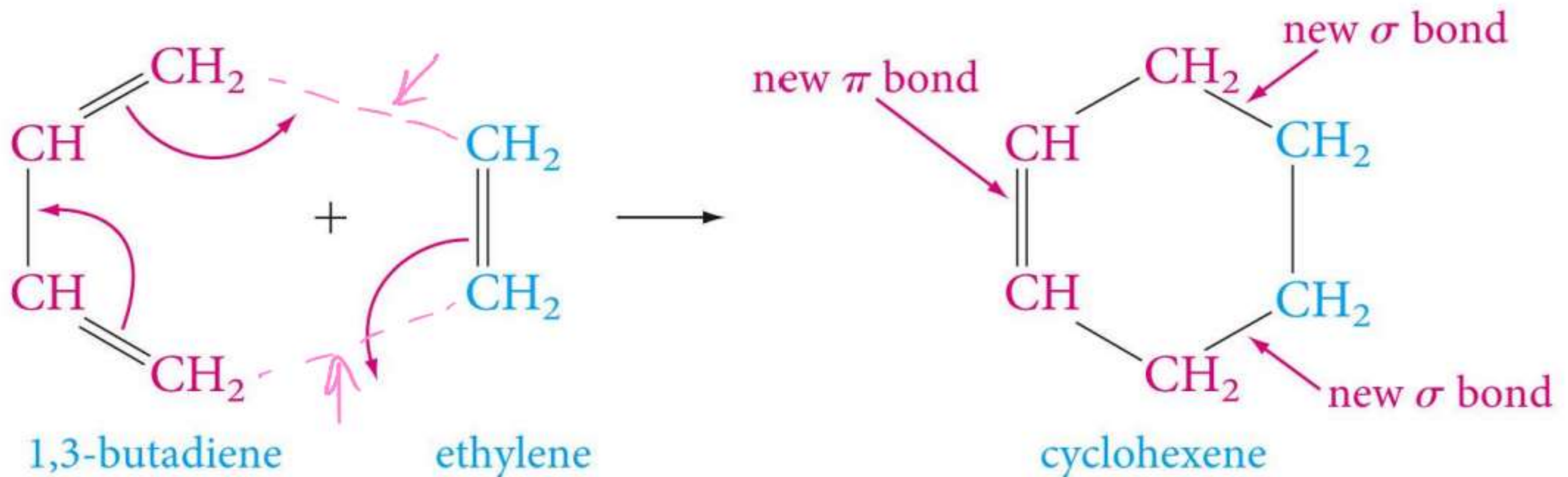
Cycloadditions: the Diels-Alder Reaction

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.

عبارة عن تفاعل بين diene و dienophile

Cycloadditions: the Diels-Alder Reaction

Diene: 1,3-butadiene
Dienophile: ethene
Product: cyclohexene



هلا انا لوعيني هاد :-

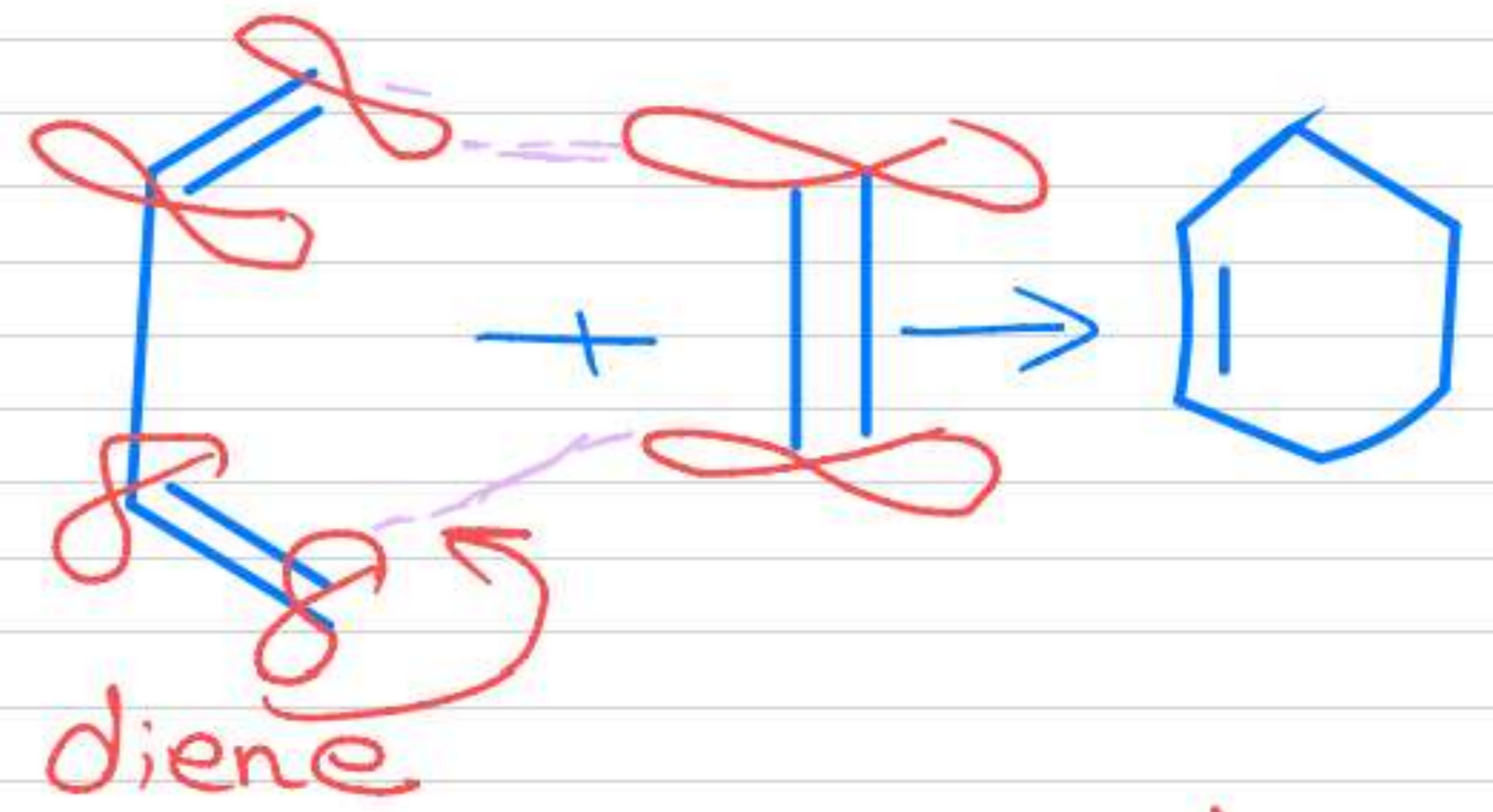
الفكرة انه علينا نتخيل انه هيا
(p orbital) وكمان نتخيل انه هيا

بينهم ()

لما بضمك عننا (p orbital) 2

متقابلةت هتبيطوف ال π

bond الموجودة بال cyclic



diene رح يتفاعل مع الكيب
رح يتيح Cyclo و فيها
double bond

Cycloadditions: the Diels-Alder Reaction

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

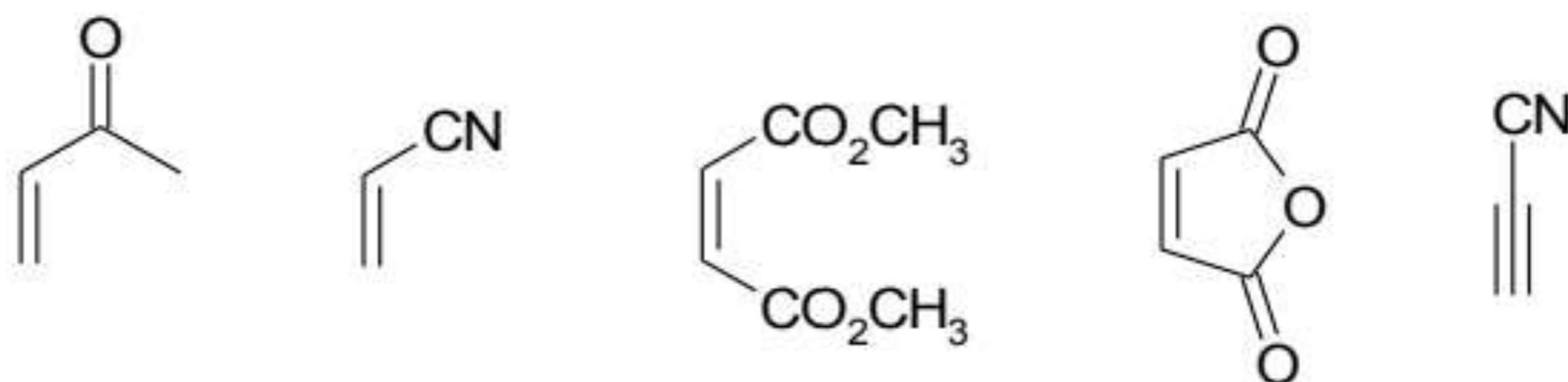
Electron withdrawing groups are groups of atoms that will withdraw electron density of the dienophile π bond which makes it a better electrophile.

Common electron withdrawing groups include: carbonyl ($-\text{C}(=\text{O})\text{R}$), cyano ($-\text{C}\equiv\text{N}$) and esters ($-\text{CO}_2\text{R}$).

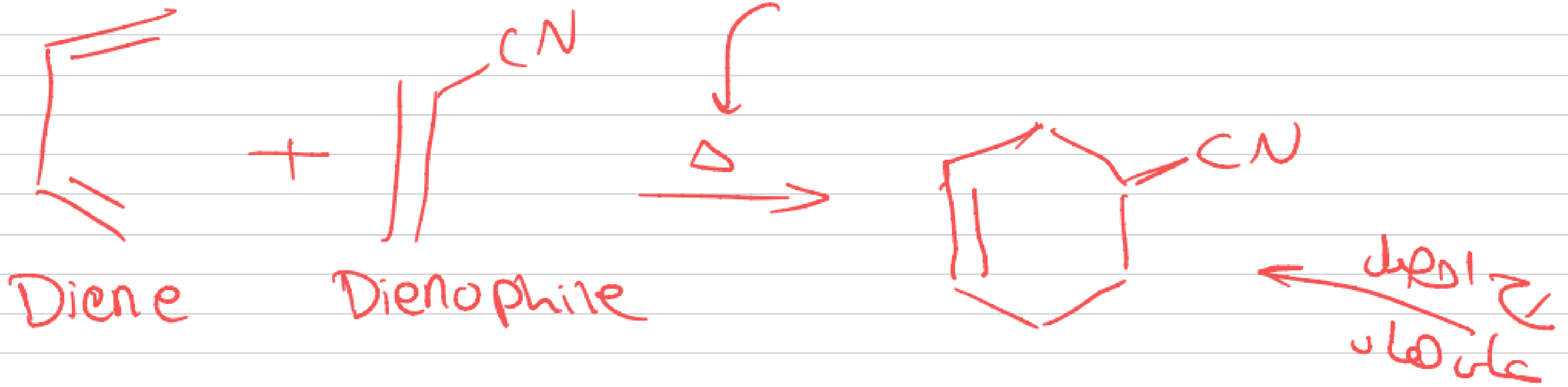
dienes



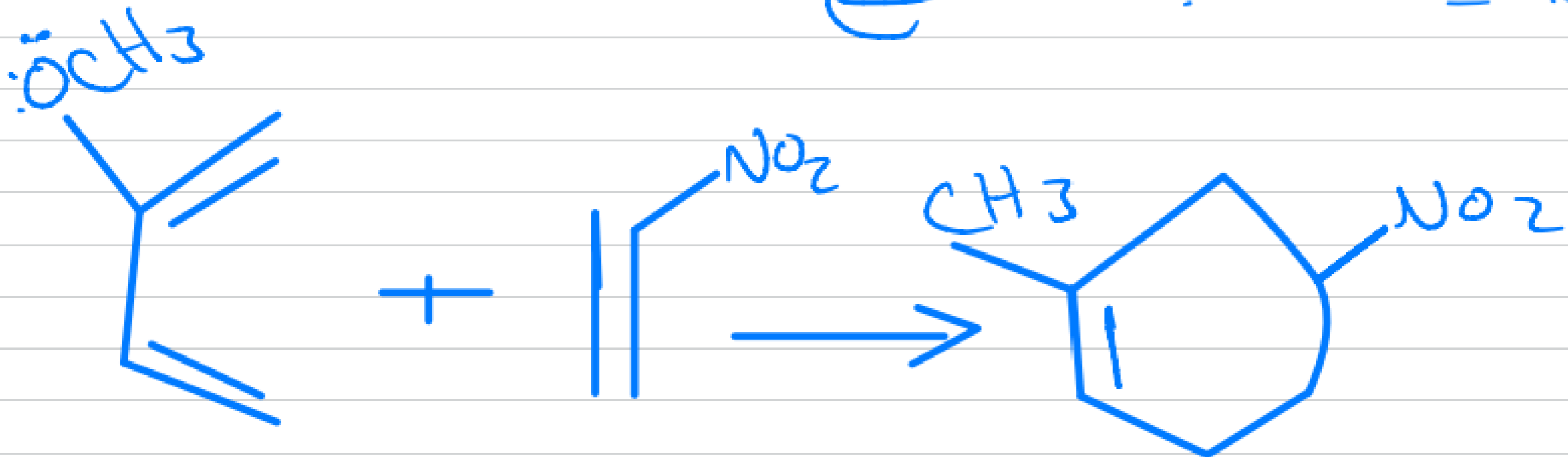
dienophiles



heat به



بشکل عام ال diene هسهول كبروا يكون عليهم مجموعات مُعطية زي CH_3 ، بينما ال dienophile كبروا يكونوا عليهم مجموعة بيتسحب ، لحتا يهت التفاعل ينشكك سريع

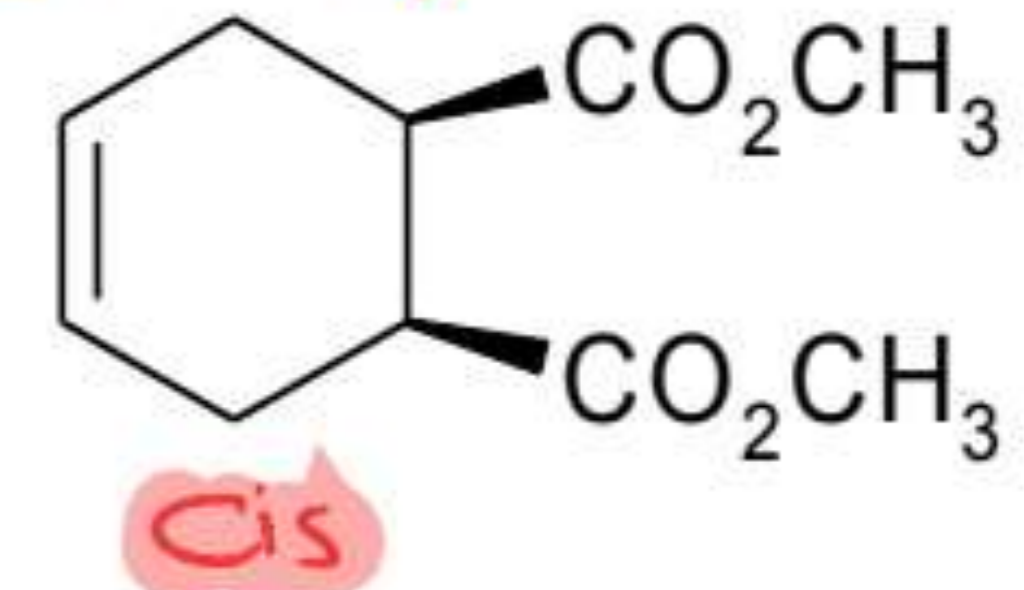
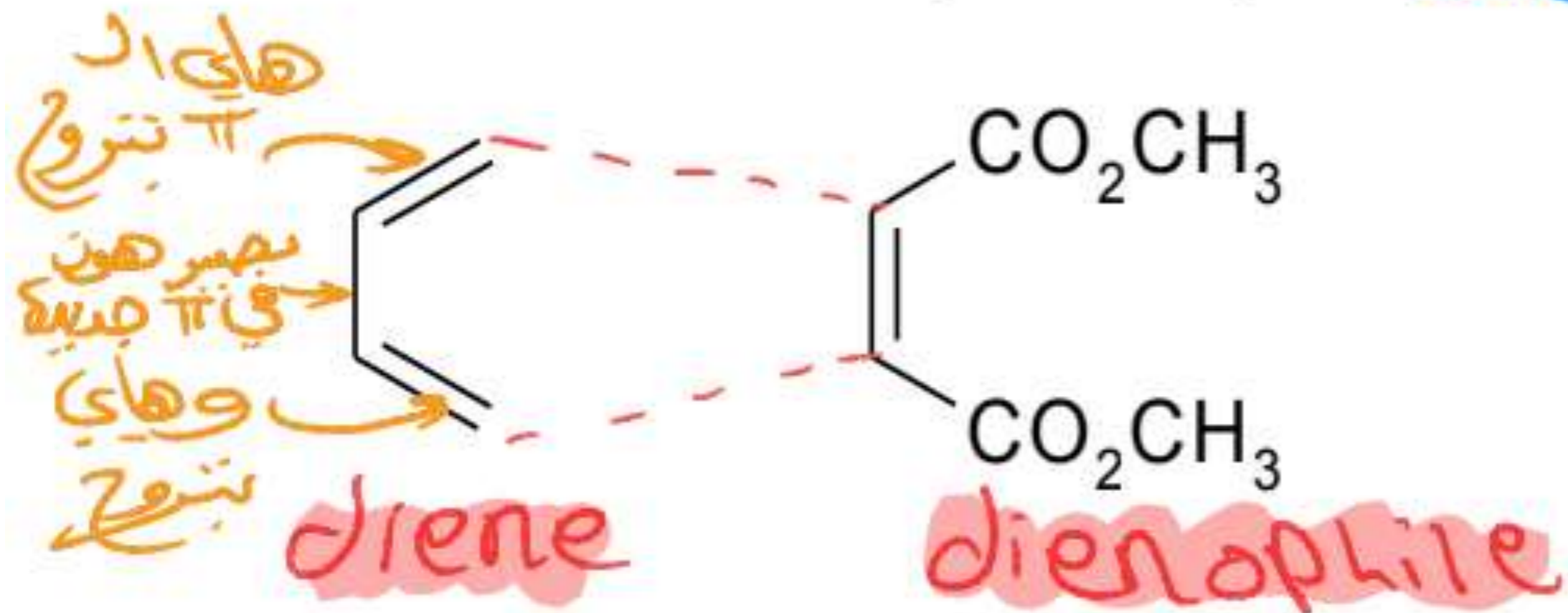


Cycloadditions: the Diels-Alder Reaction

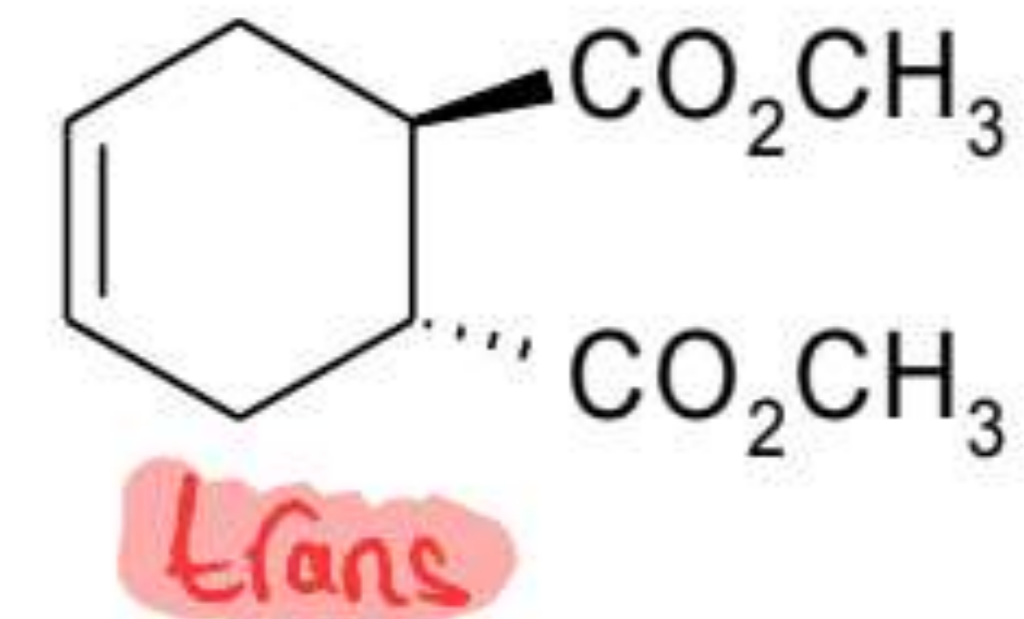
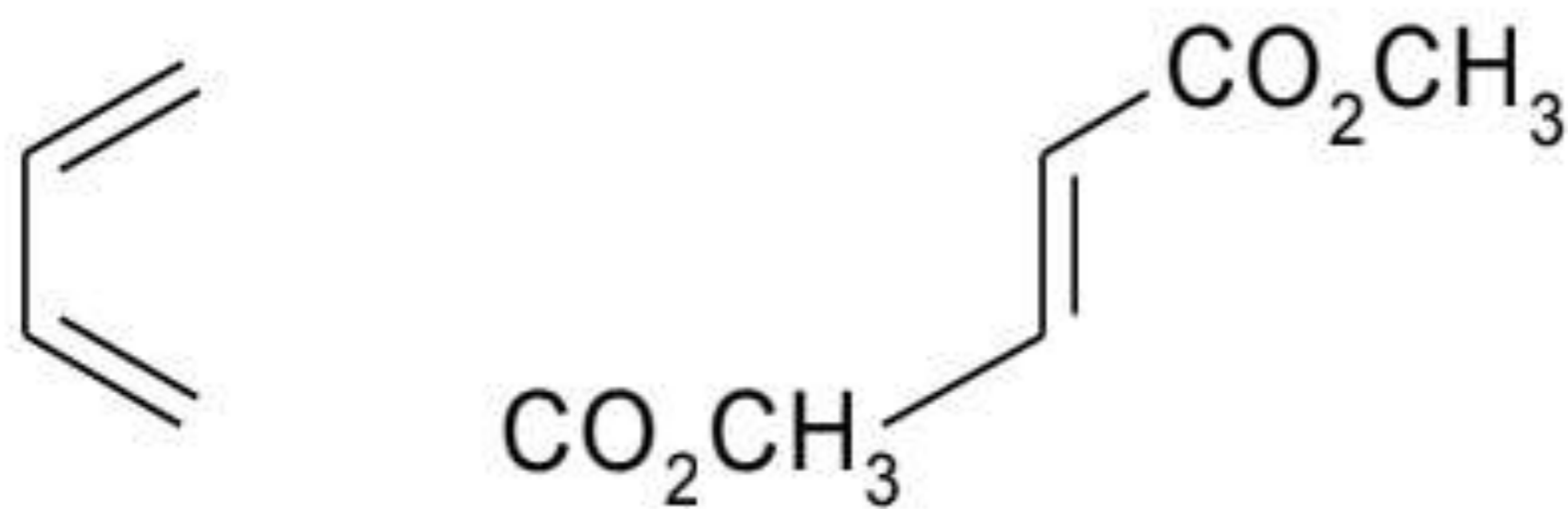
عملية التفاعل بينهم يتكون من بعض انهم يقربوا
 على بعض بنفس الوقت
 (concerted)

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.

لهذا إذا كان في Cis من الـ dienophile
 الـ Product وقتها يكون Cis

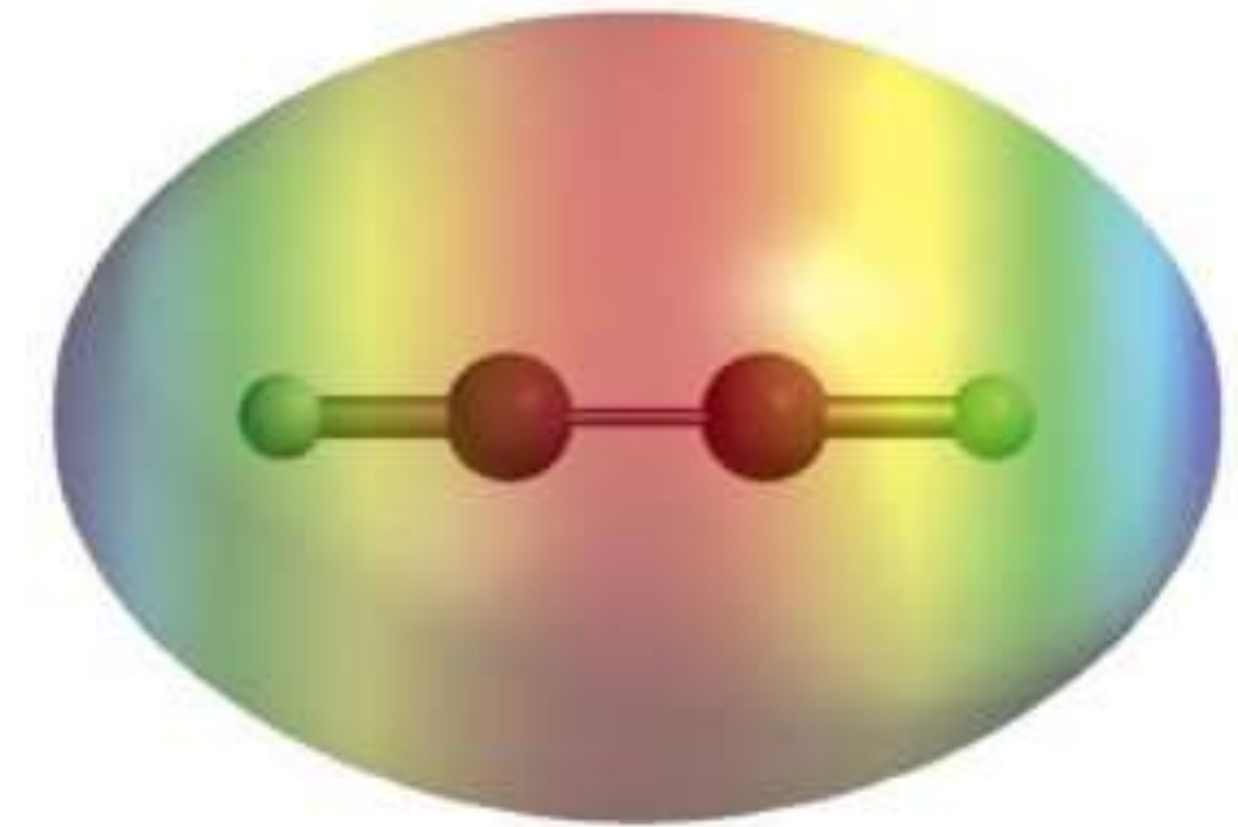


والعكس صحيح، لو اشتغلت على trans alkene



Alkynes

دو (في) عندي 2 p orbitals لكل كربون في π



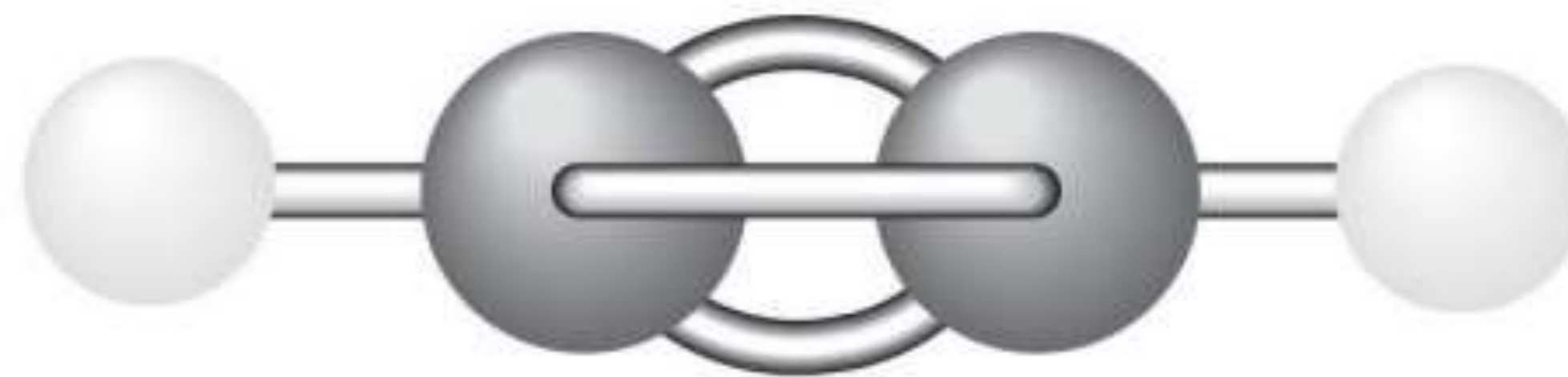
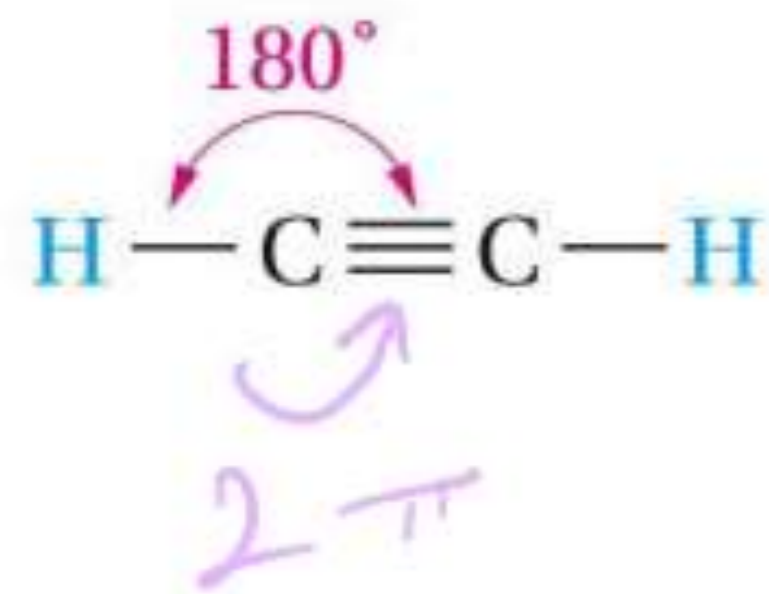
- Alkynes are **sp hybridized**

- Linear** – bond angle **180°**

- 2 σ and 2 π bond (or 1 single and 1 triple)

- $\text{C}\equiv\text{C}$ double bond $\sim 1.21 \text{ \AA}$

اقل من اقوى من ال Double bond



Alkynes: Reactions

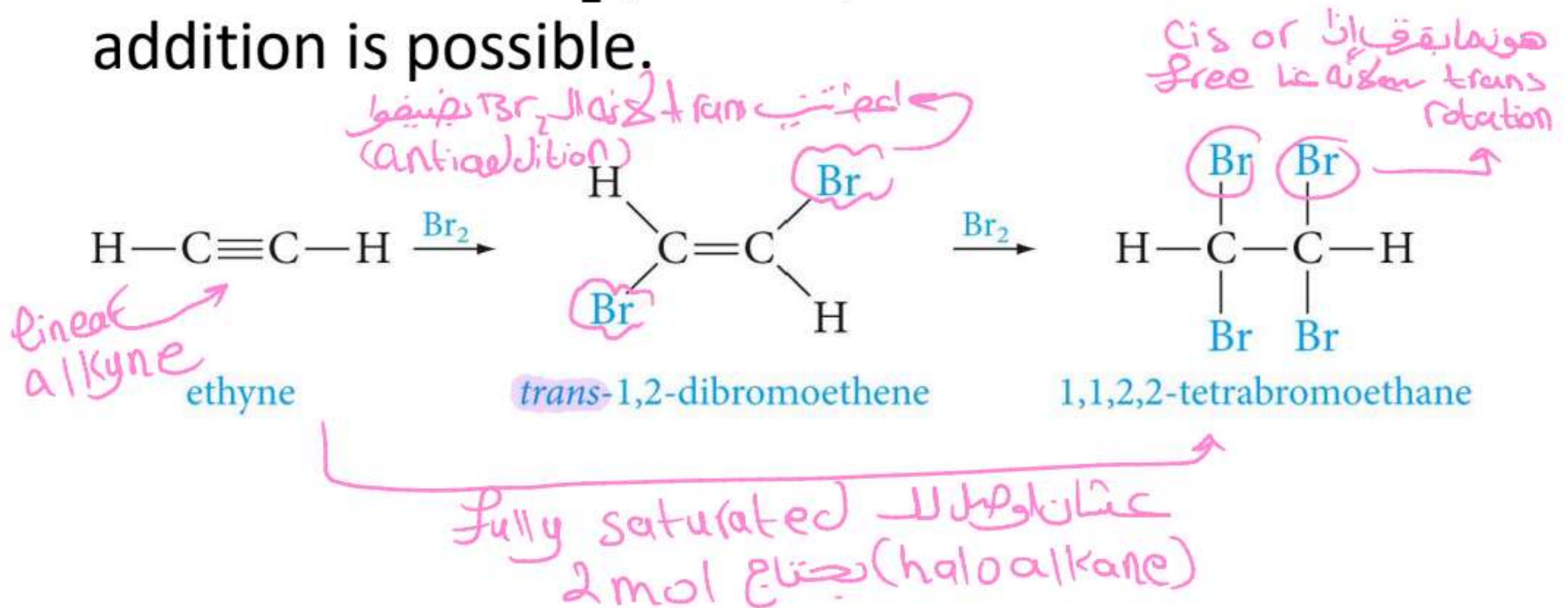
فيما قريبا من تفاعلات الألكين
ولكن الألكاين عندها 2π يعني ال IHD هي 2

Most of the reactions discussed for alkenes also apply to alkynes, although the alkynes usually react slower.

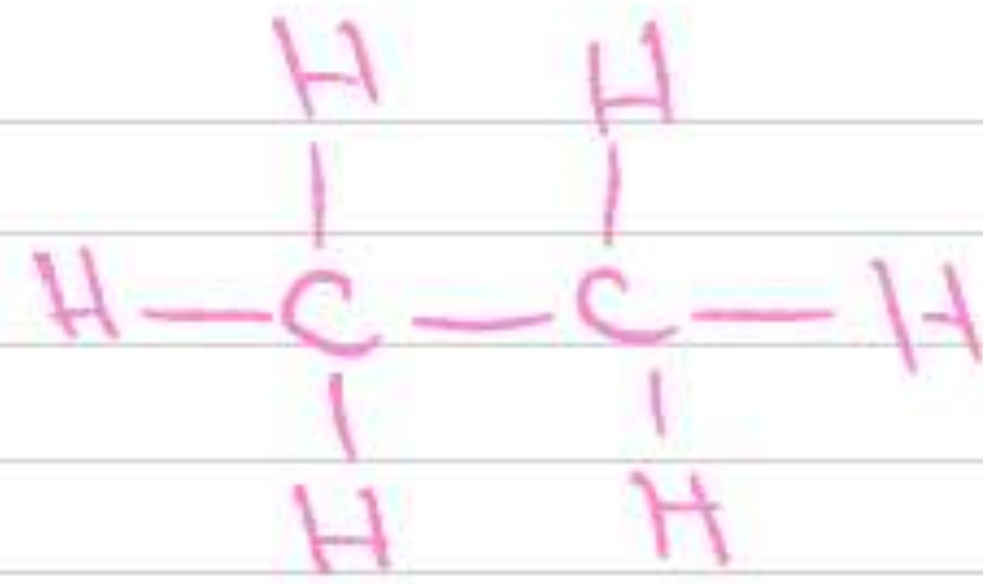
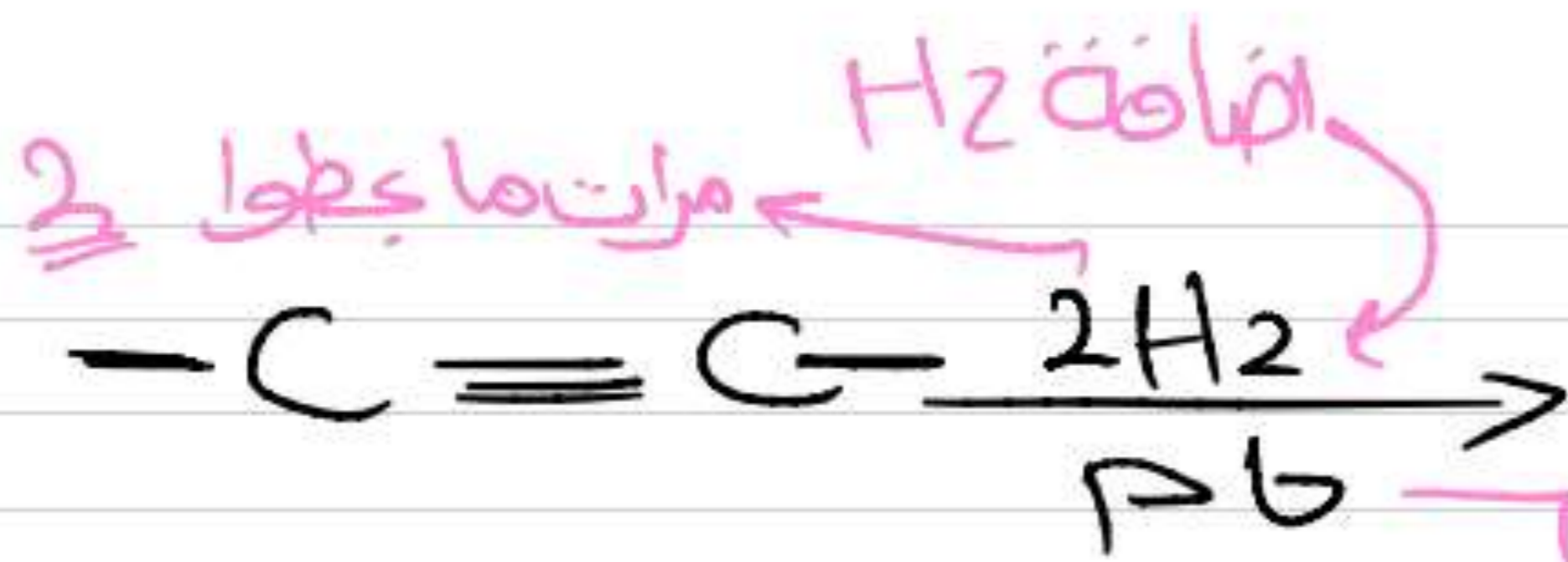
There are a couple of differences.

Alkynes: Reactions

Bromination: the first bromine adds trans to the alkyne. It can be stopped at this by controlling the amount of Br_2 present, but a second addition is possible.



* ممکن بدل لے پت مستعمل
Pt or Ni



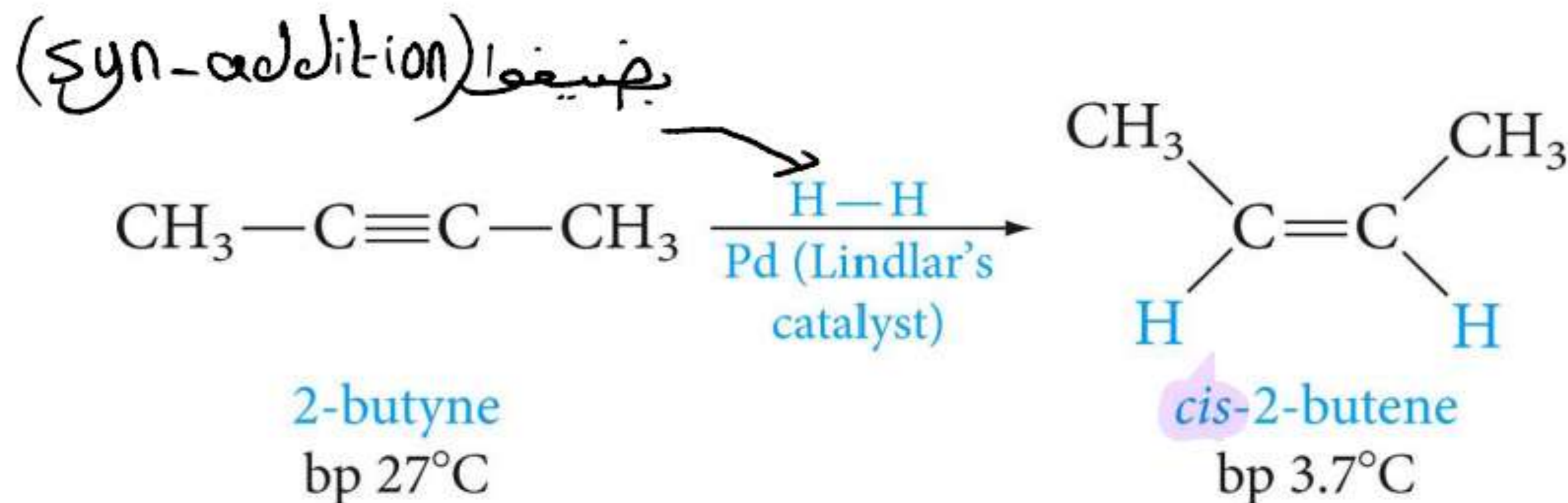
↓
Catalyst
Alkane
Alkane

↓
Alkane
Alkene

ابا عالم اسوہ (Lindlar)
لے عمل Catalyst او Reagent
لے ہار Lindlar وہ انداز Lindlar
Catalyst قادر نہ کولک Alkyne
Alkene سے طبعاً انا جاہ لے H_2
ولکن ہو ح بھیف فقط 1 mole

Alkynes: Reactions

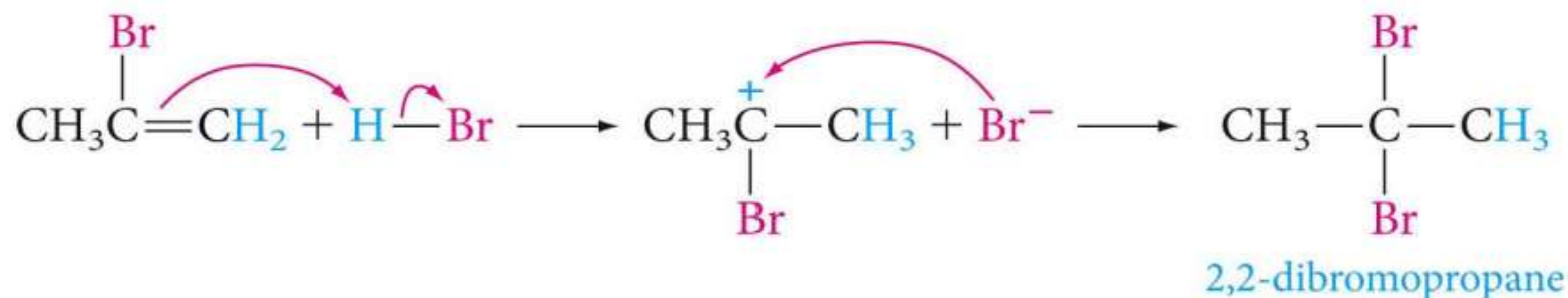
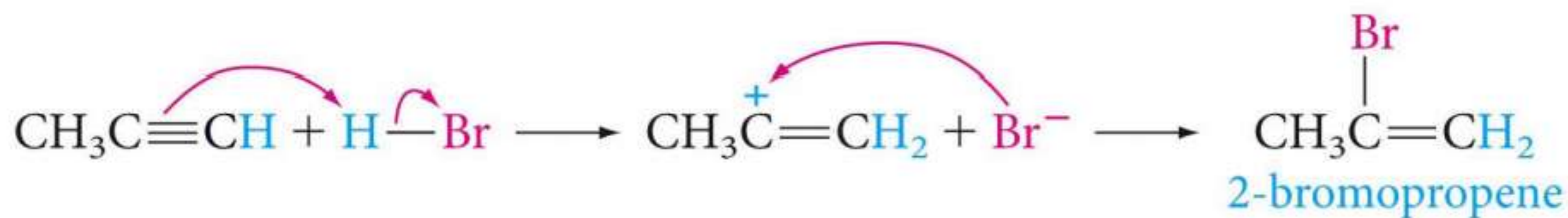
Hydrogenation: ordinary Pt or Ni catalysts produce alkanes. However a special Pd catalyst called *Lindlar's reagent* causes only 1 H₂ in a syn addition to produce a cis-alkene

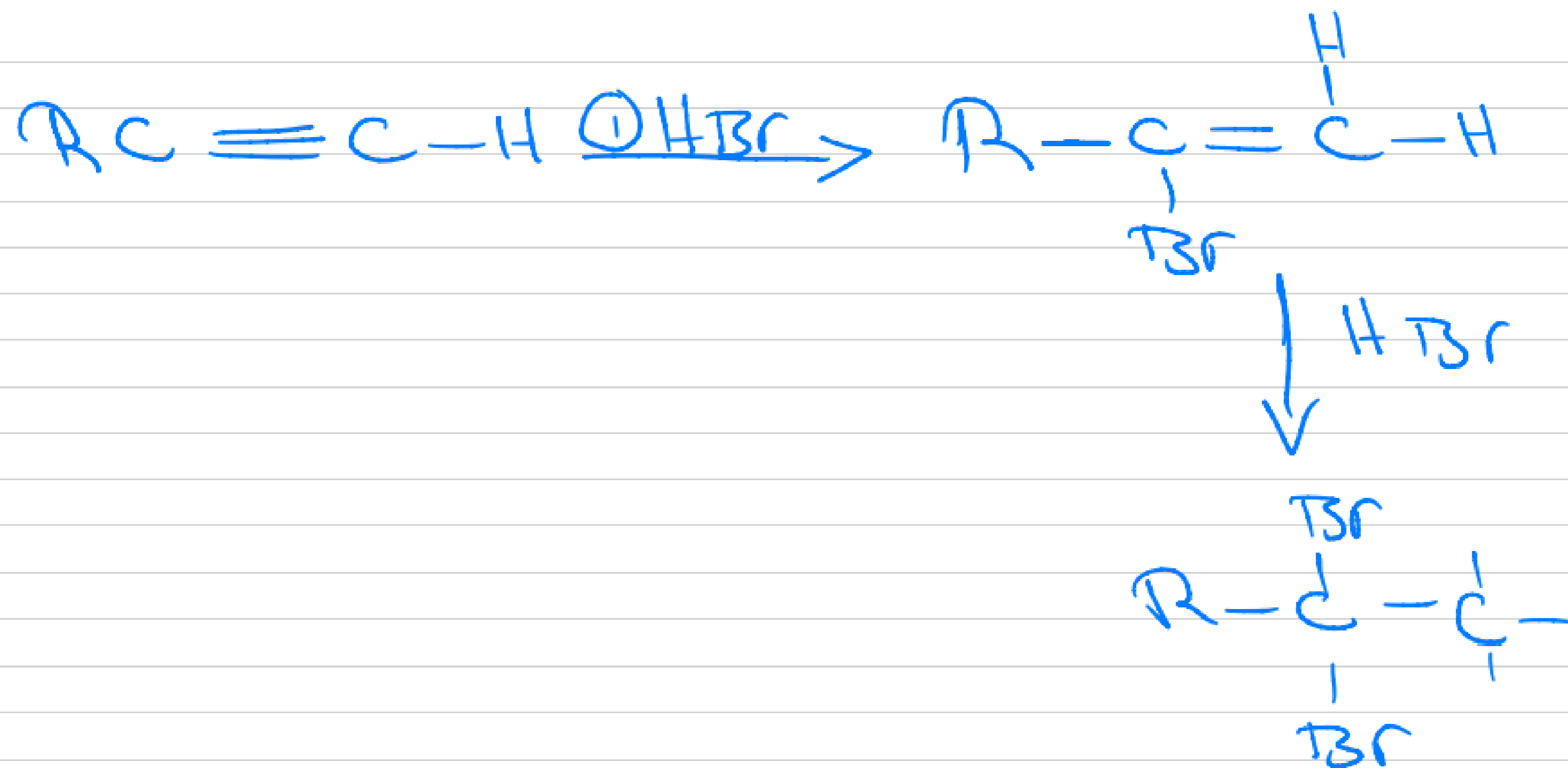


Alkynes: Reactions

Hydrohalogenation

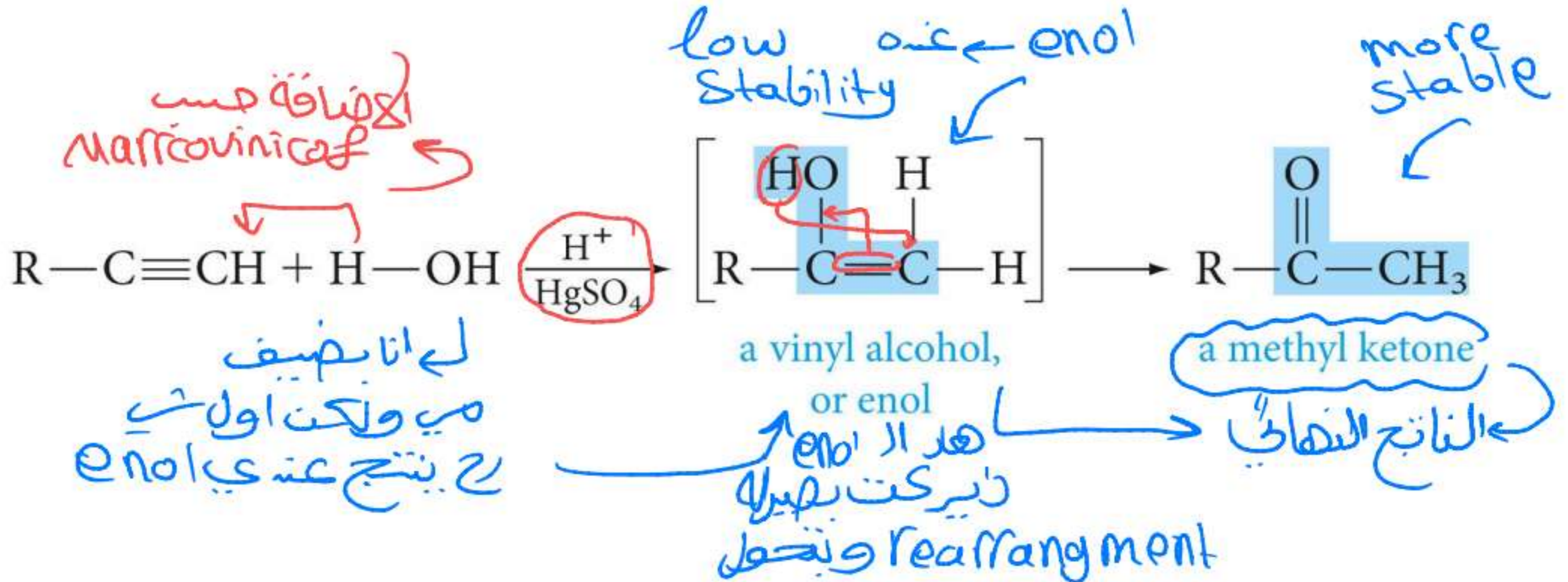
Markovnikov's rule is followed for asymmetric alkynes, $R-C\equiv C-H$





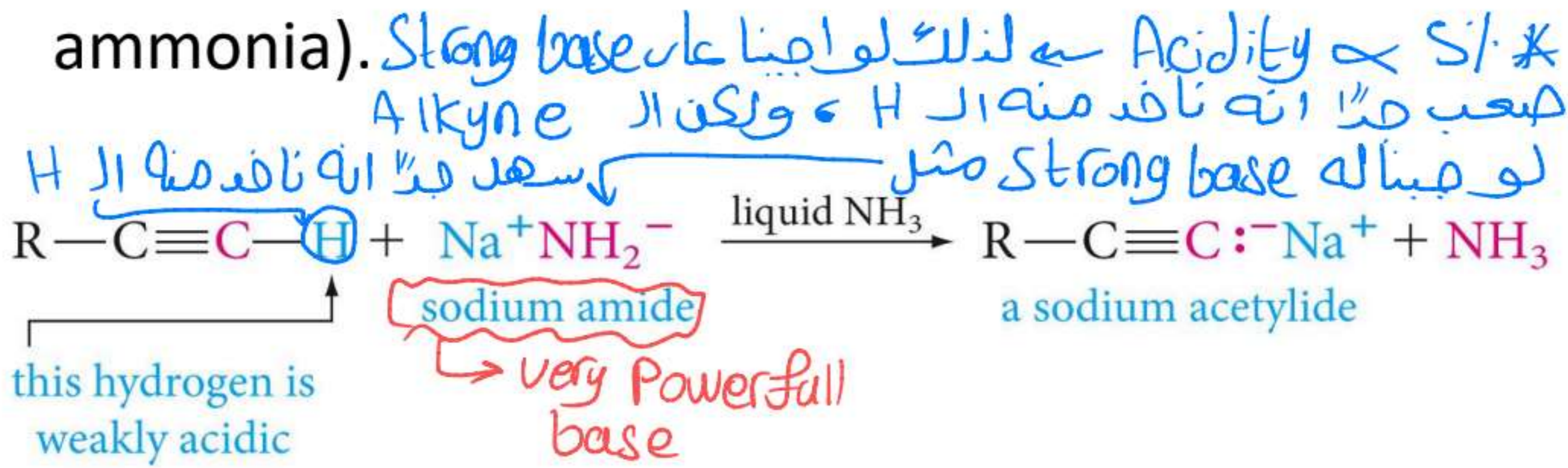
Alkynes: Reactions

Adding H₂O
 Hydration: requires an additional mercury (Hg²⁺) catalyst. The initial product, an enol, rearranges rapidly to form a ketone, i.e.



Alkynes: Acidity

The alkyne proton is quite acidic for a hydrocarbon with a pK_a of ~ 25 . This means it can be removed by strong bases such as sodium amide (made by adding metallic sodium to ammonia).



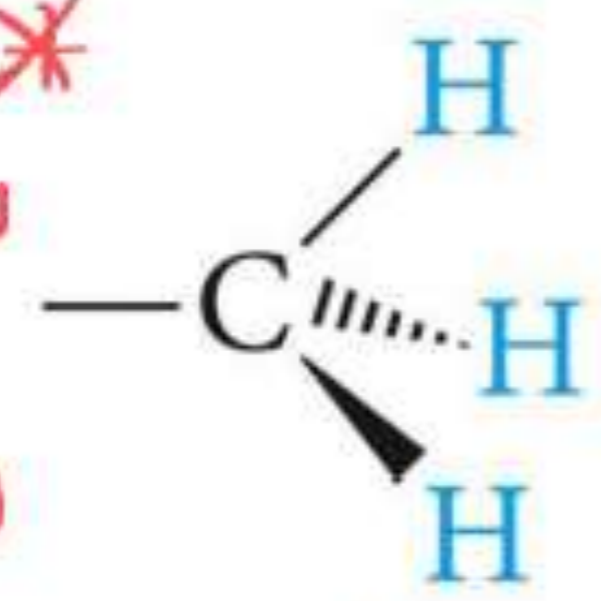
قصة ال Acidity تبعت ال Alkyne
مقارنة " بالـ Alkene و Alkane

* Note :- في علاقة
بين ال Acidity و ال
Hybridization
Atom

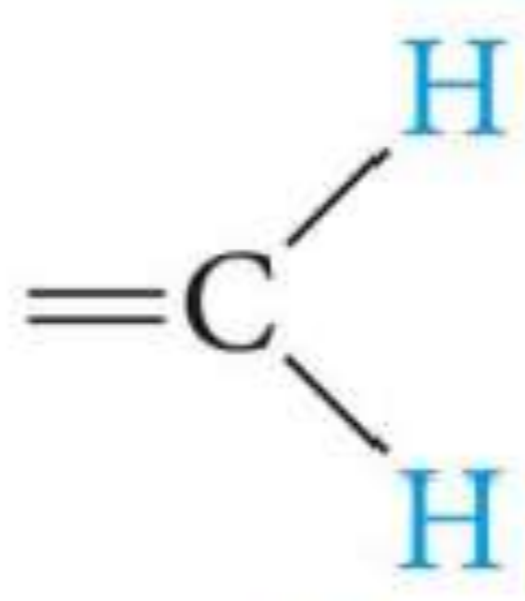
Alkynes: Acidity

The reason for the high acidity is the hybridization of the C atom in an alkyne. As the hybridization becomes more s like the acidity increases.

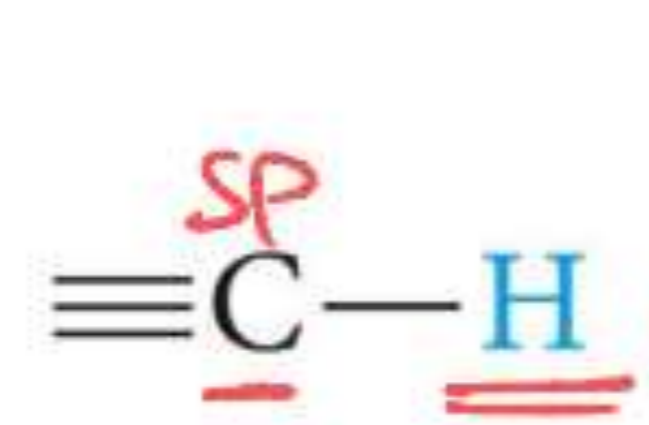
* الموضوع الها علاقة
بال Conjugated base
ان ال sp ك orbital هو
(sp) من ال sp² و ال sp³ (s) من
sp³



sp³
25% s,
75% p



sp²
33¹/₃% s,
66²/₃% p



sp
50% s,
50% p
يعني نسبة ال s
بال hybridization
هون ربطوا
نسبة ال s ال orbital
بال acidity

ال H ا إذا ارتبطت مع sp
يعني إزا في عني
Alkyne طرف منه H
هاي تعتبر more
acidic أكثر من ال
H الي سابقا مع
sp²

كلما كانت نسبة ال s اعلى
كلما كانت ال acidity اعلى
Acidity ∝ s

increasing acidity

This is very important as it is one of the few ways to generate a carbon nucleophile!