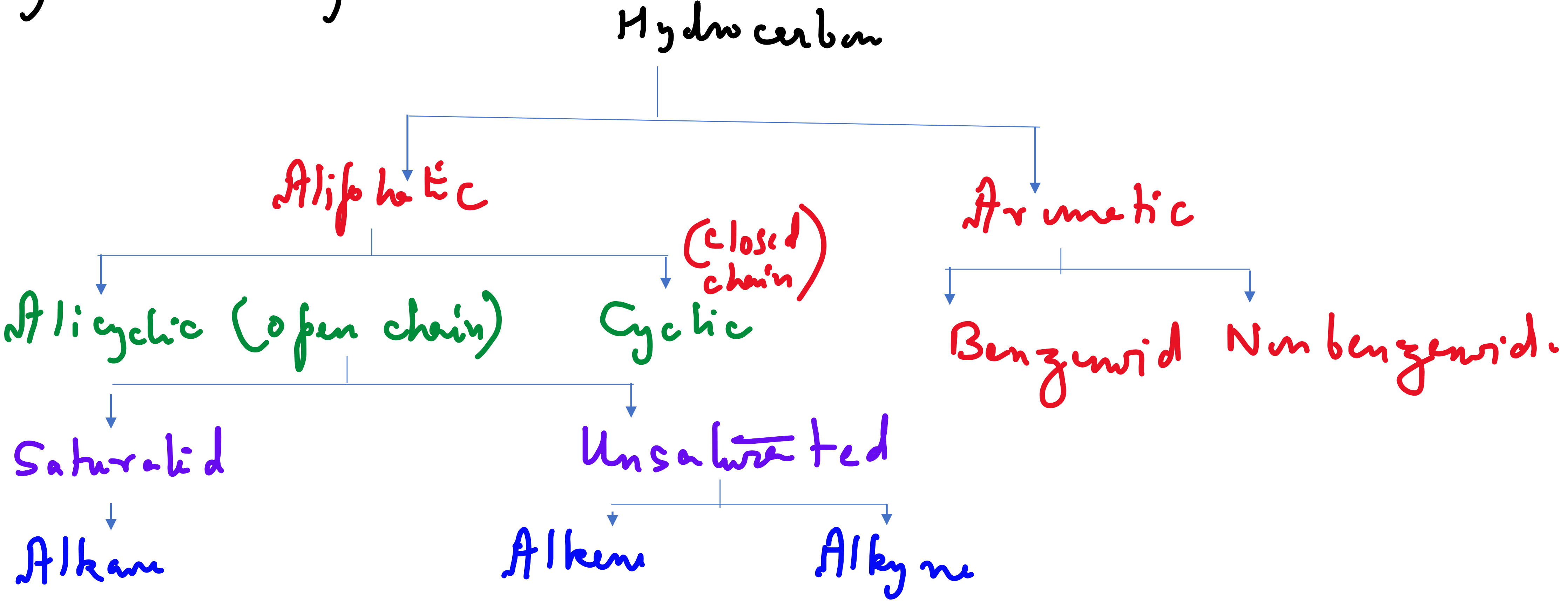
Hydrocarbons (Revision Notes)

Hydrocarbon = Compounds containing carbon & hydrogen.

Classification of hydrocarbons.



- Hydrocarbon
  - Aliphatic
    - Alicyclic (open chain)
      - Saturated
        - Alkane
      - Unsaturated
        - Alkene
        - Alkyne
    - Cyclic (closed chain)
  - Aromatic
    - Benzenoid
    - Nonbenzenoid.

Alkane

1. Open chain saturated hydrocarbon with general formula C_nH_{2n+2}

2. All the C atom present in an alkane are sp^3 hybridised i.e. single bonded.

Conformation of alkane : Conformations are the different spatial arrangement of atoms in a molecule that can be interconverted through rotation about single bonds.

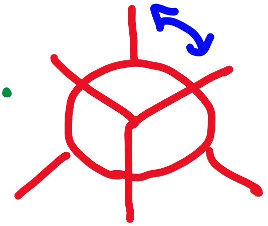
Type of conformation : 1. Eclipsed conformation
2. Staggered ,,

1. Eclipsed conformation: H atoms on two adjacent carbon atoms are closest to each other such that the dihedral angle is 0

2. Staggered conformation: H atoms on two adjacent carbon atoms are farthest from each other such that the dihedral angle is 60°

Newman representation:

C_2H_6 (Ethane)



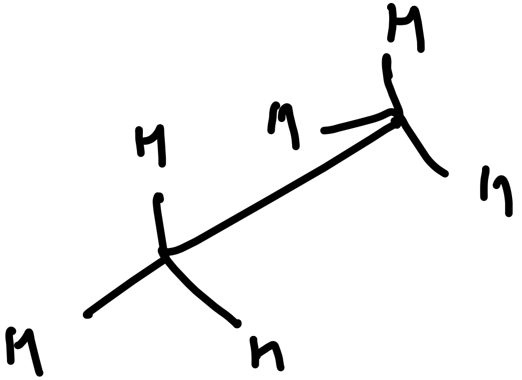
dihedral angle 60°

Staggered

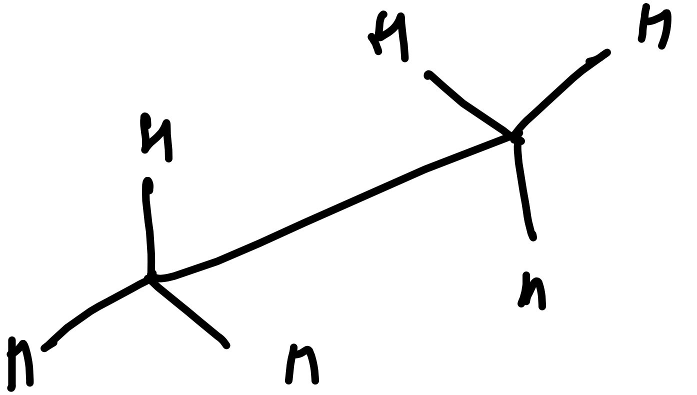
dihedral angle 0°

Eclipsed –

Sawhorse :



Eclipsed



staggered

Interconversion of eclipsed & staggered conformation is possible via single bond rotation.

Preparation of alkanes :-

1. Reduction of alkyl halides :

$$R-X + Zn: + H^{\oplus} \longrightarrow RH + Zn^{2+} + X^{\ominus}$$

$$4RX + LiAlH_4 \longrightarrow 4RH + LiX + AlX_3 \ (X \neq F)$$

$$RX + (n\,C_4H_9)_3SnH \longrightarrow RH + (n\,C_4H_9)_3SnX$$

Q. Grignard Reagent - polarity is reversal (Umpolung)

organo-metallic

$$\overset{\delta+}{R}-\overset{\delta-}{X} + 2\,Li \xrightarrow{\text{dry ether}} \overset{\ominus}{R}\,\overset{\oplus}{Li} + LiX$$

(organolithium)

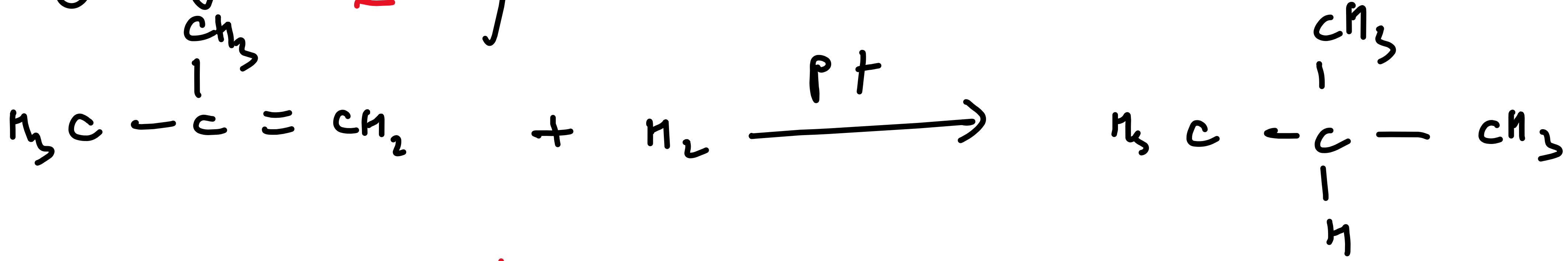
$$\overset{\ominus}{R}\,\overset{\oplus}{Li} \xrightarrow{H_2O} RH + LiOH$$

$$R-X + 2\,Mg \xrightarrow{\text{dry } Et_2O} R-MgX$$

Grignard reagent

$$R-MgX \xrightarrow{H_2O} R-H + Mg(OH)X$$

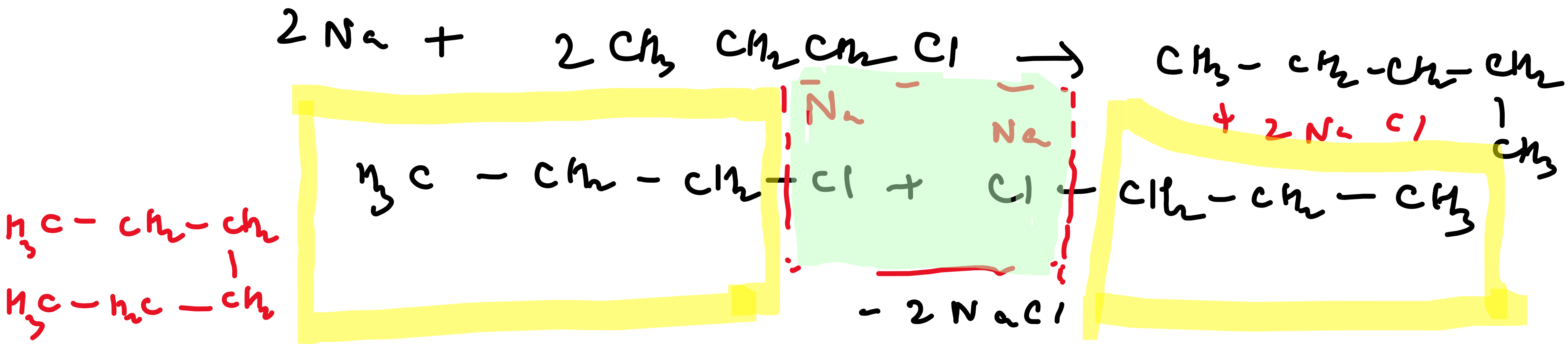
③ Hydrogenation of alkenes :



$$H_3C-\overset{CH_3}{\overset{|}{C}}=CH_2 + H_2 \xrightarrow{Pt} H_3C-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

④ Wurtz reaction

$$2R-X + 2Na \longrightarrow R-R + 2NaX$$



$$2Na + 2CH_3CH_2CH_2Cl \longrightarrow CH_3-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH_2} + 2NaCl$$

$$H_3C-CH_2-CH_2-\overset{Na}{Cl} + \overset{Na}{Cl}-CH_2-CH_2-CH_3$$

$$-2NaCl$$

$$\begin{aligned} &H_3C-CH_2-\underset{|}{CH_2} \\ &H_3C-H_2C-CH_2 \end{aligned}$$

⑤ Corey House Reaction

$$RMgX \text{ or } RLi \xrightarrow[R'X]{CuX} R-R'$$

($R = 1°, 2°$ or $3°$ & $R' = 1°$)

Involves the reaction of an organic halide with lithium diorganyl cuprate to form a new alkene.

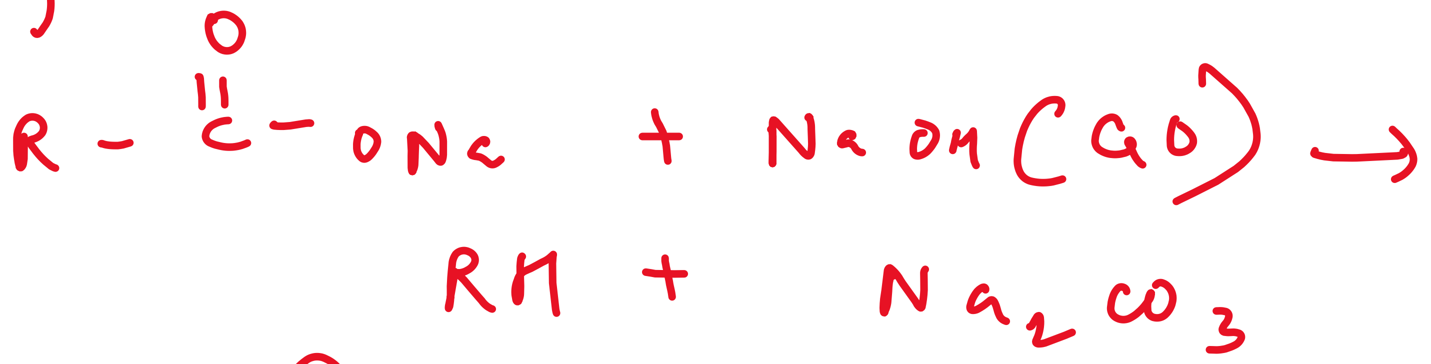
Step 1) $RX + Li \longrightarrow RLi$

Step 2) $RLi + CuI \longrightarrow \boxed{R_2CuLi}$ lithium dialkyl cuprate.

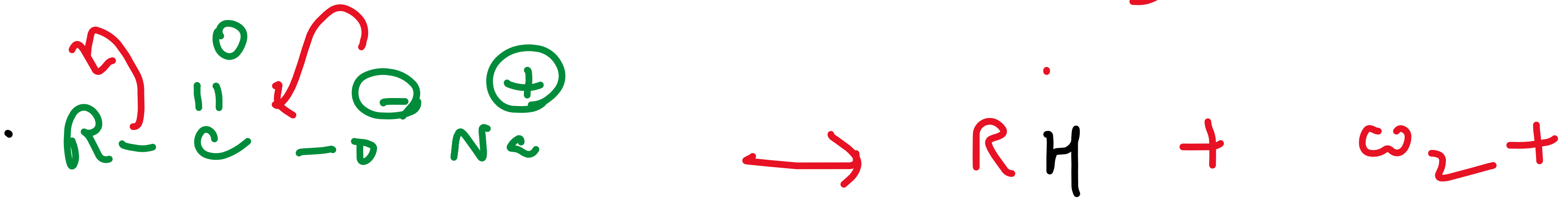
Step 3) $R_2CuLi + \boxed{R'}X \longrightarrow R-R'$

must be 1° to give a good yield.

⑥ Decarboxylation of a mixture of the sodium salt of a carboxylic acid -

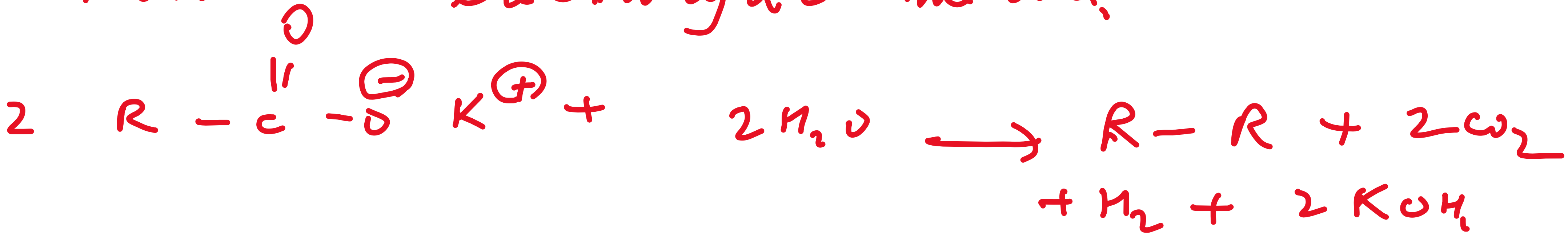


$$R-\overset{O}{\overset{\|}{C}}-ONa + NaOH(CaO) \longrightarrow RH + Na_2CO_3$$

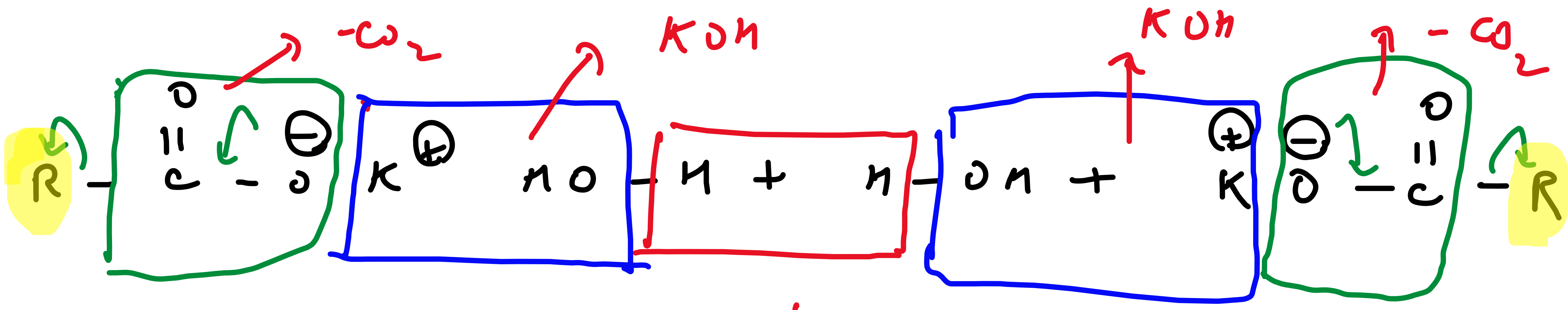


$$R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\,\overset{\oplus}{Na} \longrightarrow RH + CO_2 +$$

⑦ Kolbe's electrolytic method.



$$2\,R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\,K^{\oplus} + 2H_2O \longrightarrow R-R + 2CO_2 + H_2 + 2KOH$$



$$\downarrow$$

$$R-R + 2CO_2 + 2KOH + H_2$$

Chemical properties of Alkane (Paraffin)

↓

Latin 'parum affinum'

↓

Less reactivity

1. Direct Halogenation

Alkanes are called paraffins as they have lesser affinity towards general reagents.

(F, Cl, Br)

$$R-H + X_2 \longrightarrow RX + HX$$

Order of reactivity: $F_2 > Cl_2 > Br_2$

I_2 does not react

Mechanism: Free radical pathway. } Ionic mechanism ↓ Heterolytic cleavage of bonds.

Step I: Initiation.

homolytic cleavage

light

$$Cl \vdots Cl \xrightarrow{h\nu} 2\,Cl^{\bullet}$$

Step II: Propagation.

$$H_3C \vdots H + \dot{Cl} \longrightarrow H_3\dot{C} + H-Cl$$

$$\boxed{H_3\dot{C} + \dot{C}l} - Cl \longrightarrow H_3C - Cl + Cl^{\bullet}$$

Step III: Termination

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl - Cl$$

$$H_3C^{\bullet} + \dot{C}H_3 \longrightarrow C_2H_6 \quad | \quad H_3C - CH_3$$

$$Cl^{\bullet} + \dot{C}H_3 \longrightarrow Cl - CH_3$$

② **Nitration** Carried out by heating vapors of alkanes & HNO_3 at around 400°C to give nitroalkanes. This is also called as vapor phase nitration.

$$H_4C(g) + HNO_3(g) \xrightarrow{400^\circ C} H_3C-NO_2 + H_2O$$

④ **Combustion** (highly exothermic)

Alkanes burn readily with non luminous flame in presence of air or oxygen to give CO_2 & water along with generation of heat.

$$C_2H_6 + 7O_2 \longrightarrow CO_2 + 6H_2O + x$$

(heat)

⑤ **Aromatisation** Alkanes having 6 - 10 carbon atoms are converted into benzene & its homologues at high pressure and temperature in presence of catalyst.

$$\underset{\text{Hexane}}{C_6H_{14}} \xrightarrow[Mo_2O_3]{V_2O_5 / Cr_2O_3} \underset{\text{Benzene.}}{C_6H_6}$$

773 K & 20 atm.

⑤ Oxidation of tertiary / 3° alkane.

$$R_3CH \xrightarrow{KMnO_4} R_3COH.$$

(tertiary alcohol)

Tertiary alkanes are oxidized to tertiary alcohols in presence of $KMnO_4$.

Alkenes (Olefins)

1. Open chain, unsaturated hydrocarbon with general formula C_nH_{2n}

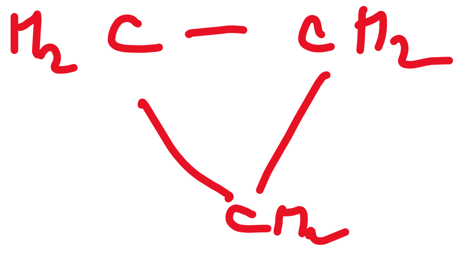
2. At least one $>C=C<$ (double bond) has to be sp^2 hybridised.

3. Allene: alkene molecule which contains at least one C that has double bonds with each of the adjacent carbon i.e. $-C=C=C-$ group.

4. Isomeric with saturated cycloalkanes.

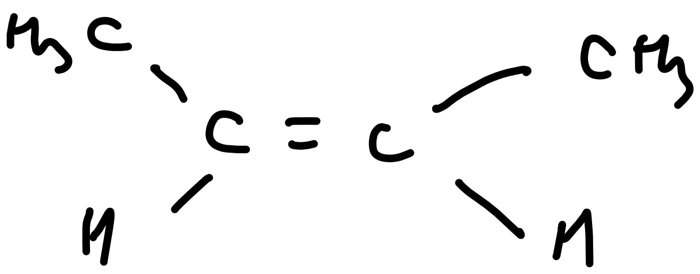
$H_3C-CH=CH_2$

C_3H_6

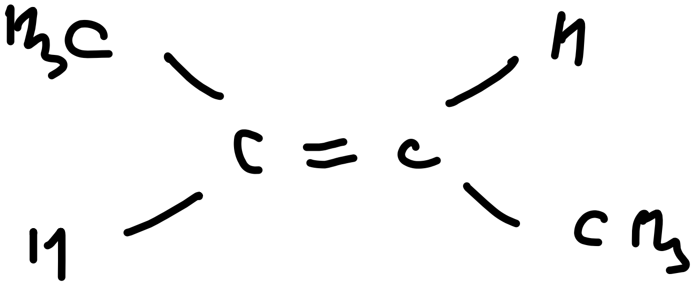


C_3H_6

Geometric Isomers.

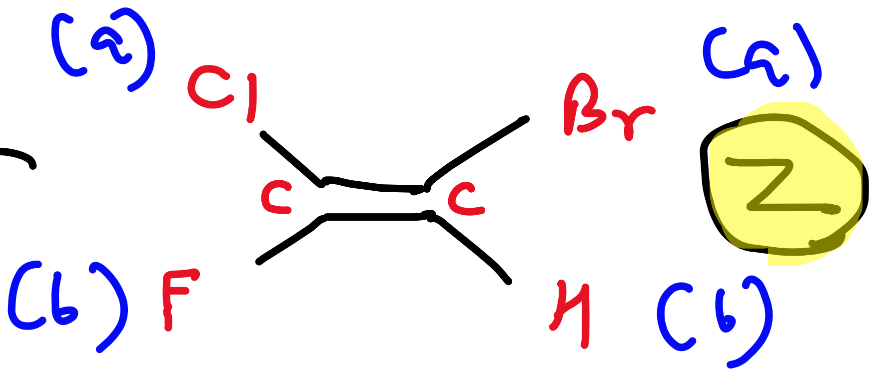


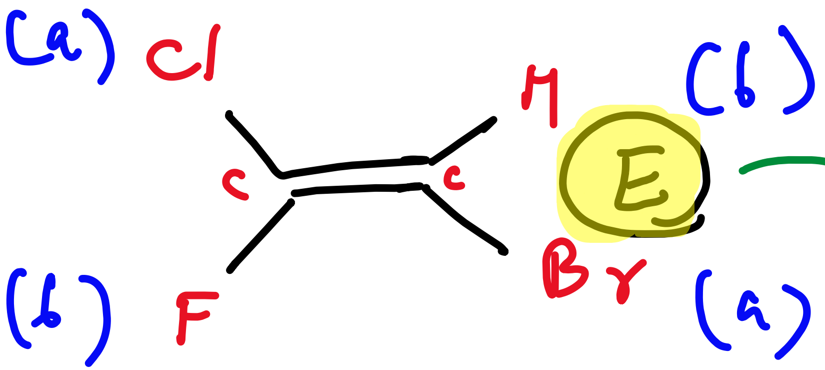
H_3C's are on the same side / called cis.



H_3C's are on the opposite site. called trans.

Z is used when the higher-priority substituents on each C are on the same side of double bond. E is used if they are on the opposite side.



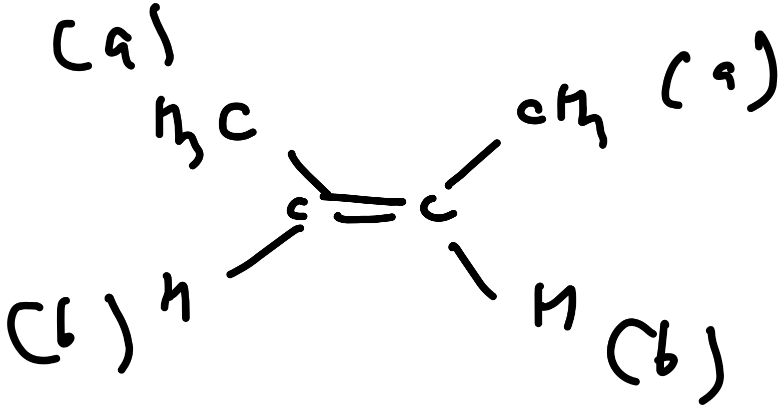


Higher priority substituents on each C are on the same side of double bond

a = higher priority
b = lower "

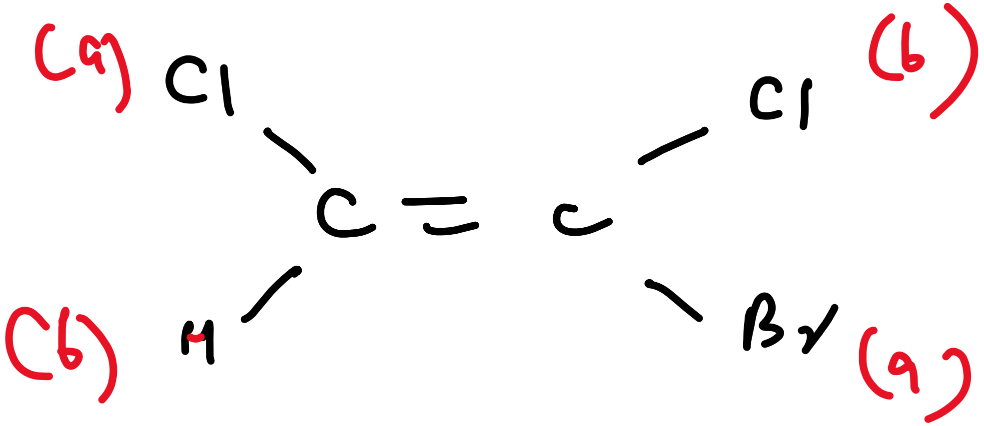
a > b

Higher priority groups are on the opp side



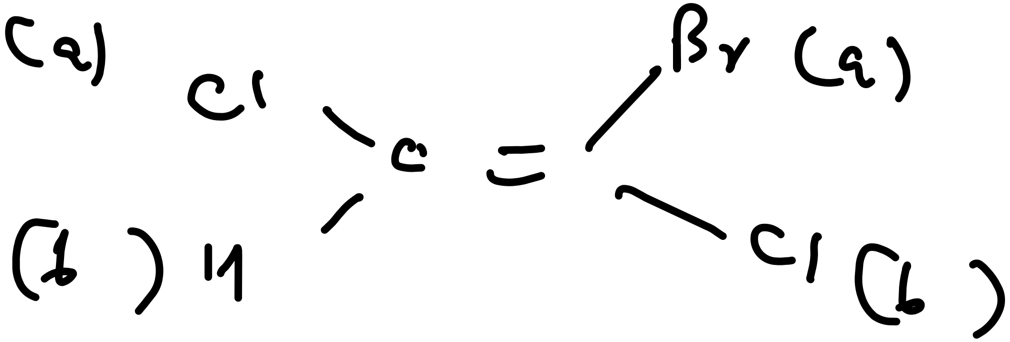
a > b

(2 Z) – but-2-ene-



a > b

(E)– 1– bromo- 1,2– dichloroethylene



(Z)– 1– bromo-1,2– dichloroethylene

cis / trans ≠ E - Z

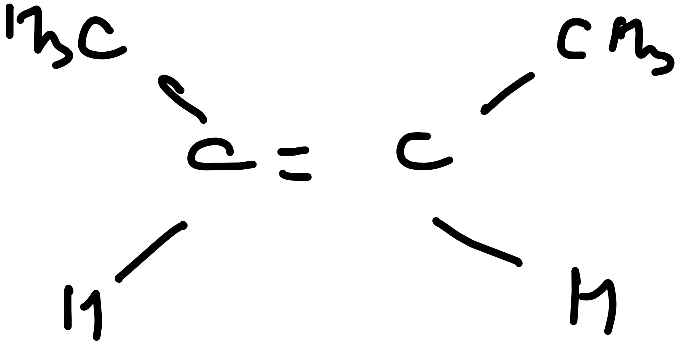
Priority ✗ based

Heats of hydrogenation: Heat of hydrogenation increases with increase in stability of alkene.

$$H_3C-CH_2-CH=CH_2 + H_2 \xrightarrow{Pt}$$

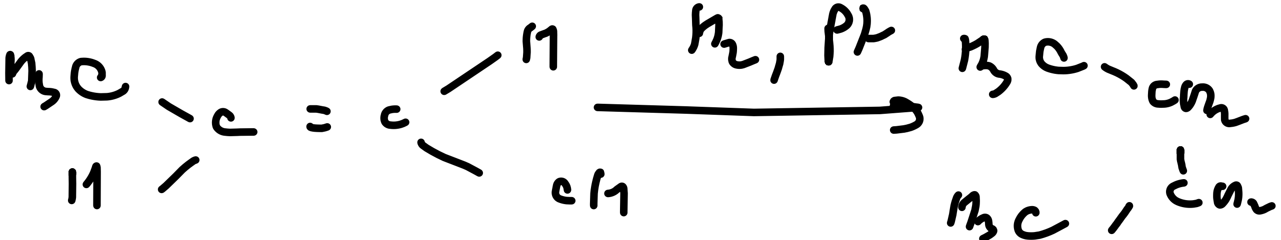
$$H_3C-CH_2-CH_2-CH_3$$

$\Delta H^\circ = -30.3$ kcal mol^{-1}



$$+ H_2 \xrightarrow{Pt}$$

$$H_3C-CH_2-CH_2-CH_3$$



$\Delta H^\circ = -28.6$ Kcal mol^{-1}

$\Delta H^\circ = -27.6$ Kcal mol^{-1}

Orders of heat of hydrogenation:

1 - Butene > cis - 2 butene > trans - 2- butene

Order of stability:

1- butene > cis - 2- butene > trans - 2- butene

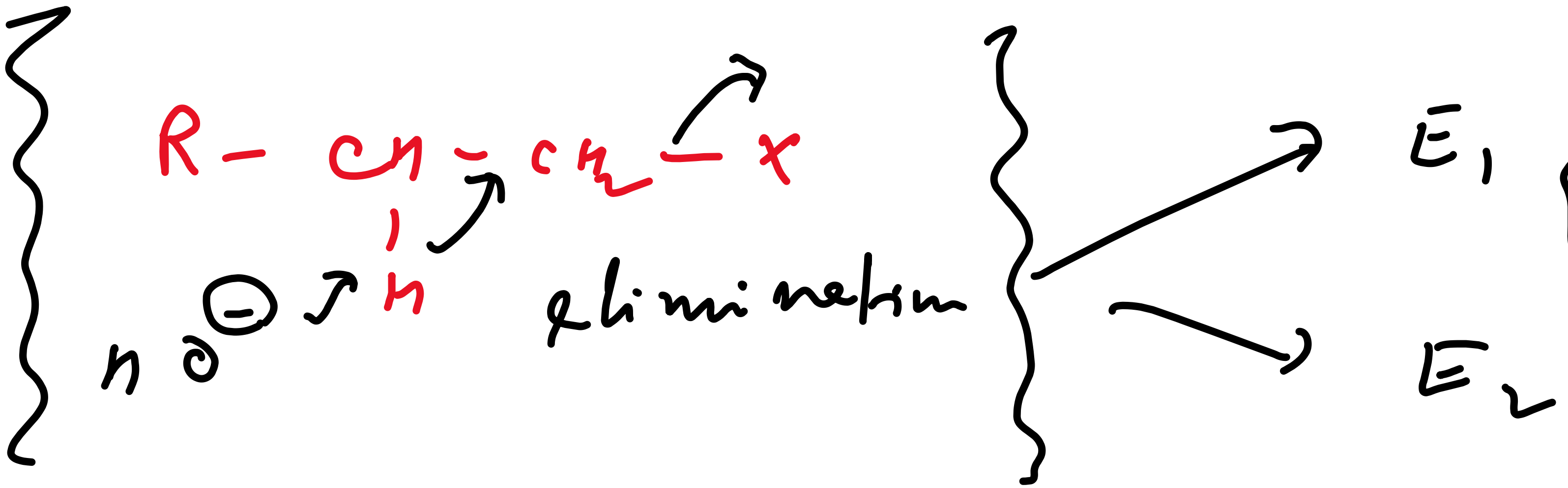
Preparation of Alkenes:

1. Cracking of petroleum:

$$R - CH_2 - CH_3 \xrightarrow{Pt \text{ or } Pd} R - CH = CH_2 + H_2$$

2. Dehydrohalogenation of alkyl halide –

$R-CH_2-CH_2-X + \text{alc. } KOH \longrightarrow RCH=CH_2$



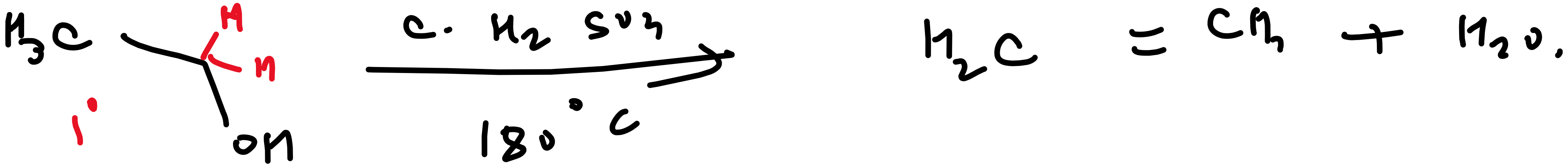
depends on substrate & reaction conditions

3. Dehydration of alcohols:

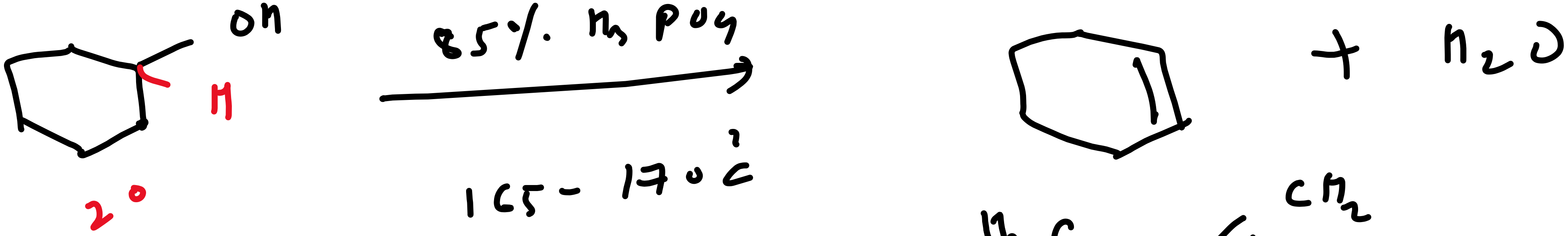
Saytzeff Rule: In dehydrohalogenation reactions, the preferred product is that alkene which has the greater no. of alkyl groups attached to the doubly bonded carbon atoms.

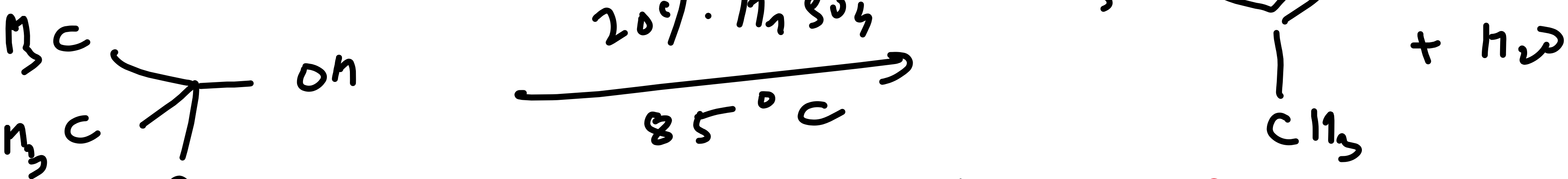
The dehydrohalogenation of 2-bromobutane yields two products 1-butene & 2-butene.

In dehydration & dehydrohalogenation, the preferential order for removal of an H is 3° > 2° > 1°.



$$H_3C-CH_2OH \xrightarrow[180^\circ C]{c.\ H_2SO_4} H_2C=CH_2 + H_2O.$$

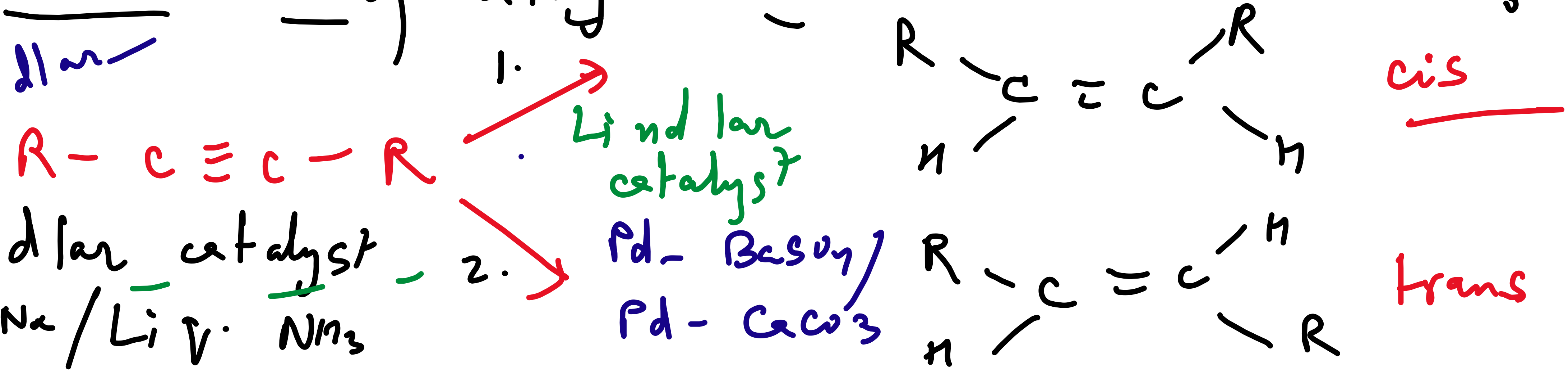




Order of reactivity : 3° > 2° > 1°

④ Reduction of alkynes :

Herbert Lindlar

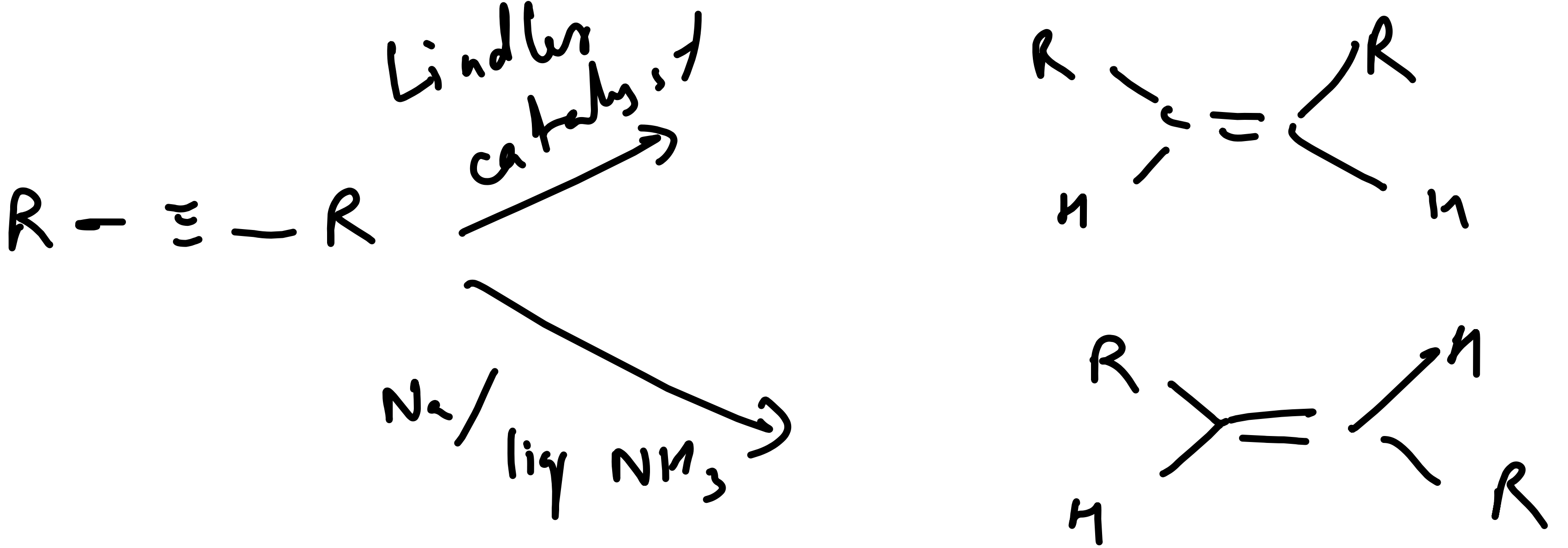


1. Lindlar catalyst

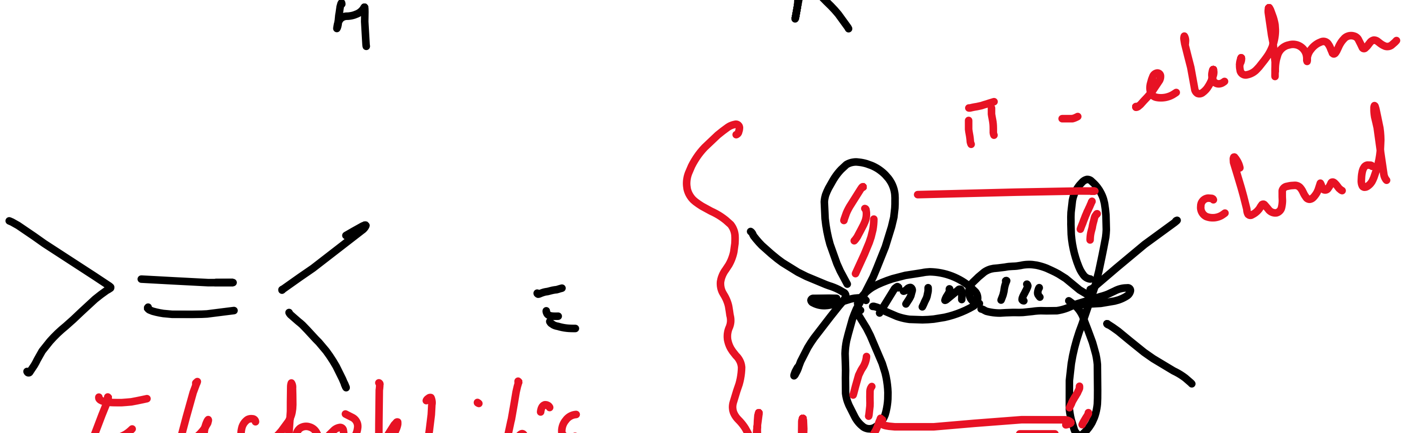
2. Na/Li in NH_3

ORGANIC CHEMISTRY

HYDROCARBON (Revision notes)

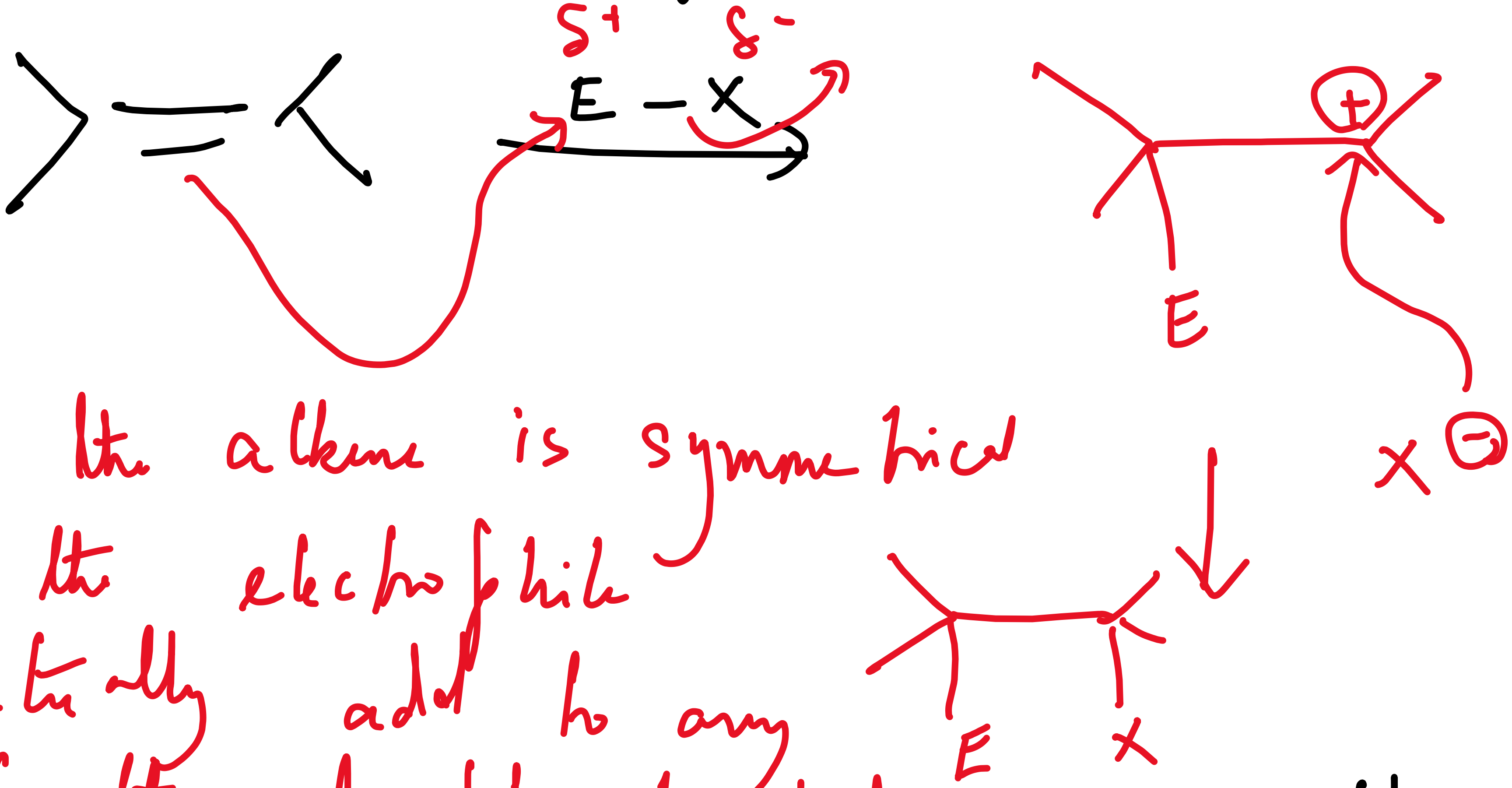


Alkene :



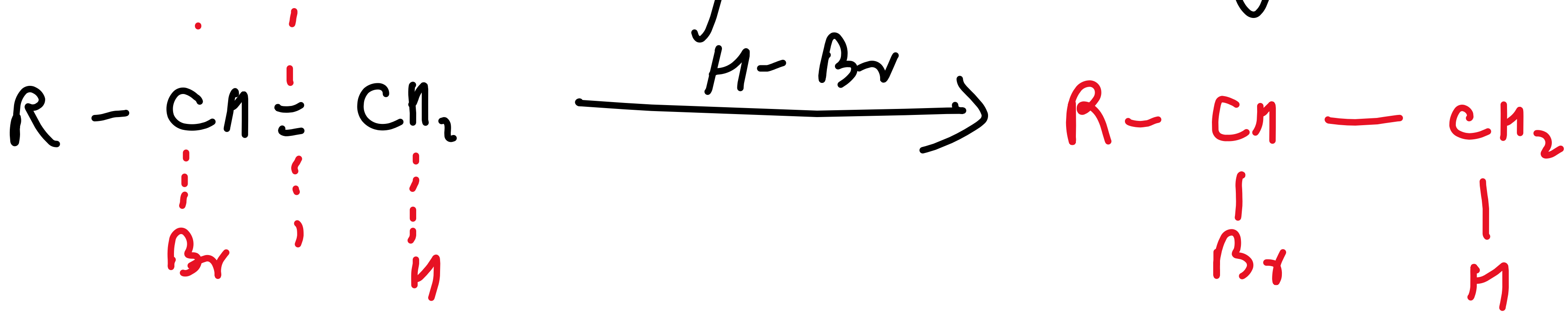
Major reaction - Electrophilic addition

Electrophilic addition of alkenes:



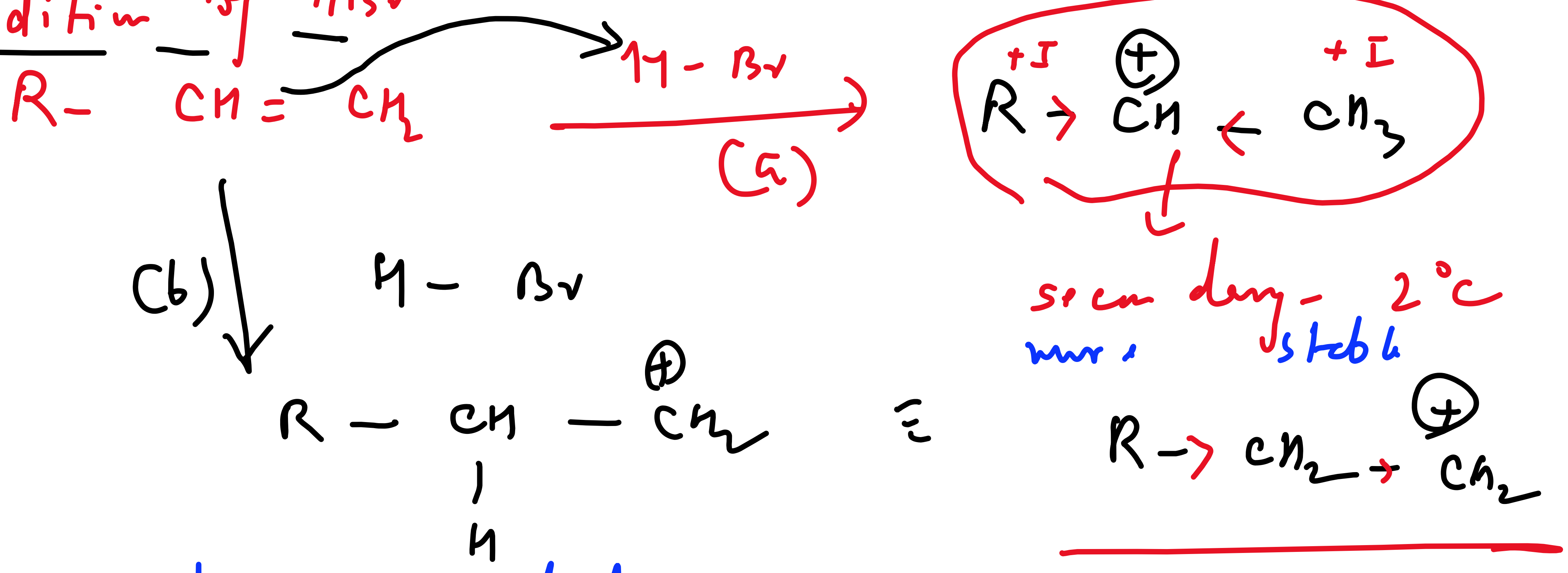
If the alkene is symmetrical then the electrophile can actually add to any one of the double bonded carbon. However, if the alkene is unsymmetrical, addition is guided by Markownikov's rule in majority of the scenario.

Markownikov's rule: The negative part of the addendum attaches to that carbon atom which contains fewer no. of hydroge atoms.



$$R-\underset{Br}{CH}=\underset{H}{CH_2} \xrightarrow{H-Br} R-\underset{Br}{\underset{|}{CH}}-\underset{H}{\underset{|}{CH_2}}$$

1. Addition of HBr



$R-CH=CH_2 \xrightarrow[(a)]{H-Br} R \rightarrow \overset{\oplus}{C}H \leftarrow CH_3$

secondary - 2°C

more stable

(b) $H-Br$

$R-\underset{\displaystyle H}{\underset{|}{CH}}-\overset{\oplus}{C}H_2 \equiv R \rightarrow CH_2 \rightarrow \overset{\oplus}{C}H_2$

less stable - 1°

MK rule is guided by carbocation stability. The H atom will attach to that carbon atom which gives rise to more stable carbocation.

Step -I:

$$R-CH=CH_2 \quad H-Br \longrightarrow R-\overset{\oplus}{C}H-\underset{\underset{H}{|}}{C}H_2 + Br^{\ominus}$$

Step II:

$$R-\overset{\oplus}{C}H-CH_3 \xrightarrow{Br^{\ominus}} R-\underset{\underset{Br}{|}}{C}H-CH_3$$

Anti M.K. addition

$$R-CH=CH_2 + HBr + (C_6H_5-CO)_2O_2 \longrightarrow R-CH_2-CH_2Br$$

(Peroxide effect)

$$H_5C_6-\overset{\overset{O}{\parallel}}{C}-O-O-\overset{\overset{O}{\parallel}}{C}-C_6H_5$$

Mechanism:

Chemical reaction → Ionic reacti
Heterolytic cleavage

→ Radical reaction
Homolytic cleavage

1. Initiation : $R-O-O-R$

$2\,RO^{\bullet}$

2. Propagation :

$CH_3-CH=CH_2 + Br^{\bullet} \longrightarrow CH_3-\dot{C}H-CH_2-Br$

$CH_3-\dot{C}H-CH_2Br + H-Br \longrightarrow$

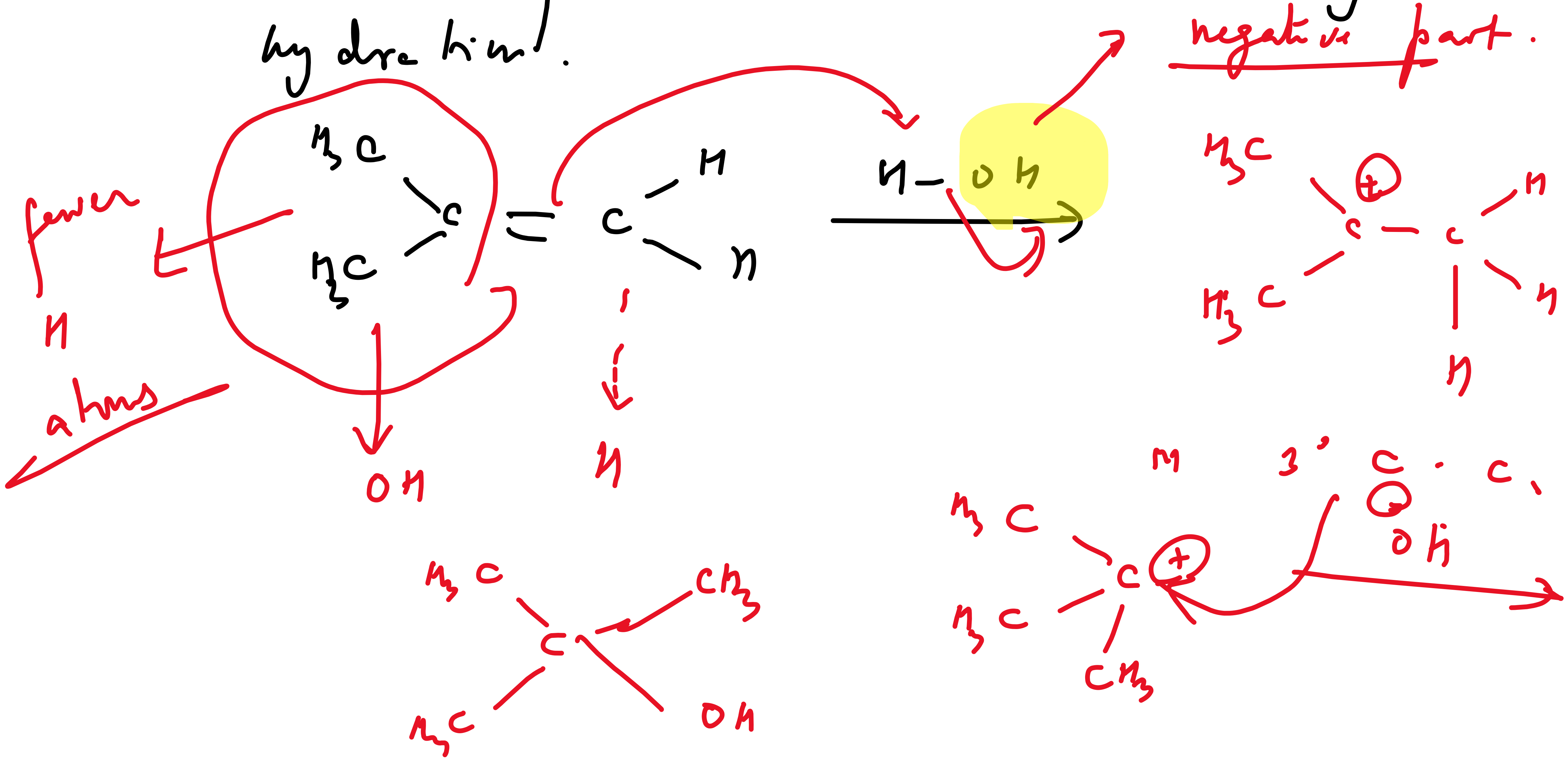
$CH_3CH_2-CH_2Br + Br^{\bullet}$

3. Termination :

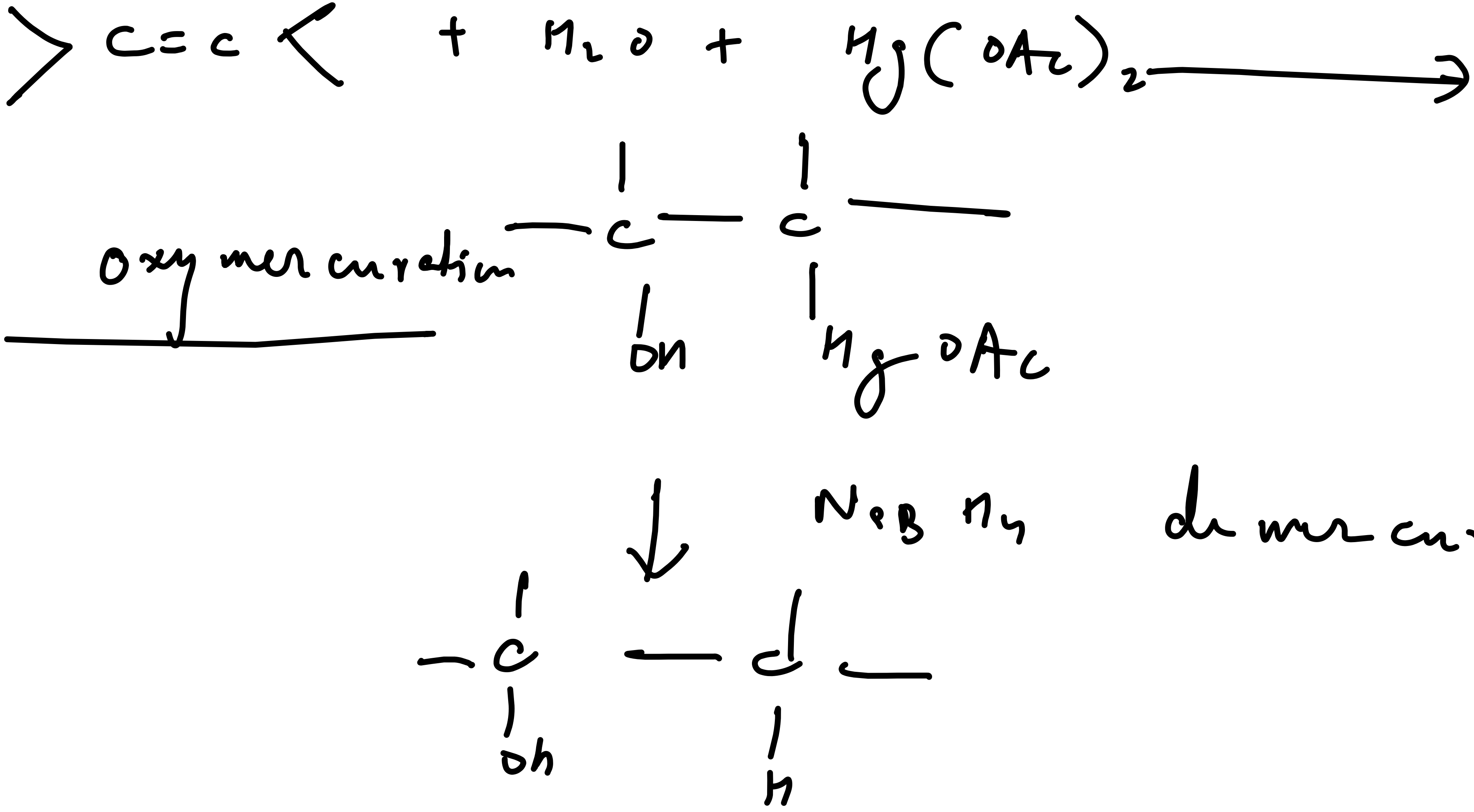
$2\,RO^{\bullet} \longrightarrow R-O-O-R$

$Br^{\bullet} + Br^{\bullet} \longrightarrow Br$

a. Addition of water to alkenes: acid catalysed hydration.



③ Oxymercuration- demercuration



$$>C=C< + H_2O + Hg(OAc)_2 \longrightarrow -\underset{\underset{OH}{|}}{\overset{|}{C}}-\underset{\underset{HgOAc}{|}}{\overset{|}{C}}-$$

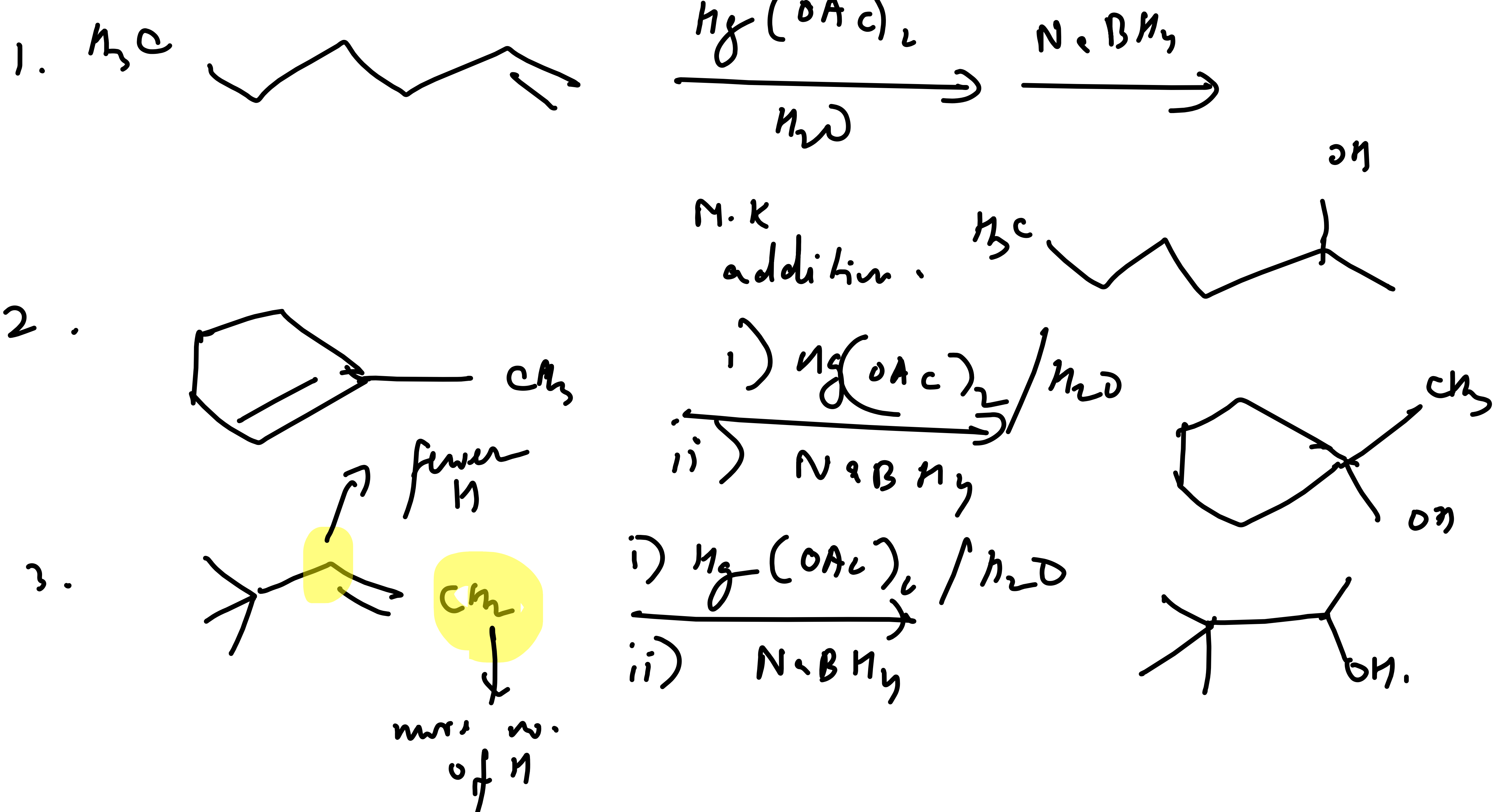
oxymercuration

$$\Big\downarrow NaBH_4$$

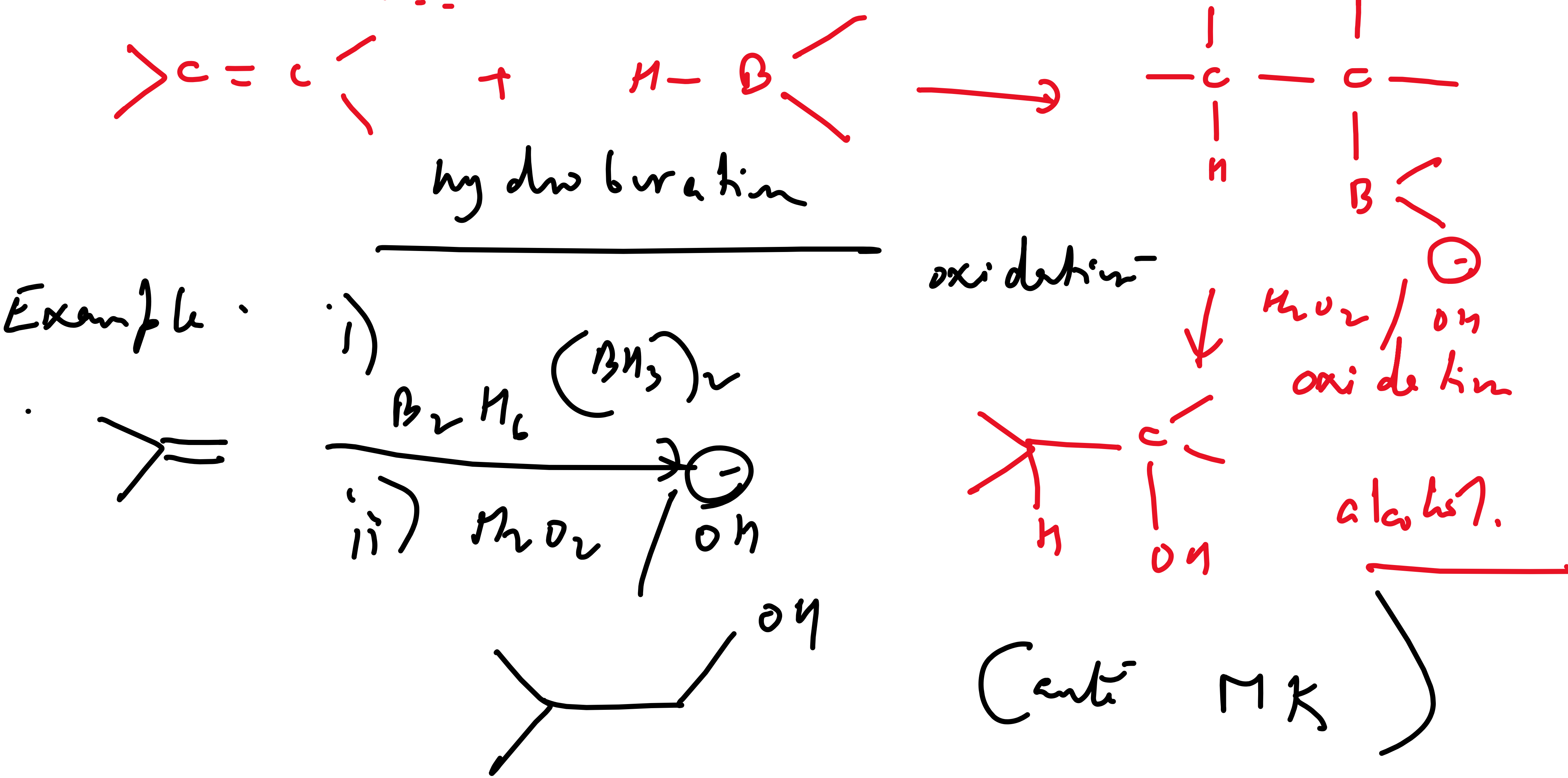
demercuration

$$-\underset{\underset{OH}{|}}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}-$$

Examples:


1.
H_3C
$Hg(OAc)_2$
H_2O
$NaBH_4$
M.K addition.
H_3C
OH
2.
CH_3
i) $Hg(OAc)_2/H_2O$
ii) $NaBH_4$
CH_3
OH
3.
fewer H
CH_2
more no. of H
i) $Hg(OAc)_2/H_2O$
ii) $NaBH_4$
OH.

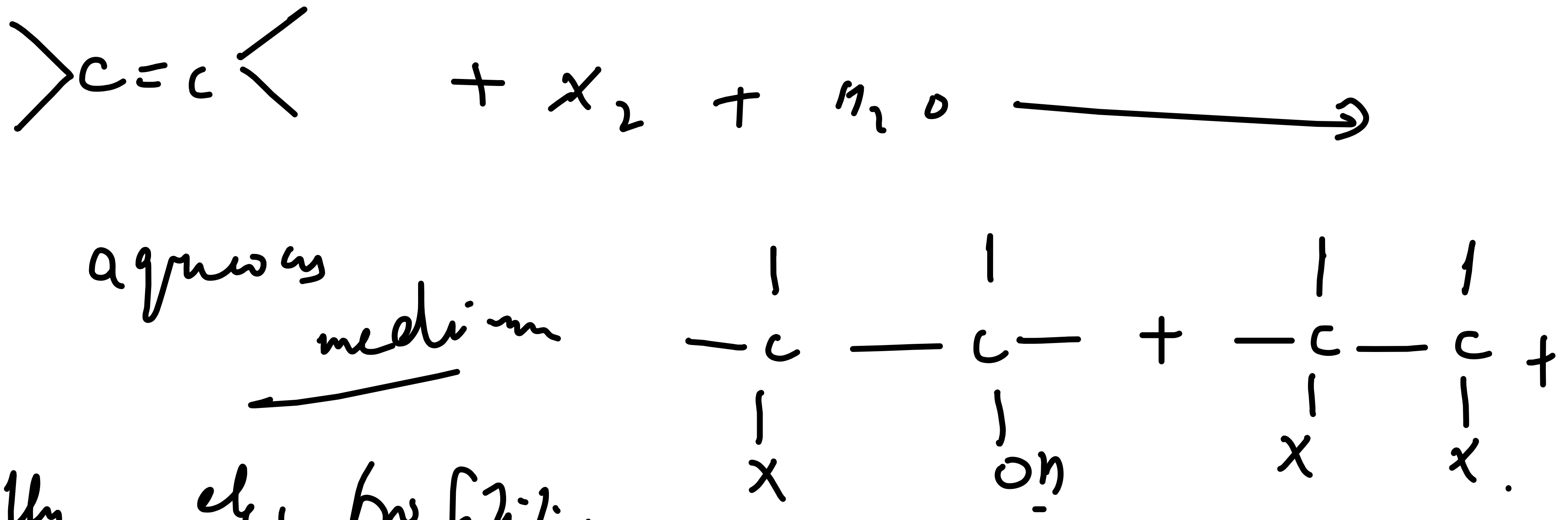
④ Hydroboration - oxidation -



Example :

(anti MK)

⑤



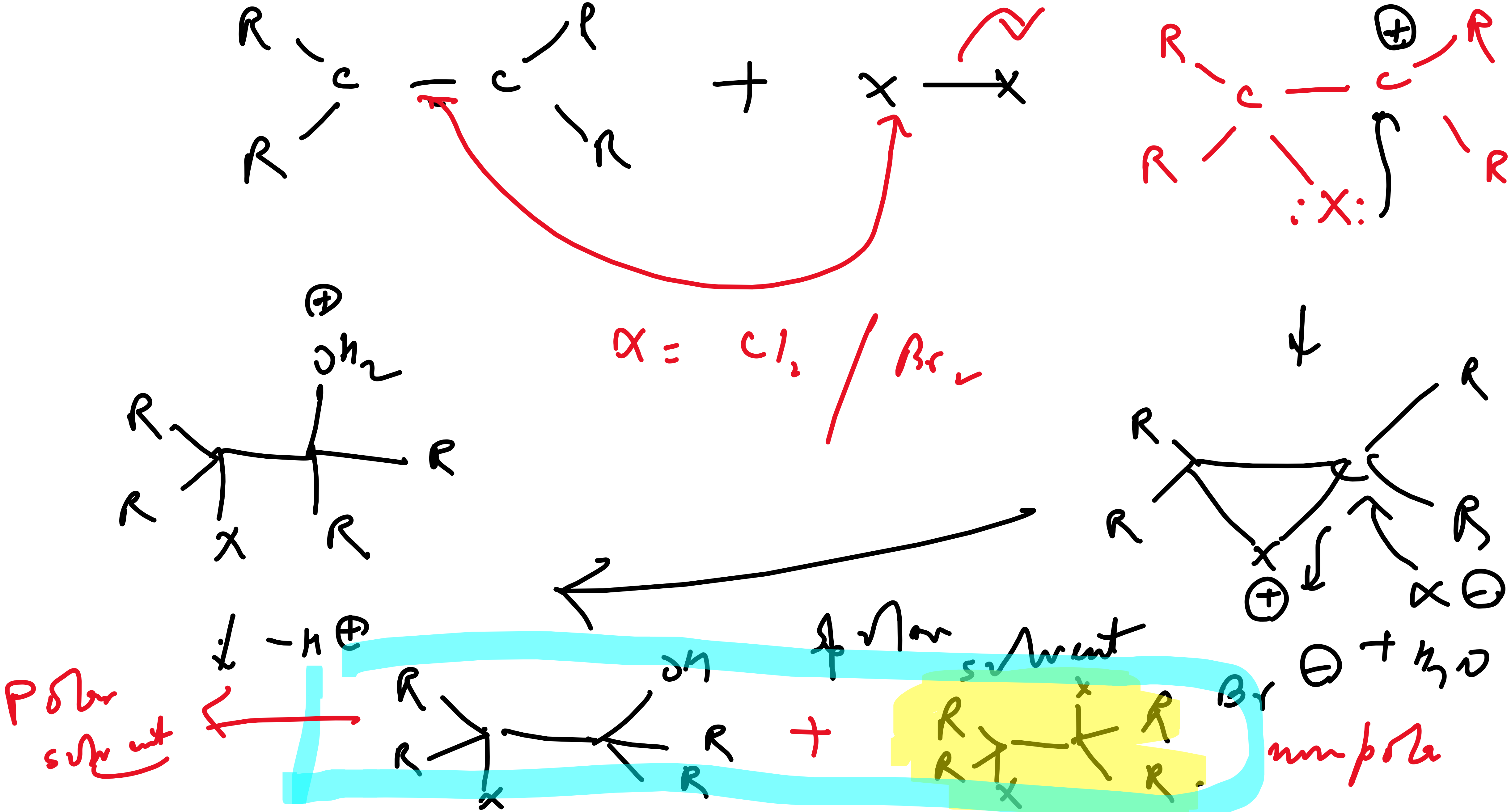
$$>C=C< \; + X_2 + H_2O \xrightarrow{} \; -\underset{X}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}- \; + \; -\underset{X}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}- \; + \; HX$$

aqueous medium

Usually electrophilic addition of halogen is carried out in nonpolar medium & it proceeds ~~throu~~gh a cyclic transition state.

$^{\ominus}OH$ & $X^{\ominus}$

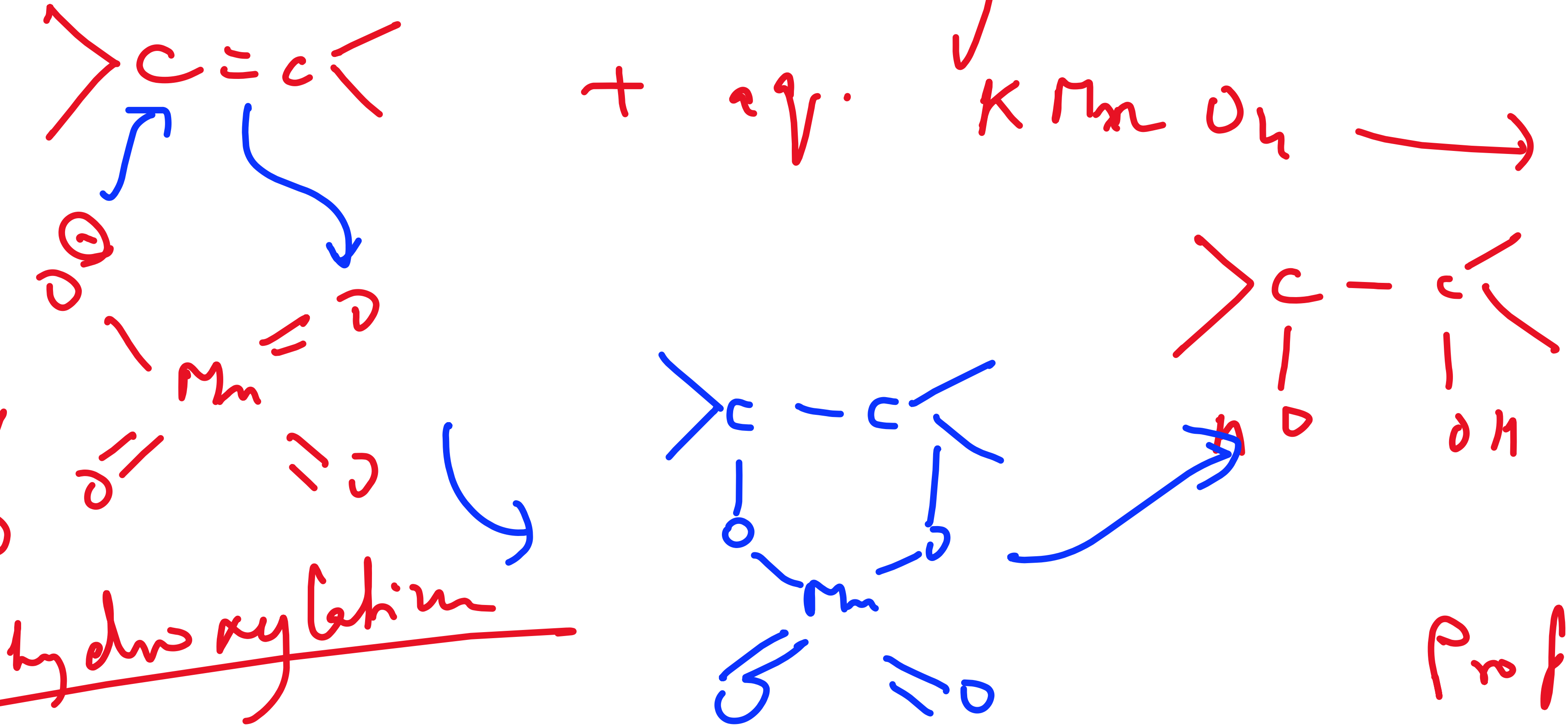
2 nucleophiles



X = Cl₂ / Br₂
⊕
:X:
X
⊕
X ⊖
⊖ + H₂O
⊕
OH₂
↓ -H⊕
OH
Polar solvent
Non polar solvent
Br
nonpolar

ⓒ Syn - hydroxylation — formation of diols.

1. OsO_4
2. $NaHSO_3/H_2O$

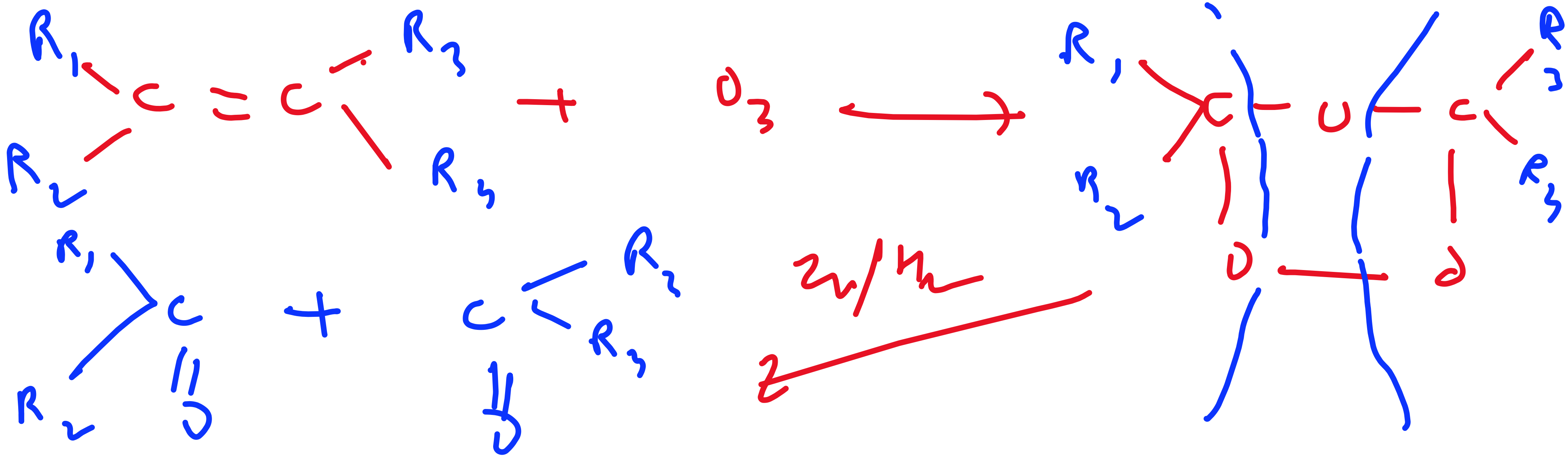


cis - hydroxylation

$CH_3-CH=CH_2 \xrightarrow[\text{ii) } NaHSO_3/H_2O]{\text{i) } OsO_4}$

Propylene glycol.

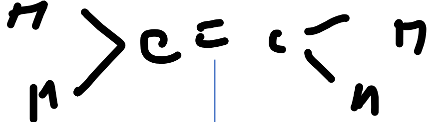
⑦ Ozonolysis :

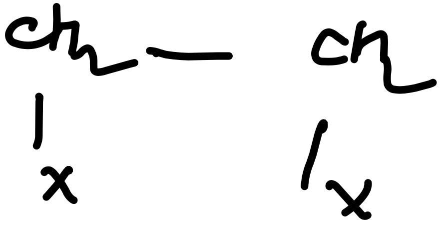
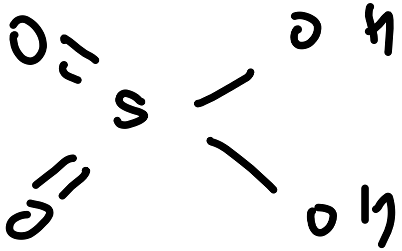
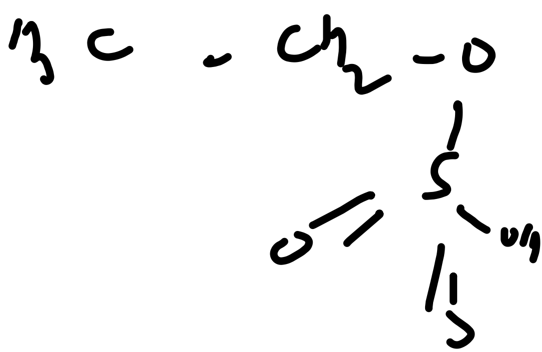


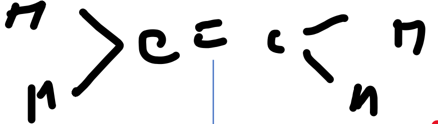
Summary :

Major reactions of alkene is electrophilic addition.

Examples of electrophilic polar addition reaction



Reagent Name	Structure	Product name	Structure
1. Halogens	$X-X$	Ethylene dihalide.	 CH_2X-CH_2X
2. Hydrogen halide	$H-X$	Ethyl halide	CH_3-CH_2-X
3. Hypohalous acid	$X-OH$	Ethylene halohydrin	H_2CX-CH_2OH
4. Sulfuric acid (cold)		Ethyl bisulfite	



Reagent Name	Structure	Product name	Structure
5. Water	H– OH M.K	Ethyl alcohol	H_3C-CH_2-OH
c. Borane	$H_2B:H$ anti M.K.	Ethyl borane	$(H_3CCH_2BH_2)$ ↓ $(H_3C-CH_2)_3-B$

all the 3 hydrogen atoms of $\cdot BH_3$ gets substituted with alkyl group.

⑦ Peroxy formic acid	$H-\overset{O}{\overset{\parallel}{C}}-O\,\vdots\,OH$	Ethylene glycol	$\underset{OH}{CH_2}-\underset{OH}{CH_2}$

Alkyne : 1. Unsaturated open chain hydrocarbon with general formula,

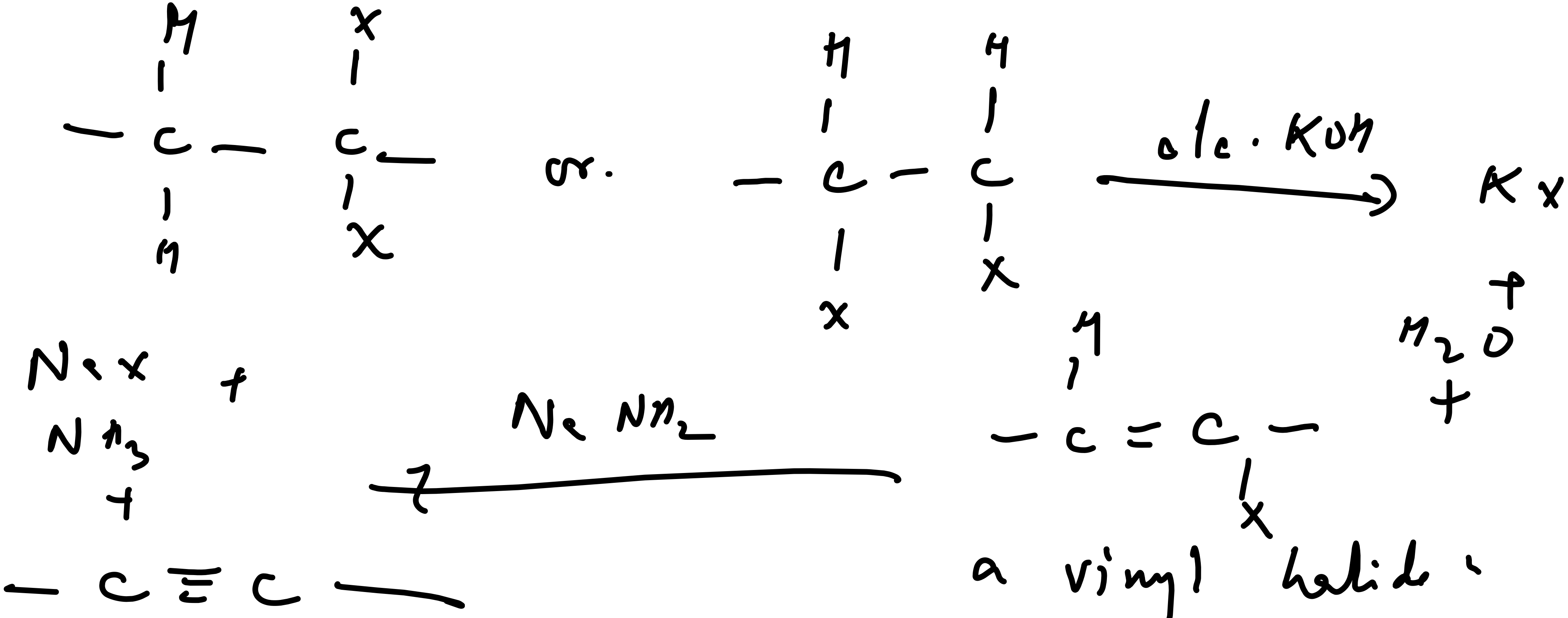
C_nH_{2n-2}

2. At least one $-C\equiv C-$ (triple bond) group i.e. sp hybridisation is present throughout the chain.

3. Physical properties of alkynes are similar to those of the corresponding alkenes

Preparation :

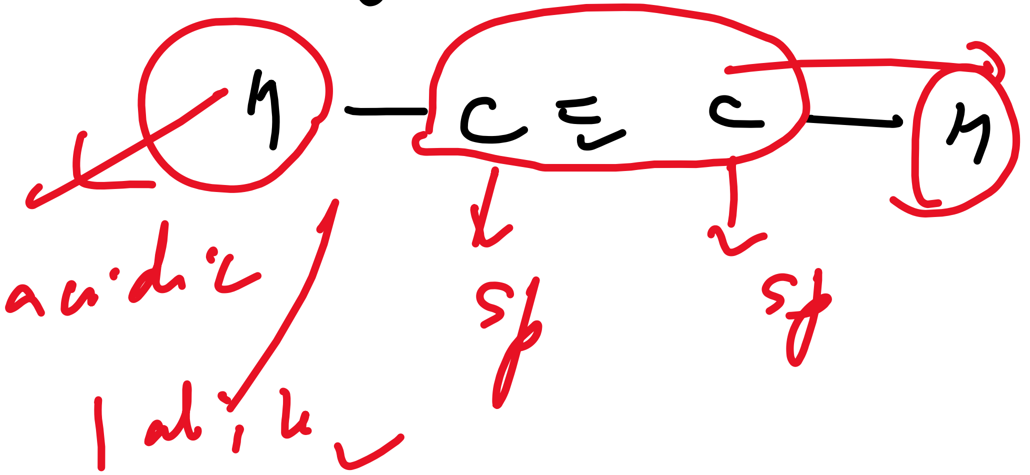
1. Dehydrohalogenation of vic-dihalides or gem-dihalides.



2. Dehalogenation of vic-tetrahalogen compounds.

$$H_3C-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-CH_3 + 2Zn \xrightarrow[\Delta]{EtOH} H_3C-C\equiv C-CH_3 + 2ZnBr_2$$

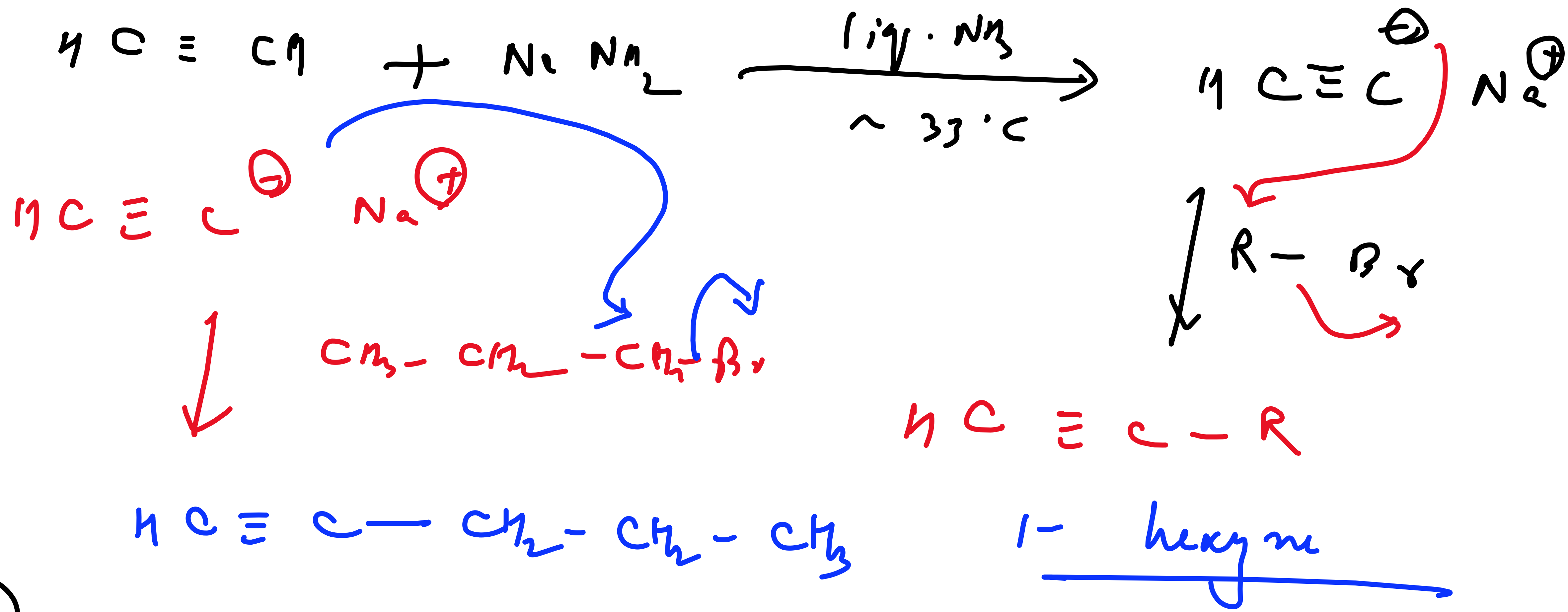
3. Acetylene ⟶ Substituted acetylene.



highly electronegative

s character : 50%

Acetylene is acidic



$$HC\equiv CH + NaNH_2 \xrightarrow[\sim 33^{\circ}C]{liq.\ NH_3} HC\equiv C^{\ominus}\ Na^{\oplus}$$

$$R-Br$$

$$HC\equiv C-R$$

$$HC\equiv C^{\ominus}\ Na^{\oplus}$$

$$CH_3-CH_2-CH_2-Br$$

$$HC\equiv C-CH_2-CH_2-CH_3$$

1- hexyne

④ $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

⑤ Kolbe's electrolysis.

$$\begin{matrix} CH-CO_2Na \\ \| \\ CH-CO_2Na \end{matrix} \xrightarrow[\text{electric current}]{H_2O}$$

$$\begin{array}{c} CH \\ ||| \\ CH \end{array} + 2CO_2 + 2NaOH + H_2$$

Chemical Properties:

1. **Hydrogenation:** $R - C \equiv C - CH_2 - CH_3 +$

$$\xrightarrow{2H_2} H_3C - CH_2 - CH_2 - CH_2 - CH_3 .$$

2. **Hydrohalogenation**

MK addition: $R - C = CH + HBr \longrightarrow \begin{array}{c} RCBr \\ || \\ CH_2 \end{array}$

$+ HBr$

$R-CBr_2-CH_3$

Anti M. K.

$R-C\equiv CH + HBr$ + peroxide :

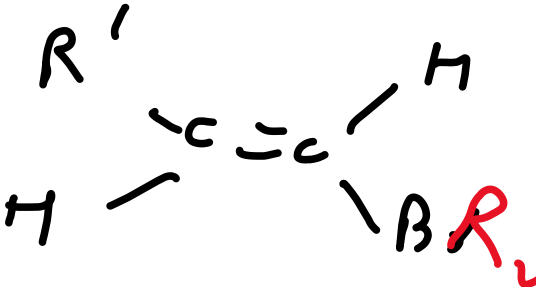
$R-CH=CHBr$.

3. <u>Hydration</u>

$$CH\equiv CH + H_2O \xrightarrow[Hg^{+}]{H_2SO_4} H_2C=CHOH + H_3C\,CHO$$

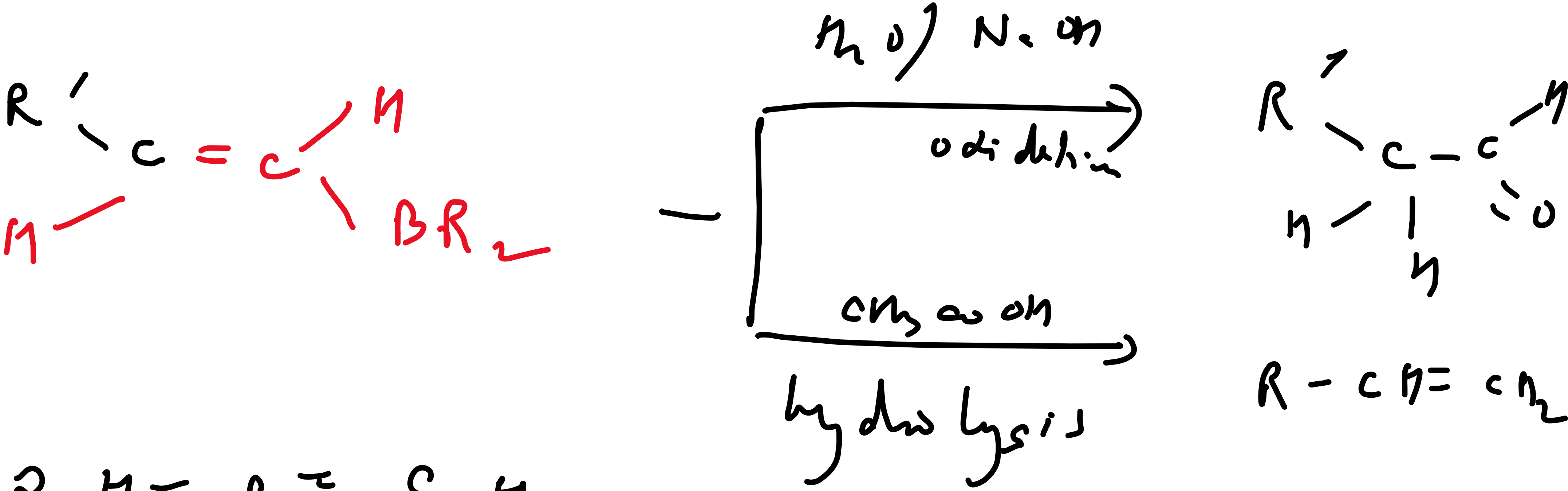
4. Addition of BH_3

$R'C\equiv C-H + R_2BH \longrightarrow$



poorer H.

anti M. K.

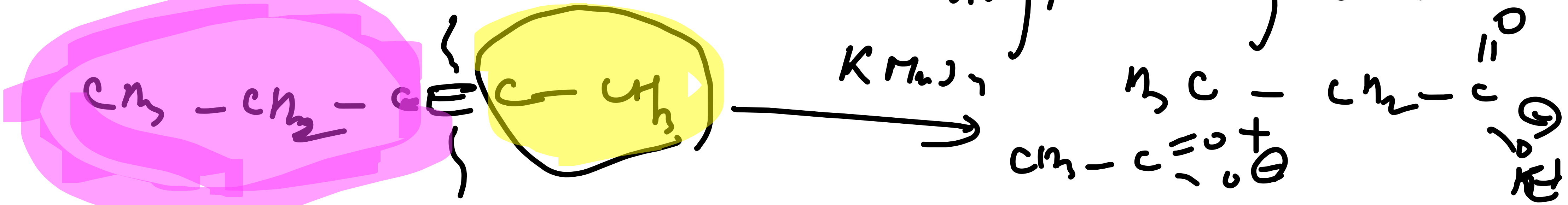


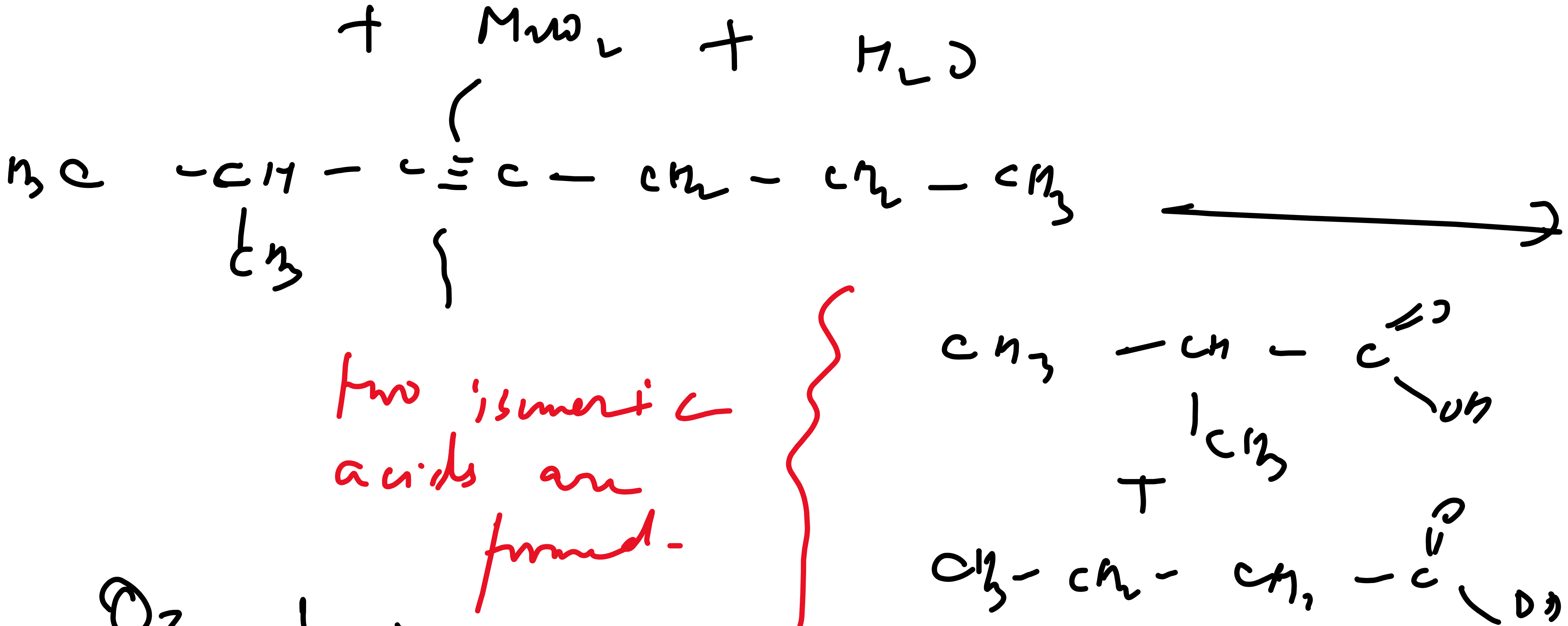
⑤ $2\,H-C\equiv CH$

$$\downarrow\ Cu(NH_3)_2^{\oplus}\,Cl^{\ominus}\,/\,H_2O$$

$H_2C-CH-C\equiv CH$ vinyl acetylene.

⑥



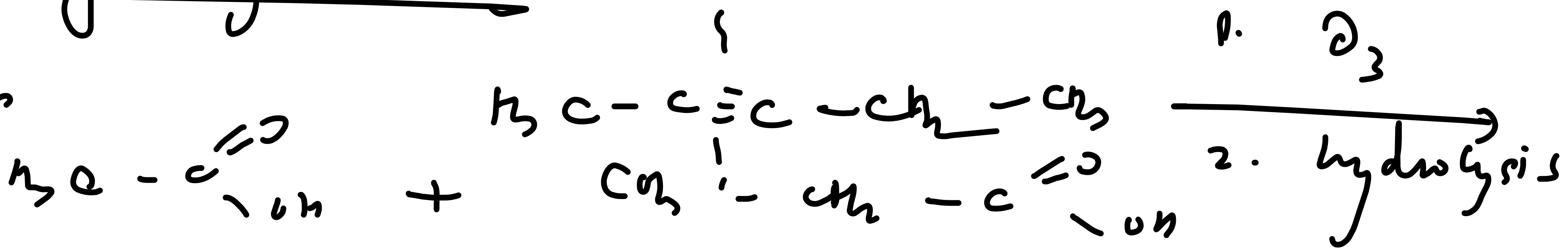


$$H_3C-\underset{CH_3}{\underset{|}{CH}}-C\equiv C-CH_2-CH_2-CH_3 \longrightarrow \underset{CH_3}{\underset{|}{CH_3-CH}}-C\overset{=O}{\underset{OH}{}} + CH_3-CH_2-CH_2-C\overset{=O}{\underset{OH}{}} + MnO_2 + H_2O$$

two isomeric acids are formed.

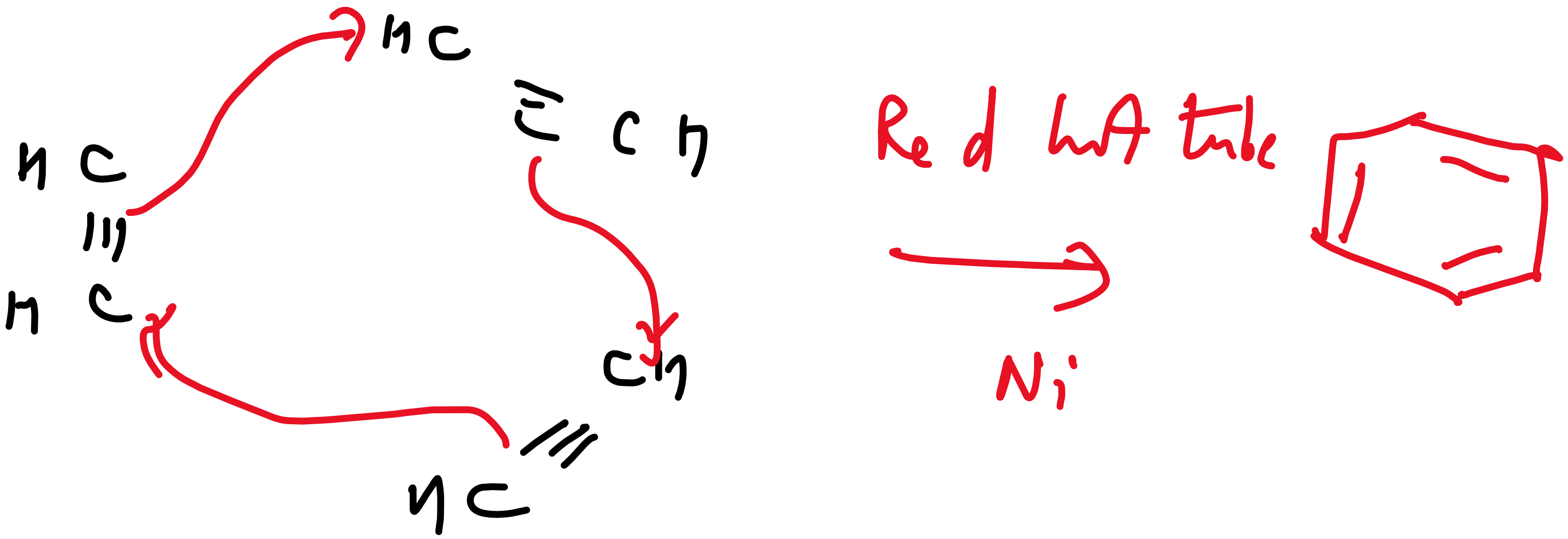
7. Ozonolysis

acid formations



$$H_3C-C\equiv C-CH_2-CH_3 \xrightarrow[\text{2. hydrolysis}]{\text{1. } O_3} H_3C-C\overset{=O}{\underset{OH}{}} + CH_3-CH_2-C\overset{=O}{\underset{OH}{}}$$

8. Cyclic Polymerization

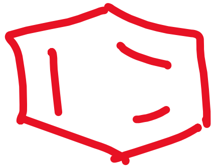


Aromatic Hydrocarbons -

Conditions of aromaticity :

1. The compound must be cyclic .
2. Have planarity in geometry.
3. Complete delocalization of electrons over ring.
4. Follow Huckel's rule of aromaticity i.e. total no. of electrons in a ring must be $4n + 2$ where n = an integer.

If $n =$ integer, then a system is aromatic

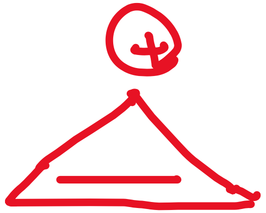


Total no. of electrons = 6

$\therefore 4n + 2 = 6$

$$\Rightarrow n = \frac{6-2}{4} = \underset{\text{integer.}}{\underset{\downarrow}{\boxed{1}}}$$

$\therefore$ Benzene is aromatic



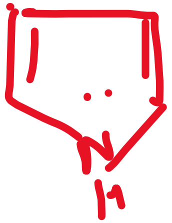
aromatic

Total no. of electrons = 2

$4n + 2 = 2$

$\therefore n = 0$

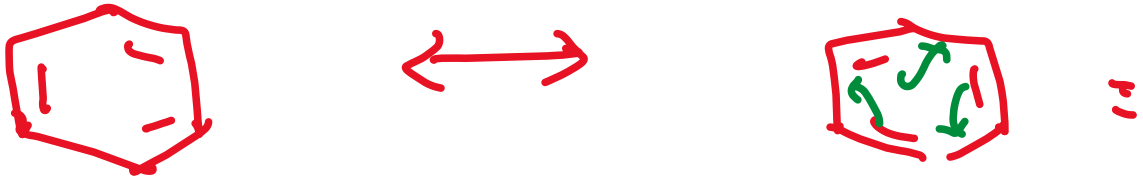
aromatic



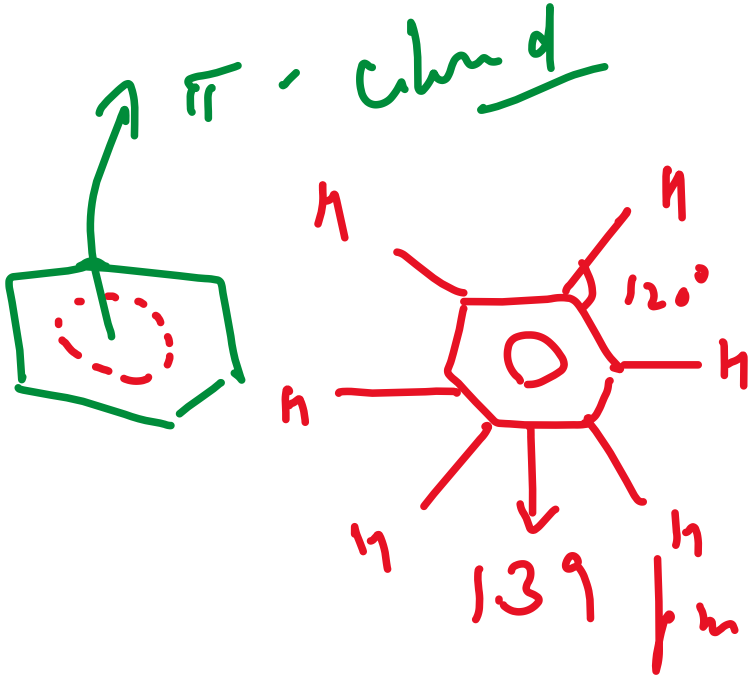
Total no. of electrons = 6

$n = 1$ (including lone pair)

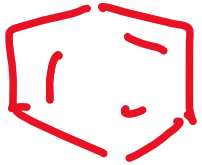
Benzene - C_6H_6



A Kekule structure B



2.



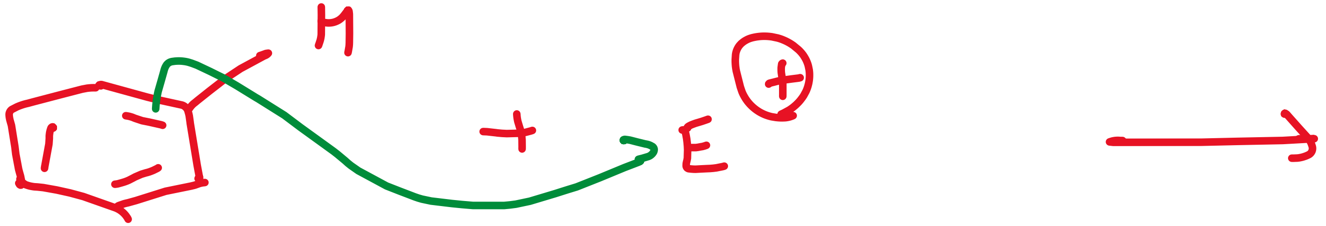
Major reaction:

Electrophilic substitution -

Due to presence of delocalizing π- electron cloud, benzene ring can be easily attacked by the electrophiles.

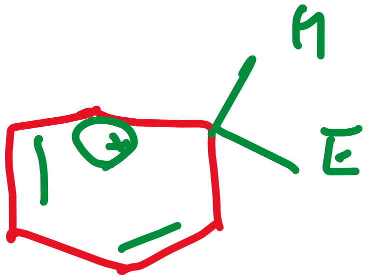
Mechanism:

Step I:

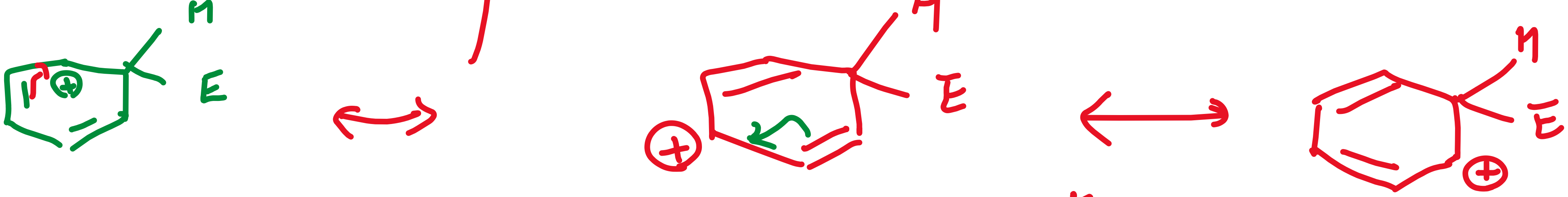


Benzene

Electrophile



Electrophilic attack on a π bond by an electrophile to form carbocation



resonance-stabilized

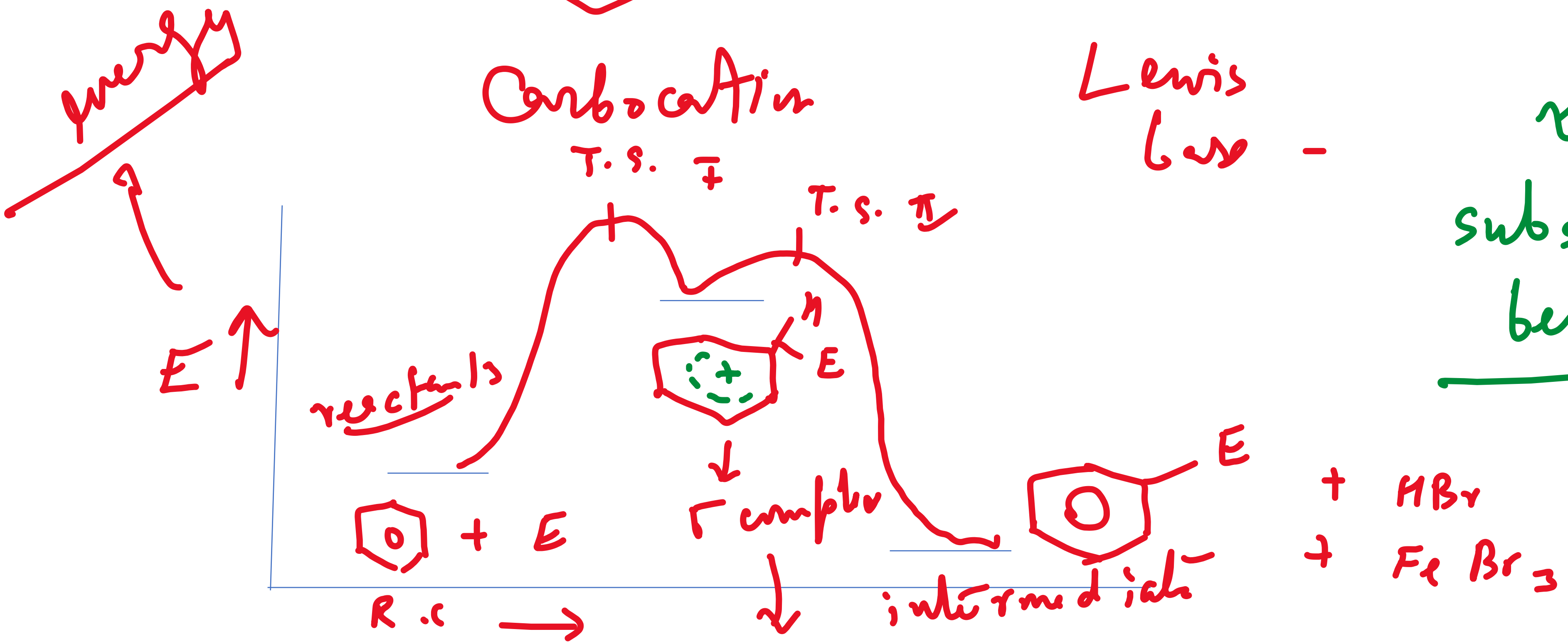
σ complex

Step II: Deprotonation of the carbocation to restore its aromaticity.

Carbocation

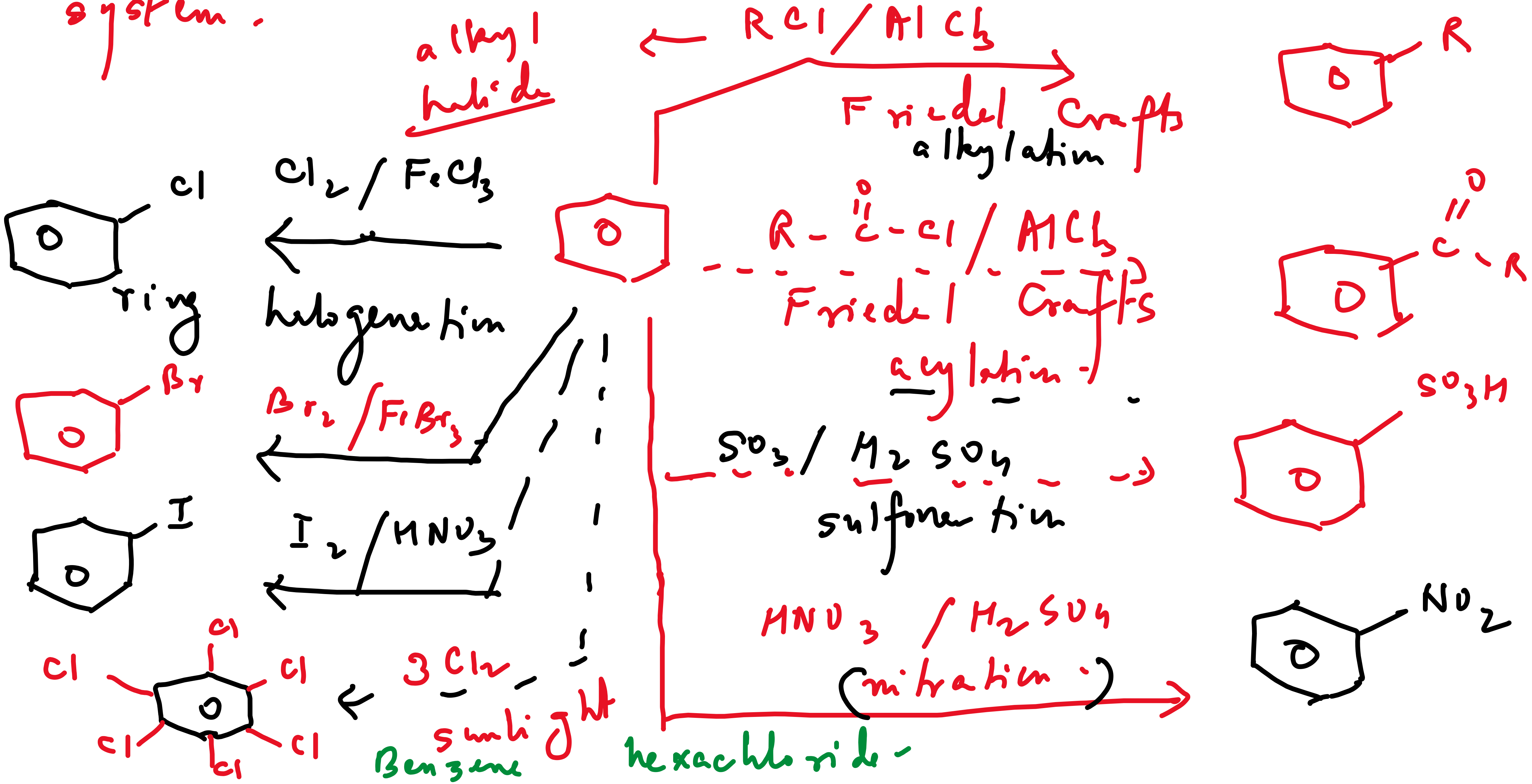
Lewis base -

substituted benzene



R.C. = reaction coordinate

Electrophilic substitution reactions in benzene system.



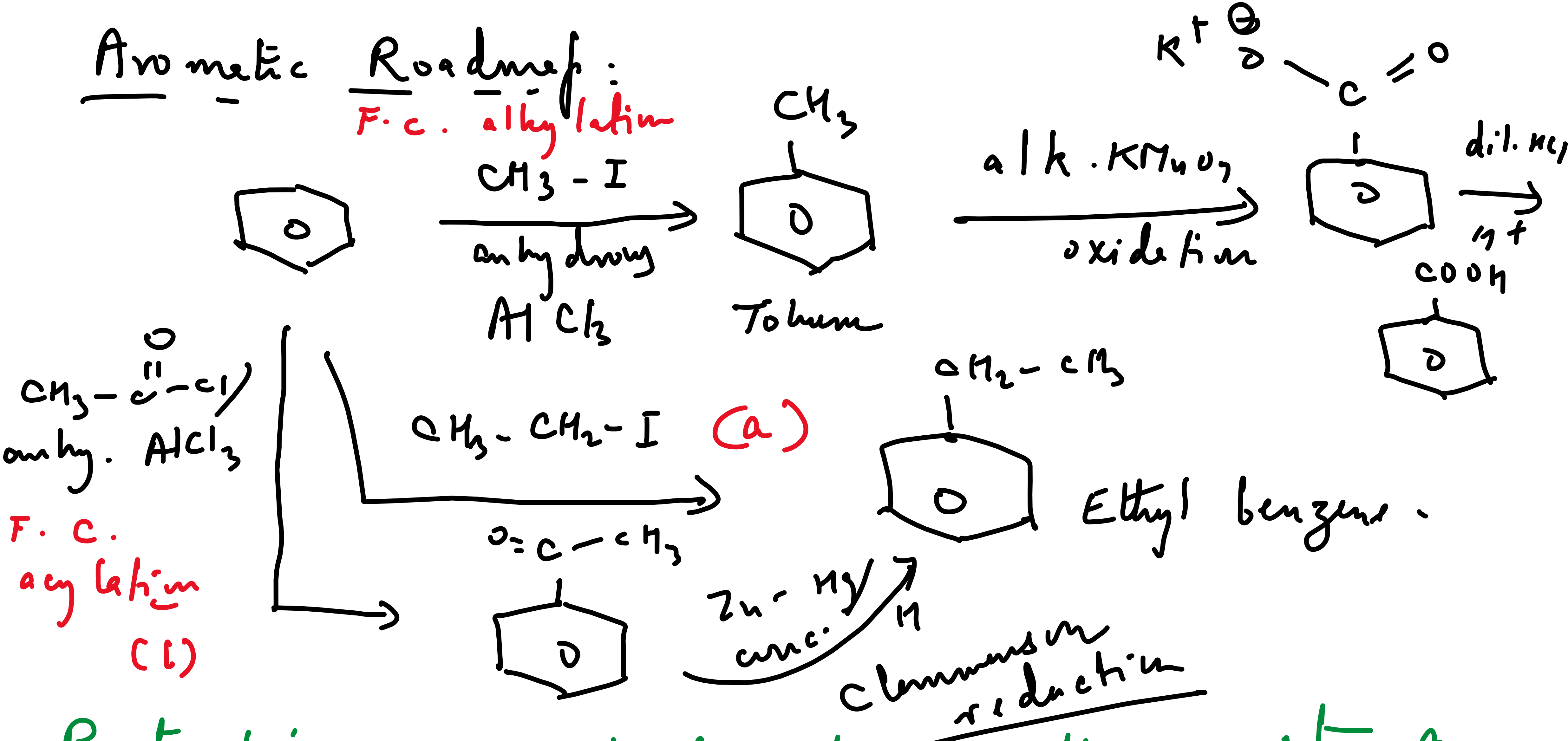
Anti aromatic hydrocarbons

Highly unstable compounds.

Number of electrons (π electrons) in ring = $4n$.

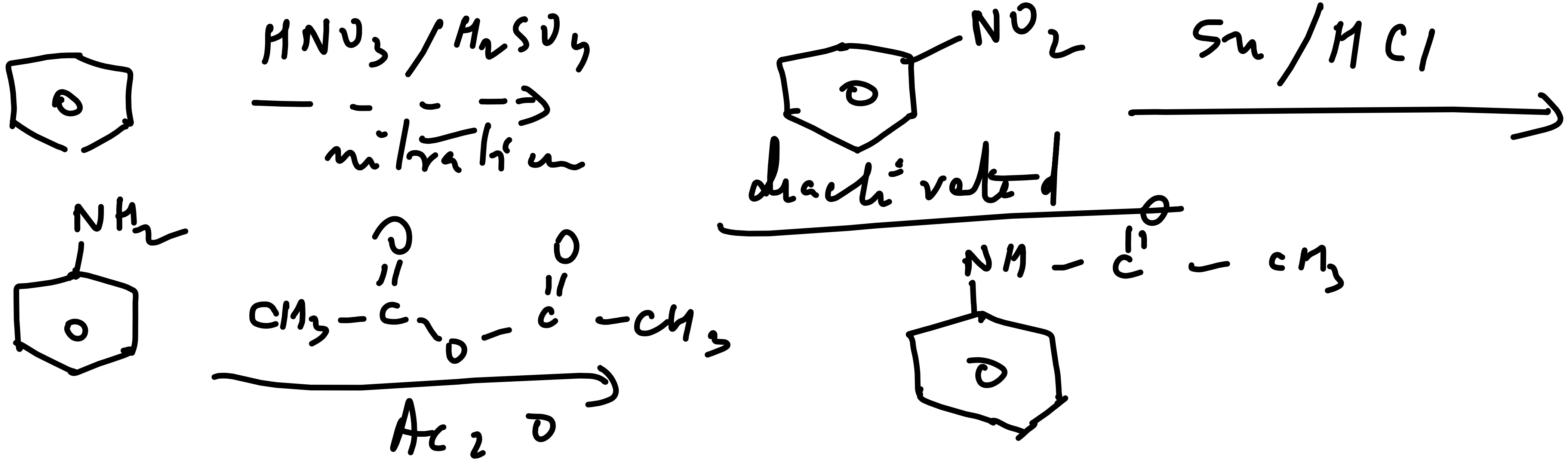
These hydrocarbons do not obey Huckel's rule of aromaticity.

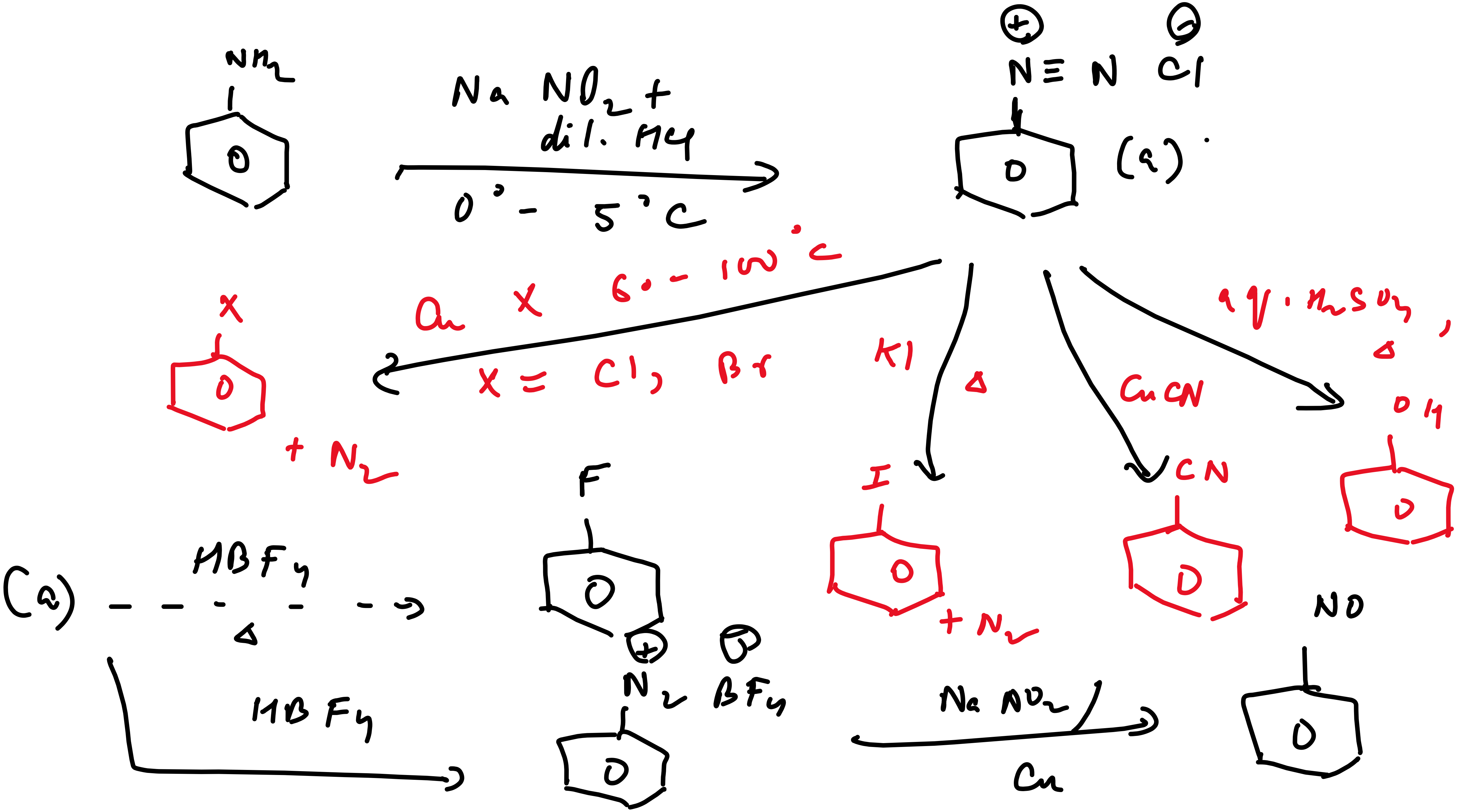
Aromatic Roadmap :



Route b is more preferred than route a - $-CH_3$ being $+I$ / activating group - once (alkyl group) introduced into the benzene ring the ring becomes highly activated and has a tenacity to undergo further electrophilic substitution forming polyalkylated products. The reaction does not stop at monoalkylation.

Subsequently, the better strategy is to use F.C. acylation instead of alkylation, following Clemmensen's reduction, because $-\overset{O}{\overset{\|}{C}}-CH_3$ (acyl) groups are deactivating. Once $-COCH_3$ group is introduced into the benzene ring, the reaction stops to monoacylation, which on further reduction with Zn-Hg & HCl undergoes Clemmensen's reduction to form the monoacylated product selectively.




NH2
NaNO2 + dil. HCl
0° - 5°C
⊕ N≡N Cl ⊖
(a)
Cu X 60 - 100°C
X = Cl, Br
X
+ N2
KI
Δ
I
+ N2
CuCN
CN
aq. H2SO4, Δ
OH
(a) HBF4 Δ
F
HBF4
⊕ N2 ⊖ BF4
NaNO2 / Cu
NO2