CH 14 Hydrocarbon

Friday, June 13, 2025 5:03 PM

Free Radical Mechanism

IGCSE $CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$

* Alkene Addition Reactions

→ * Alkene oxidation Reaction AS | A2

Alkane $C-C-H \rightarrow \left[\underset{EN}{C} \overset{\cdot}{\underset{\times}{-}} \underset{EN}{H} \right]$ non polar.

Alkane is unreactive $\overset{+\delta}{C} \overset{\cdot}{\underset{\times}{-}} \overset{-\delta}{Cl}$

C ✗ E.N
Cl ✓ attracting the ē pair towards itself $\overset{+\delta}{C} \overset{\cdot}{\underset{\times}{-}} Cl$

If bond is non polar it is considered strong bond and can't be broken easily

$\underbrace{C-C}_{\text{non polar}}$ & $\underbrace{C-H}_{\text{non polar}}$

Alkane Reactions

- Free Radical substitution
- Combustion
- Cracking

Cracking Breakdown of long chain hydrocarbon (less demand) into small chain hydrocarbon (more useful).

Condition : High temp
" Pressure

Catalyst $\underset{\text{alumina}}{Al_2O_3}$ and $\underset{\text{silica}}{SiO_2}$

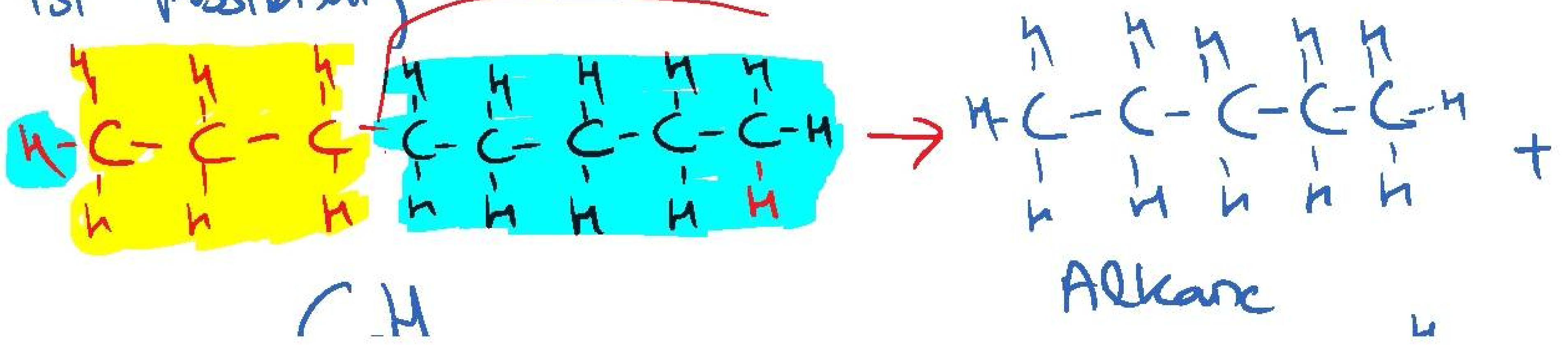
1st Possibility

longer chain hydrocarbon → small Alkane + Alkene
Alkane

2nd Possibility

longer Chain Alkane → Alkene + hydrogen gas

1st Possibility



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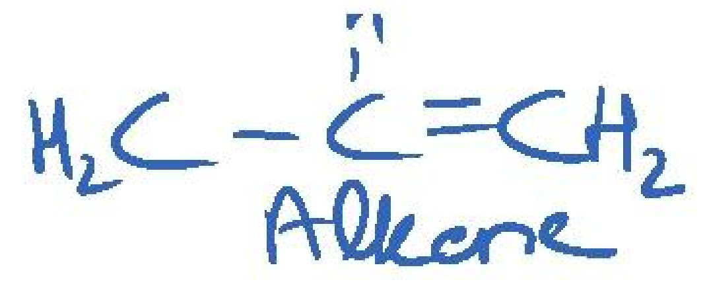
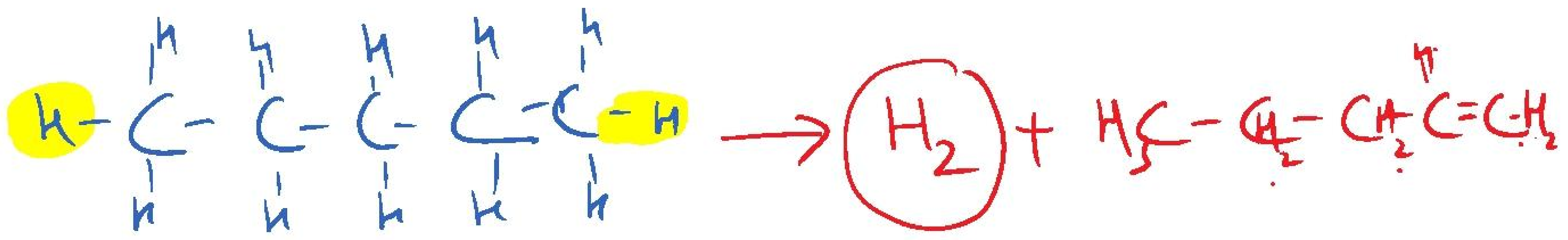


Alkene



Alkane C_5H_{12}

H_2 gas → fuel

→ Alkene is use as Feedstock For different Industries
→ Alkane
→ Alcohol
→ Polymers

Alkane → Fuel

less Carbon Small Carbon chain is Considered best fuel because it is highly flammable

Carbon number $\propto \frac{1}{\text{Flammability}}$

Combustion

Burning of fuel in the presence of O_2

Complete Combustion
excess of O_2
CO_2, H_2O

Incomplete Combustion
limited amount O_2
CO, C (soot), H_2O, CO_2

Complete Combustion

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

$C_8H_{18} + 12.5\overset{③}{O_2} \longrightarrow \underbrace{\overset{①}{8CO_2}}_{16} + \overset{②}{9H_2O}$ $\frac{\cancel{18}\,9}{\cancel{2}}$

16 + 9

$\frac{\boxed{25}\text{ Oxygen}}{2}$

$C_xH_{ⓨ} + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$

$C_{\underset{x}{②}}H_{\underset{y}{⑥}} + \qquad \rightarrow 2CO_2 + 3H_2O$

Incomplete Combustion

$\boxed{\frac{2CH_4}{2} + \frac{\cancel{3}O_2}{2}}$ $15O_2$ $\longrightarrow 2CO + \overset{4}{\cancel{2}}H_2O$

$CH_4 + \boxed{2O_2} \longrightarrow CO_2 + 2H_2O$

$\boxed{CO_2}$ Green house sheet / glass

↓

Green House Gas

$\boxed{CO}$ silent killer

↓

Toxic gas

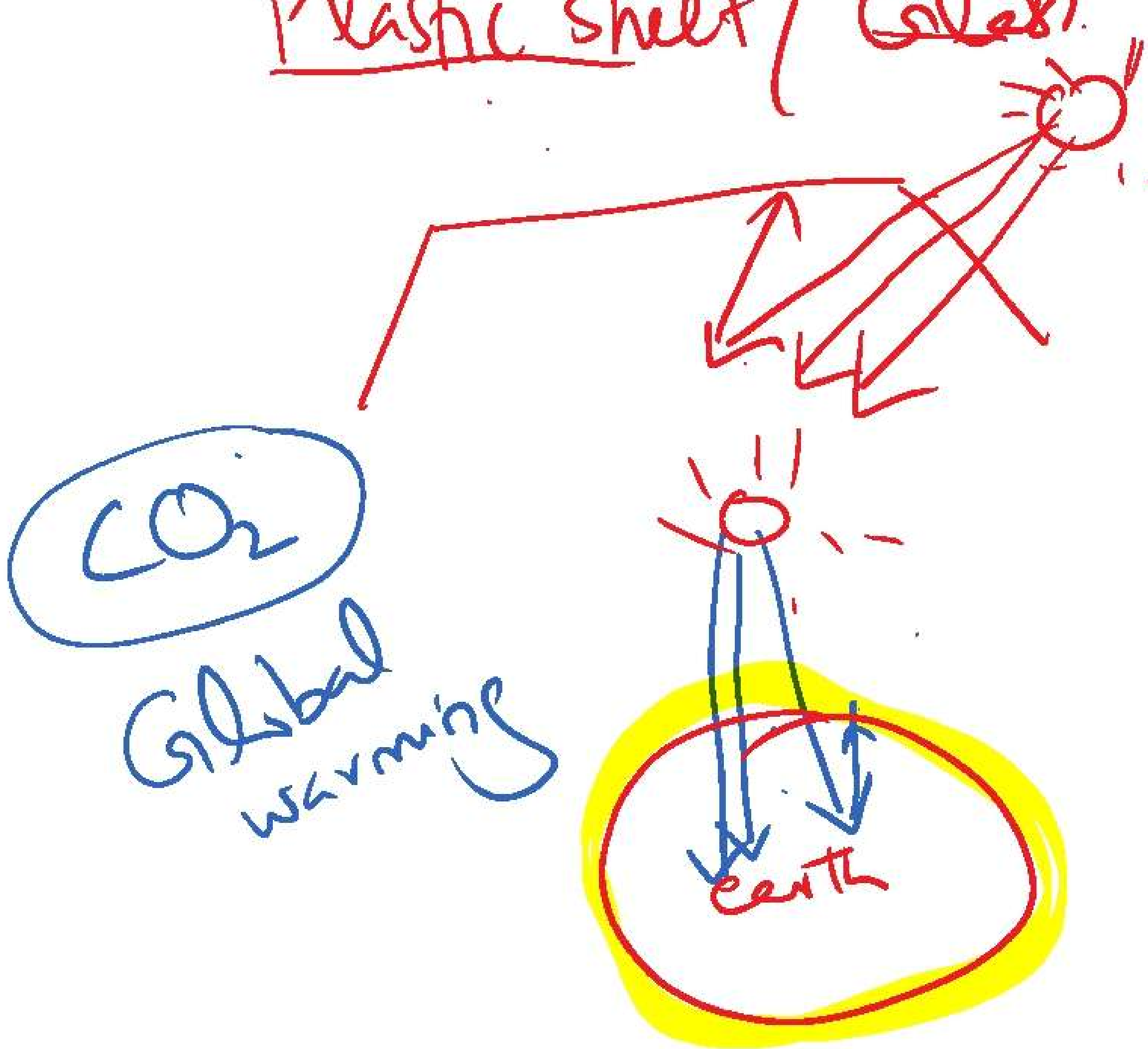
colourless

odourless gas

Hb-CO

suffocation

Plastic sheet / Glass



CO_2, CO

NO Oxides of Nitrogen

NO_2

N_2 78%

inert gas

Triple bond

$N \equiv N$

Natural Process

(1) $N_2 + O_2 \xrightarrow{\text{Lightening}}$ NO (P), NO_2 (P) Pollutants (P)

$NO + O_2 \longrightarrow$

primary pollutants

(2) (Manmade) Car exhaust fumes

↓

(1) Unburnt hydrocarbons

(P) oxides of nitrogen NO, NO_2 + (2) VOCs (Volatile organic compounds) (P)

Photochemical smog ← (PAN) ← secondary pollutant

Peroxyacetyl nitrate

→ Harmful for lungs

→ eyes irritation

NO & $NO_2 + H_2O \longrightarrow HNO_3$

Imp How Acid Rain is formed

$SO_2 + O_2 \xrightarrow[400\text{-}450]{V_2O_5} SO_3$

⇒ NO_2 is acting as a Catalyst

$SO_2 + NO_2 \longrightarrow SO_3 + NO$

$NO + \frac{1}{2}O_2 \rightarrow \boxed{NO_2}$ (regenerated)

$SO_3 + H_2O \rightarrow H_2SO_4$

Catalytic removal → Platinum

Harmful gases: CO → CO_2; NO, NO_2 → N_2 → Harmless gases

$2CO + O_2 \rightarrow CO_2$

$$\boxed{2CO + 2NO \rightarrow 2CO_2 + N_2}$$

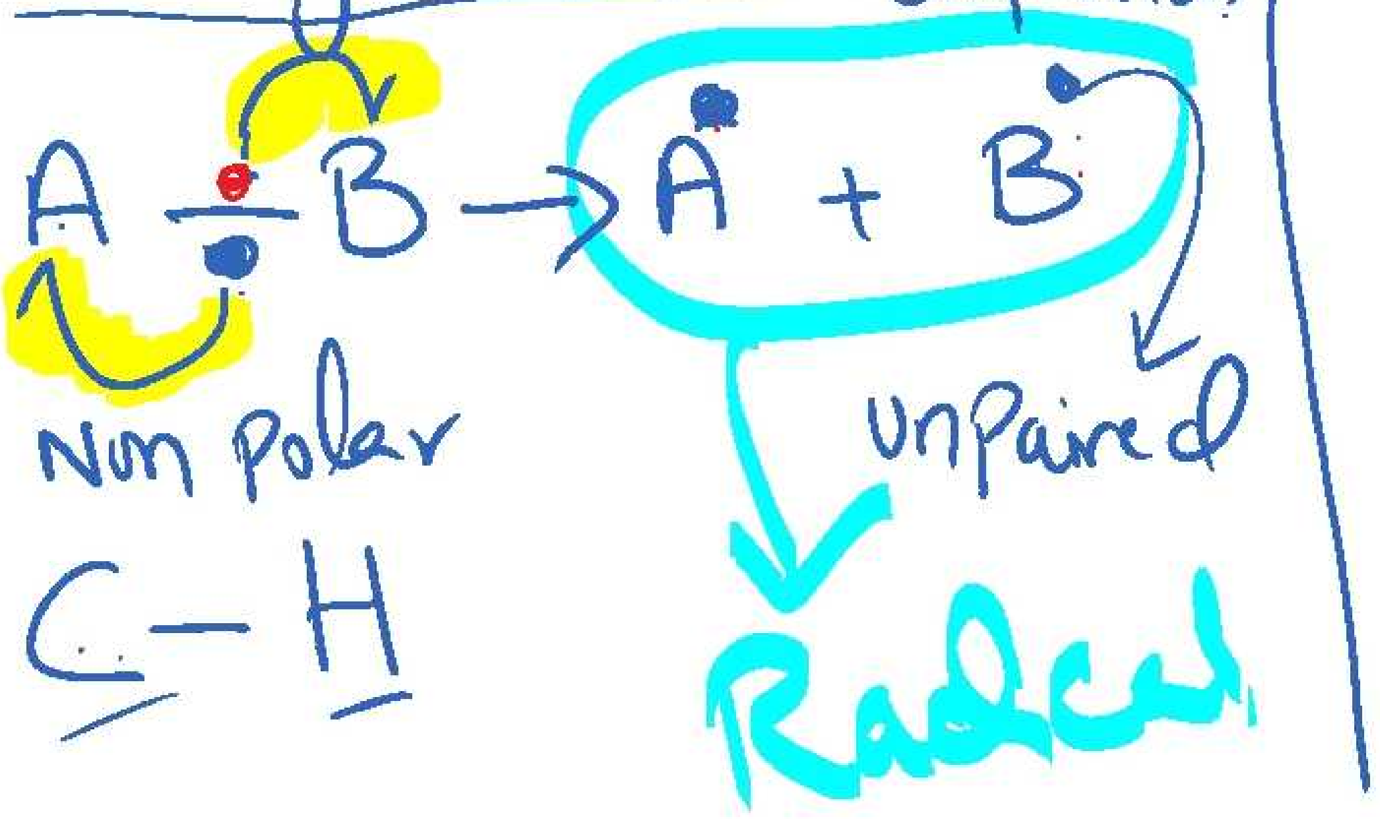
(1) CO	Incomplete combustion	Toxic gas	$CO + O_2 \rightarrow CO_2$
(2) oxides of nitrogen NO, NO_2	oxidation of nitrogen in car engines	Dissolve in and react in H_2O ~~with~~ to form acid rain	$2CO + 2NO \rightarrow 2CO_2 + N_2$
(3) VOCs	unburnt hydrocarbon from fuel in car engines	react with oxides of nitrogen and form PAN	Unburnt hydrocarbon must be oxidized to CO_2 & H_2O
(4) PAN VOCs + oxides of nitrogen	photochemical reaction of VOCs and nitrogen oxides in the atmosphere	photochemical smog	

Free Radical (Mechanisms)

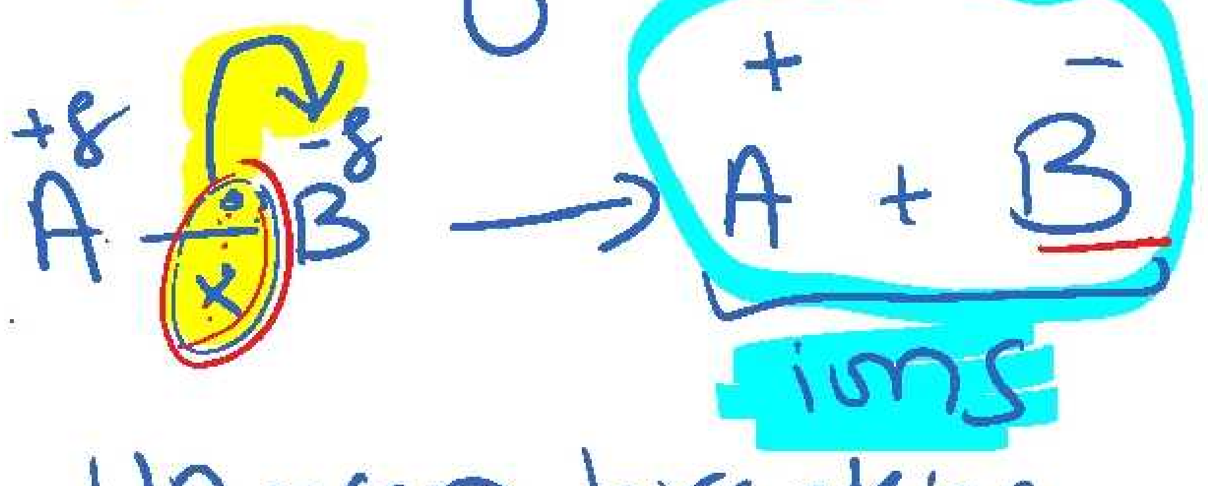
Substitution Reaction

photochemical reactions

Homolytic fission — same — will happen in non polar compounds



Heterolytic (Polar)

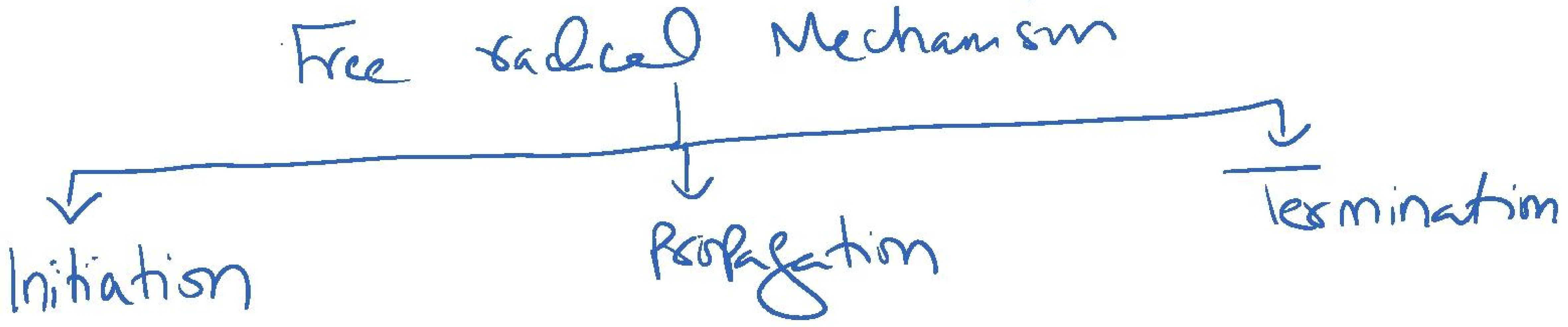


Uneven breaking of bonds.

Free Radical An atom or group of atoms which has unpaired electron.

In free radicals bond split evenly each atom will get one of the 2 e⁻s

→ Free radicals are highly reactive
→ " " are neutral.

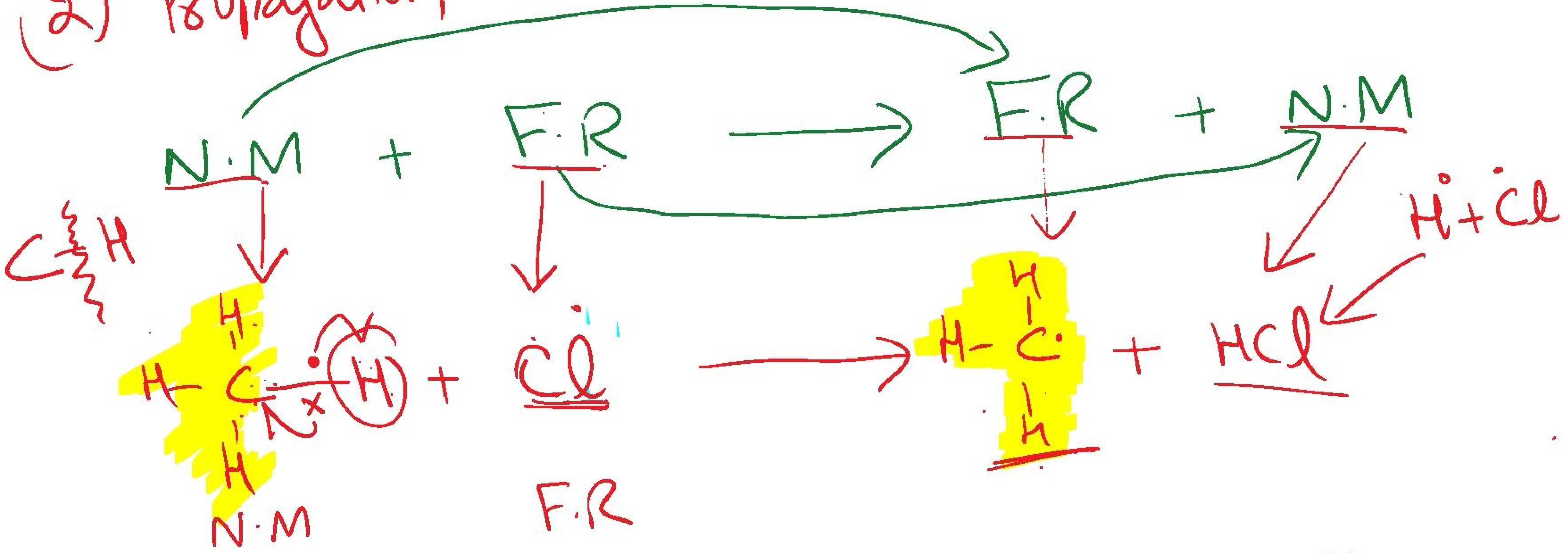


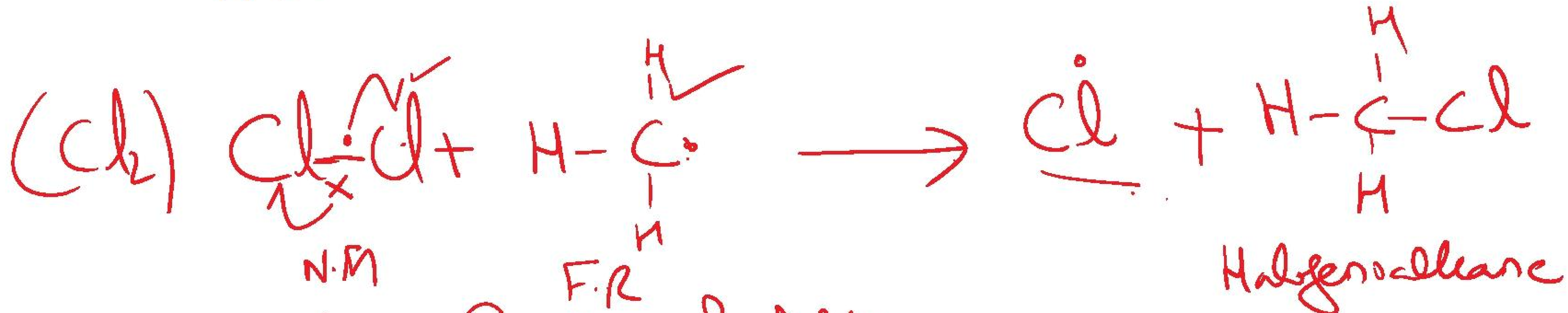
$\underline{N\cdot M}$ $\xrightarrow{hv}$ Free radical + free radical
normal molecule

(1) Initiation:-


$Cl-Cl \xrightarrow{hv} \dot{Cl} + \dot{Cl}$

(2) Propagation





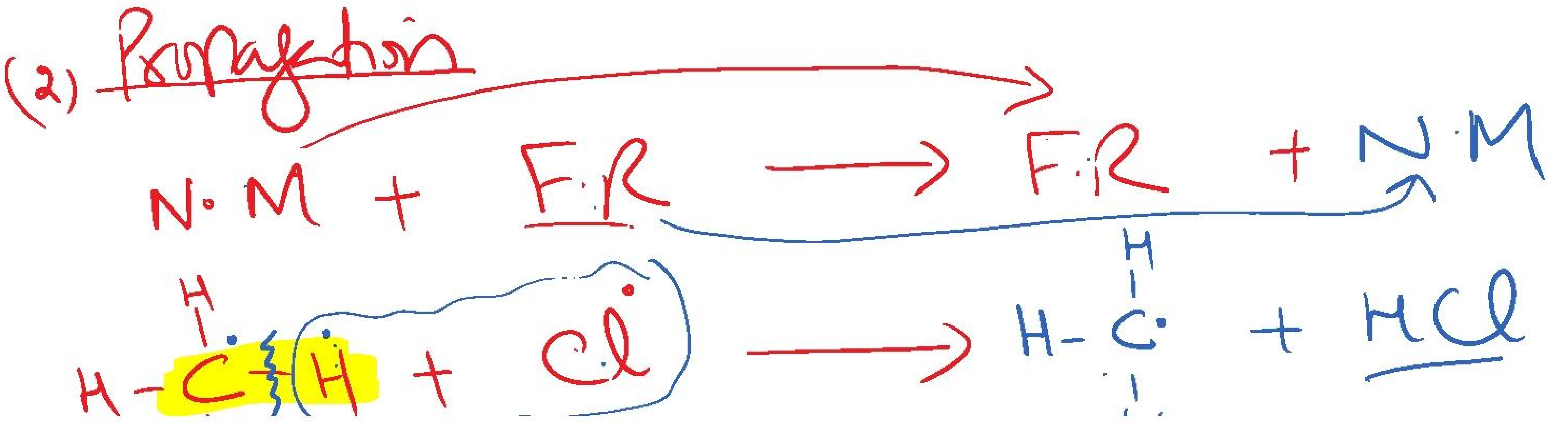
Substitution Reaction of Alkane

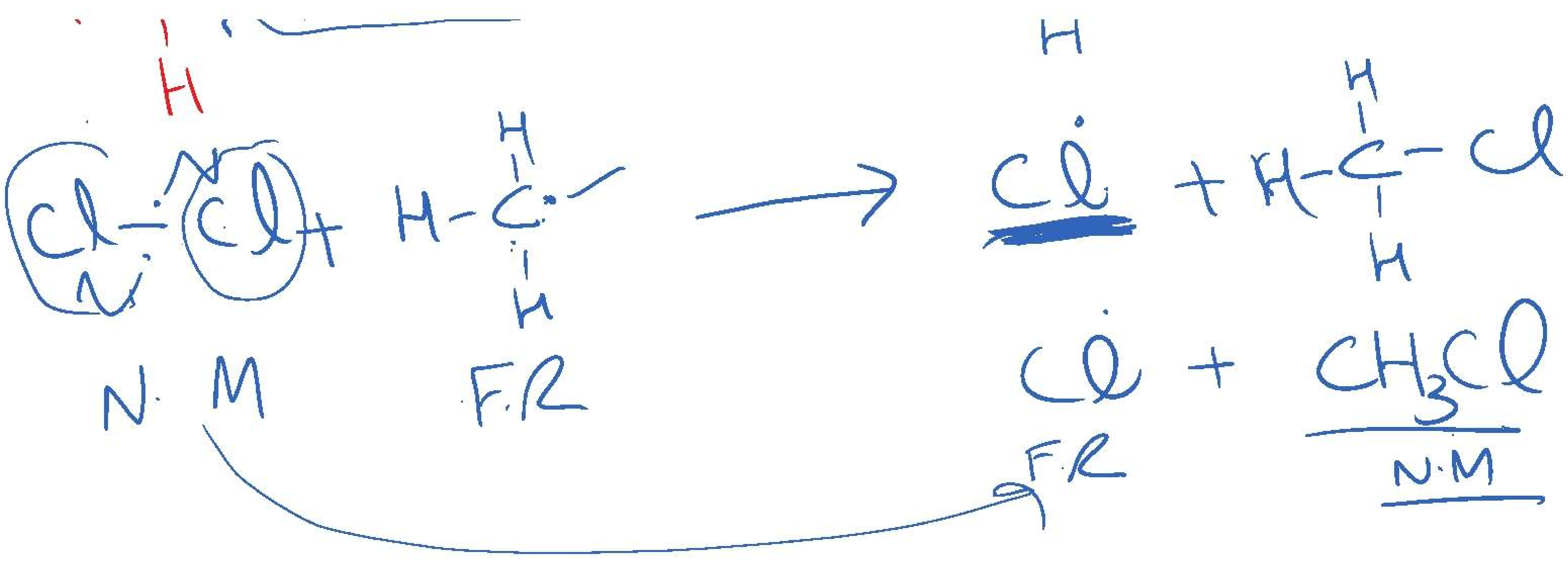
IG $CH_4 + Cl_2 \xrightarrow{hv} \boxed{CH_3Cl} + HCl$

Mechanism.

(1) Initiation (Cl₂) $Cl-Cl \xrightarrow{hv} \dot{Cl} + \dot{Cl}$

(2) Propagation





Termination step (opposite to initiation)

Free radical + free radical → N· M

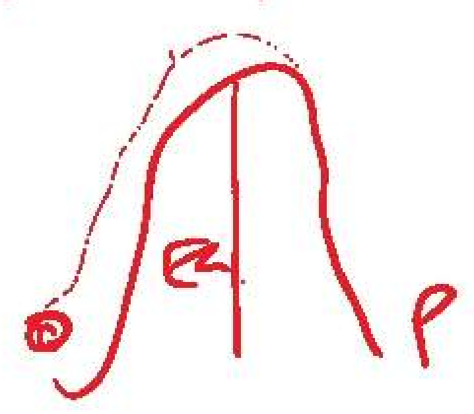
$\dot{Cl} + \dot{Cl} \longrightarrow Cl_2$

$\dot{Cl} + \dot{C}H_3 \longrightarrow CH_3Cl$

$\dot{H} + \dot{C}l \longrightarrow HCl$

→ Termination step is the fastest step because free radicals are reacting together and this step will have low activation energy.

(highly reactive)



→ Free Radicals are endothermic reactions because they need sunlight to initiate the reaction.

IG $CH_4 + Cl_2 \xrightarrow{h\nu} \boxed{CH_3Cl} + HCl$

overall reaction

I $\underset{N\cdot M}{Cl_2} \longrightarrow \dot{Cl} + \dot{Cl}$

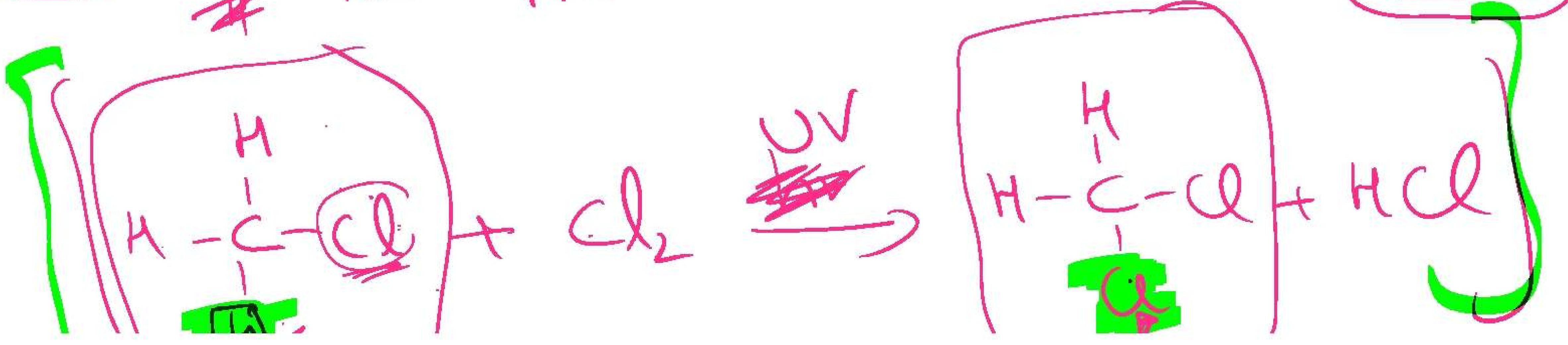
P $\underset{N\cdot M}{CH_4} + \underset{F.R}{\dot{Cl}} \longrightarrow \dot{C}H_3 + HCl$

$CH_3 + Cl_2 \longrightarrow \boxed{CH_3Cl} + \dot{Cl}$

T $\underset{F.R}{\dot{Cl}} + \underset{F.R}{\dot{Cl}} \longrightarrow Cl_2$

$CH_4 + Cl_2$
↓
CH_3Cl

#

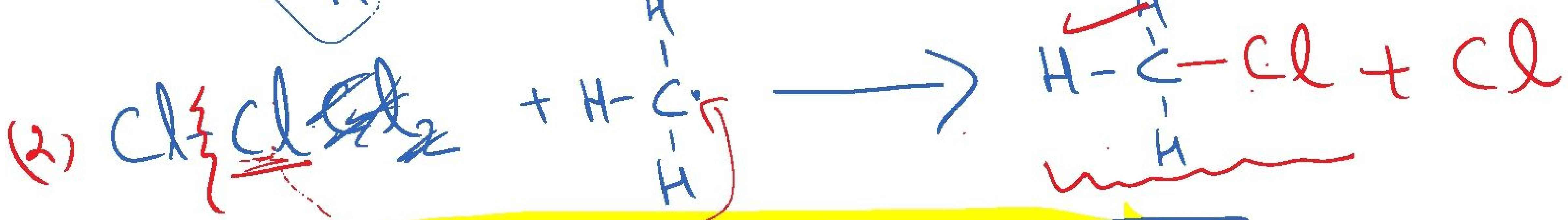


Initiation. $Cl-Cl \rightarrow \dot{Cl} + \dot{Cl}$

Propagation

$N{\cdot}M + F{\cdot}R \rightarrow F{\cdot}R + N{\cdot}M$

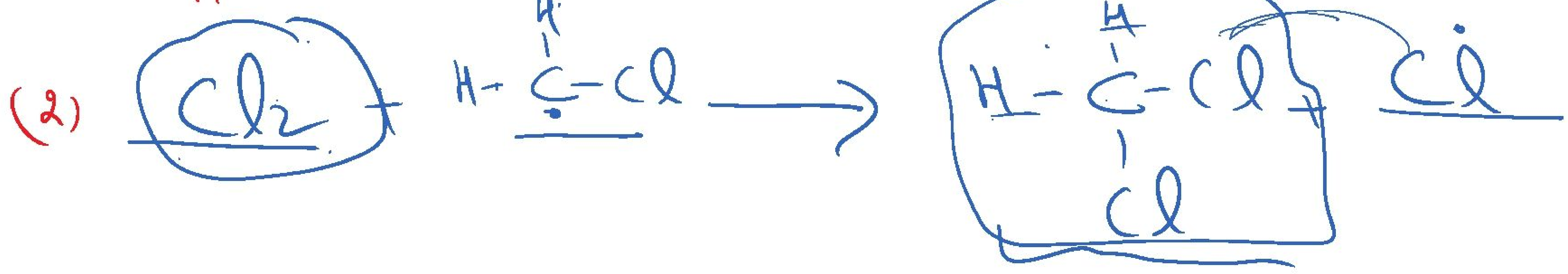
(1) $H-\overset{H}{\underset{H}{C}}-H + \dot{Cl} \rightarrow H-\overset{H}{\underset{H}{\dot{C}}} + HCl$



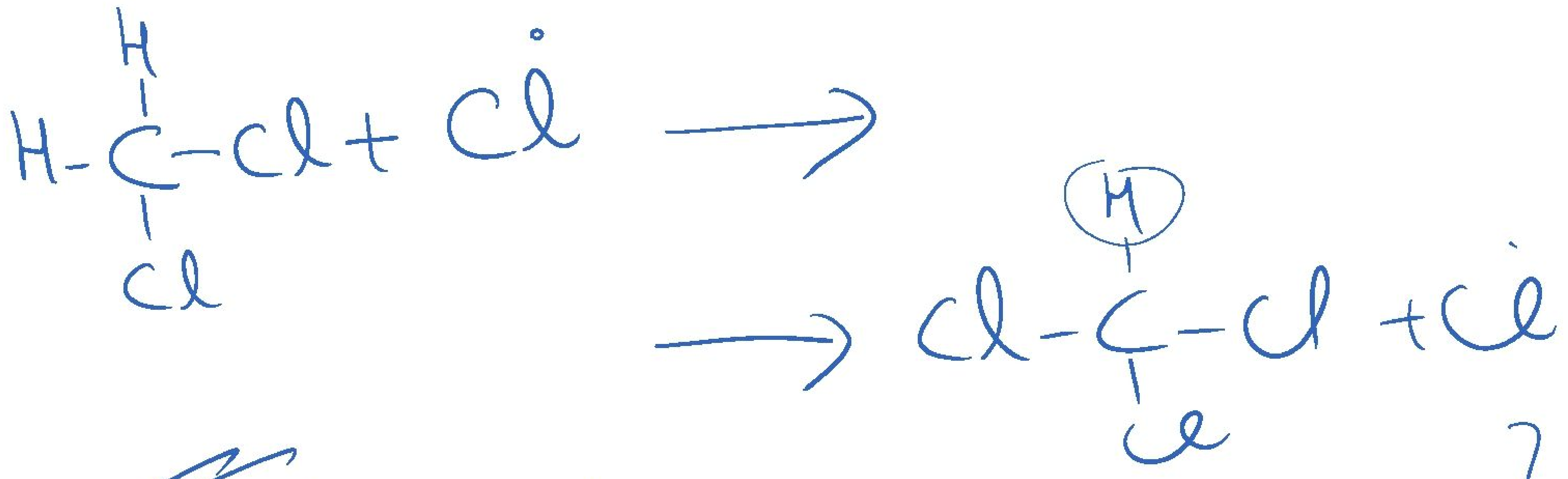
(2) $Cl\,Cl\,\cancel{Cl_2} + H-\overset{H}{\underset{H}{\dot{C}}} \rightarrow H-\overset{H}{\underset{H}{C}}-Cl + \dot{Cl}$

$N{\cdot}M + F{\cdot}R \rightarrow \boxed{F{\cdot}R} + N{\cdot}M$

(1) $H-\overset{H}{\underset{H}{C}}-Cl + \dot{Cl} \rightarrow H-\overset{H}{\underset{\cdot}{C}}-Cl + HCl$



(2) $Cl_2 + H-\overset{H}{\underset{\cdot}{C}}-Cl \rightarrow \boxed{H-\overset{H}{\underset{Cl}{C}}-Cl} + \dot{Cl}$



$H-\overset{H}{\underset{Cl}{C}}-Cl + \dot{Cl} \rightarrow$

$\rightarrow Cl-\overset{H}{\underset{Cl}{C}}-Cl + \dot{Cl}$

$\dot{C}H_3$, $\dot{C}H_2Cl$

Terminat

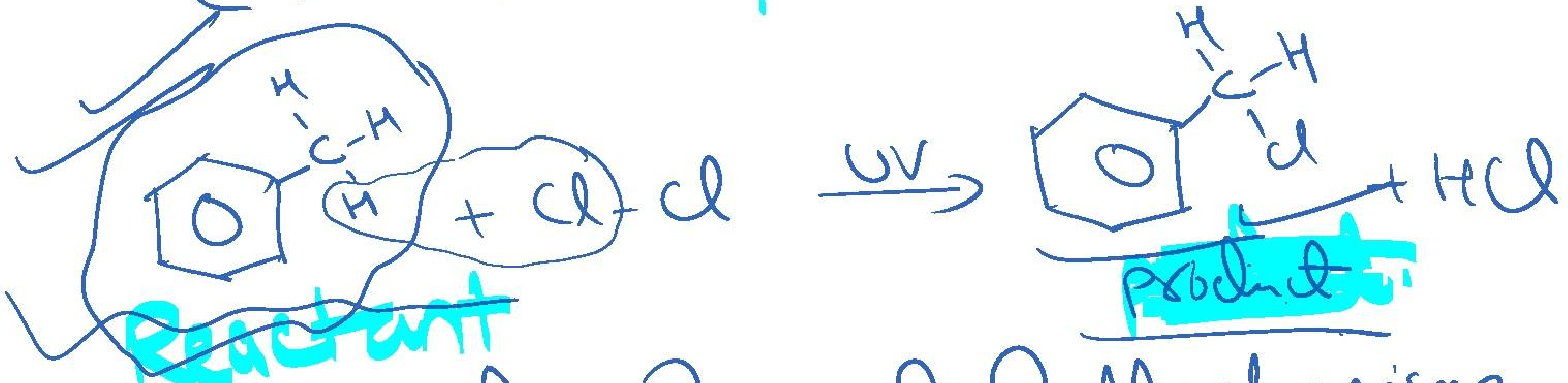
$\dot{C}H_3 + \dot{C}H_2Cl \rightarrow CH_3-CH_2-Cl$

$\dot{C}H_3 + CH_3 \rightarrow CH_3-CH_3$

In free radical substitution Reactions

→ You will break non Polar bond (C–H, Cl–Cl)
by homolytic fissions

→ Replace H with halogen

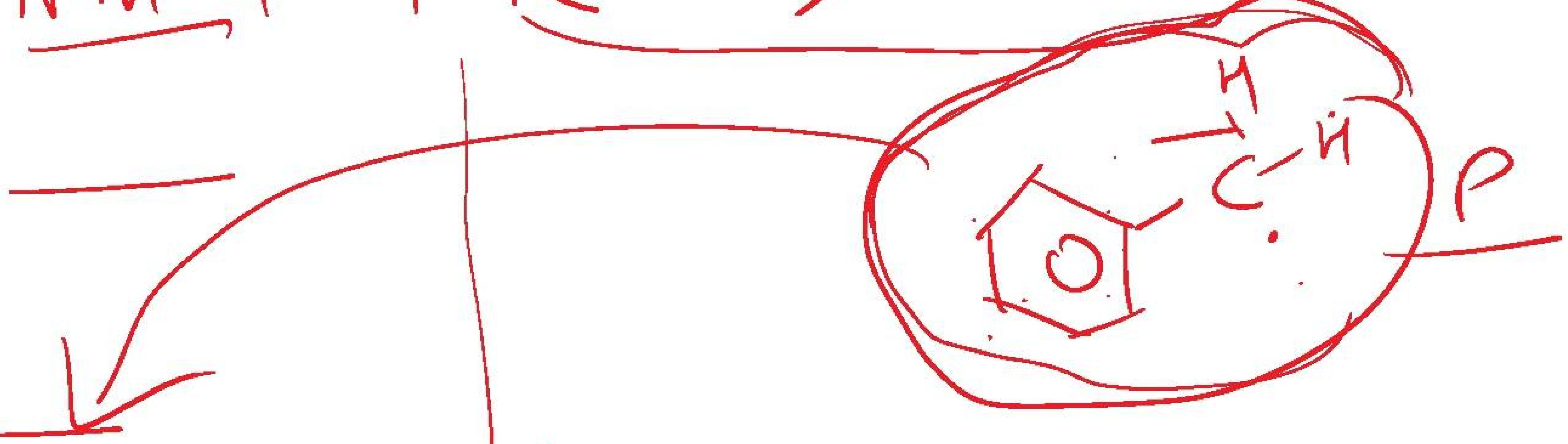


Write down free radical Mechanism for this reaction and how many steps are involved, write down each step.

Initiation : $Cl_2 \xrightarrow{UV} \dot{Cl} + \dot{Cl}$

Propagation:

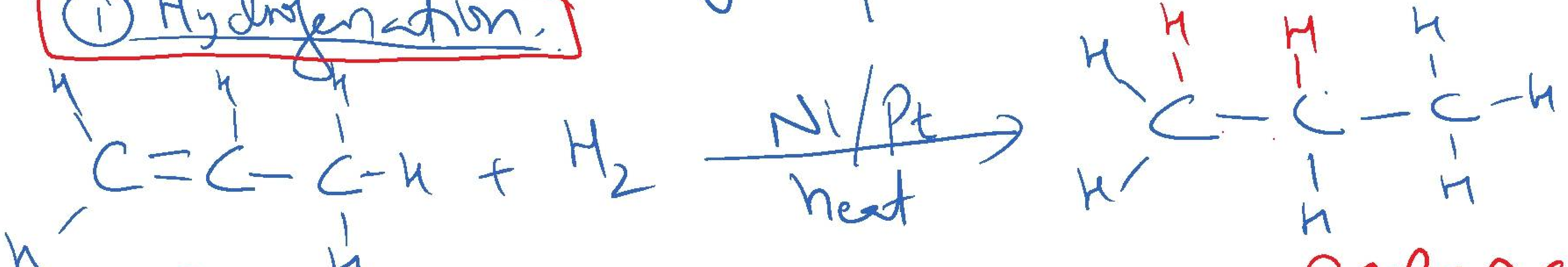
N·M + F·R → F·R + N·M



Cl ~~__~~ + ~~__~~

Production of Alkane

① Hydrogenation.



$CH_2=CH-CH_3 + H_2 \xrightarrow[\text{heat}]{Ni/Pt} CH_3-CH_2-CH_3$

Propene

Propane

② Cracking*

higher hydrocarbon → Alkane + Alkene

Crud oil

↓

fractional distillation

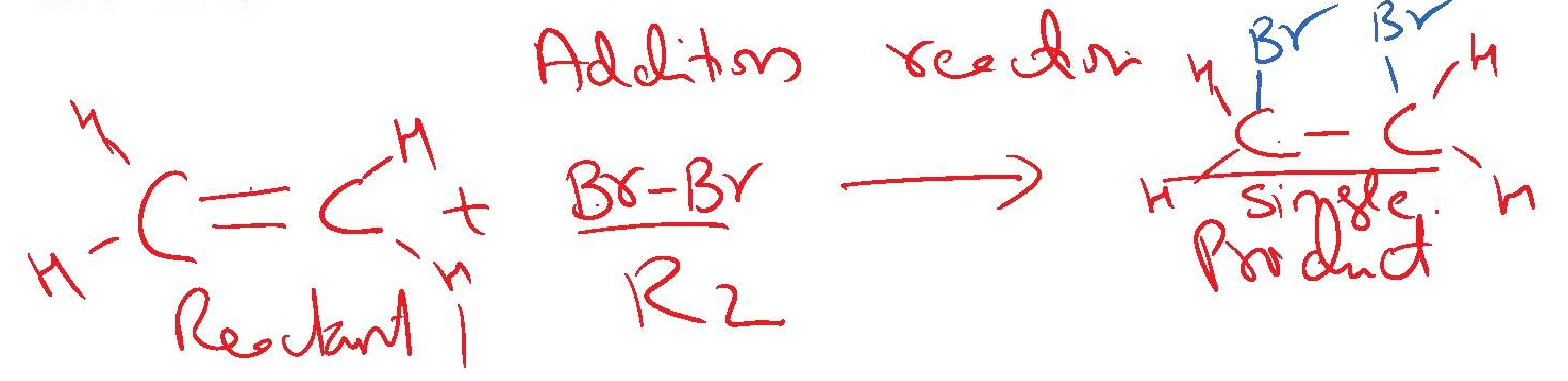
Refinary [illegible]

Bitumens

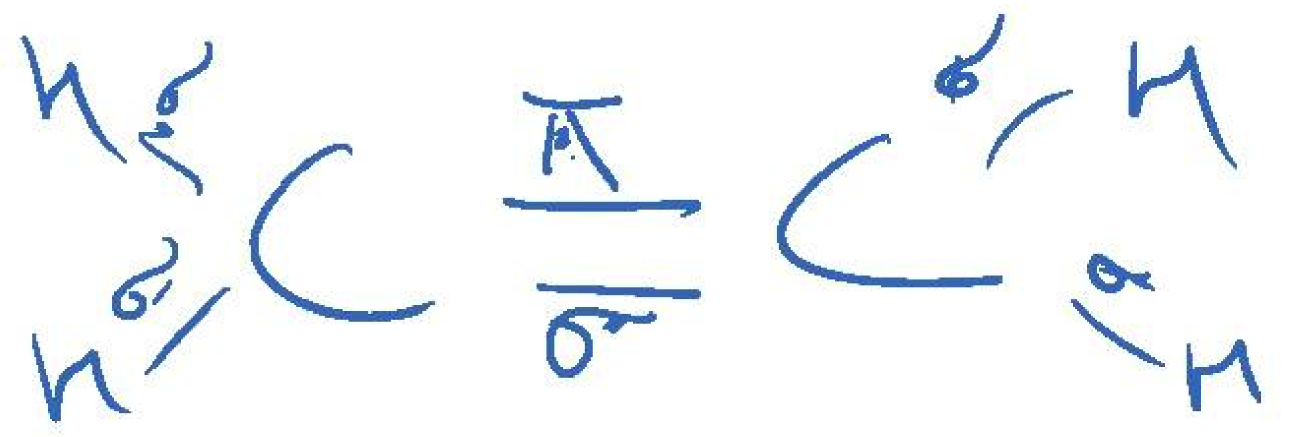
CnH2n

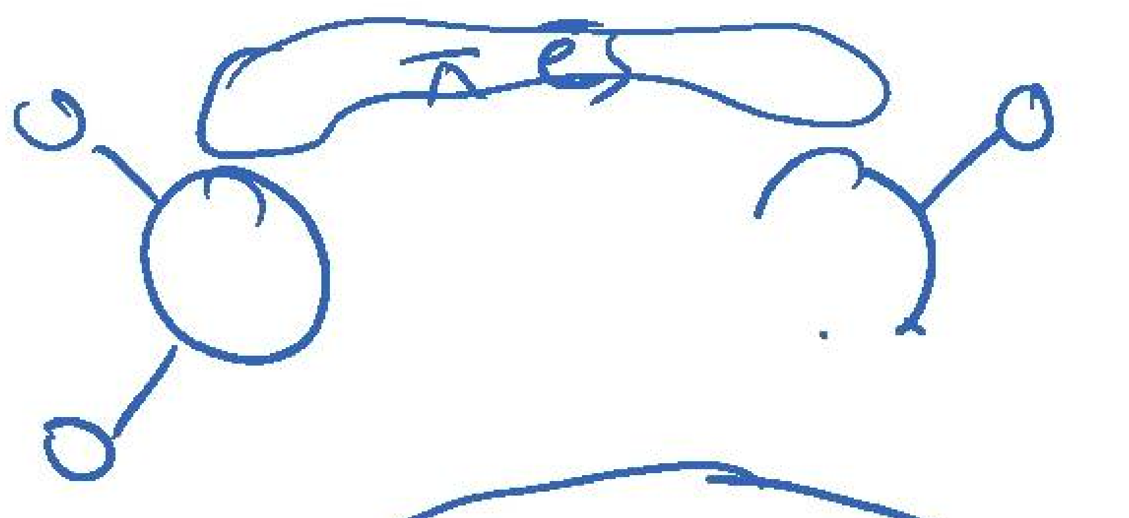
Alkene Reactions

Addition reaction



Adding an atoms in a molecule by breaking π bond
Alkene are reactive due to the presence of π bond - Weaker





Nucleophile (Nu)

$\bar{e}$ rich specie

(1) Central atom of a molecule has lone Pair $H_2\ddot{O}$, $\ddot{N}H_3$

(2) have negative charge
$:\ddot{O}\overline{H}$, $:\overline{Cl}$, $:\overline{CN}$

(3) Multiple bonds between same atoms like
✓ C=C (Alkene) $C\overset{\times}{\equiv}C$ (Alkyne)

Electrophile (E)

electron deficient speci

(1) have positive charge | +δ charge

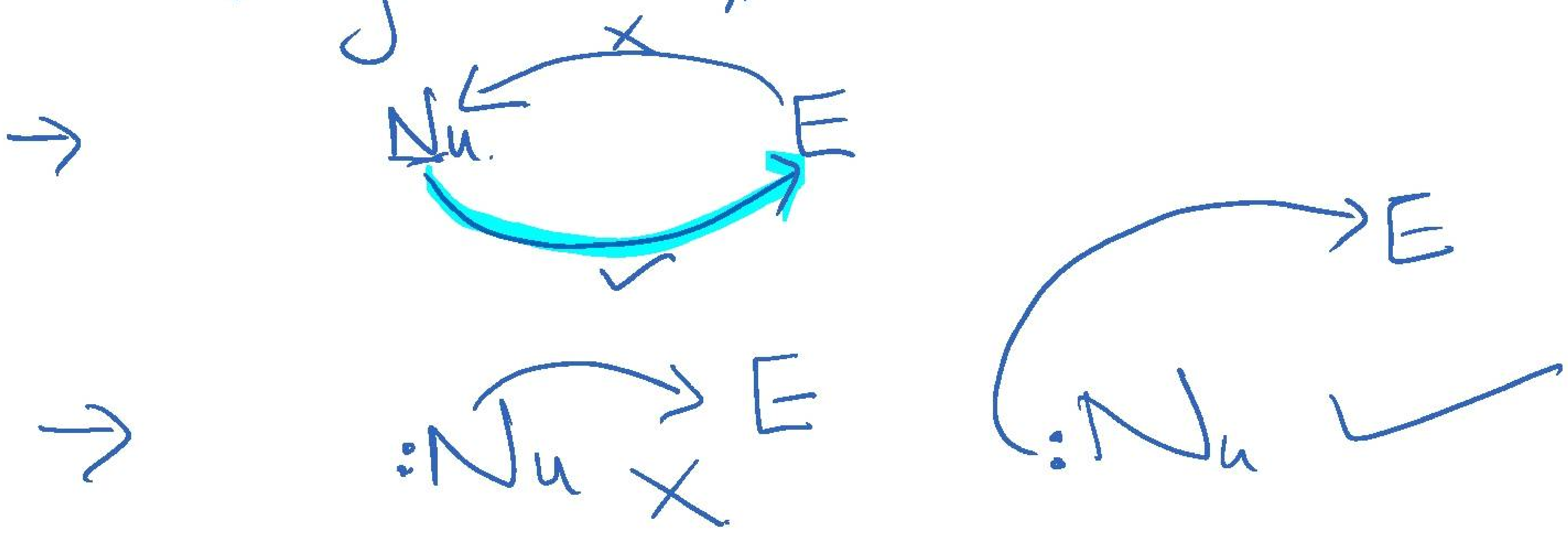
$\boxed{\overset{+\delta}{H}} - \overset{-\delta}{Cl}$

↓

E

$\underset{+}{C} \rightarrow E$

Mechanism → (Dipoles, charges, lone pair on Nu and Curly arrows).



(1) Addition of Hydrogen (Hydrogenation)

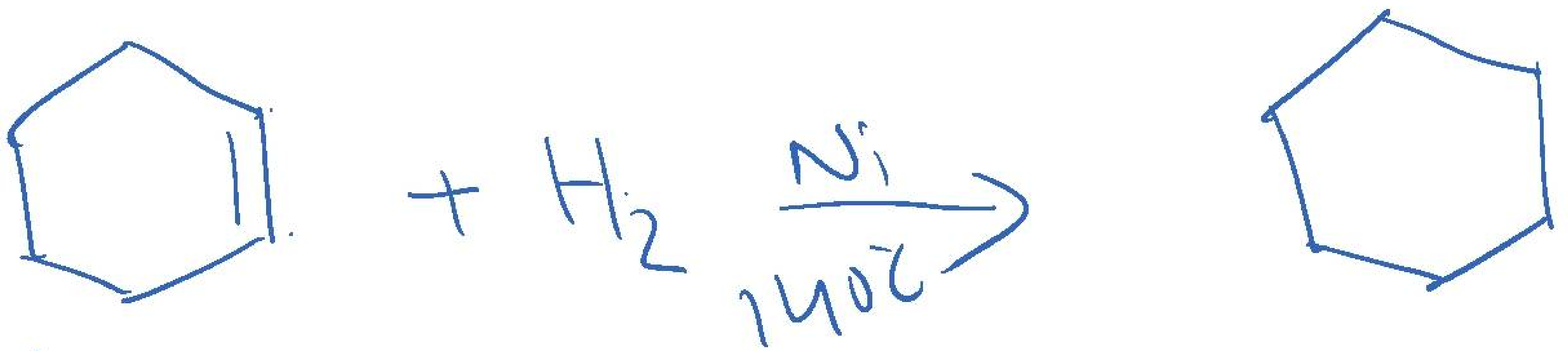
$H_2C=CH_2 + H_2 \xrightarrow[140^\circ C]{Ni\ Catalyst} \underset{H}{H_2C} - \underset{H}{CH_2}$

Unsaturated Saturated

Industrial Importance

Vegetable oil + H_2 $\xrightarrow[140^\circ C]{Ni}$ Margarine (Ghee)

Alkene Alkane



Cycloalkene

(2) Addition of Halogen Cl_2/Br_2

$CH_3-CH=CH_2 + Cl_2 \longrightarrow CH_3-\overset{Cl}{CH}-\overset{Cl}{CH_2}$

1,2-dichloropropane

$H_2C=CH_2 + Br_2 \longrightarrow \underset{Br}{H_2C} - \underset{Br}{CH_2}$

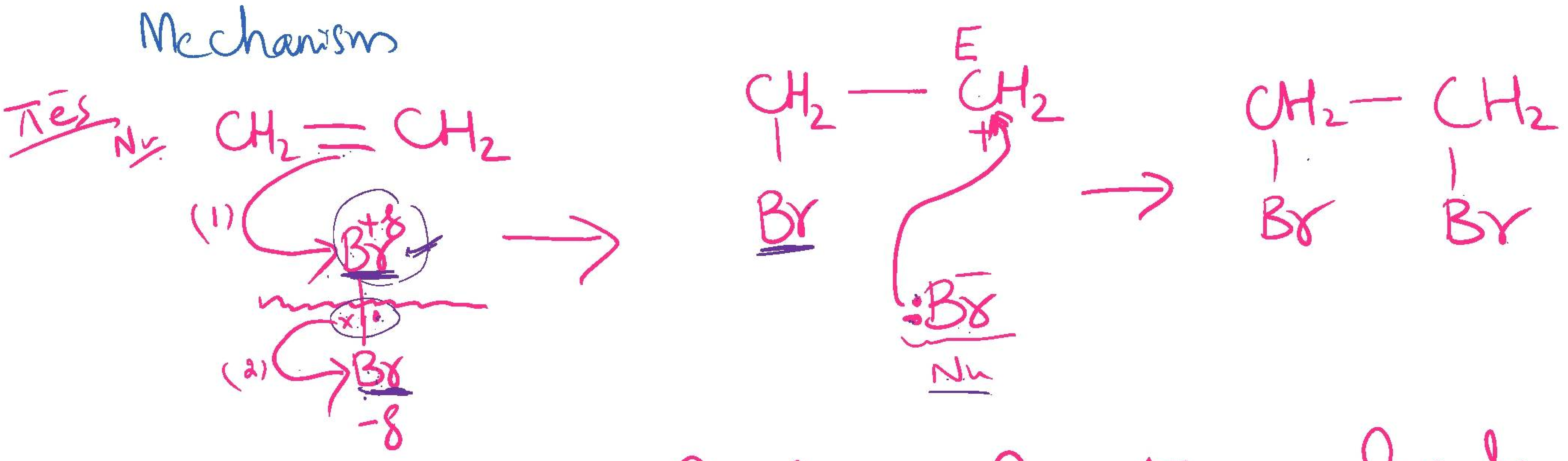
Alkene reddish brown

Chemical Test to detect unsaturation (C=C)

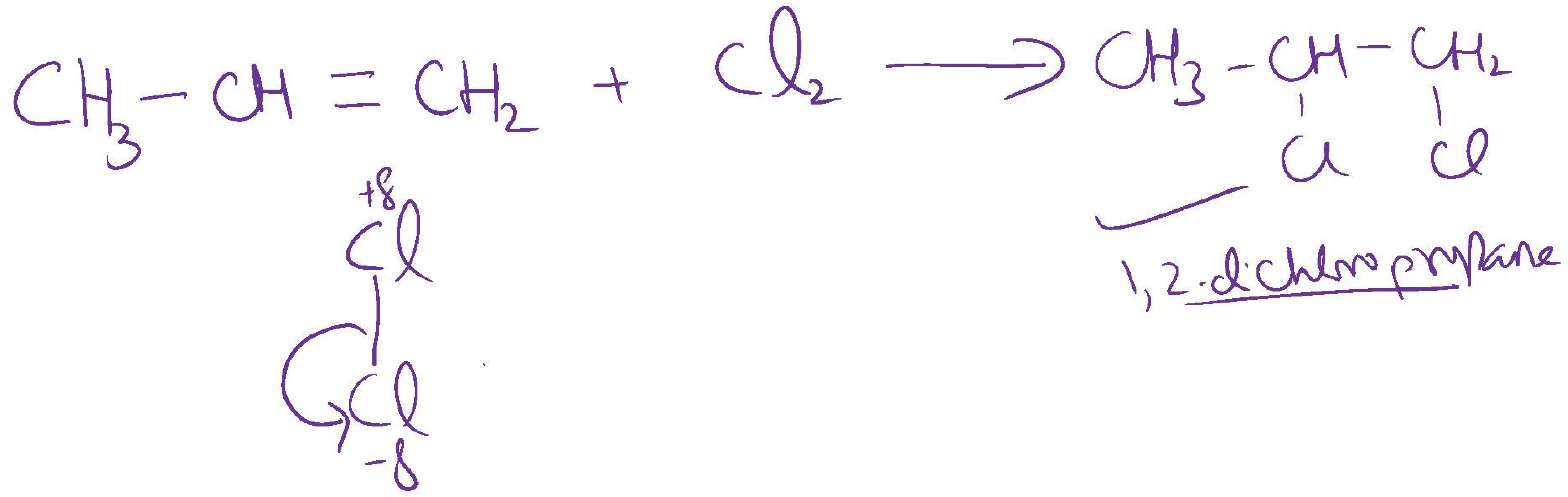
① Reddish Brown / orange Colour of Br_2 will be decolourise.

$\text{Alkane} + \underline{Br_2} \longrightarrow$ No reaction

Mechanism



As the Bromine molecule and ethene molecule approach each other, the area of high electronic density around C=C repels the pair of ēs in Br – Br bond away from the nearer Br atom ($Br^{+\delta}$) this makes nearer Br slightly positive and far $Br^{-\delta}$.

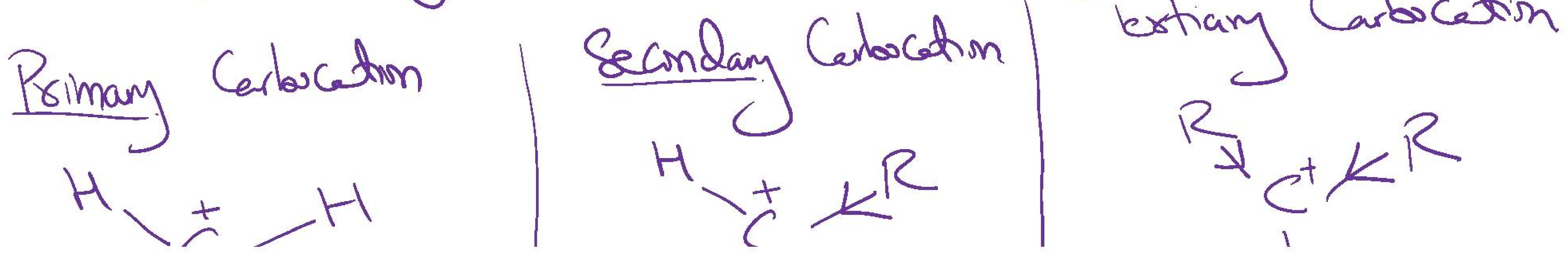


$$CH_3 - CH = CH_2 + Cl_2 \longrightarrow CH_3 - \underset{Cl}{CH} - \underset{Cl}{CH_2}$$

1,2-dichloropropane

(3) Addition of HX (HCl, HBr, HI)

Stability of Carbocation ($\overset{+}{C}$)

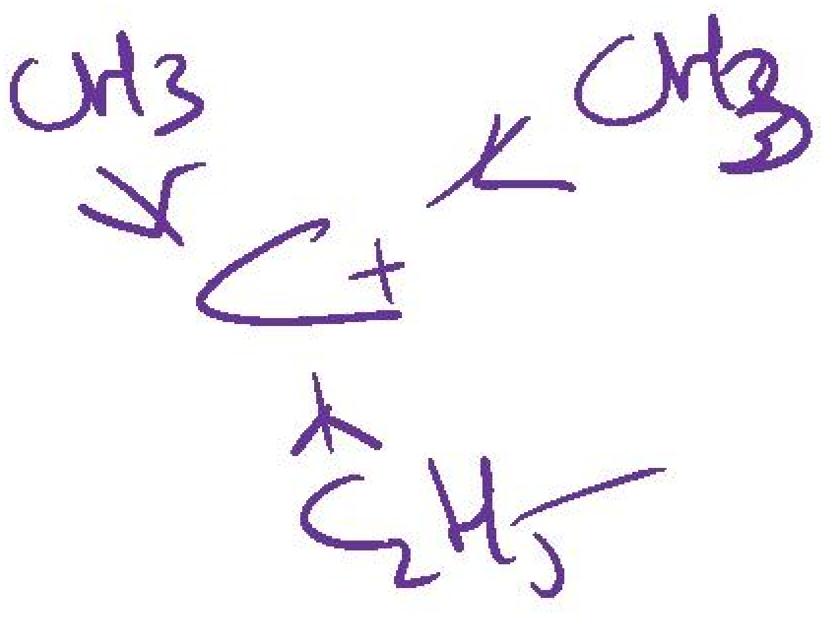


R = Alkyl group are electron donating groups

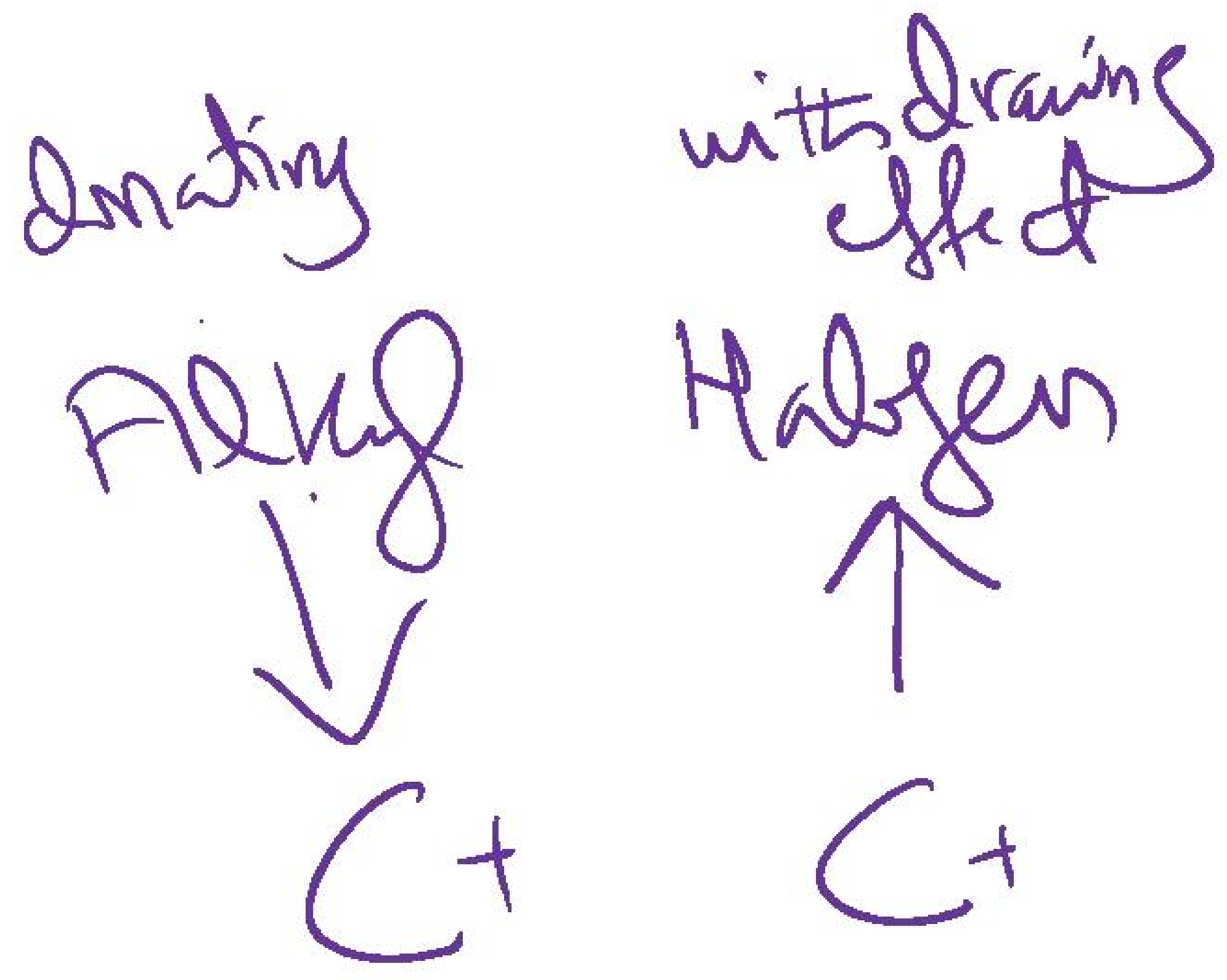
T > Sec > Primary

Q. Why tertiary Carbocation is more stable?

A In tertiary Carbocation there are 3 alkyl groups and alkyl groups are electron donating groups. as a result charge density on positively charged Carbon atom will increase making tertiary more stable.



electron Donating Inductive effect.



HX →

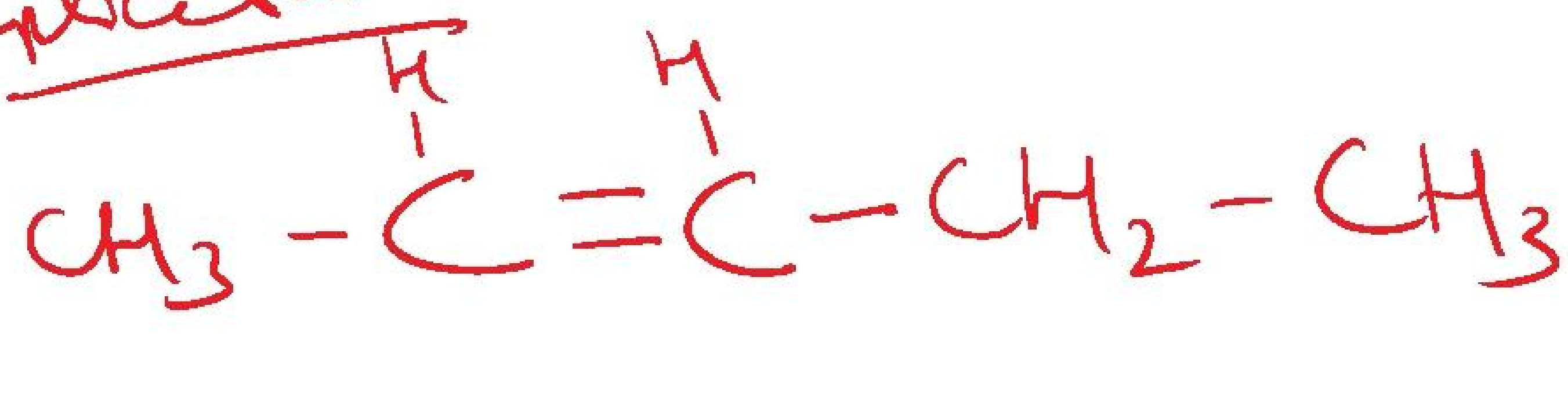
Simple ~~Symmetrical Alkene~~

$$CH_3-CH_2-\overset{H}{C}=\overset{H}{C}-CH_2-CH_3$$

HX

Unsymmetrical Alkene

Complicated



$$CH_3-\overset{H}{C}=\overset{H}{C}-CH_2-CH_3$$

H H Cl H

$H_2C=CH_2 + HCl \rightarrow$

CH_3-CH_2-Cl

symmetric alkene

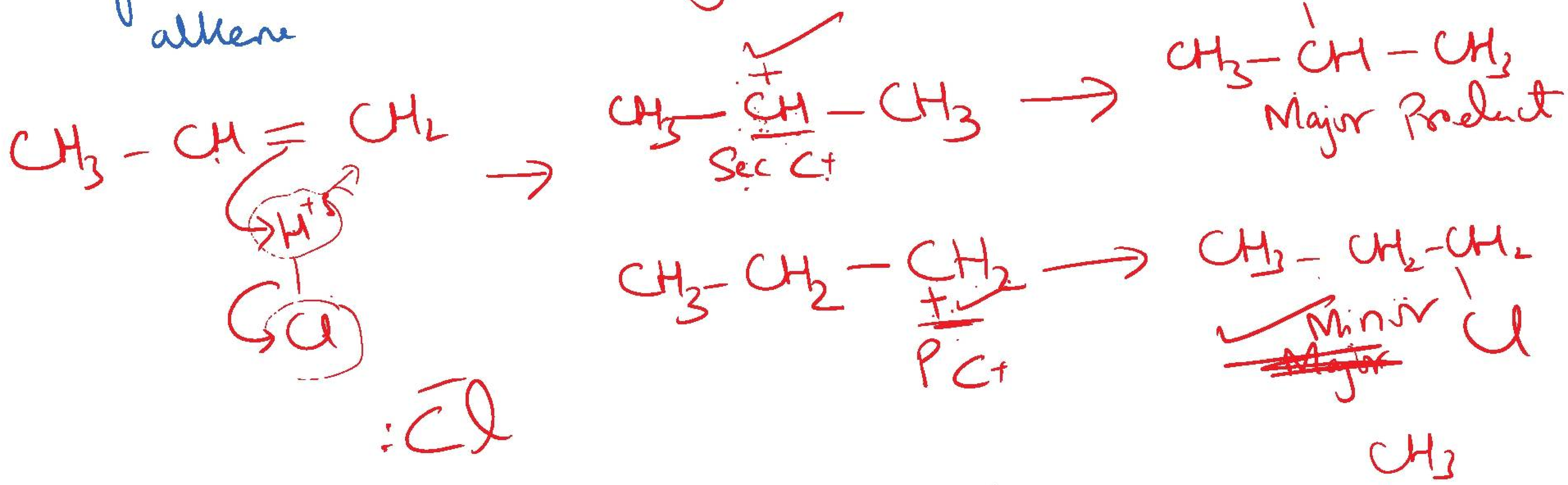
IUPAC ✓ Chloro ethane

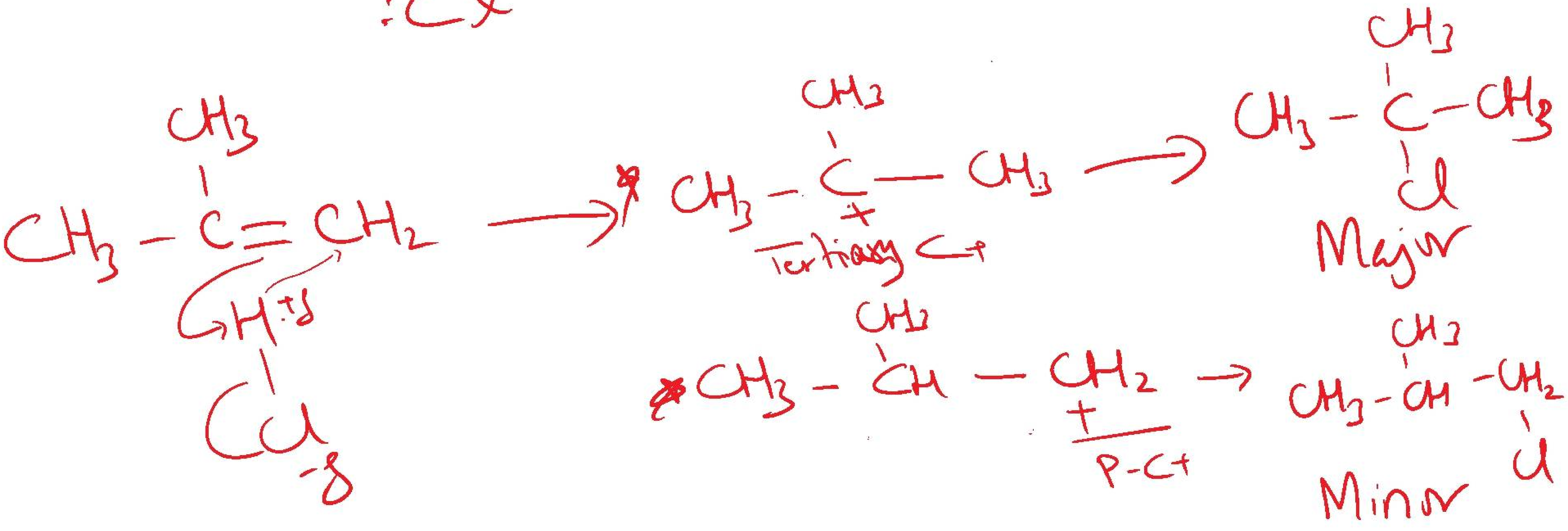
Common name - ethyl chloride

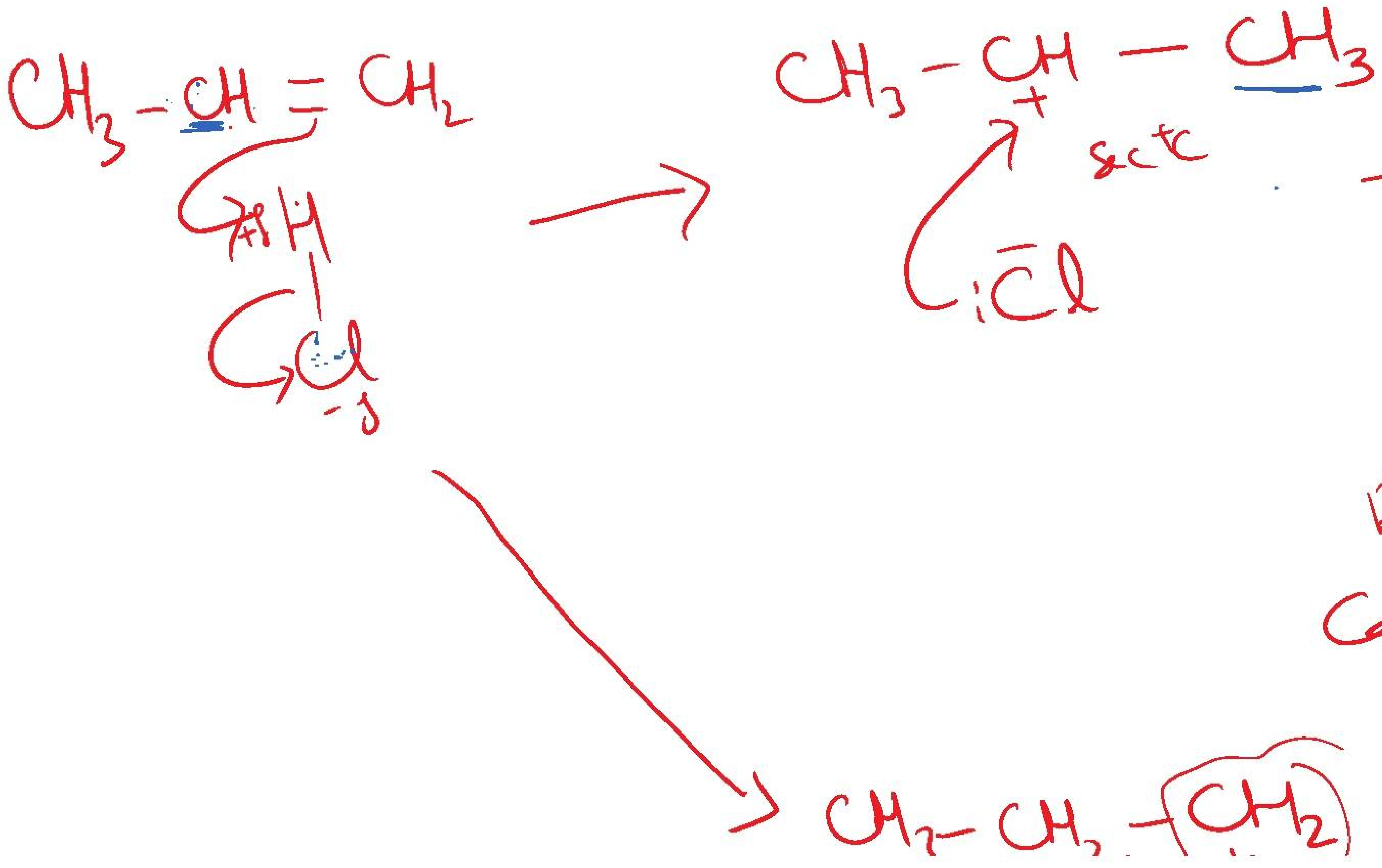
Mechanism

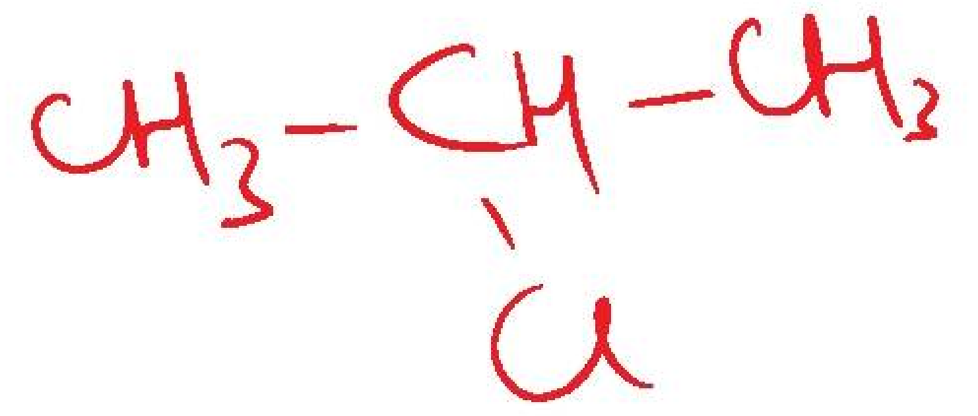
$CH_3-CH=CH_2 + \overset{+\delta}{H}\overset{-\delta}{Cl} \rightarrow$ Major / Minor Product ?

Unsymmetrical alkene



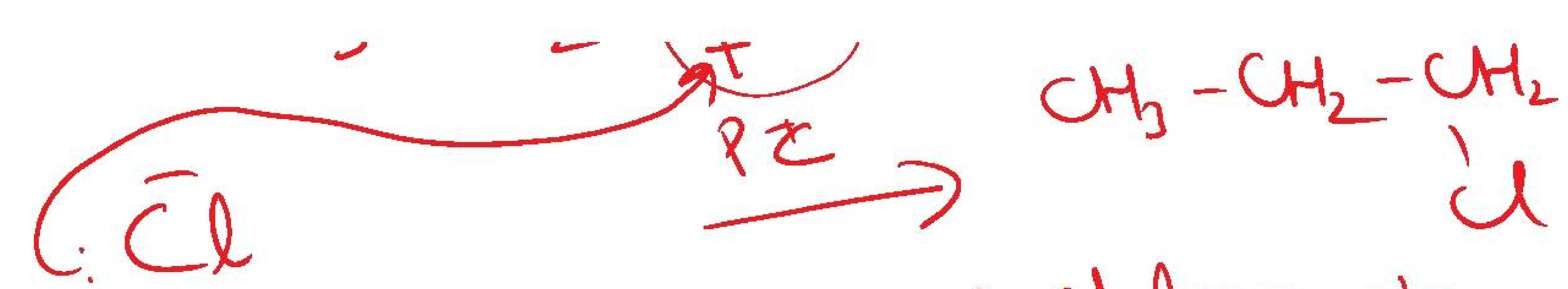






2-Chloro pentane
Major Product

Because secondary Carbocation is more stable than P-+C



$CH_3-CH_2-\underset{Cl}{C}H_2$

1-Chloropentane
Minor Product

Q. Why 2-chloropentane is Major product?
Ans During the formation of 2-chloropentane secondary carbocation is formed which is more stable than primary.

Markownikov's Rule

During the addition of in unsymmetrical alkene, the negative part of adding molecule (Cl) will attack to that carbon which has least number of hydrogen. (Major product)

$CH_3-CH_2-CH_2-CH=\overset{h}{C}H_2 + HCl \longrightarrow$?

Addition of Steam
(Mechanism is not included)

Conditions : Temperature 330°C
Pressure : 60 atm
Catalyst : Con H_3PO_4

CH_3-CH_2-OH

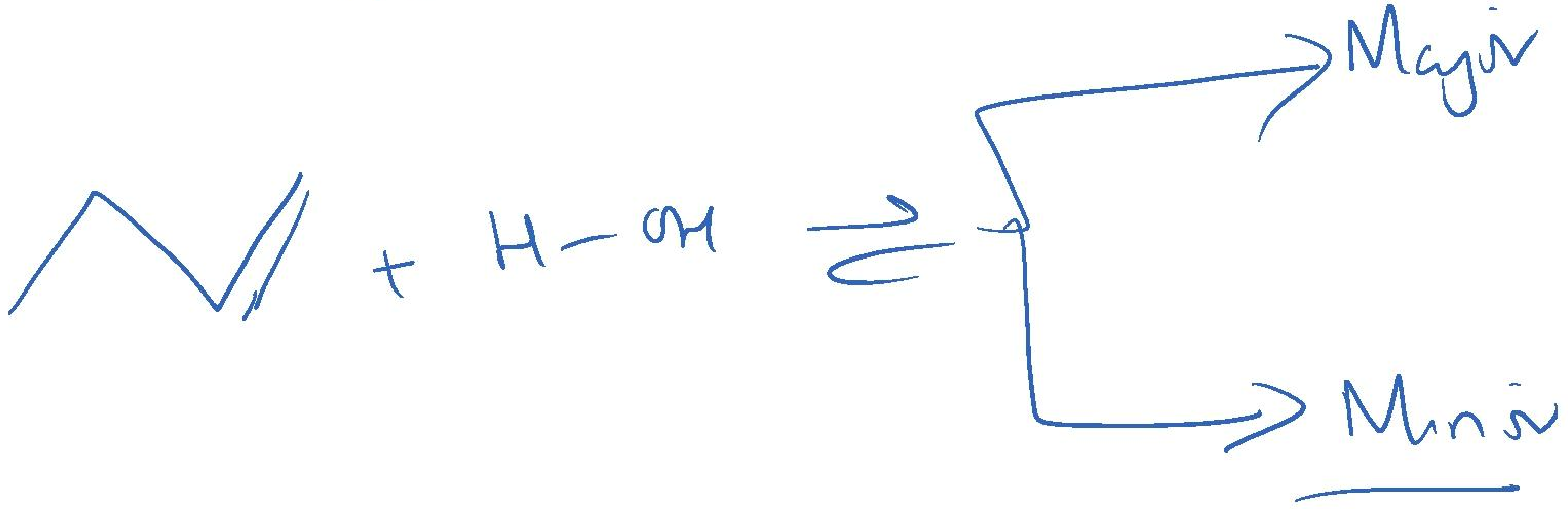
H′ Alkene ′H H–OH Alcohol

$CH_3-\overset{+}{CH}=\overset{+}{CH_2} + \underset{(g)}{H_2O} \rightleftharpoons$ → Major (will follow Markovnikov rule) / → Minor

H⁺, OH

H^+ – $\ddot{O}H$

Unsymmetrical Alkene → Major / Minor



Propan-2-ol

Most important Oxidation of Alkene

Oxidising agent which ~~od~~ oxidises others

e.g. $KMnO_4$ (purple in colour)

$\underbrace{KMnO_4 + \text{dil } H_2SO_4} \longrightarrow [O]$ most reactive atomic Oxygen

Oxidation of Alkene

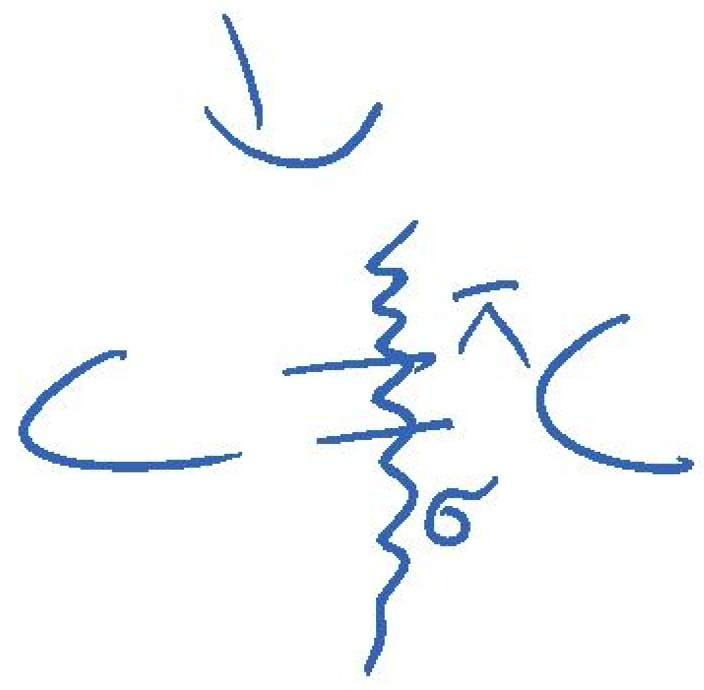
① Cold dilute

② Hot Concentrated Acidified $KMnO_4$

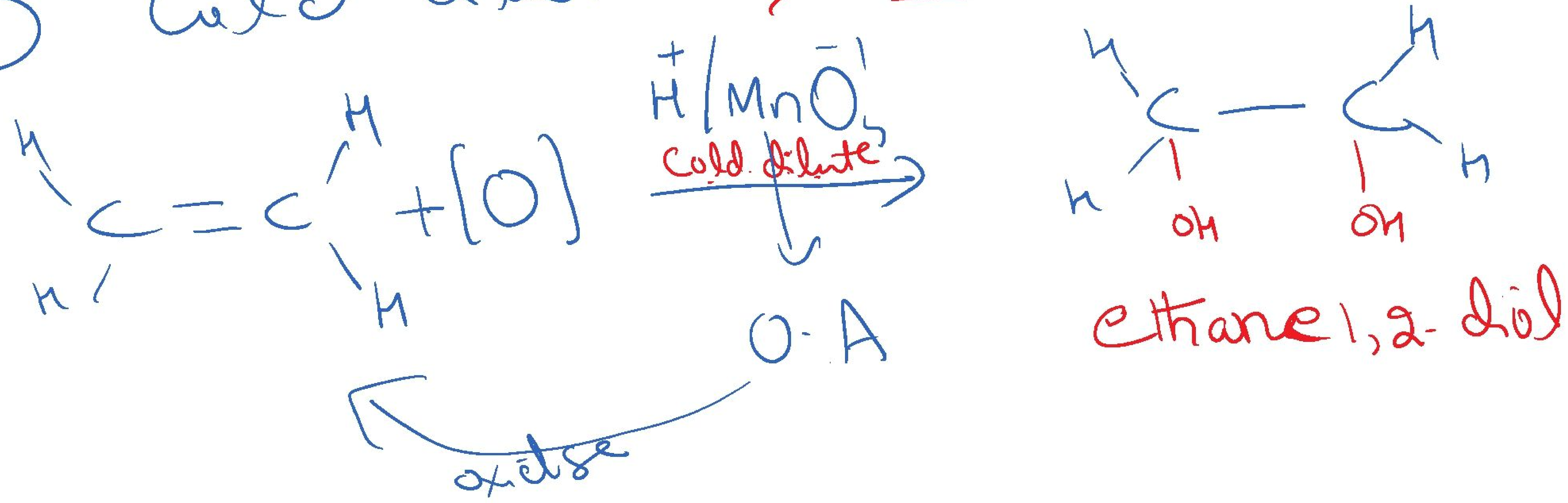
Acidified KMnO4

↓

Attack on π bond of an Alkene

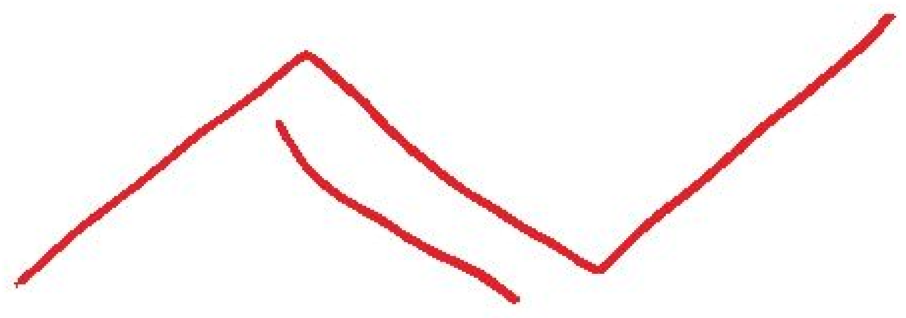


① Cold dilute ⟶ (Diol) Product

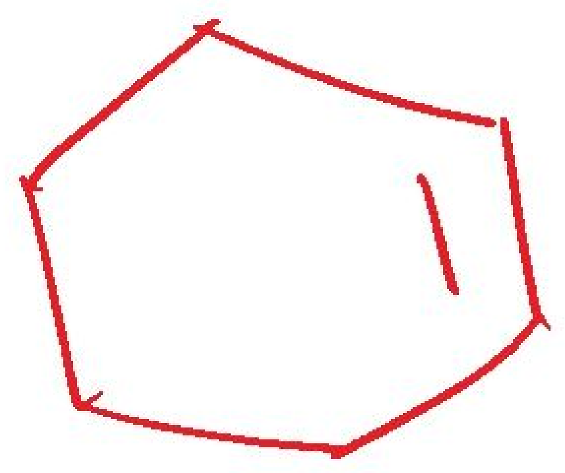


ethane 1,2-diol

$CH_3-CH=CH_2 + 2[O] \xrightarrow[H_2SO_4\,(aq)\ Cold]{KMnO_4}$?

(1)  $+ [O] \longrightarrow$ H.W

Observation

(2)  $+ [O] \longrightarrow$? H.W

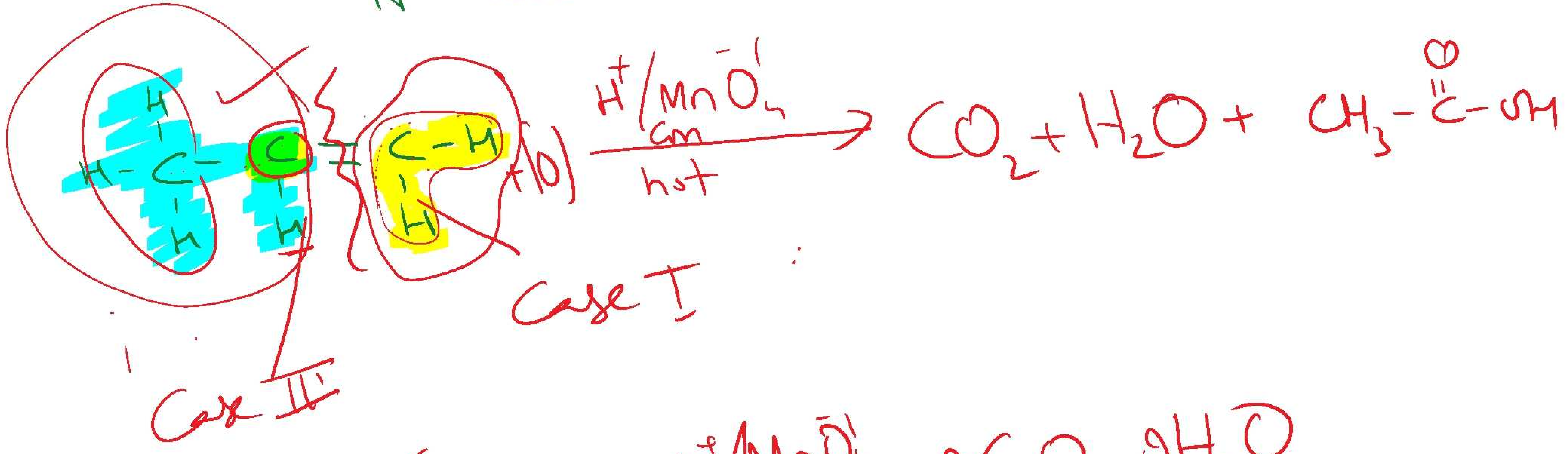
Oxidation of an Alkene using Hot Concentrated KMnO4
Acidified

$H_2C=CH_2 \longrightarrow 2CO_2 + 2H_2O$

Case 1 If double bond carbon atom has 2H then it will oxidise into CO_2 & water.

Case II If double bond carbon atom has one H atom and one alkyl group then it will oxidise into carboxylic acid

Case III If double bonded carbon atom has 2 alkyl groups and no H atom, it will oxidise to ketone.



$$CH_3-CH=CH_2 + [O] \xrightarrow[\text{hot}]{H^+/MnO_4^-\ \text{con}} CO_2 + H_2O + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

$$H_2C=CH_2 + [O] \xrightarrow[\text{Heat}]{H^+/MnO_4^-\ \text{con}} 2CO_2 + 2H_2O$$

$$\underset{1}{CH_3-CH}=\underset{2}{CH-CH_3} + [O] \xrightarrow{} \boxed{2CH_3-\overset{O}{\overset{\|}{C}}-OH}$$

Alkene symmetrical ⟶ same product

Alkene Unsymmetrical ⟶ Different product

$$CH_3-CH=CH-CH_2-CH_3 + [O] \xrightarrow{} CH_3-\overset{O}{\overset{\|}{C}}-OH$$

ethanoic acid
+
Propanoic acid

Practice Q

$X + [O]$ | $CH_3-CH_2-C\equiv C-CH_2-CH_3$

$\xrightarrow[H^+/MnO_4^-]{\text{hot Conc}}$ $2CH_3CH_2COOH$

$CH_3CH_2-COOH + CH_3CH_2COOH$

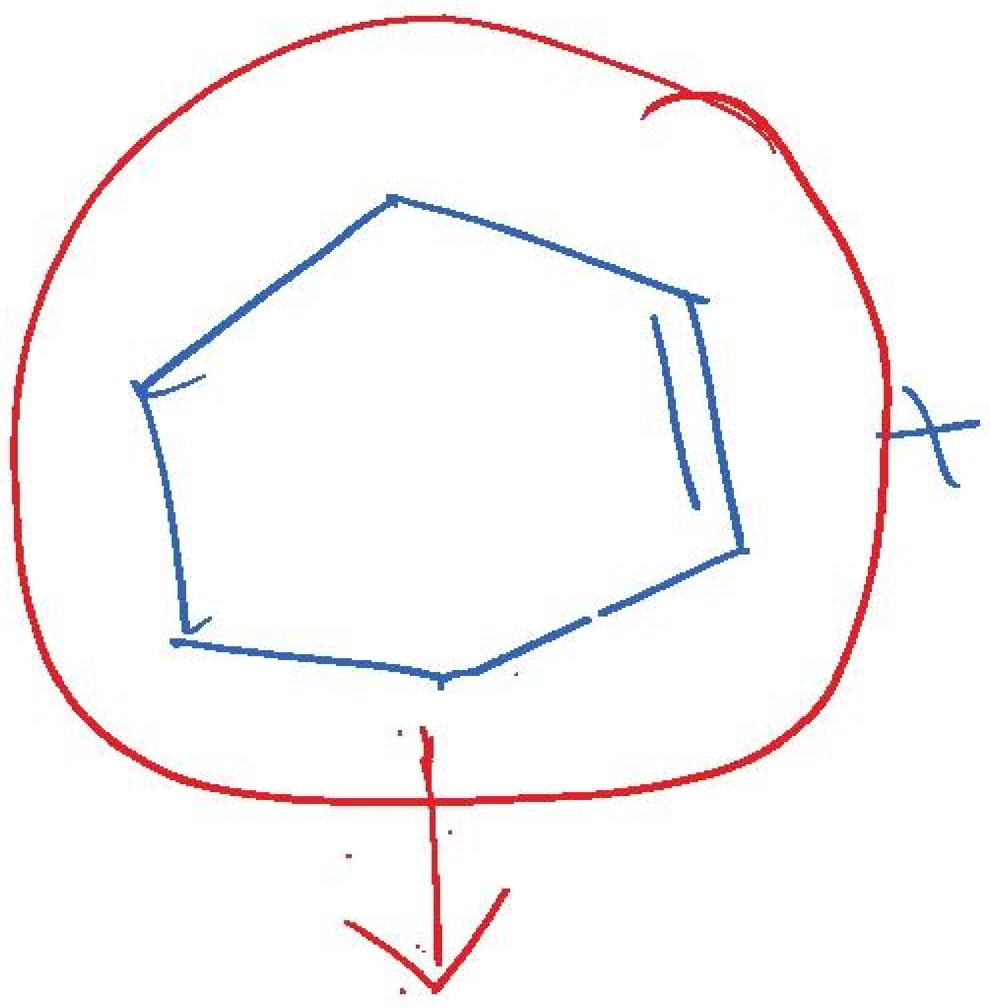
Propanoic acid

Case II What is X ?

$H-C\equiv C-\overset{H}{\underset{H}{C}}-H$

$CO_2, H_2O,$ CH_3COOH

skeletal →



$+ [O]$ $\xrightarrow[H^+/MnO_4^-]{\text{hot, Conc}}$? ?

Display Structure