

# ALKYL HALIDES

## aka Halogenoalkanes

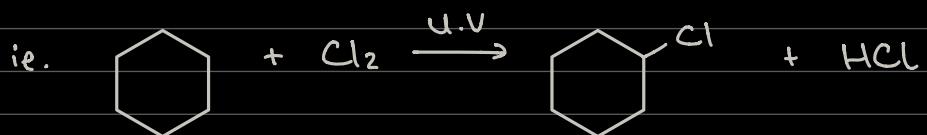
- Functional group is the carbon-halogen bond



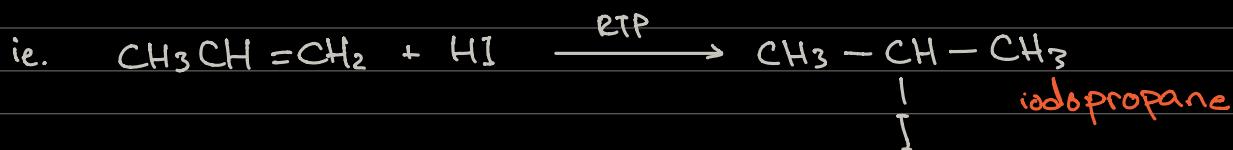
## PREPARATION

## 1. From alkanes

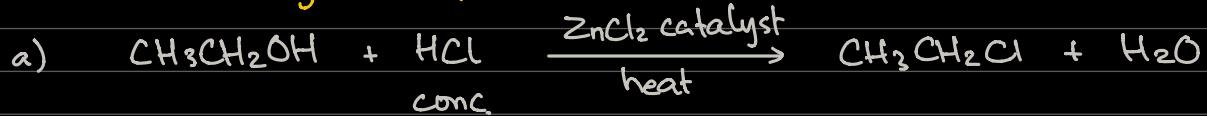
Free Radical Substitution of alkanes results in alkyl halides



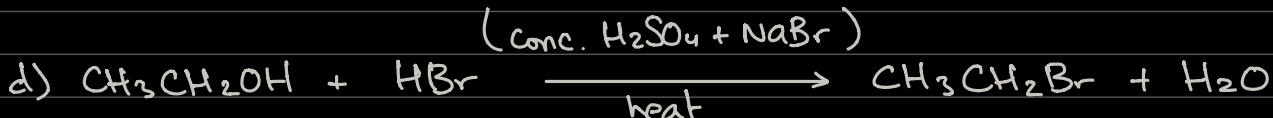
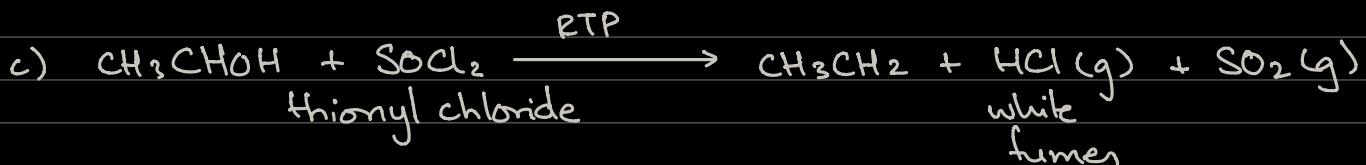
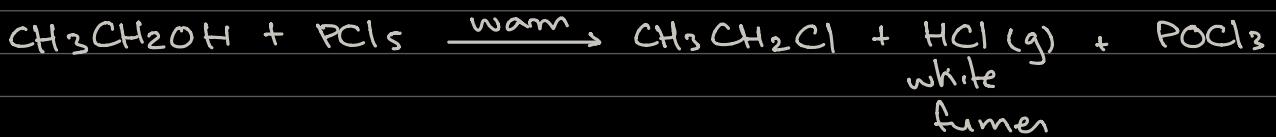
## 2. From Alkenes by electrophilic addition

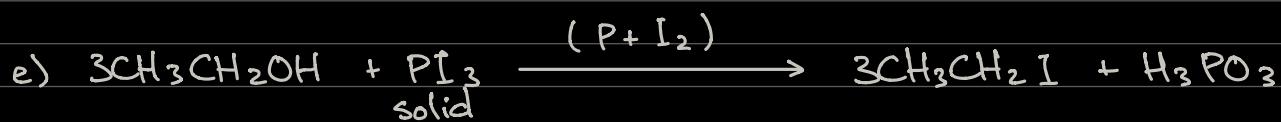


3. From alcohols by nucleophilic substitution



b) By using a chlorinating agent i.e.  $\text{PCl}_3$ ,  $\text{PCl}_5$ ,  $\text{SOCl}_2$





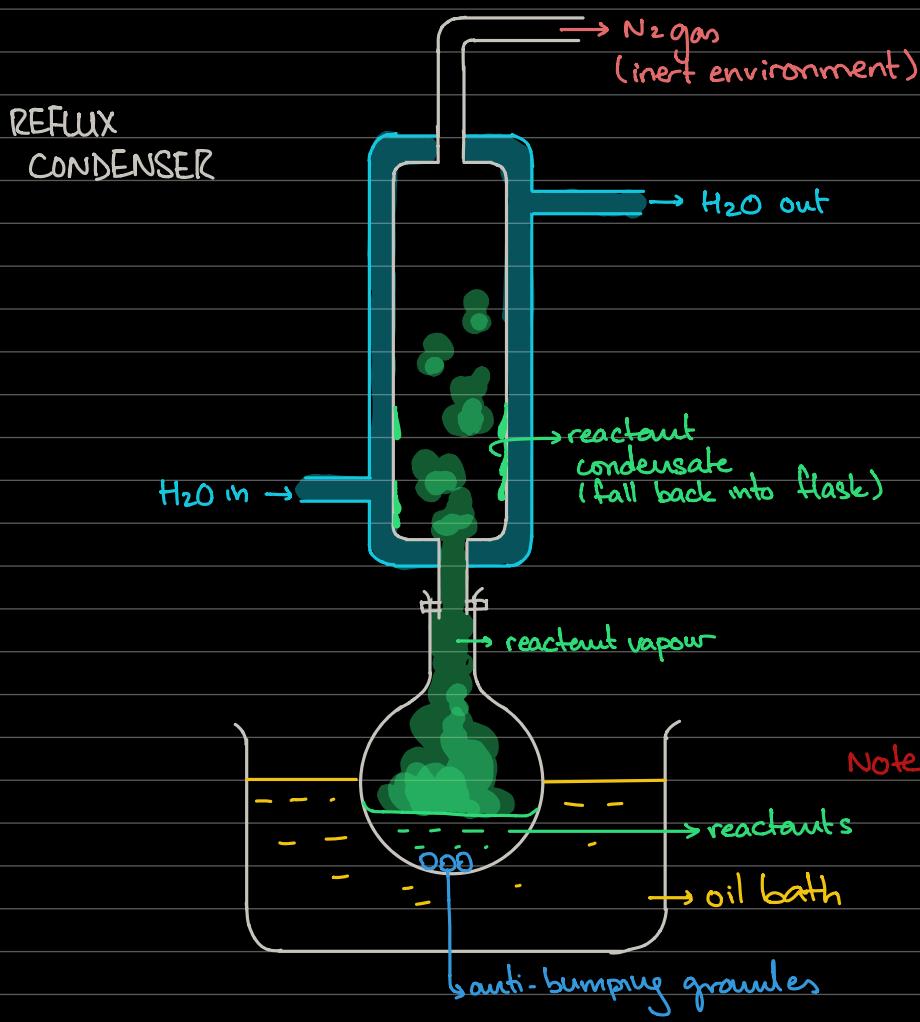
## REACTIONS OF ALKYL HALIDES

Mechanism: Nucleophilic Substitution ( $\text{S}\text{N}$ )

$\text{SN}_1$   
Nucleophilic substitution  
unimolecular

$\text{SN}_2$   
Nucleophilic substitution  
bimolecular

For organic reactions: experiments are done by "heating under reflux"



- Reasons for reflux:
1. Ensure that reaction goes to completion
  2. Increases the rate of reaction
  3. Ensures that the volatile reactants or products are not lost by evaporation when boiling

Note: Organic compounds are flammable, so they are never heated over a naked flame. Possible alternatives:

- water / steam bath
- oil bath
- electric heating mantle

## REACTIVITY OF ALKYL HALIDES

Determined primarily by bond energy and secondarily by bond polarity

### 1. Bond Polarity



where X is a halogen  
hence, this bond is polar



Most Polar



Least Polar

Based on only polarity, we would predict that C-F is the most reactive and C-I is the least reactive

### 2. Bond Energy

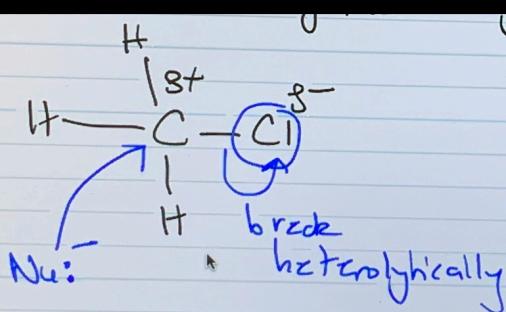
kJ/mol

C — F	467	strongest bond
C — Cl	346	
C — Br	290	
C — I	288	weakest bond

Based on the bond energy data, C-I is most reactive as its bond energy is the lowest.

But since bond energy is the PRIMARY determinant of reactivity, C-I would be considered more reactive than C-F

↳ However, bond polarity is also important as it's used to predict the type of reaction and the nature of the reagent that will attack the alkyl halide

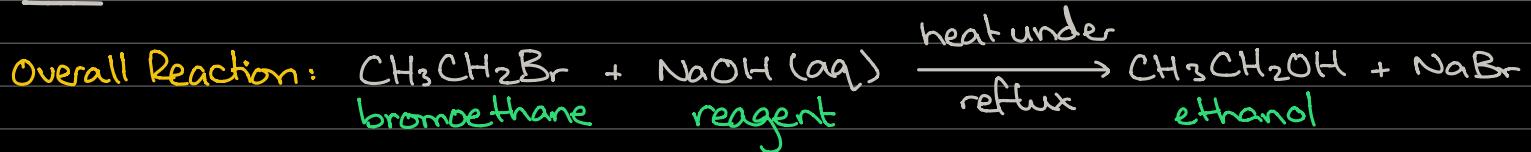


Nucleophilic Substitution

C<sup>δ+</sup> is an electron deficient carbon, so C<sup>δ+</sup> attracts nucleophiles

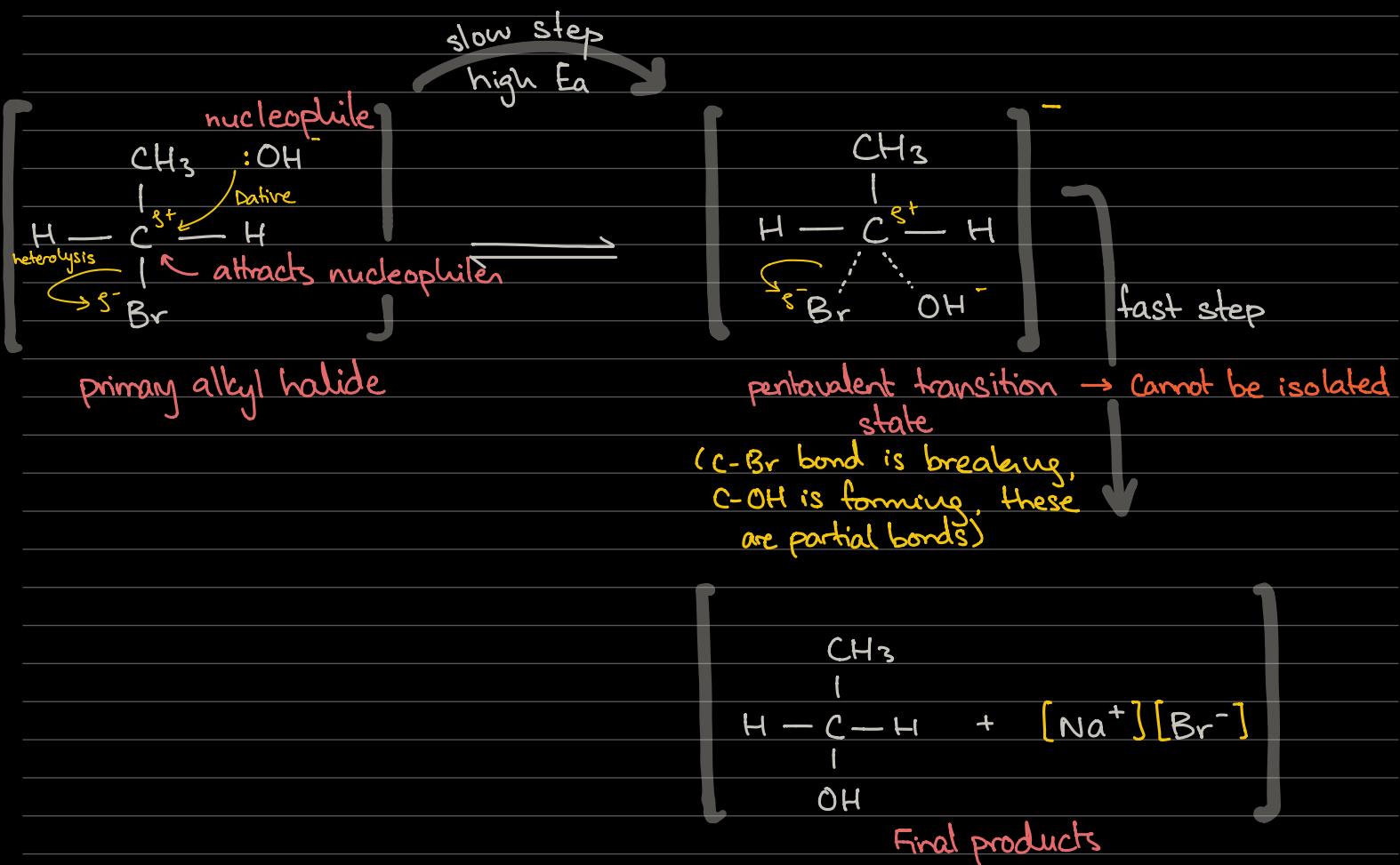
# REACTION OF ALKYL HALIDES WITH AQ. NaOH (Hydrolysis)

Sn<sub>2</sub>



## Mechanism:

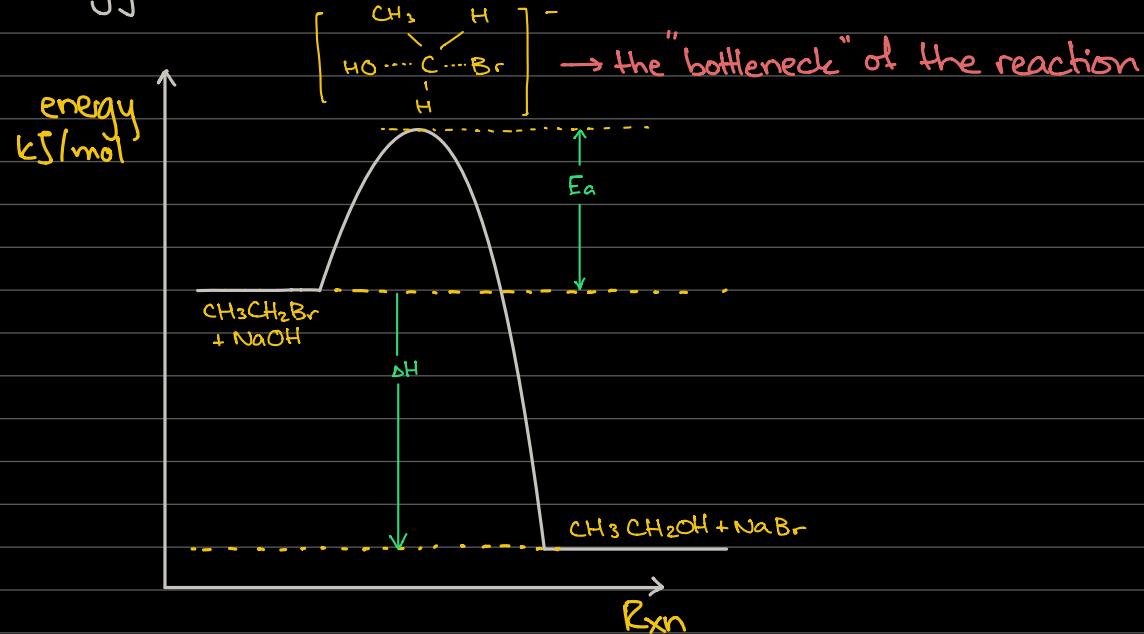
$\text{C-H}$  413  
 $\text{C-Br}$  290



- The nucleophile ( $\text{OH}^-$  ion) is attracted to the  $\text{C}^+$  carbon of the C-Halogen bond
  - It approaches the molecule from the opposite side to the halogen, to minimise repulsion from the partially negatively charged bromine
    - ↳ So its attack is not impeded by the  $\text{Br}^{3-}$

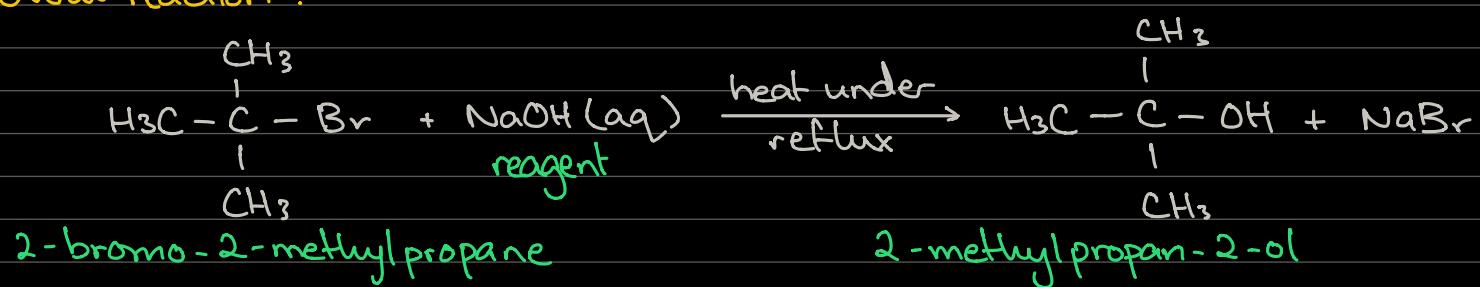
- A pentavalent transition state is formed simultaneously  
↳ It is a charged activated complex
- The  $\text{C}^{\delta+} \cdots \text{Br}^{\delta-}$  bond breaks heterolytically to form the product (ethanol) and the bromide ion is released
- The reaction is called "nucleophilic" as the first step involves an attack by a nucleophile

Energy Profile of this reaction:

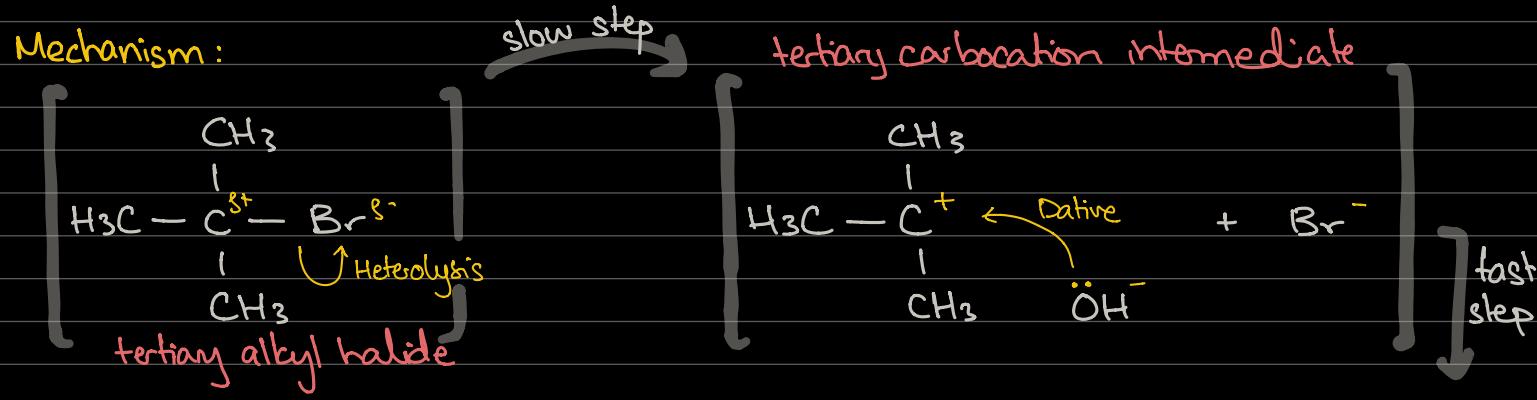


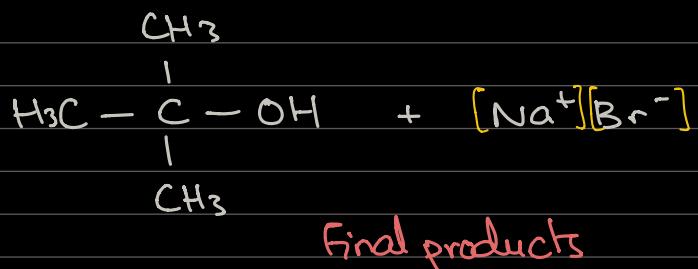
## SN

Overall reaction :



Mechanism:





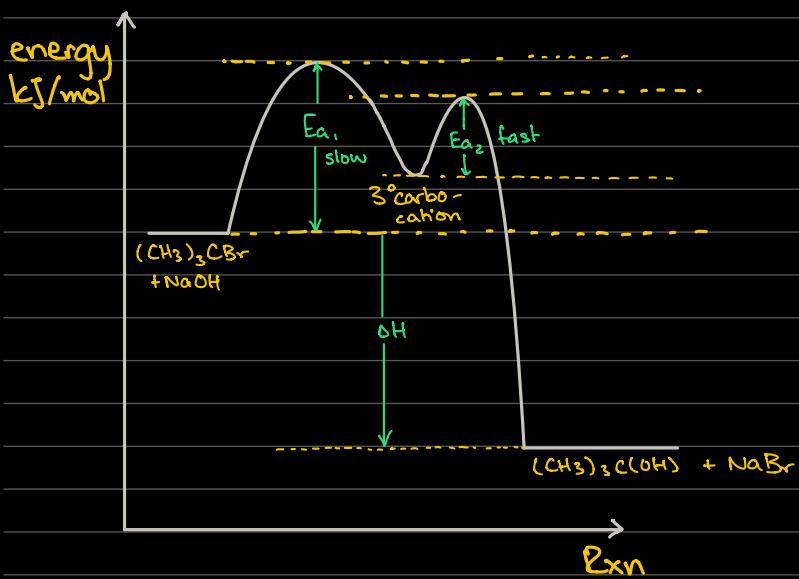
- The reaction starts out by the heterolytic fission of the C-Br bond (due to collisions), to form a  $3^\circ$  carbocation
- The carbocation is readily attacked by the nucleophile ( $\text{OH}^-$ ) to form the product alcohol

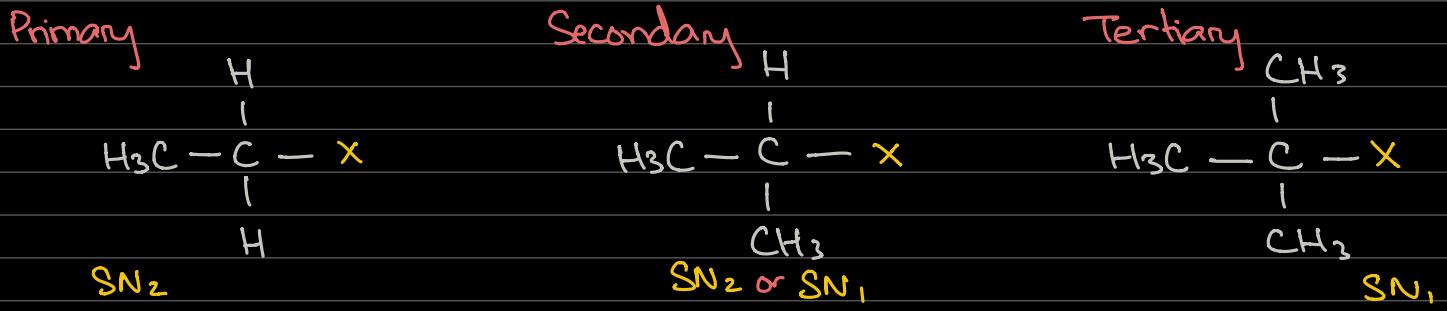
$$\text{Rate} \propto [(\text{CH}_3)_3\text{CBr}]$$

↳ rate depends on the concentration of only one species (alkyl halides), as only the alkyl halide is involved in forming the carbocation intermediate

↳ Hence, the reaction is unimolecular

Energy profile of this reaction (exothermic reaction)

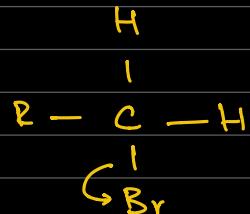




$X$  = Halogen atom

Why is this the case?  $\rightarrow S_{N}1$  vs  $S_{N}2$  depends on type of alkyl halide

i.e. a primary alkyl halide



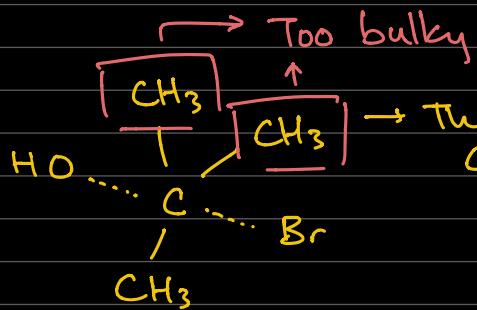
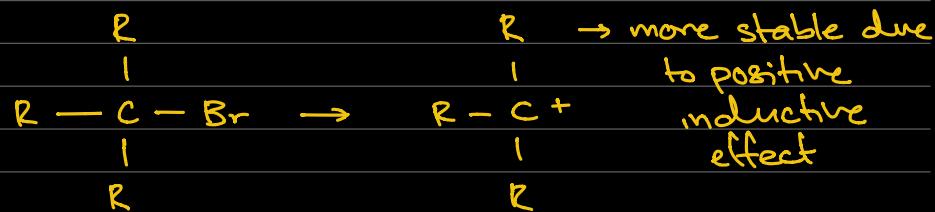
If it forms a carbocation, it will be a  $1^\circ$  one.

it will be a  $1^\circ$  one.

↳ not very stable

→ Hence 1' alkyl halides prefer to go through the  $S_N2$  mechanism, forming a pentavalent transition state

A  $3^\circ$  alkyl halide

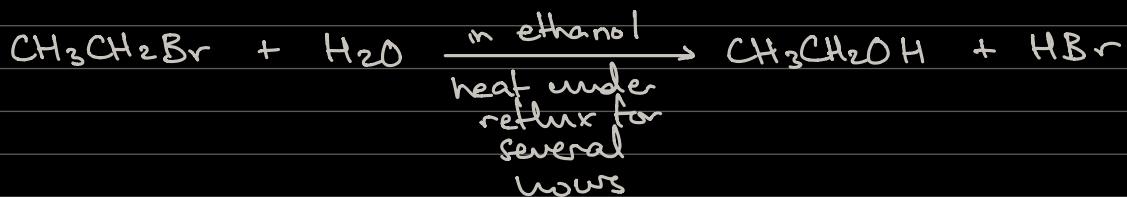


↳ i.e., there is not enough space for the pentavalent transition state to form, so it goes through the carbocation intermediate

## REACTION OF ALKYL HALIDES WITH WATER

(Hydrolysis)

- $\text{H}_2\text{O}$  is a weak nucleophile, so the reaction with water and alkyl halide is very slow



Because this reaction is so slow, hydrolysis is usually carried out by using  $\text{NaOH}$  (aq)

## REACTION OF ALKYL HALIDES WITH AMMONIA

- $\text{NH}_3$  is a nucleophile because it has a lone pair of electrons so it can attack the partially positively charged carbon

- Product is an amine



Types of Amines:

$1^\circ$  amine



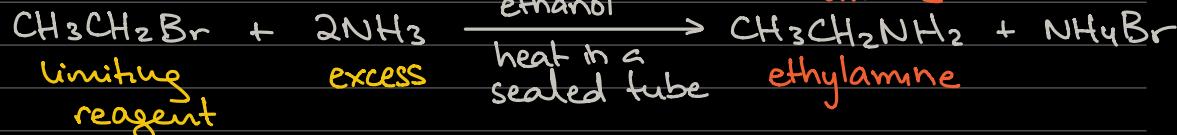
$2^\circ$  amine



$3^\circ$  amine



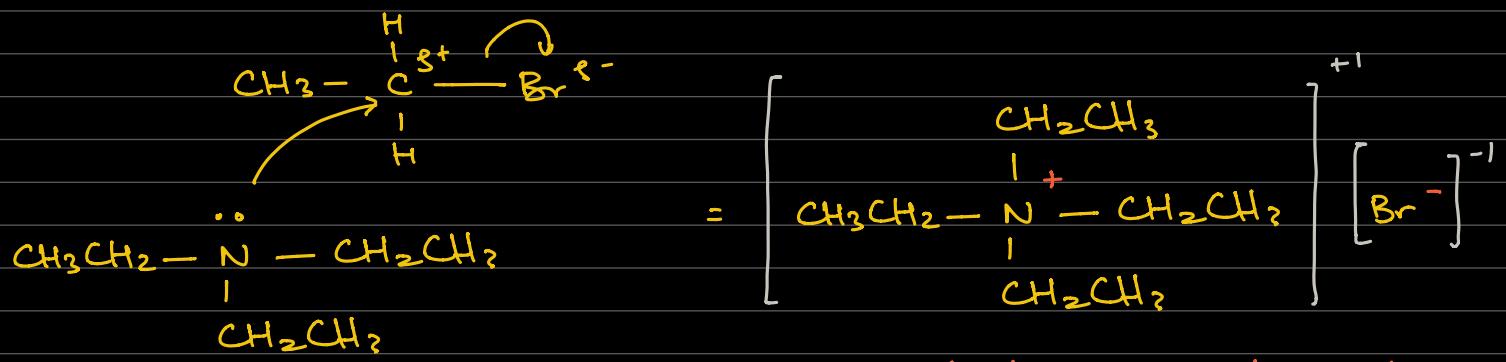
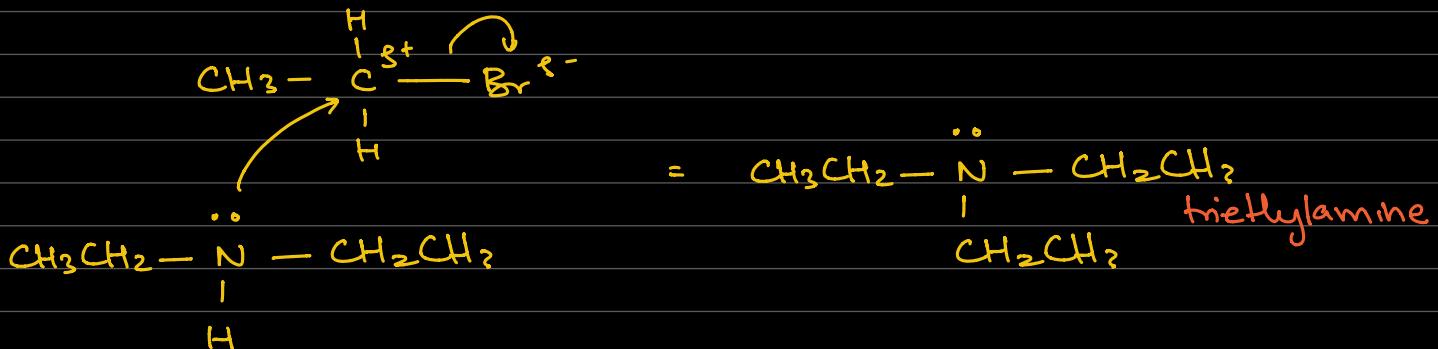
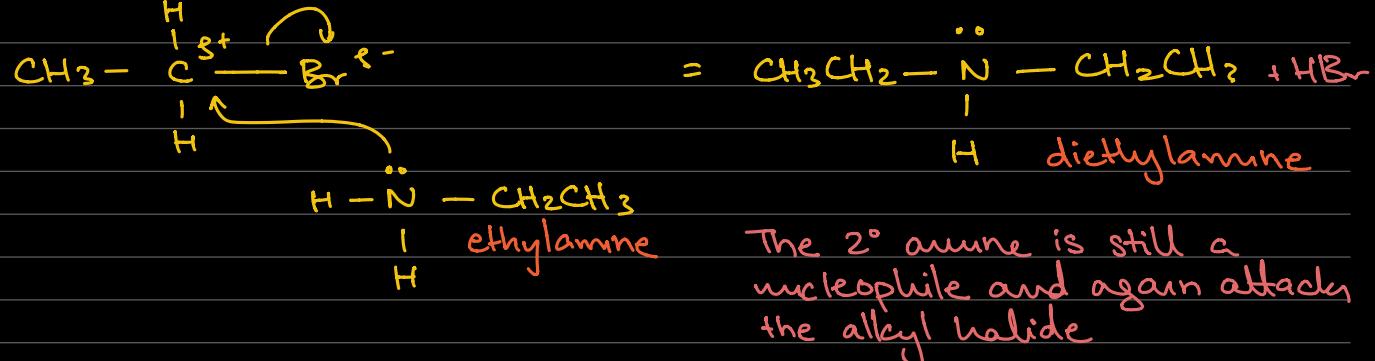
Overall Reaction:



- To stop the reaction at the  $1^\circ$  amine stage, excess  $\text{NH}_3$  should be used

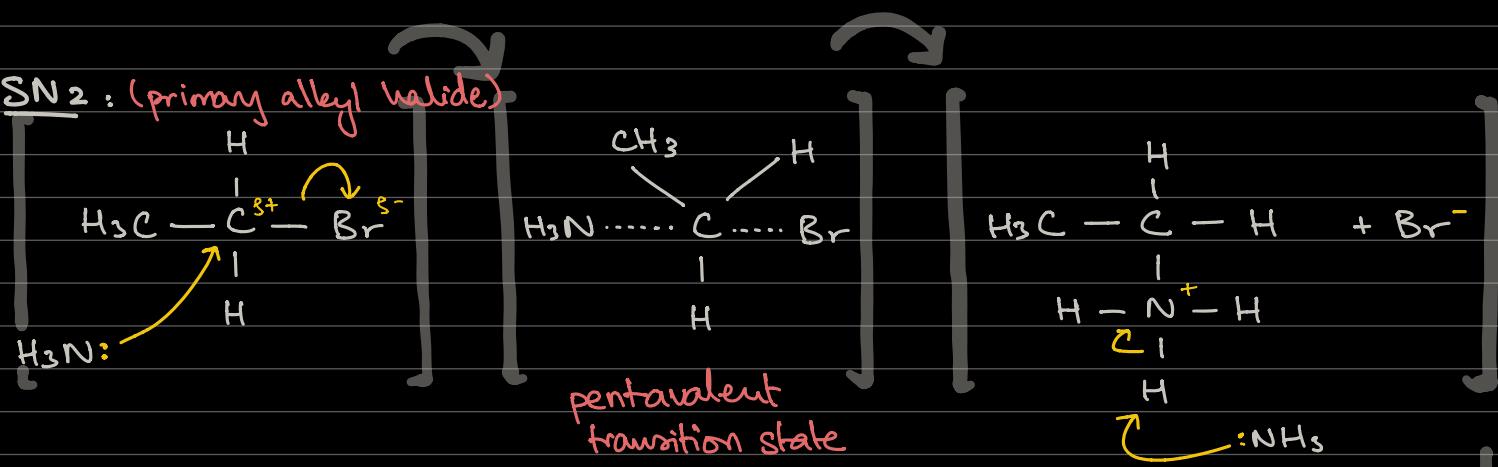
- If  $\text{NH}_3$  (g) is limiting and  $\text{CH}_3\text{CH}_2\text{Br}$  is in excess:

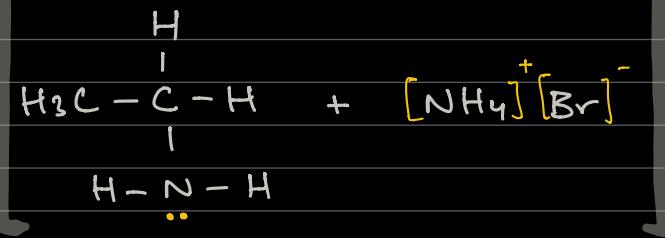
The primary amine product  $\text{CH}_3\text{CH}_2\ddot{\text{N}}\text{H}_2$  (a nucleophile) will attack the unreacted  $\text{CH}_3\text{CH}_2\text{Br}$  to form a  $2^\circ$  amine.



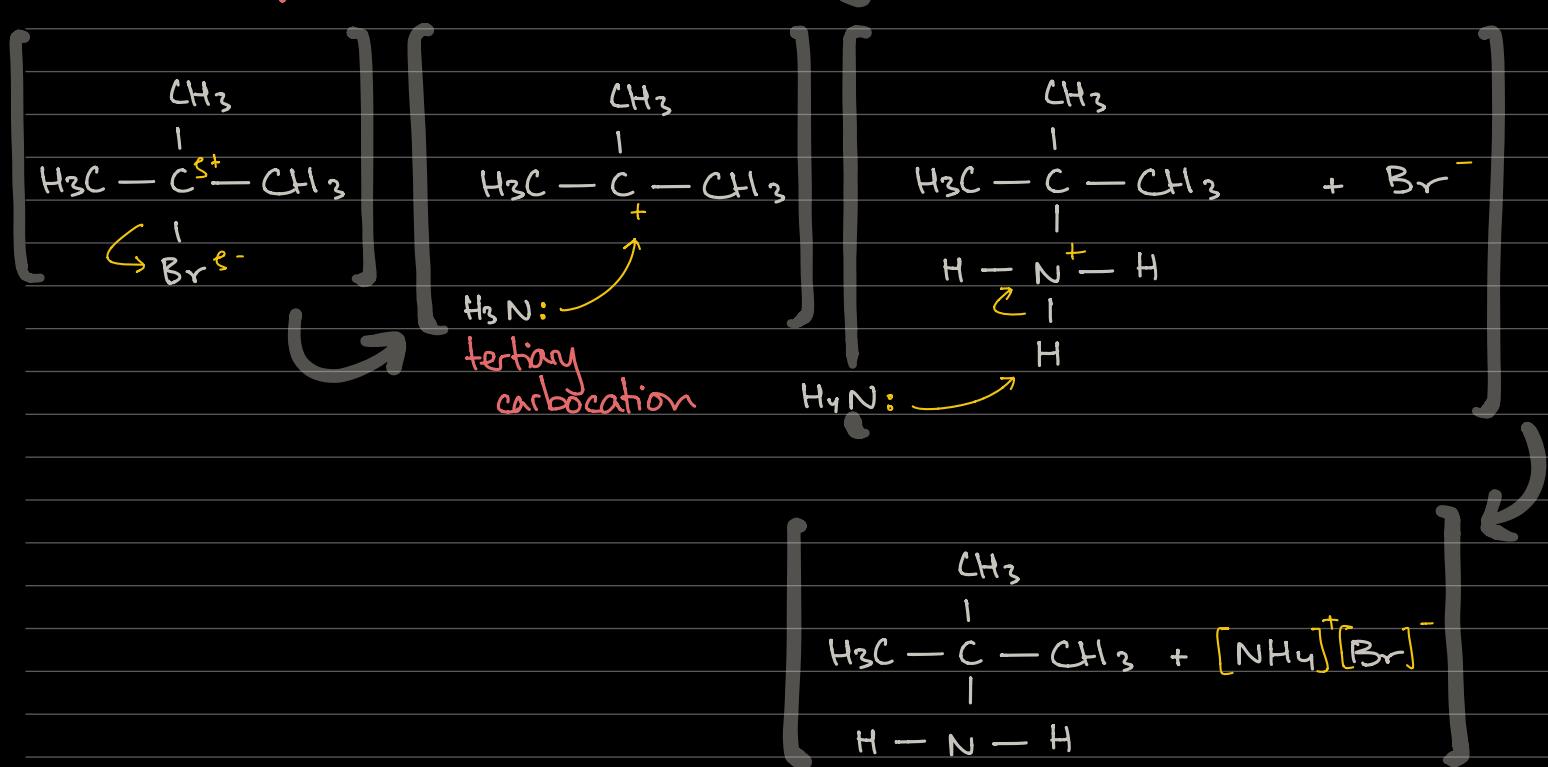
N finally uses up its lone pair because it has no more Hs to give up

- If we want to make the primary amine only, use a large excess of ammonia





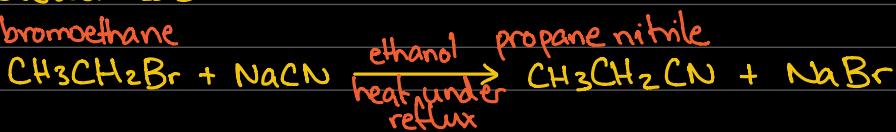
$\text{SN}_1$ : ( $3^\circ$  alkyl halide)



## REACTION OF ALKYL HALIDES WITH SODIUM CYANIDE IN ETHANOL

- Produces a nitrile

### Overall Reaction:



Note: Difference bw. cyanide and nitrile

$\hookrightarrow [C \equiv N]^+$   
cyanide  $\rightarrow$  inorganic compounds  
ie. sodium cyanide ( $NaCN$ )

$\text{R}-\text{C}\equiv\text{N}$ :  
nitrile  $\rightarrow$  organic compounds  
ie. propane nitrile  $\text{CH}_3\text{CH}_2\text{CN}$

- This is an important reaction in organic synthesis as it can be used to elongate/lengthen the carbon chain
  - In the above example, the alkyl halide is a  $1^\circ$  one, hence it <sup>always</sup> undergoes a  $\text{SN}_2$  reaction

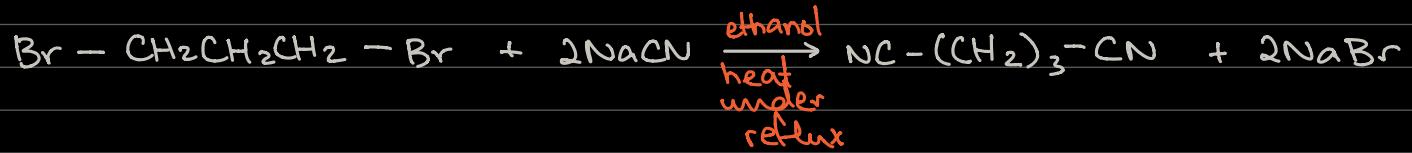
- Below is an example where a 2° alkyl halide undergoes a SN reaction (SN<sub>2</sub> or SN<sub>1</sub>)



- 3° alkyl halide (SN<sub>1</sub> only)



More examples :

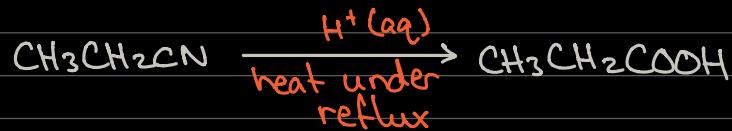


- Nitriles can be converted to other functional groups easily
- Possible conversions :



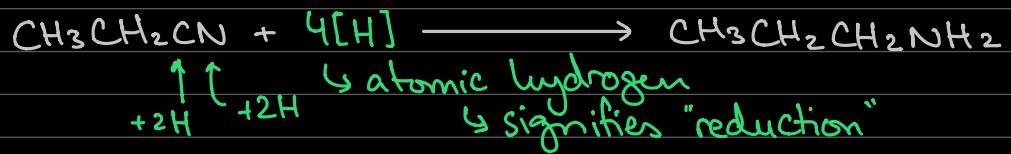
### HYDROLYSIS of nitriles

- By heating the RCN under reflux with dilute aqueous acid, ie. HCl



## REDUCTION of nitriles

a) Na metal in ethanol as solvent  $\rightarrow$  H<sub>2</sub> gas is evolved, which acts as the required reducing agent



Reagent: Na(s)

Condition: ethanol, rtp

OR

b) NaBH<sub>4</sub> in water as a solvent

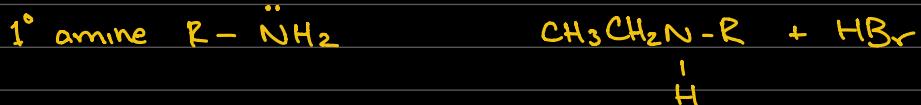
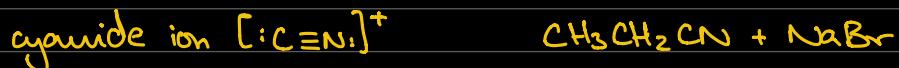


Reagent: NaBH<sub>4</sub>

Condition: water, rtp

## SUMMARY of Nucleophilic Substitution Rxns:

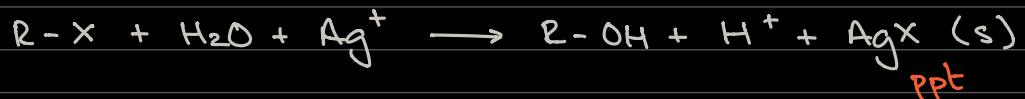
Nucleophile      Product formed when it is reacted with CH<sub>3</sub>CH<sub>2</sub>Br



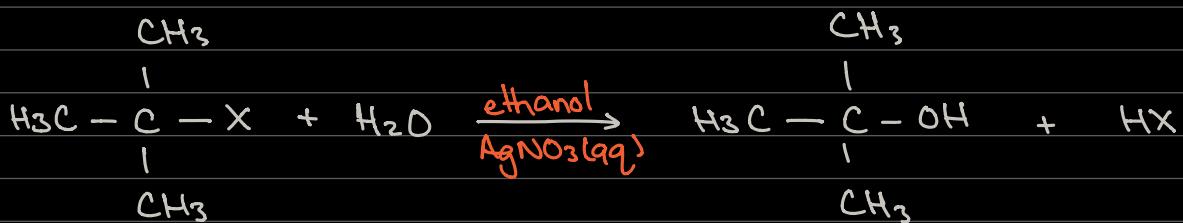
$\begin{matrix} | \\ \text{H} \end{matrix}$   
1° amine

## COMPARING THE RATE OF HYDROLYSIS OF R-X (where X = Cl vs. Br vs. I)

- Based on the identification test for halide ion test ( $\text{AgNO}_3$ )
- Rates of hydrolysis can be studied by dissolving the alkyl halide in ethanol and water and adding  $\text{AgNO}_3\text{(aq)}$  to the reaction mixture
- As the alkyl halide slowly hydrolyses, the halide ion ( $X^-$ ) is released and forms a ppt with  $\text{AgNO}_3\text{(aq)}$ .



Example:



### SUMMARY

Compound	Observation	Color of ppt.
$(\text{CH}_3)_3\text{C}-\text{Cl}$	Slight cloudiness after 1 hour	white $\text{AgCl(s)}$
$(\text{CH}_3)_3\text{C}-\text{Br}$	Cloudiness after a few minutes	pale cream $\text{AgBr(s)}$
$(\text{CH}_3)_3\text{C}-\text{I}$	Thick precipitate within a minute	pale yellow $\text{AgI(s)}$

Q. Explain this observation with reference to the Data Booklet

- Iodoalkanes are the most reactive, as the C-I bond energy is the lowest (240 kJ/mol) whereas the chloroalkane is the least reactive with the highest bond energy (340 kJ/mol)

↳ Therefore, the reaction / hydrolysis is fastest for iodoalkanes



# EUMINATION REACTIONS OF ALKYL HALIDES

- Whether the alkyl halide undergoes nucleophilic substitution or elimination depends on the reaction conditions or the solvent being used

(in ethanol)

Reagent: ethanolic NaOH or ethanolic KOH

Condition:

why KOH:

KOH is better for this reaction because it is more soluble in ethanol than NaOH

- Q. How is elimination different from substitution?

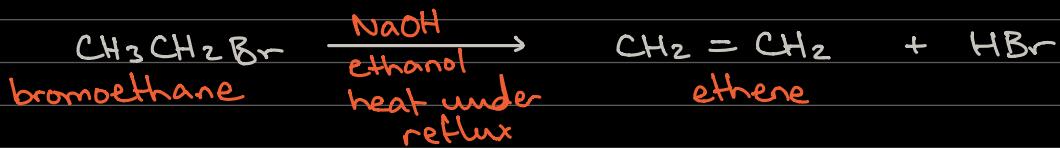
In elimination, we are removing a small molecule from the starting material

- OH<sup>-</sup> ion behaves as a base and not as a nucleophile

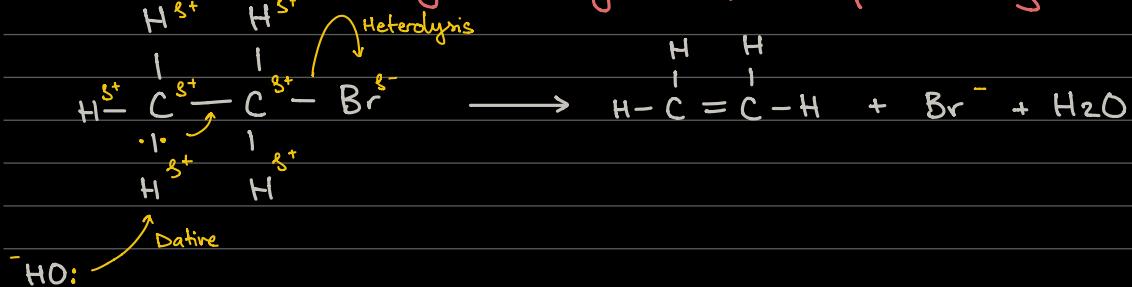
- A base is a proton (H<sup>+</sup>) acceptor, i.e. OH<sup>-</sup> + H<sup>+</sup> → H<sub>2</sub>O
- An acid is a proton (H<sup>+</sup>) donor

- In ethanol, NaOH behaves as a base

Overall Reaction :



Mechanism: (Not really in our syllabus, but predicting the organic product is)



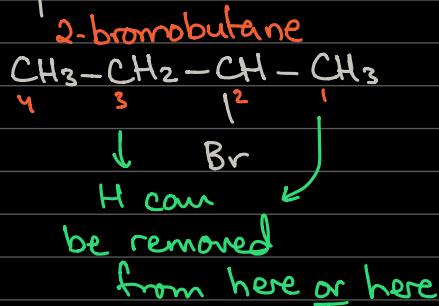
- The H<sup>δ+</sup> from the carbon adjacent to where the halogen is attached is removed

- The EN halogen creates a δ<sup>+</sup> charge on all the hydrogens so the H<sup>δ+</sup> are acidic in nature

- The OH<sup>-</sup> ion behaves as a base in ethanol, and deprotonates the alkyl halide

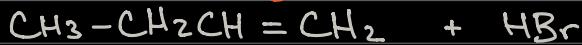
- As a result, the  $\text{H}^+$  and the Br are eliminated and an alkene is produced

Example:



If we remove  $\text{H}^+$  from C<sub>1</sub>:

but-1-ene



If we remove  $\text{H}^+$  from C<sub>3</sub>:

cis-but-2-ene and trans-but-2-ene



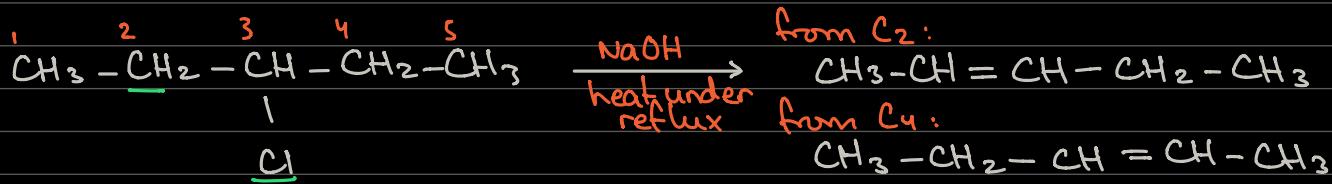
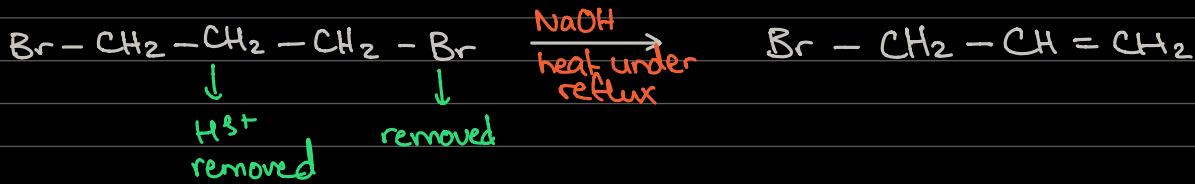
Q. How many alkenes formed as a result of this reaction?

Ans. 3:

1. But-1-ene
2. cis-but-2-ene
3. trans-but-2-ene

→ 3 different alkenes

Example:



↳ same product

pent-2-ene

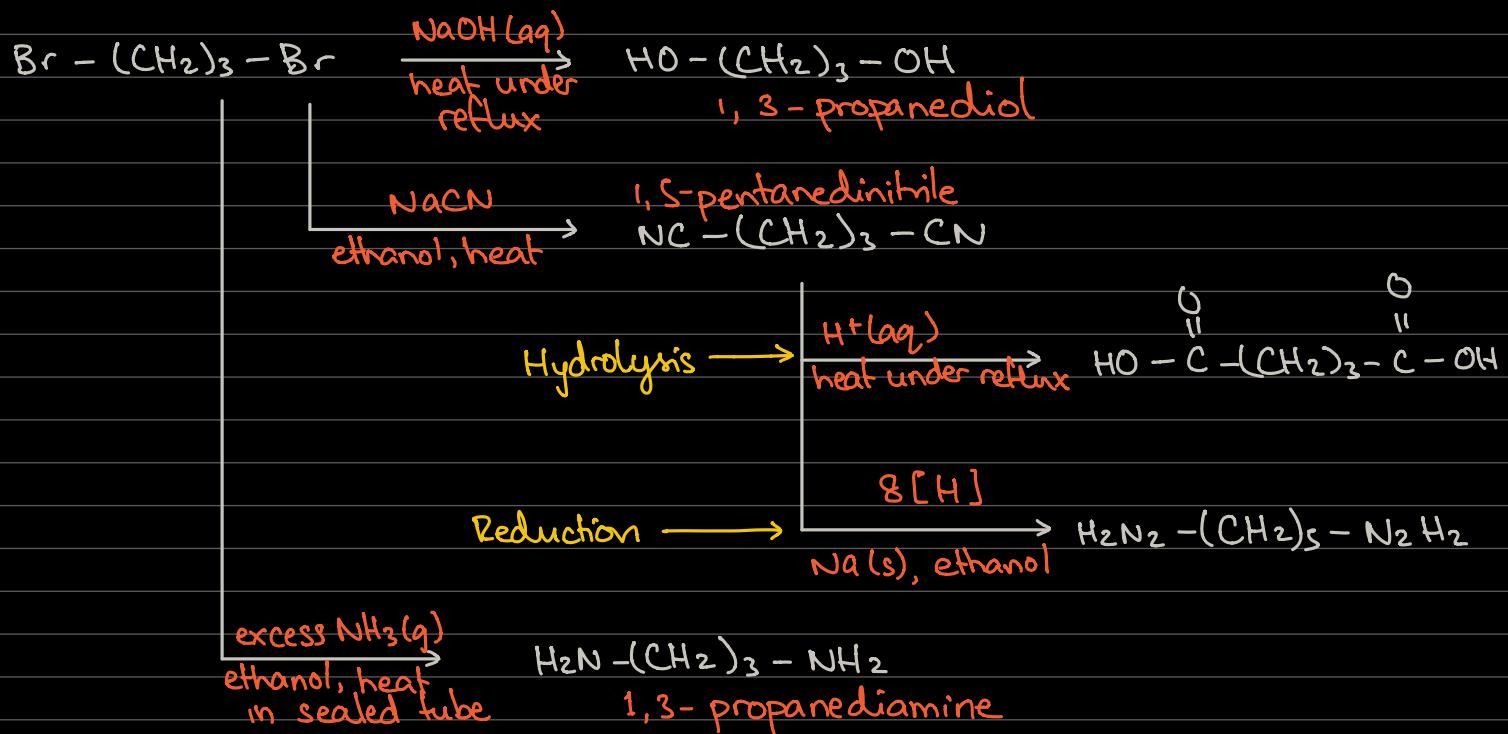
Q. How many alkenes produced?

Ans. 1. cis-pent-2-ene

2. trans-pent-2-ene

→ 2 different alkenes

# REVISION OF NUCLEOPHILIC SUBSTITUTION



## USES OF ALKYL HALIDES

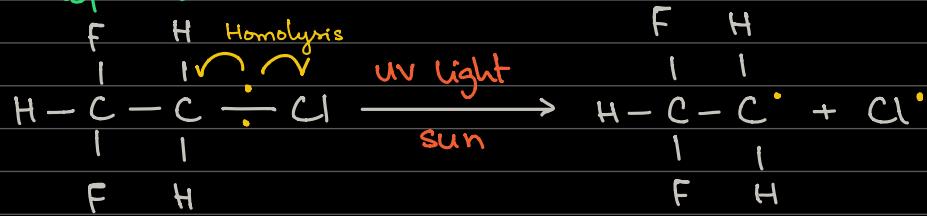
1. Used as CFCs ( chlorofluorocarbons )

↳ Properties of CFCs that made them useful :

- they were inert and non toxic
  - they are volatile and have low boiling points
  - can be compressed easily

Because of these properties, they could be used as aerosol propellants, refrigerants, and coolants.

But they have been phased out as they generate the chlorine free radical which has destroyed the ozone ( $O_3$ ) layer in the stratosphere (upper atmosphere)



2. Anesthetics : Chloroform ( $\text{CHCl}_3$ ) → not used anymore

Generally known as a class of compounds called "Haloethanes"  
ie.  $\text{CF}_3\text{CHBrCl}$

3. Fire retardants / extinguishers : known as "Halons"  
ie.  $\text{CBrClF}_2$

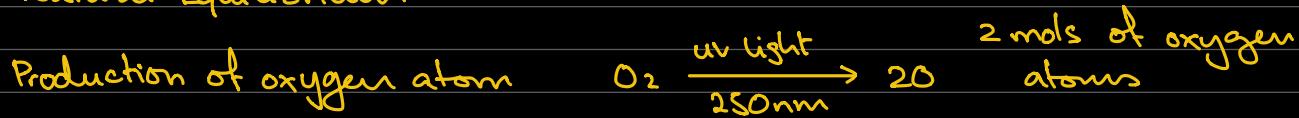
4. Used to make polymers : ie. Teflon, PVC, etc.

5. Solvents : ie.  $\text{CH}_2\text{Cl}_2 \rightarrow$  paint remover  
 $\text{CCl}_4 \rightarrow$  non-polar solvent

6. Insecticides : DDT  $\rightarrow$  highly toxic

7. Herbicides

Ozone depletion in the stratosphere  
natural Equilibrium



Natural Ozone formation

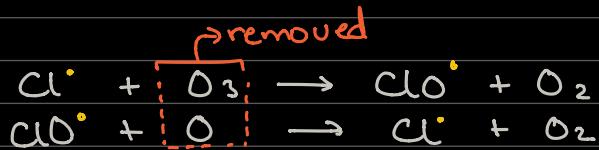


Natural Ozone depletion



} Equilibrium occurs naturally

The  $\text{Cl}^\cdot$  free radical disrupts the equilibrium by acting as a catalyst for breaking up ozone



Double depletion effect as it is removing atomic oxygen and  $\text{O}_3$  from the natural equilibrium process