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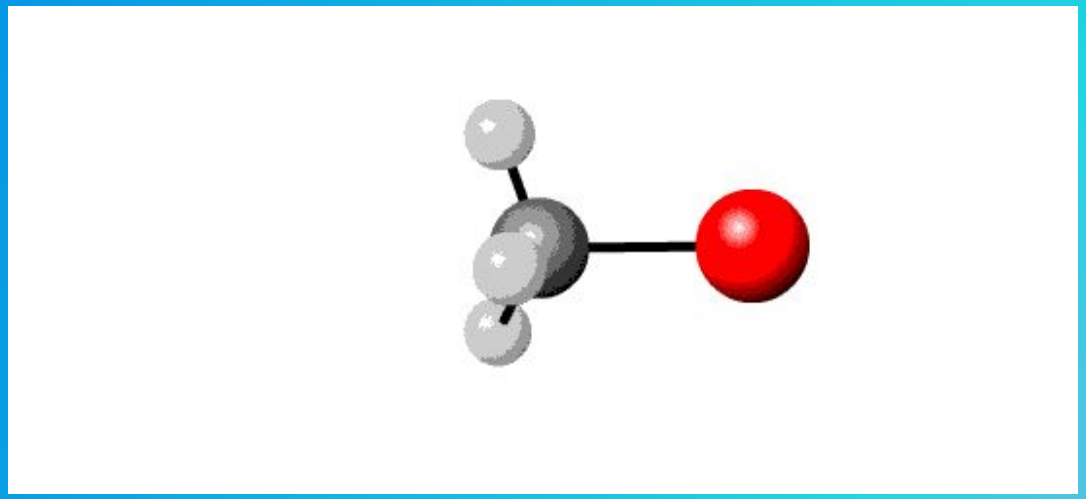
Substitution reactions of halogenoalkanes



Learning Objectives

- Recognise that halogenoalkanes will react with nucleophiles
- Understand the mechanism of nucleophilic substitution reactions
- Be able to write equations and mechanisms for a general case and some common examples

Success Criteria

- Define the term *nucleophilic substitution*.
- Explain the differences between S_N1 and S_N2 mechanisms.
- Write equations and examples of nucleophilic substitution reactions.
- Outline and draw S_N1 and S_N2 mechanisms for halogenoalkane reactions.

Keywords

- Nucleophile
- Substitution
- Nucleophilic substitution
- Nucleophilic substitution unimolecular (S_N1)
- Nucleophilic substitution bimolecular (S_N2)
- rate-determining step (slowest step)
- primary, secondary, tertiary halogenoalkane
- steric effect / steric hindrance
- carbocation intermediate
- transition state

Polar bonds and nucleophiles

The carbon–halogen bond in halogenoalkanes is polar because all halogens are more electronegative than carbon.

The polar bond means that the carbon atom has a small positive charge (δ+), which attracts substances with a lone pair of electrons. These are **nucleophiles**, meaning 'nucleus (positive charge) loving'. Examples include:

ammonia

cyanide

hydroxide

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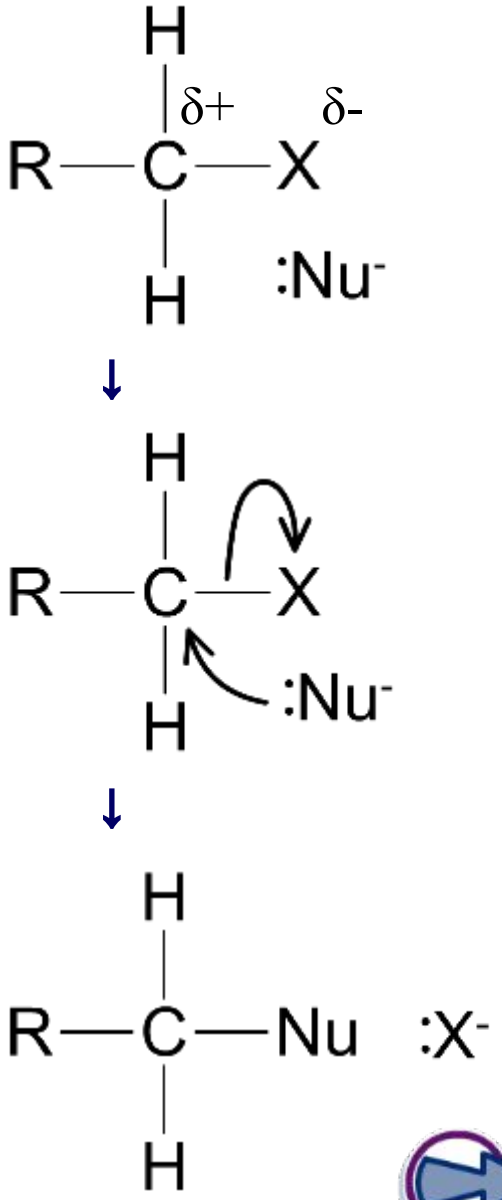
Reaction with nucleophiles

Nucleophiles (Nu^-) attack the carbon of a carbon–halogen (C–X) bond, because the electron pair on the nucleophile is attracted towards the small positive charge on the carbon.

The electrons in the C–X bond are repelled as the Nu^- approaches the carbon atom.

The Nu^- bonds to the carbon and the C–X bond breaks. The two electrons move to the halogen, forming a halide ion.

The halide is substituted, so this is a **nucleophilic substitution reaction**.



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Rate of nucleophilic substitution

The rate of a nucleophilic substitution reaction depends on the strength of the carbon–halogen bond rather than the degree of polarization in the bond.

Bond	Strength ($kJ\,mol^{-1}$)
C–F	484
C–Cl	338
C–Br	276
C–I	238

The C–I bond is the weakest and so most readily undergoes nucleophilic substitution. The rate of reactions involving iodoalkanes is the highest.

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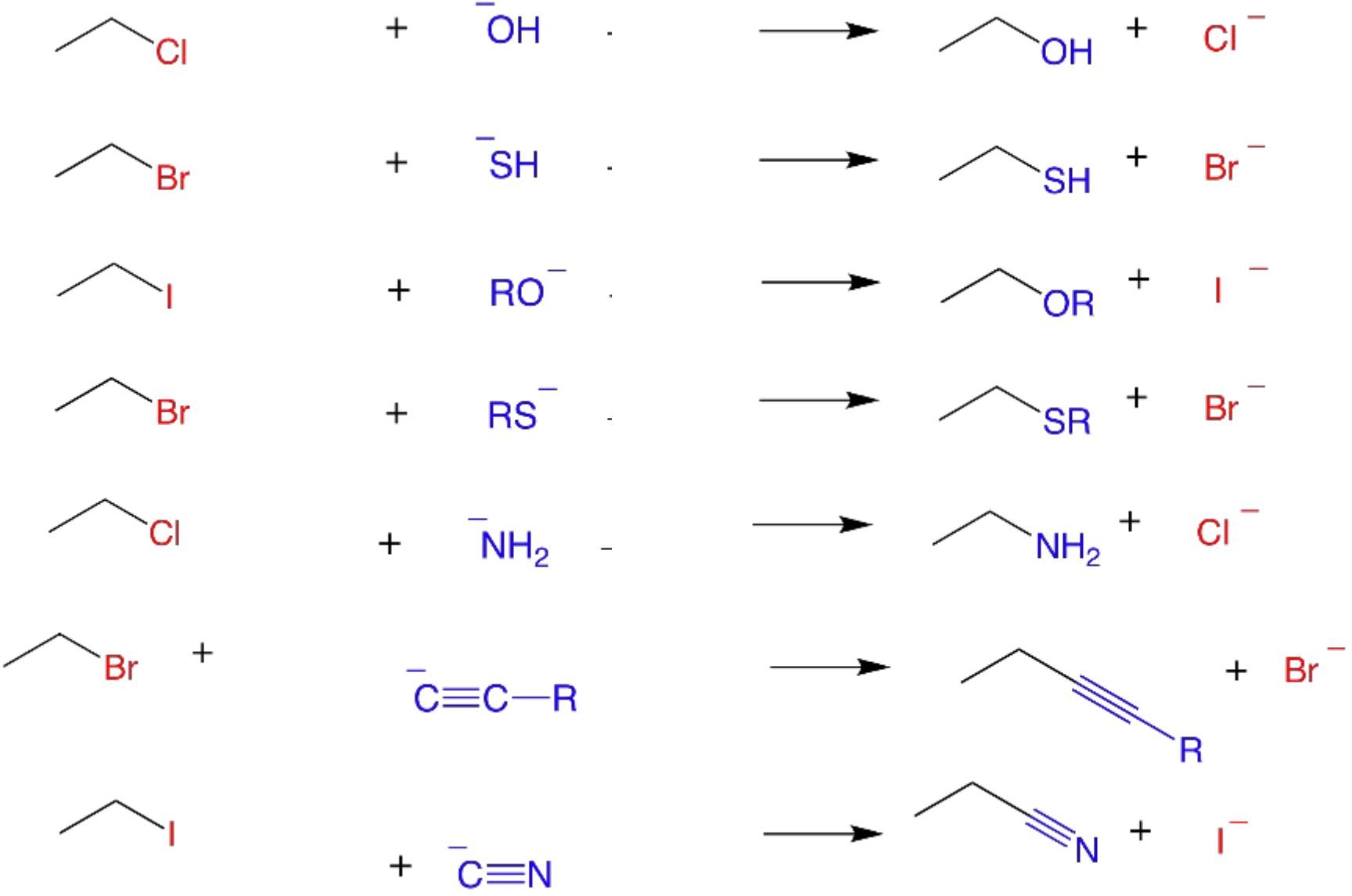
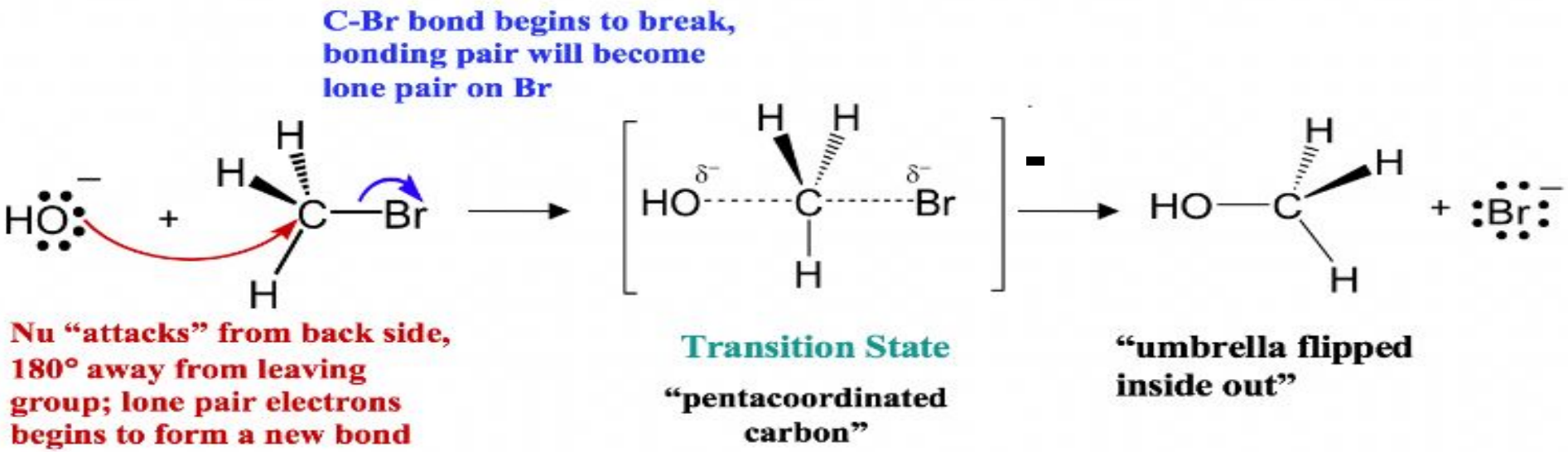
Halogenoalkanes Nucleophiles Substitution reactions



S_N2

Substitution **Nucleophilic** **Bimolecular**

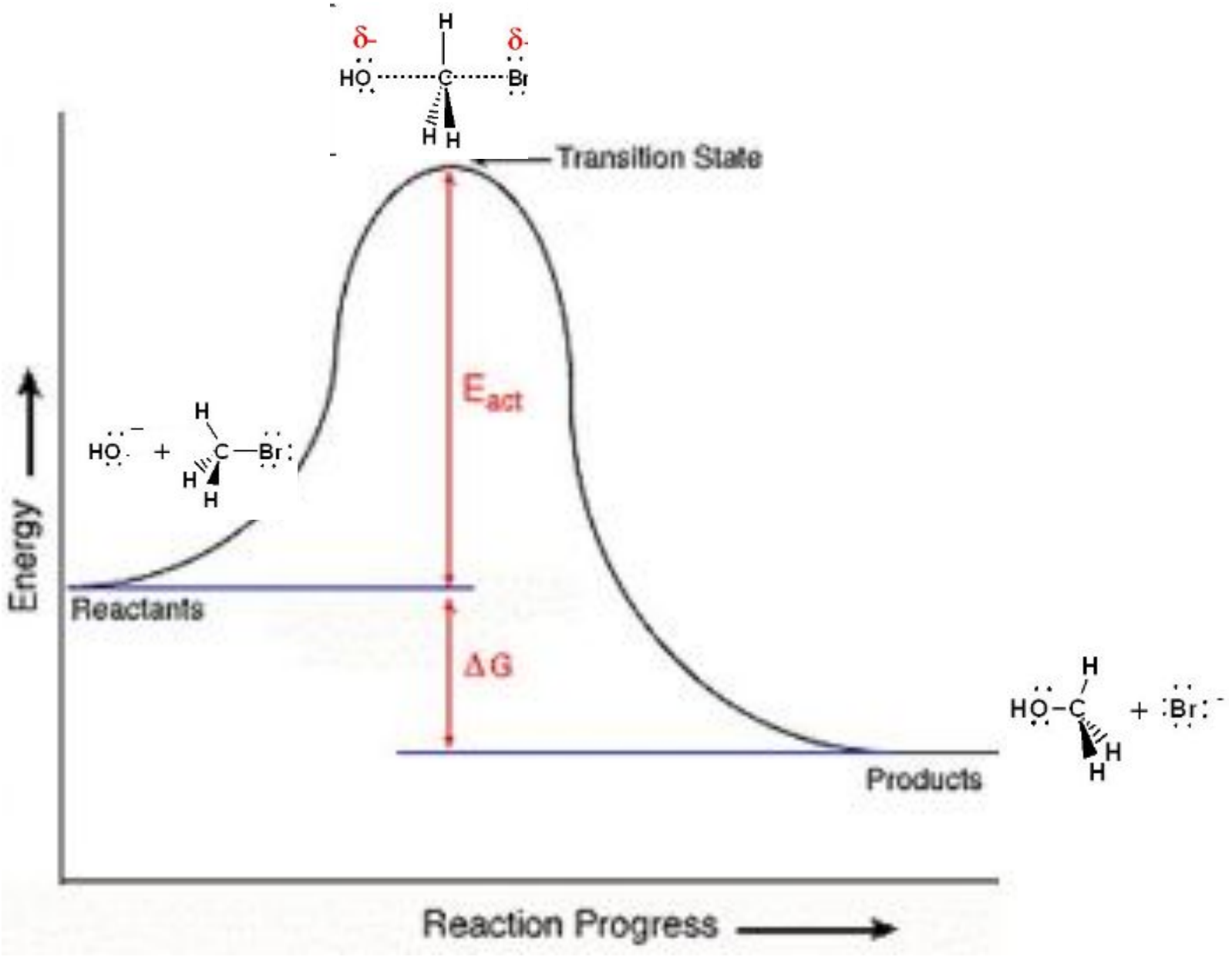


- Rate-Determining Step involves 2 components

$$\textbf{rate} = k[\textbf{halogenoalkane}]^m[\textbf{nucleophile}]^n$$

- **Simultaneous** bond-making and bond-breaking steps
- S_N2 reactions do **not** proceed via an intermediate
- Occurs in **primary** and **secondary** halogenoalkanes

ENERGY PROFILE for S_N2



S_N2 MECHANISM

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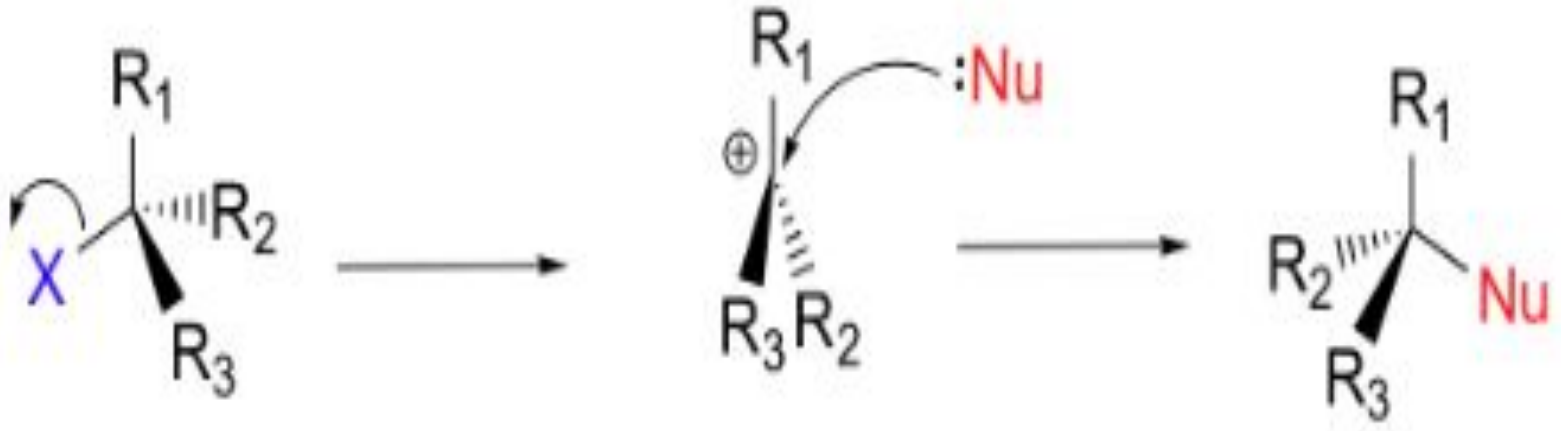
S_N1

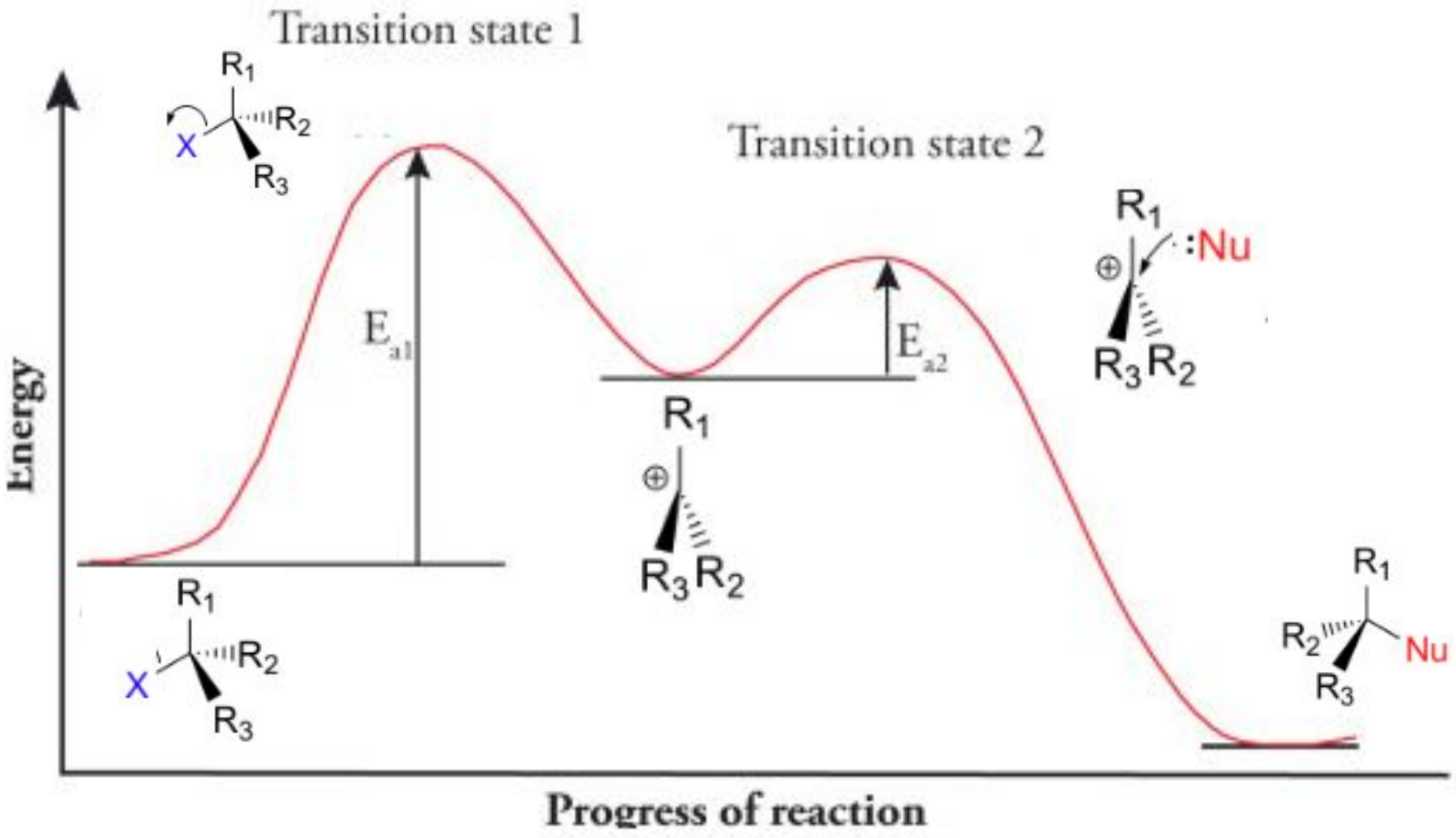
Substitution **Nucleophilic** **Unimolecular**



- Rate-Determining Step involves 1 component only

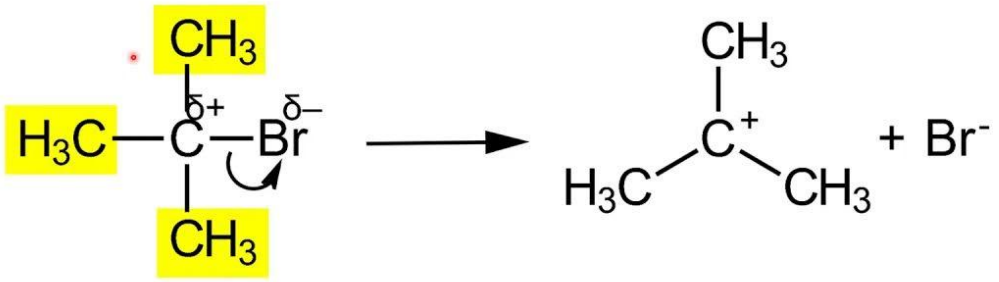
  rate = *k*[halogenoalkane]
- Bond-breaking takes place first then bond-making occurs later.
- S_N1 reactions proceed via an intermediate carbocation.
- Occurs in **secondary** and **tertiary** halogenoalkanes

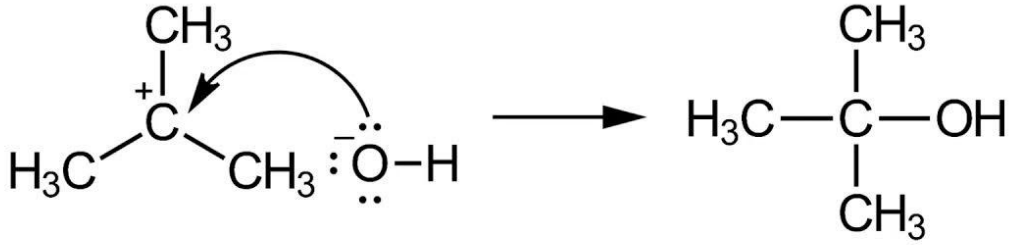
ENERGY PROFILE for S_N1



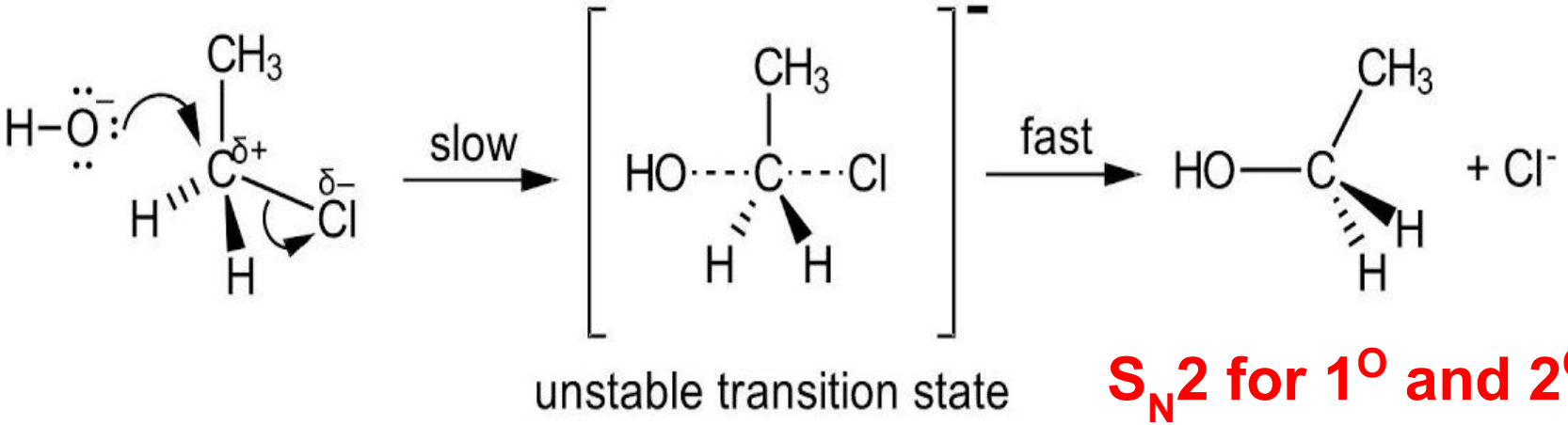
S_N1 MECHANISM

Summary of Mechanisms





S_N1 for 3^O Halogenoalkanes



S_N2 for 1^O and 2^O Halogenoalkanes

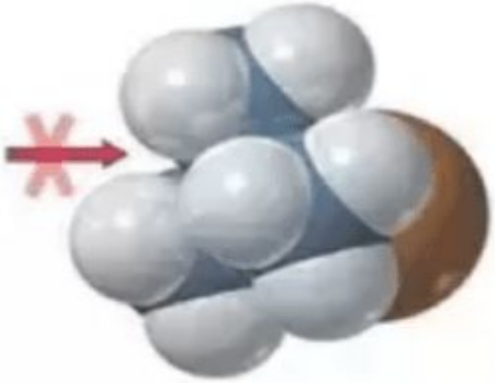
Why do tertiary halogenoalkanes unlikely to proceed via S_N2 mechanism?

Also known as the "bulkiness" of the groups attached

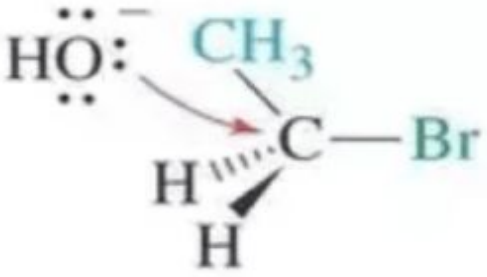
Steric Effects

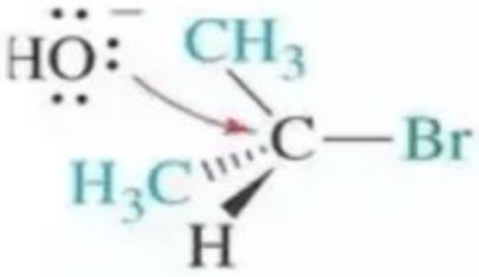
ethyl bromide (1°)
attack is easy

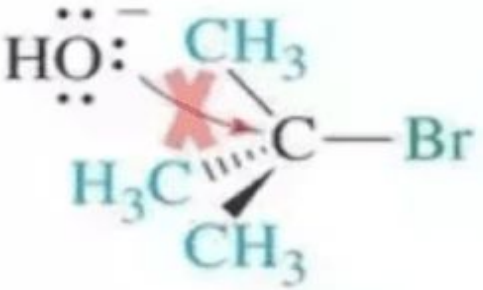
isopropyl bromide (2°)
attack is possible



t-butyl bromide (3°)
attack is impossible

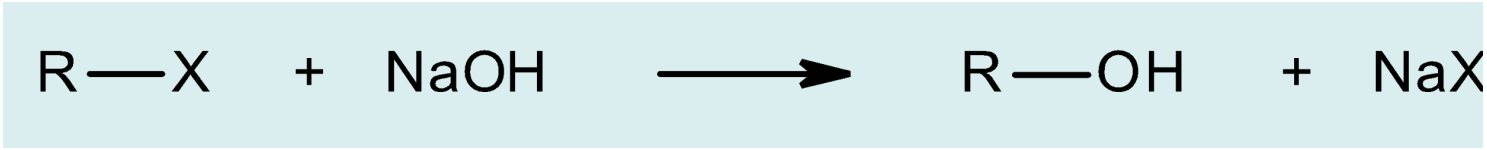


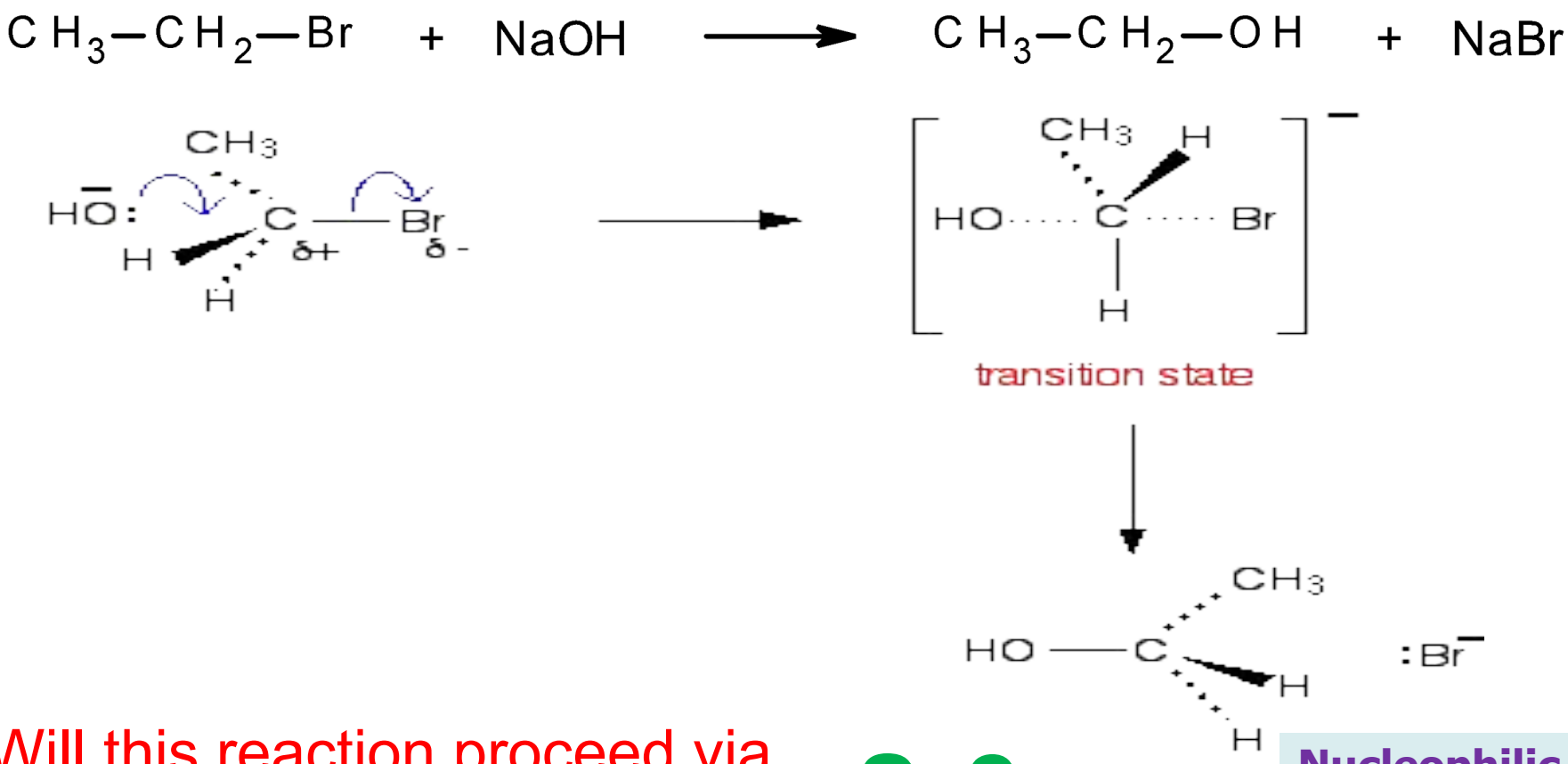




e.g. bromoethane + aqueous warm NaOH

Conditions: aqueous, warm



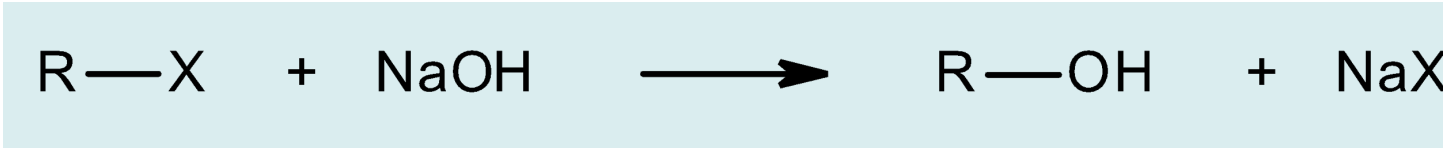


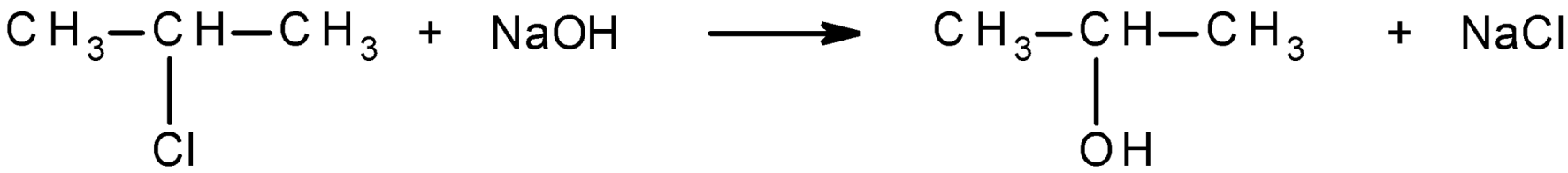
Will this reaction proceed via S_N1 or S_N2 mechanism?

S_N2

Nucleophilic substitution

e.g. 2-chloropropane + NaOH **Aqueous and warm**





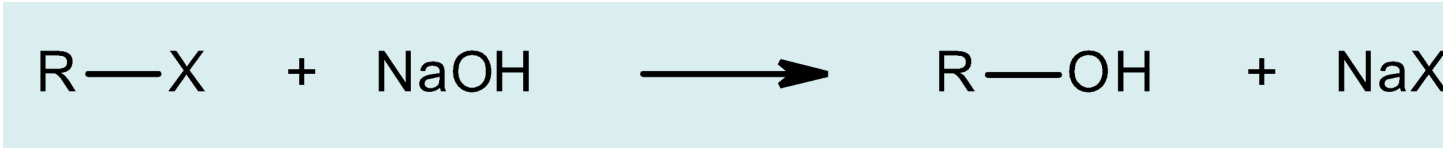
Task 1: Outline and draw the mechanism for this reaction.

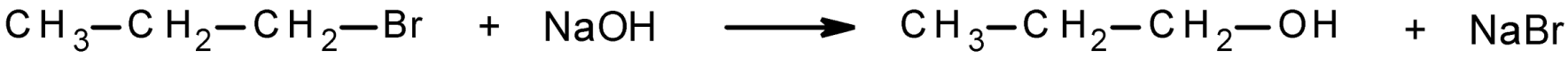
Will this reaction proceed via S_N1 or S_N2 mechanism?

S_N1 or S_N2

Nucleophilic substitution

e.g. 1-bromopropane + NaOH **Aqueous and warm**





Task 2: Outline and draw the mechanism for this reaction.

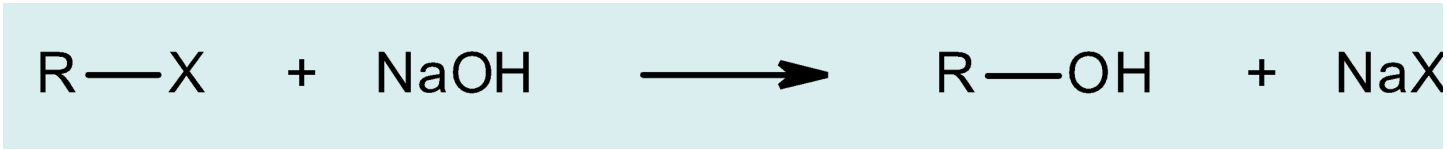
Will this reaction proceed via S_N1 or S_N2 mechanism?

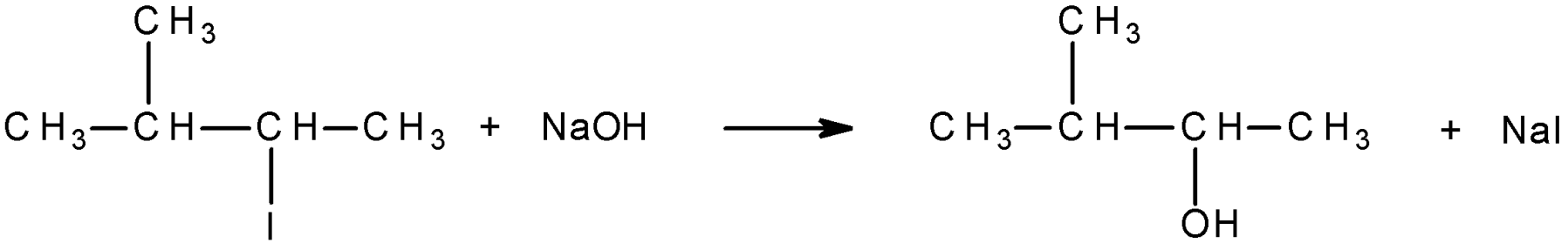
S_N2

Nucleophilic substitution

e.g. 2-iodo-3-methylbutane + NaOH

Aqueous and warm





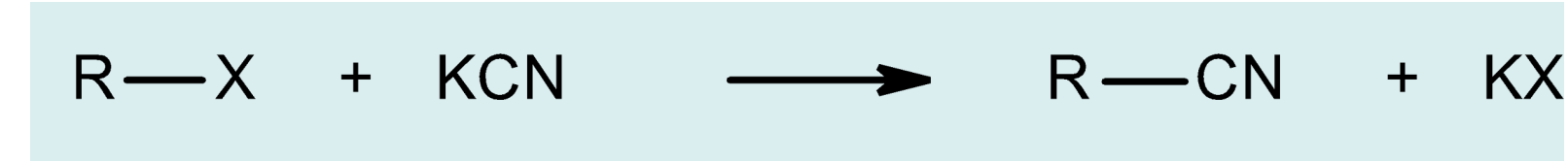
Task 3: Outline and draw the mechanism for this reaction.

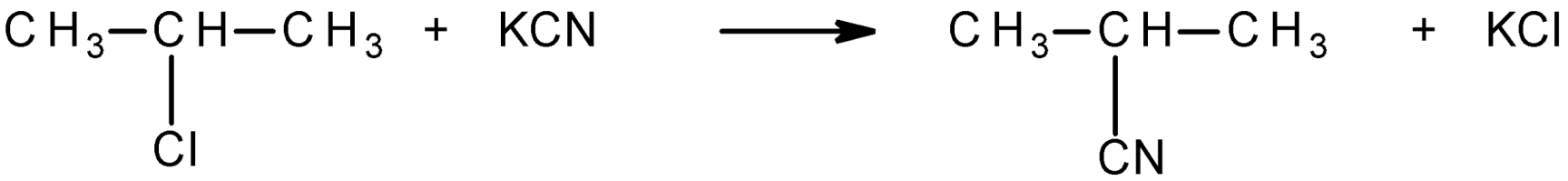
Will this reaction proceed via S_N1 or S_N2 mechanism?

S_N1 or S_N2

Nucleophilic substitution

e.g. 2-chloropropane + ethanolic KCN, boil under reflux





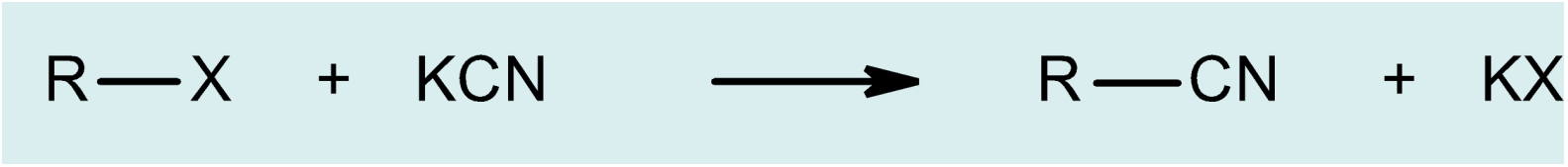
Task 4: Outline and draw the mechanism for this reaction.

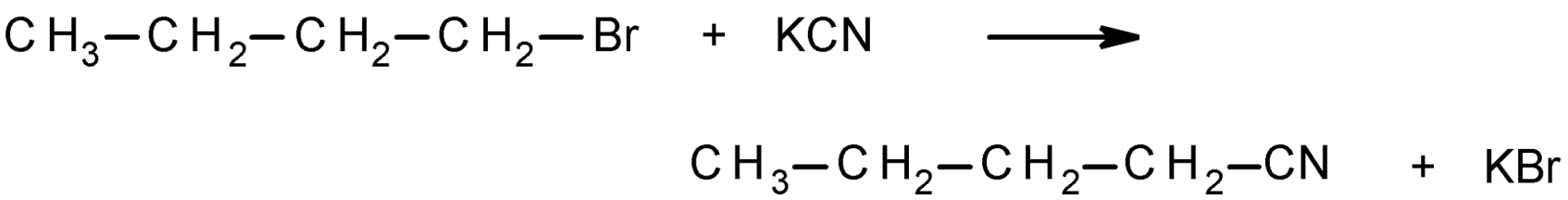
Will this reaction proceed via S_N1 or S_N2 mechanism?

S_N1 or S_N2

Nucleophilic substitution

e.g. 1-bromobutane + ethanolic KCN, boil under reflux





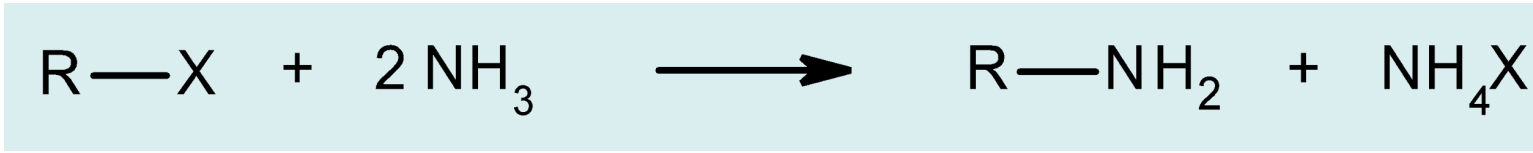
Task 5: Outline and draw the mechanism for this reaction.

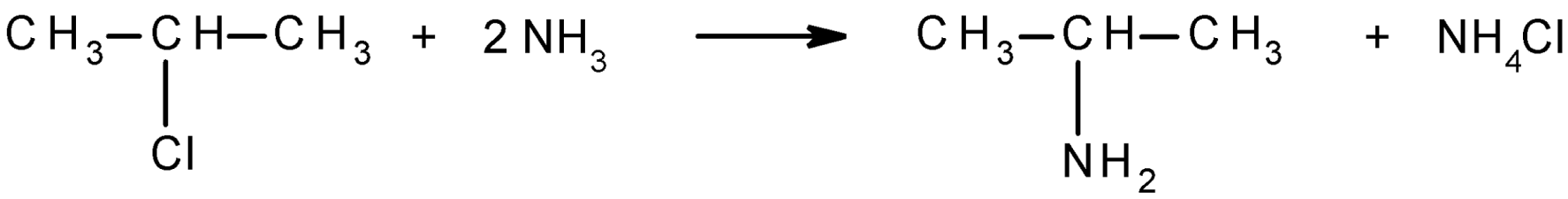
Will this reaction proceed via S_N1 or S_N2 mechanism?

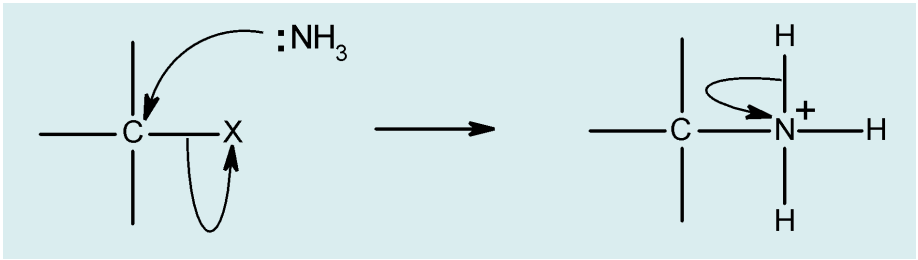
S_N2

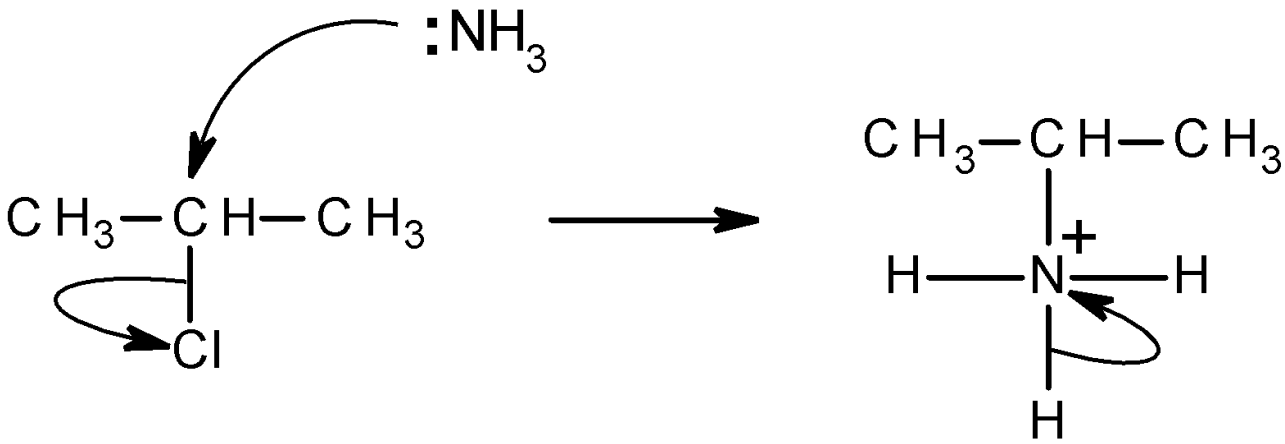
Nucleophilic substitution

e.g. 2-chloropropane + excess hot conc. NH_3



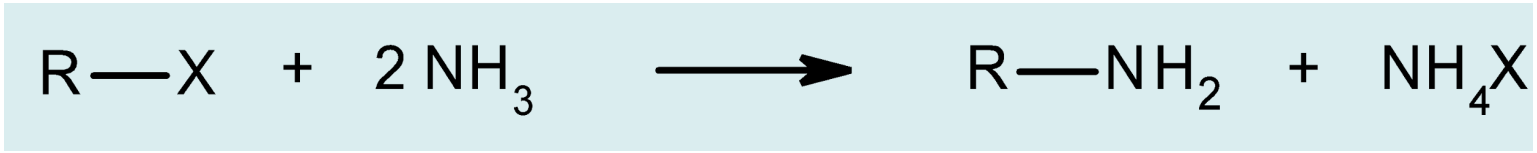


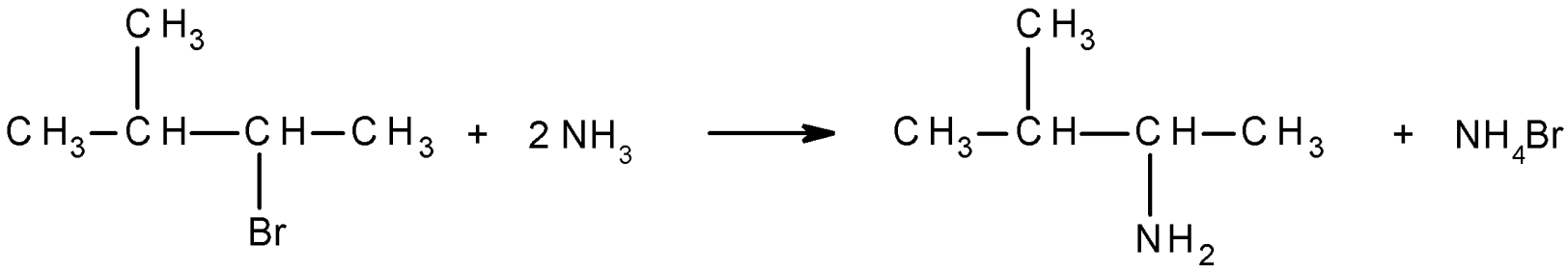


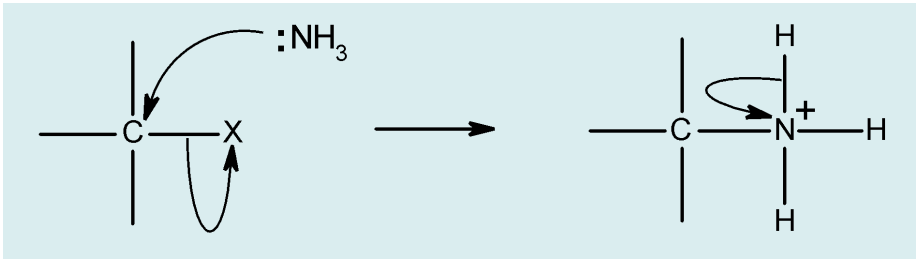


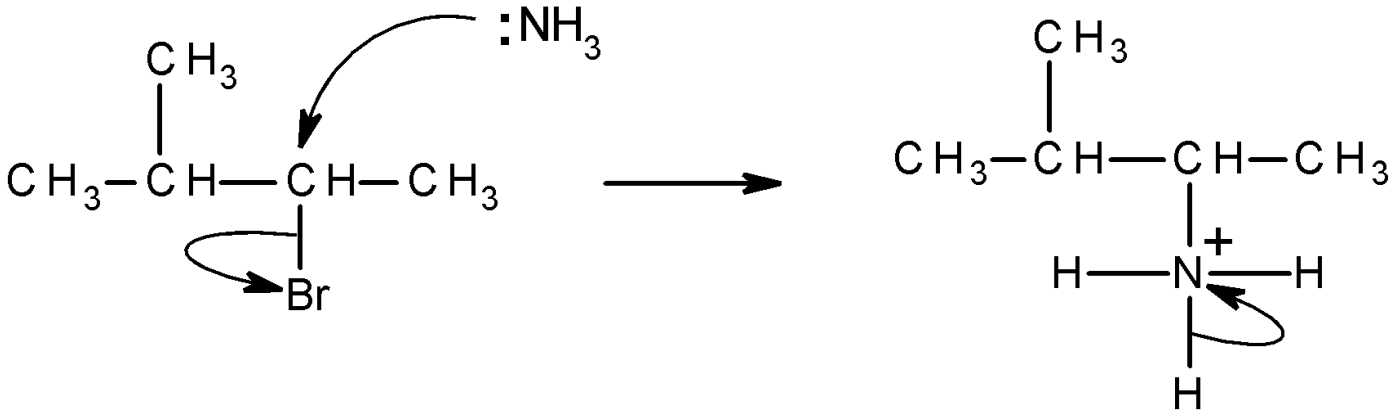
Nucleophilic substitution

e.g. 2-bromo-3-methylbutane + excess hot conc. NH_3







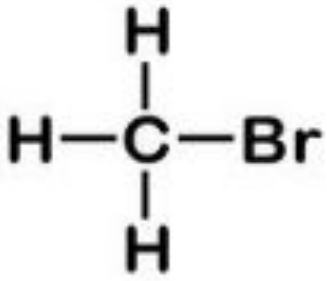
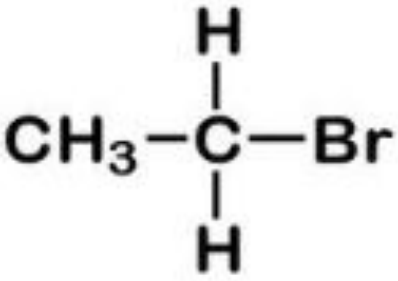
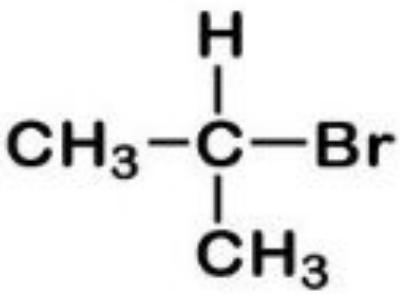
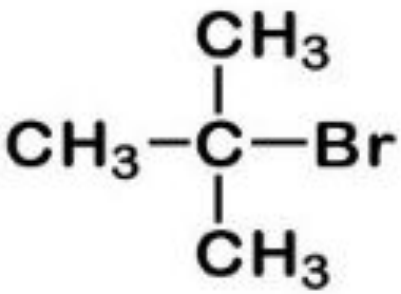


Nucleophilic substitution

Comparison between S_N1 and S_N2 mechanism

S_N1	S_N2
A two-step mechanism (as the leaving group leaves, the substrate forms a **carbocation intermediate**)	A one-step mechanism (the reaction happens in a single **transition state**)
A **unimolecular** rate-determining step (depends on haloalkane concentration only)	A **bimolecular** rate-determining step (depends on both haloalkane and nucleophile concentrations)
Reactivity order: 3^o halogenoalkane > 2^o > 1^o > methyl	**Reactivity order:** methyl > 1^o halogenoalkane > 2^o > 3^o

Summary

methyl	primary	secondary	tertiary
			
SN2	SN2	SN2 SN1	SN1

Reflection

- What has been learned
- What remained unclear
- What is necessary to work on