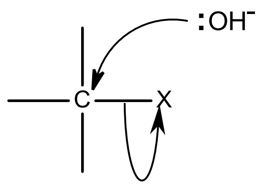
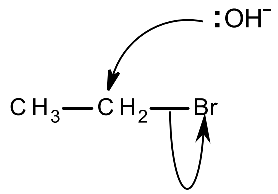
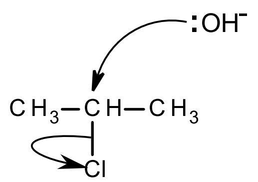
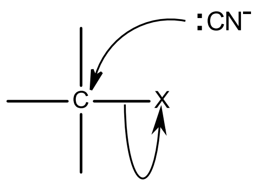
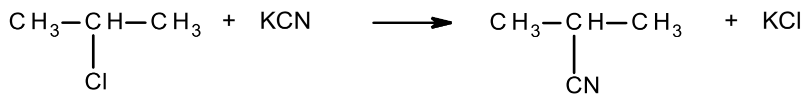
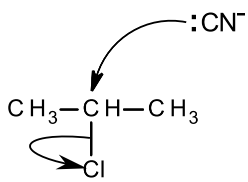
REACTIONS OF HALOGENOALKANES 1

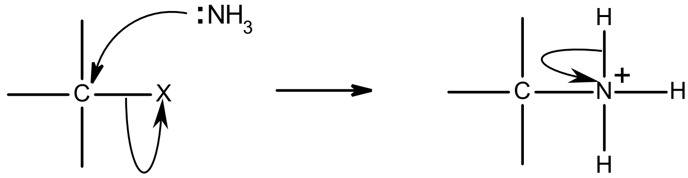
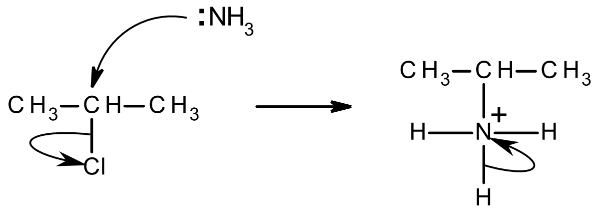
NUCLEOPHILIC SUBSTITUTION	Halogenoalkanes are susceptible to attack by **nucleophiles** (lone pair donors) such as OH^-, CN^- and NH_3. This is because the halogen atom is more electronegative than carbon atoms and so the C of the C-halogen bond is $\delta+$. In a **substitution** reaction, the halogen atom is replaced by another atom/group. The rate of the reaction is partly affected by the strength of the C-halogen bond. The longer the bond, the weaker the bond, the more easily it breaks and the faster the reaction. Therefore, in terms of rate: C-I > C-Br > C-Cl > C-F.

NUCLEOPHILIC SUBSTITUTION 1 – reaction with warm, aqueous NaOH	
Reagent	NaOH
Conditions	aqueous, warm
What happens	halogen atom is replaced by OH group
Overall equation	R—X + NaOH ⟶ R—OH + NaX
Mechanism	**nucleophilic substitution** 
Example 1	e.g. bromoethane + aqueous NaOH CH_3-CH_2-Br + NaOH ⟶ CH_3-CH_2-OH + NaBr **nucleophilic substitution** 
Example 2	e.g. 2-chloropropane + aqueous NaOH $CH_3-CH(Cl)-CH_3$ + NaOH ⟶ $CH_3-CH(OH)-CH_3$ + NaCl **nucleophilic substitution** 

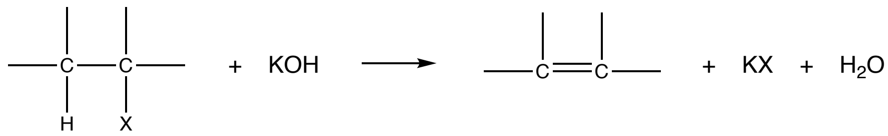
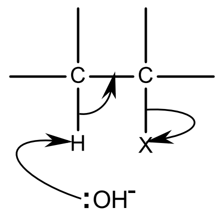
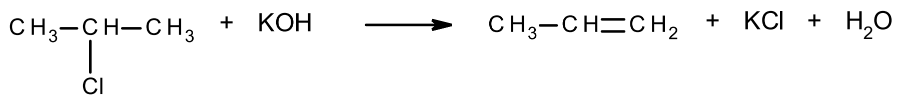
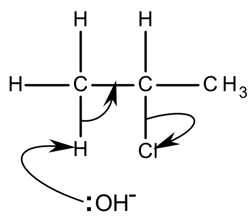
Example 3	e.g. 1-bromopropane + aqueous NaOH
Example 4	e.g. 2-iodo-3-methylbutane + aqueous NaOH

NUCLEOPHILIC SUBSTITUTION 2 – reaction with KCN	
Reagent	KCN
Conditions	Aqueous ethanol, warm
What happens	halogen atom is replaced by CN group
Overall equation	R—X + KCN ⟶ R—CN + KX
Mechanism	**nucleophilic substitution** 
Example 5	e.g. 2-chloropropane + KCN in aqueous ethanol  **nucleophilic substitution** 

Example 6	e.g. 1-bromobutane + KCN in aqueous ethanol

NUCLEOPHILIC SUBSTITUTION 3 – reaction with NH_3	
Reagent	NH_3
Conditions	Excess concentrated ammonia dissolved in ethanol at pressure in a sealed container
What happens	first molecule of NH_3: halogen atom is replaced by NH_2 group second molecule of NH_3: leads to formation of NH_4X
Overall equation	$R{-}X + 2\,NH_3 \longrightarrow R{-}NH_2 + NH_4X$
Mechanism	**nucleophilic substitution** 
Example 7	e.g. 2-chloropropane + excess conc NH_3 $CH_3{-}CH(Cl){-}CH_3 + 2\,NH_3 \longrightarrow CH_3{-}CH(NH_2){-}CH_3 + NH_4Cl$ **nucleophilic substitution** 
Example 8	e.g. 2-bromo-3-methylbutane + excess conc NH_3

ELIMINATION	When halogenoalkanes react with OH^- ions, an elimination reaction can compete with the nucleophilic substitution reaction. Elimination is favoured if hot, ethanolic KOH is used instead of warm, aqueous NaOH. In elimination, an H and X are removed from adjacent C atoms giving an alkene. In elimination, the OH^- ion acts as a base. In substitution, the OH^- ion acts as a nucleophile.

ELIMINATION – reaction with hot, ethanolic KOH	
Reagent	KOH
Conditions	Ethanolic, hot
What happens	The halogen atom and one H atom from an adjacent C atom is removed giving an alkene (note that elimination cannot happen if there is no H on an adjacent C atom). A mixture of alkenes could be formed depending on which of the adjacent C atoms the H is lost from.
Overall equation	
Mechanism	**elimination** 
Example 9	e.g. 2-chloropropane + hot, ethanolic KOH  **elimination** 
Example 10	e.g. 2-bromobutane + hot, ethanolic KOH (to give but-2-ene)