Substitution Reactions of alkyl halides

1. Substitution by hydroxyl group (Hydrolysis)

$$RX + KOH(aq) \xrightarrow{\text{Boil}} ROH + KX$$

$$CH_3CH_2Br \xrightarrow{Ag_2O/H_2O} CH_3CH_2OH + AgBr$$

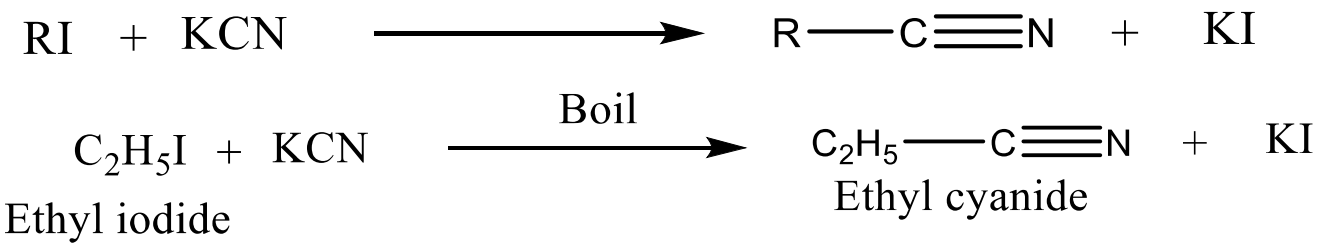
2. Subsitution by alkoxy group (Formation of Ethers)- On treatment with sodium alkoxide or dry silver oxide, ether is formed. The reaction is called ***Willamson's reaction*** *and quite useful for the synthesis of unsymmetrical ethers.*

$$\underset{\text{Alkyl halide}}{RX} + \underset{\text{Sod. alkoxide}}{R'ONa} \longrightarrow NaX + ROR'$$

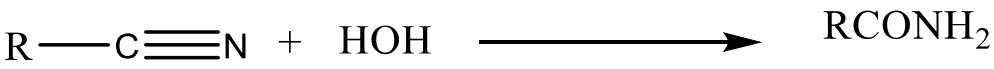
$$C_2H_5Br + C_2H_5ONa \longrightarrow C_2H_5O{-}C_2H_5 + NaBr$$

$$2C_2H_5Br + \underset{(dry)}{Ag_2O} \longrightarrow C_2H_5O{-}C_2H_5 + NaBr$$

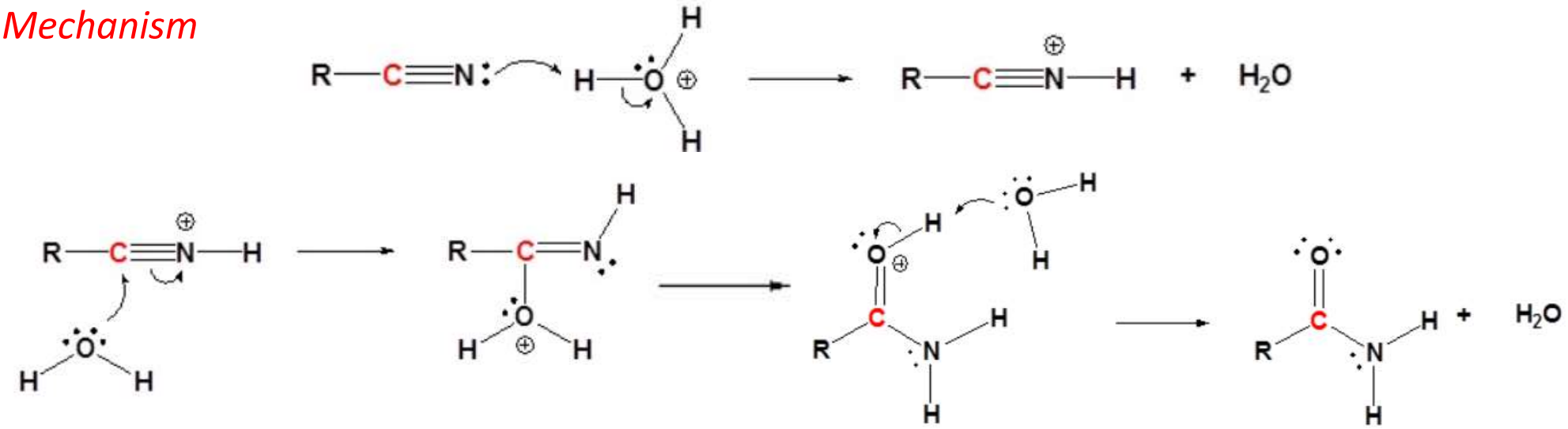
3. ***Substitution by Cyano group-*** *On heating with alcoholic solution of potassium cyanide, we get alkyl cyanide*.



(i) ***Controlled hydrolysis*** *of alkyl halide with conc. HCl (or alkaline H_2O_2) at low temperature yields amide*.

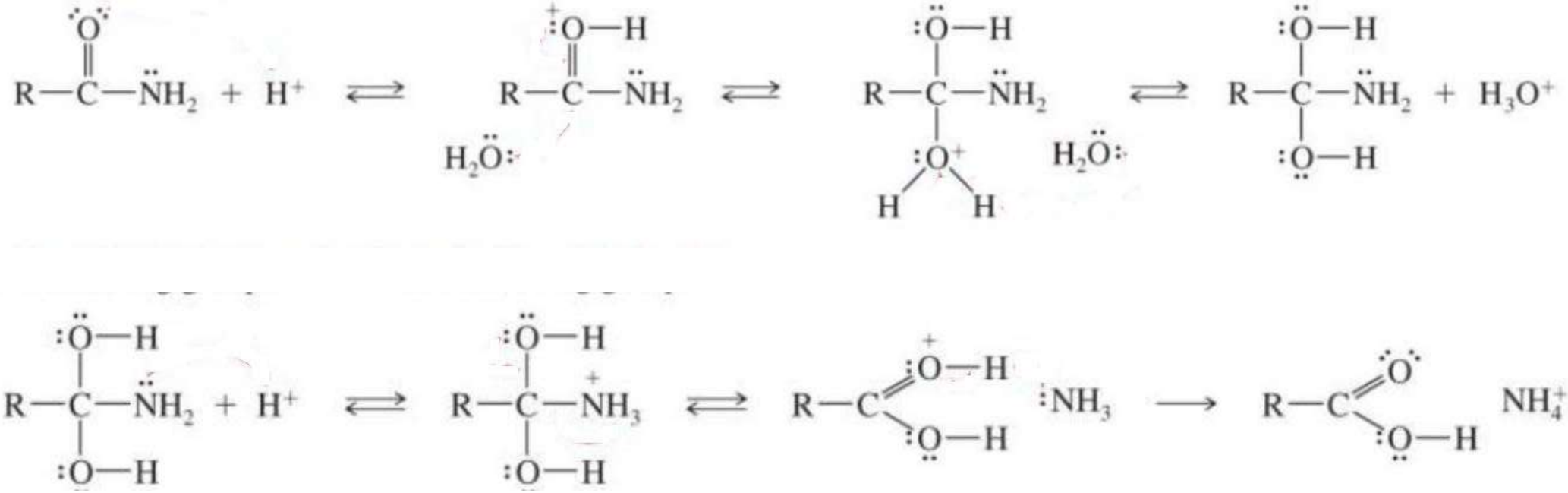


Mechanism

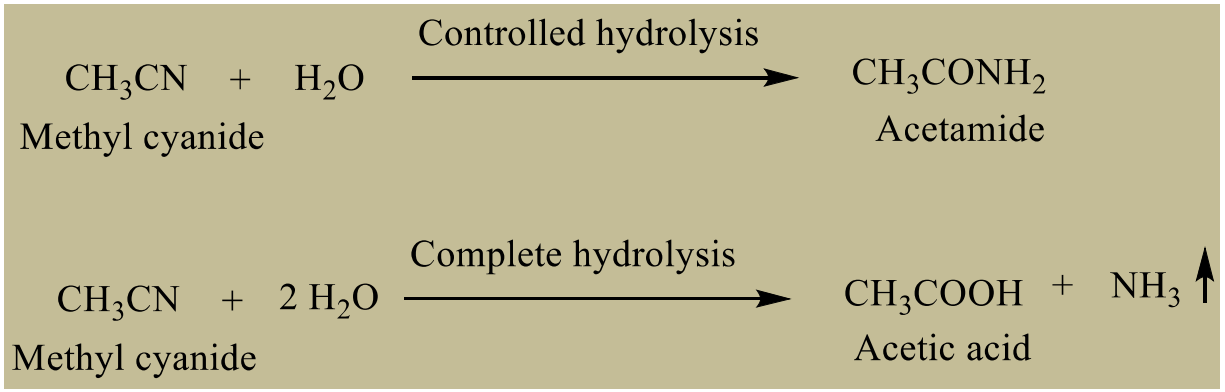


Note- An **amide** is a compound with the general formula RC(=O)NR'R", where R, R', and R" represent organic groups or hydrogen atoms

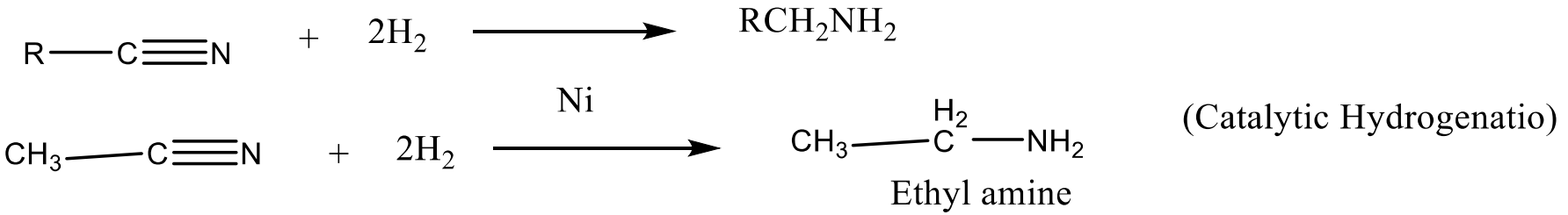
(ii) ***Complete hydrolysis*** *of alkyl cyanide on boiling with dilute acid, yield an acid*.



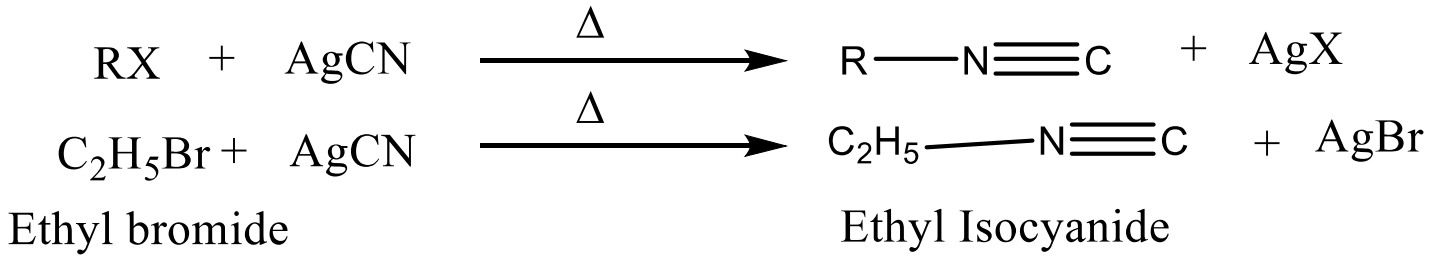
Source- 2010 Pearson Prentice Hall, Inc.



(iii) *Alkyl cyanide can also be reduced to primary amines by heating with hydrogen in presence of Nickel*

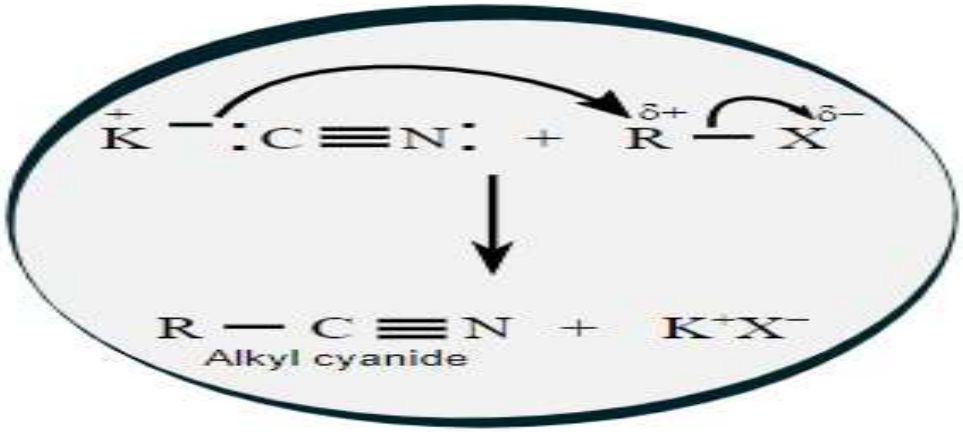


3. ***Substitution by Isocyanide group-*** *Alkyl halide on reaction with silver cyanide at high temperature yields alkyl isocyanide.*

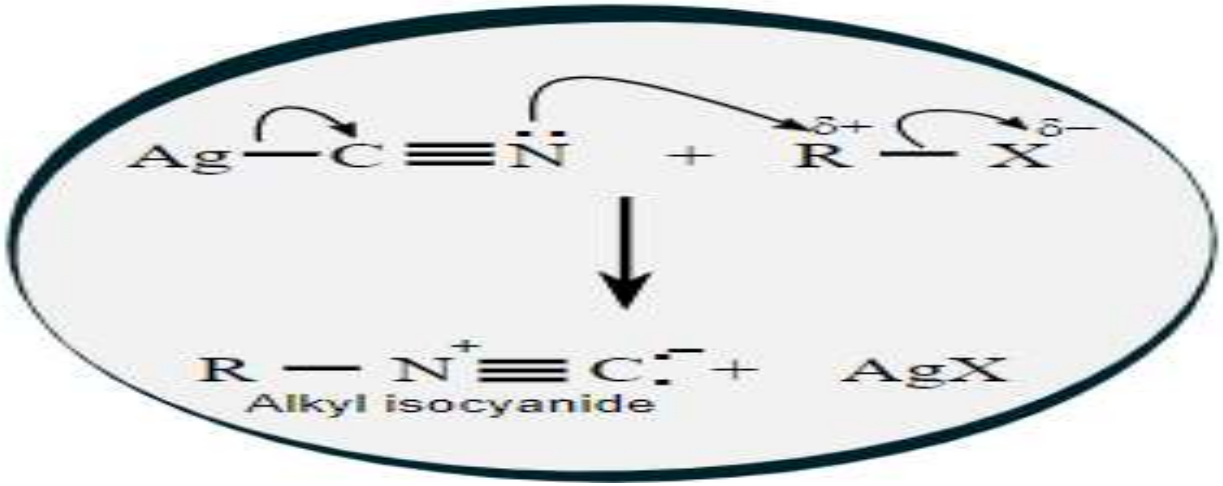


Note- *Alkyl halides give alkyl cyanides with Potassium cyanide* (*KCN*) *but alkyl isocyanides with Silver cyanide* (*AgCN*).

Reason- *KCN is predominately ionic, in solution it gives cyanide ion. In cyanide ion both carbon and nitrogen can donate electrons but reaction takes place through carbon atom since C-C bond is stronger than C-N bond*



On the other hand AgCN is predominantly covalent. Therefore, only nitrogen electron pair is available for bond formation. As a result, alkyl isocyanides are obtained as major products.



5. **Action of silver acetate**- *Alkyl halide reacts with silver acetate to form ester*

$$RI + CH_3COOAg \xrightarrow{\Delta} CH_3COOR + AgI$$

$$CH_3I + CH_3COOAg \xrightarrow{\Delta} CH_3COOCH_3 + AgI$$

Methyl iodide — Methyl acetate

6. **Substitution by amino group**-

a) *When alkyl halide is in small amount, primary amines result*

$$CH_3CH_2Br + HNH_2 \longrightarrow CH_3CH_2NH_2 + HI$$

Ethyl bromide — Ethyl amine (1^o)

b) *When alkyl halide is in excess, then a mixture of amine (1^o, 2^o and 3^o) get formed. The tertiary amine further reacts with alkyl halide to form a quaternary salt*.

$$C_2H_5I + HNH_2 \longrightarrow C_2H_5NH_2 + HI$$

Ethyl bromide — Ethyl amine (1^o)

$$C_2H_5I + C_2H_5NH_2 \longrightarrow (C_2H_5)_2NH + HI$$

Diethyl amine (2^o)

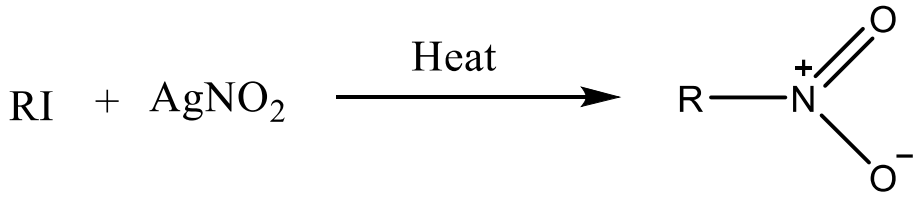
$$C_2H_5I + (C_2H_5)_2NH \longrightarrow (C_2H_5)_3N + HI$$

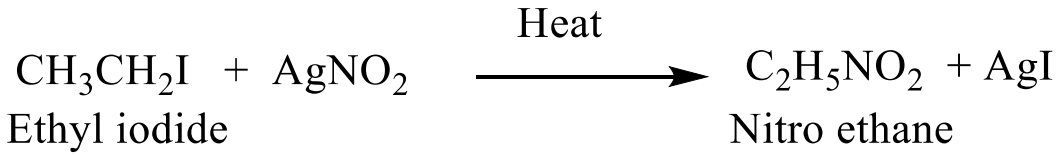
Triethyl amine (3^o)

$$C_2H_5I + (C_2H_5)_3N \longrightarrow [(C_2H_5)_4N]^+I^-$$

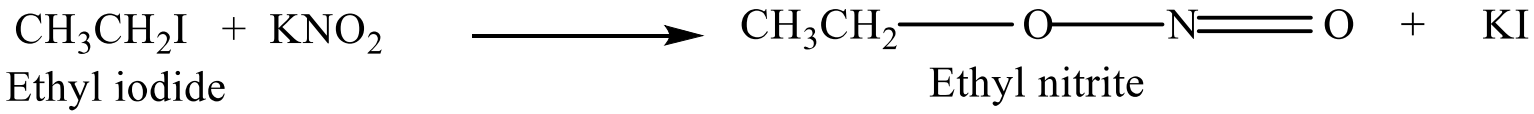
Tetraethyl ammonium iodide (4^o)

7. ***Subsitution by nitro group (formation of Nitroalkanes)***- *When heated with silver nitrite, nitroalkane results.*

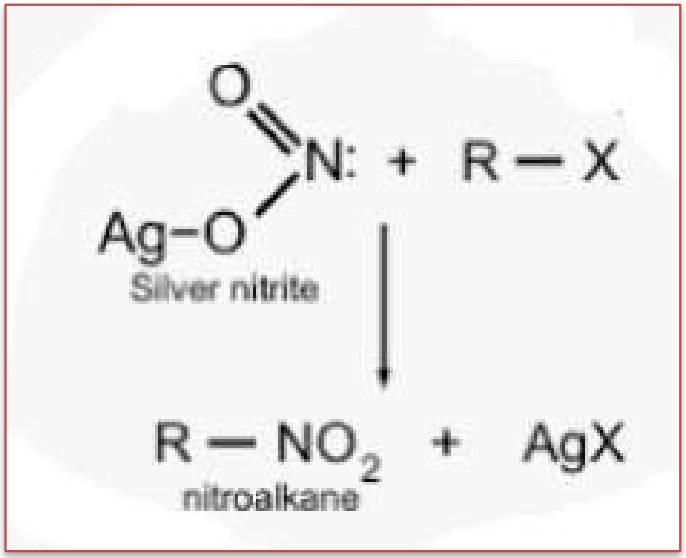


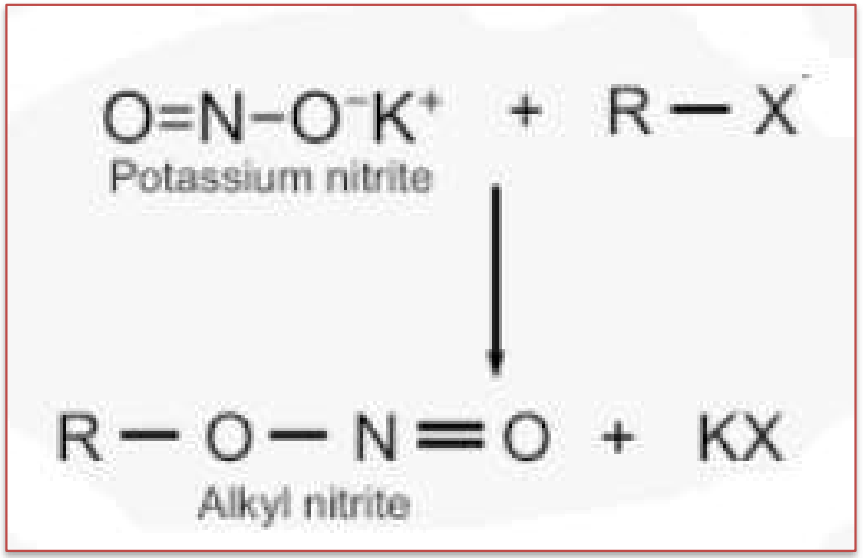


8. ***Subsitution by nitrite group (formation of alkyl nitrites)***- *On treatment with aqueous solution of potassium nitrite, we get alkyl nitrite.*



Note- *Alkyl halides give nitroalkane with Silver nitrite* ($AgNO_2$) *but with potassium nitrite* (KNO_2), *it give alkyl nitrite*.





Reason- *KNO_2 is predominately ionic, nucleophilic attack by the oxygen bearing negative charge mainly gives alkyl nitrites. On the other hand, $AgNO_2$ is a covalent compound and both oxygen and nitrogen atoms carry lone pair of electrons. Since nitrogen is less electronegative than oxygen, lone pair of electrons on nitrogen is more available for bond formation. As a result, nitroalkane is the dominant product*.