The role of dry HCl is it protonates the oxygen atom of carbonyl compounds and therefore encreases the electrophilic character of carbonyl carbon.

$$\underset{\text{(Aldehyde)}}{\overset{R}{\underset{H}{>}}C=O} + \underset{\text{Monohydric alcohol).}}{R'-OH} \xrightleftharpoons{HCl\ gas} \underset{\text{(Hemiacetal)}}{\overset{R}{\underset{H}{>}}C(OR')(OH)} \xrightleftharpoons[HCl\ gas]{R'OH} \underset{\text{Acetal (gem-dialkoxy Compound)}}{\overset{R}{\underset{H}{>}}C(OR')_2} + H_2O$$

(Alkoxy alcohol)

$$\overset{R}{\underset{R}{>}}C=O + \underset{CH_2-OH}{\overset{CH_2-OH}{|}} \xrightarrow[\text{dil. HCl.}]{HCl\ gas} \overset{R}{\underset{R}{>}}C\underset{O-CH_2}{\overset{O-CH_2}{|}} + H_2O.$$

(B) Nucleophilic addition reaction followed by elemination:

Addition of ammonia & their derivatives:

The derevative of NH_3 are five mainly in which one hydrogen of NH_3 is removed and other part is added (which is also called Z).

The derivative of NH_3 are as follows

1. Ammonia — NH_3 or NH_2-H
2. Hydroxylamine: NH_2-OH
3. Hydrazine NH_2-NH_2
4. Phenyl hydrazine $NH_2-NH\cdot C_6H_5$ or $NH_2-NH-C_6H_5$
5. 2,4 dinitrophenyl hydrazine: $NH_2-NH-C_6H_3(NO_2)_2$ (2,4 DNP)
6. Semicarbazide $NH_2-NH-CONH_2$

During reaction H_2 of above Compound will combine with 'O' of C=O & it will

be eliminated in the form of water and test part will be added (Must contain C=N) to form final product.

The chemical reactions are as follows:-

~~Test for Carbonyl~~:-

1. With Ammonia:- It form Imine.

$$>C=O + H_2N-H \longrightarrow >C=NH + H_2O$$

Aldehyde/Ketone — Ammonia — Imine

2. With hydroxylamine:- It form oxime.

$$>C=O + H_2N.OH \longrightarrow >C=N.OH + H_2O$$

Aldehyde/Ketone — Hydroxylamine — oxime.

3. With hydrazine:- It form hydrazone.

$$>C=O + H_2N.NH_2 \longrightarrow >C=N.NH_2 + H_2O$$

Aldehyde/Ketone — Hydrazine — Hydrazone.

4. With Phenylhydrazine:- It form phenyl hydrazone.

$$>C=O + H_2N.NH-C_6H_5 \longrightarrow >C=N.NH-C_6H_5 + H_2O$$

Aldehyde/Ketone — Phenylhydrazine — Phenylhydrazone.

5. With 2,4-dinitrophenylhydrazine:- It forms 2,4-dinitrophenylhydrazone.

$$>C=O + H_2N-NH-C_6H_3(NO_2)_2 \longrightarrow >C=N.NH-C_6H_3(NO_2)_2 + H_2O$$

Aldehyde/Ketone — (2,4 DNP) — 2,4-dinitrophenyl hydrazone.

Note: The Colour of 2,4-DNP dinitrophenyl hydrazone may have red, orange or yellow (ROY) Colour.

6. With Semicarbazide :- It forms Semicarbazone.

$>C=O + H_2N\cdot NH\cdot CONH_2 \longrightarrow >C=N\cdot NH\cdot CONH_2 + H_2O$

Aldehyde / Ketone — Semicarbazide — Semicarbazone

[C] Reduction reaction :-

When Aldehyde or ketone is reduced then it may form alcohol or alkane which depends on the type of reagent. For example in presence of LiAlH4, NaBH4, Na/C2H5OH, H2/Ni or Pt or Pd Aldehyde or Ketone is reduced to Alcohol but in presence of Na-Hg/HCl, NH_2-NH_2/KOH/Glycol, HI/Red P it form alkane. Reagent in presence of LiAlH4/NaBH4/Na/C2H5OH/H2/Ni, Pd, Pt →

$H-\overset{O}{\overset{\|}{C}}-H + 2[H] \xrightarrow[\text{or } H_2/Ni]{LiAlH_4 \text{ or } NaBH_4} CH_3-OH$

Methanal — Methanol (1° Alc)

$CH_3-\overset{O}{\overset{\|}{C}}-H + 2[H] \xrightarrow[\text{or } H_2/Ni]{LiAlH_4 \text{ or } NaBH_4} CH_3-CH_2-OH$

(Ethanol) (1° Alc)

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 2[H] \xrightarrow[\text{or } H_2/Ni]{LiAlH_4 \text{ or } NaBH_4} CH_3-\overset{OH}{\overset{|}{C}}H-CH_3$

(Propane 2-ol) (2° Alc)

Note: On reduction in presence of LiAlH4 or NaBH4 or H2/Ni or Pd or Pt aldehyde is reduced to 1° Alcohol whereas ketone is reduced to 2° Alcohol.

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Reduction in presence of Zn-Hg or Na-Hg | HCl or NH_2-NH_2 | KOH | Glycol :-

1. Clemmensen reduction: When aldehyde or ketone is reduced in presence of Zinc-Amalgum (Zn-Hg) or Na-Hg | HCl then alkane is formed.

$$>C=O + 4[H] \xrightarrow[HCl]{Zn-Hg} >CH_2 + H_2O$$
(Alkane)

2. Wolf Kishner reduction → When Aldehyde or ketone is reduced in presence of NH_2-NH_2 first it form hydrazone and further when treated in presence of KOH or NaOH | Ethylene Glycol & Heat it gives alkane & N_2.

$$>C=O + H_2N\cdot NH_2 \xrightarrow{-H_2O} >C=N\cdot NH_2 \xrightarrow[\Delta]{KOH/Glycol} >CH_2 + N_2$$
Hydrazone

(D) Oxidation :→

Oxidation of Aldehyde and ketone is possible by two types of oxidising agent one is strong oxidising agent i.e $KMnO_4$ or $K_2Cr_2O_7$ | H+ and other is by weak oxidising agent like Tollen's reagent $[Ag(NH_3)_2]^+$ & Fehling solution (A mixture of Na-K-tartarate & Cuso4 solution) in basic medium.

Imp Note : Tollen's reagent $[Ag(NH_3)_2]^+$ & Fehling solution (equimolar mixture of Na-K tartarate & $CuSO_4$ solution) are used to identify Aldehyde & Ketone. Aldehyde gives positive test of Tollen's reagent & Fehling solution whereas Ketone do not respond for this, in this way we can identify Aldehyde & Ketone.

When aldehyde is oxidised in presence of $KMnO_4$ or $K_2Cr_2O_7/H^+$ then it gives carboxylic acid having same no. of carbon atom, but when ketone is oxidised by strong oxidising agent like $KMnO_4$ or $K_2Cr_2O_7$ in acidic medium it gives carboxylic acid but no. of carbon atom decreases by one.

$$R-CHO + [O] \xrightarrow{KMnO_4} R-COOH \text{ or } R-\overset{O}{\overset{\|}{C}}-OH$$

$$CH_3-CHO + [O] \xrightarrow{KMnO_4} R-\overset{O}{\overset{\|}{C}}-OH$$

$$CH_3-\overset{2}{\overset{O}{\overset{\|}{C}}}-\overset{3}{CH_3} + [O] \xrightarrow{KMnO_4} \overset{2}{CH_3}-\overset{1}{\overset{O}{\overset{\|}{C}}}-OH.$$

Tollen's test :→ Ammonical silver nitrate solution ($NH_4OH + AgNO_3$) is called Tollen's reagent. NH_4OH & $AgNO_3$ on combination gives a complex compound i.e $[Ag(NH_3)_2]^+$ is also called Tollen's reagent.

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Tollen's reagent is a kind of ~~reagent~~ mild or weak oxidising agent which convert R-CHO to R-COO⁻ (carboxylate) & give silver mirror (Ag↓) which is the test of Aldehyde, because ketone do not give this test. Reaction take place in basic medium.

$$R-\overset{O}{\overset{\|}{C}}-H + 2[Ag(NH_3)_2]^{+} + 3OH^- \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^- + 2Ag\downarrow + 4NH_3 + H_2O$$

$$R-\overset{O}{\overset{\|}{C}}-R + 2[Ag(NH_3)_2]^{+} + 3OH^- \longrightarrow \text{No reaction. (Silver mirror)}$$

Fehling solution test :→

Na-K-tartarate (Rochelle salt) & $CuSO_4$ solution are mixed in equimolar ratio, this mixture is called Fehling solution, which oxidises to Aldehyde & give carboxylate ion including red ppt of Cu_2O, which is the test for aldehyde, ketone do not give this test.

$$R-\overset{O}{\overset{\|}{C}}-H + 2Cu^{2+} + 5OH^- \longrightarrow R-COO^- + Cu_2O + 3H_2O$$

(Red ppt)

$$R-\overset{O}{\overset{\|}{C}}-H + 2Cu^{2+} + 5OH^- \longrightarrow \text{No reaction.}$$