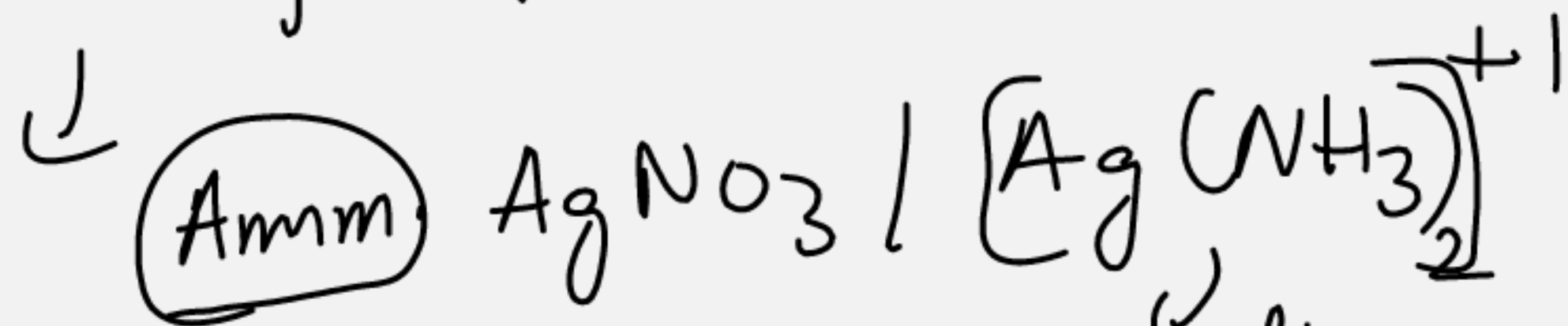
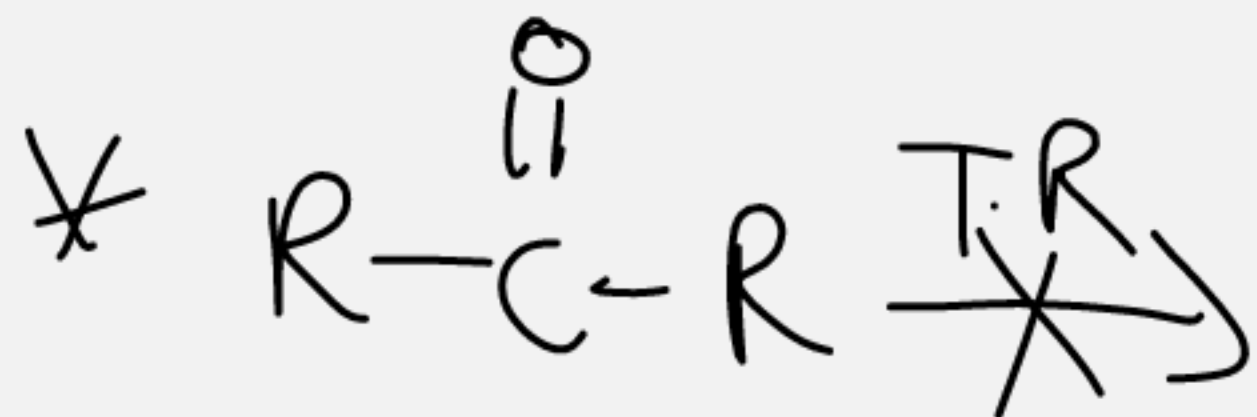
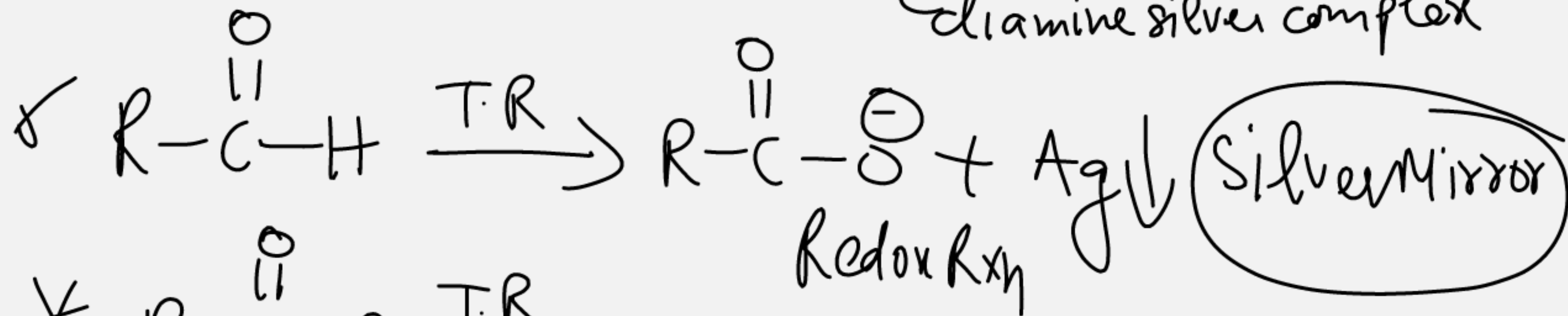


Test for Aldehydes

① Tollen's Reagent / Test



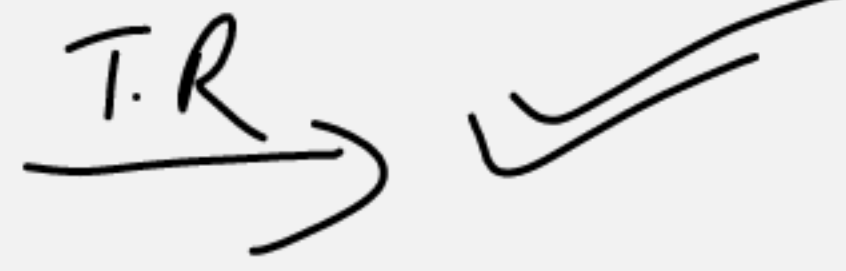
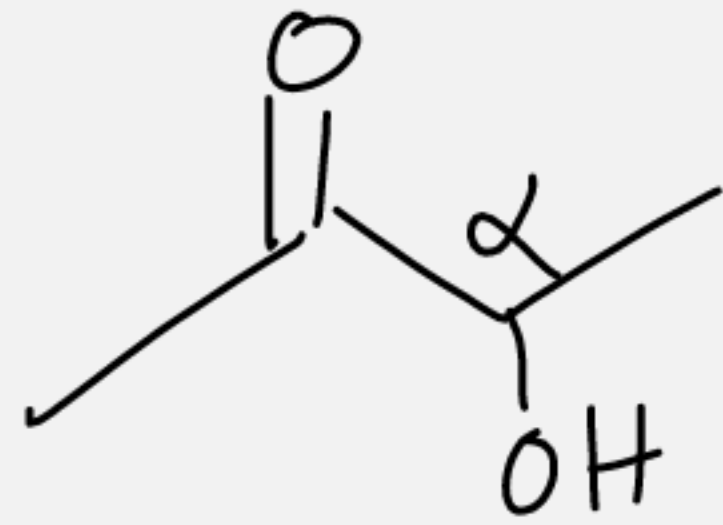
↓ diamine silver complex



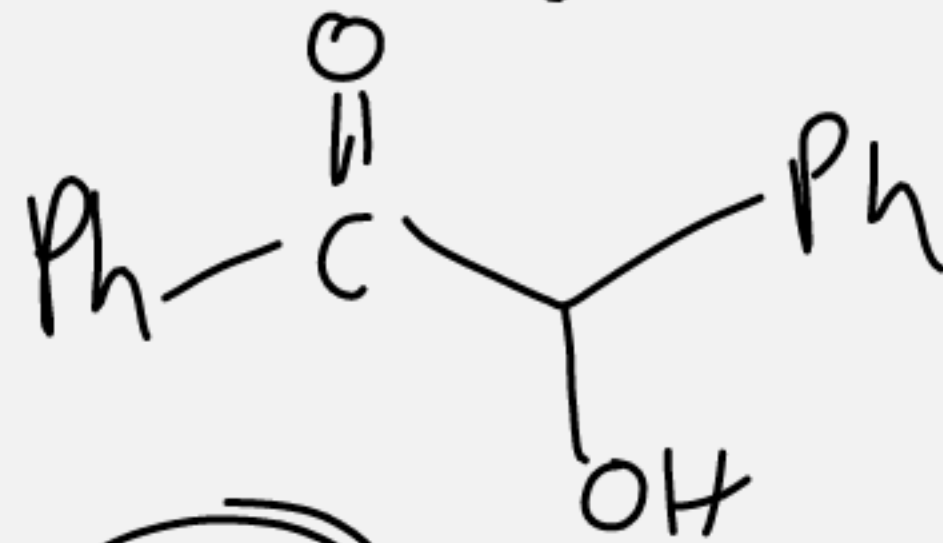
~~except~~

Exception

①



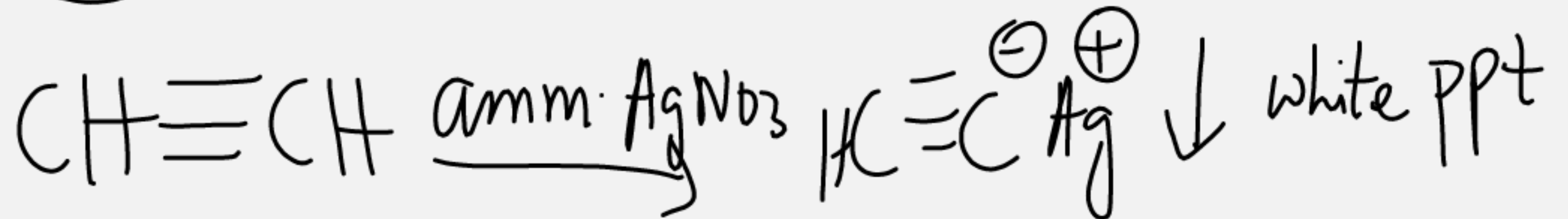
α -hydroxy Carbonyl

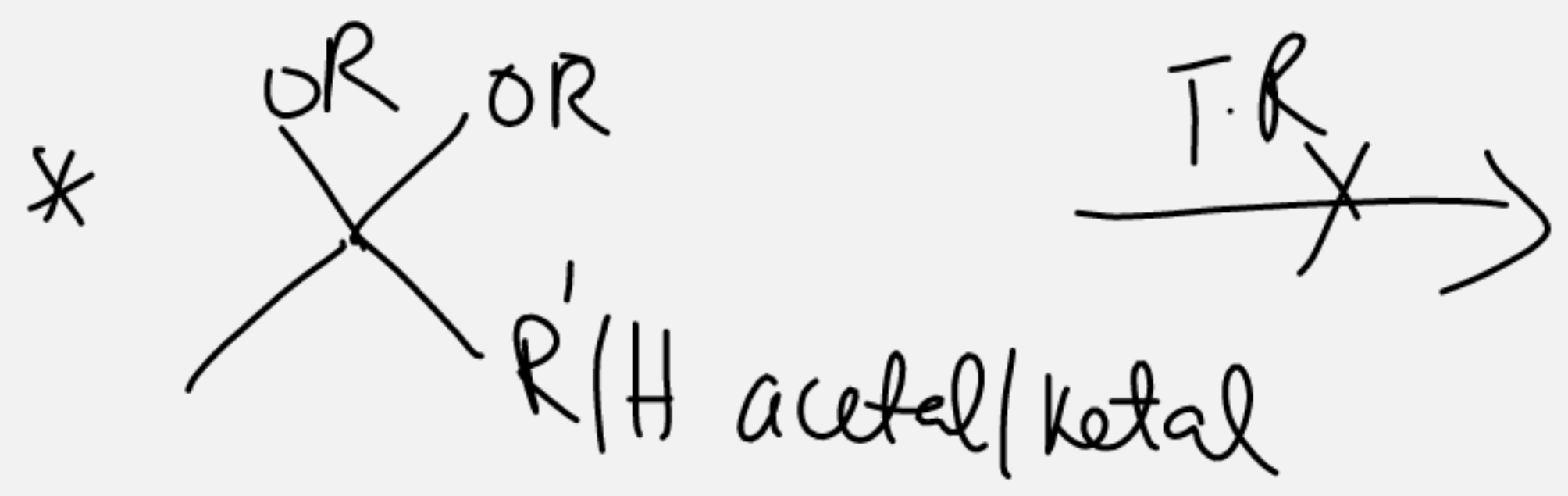


②



③

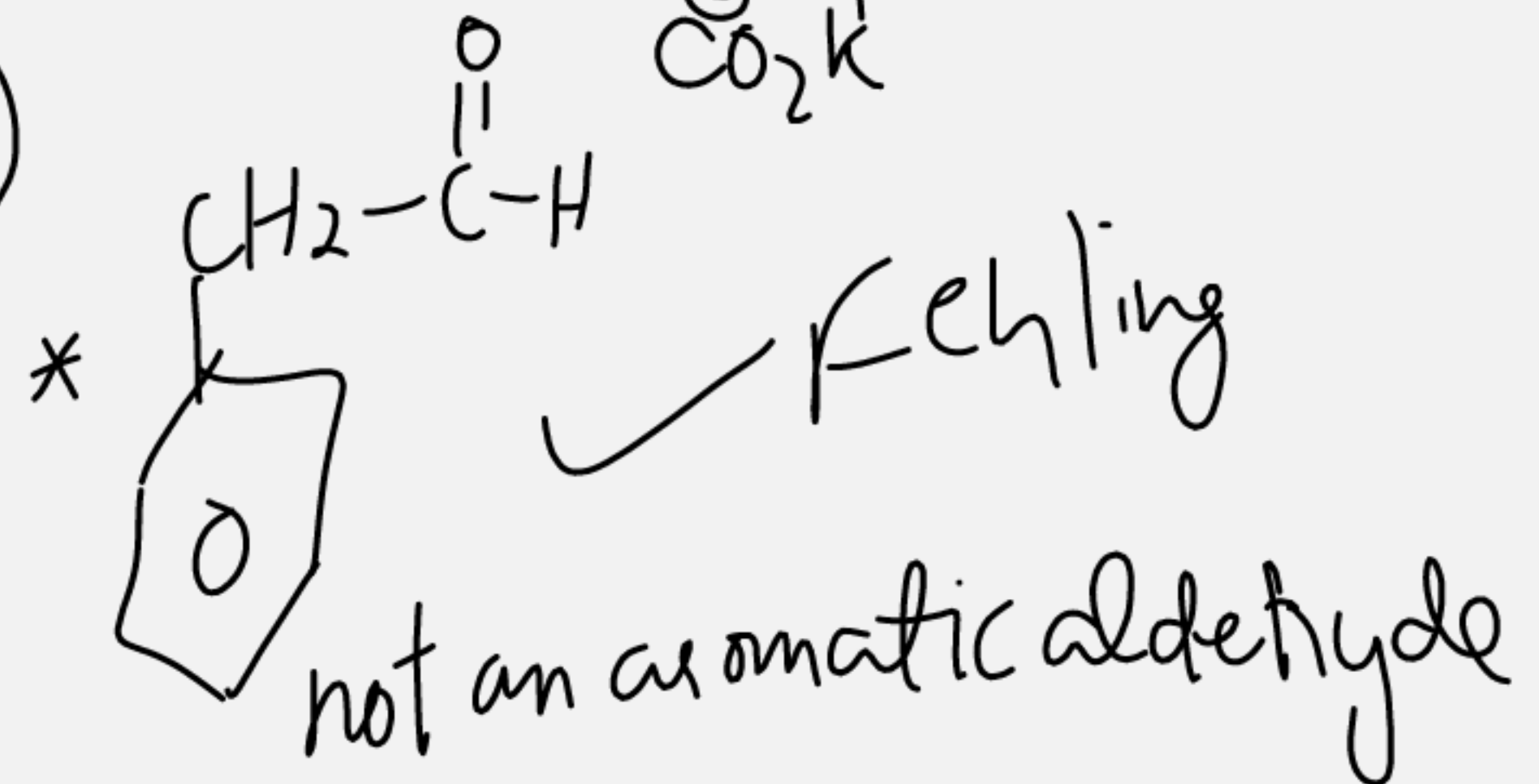
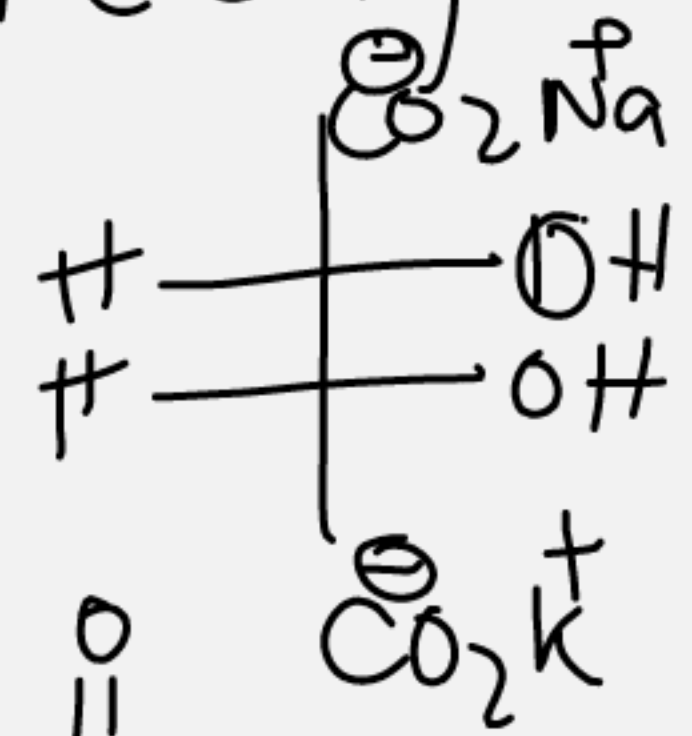
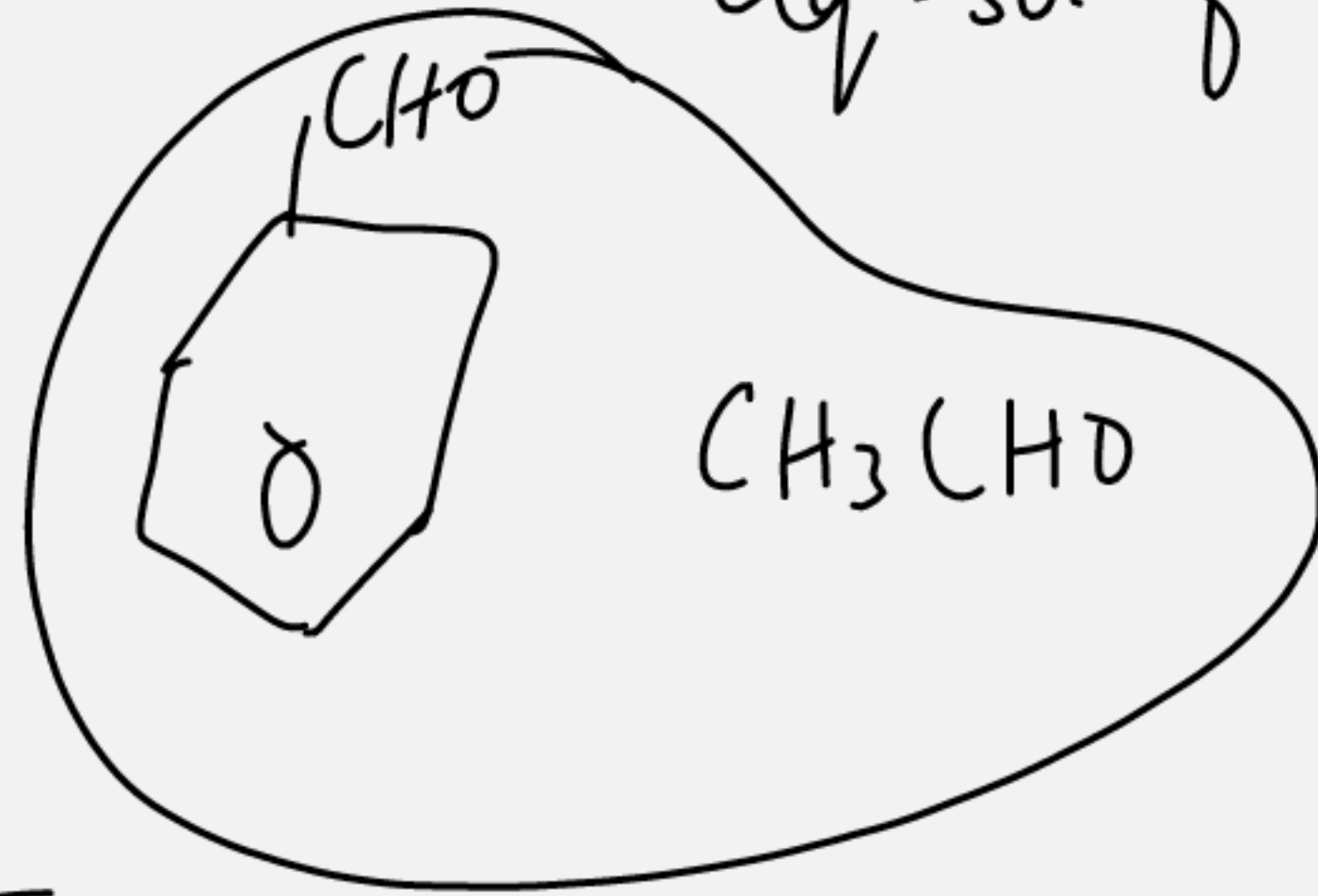




Stable in basic medium.

Fehling Test

Fehling Reagent = Fehling sol. A + Fehling sol. B
aq. soln of CuSO_4



Benedict Test

Same as Fehling

CuSO_4 + citric acid

Obs \rightarrow Cu_2O ↓ red ppt

* 2,4 DNP Test (Brady's Reagent)

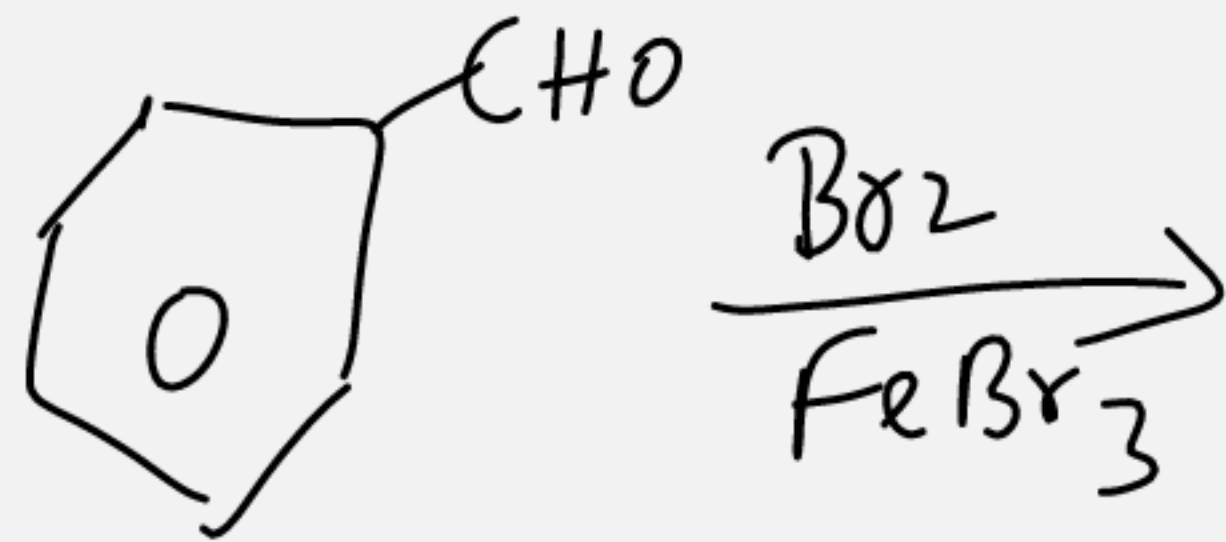
* Schiff Reagent → To differentiate b/w aldehyde & ketone
Obs → pink colour when it is aldehyde

Biomolecules

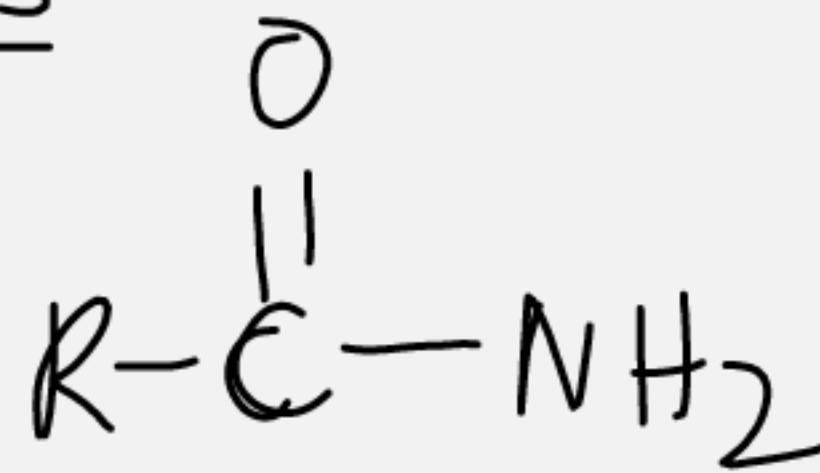
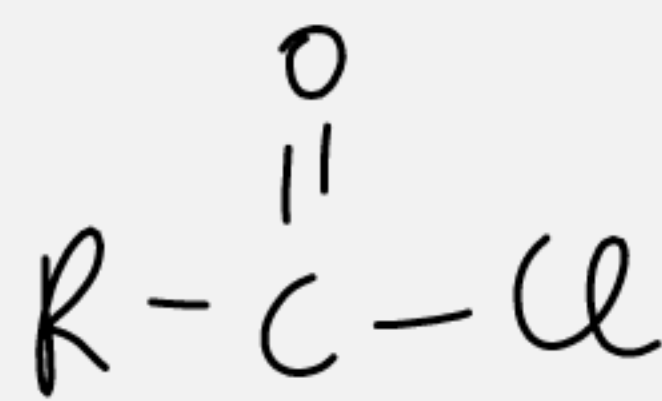
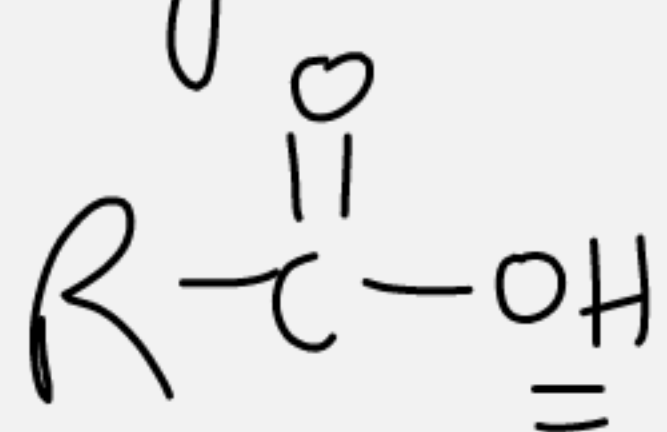
* Biuret test ⇒ Test for protein & peptide
↓
polypeptide

* Ninhydrin Test ⇒ || || Protein & Amino Acid

Obs → deep Purple anion (Ruhman's Purple)



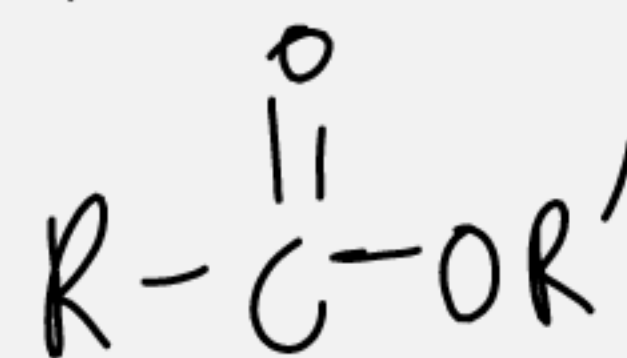
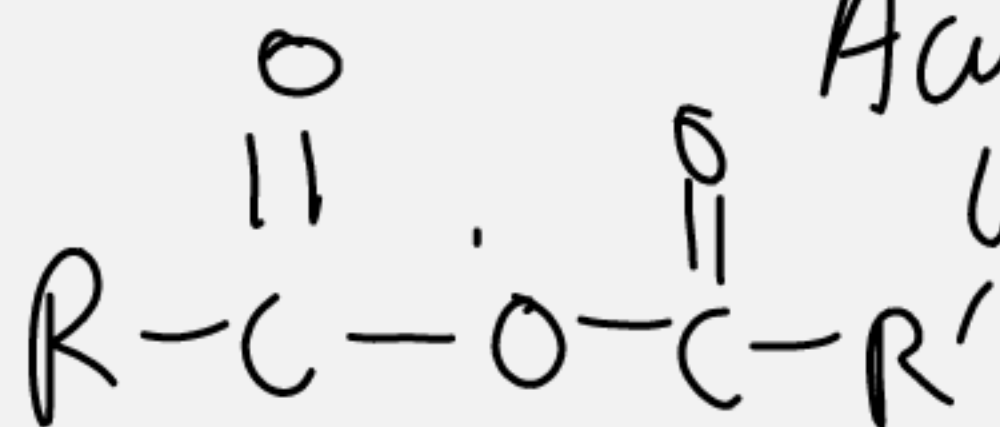
Carbonylic Acid & Derivatives



Acid chloride

Amide

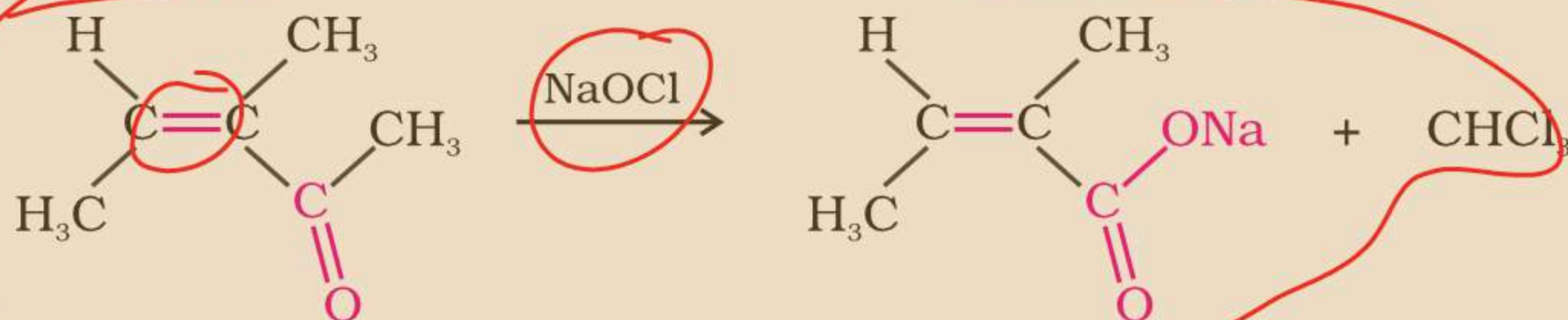
Acyl chloride



Ester

anhydride

are oxidised by sodium hypohalite to sodium salts of



corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to haloform. This oxidation does not affect a carbon-carbon double bond, if present in the molecule.

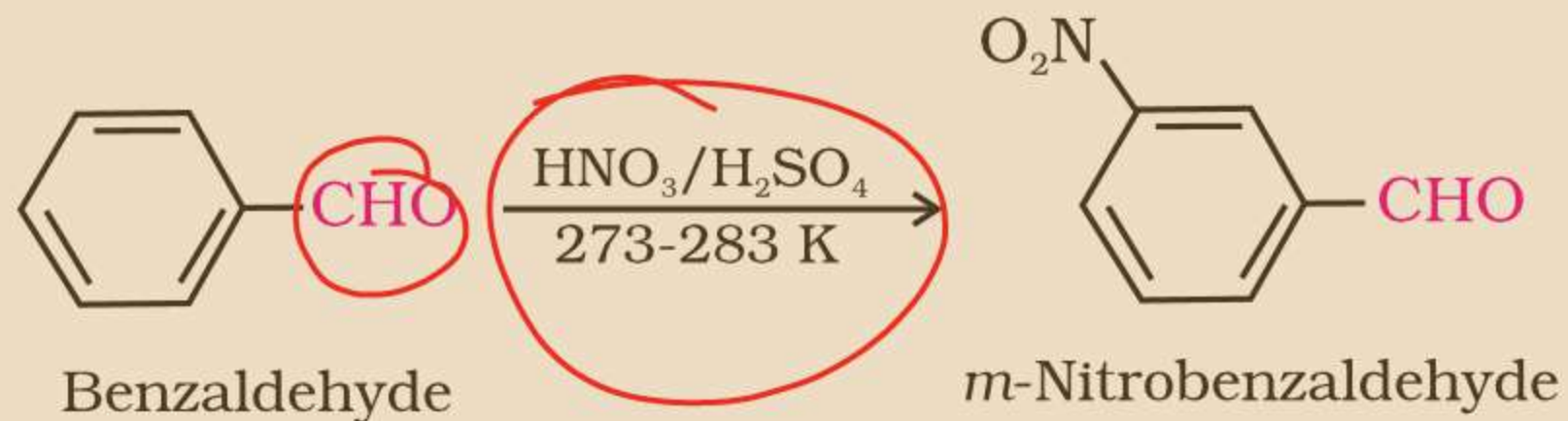
Iodoform reaction with sodium hypoiodite is also used for detection of CH_3CO group or $\text{CH}_3\text{CH}(\text{OH})$ group which produces CH_3CO group on oxidation.

Example 12.4

An organic compound (A) with molecular formula $\text{C}_8\text{H}_8\text{O}$ forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula $\text{C}_7\text{H}_6\text{O}_2$. Identify the compounds (A) and (B) and explain the reactions involved.



- (ii) *Electrophilic substitution reaction:* Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta*-directing group.



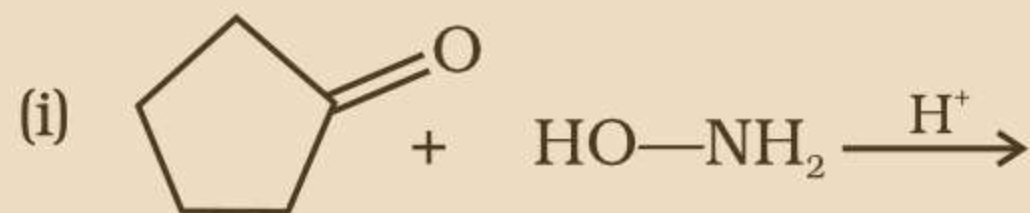
Intext Questions

12.4 Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

- (i) Ethanal, Propanal, Propanone, Butanone.
 (ii) Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone.

Hint: Consider steric effect and electronic effect.

12.5 Predict the products of the following reactions:



Benzene

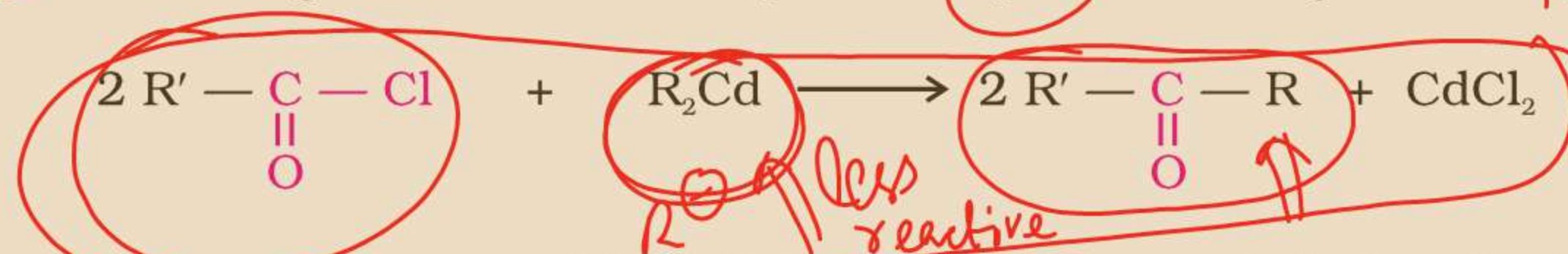
Benzaldehyde

This reaction is known as **Gatterman-Koch** reaction.

12.2.3 Preparation of Ketones

1. From acyl chlorides

Treatment of acyl chlorides with dialkylcadmium, prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones.

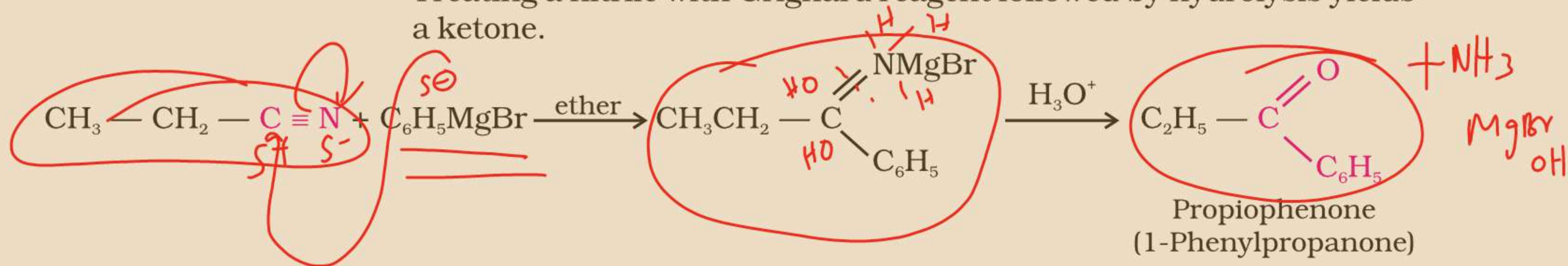


363 Aldehydes, Ketones and Carboxylic Acids



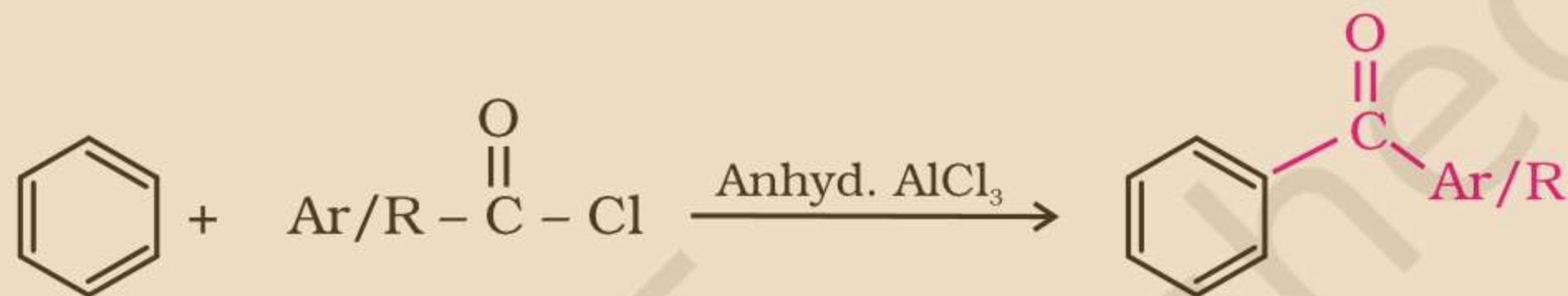
2. From nitriles

Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.



3. From benzene or substituted benzenes

When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, it affords the corresponding ketone. This reaction is known as **Friedel-Crafts acylation reaction**.



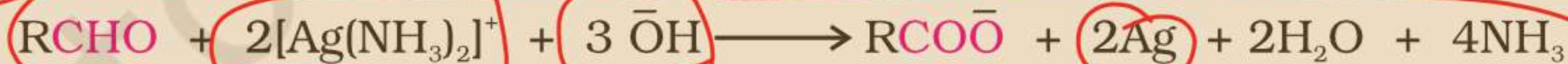
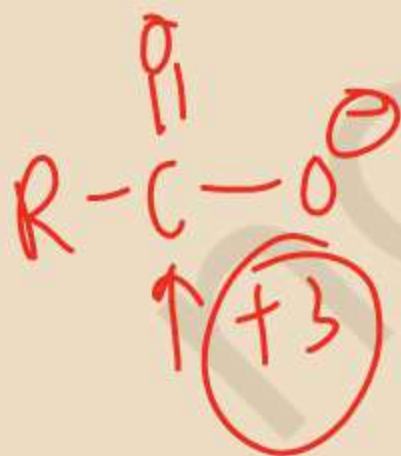
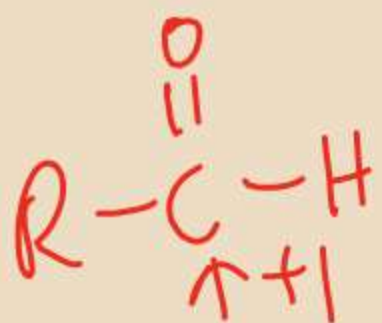
Example 12.1

Give names of the reagents to bring about the following transformations:



The mild oxidising agents given below are used to distinguish aldehydes from ketones:



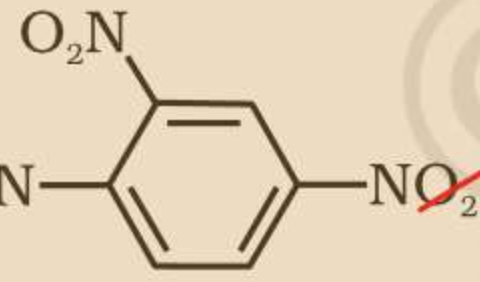
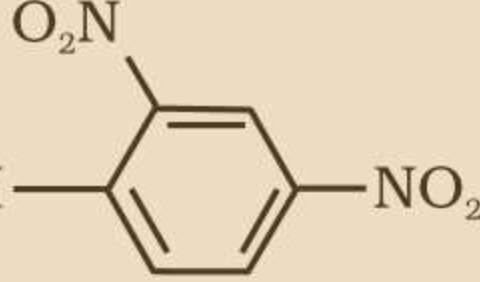
(i) *Tollens' test*: On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.



(ii) *Fehling's test*: Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are oxidised to corresponding carboxylate anion.

* Aromatic aldehydes do not respond to this test.



—OH	Hydroxylamine	>C=N—OH	Oxime
—NH_2	Hydrazine	>C=N—NH_2	Hydrazone
—HN— 	Phenylhydrazine	>C=N—NH— 	Phenylhydrazone
—HN— 	2,4-Dinitrophenylhydrazine	>C=N—NH— 	2,4 Dinitrophenylhydrazone
—NH—C(=O)—NH_2	Semicarbazide	$\text{>C=N—NH—C(=O)—NH}_2$	Semicarbazone

* 2,4-DNP-derivatives are yellow, orange or red solids, useful for characterisation of aldehydes and ketones.

2. Reduction

- (i) *Reduction to alcohols:* Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride (NaBH_4) or lithium aluminium hydride (LiAlH_4) as well as by catalytic hydrogenation (Unit 11, Class XII).
- (ii) *Reduction to hydrocarbons:* The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc-

