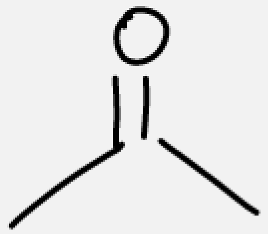
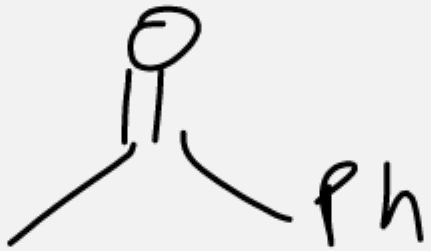
Q. Which of the following will react with NH_2OH (hydroxyl amine) to produce 2 oximes (including S.I)

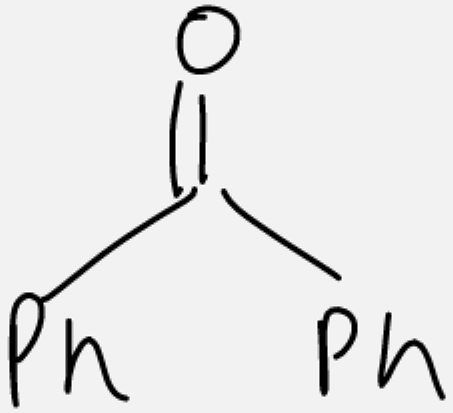
a)

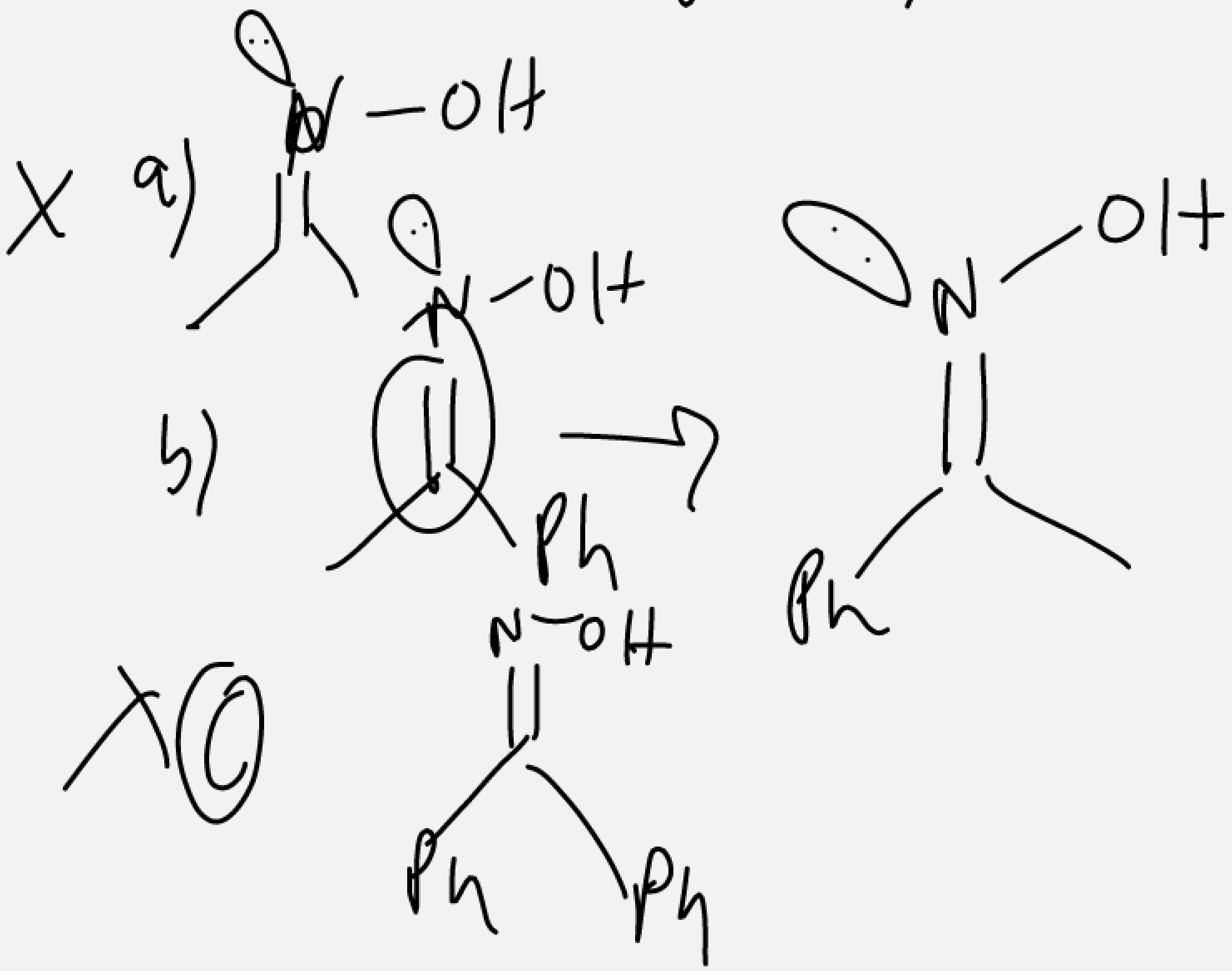


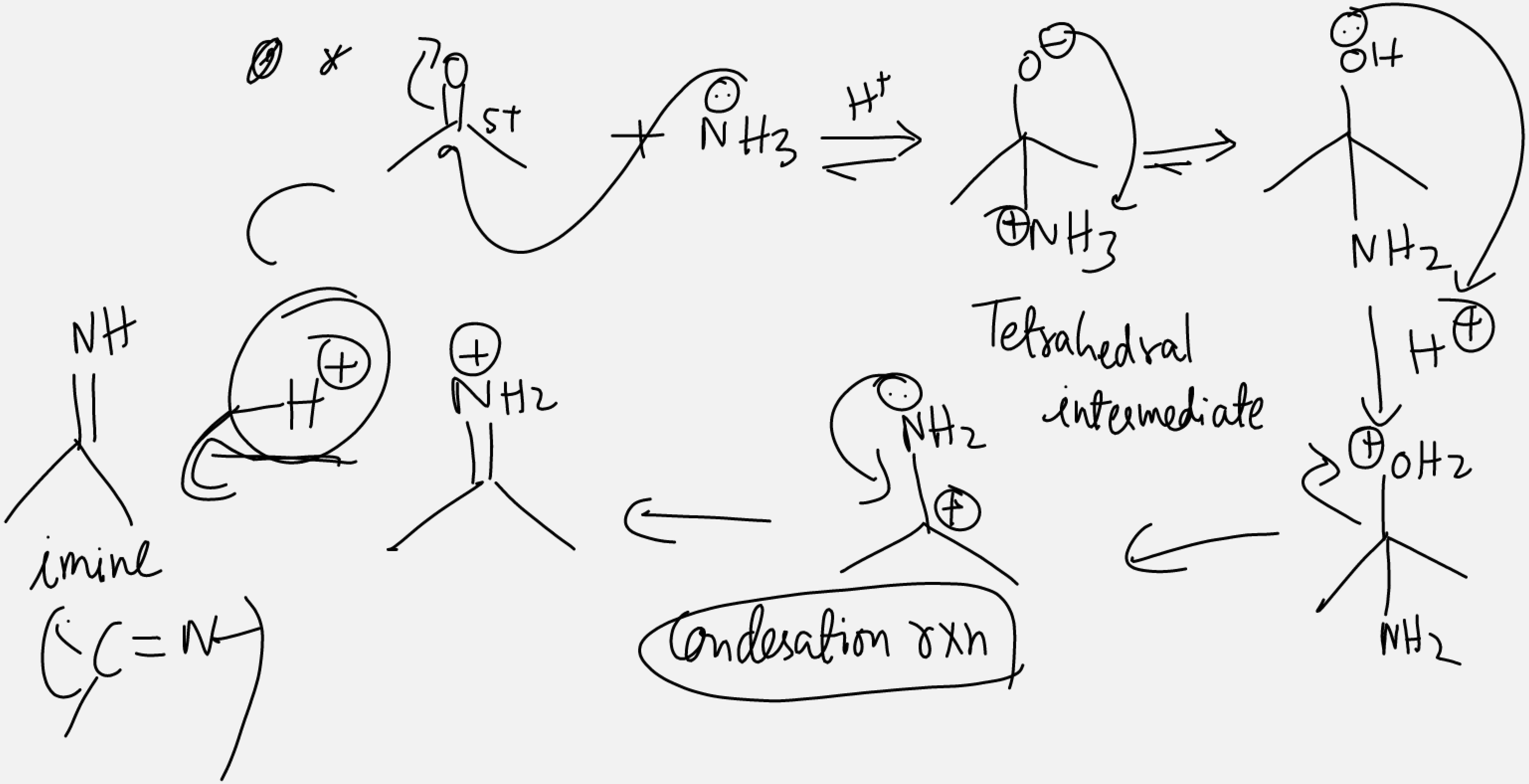
b)



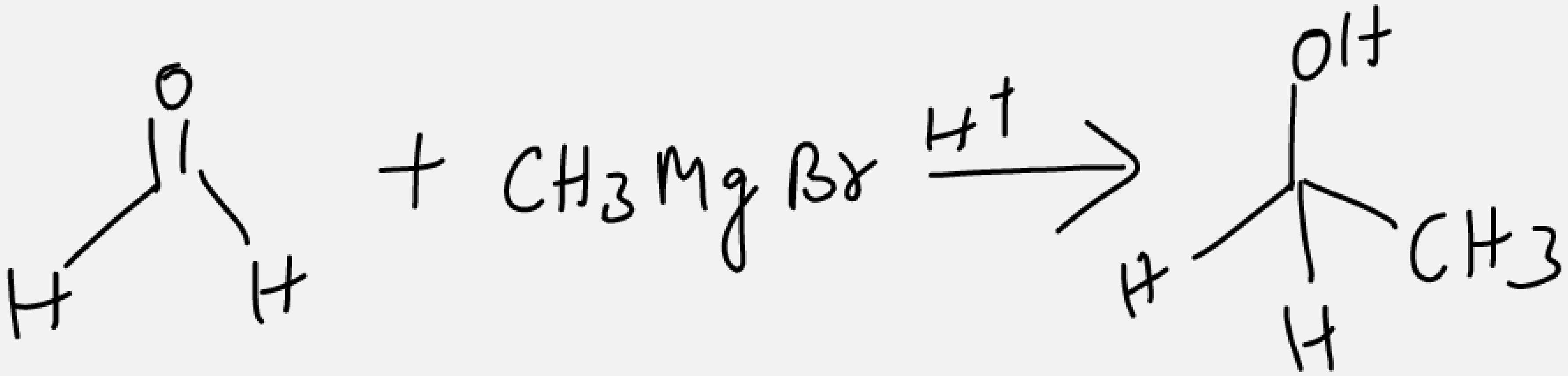
c)



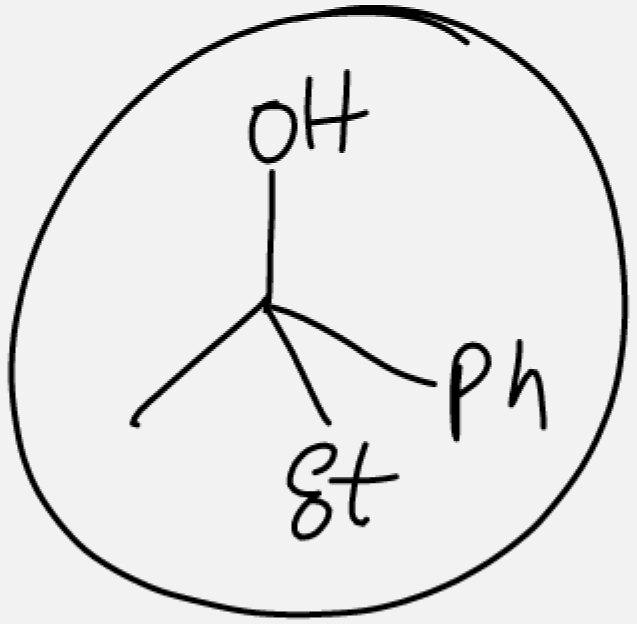



δ+
O
NH3
H+
O−
+NH3
OH
NH2
Tetrahedral intermediate
H+
+OH2
NH2
NH2
+
Condesation rxn
+NH2
H+
NH
imine
C=N

*



1° alcohol (Ethanol)



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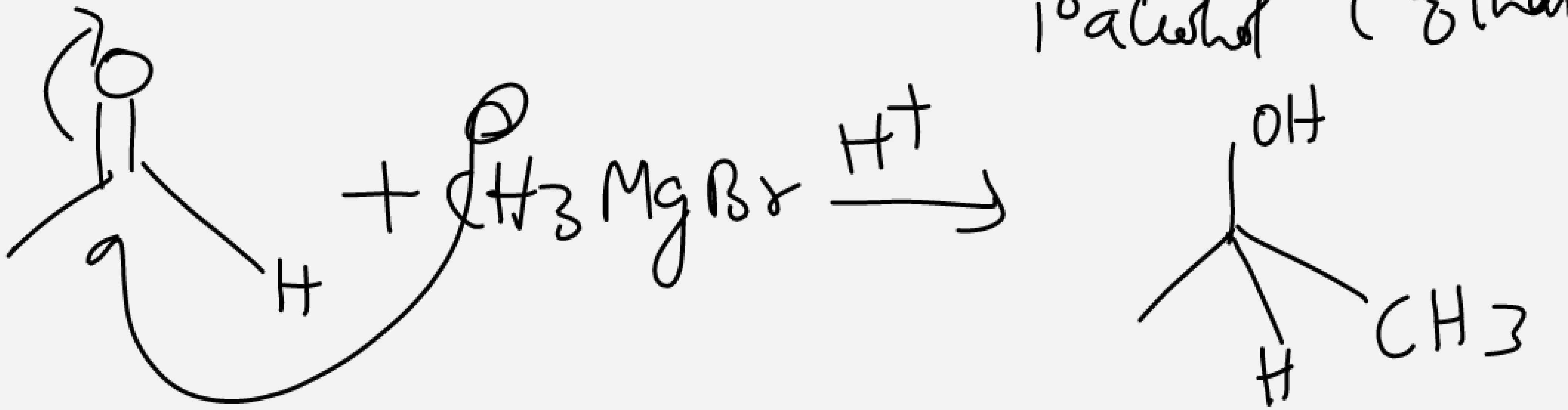
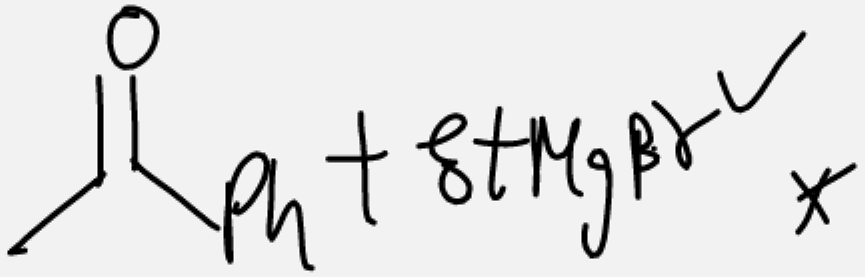


(propan-2-ol)

2° alcohol



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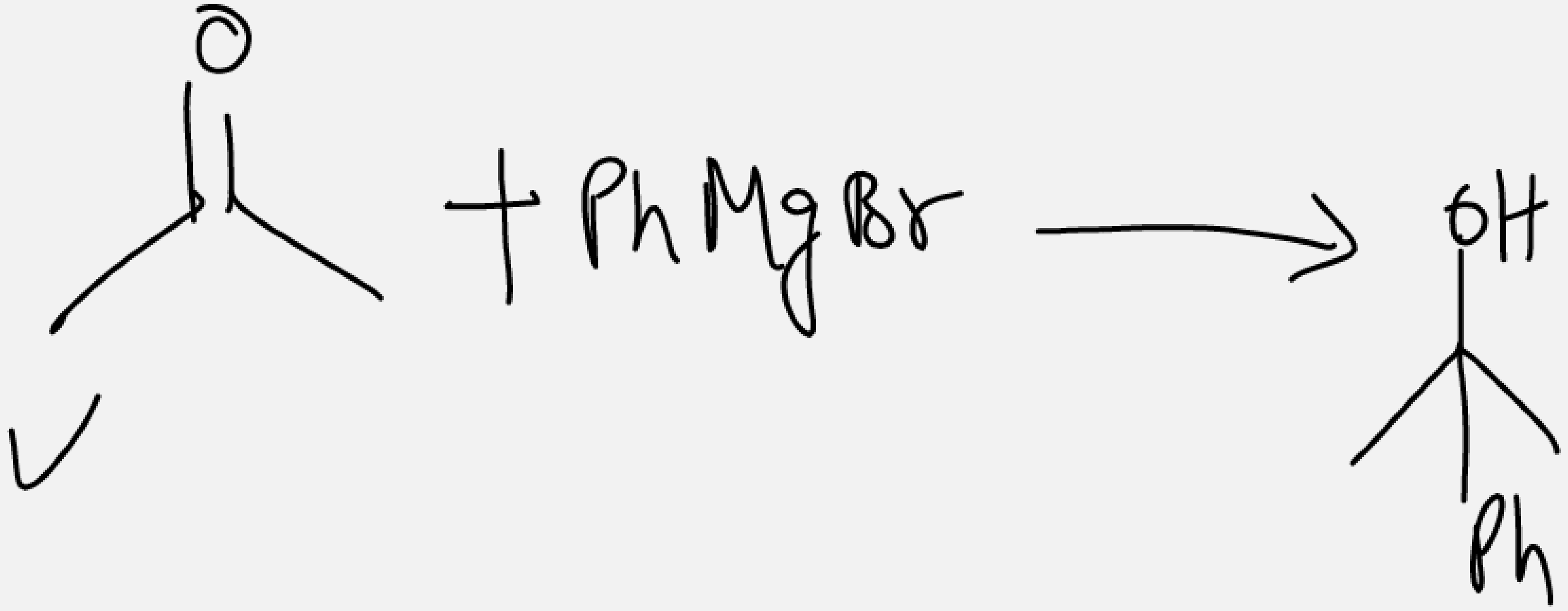
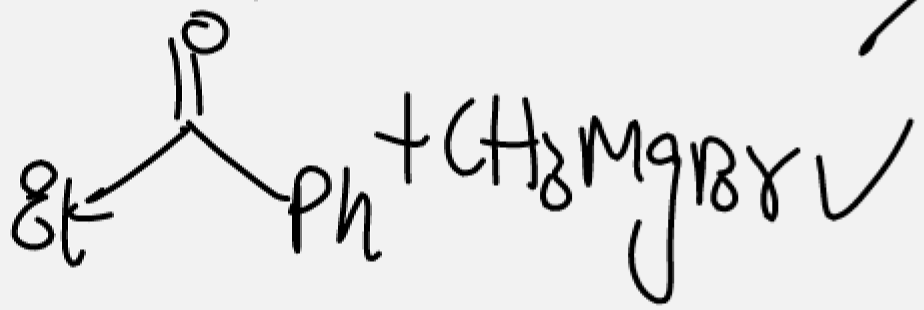


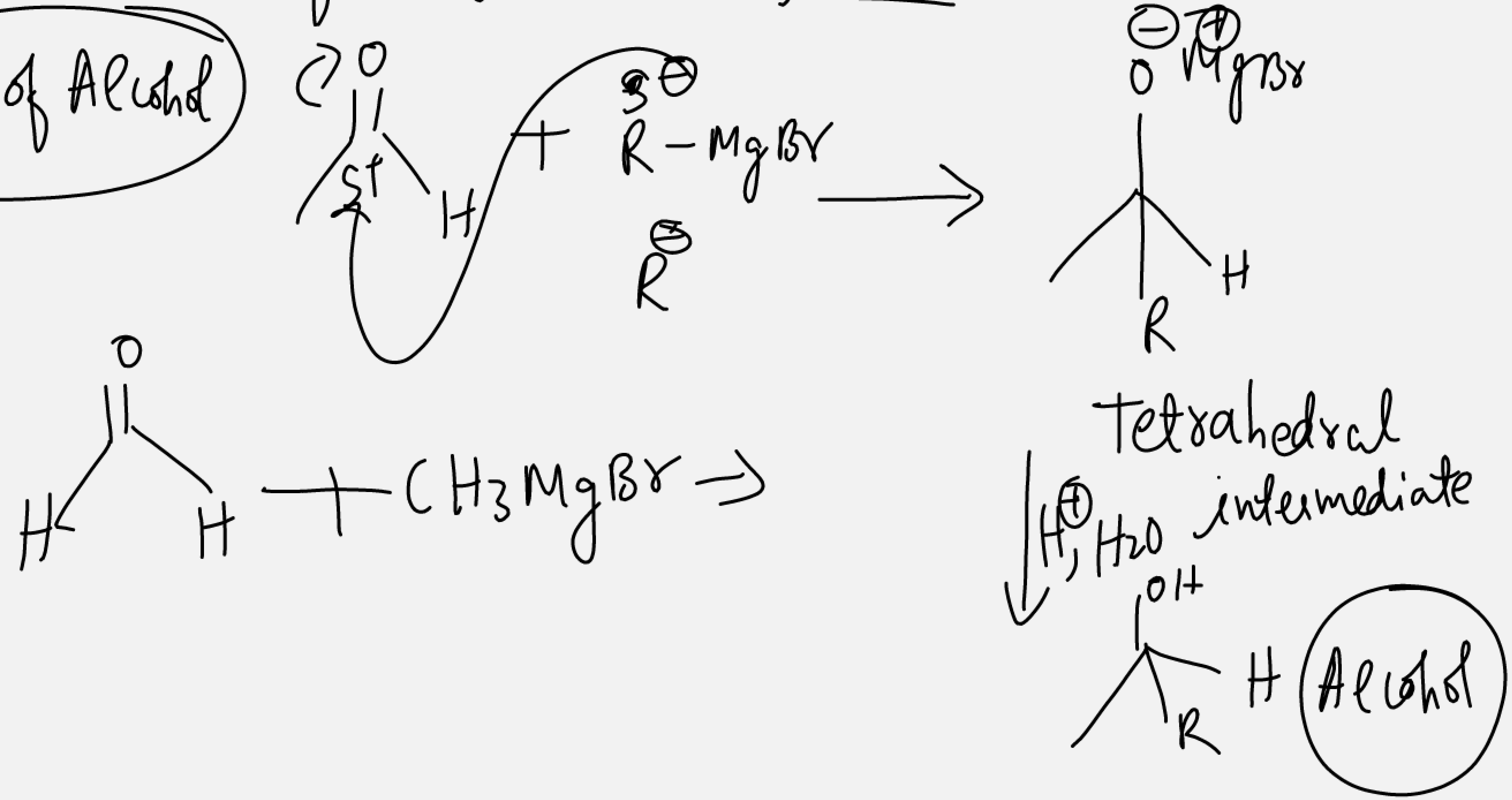
3° alcohol



3 Addition of Grignard Reagent

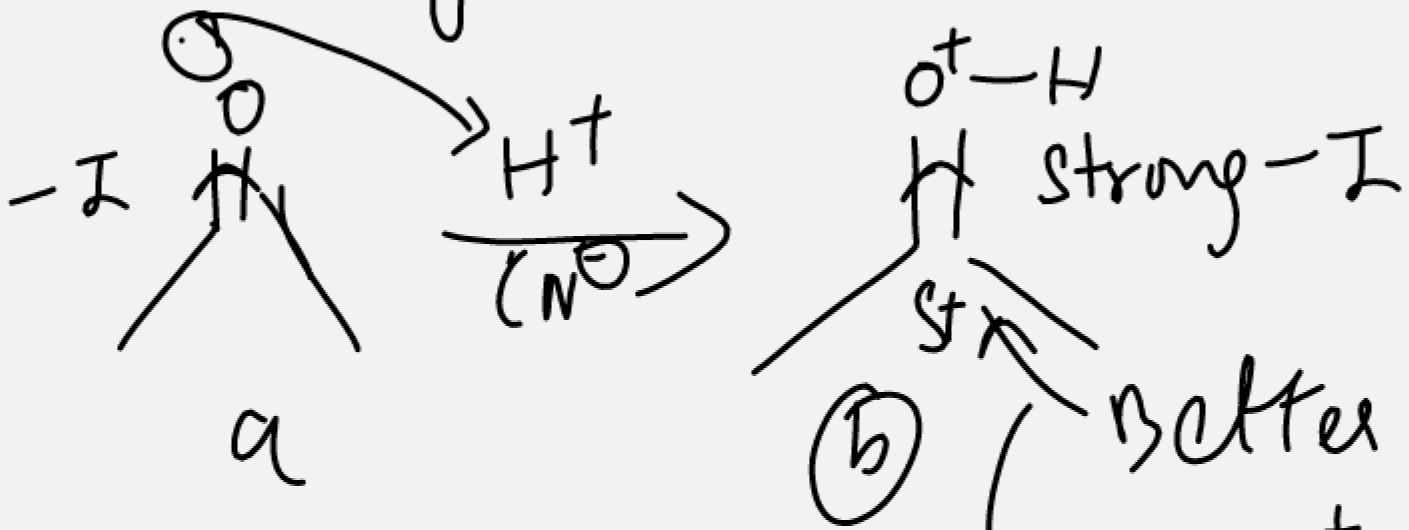
Preph of Alcohol

Eg



* Acid & Base Catalysis can increase rate of Nu add^n rxn

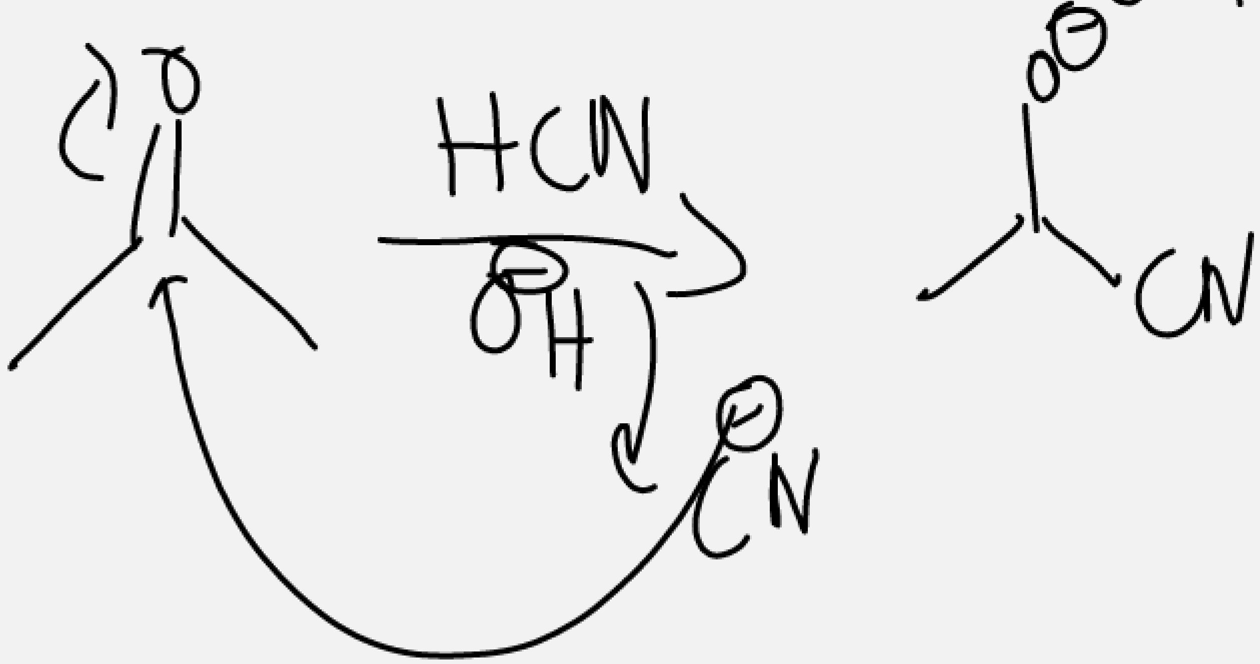
Acid makes Aldehydes Ketones better E^+



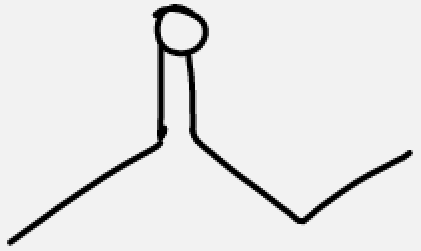
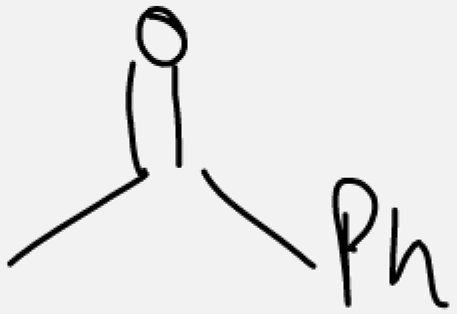
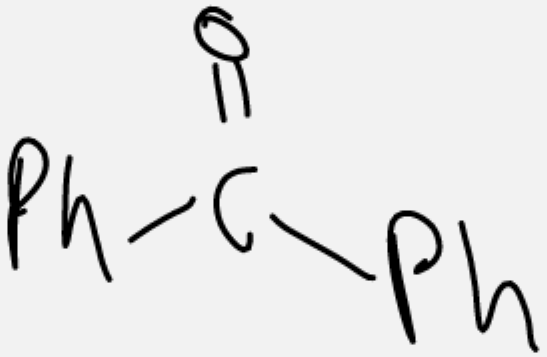
Better E^+ than ⓐ

more δ+

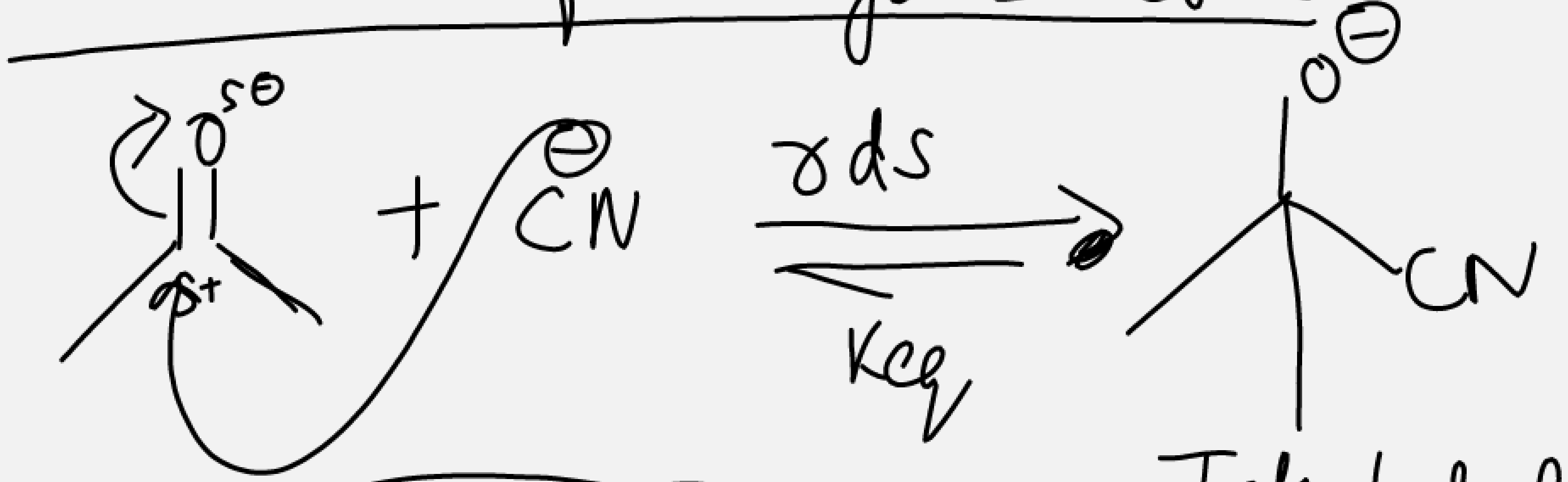
and base makes Nu better Nucleophiles



Keq for $\overset{\ominus}{C}N$ addition

	Keq
$CH_3CHO \rightarrow$	1400
$PhCHO \rightarrow$	210
 $\rightarrow$	38
 $\rightarrow$	0·8
 $\rightarrow$	very small

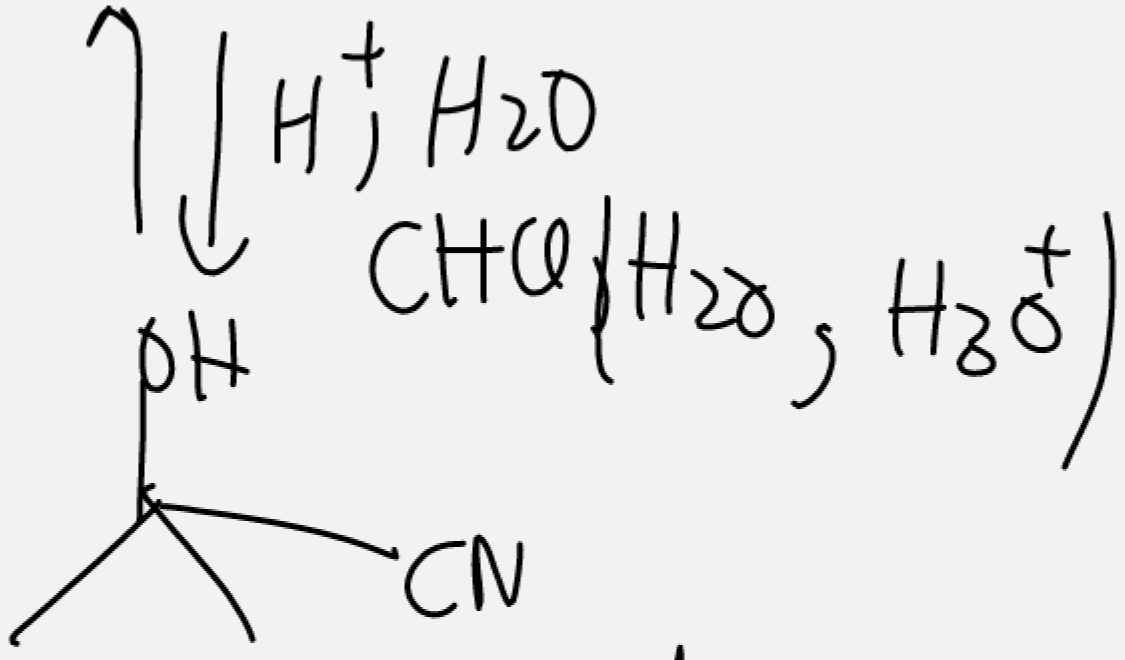
Chemical Rxn of Aldehyde & Ketone



Tetrahedral intermediate

Nucleophilic Add^n rxn

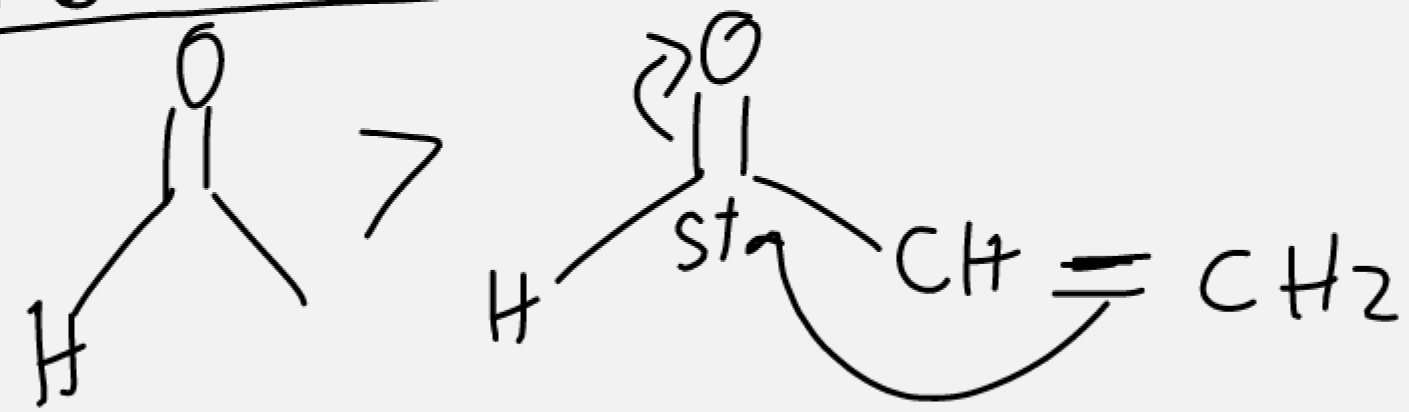
$Keq_{\text{aldehye}} > Keq_{\text{ketone}}$



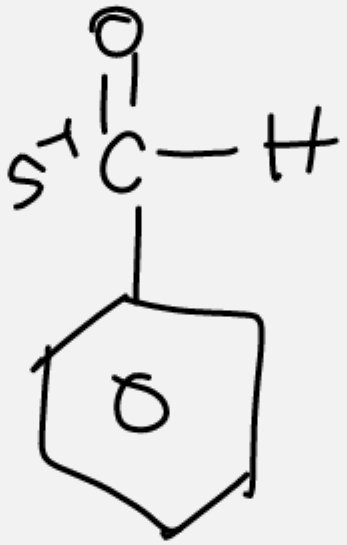
Cyanohydrin

Q.

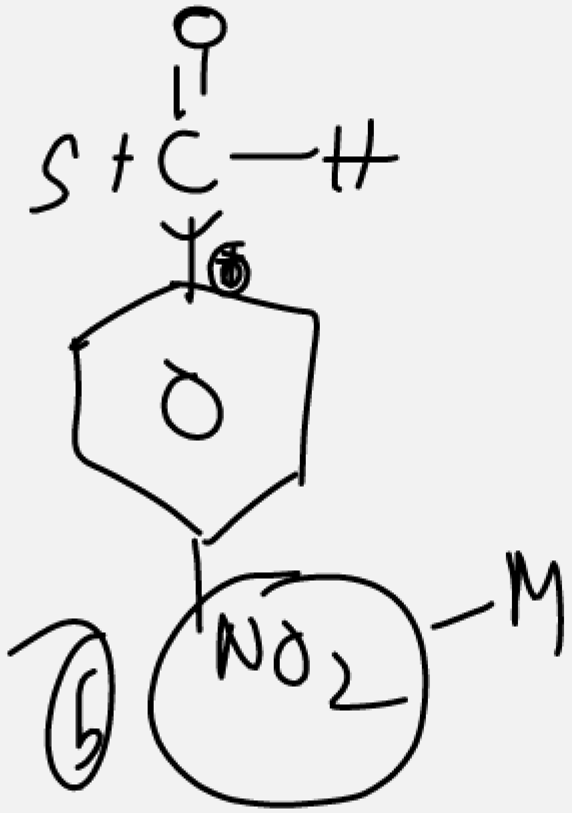
Reactivity order towards Nu



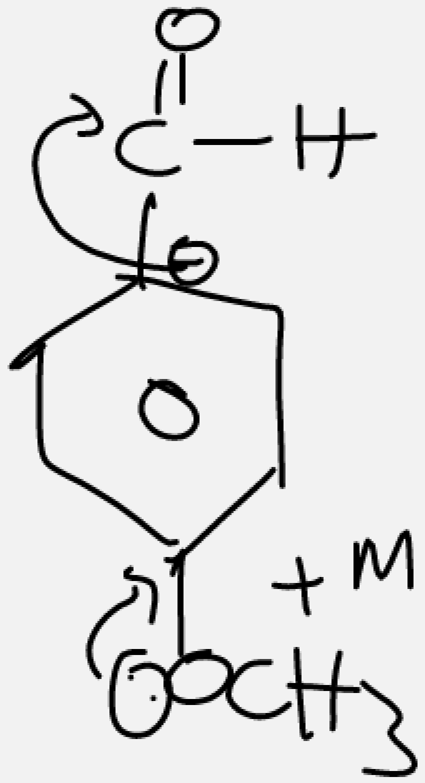
Q.



a



b

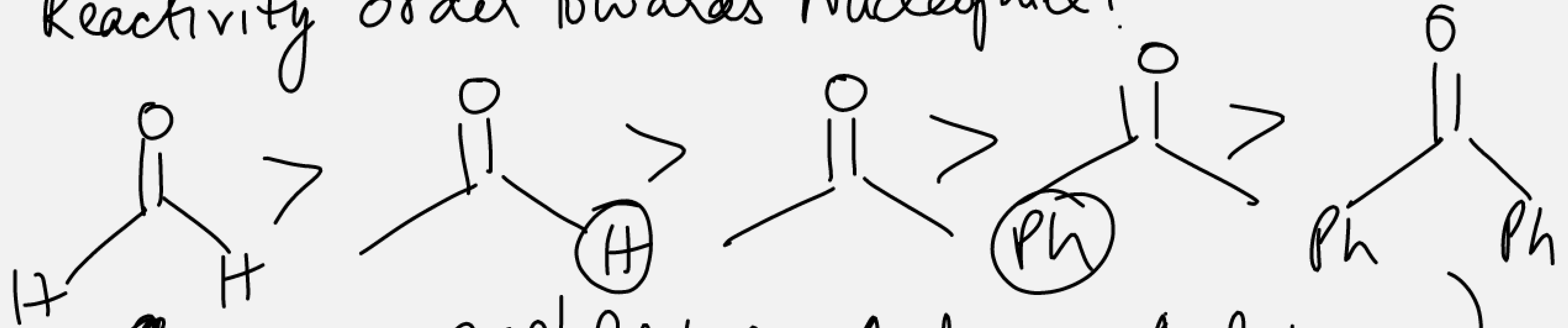


c

b > a > c

Ex NCERT.

Comment on Reactivity order towards Nucleophile?



formaldehyde (Methanal)

acetaldehyde (Ethanal)

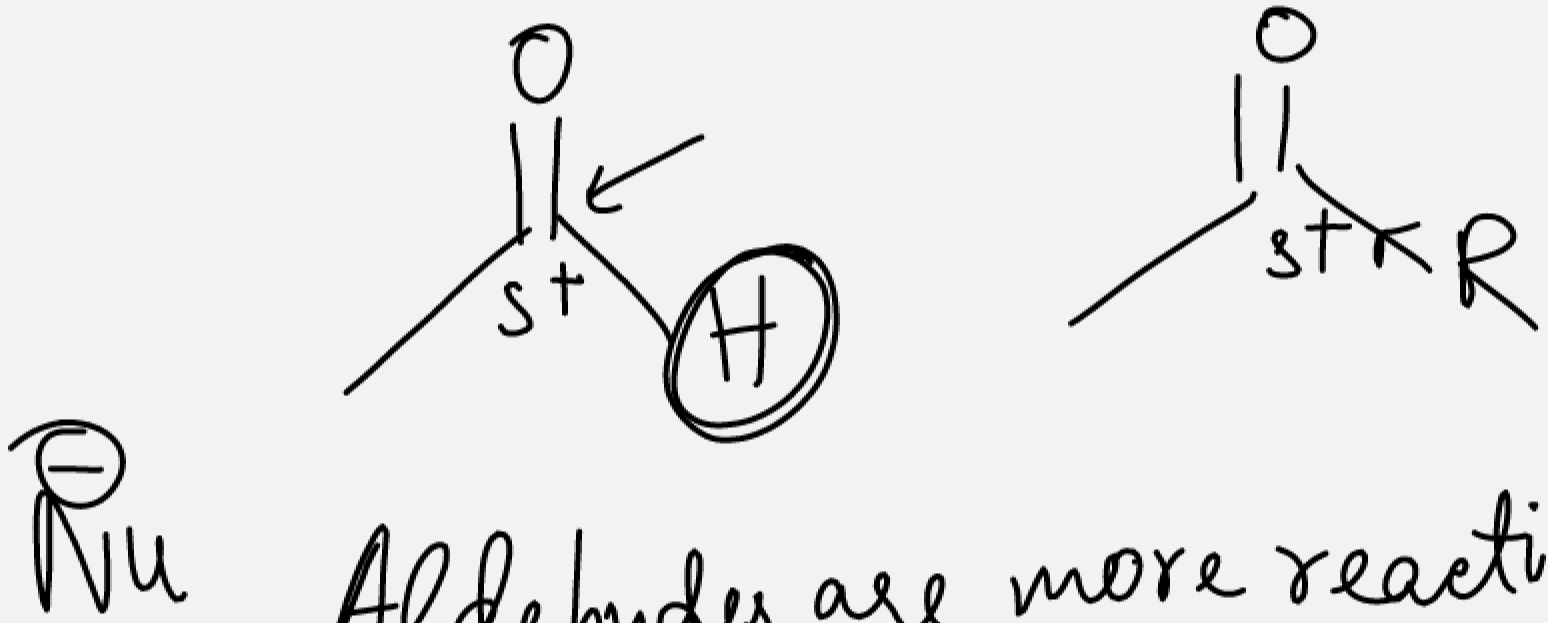
Acetone (Propan-2-one)

Acetophenone

Benzophenone

Reason Both electronic & steric factor.

Reactivity of Carbonyl Compounds



Aldehydes are more reactive than Ketone towards Nucleophilic attack due to —

1) Electronic reason → More δ^+ on aldehyde Carbonyl carbon.

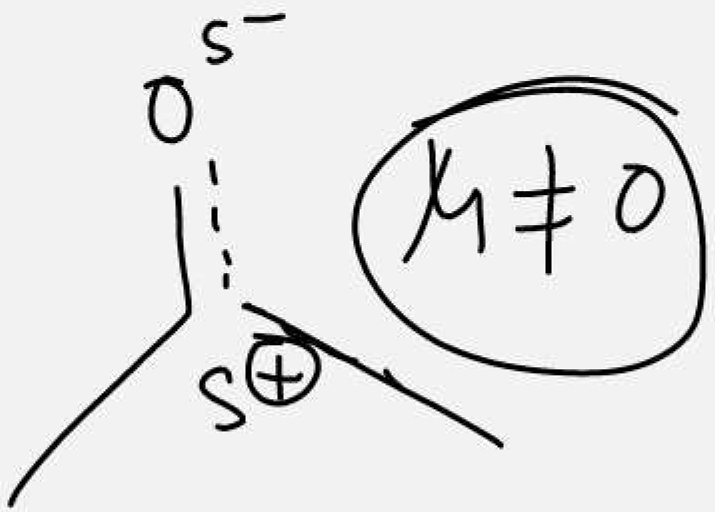
2) Steric reason → Less Steric hindrance on aldehyde. Nu can easily approach.

Carbonyl Compounds (Aldehyde & Ketones)

*

Aldehyde

ketone



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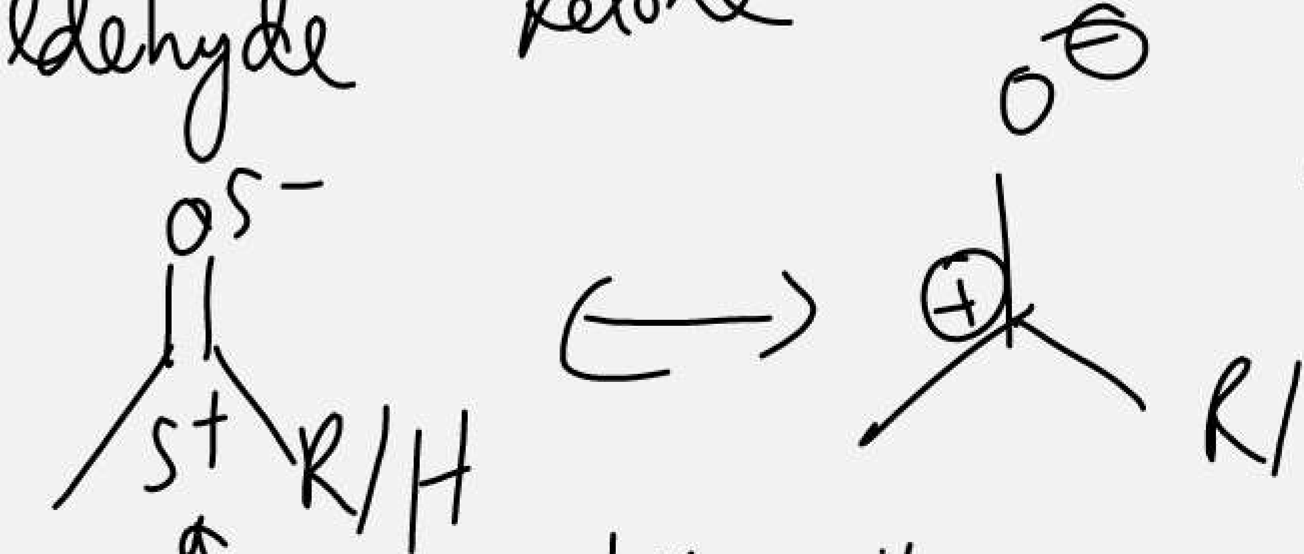
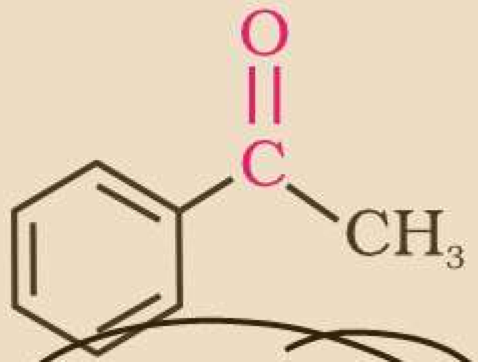


↑ electrophilic site

The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group. The locations of substituents are indicated by Greek letters, α α′, β β′ and so on beginning with the carbon atoms next to the carbonyl group, indicated as αα′. Some ketones have historical common names, the simplest dimethyl ketone is called acetone. Alkyl phenyl ketones are usually named by adding the name of acyl group as prefix to the word phenone. For example

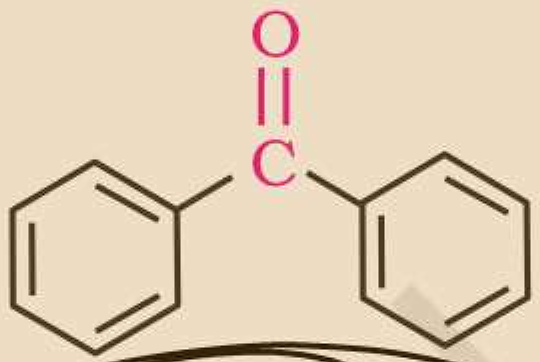
$CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3$

Acetone



Acetophenone

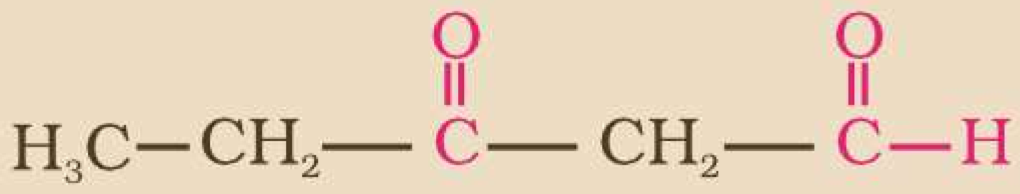
Propiophenone



Benzophenone

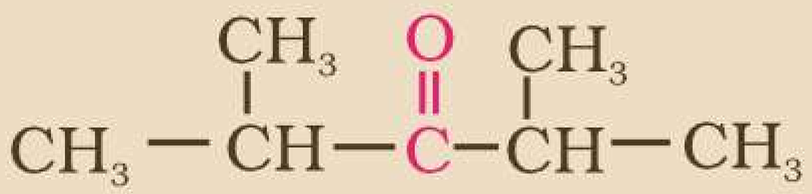
(b) IUPAC names

The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending *–e* with *–al* and *–one* respectively. In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group while in case of ketones the numbering begins from the end nearer to the carbonyl group. The substituents are prefixed in alphabetical order along with numerals



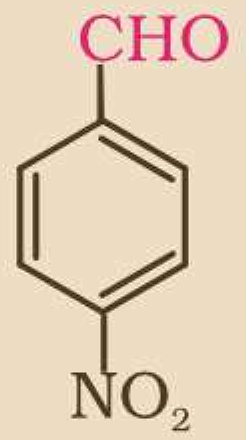
$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$

3-Oxopentanal

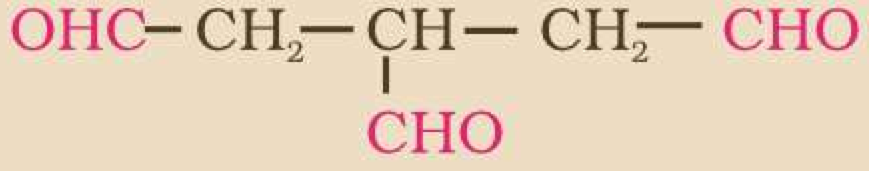


$CH_3-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{CH}}-CH_3$

2,4-Dimethylpentan-3-one



4-Nitrobenzenecarbaldehyde
or
4-Nitrobenzaldehyde



$OHC-CH_2-\underset{CHO}{\underset{|}{CH}}-CH_2-CHO$

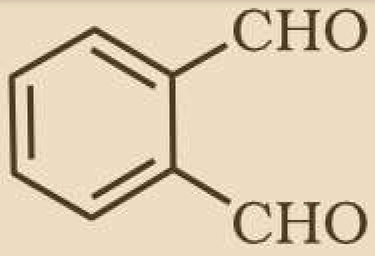
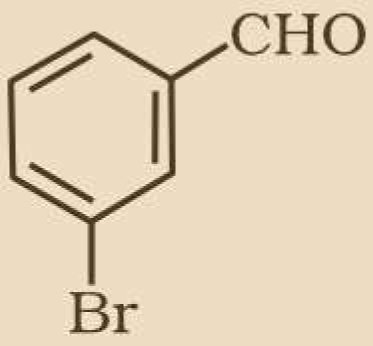
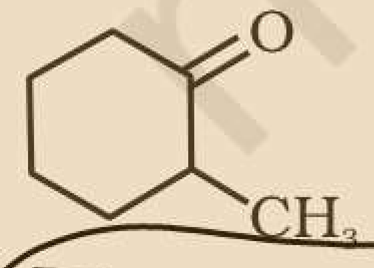
Propane–1,2,3-tricarbaldehyde

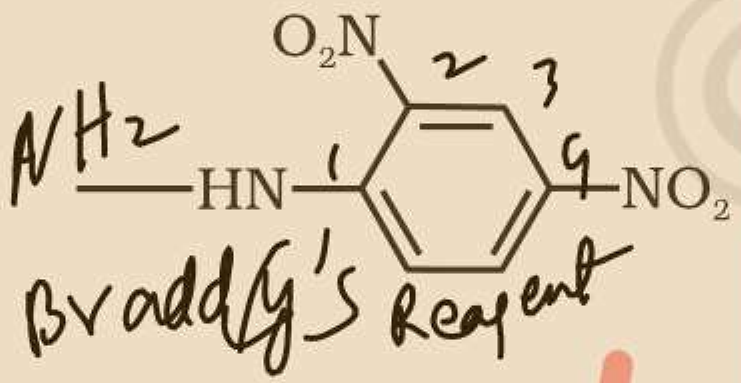
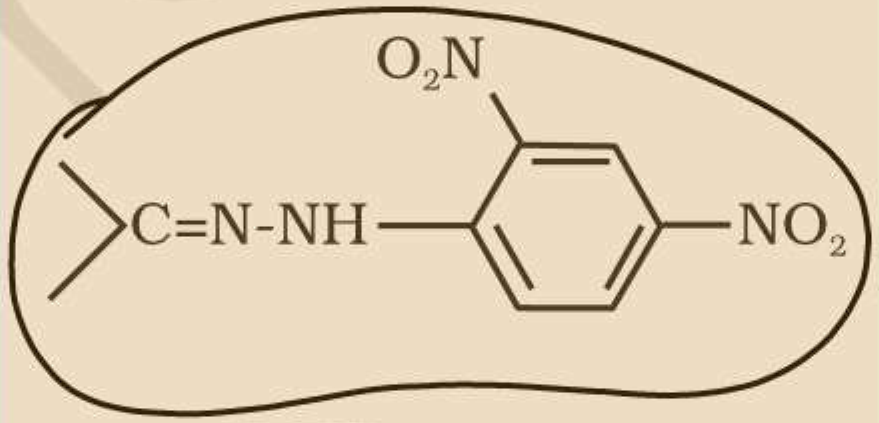
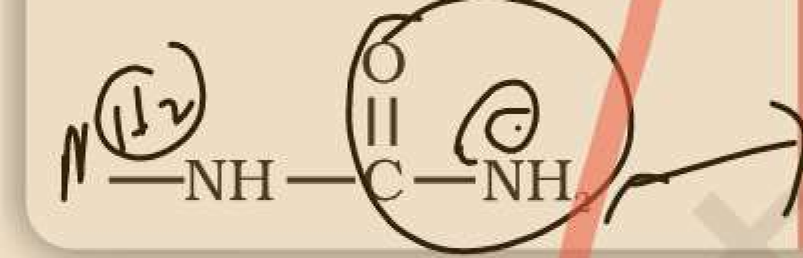
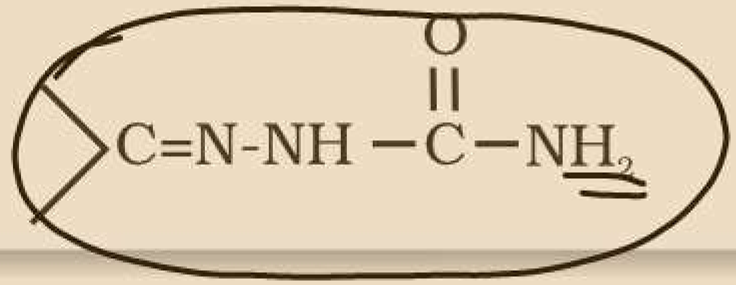
[Note: To give identical treatment to all aldehydic groups, the compound is named as shown above.]

The common and IUPAC names of some aldehydes and ketones are given in Table 12.1.

Table 12.1: Common and IUPAC Names of Some Aldehydes and Ketones

Structure	Common name	IUPAC name
Aldehydes		
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal

	Phthaldehyde	Benzene-1,2-dicarbaldehyde
	*m*-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde or 3-Bromobenzaldehyde
Ketones		
$CH_3COCH_2CH_2CH_3$	Methyl *n*-propyl ketone	Pentan-2-one
$(CH_3)_2CHCOCH(CH_3)_2$	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α-Methylcyclohexanone	2-Methylcyclohexanone
$(CH_3)_2C{=}CHCOCH_3$	Mesityl oxide	4-Methylpent-3-en-2-one

-R	Amine	$>C=NR$	Substituted imine (Schiff's base)
$-OH$	Hydroxylamine	$>C=N-OH$	Oxime
$-NH_2$	Hydrazine	$>C=N-NH_2$	Hydrazone
	Phenylhydrazine		Phenylhydrazone
 	2,4-Dinitrophenyl-hydrazine		2,4 Dinitrophenyl-hydrazone
 $-NH-\overset{O}{\overset{\|\|}{C}}-NH_2$ 	Semicarbazide	 $>C=N-NH-\overset{O}{\overset{\|\|}{C}}-NH_2$	Semicarbazone

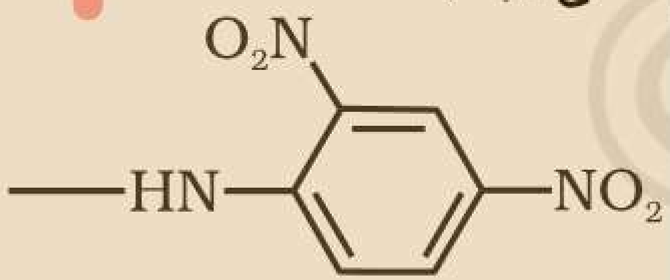
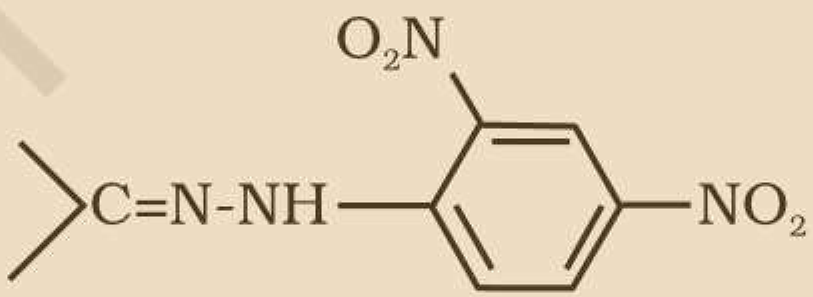
* 2,4-DNP-derivatives are yellow, orange or red solids, useful for characterisation of aldehydes and ketones.

2. Reduction

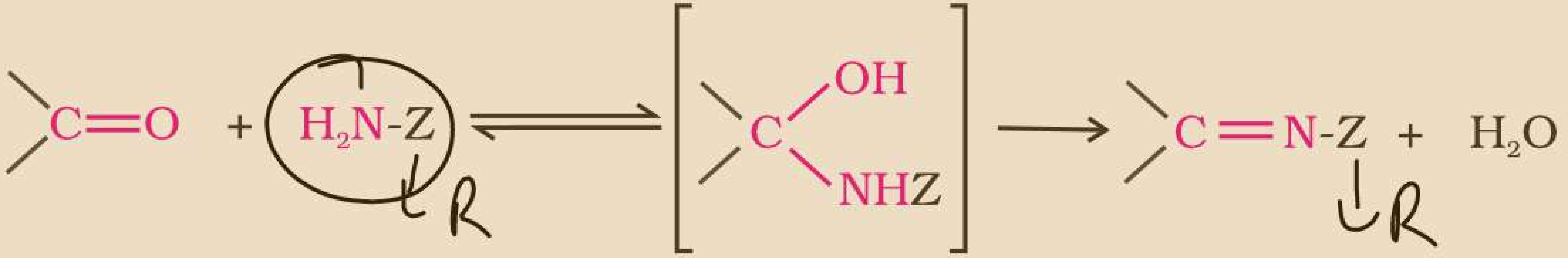
(i) *Reduction to alcohols:* Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium

Z = Alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$, etc.

Table 12.2: Some N-Substituted Derivatives of Aldehydes and Ketones (>C=N-Z)

Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	$>C=NH$	Imine
-R	Amine	$>C=NR$	Substituted imine (Schiff's base)
-OH NH_2-OH	Hydroxylamine	$>C=N-OH$ oxime	Oxime
$-NH_2$ NH_2-NH_2	Hydrazine	$>C=N-NH_2$	Hydrazone
	Phenylhydrazine $NH_2-NH-Ph$		Phenylhydrazone
	2,4-Dinitrophenyl-hydrazine		2,4 Dinitrophenyl-hydrazone
$\overset{O}{\parallel}$	Semicarbazide	$>C=N-NH-\overset{O}{\overset{\parallel}{C}}-NH$	Semicarbazone

group of aldehydes and ketones. The reaction is reversible and catalysed by acid. The equilibrium favours the product formation due to rapid dehydration of the intermediate to form >C=N-Z.



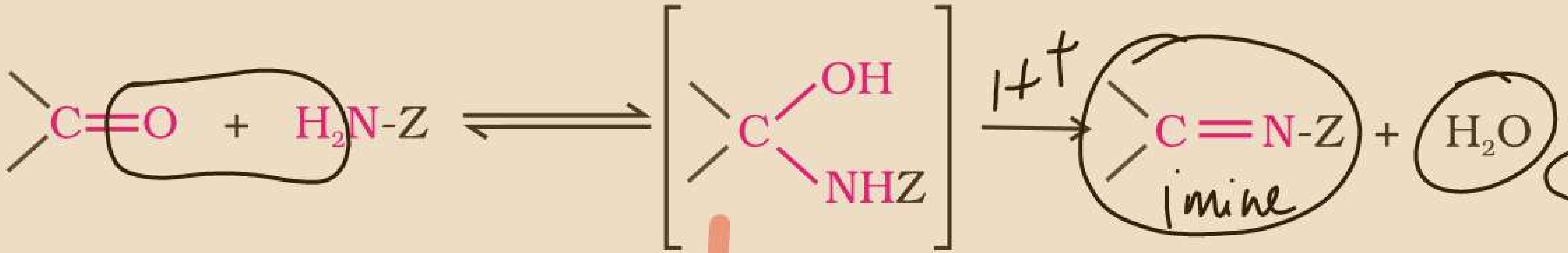
Z = Alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$, etc.

Table 12.2: Some N-Substituted Derivatives of Aldehydes and Ketones (>C=N-Z)

Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	>C=NH	Imine C=N-H R
-R	Amine	>C=NR	Substituted imine (Schiff's base)
—OH	Hydroxylamine	>C=N–OH	Oxime
—NH_2	Hydrazine	>C=N–NH_2	Hydrazone
	Phenylhydrazine		Phenylhydrazone

are hydrolysed with aqueous mineral acids to yield corresponding aldehydes and ketones respectively.

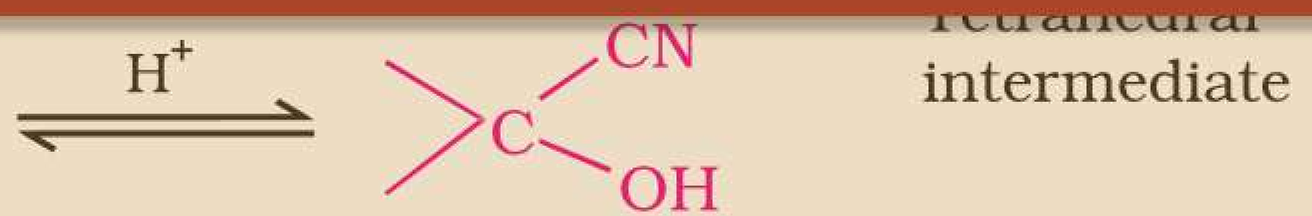
(e) *Addition of ammonia and its derivatives*: Nucleophiles, such as ammonia and its derivatives H_2N-Z add to the carbonyl group of aldehydes and ketones. The reaction is reversible and catalysed by acid. The equilibrium favours the product formation due to rapid dehydration of the intermediate to form >C=N-Z.



Z = Alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$, etc.

Table 12.2: Some N-Substituted Derivatives of Aldehydes and Ketones (>C=N-Z)

Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	$>C=NH$	Imine
-R	Amine	$>C=NR$	Substituted imine (Schiff's base)
—OH	Hydroxylamine	$>C=N–OH$	Oxime



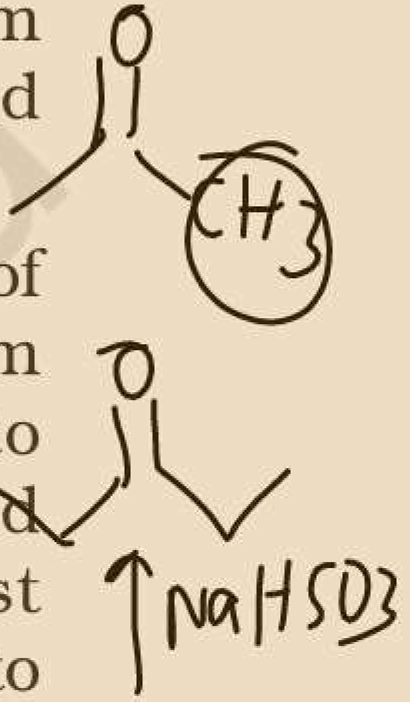
Cyanohydrin

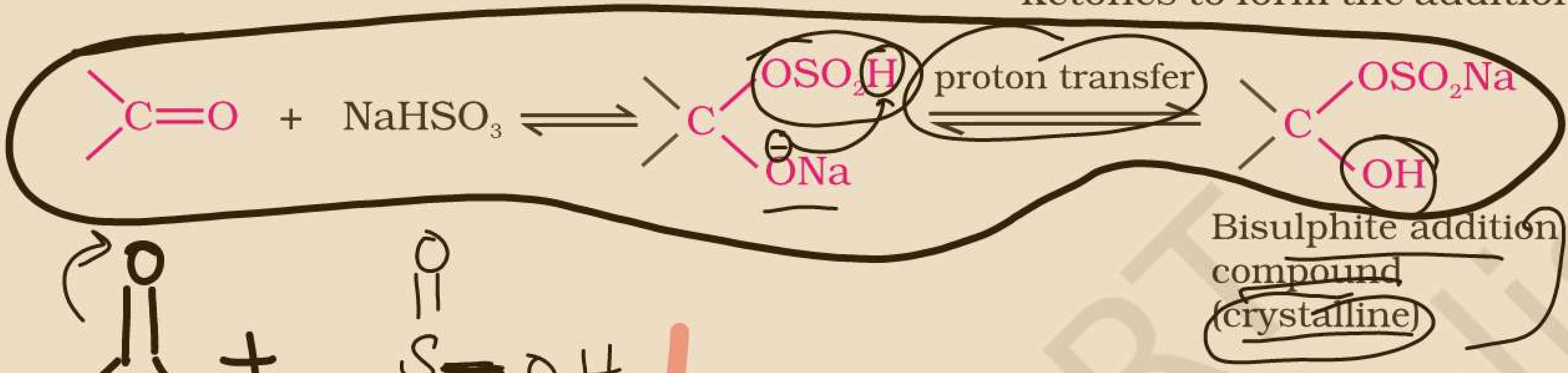
cyanohydrin.

Cyanohydrins are useful synthetic intermediates.

→ $NaHSO_3$

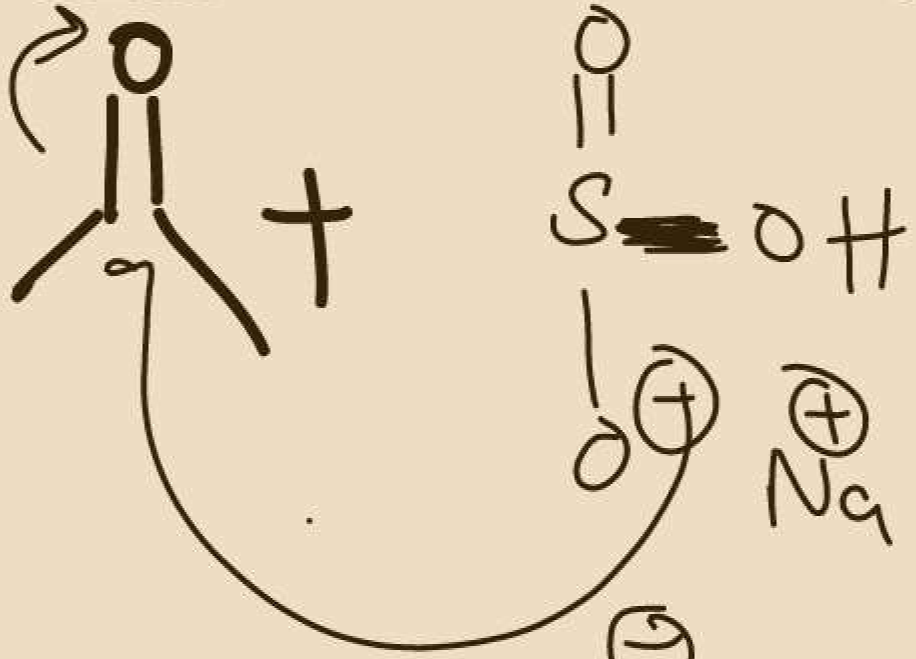
(b) *Addition of sodium hydrogensulphite:* Sodium hydrogensulphite adds to aldehydes and ketones to form the addition products.





Bisulphite addition compound (crystalline)

The position of the equilibrium lies largely to the right hand side for most aldehydes and to the left for most ketones due to steric reasons. The hydrogensulphite addition compound is water soluble and can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali. Therefore, these are useful for separation and purification of aldehydes.

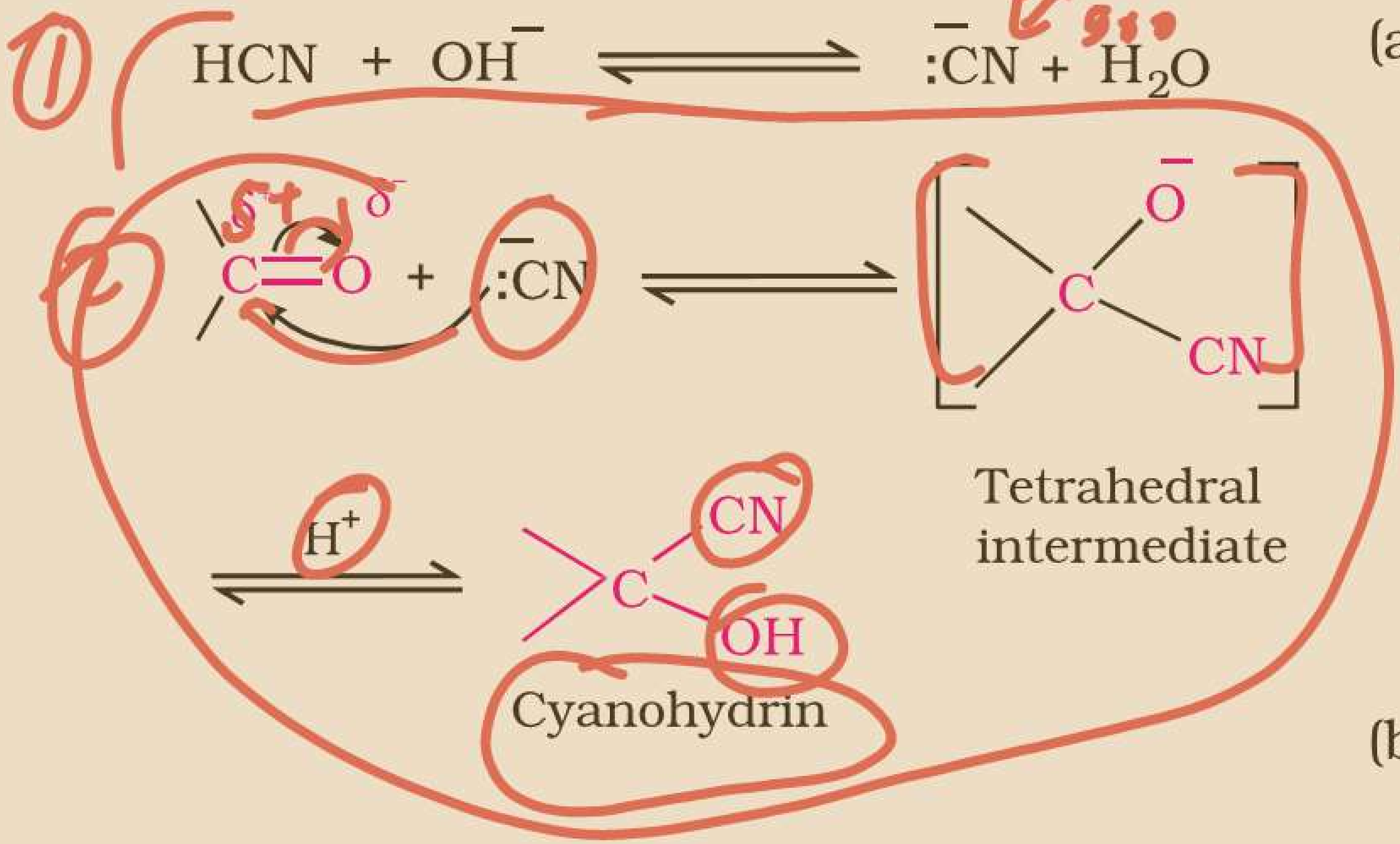


$RSO_3H + RO^{\ominus} \rightarrow$

(c) *Addition of Grignard reagents:* (refer Unit 11, Class XII).

(d) *Addition of alcohols:* Aldehydes react with one equivalent of monohydric alcohol in the presence of dry hydrogen chloride to yield alkoxyalcohol intermediate, known as hemiacetals, which further react with one more molecule of alcohol to give a *gem*-dialkoxy

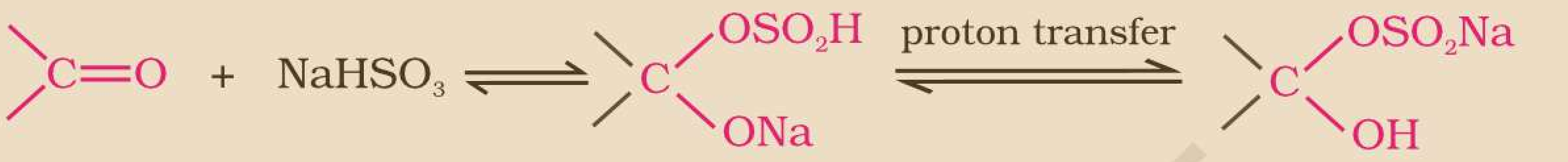
(iii) Some important examples of nucleophilic addition and nucleophilic addition-elimination reactions:



(a) *Addition of hydrogen cyanide (HCN)*: Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins. This reaction occurs very slowly with pure HCN. Therefore, it is catalysed by a base and the generated cyanide ion (CN^-) being a stronger nucleophile readily adds to carbonyl compounds to yield corresponding cyanohydrin.

Cyanohydrins are useful synthetic intermediates.

(b) *Addition of sodium hydrogensulphite:* Sodium hydrogensulphite adds to aldehydes and ketones to form the addition products.

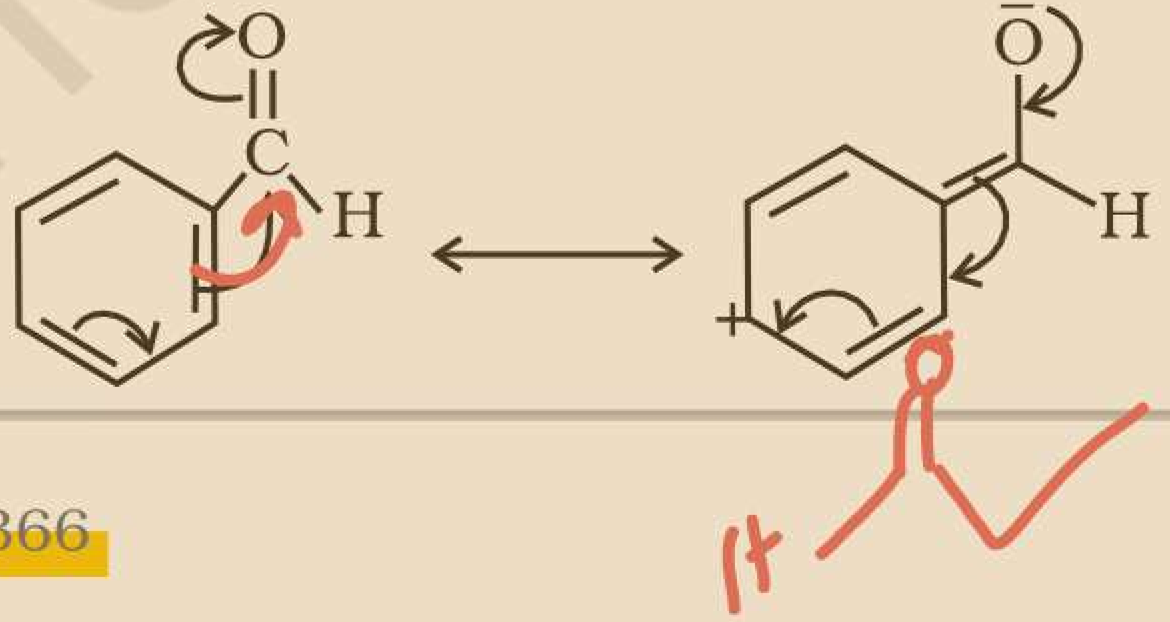


Bisulphite addition compound (crystalline)

The position of the equilibrium lies largely to the right hand side for most aldehydes and to the left for most substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl carbon more effectively than in former.

Example 12.3 Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

Solution The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal.



Nu^- and H^+ across the carbon oxygen double bond as shown in Fig. 12.2.

Fig.12.2: *Nucleophilic attack on carbonyl carbon*

(ii) Reactivity

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl carbon more effectively than in former.

Example 12.3 Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

Solution The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal.