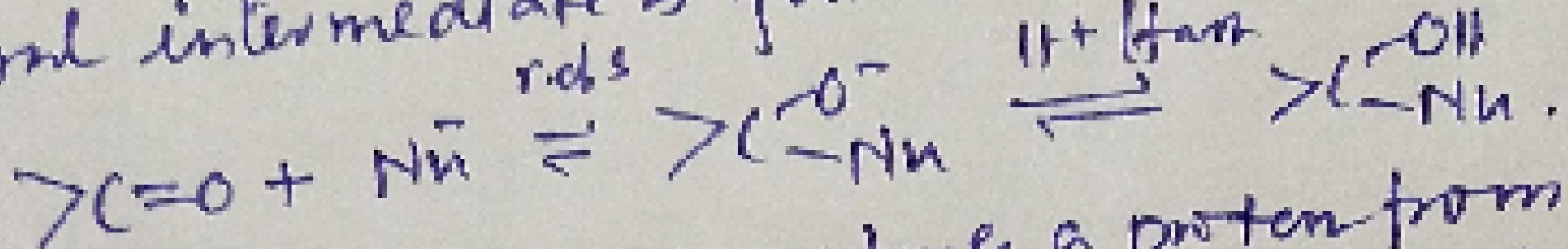


(1)

CARBONYL COMPOUND:

(Aldehyde & ketone)

Aldehyde & ketone undergoes nucleophilic addition reaction. A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group. The hybridization of carbon changes from sp^2 to sp^3 in this process. A tetrahedral intermediate is formed.



This intermediate captures a proton from the acidic medium to give the electrically neutral product.



The reactivity of aldehyde/ketone towards nu. More is the δ^+ charge on carbonyl carbon, more will be reactivity.

Examples of nucleophile.

i) $\text{HCN} + \text{Base}$ or NaCN/KCN . [carbon is the donor atom].

ii) $\text{H}_2\text{N} + \text{Base}$ or $\text{NaNH}_2/\text{KNH}_2$.

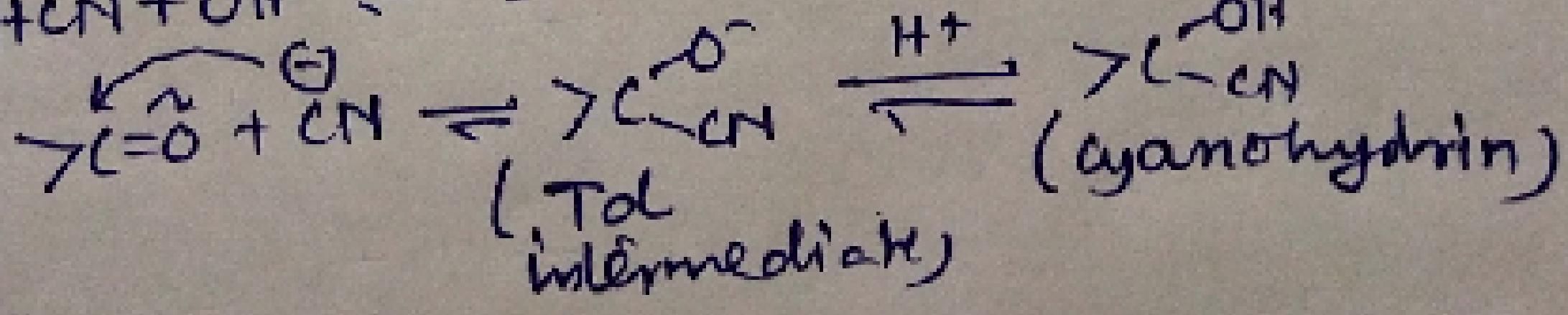
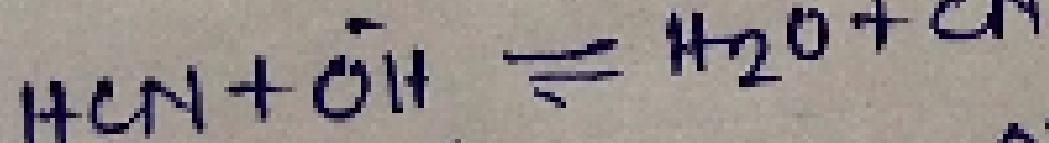
iii) NaHSO_3 [S is the donor atom]

iv) H_2O . [oxygen is the donor atom]

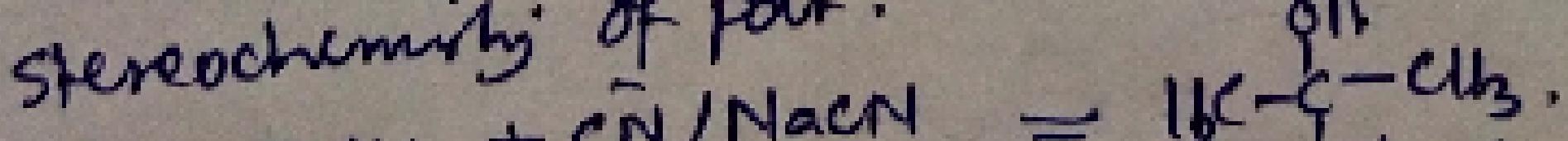
v) $\text{H}_2\text{N}-\text{Z}$ system. (N is the donor atom).

vi) NH_2^- & systems. (N is the donor atom).

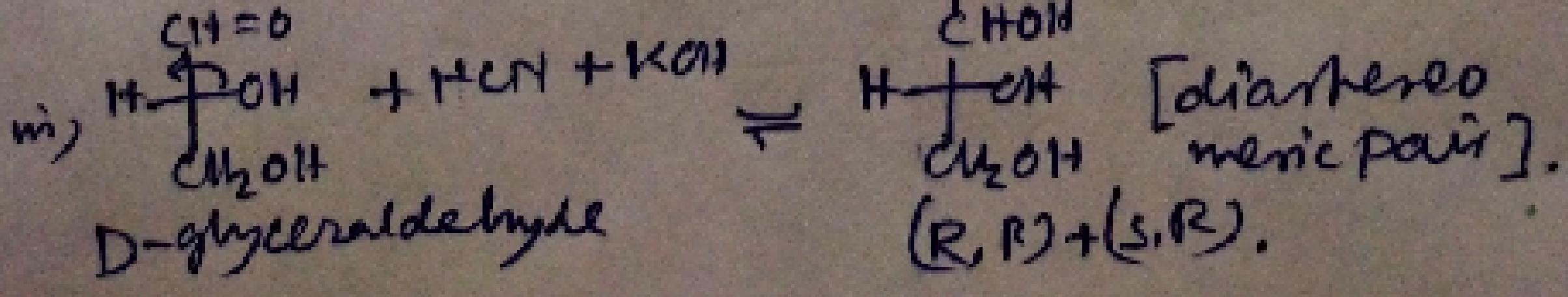
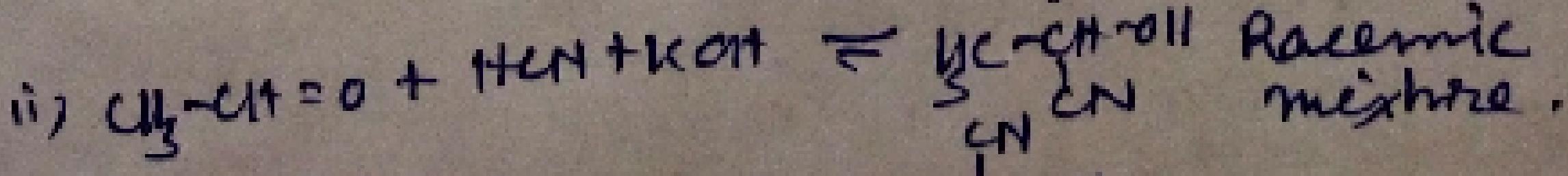
vii) ROH . (oxygen is the donor atom).

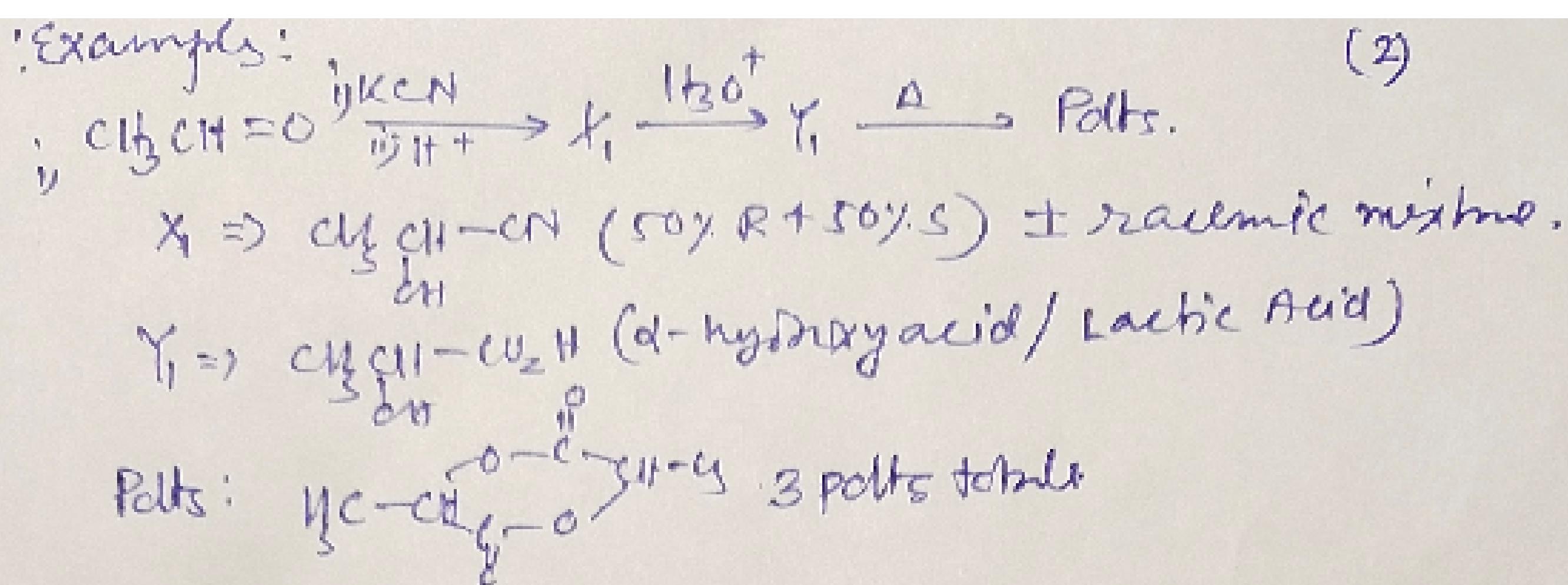


Stereochemistry of polt.

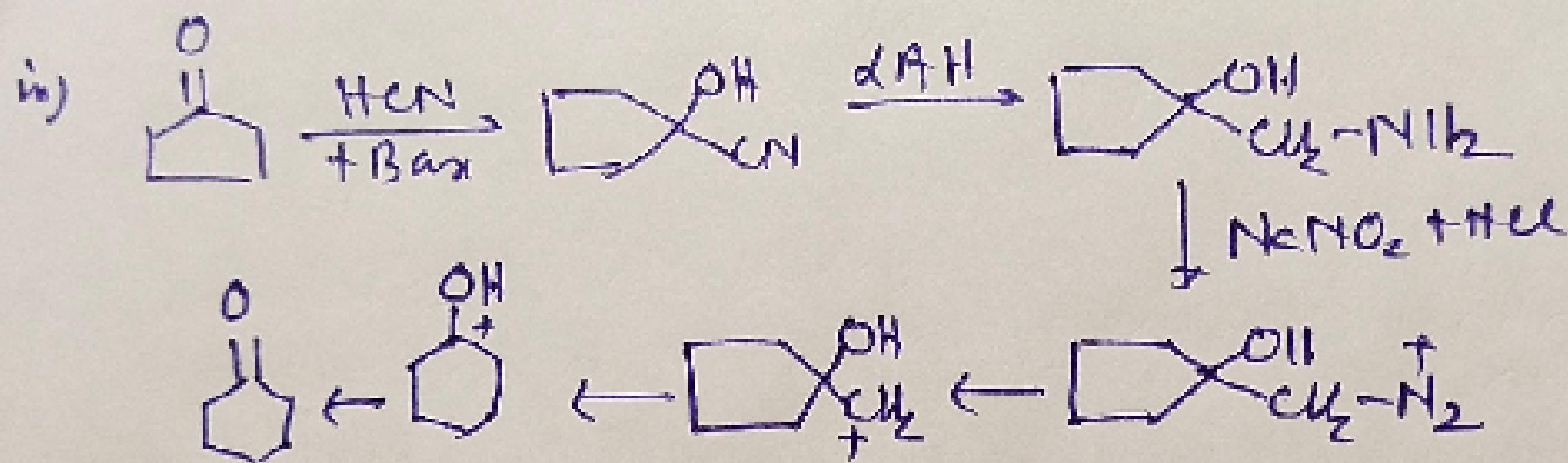


followed by H^+ $\xrightarrow{\text{H}^+}$ $\text{CH}_3\text{C}_2\text{H}_5\text{CN}$ optically inactive





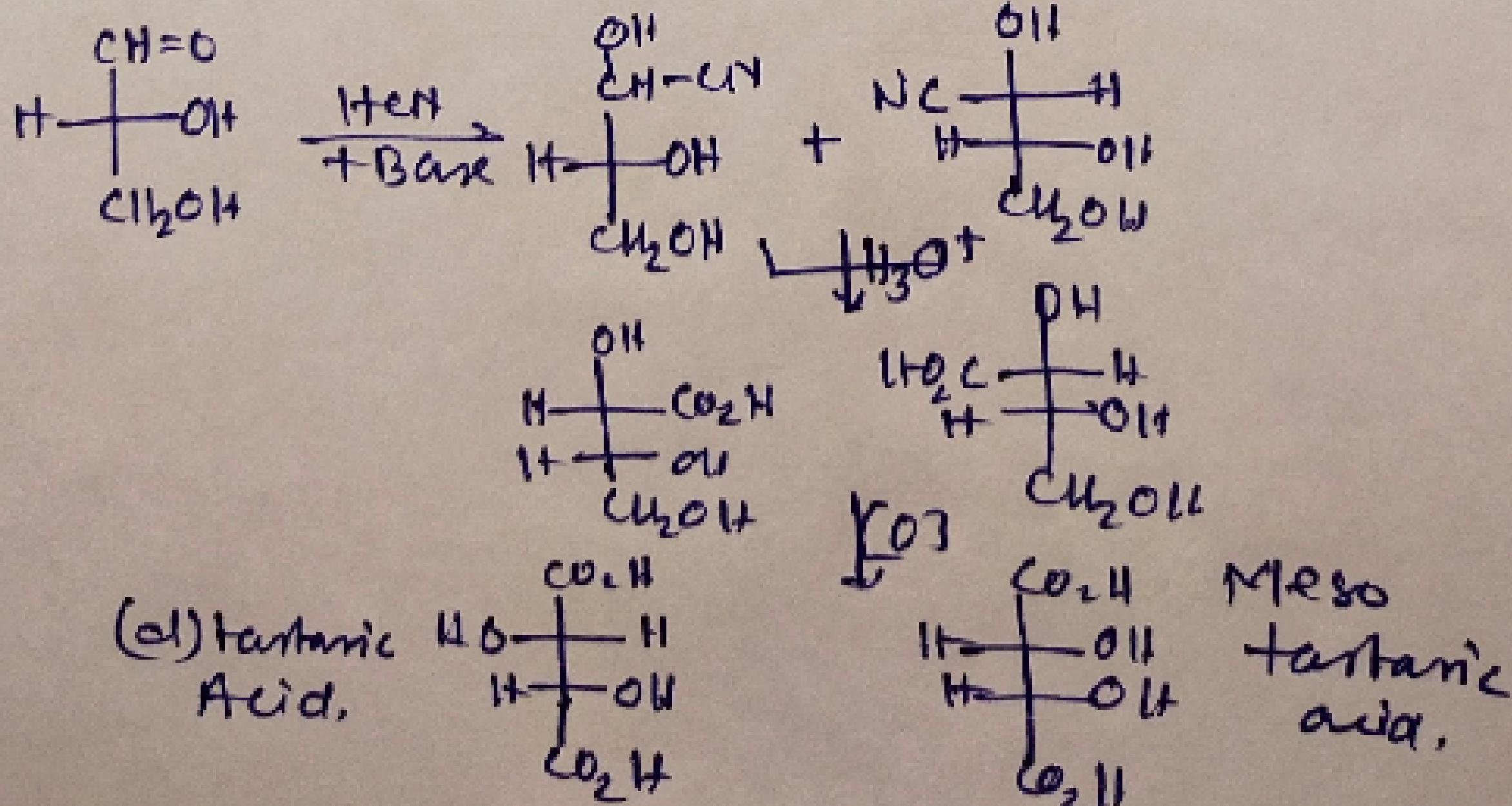
i) \pm glyceraldehyde $\xrightarrow[\text{HCOH}]{\text{HCN}}$ Total 4 pelts.
 $\quad\quad\quad$ (2 pairs of racemic mixtures)
 Optically inactive / reversible.



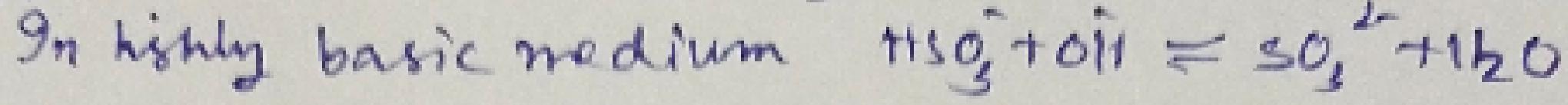
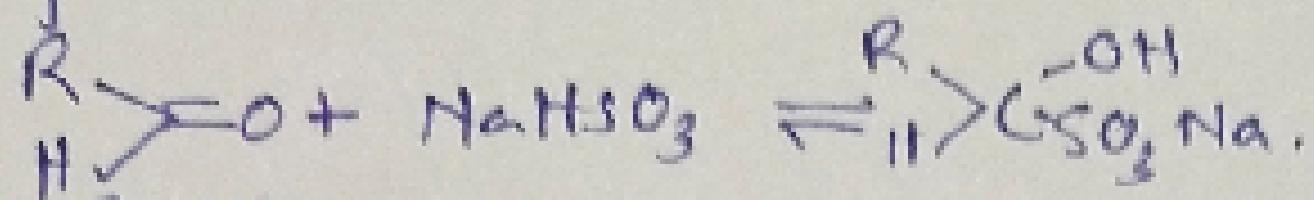
iii) R-glyceraldehyde $\xrightarrow[\text{Base}]{\text{HCN}}$ M + N (m.f. $\text{C}_4\text{H}_7\text{NO}_3$)

M $\xrightarrow{\text{H}_3\text{O}^+}$ P ($\text{C}_4\text{H}_8\text{O}_5$) $\xrightarrow{[0]}$ Meso tartaric acid.

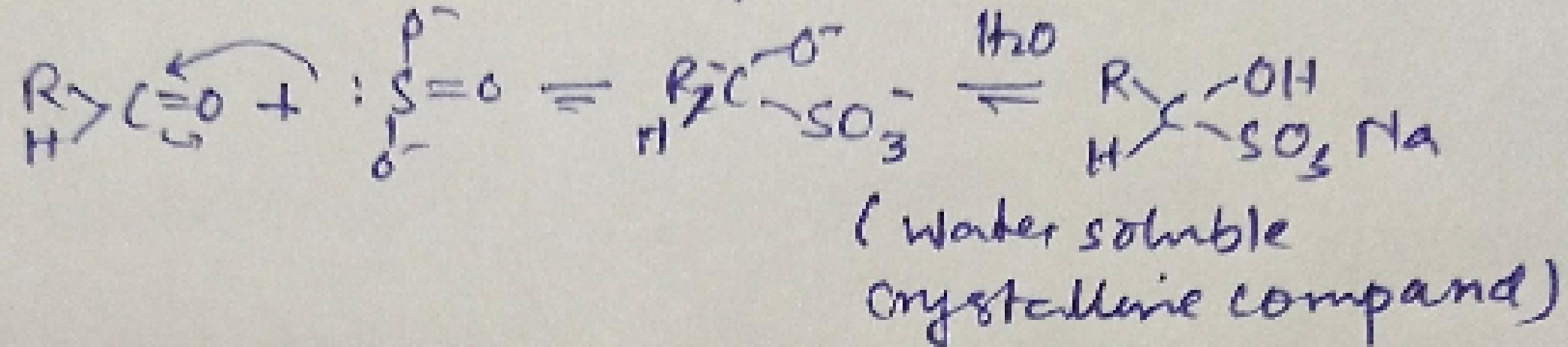
N $\xrightarrow{\text{H}_3\text{O}^+}$ Q ($\text{C}_4\text{H}_8\text{O}_5$) $\xrightarrow{[0]}$ (+) tartaric acid.



Sodium hydrogen sulphite adds to aldehydes & ketones to form the addition products. (3)



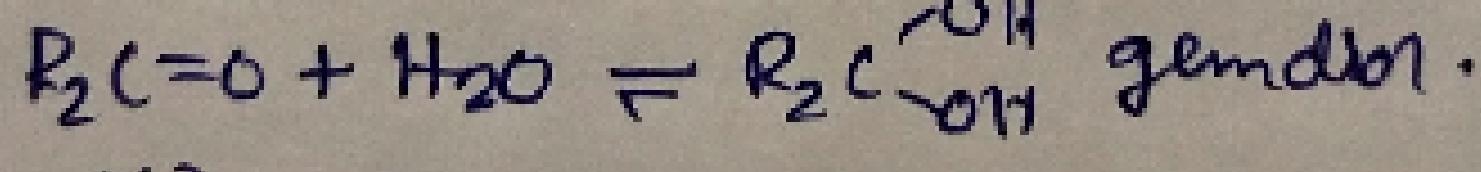
SO_3^{2-} is the effective nucleophile.



The position of the equilibrium lies largely to the right hand side for most aldehydes & to the left for most ketones. This reaction is applicable for all aldehydes, ketones having ketomethyl groups & cyclic ketones. [\square : $\square = \text{O}$].

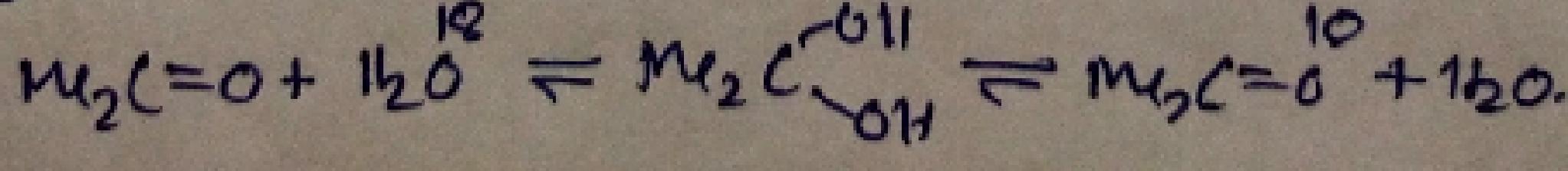
The product if heated with dilute acid, carbonyl compound can be regenerated. This reaction is used as means of separating carbonyl compounds from non-carbonyl compounds.

iii) H_2O : Most carbonyl compounds undergo reversible hydration in aqueous solution.



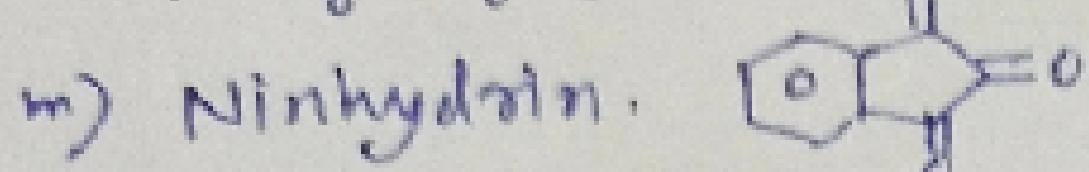
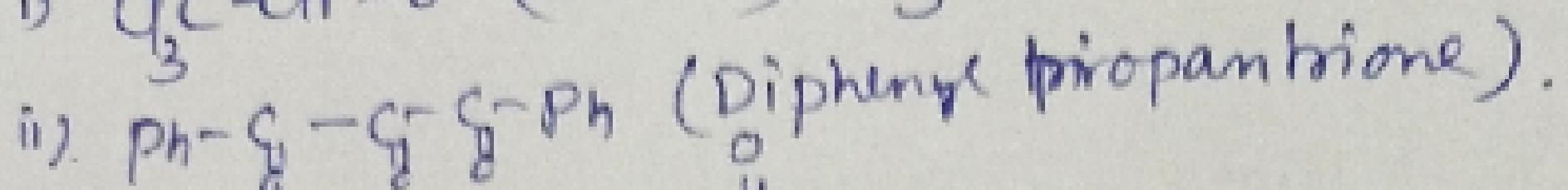
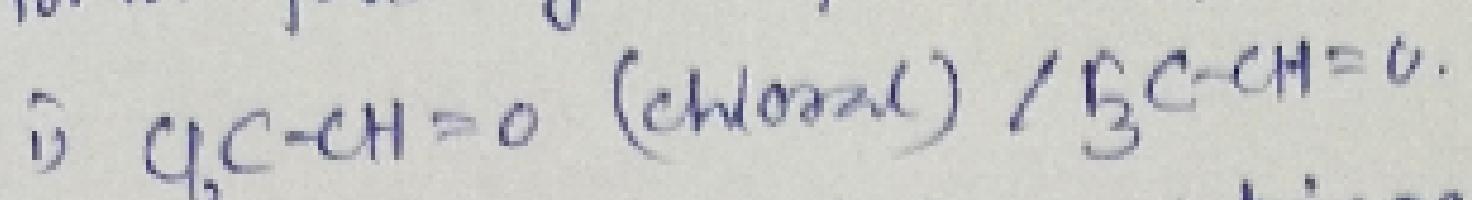
K_{eq} (at 20°C) for most aldehydes & all ketones.

HCHO	2×10^3	Eqn^m is shifted to forward direction.
$\text{CH}_3\text{CH}_2\text{CHO}$	1.4	So gemdiol formed can not be isolated.
CH_3COCH_3	2×10^{-3}	

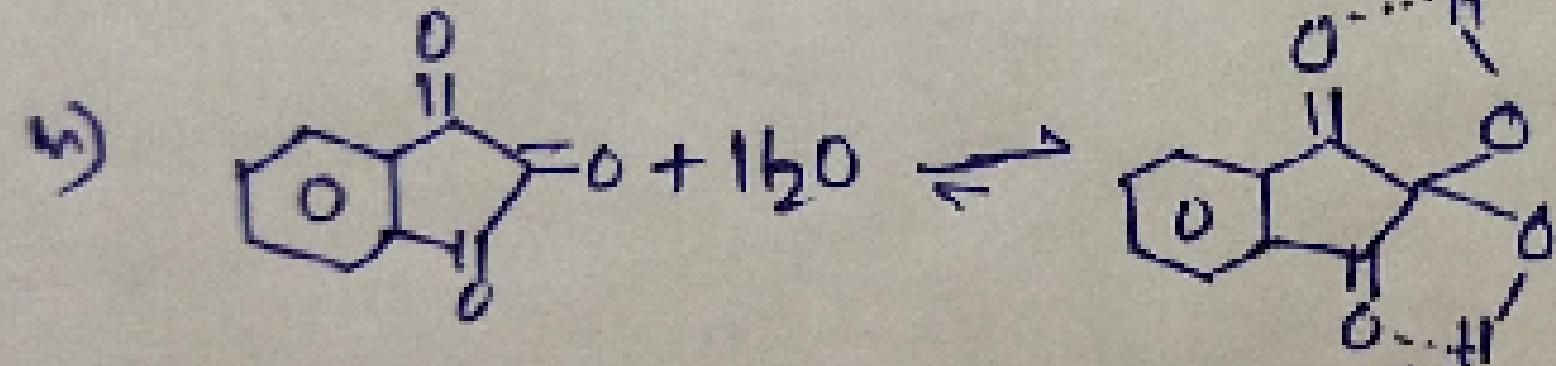
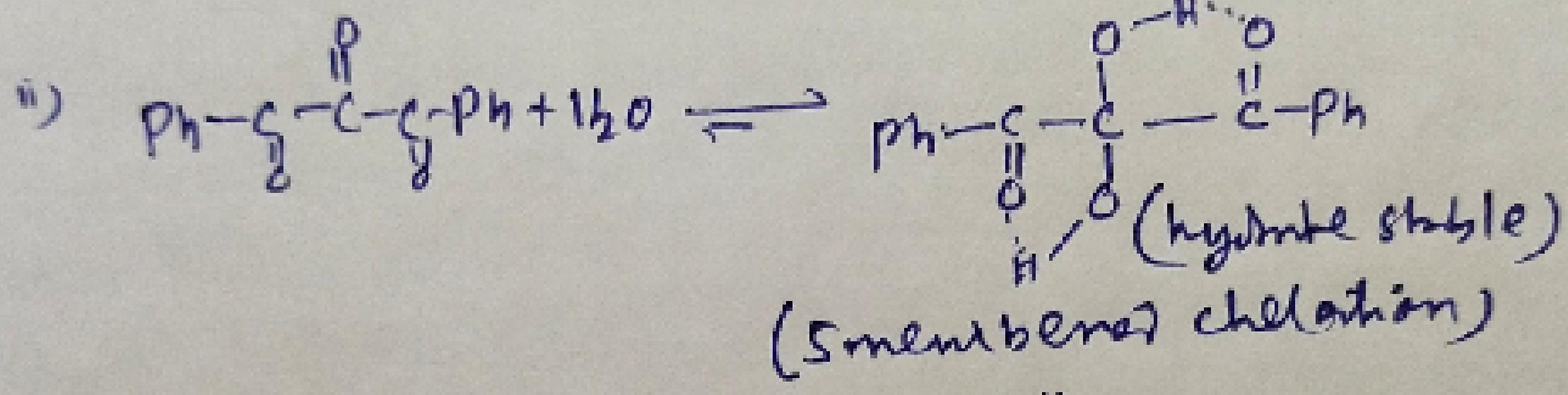


By this way $\text{Me}_2\text{C}(=\text{O})$ can be converted into $\text{Me}_2\text{C}(=\text{O})^{10}$.

for the following compounds gemdiol can be formed. 4

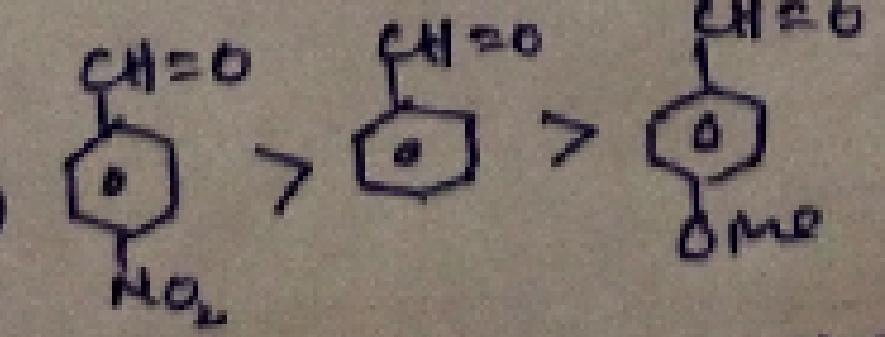
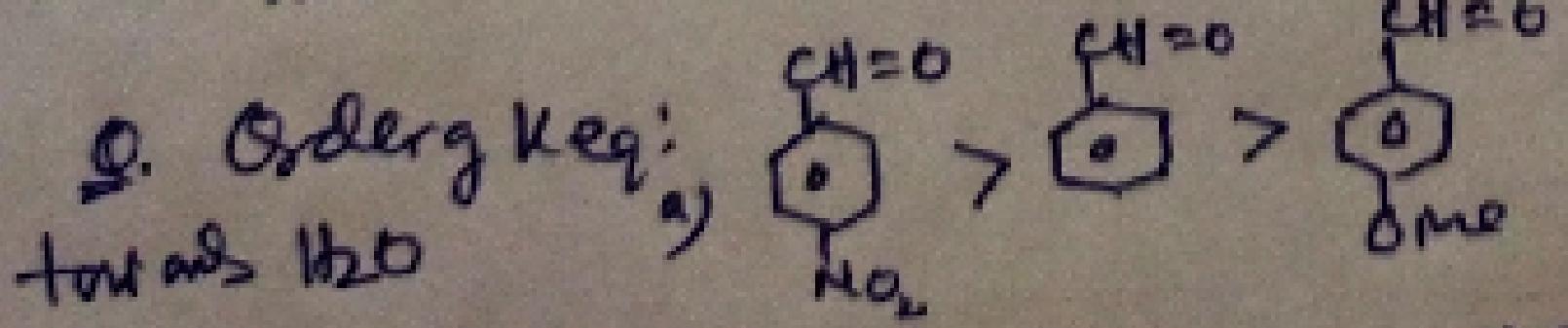


The reason, gemdiols are stable due to intramolecular hydrogen bonding.



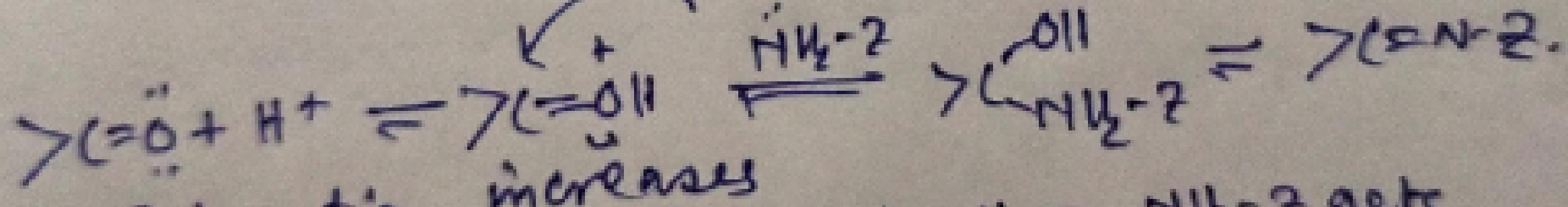
cyclopentanone also forms readily isolable hydrate.

driving force is provided by relief of angle strain
on going from carbonyl compound ($\text{C}-\text{C}-\text{C}$ bond angle is 60° , compared with normal sp^2 value of 120°) to hydrate ($\text{C}-\text{C}-\text{C}$ bond angle = 60° compared with normal sp^3 value of 109.28°).



$\text{N}^{+}\text{H}_2\text{-2}$: (Adding ammonia & its derivative) 5
 Nucleophiles such as NH_3 & its derivative $\text{N}^{+}\text{H}_2\text{-2}$ add to the carbonyl system. The reaction is reversible & catalyzed by acid ($\text{pH}=5\text{ to }6$ reaction rate is optimum). The eqn^m favours the product formation due to rapid dehydration of the intermediate to form >C=NH-2 .

	Reagent:	derivative:	Product:
a) -H	NH_3 (Ammonia)	>C=NH	Imine
b) -R	RNH_2 (Primary amine)	>C=NR .	Schiff's base.
c) -OH	$\text{N}^{+}\text{H}_2\text{OH}$ (Hydroxylamine)	>C=N-OH	Oxime
d) - N^{+}H_2	$\text{N}^{+}\text{H}_2\text{-NH}_2$ (Hydrazine)	>C=N-NH_2	Hydra zone
e) - $\text{N}^{+}\text{H}-\text{Ph}$	$\text{N}^{+}\text{H}_2\text{-NH-Ph}$ (Phenyl hydrazine)	>C=N-NH-Ph	Phenyl Hydra zone
f) - $\text{N}^{+}\text{H}-\text{C}_6\text{H}_3(\text{NO}_2)_2$	2,4, D.N.P Dinitrophenyl hydrazine	$\text{>C=N-NH-C}_6\text{H}_3(\text{NO}_2)_2$	zone
g) - $\text{NH}_2-\text{C}_6\text{H}_4-\text{NH}_2$	$\text{N}^{+}\text{H}_2\text{-NH-C}_6\text{H}_4\text{-NH}_2$. (Semi carbazide)	$\text{>C=N-NH-C}_6\text{H}_4\text{-NH}_2$	Semicarbazone.



Protonation increases
electrophilic character
of carbonyl system

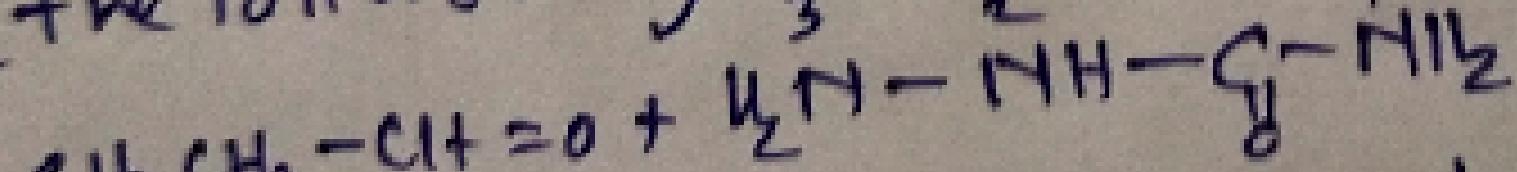
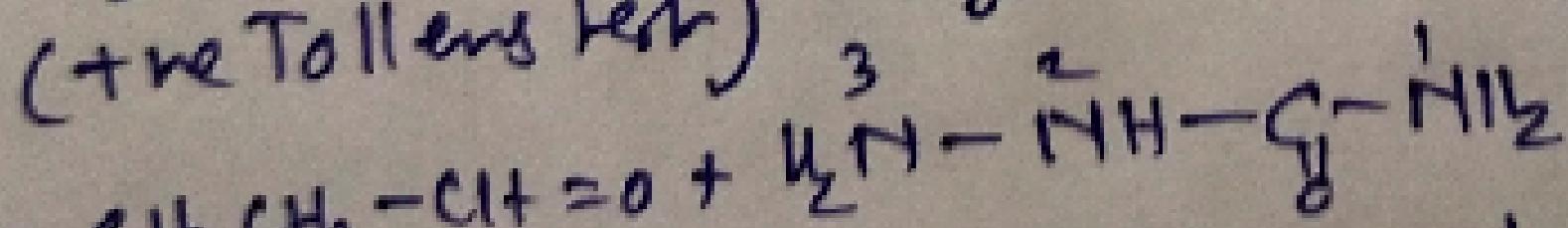
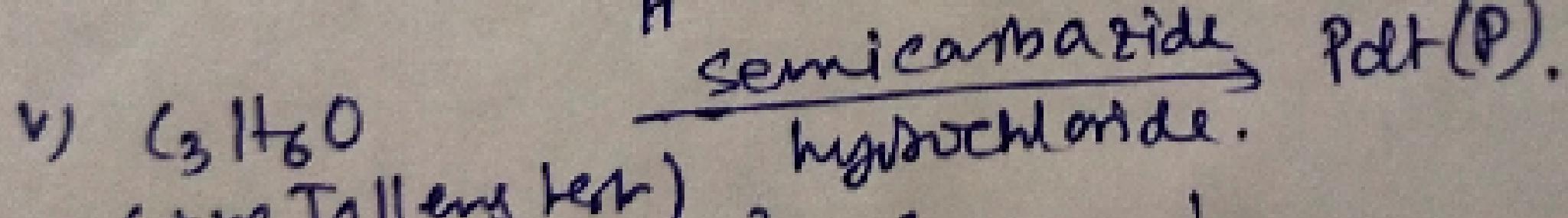
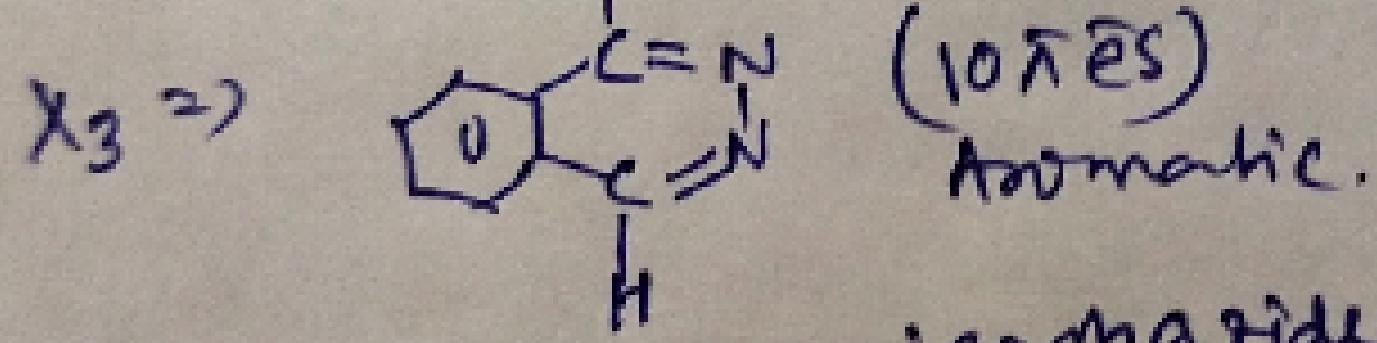
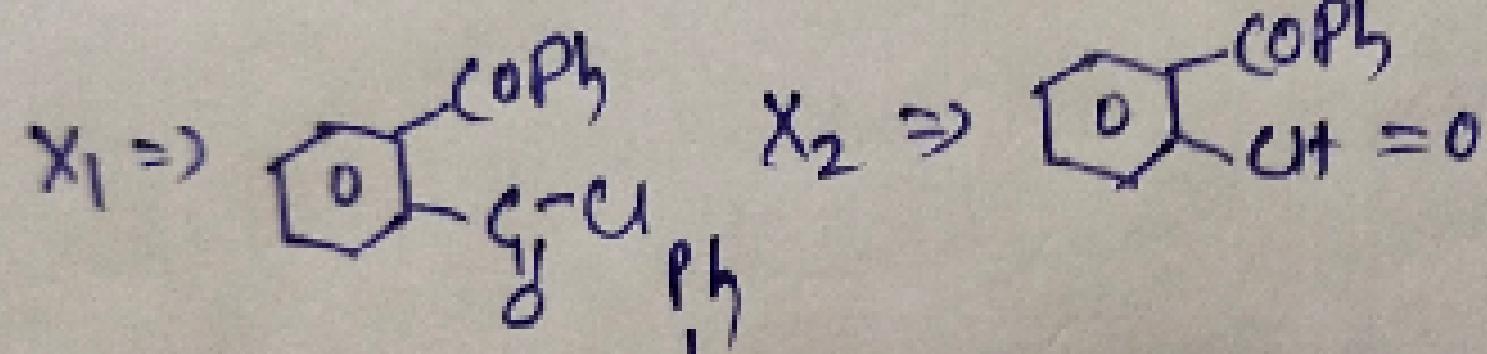
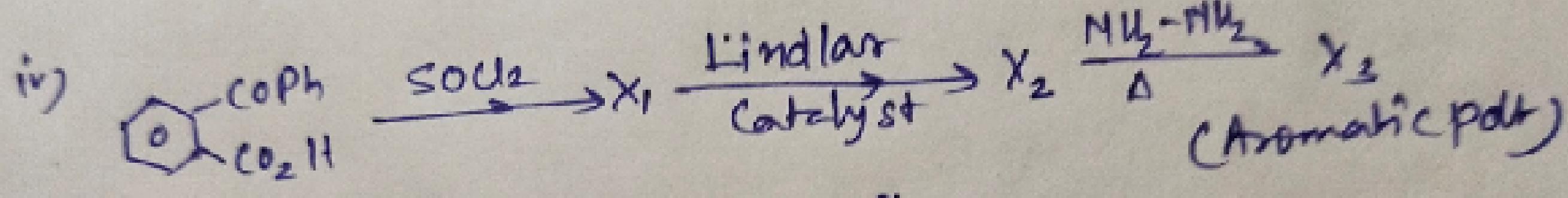
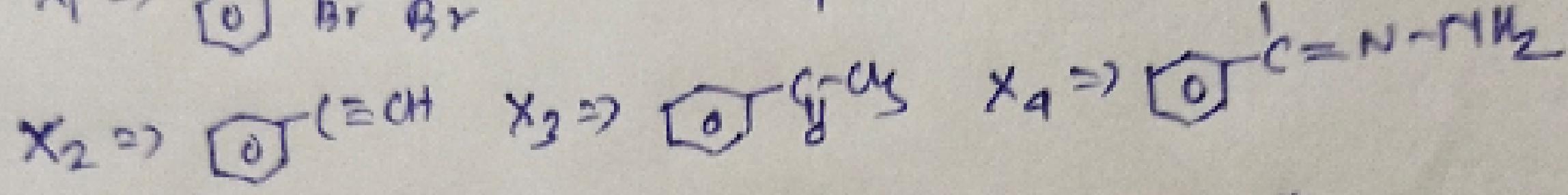
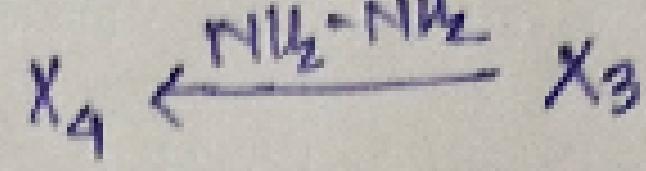
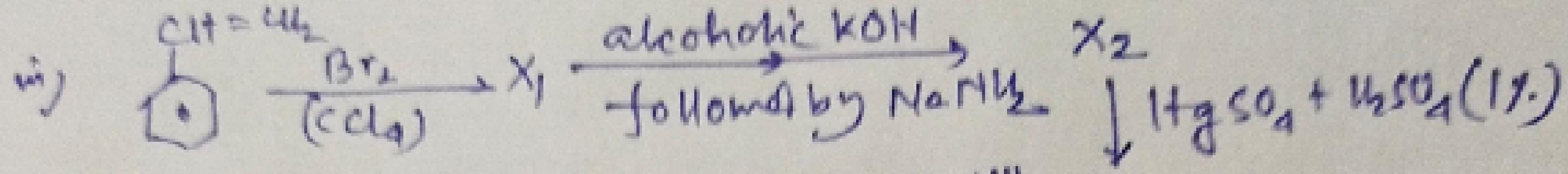
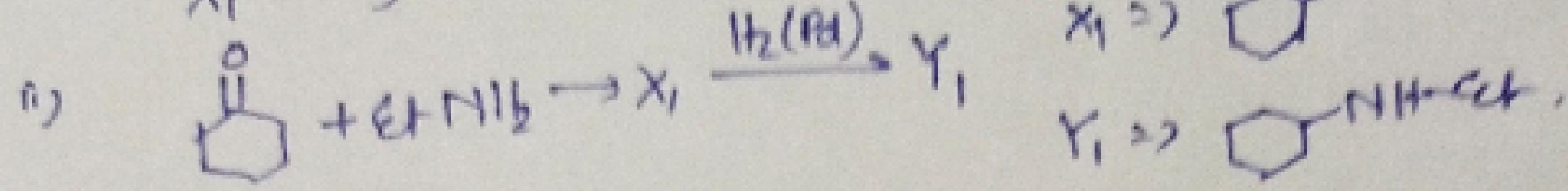
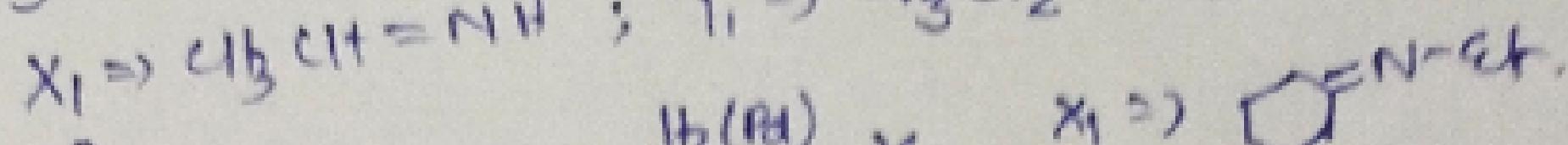
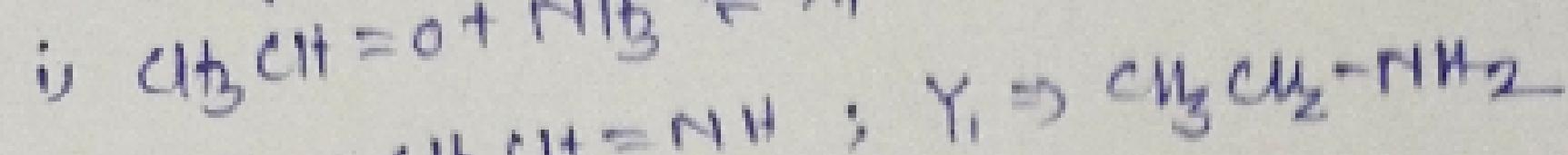
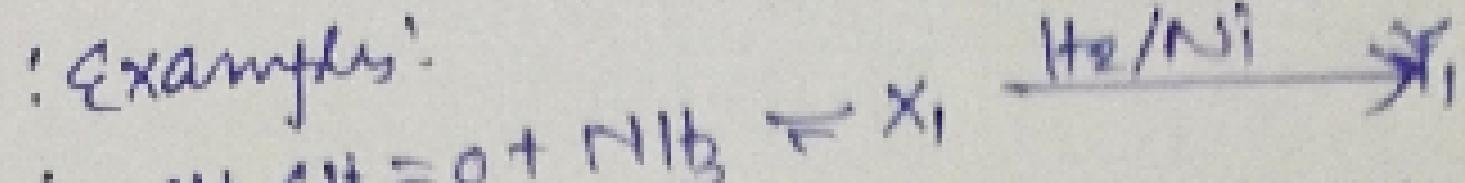
At $\text{pH}=0$, $\text{N}^{+}\text{H}_2\text{-2}$ gets
protonated, so donating
ability of $\text{N}^{+}\text{H}_2\text{-2}$ is lost.

: Points to be noted:

- 2,4 DNP derivatives are yellow, orange or red solids, it is used to identify all aldehydes & ketones. 2,4, D. N. P also used to distinguish a carbonyl compound from noncarbonyl compound.
- Semicarbazone are white crystals.
- Schiff base is formed when 1° aliphatic/aromatic amine reacts with aldehyde.

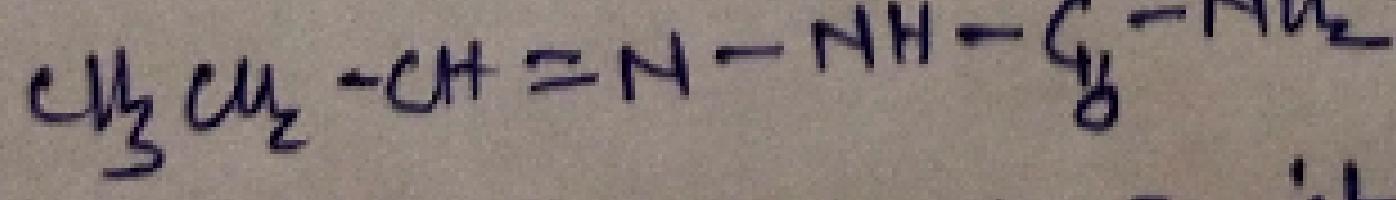
b

Example:



(N^5 is the donor atom)

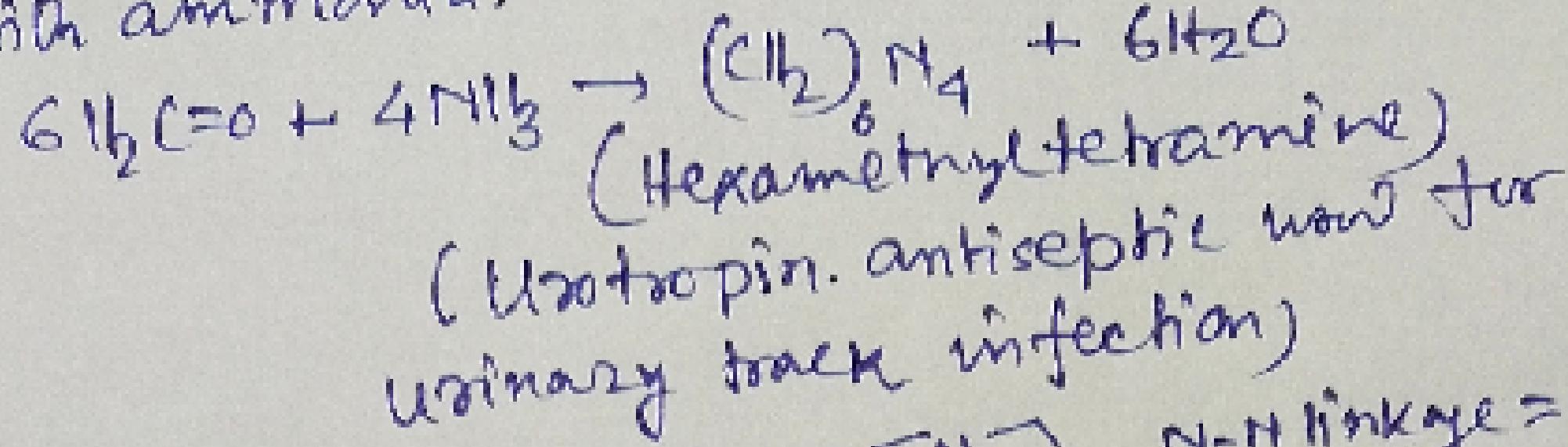
Pure lone pair of electron.



vi) The smallest aldehyde & its next higher homologue reacts with NH_2OH . What are the total no. of organic products. Ans: 3

vii) What will be the product when formaldehyde reacts with ammonia? 7

with ammonia.



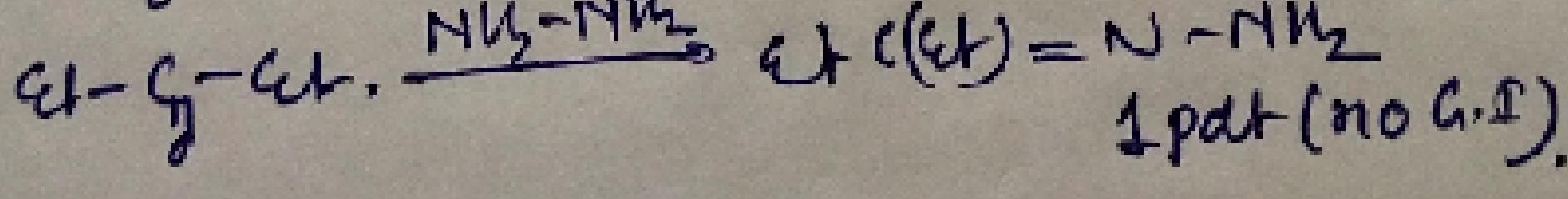
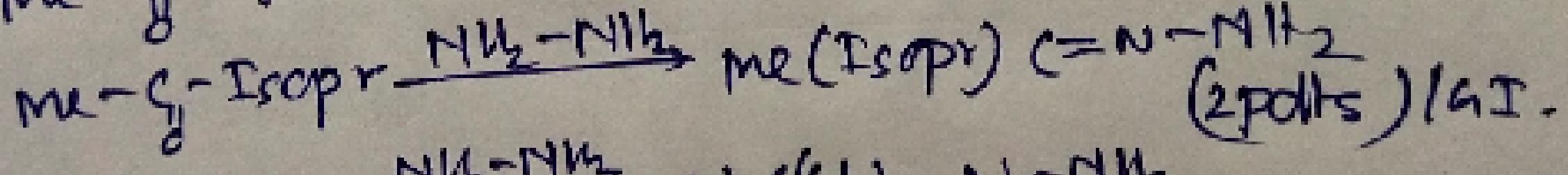
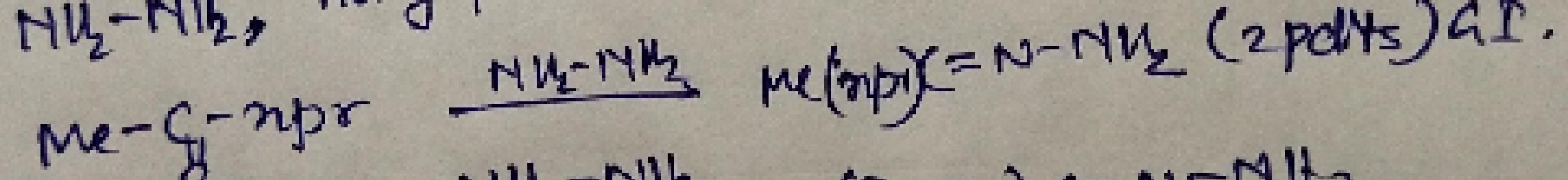
Structure of Urotoxin.



N-N linkage = 0.

- vn) distinguish $\text{CH}_3-\text{C}(=\text{O})-\text{CH}_3$ vs $\text{CH}_3-\text{CH}(\text{C}(=\text{O})-\text{CH}_3)$ 2.U.D.N.P
- b) $\text{CH}_3\text{CH}=\text{O}$ vs $\text{CH}_3-\text{C}(=\text{O})-\text{CH}_3$ Tollen's / Fehling
- c) $\text{CH}_3\text{CH}=\text{O}$ vs $\text{CH}_3\text{CH}_2\text{CH}=\text{O}$ Iodoforn
- d) 2 butanone, 3 pentanone Iodoforn or NaHSO_3 .

ix) Ketone ($\text{M.wt} = 86$) which reacts with NH_2-NH_2 , no. of possible hydrazones.

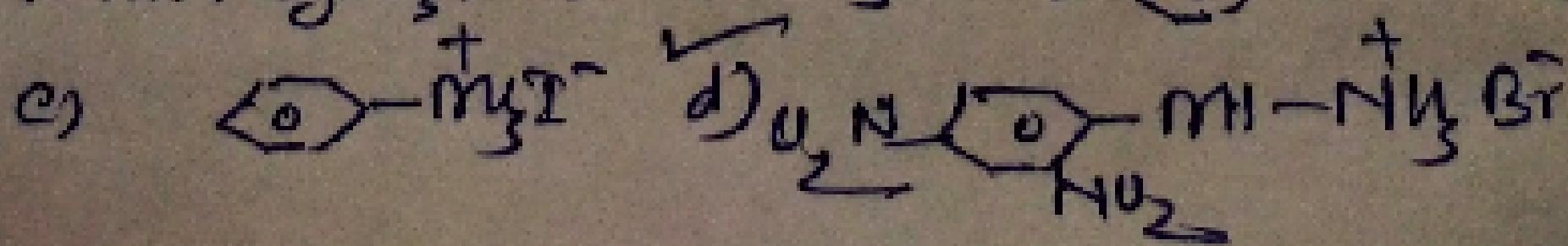


x) Compound X ($\text{C}_3\text{H}_6\text{O}$) gives -ve 2.U.D.N.P test.
Also X does not react with sodium methyl.

What is X? $[\text{CH}_3\text{O}-\text{CH}=\text{CH}_2]$ Ans?

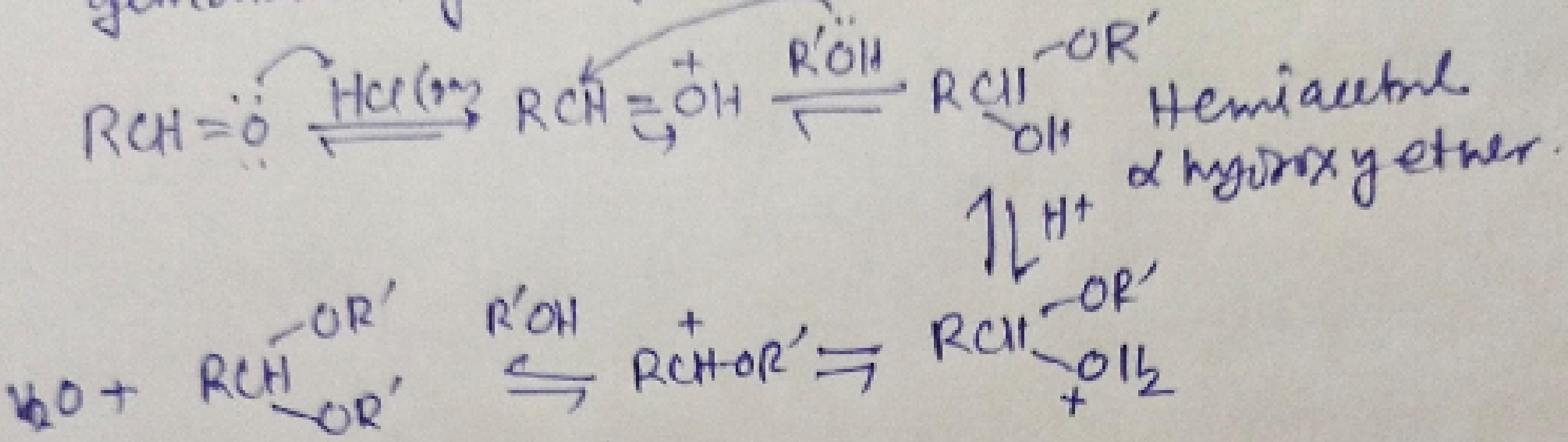
xi) Which compound reacts with aldehydes to form hydrazone ($=\text{N}-\text{NH}$ linkage) & yellow

ppt with AgNO_3 . a) $\text{NH}_2-\overset{+}{\text{NH}_3}\text{Cl}$ b) $\text{O}=\text{N}-\text{NH}_2\text{Cl}$

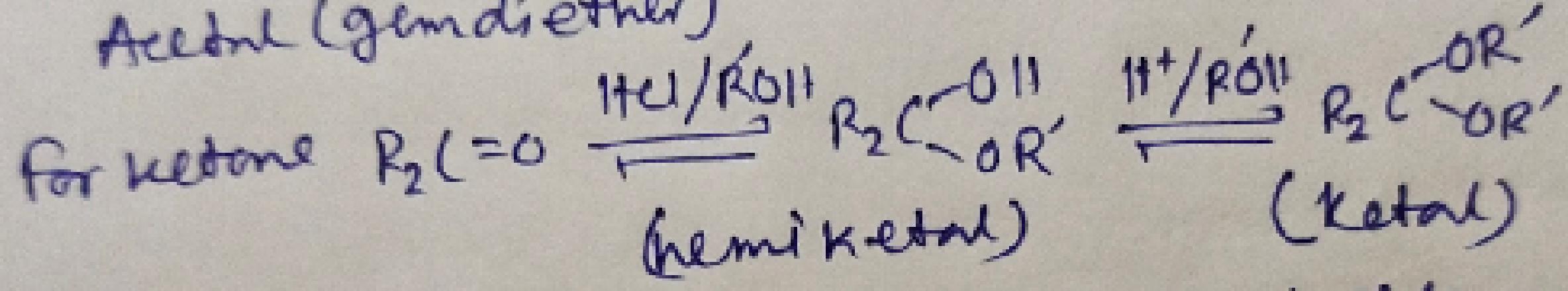


ROH:

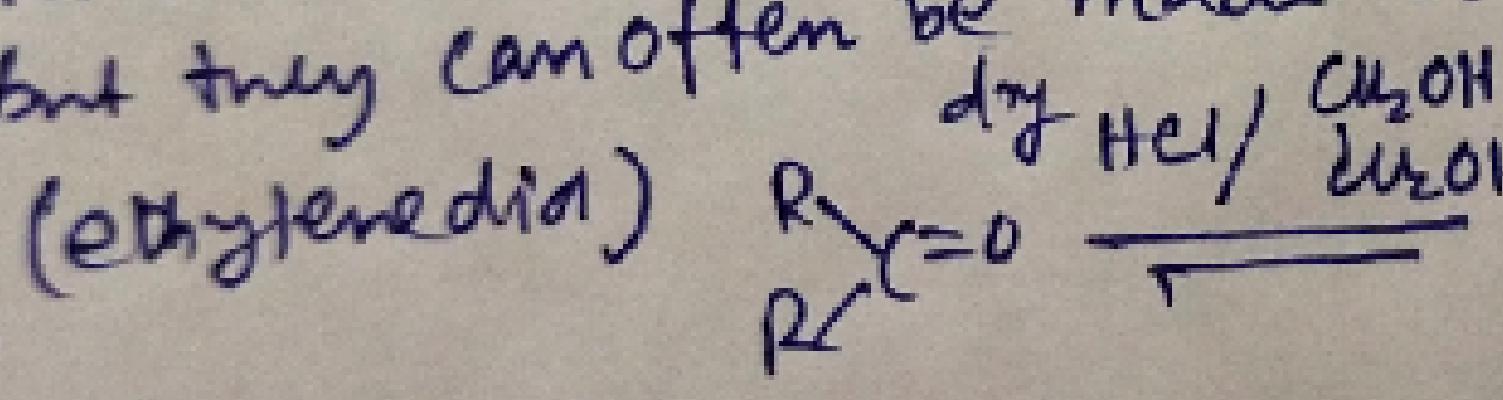
Aldehydes react with one equivalent monohydric 8 alcohol in presence of dry HCl to yield alkoxy alcohol intermediate, known as hemiacetal, which further react with one more molecule of alcohol to give a geminaloxy compound known as acetal.



Acetal (gemdiether)

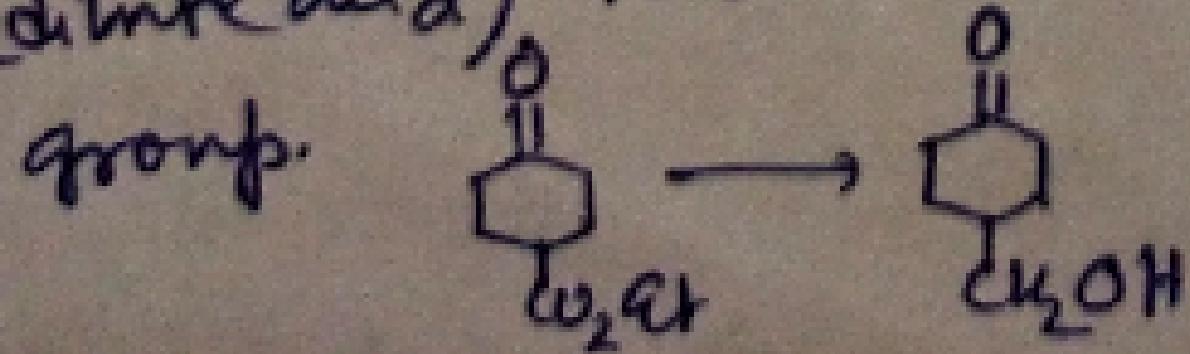


for ketone the reaction lies to reactant side, but they can often be made to react with 1,2 diol.

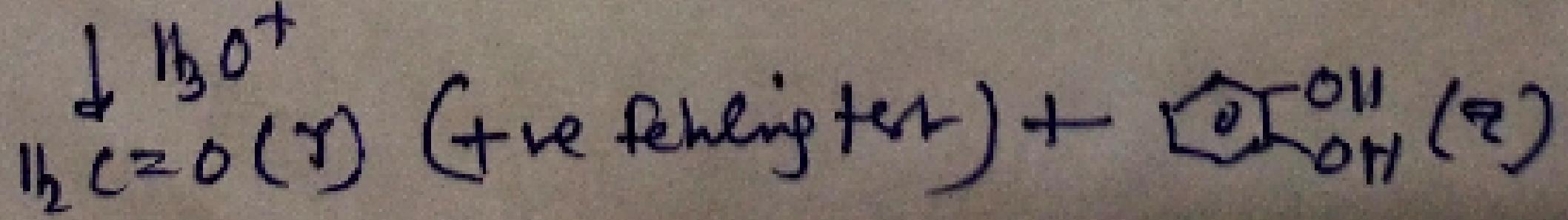
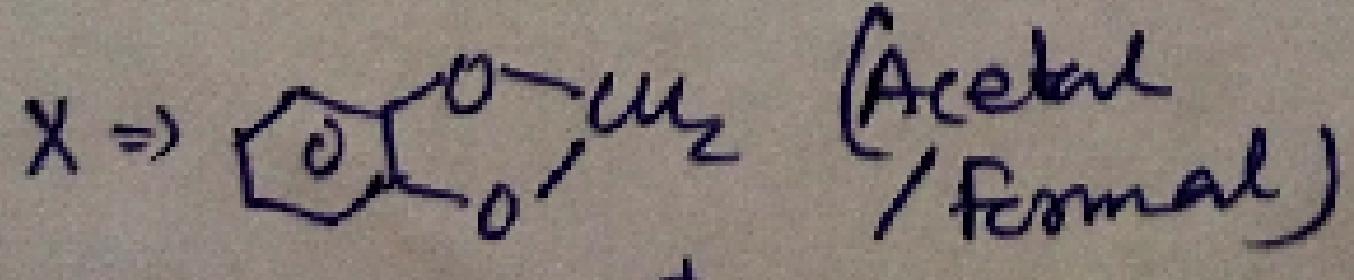
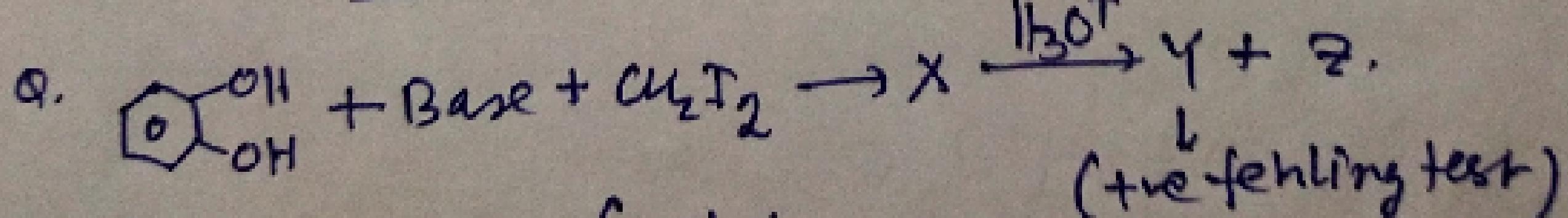
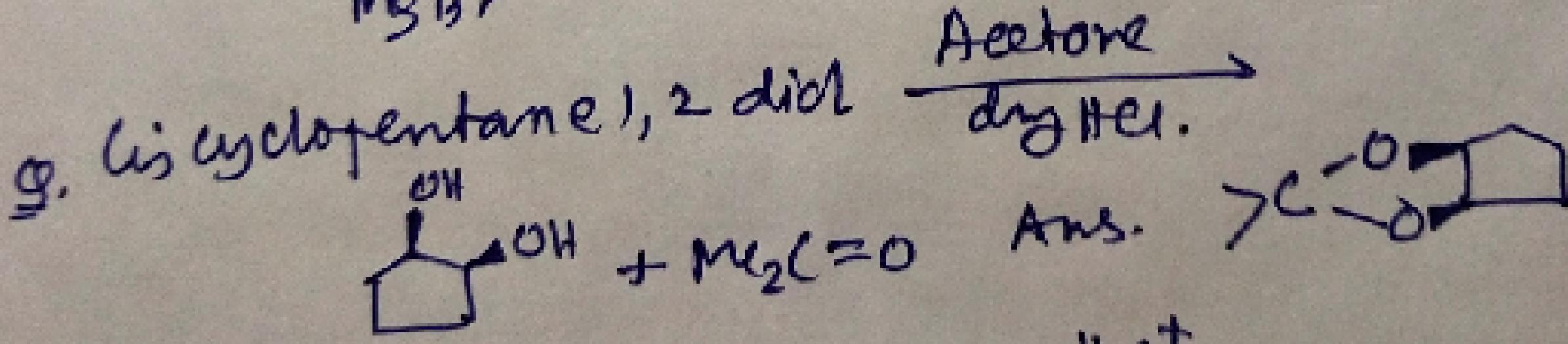
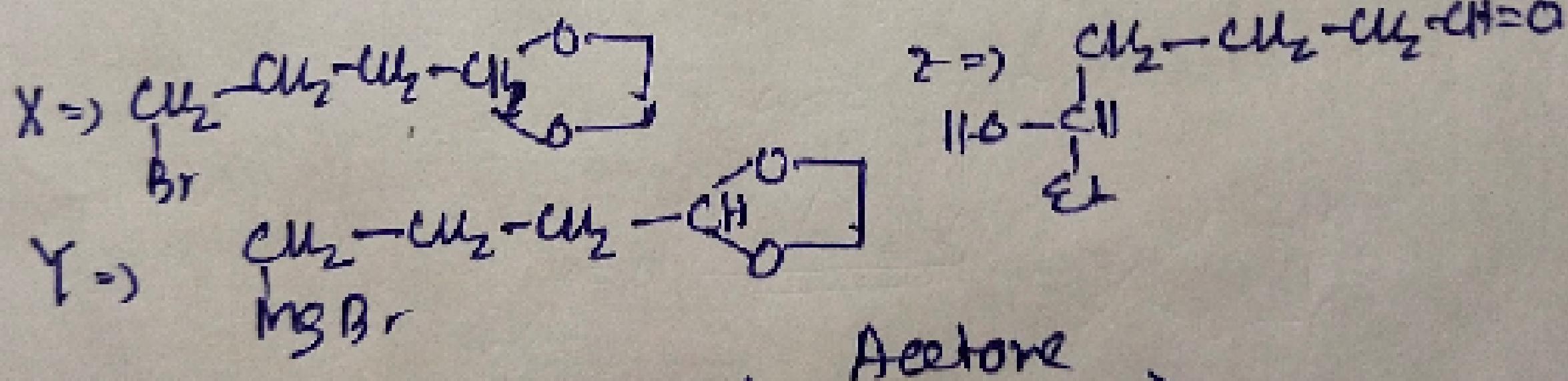
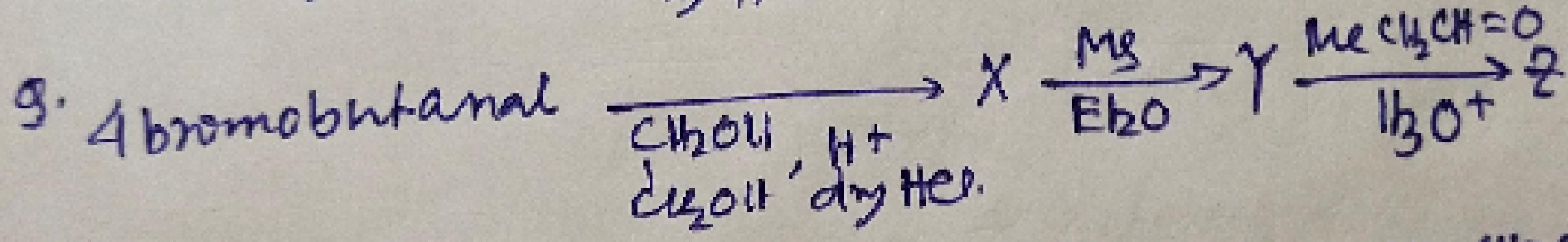
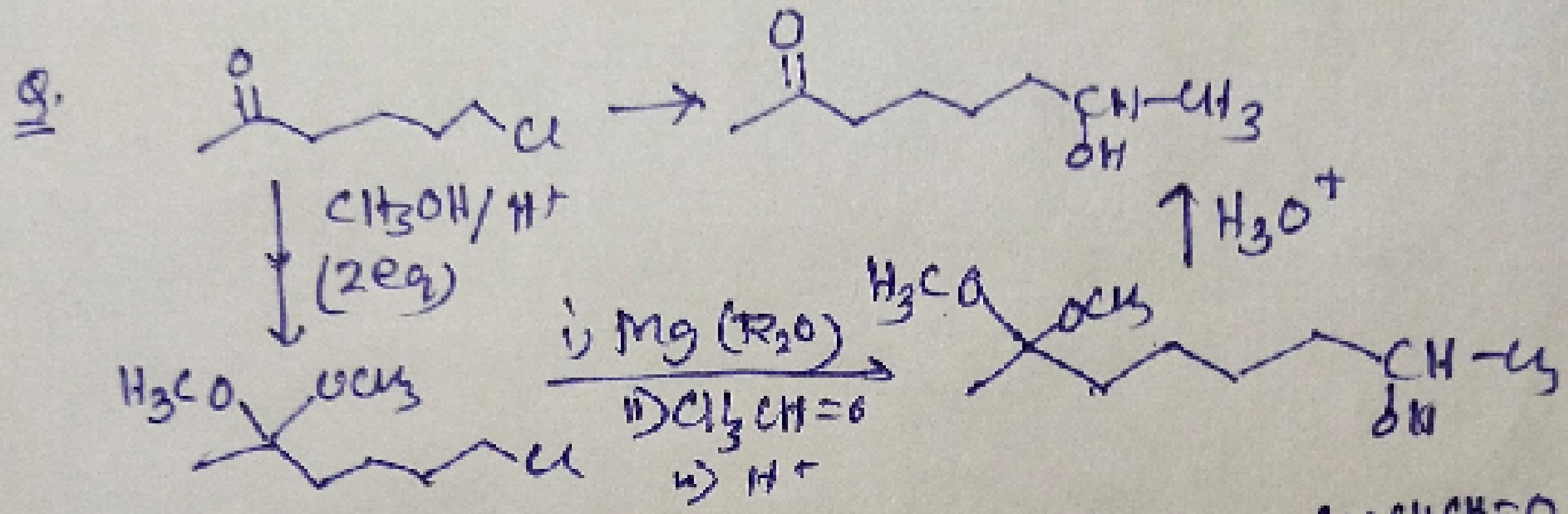
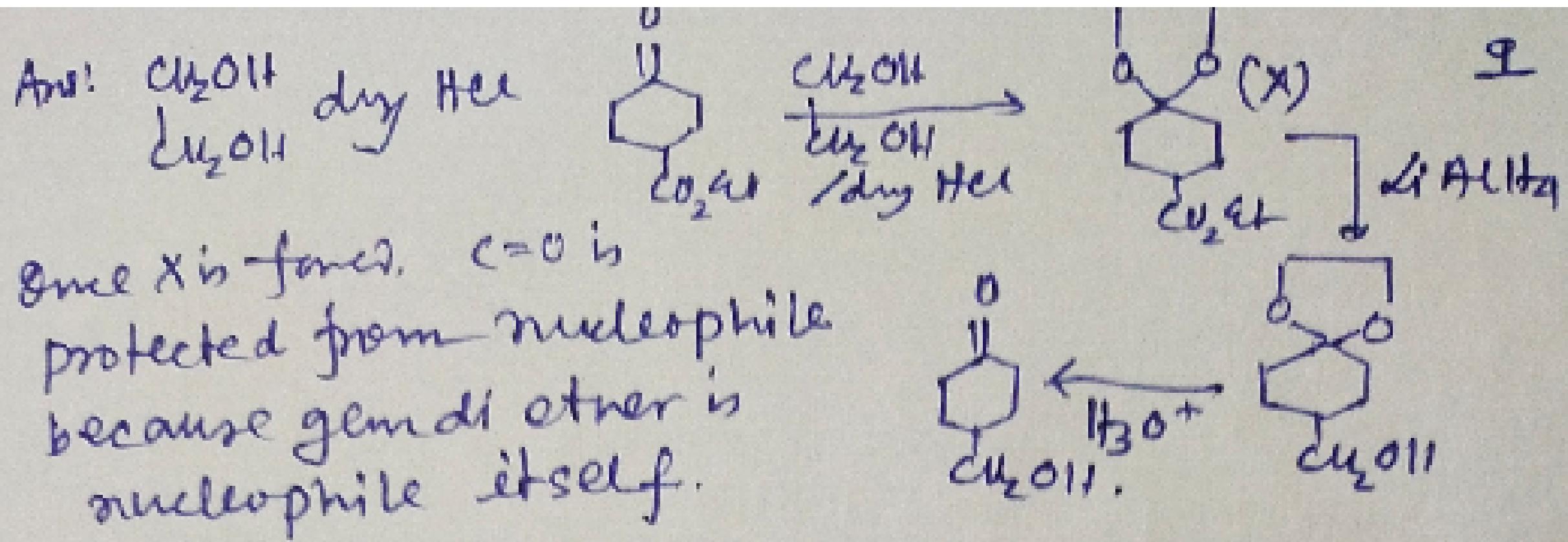


Ethylene glycol acetate

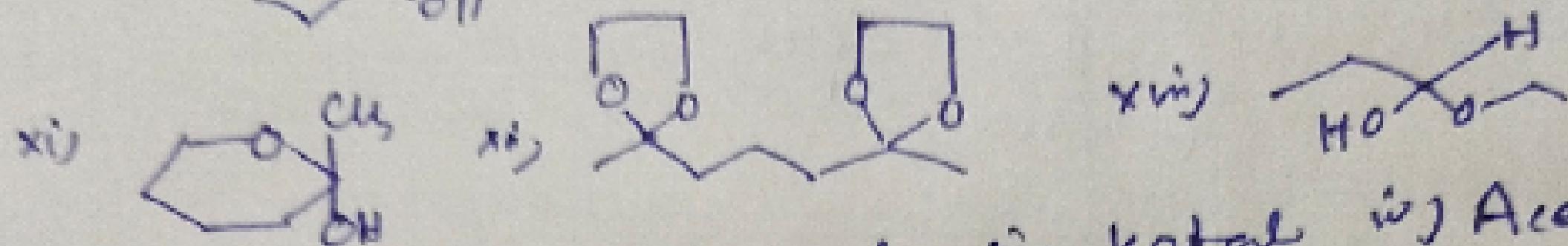
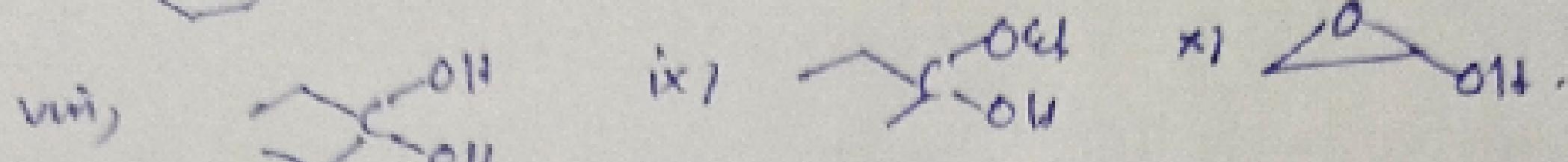
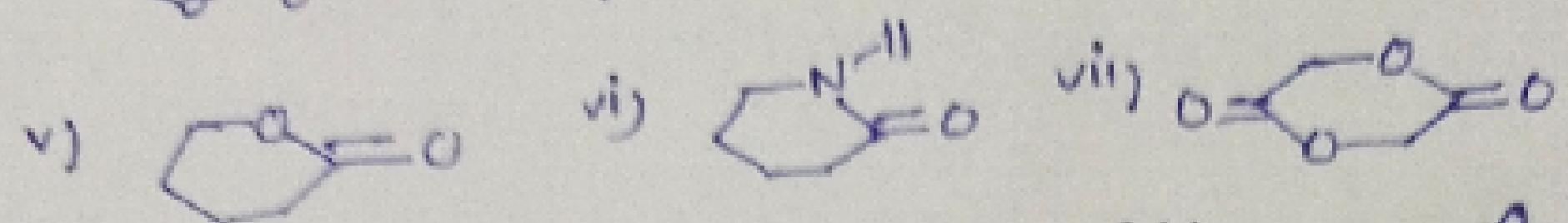
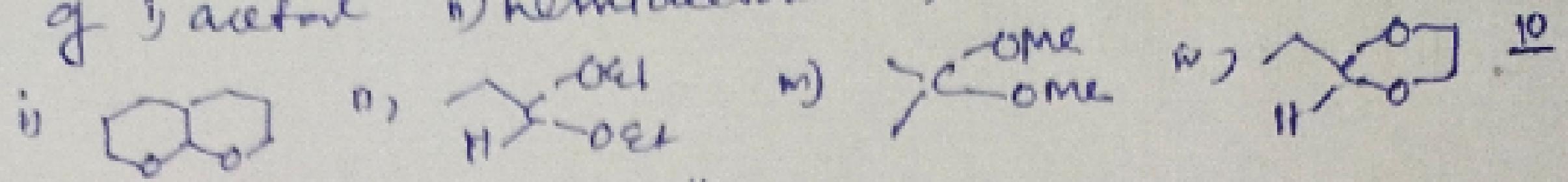
To shift the equilibrium in forward direction, (acetal/ketal formation), the H₂O has to be removed by using excess acid catalyst (passing H₂ gas continuously). The hydrolysis of acetal/ketal (backward reaction) can be carried out in presence of HgO^+ (dilute acid). This reaction is used to protect carbonyl group.



To carry out the following conversion, what should be the reagents and?



a. How many of following compounds are example
of i) acetone ii) hemiacetal. iii) Ketol iv) Hemiketal



i) cyclic acetone. ii) Acetal. iii) Ketol iv) Acetone

v) Lactone vi) Lactum vii) Lactide viii) geminal.

ix) hemiketal. x) hemiacetal xi) hemiketal.
(cyclic)

xii) Ketol (cyclic) xiii) Hemiacetal.

