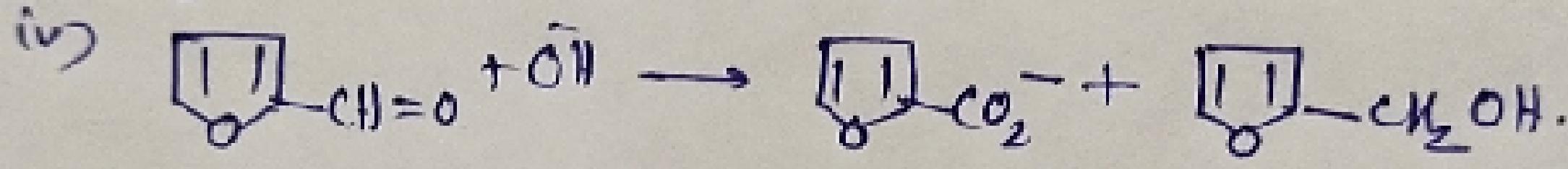
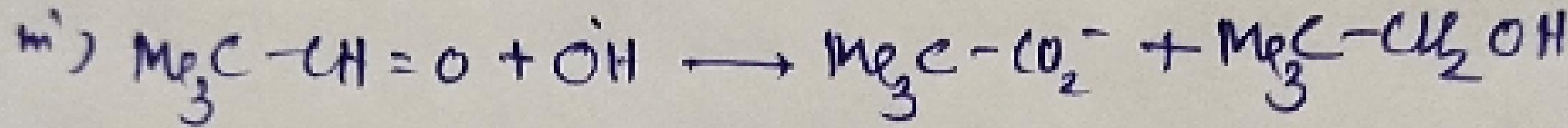
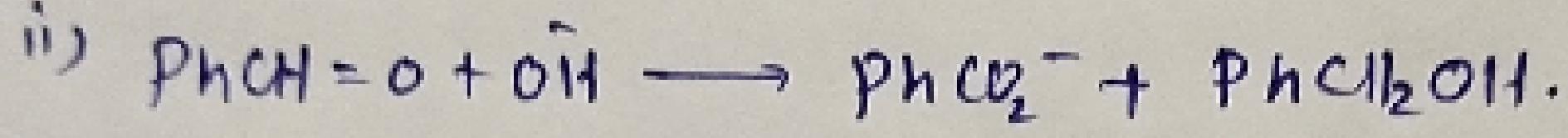
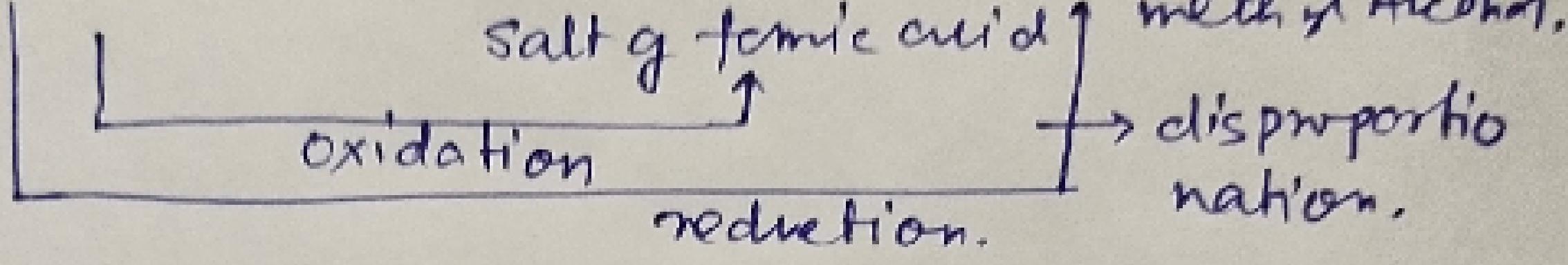
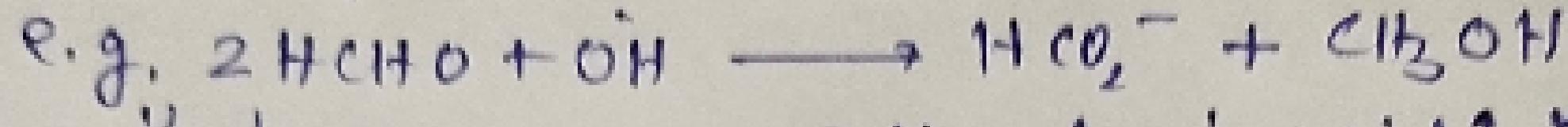


Name reaction:

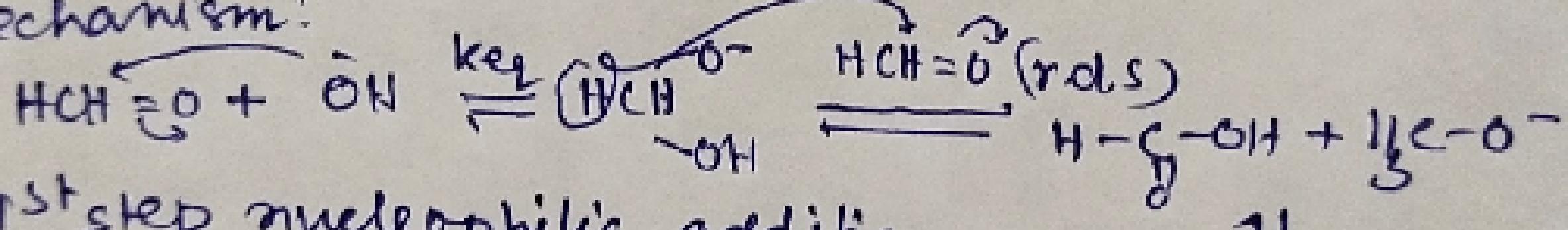
①

Cannizzaro Reaction:

Carbonyl compound (Aldehyde) with no  $\alpha$  hydrogen in presence of base ( $\text{NaOH} / \text{KOH}$ ) undergoes disproportionation reaction & converted into mixture of salt of acid & alcohol.



Mechanism:



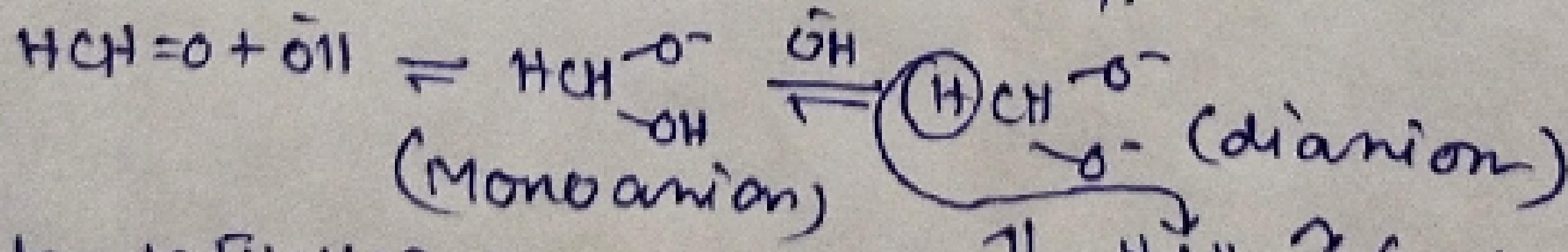
$\Rightarrow$  1<sup>st</sup> step nucleophilic addition

$\Rightarrow$  2<sup>nd</sup> step, r.d.s. H<sup>+</sup> shift takes place  $\text{H}-\text{C}(\text{O}^-)-\text{OH} + \text{CH}_3\text{OH}$ .  
to  $\text{HCHO=O}^{\text{--}}$

$\Rightarrow$  3<sup>rd</sup> step; proton exchange takes place.

$$\Rightarrow \text{rate} = k \frac{[\text{CH}_3\text{OH}]}{[\text{HCHO}]} = k' \frac{[\text{HCHO}]}{[\text{OH}^-]} [\text{OH}^-]^2$$

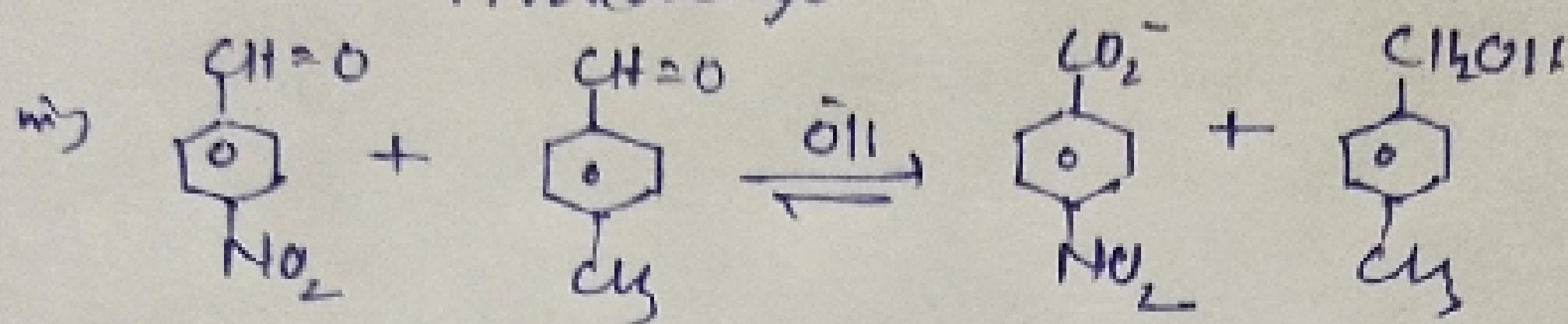
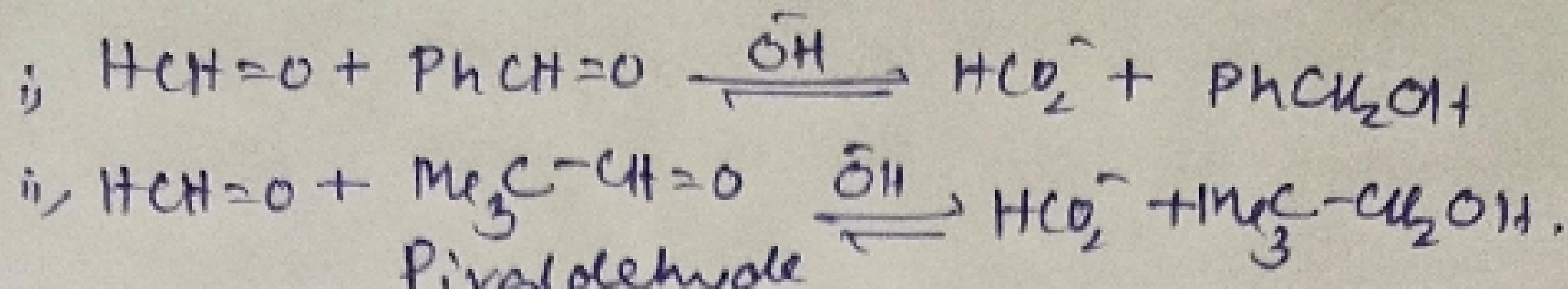
At very high conc<sup>n</sup> of OH<sup>-</sup>, order = 4.



$$\begin{aligned} \text{rate} &= k \frac{[\text{HCHO}]}{[\text{dianion}]} [\text{dianion}] \\ &= k' \frac{[\text{HCHO}]}{[\text{OH}^-]} [\text{OH}^-] [\text{monoanion}] \quad \text{H}-\text{C}(\text{O}^-)-\text{OH} + \text{HCO}_2^- \\ &= k'' \frac{[\text{HCHO}]}{[\text{OH}^-]} [\text{OH}^-]^2 \end{aligned}$$

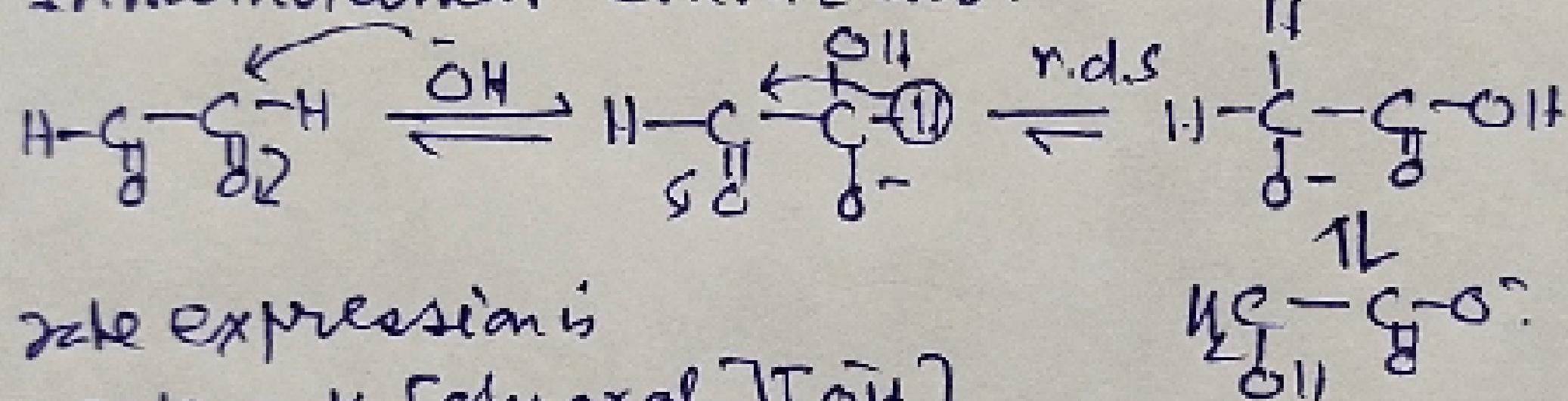
Crossed Cannizzaro:

(2)



Actually, the carbonyl carbon on which  $\delta+$  charge is more, will be attacked by  $\text{OH}^-$ . The carbonyl compound which is first attacked by  $\text{OH}^-$  is always oxidised.

: Intramolecular Cannizzaro:



So, order of Cannizzaro reaction is

i) 3 [simple Cannizzaro; low conc. of  $\text{OH}^-$ ].

ii) 4. [simple Cannizzaro; high conc. of  $\text{OH}^-$ ].

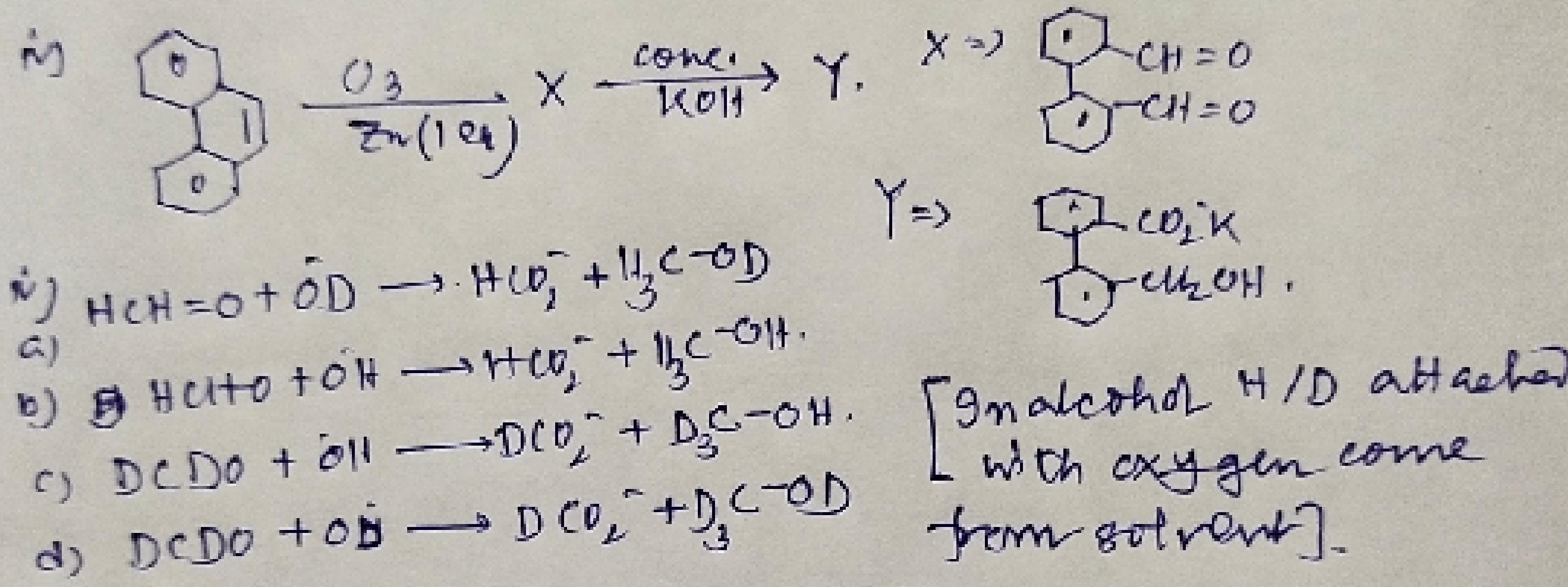
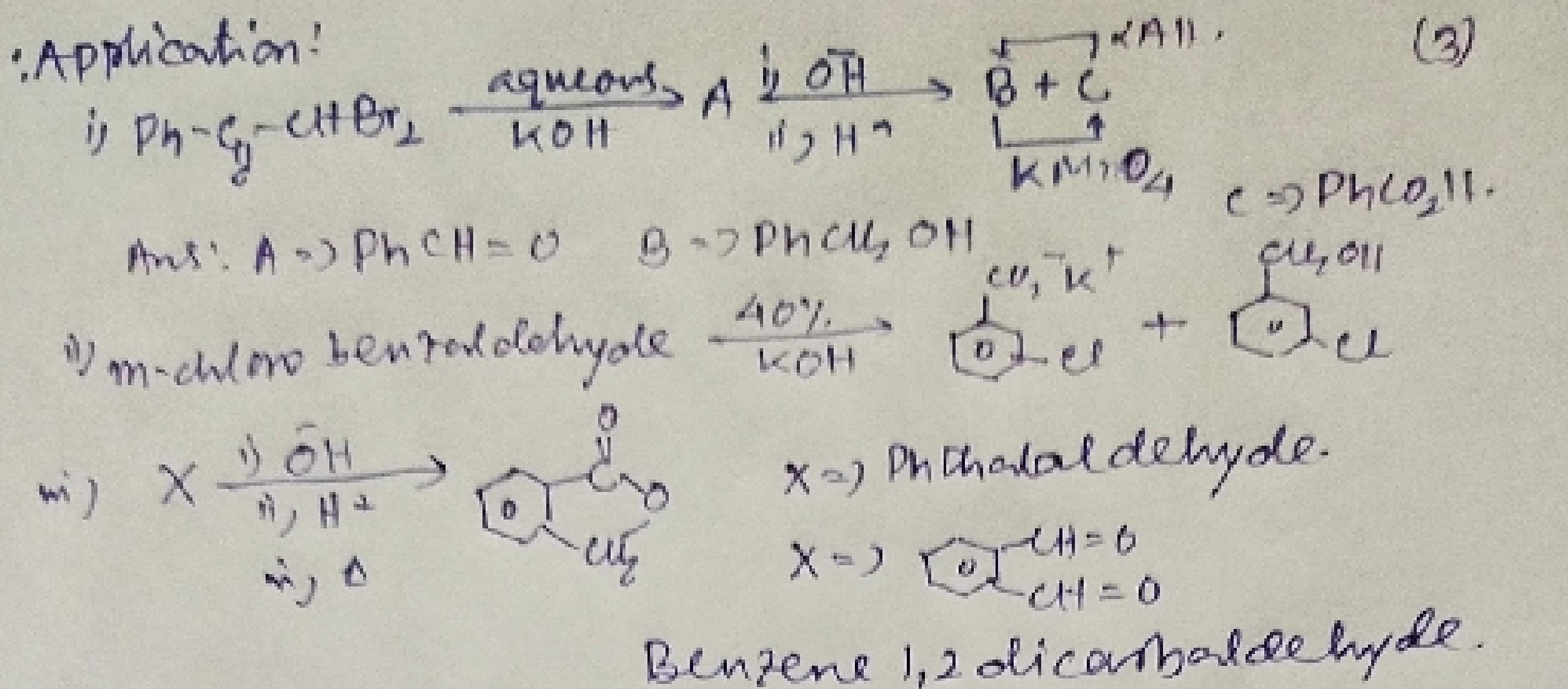
Where dianion is also found as intermediate.

iii) 2 [intracannizaro reaction].

$\Rightarrow$  simple Cannizzaro is disproportionation reaction  
but crossed Cannizzaro is simple redox reaction

$\Rightarrow \text{Ph}-\text{C}_2=\text{O} + \text{OH}^- \rightleftharpoons \text{PhCH}-\text{CO}_2^-$  is example of  
intra crossed Cannizzaro reaction.

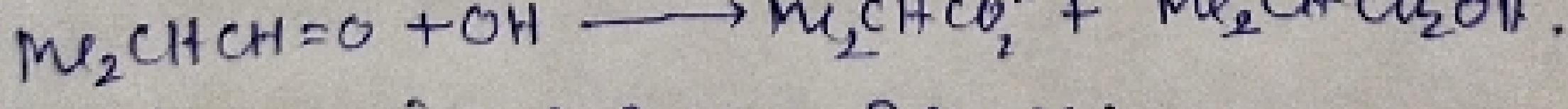
$\Rightarrow \text{Ph}-\text{C}_2=\text{O} \xrightarrow[\text{Catalyst}]{\text{Linollar}} \text{PhCH=O} \xrightarrow[+\text{KOH}]{\text{H}_2\text{O}} \text{PhCH}_2\text{CH} + \text{HCO}_2^-$



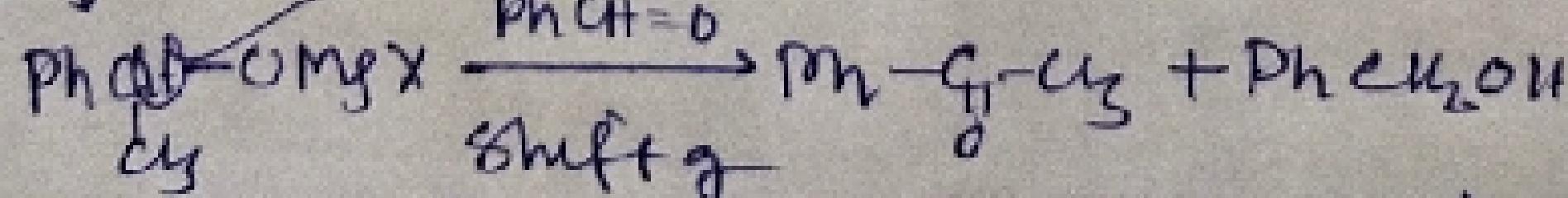
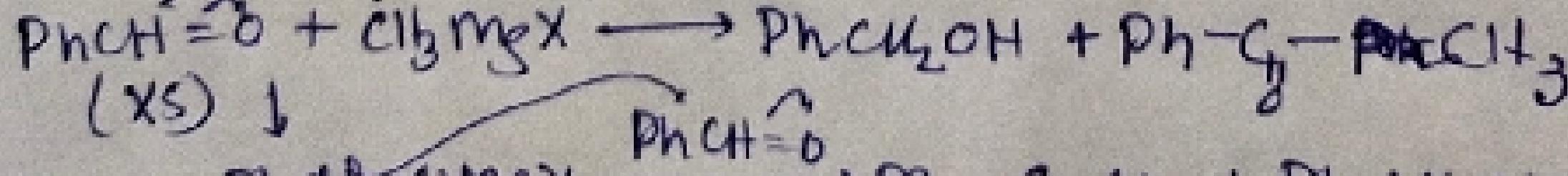
v) Exception:  
 $\text{C}_3\text{H}_7\text{CH=O}$  gives -ve Cannizzaro test. [no  $\alpha\text{H}$ ].

$\text{Me}_2\text{CH}-\text{CH=O}$  gives +ve Cannizzaro test [ $\alpha\text{H}$  present].

Explanation:  $\text{C}_3\text{H}_7\text{CH=O} + \text{OH}^- \rightleftharpoons \text{C}_3\text{H}_7\text{CH}(\text{O}^-)\text{O}^-$  [i.e.,  $\text{C}_3\text{H}_7$  acts as L.G.]

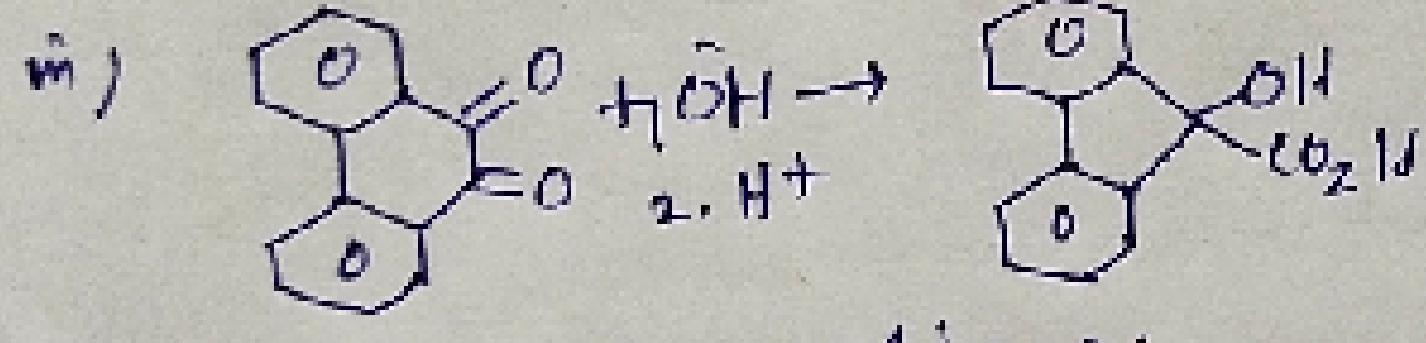
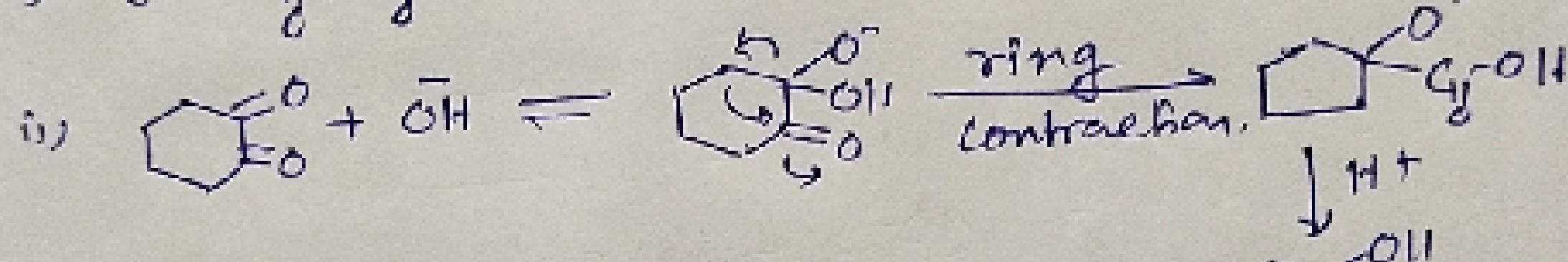
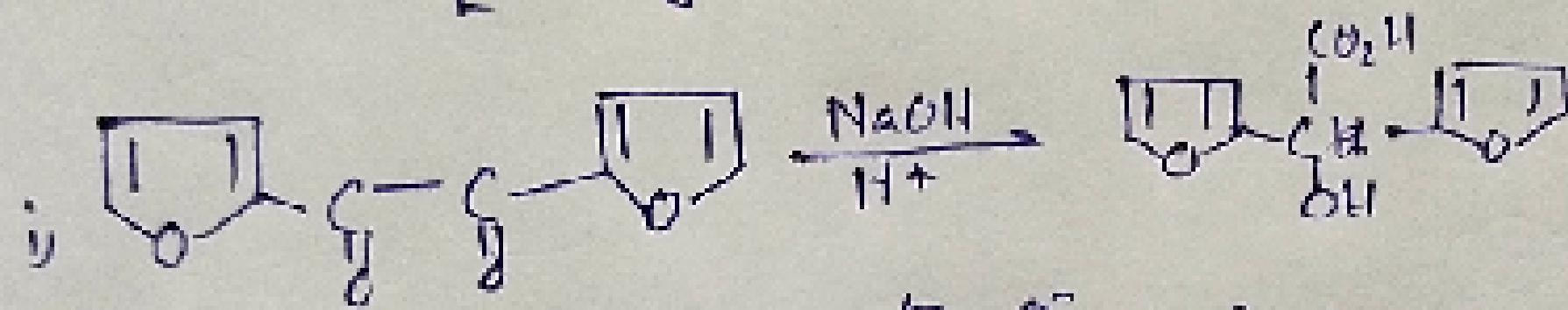
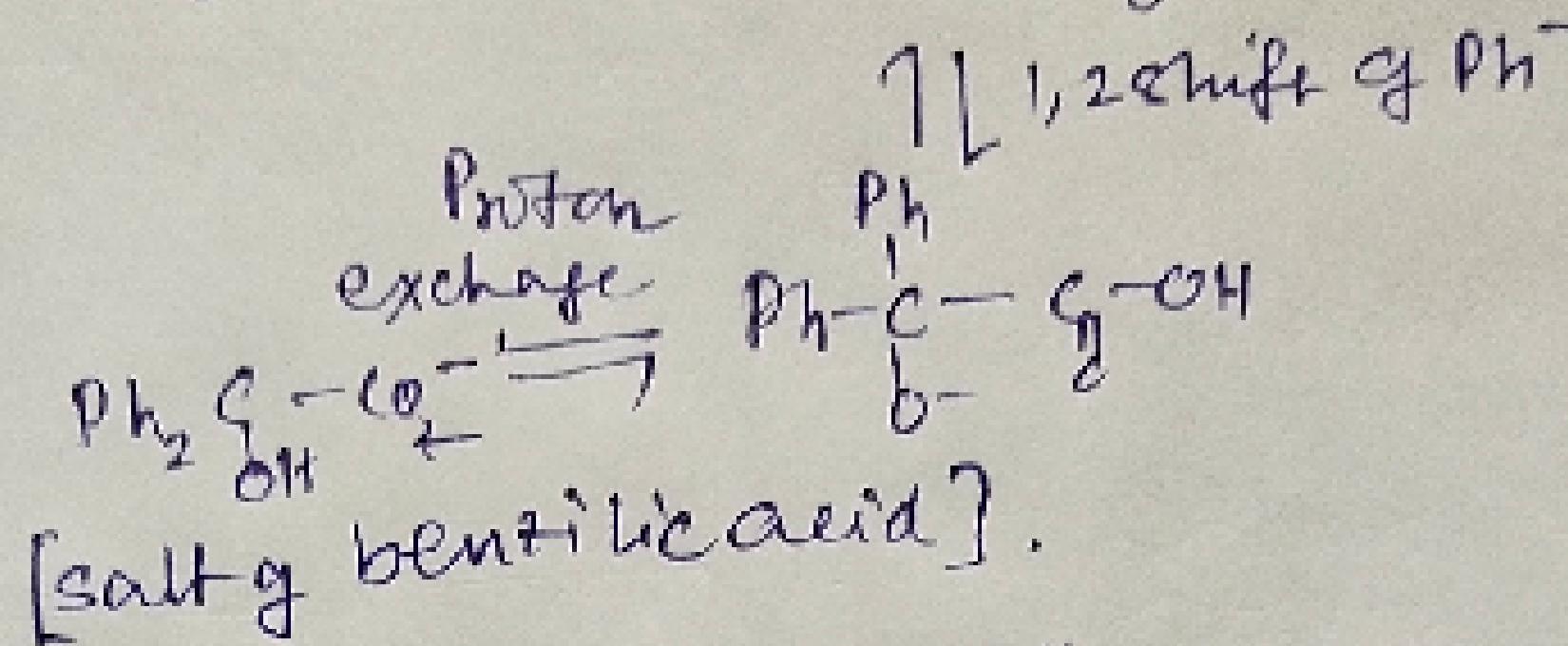
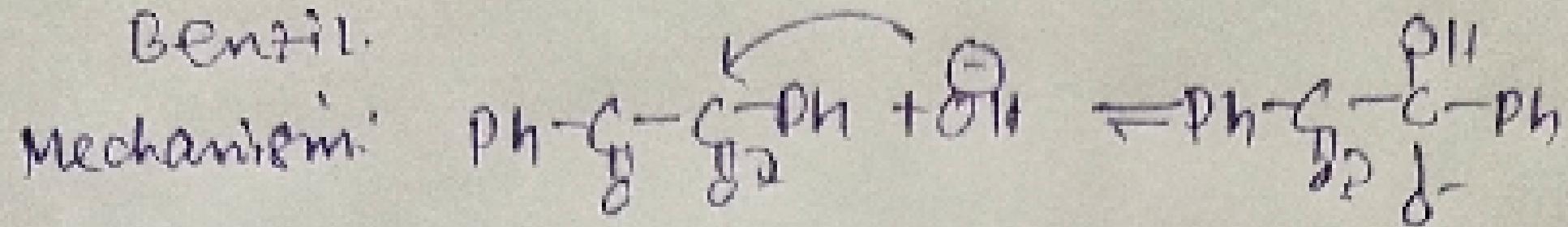
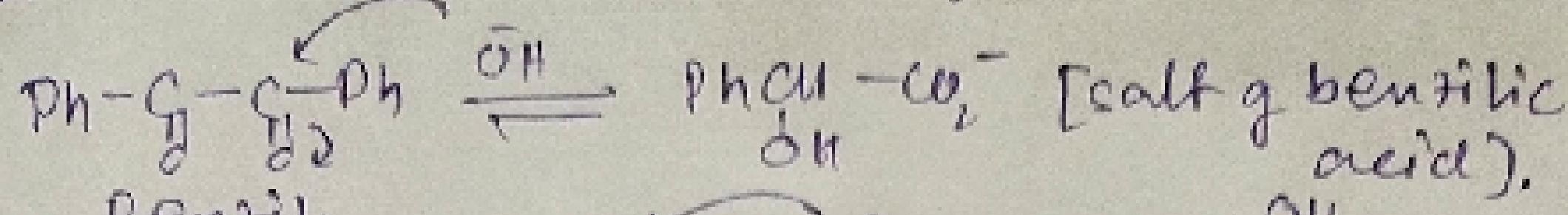
$$\text{HCO}_2^- + \text{CH}_3\text{Cl}_2 \xrightleftharpoons{\text{H}_2\text{O}} \text{CCl}_3 + \text{HCO}_2^-$$


Cannizzaro in presence of  $\text{RMgX}$ :

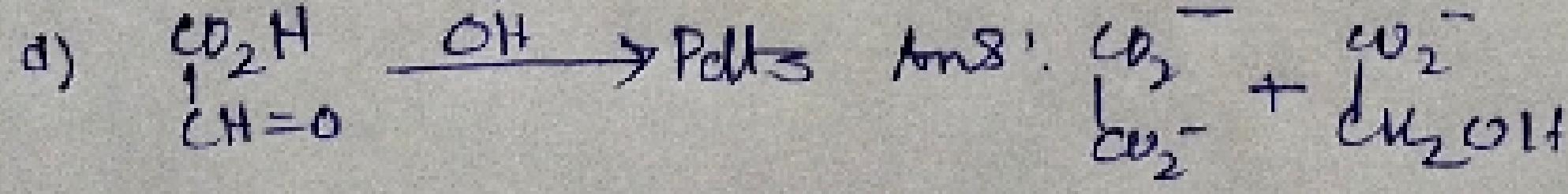
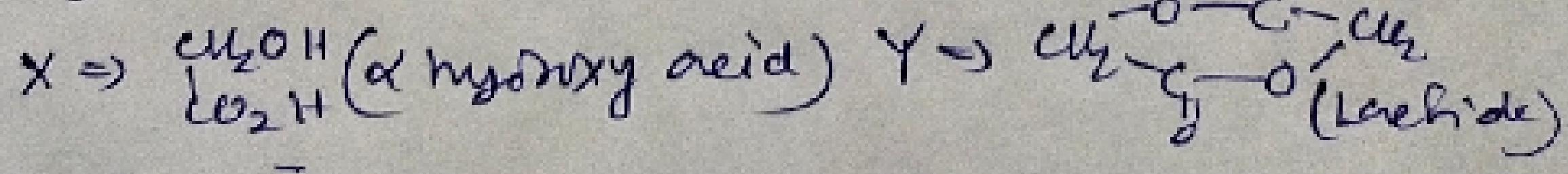
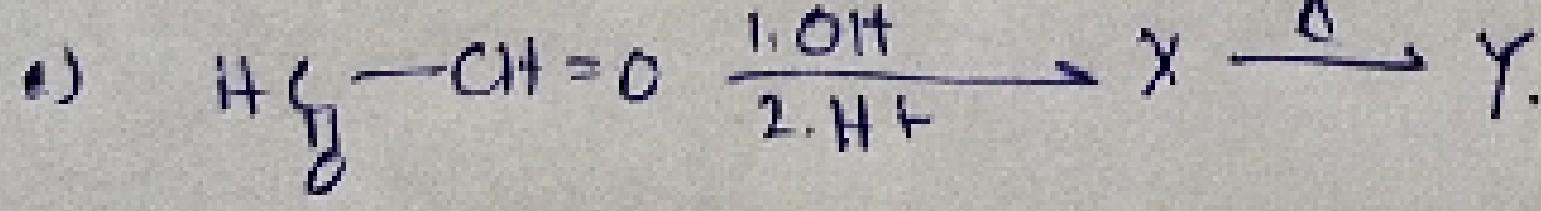
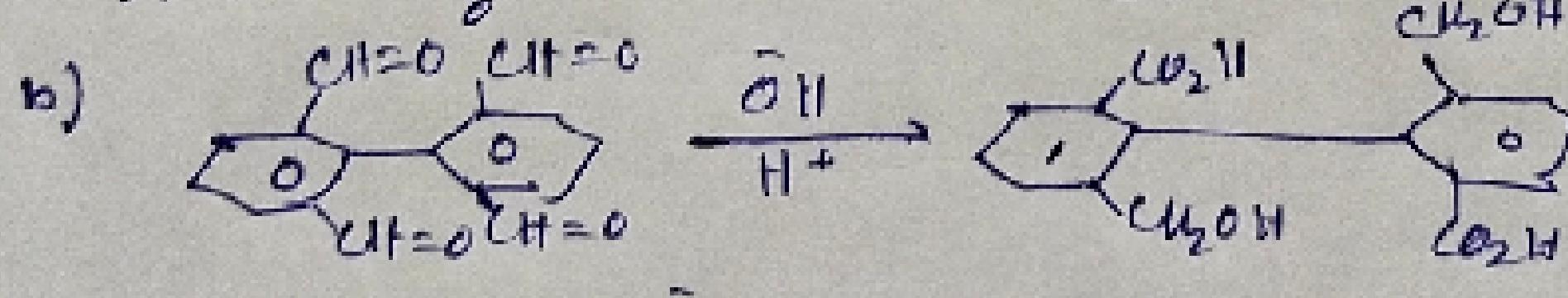
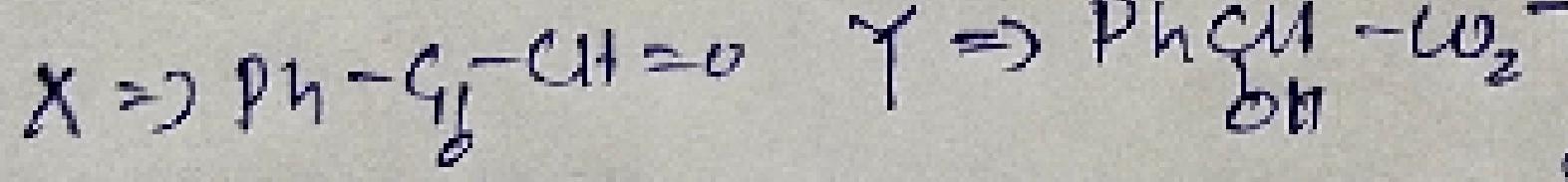
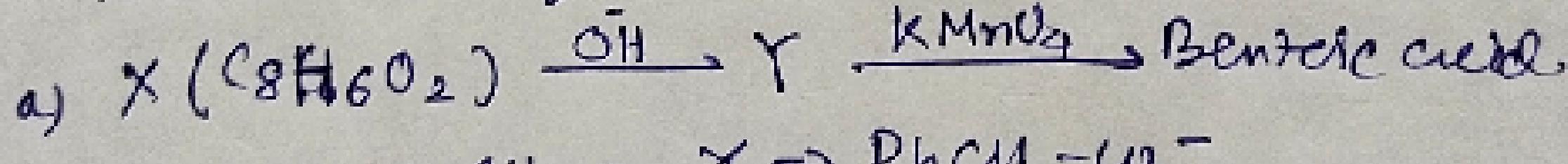


Shift + g  
 $\text{H}^-$  from 1 molecule to another.

## Benzil-Benzoic Acid rearrangement: (4)



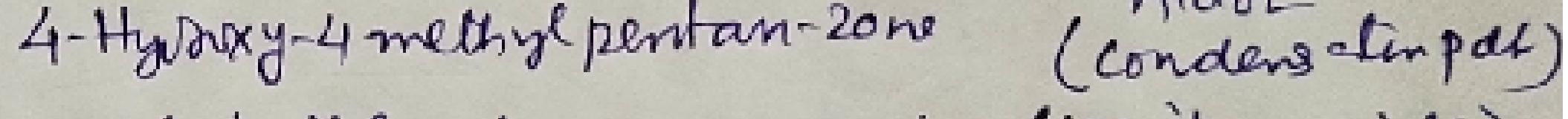
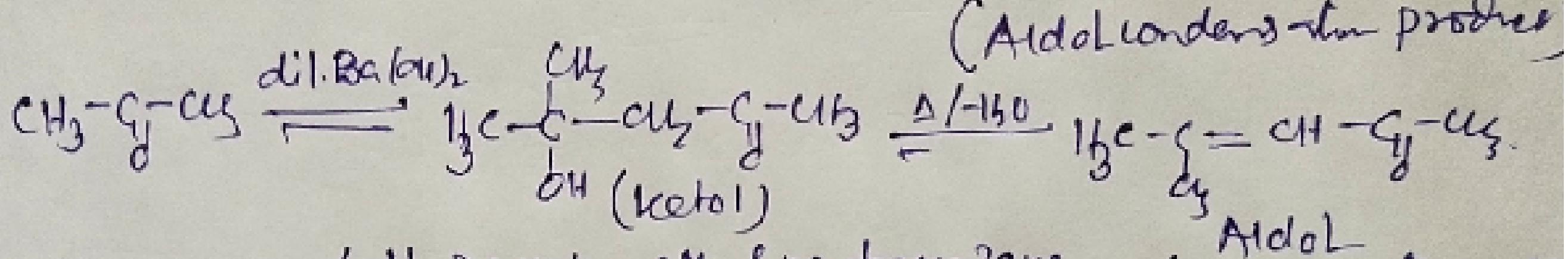
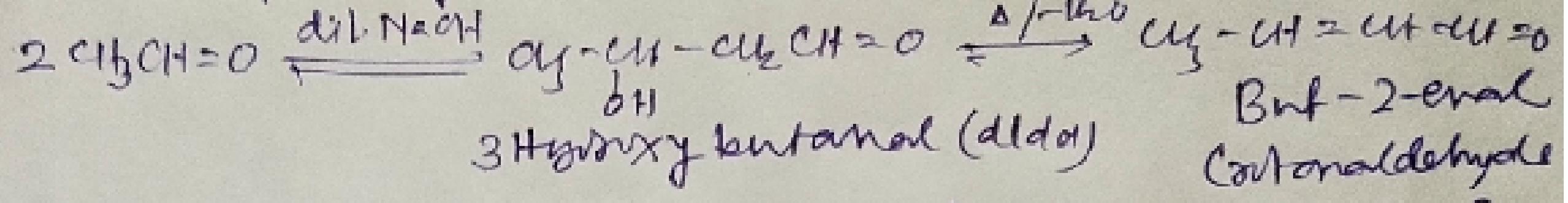
: some more questions:



### Aldol condensation:

(5)

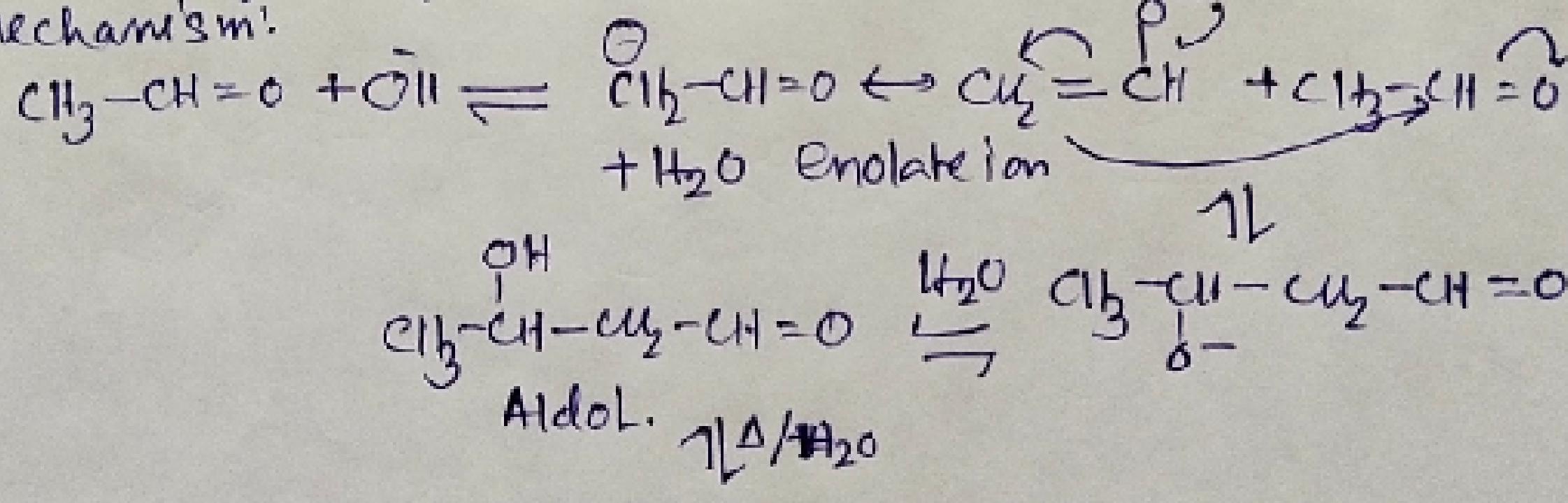
Carbonyl compds (aldehyde / ketone) having at least one  $\alpha$  hydrogen undergo a reaction in presence of dilute KOH as catalyst to give  $\beta$ -hydroxy aldehyde (aldol) or  $\beta$ -hydroxy ketone (ketol) respectively. This is known as Aldol reaction.



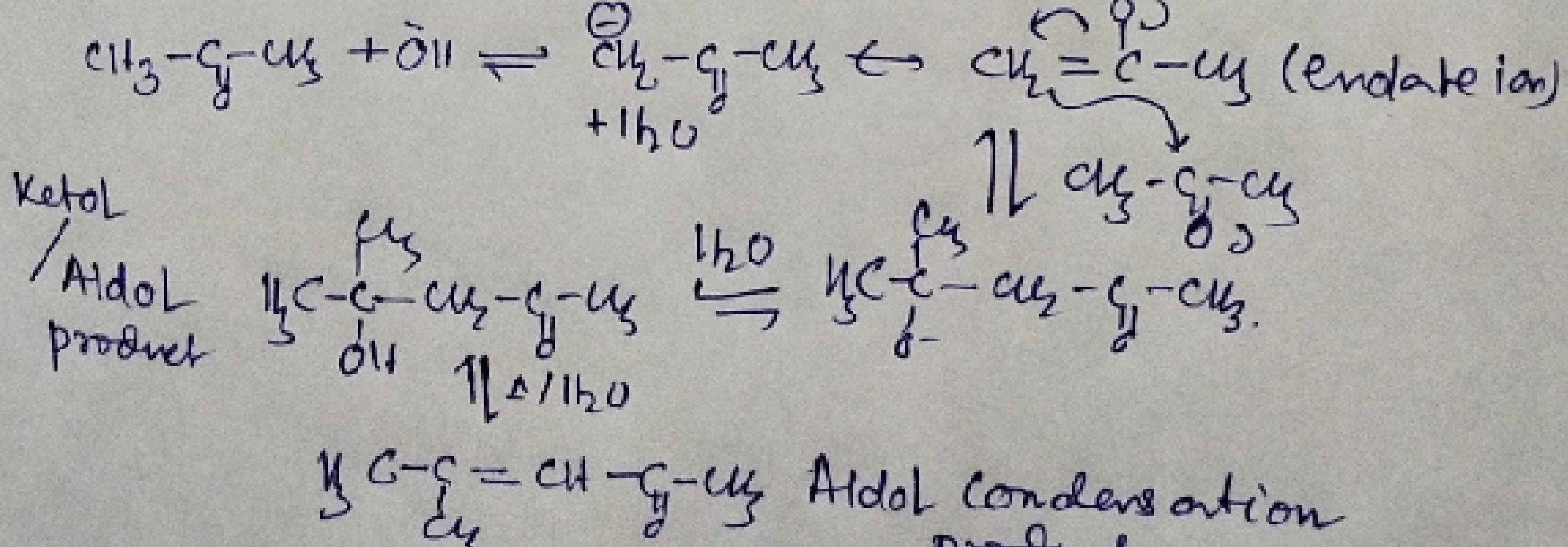
IVPAC name: 4-methyl pent-3-en-2-one.  $\angle$  (Mesityl oxide)

The aldol + ketol readily lose water to give  $\beta$  unsaturated carbonyl compounds which are aldol condensation products.

Mechanism:



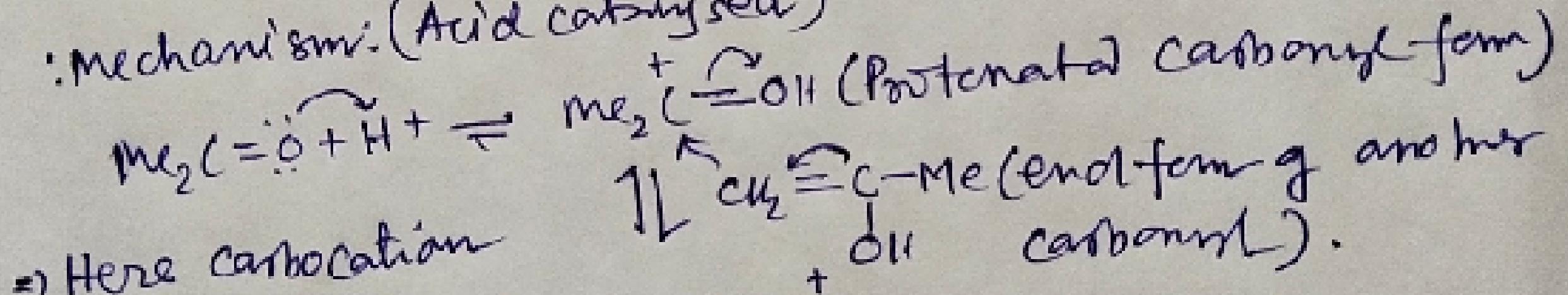
$\alpha, \beta$  unsaturated carbonyl compound.



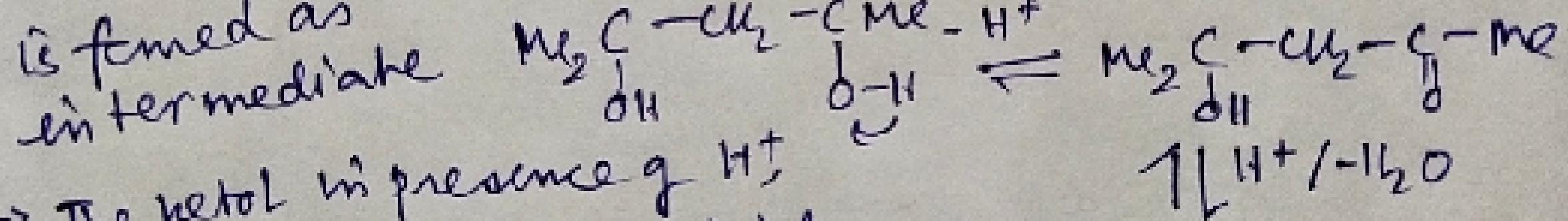
Points to be noted

- ⇒ In case of  $\text{CH}_3\text{CH}=\text{O}$  (Aldehyde) the equilibrium found to lie right over in favour of add. which indicates step(2) is more rapid than the reverse of step(1). ⑥
- ⇒ In case of  $\text{CH}_3\text{C}_2\text{H}_5$  (ketone), the equilibrium is found to lie far left. which indicates ketone is much less reactive than aldehyde towards nucleophile.
- ⇒ The reaction eqn<sup>m</sup> can be shifted to forward by mixing hot propanone & solid  $\text{Ba(OH)}_2$  (base catalyst) & repetitive siphoning/distillation. By this way equilibrium mixture (having 2% ketol + 98% ketone) is distilled. Here only propanone ( $\text{bp } 56^\circ$ ) will distill out; the 2% ketol ( $\text{bp } 164^\circ$ ) will be left behind. A second siphoning will add a further  $\approx 2\%$  diacetone aldehyd. & so on. So it's time consuming.
- ⇒ To get high % ketol /  $\alpha,\beta$ -unsaturated ketone, acid catalyst aldol condensation should be used np.

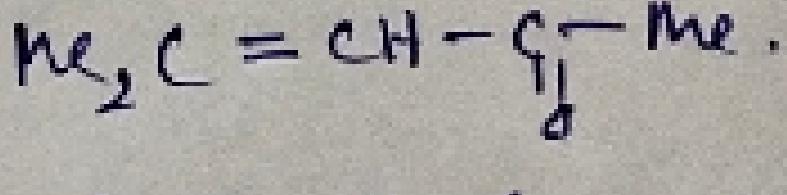
Mechanism (Acid catalysed)



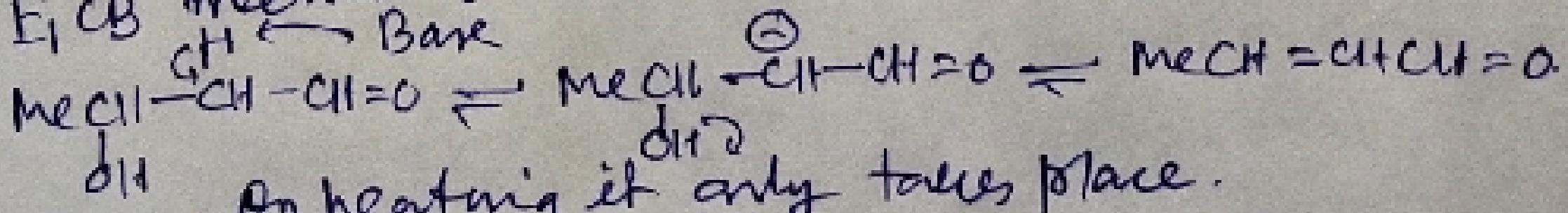
⇒ Here carbocation



⇒ The ketol in presence of  $\text{H}^+$  readily dehydrates to yield  $\alpha,\beta$ -unsaturated ketone.



Base catalysed dehydration of aldol is example of E<sub>1</sub>CB mechanism.

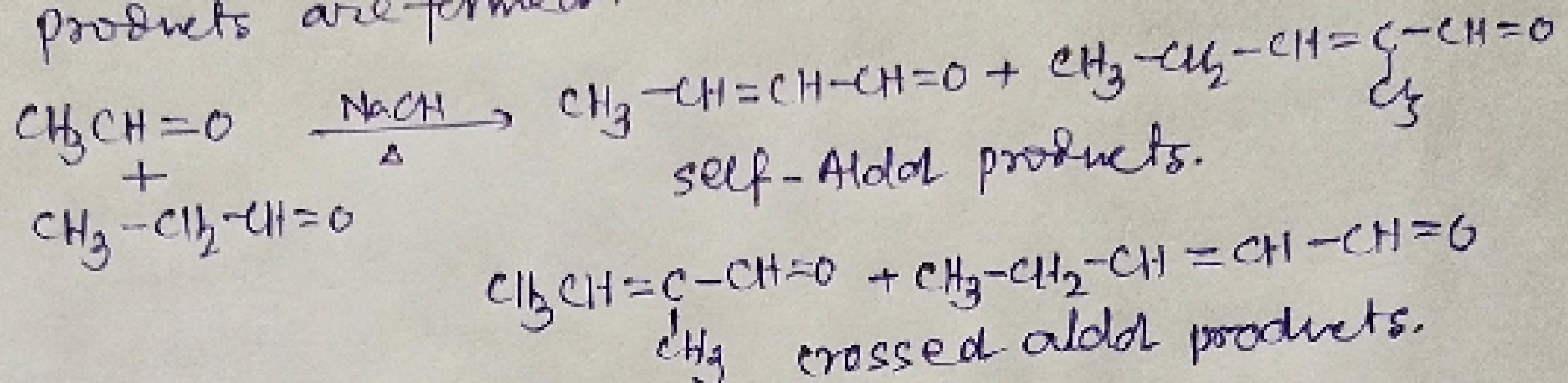


On heating it only takes place.

; Crossed Aldol Condensation:

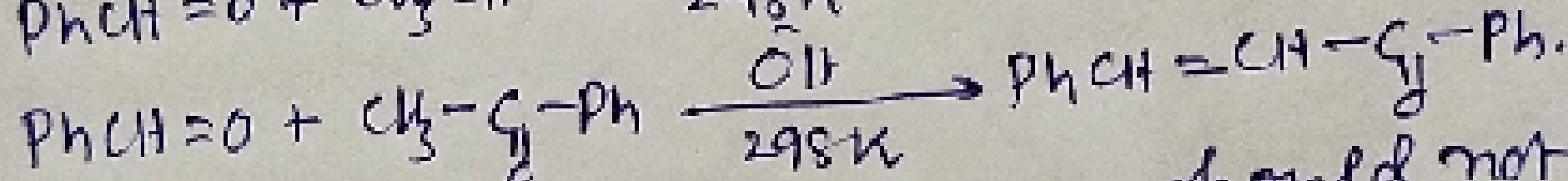
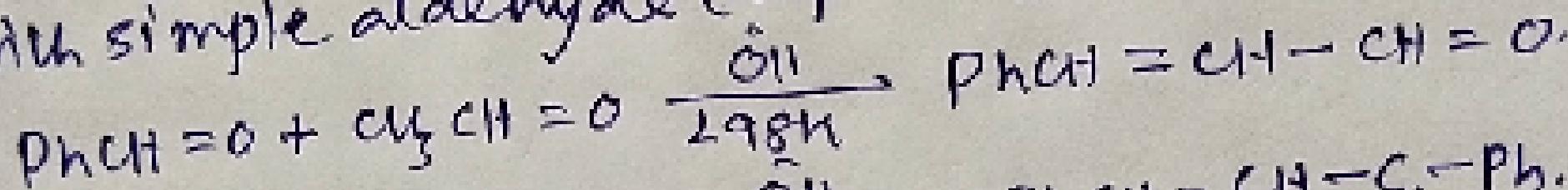
(7)

When aldol condensation is carried out between two different aldehydes/ketones having  $\alpha$ -H, it gives mixture of four products. e.g. A mixture of ethanol & propanal undergoes aldol condensation then self aldol & crossed aldol products are formed.

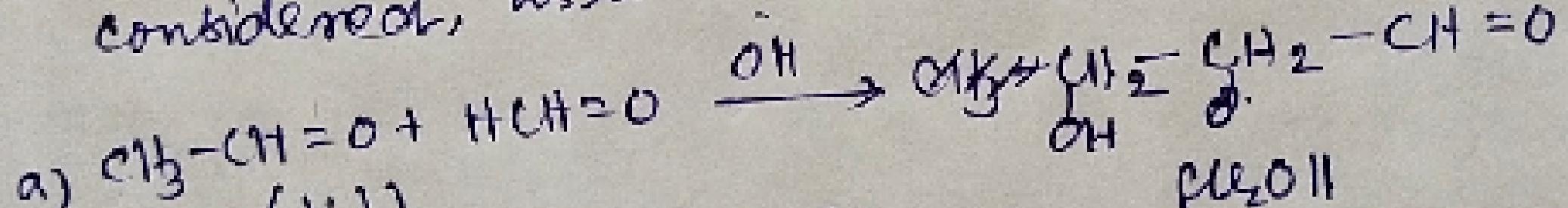


It is of no synthetic utility.

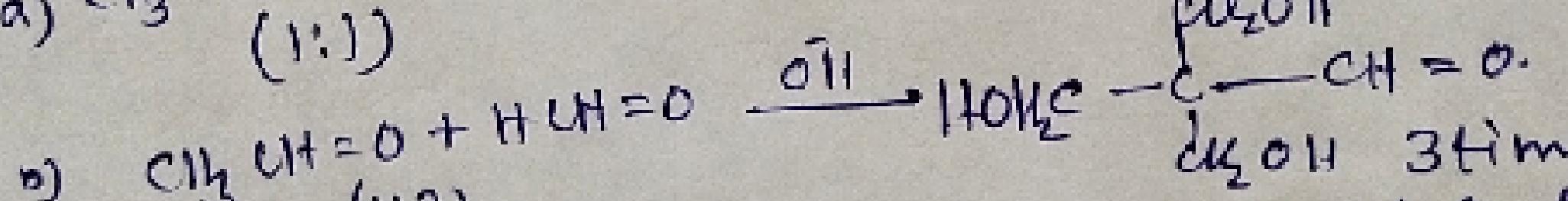
Crossed aldol can be of synthetic utility, where one aldehyde (aromatic aldehyde) with no  $\alpha$ -H reacts with simple aldehyde (aliphatic) with  $\alpha$ -H.



$\Rightarrow$  In presence of Aldol, Cannizaro should not be considered, as it is extremely slow.

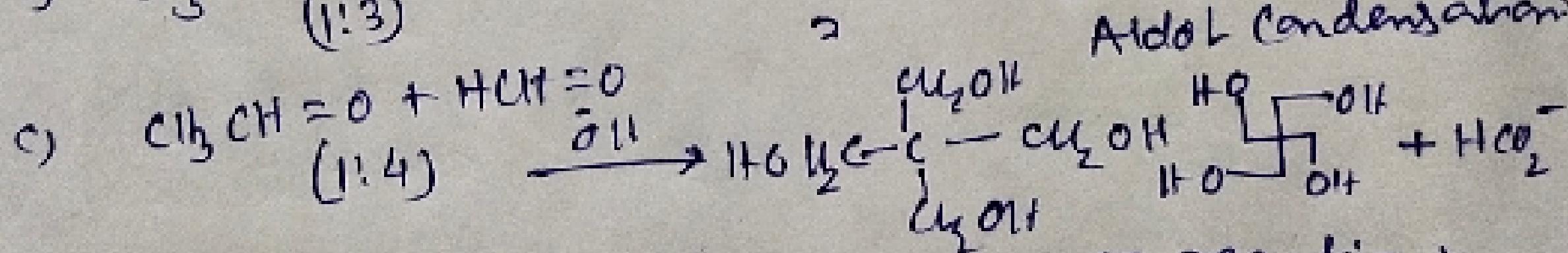


(1:1)

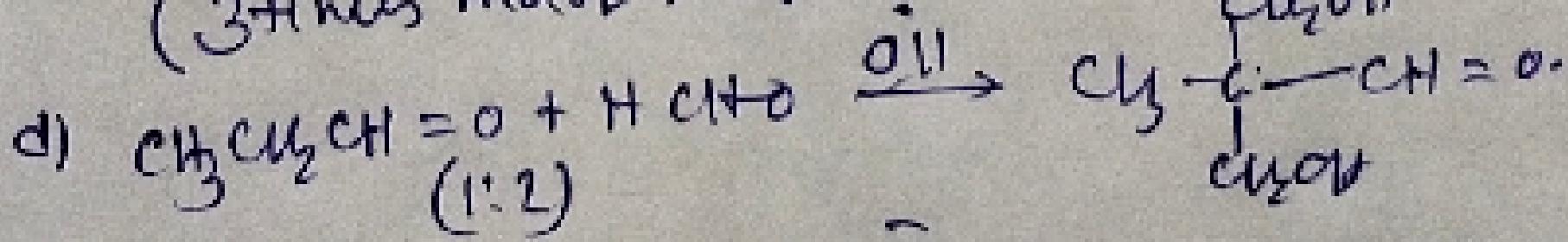


(1:3)

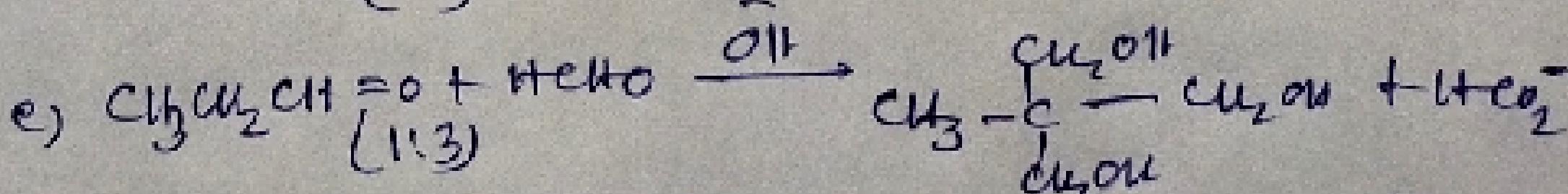
$\xrightarrow[3\text{ times}]{\text{Cu(OH)}} \text{Aldol condensation}$



(3 times Aldol + crossed Cannizaro reaction)

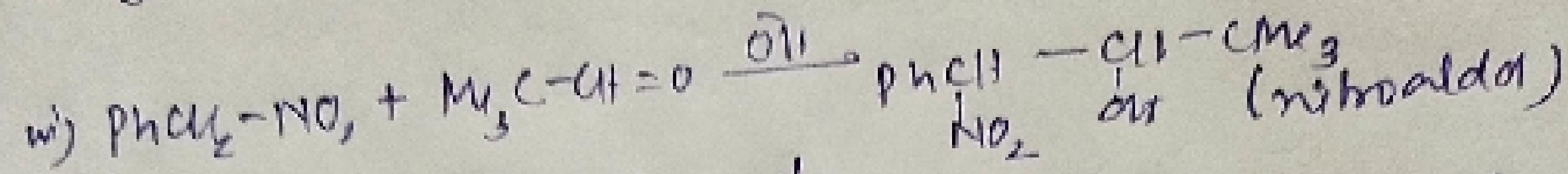
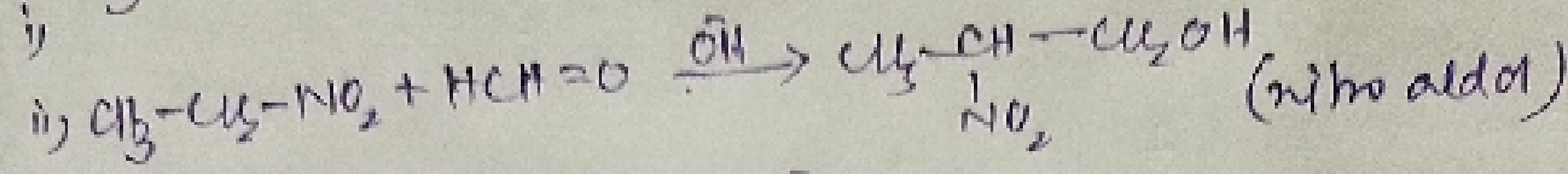
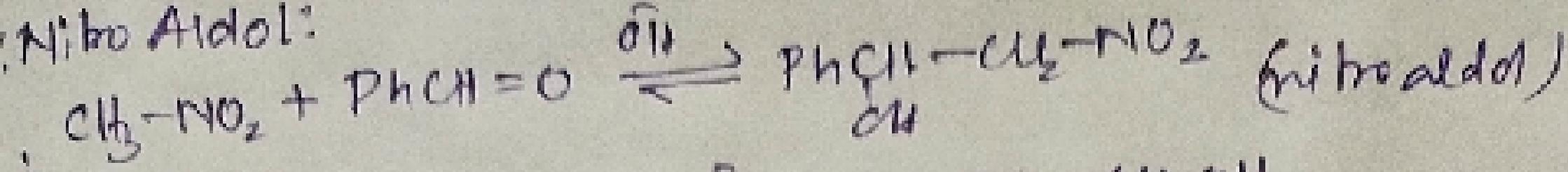


(1:2)



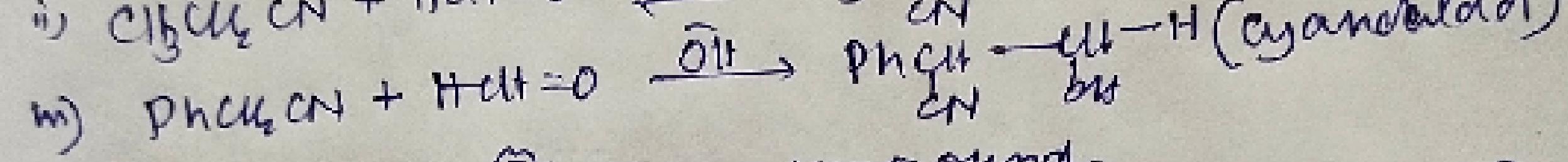
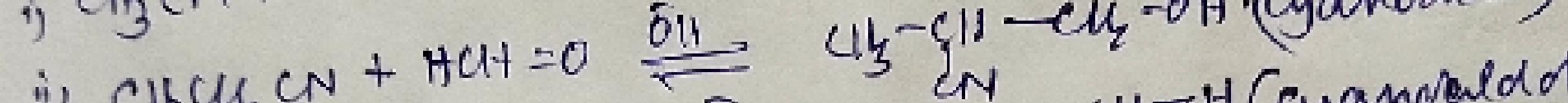
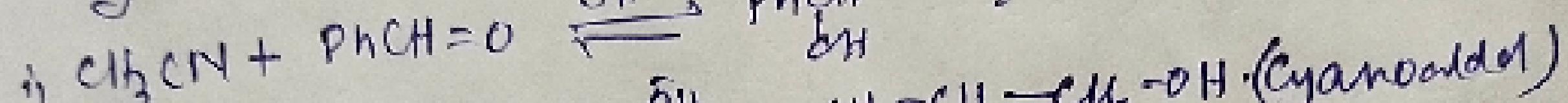
(8)

: Nitro Aldol:



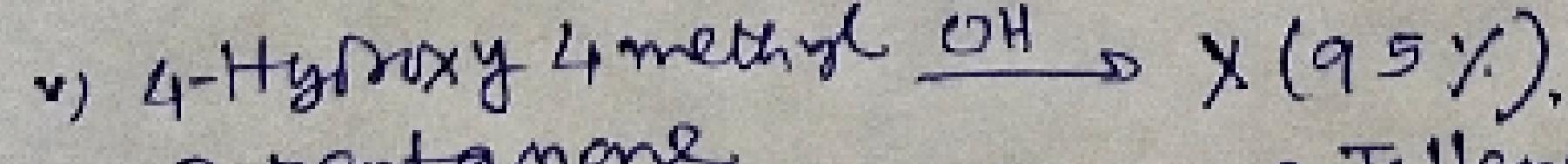
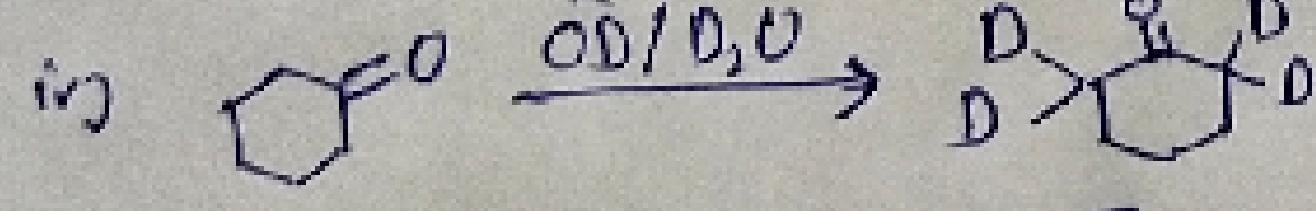
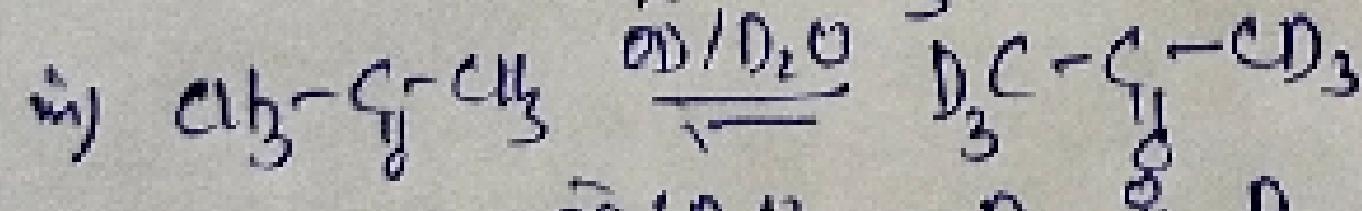
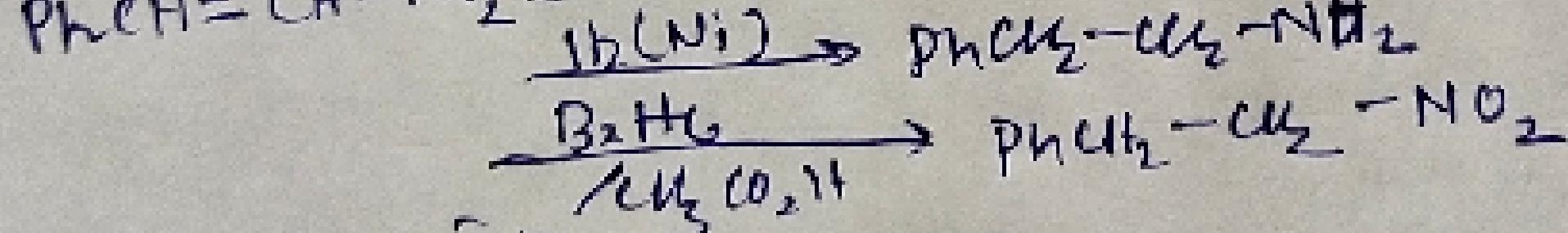
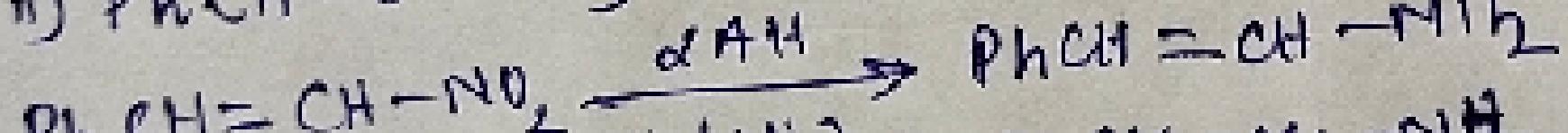
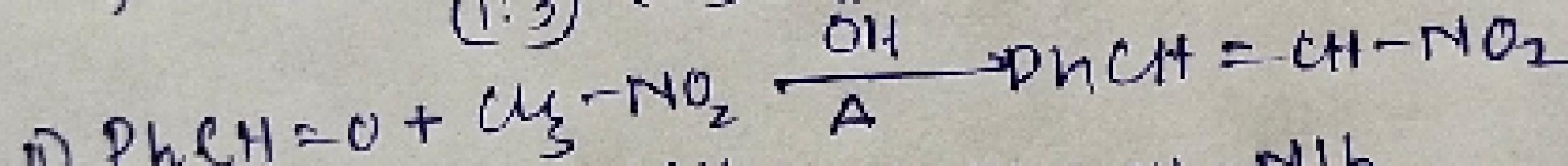
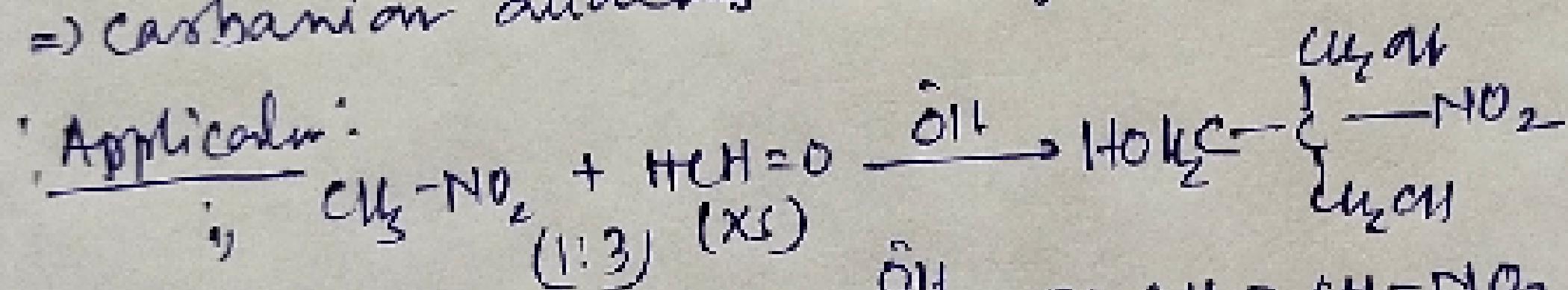
$\Rightarrow$  Here source of  $\text{O}^-$  is nitro cpd  
 $\Rightarrow$  carbanion attacks carbonyl carbon [nucleophilic addition]

: Cyano Aldol:



$\Rightarrow$  Here source of  $\text{O}^-$  is cyano compound.  
 $\Rightarrow$  carbanion attacks carbonyl carbon [nucleophilic addition].

: Application:

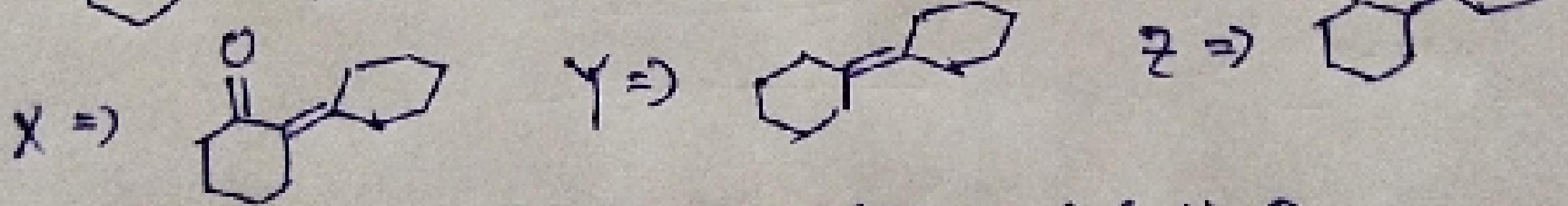
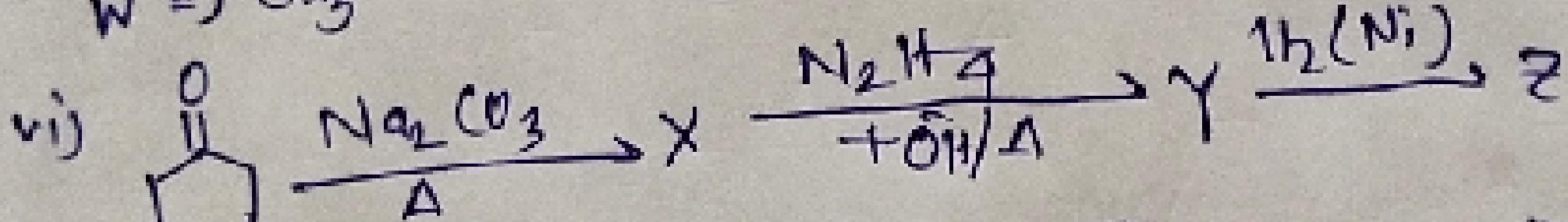
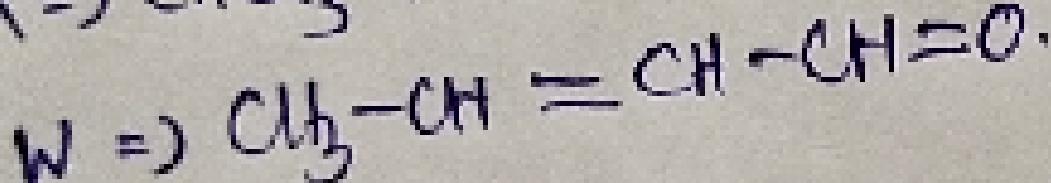
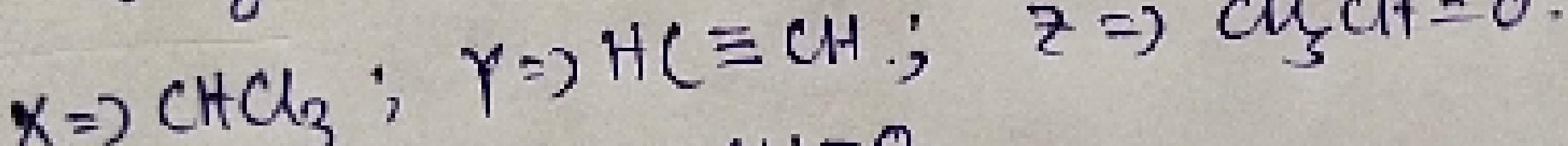
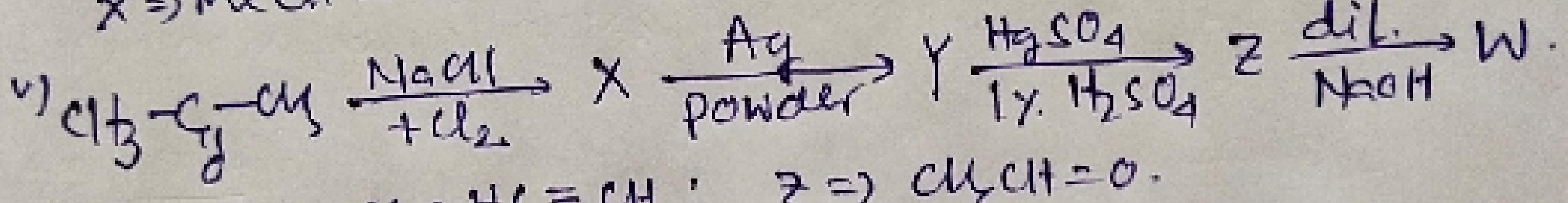
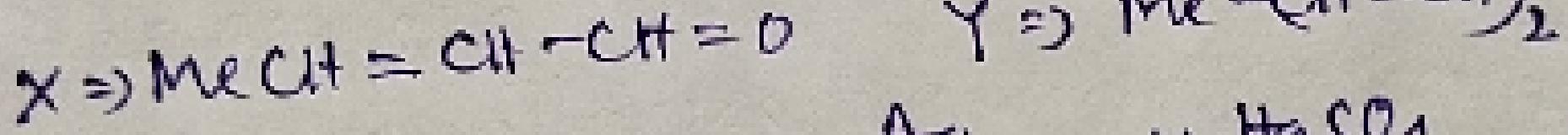
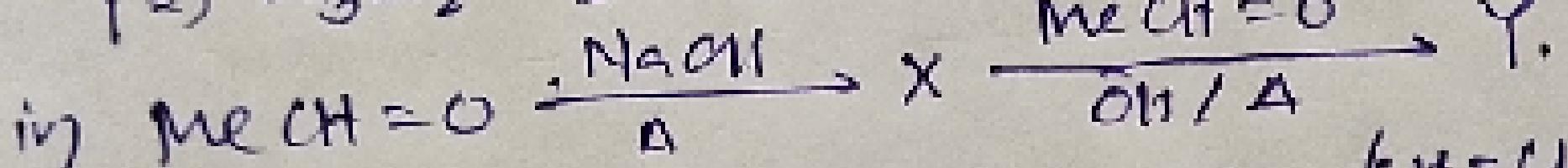
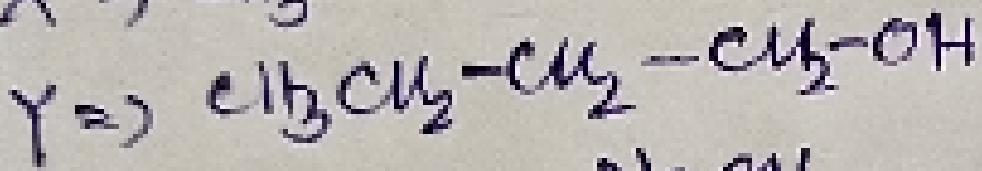
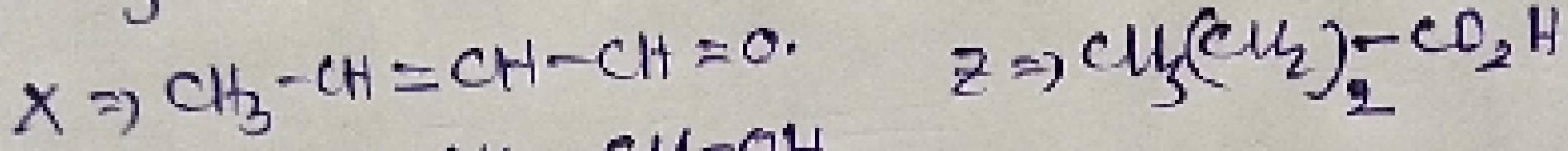
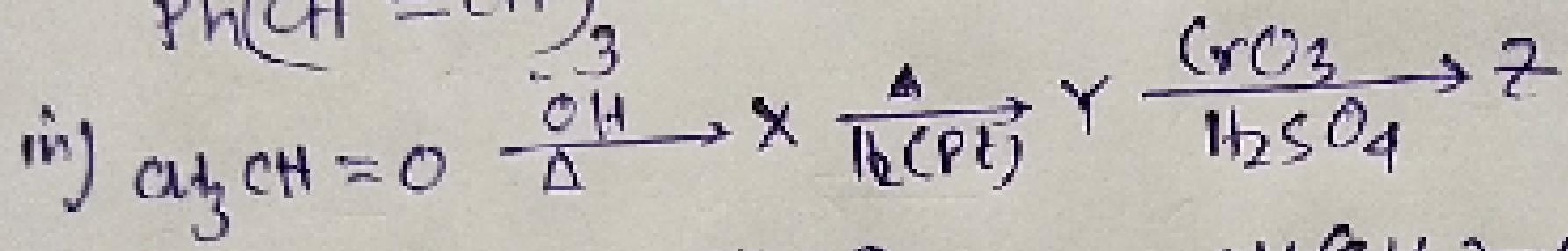
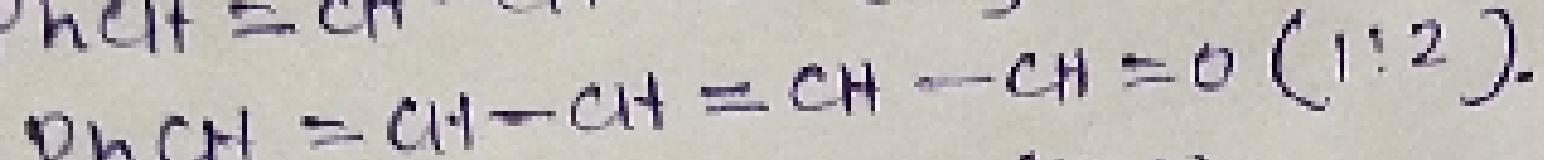
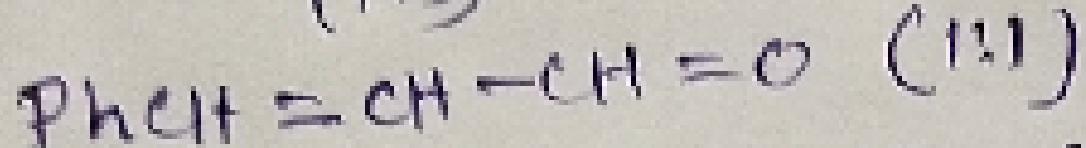
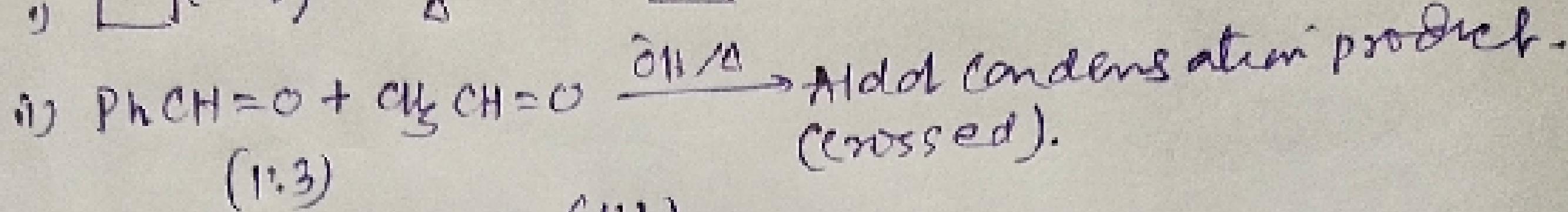
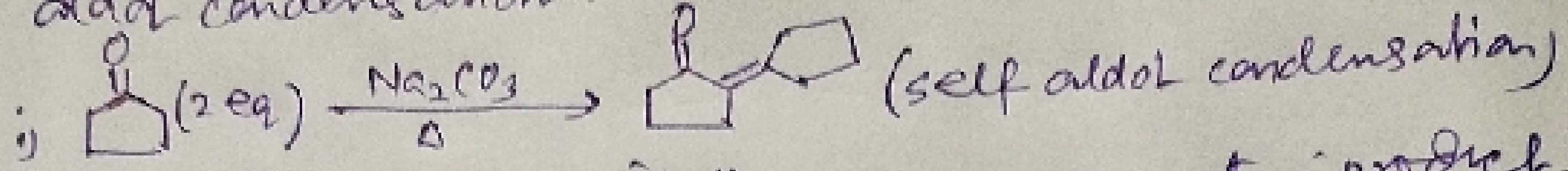


2 pentanone

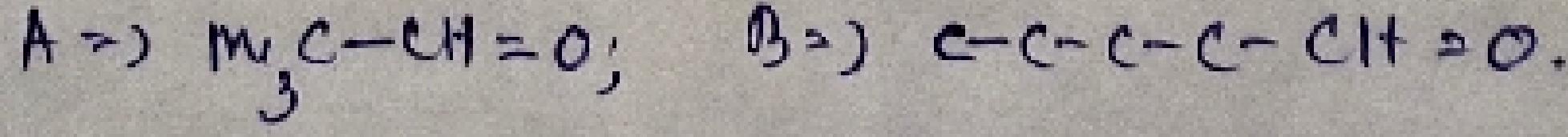
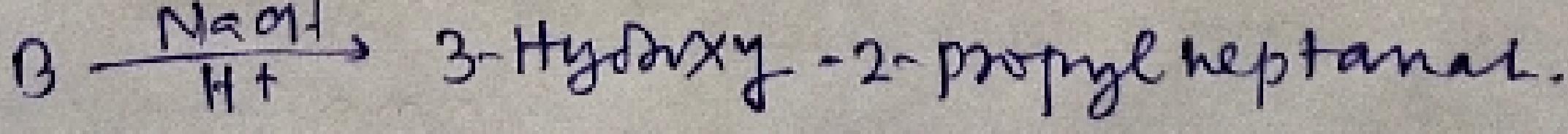
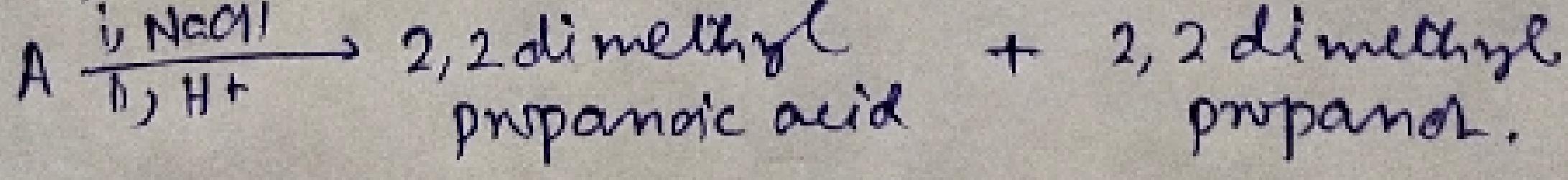
 $\text{X} \rightarrow$  -ve Tollens test. $\text{X} \Rightarrow$  Acetone $\text{X} \Rightarrow$  gives +ve iodoferm test.

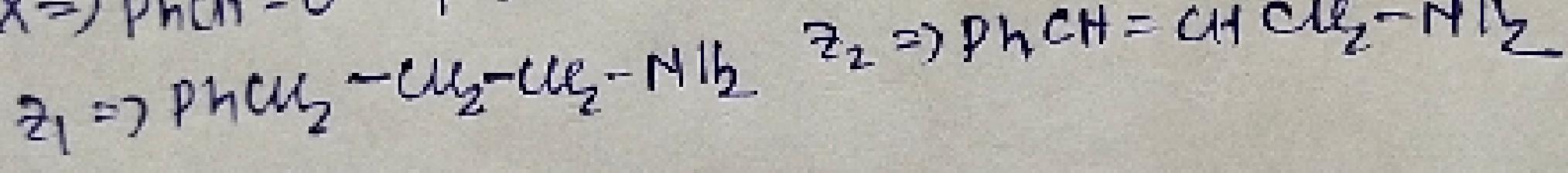
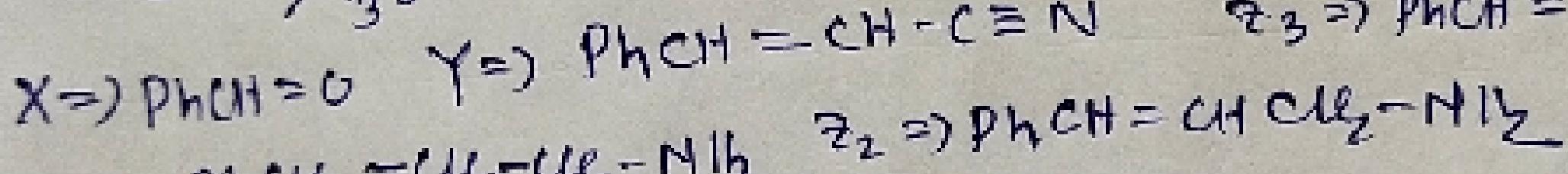
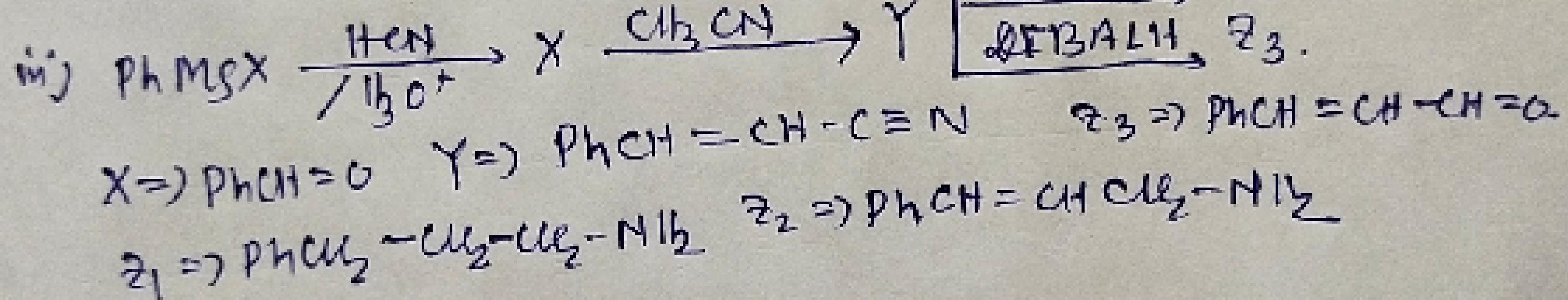
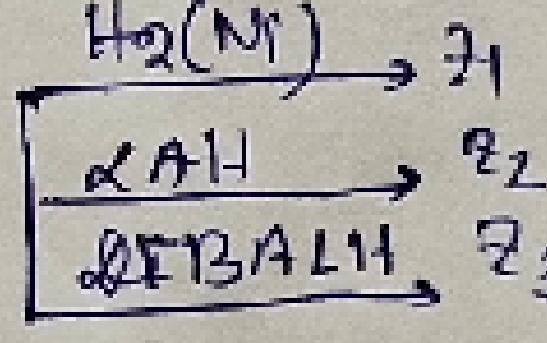
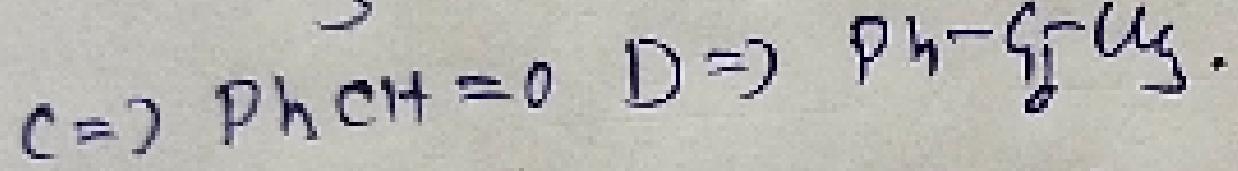
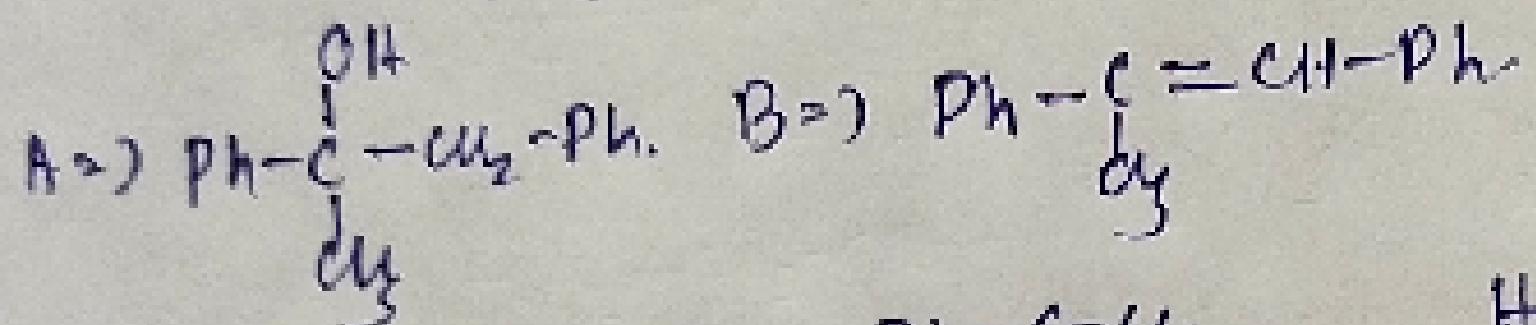
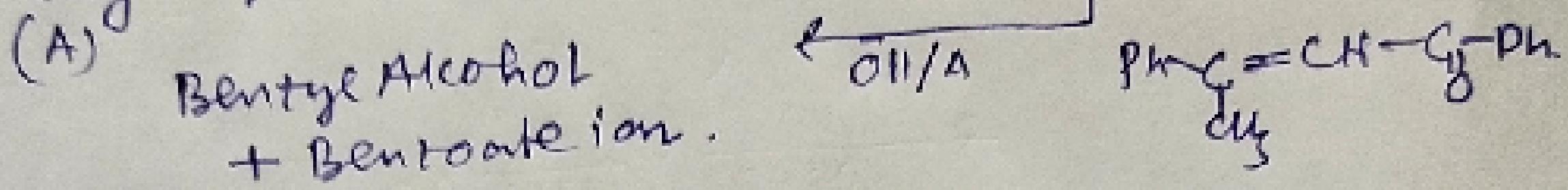
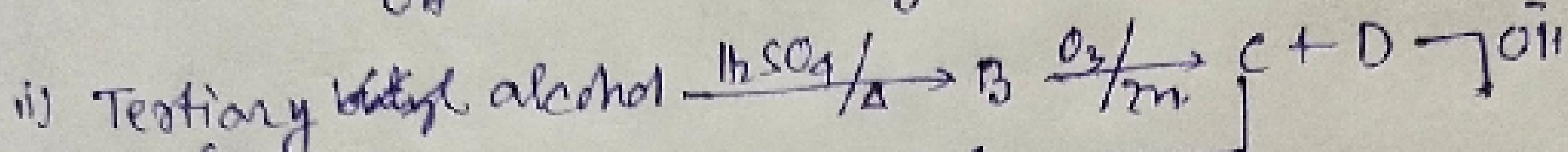
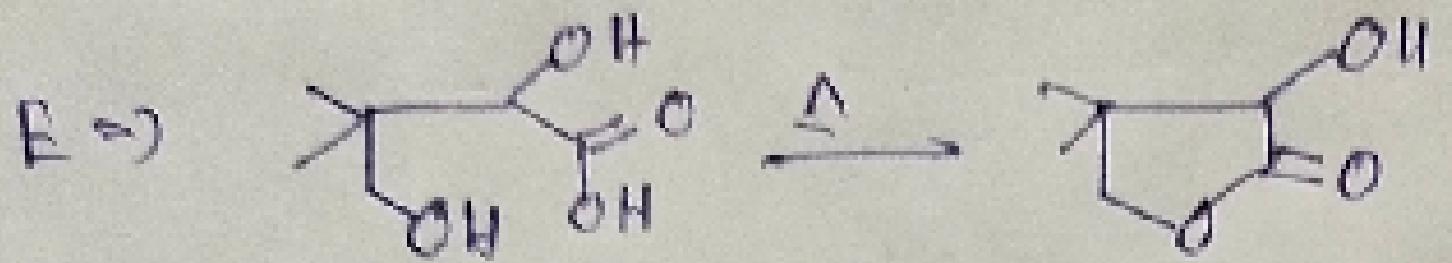
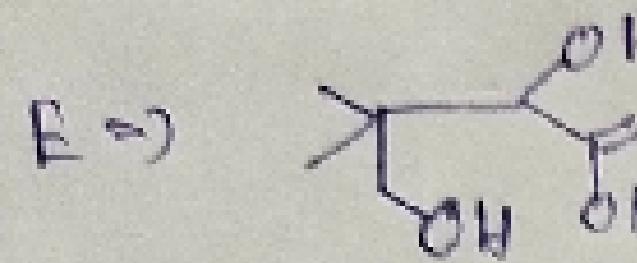
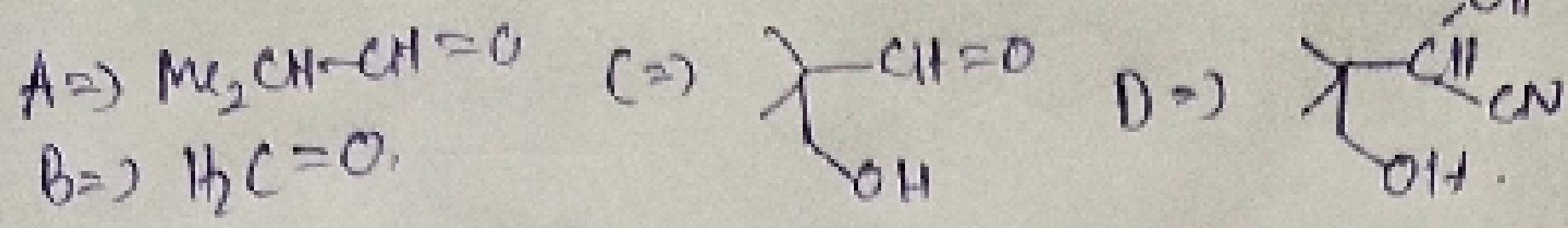
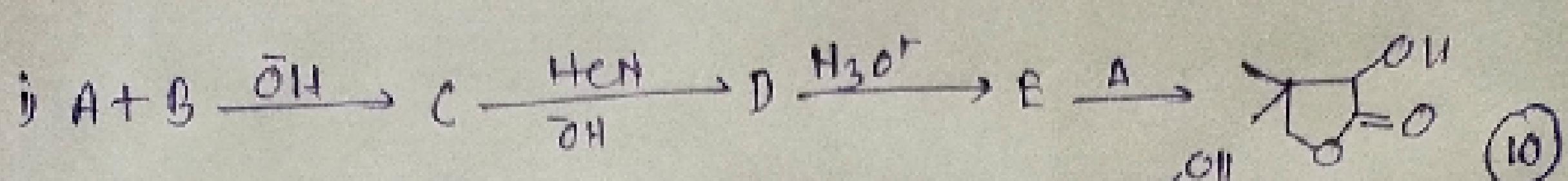
Retro Aldol (Backward Aldol).

⇒ instead of NaOH,  $\text{Na}_2\text{CO}_3 / \text{K}_2\text{CO}_3, \Delta$  can be used in  
α) add condensation.



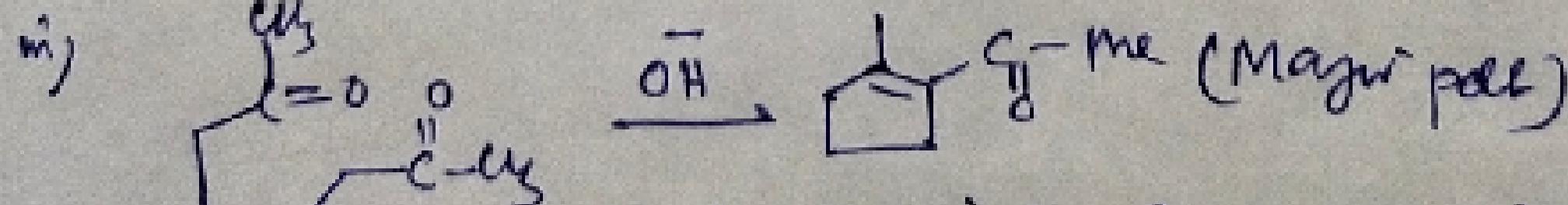
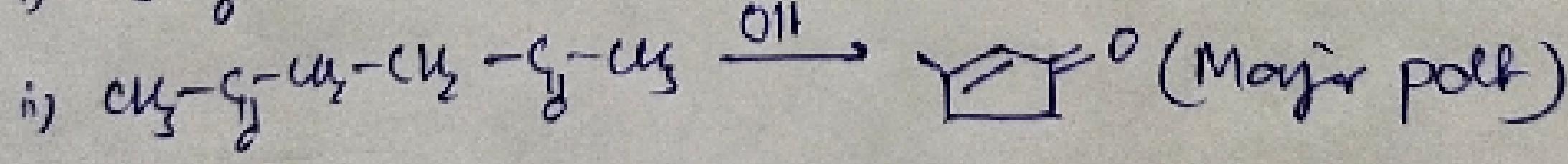
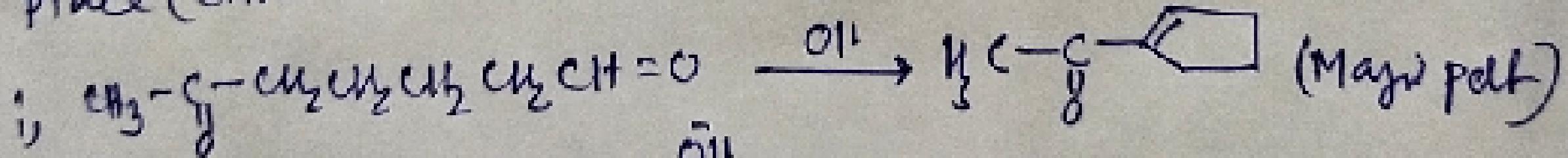
vii) A, B → two compounds with m.f  $C_5\text{H}_10\text{O}$ .





iv) Intra Aldol:

Aldol reaction with suitable dicarbonyl compounds can be intramolecular aldol i.e. cyclisation takes place (either 5/6 membered ring is formed).



Points:  $\Rightarrow$  carbocation is formed in such a way so that it reacts with aldehyde system.

$\Rightarrow$  during cyclisation 5/6 membered ring is formed.

