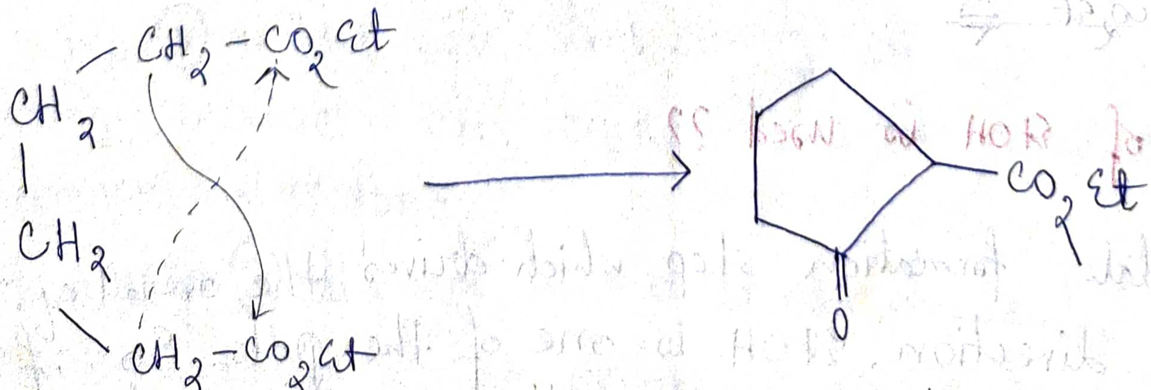
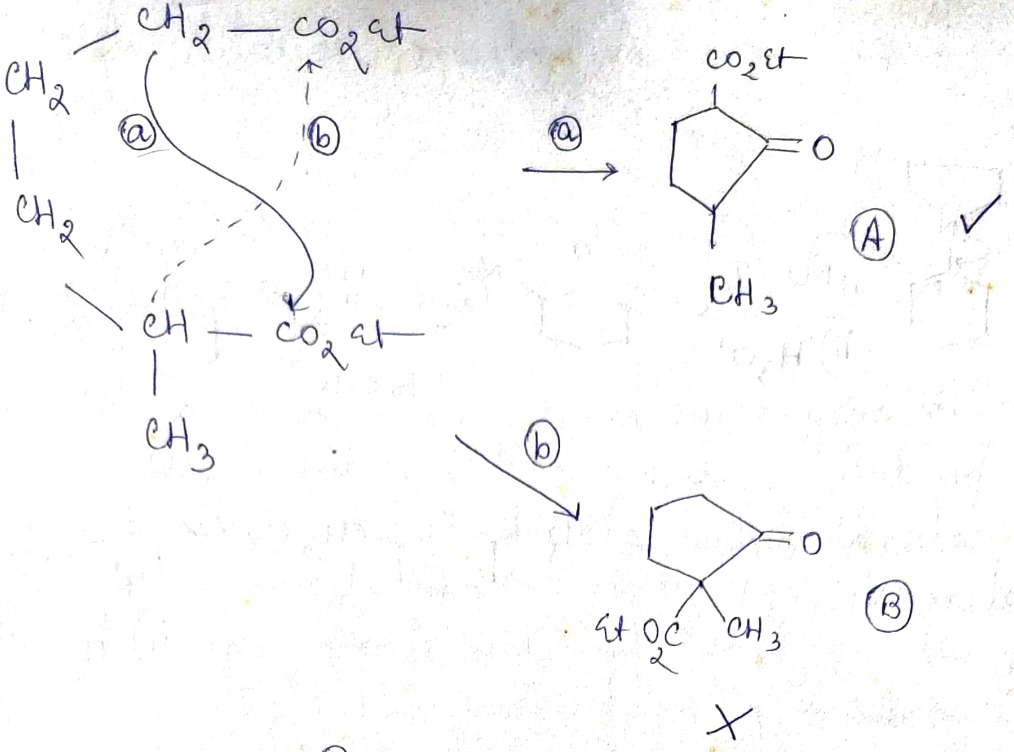
▨ Dieckmann rxn :- (intramolecular claisen condensation)



di ethyl adipate

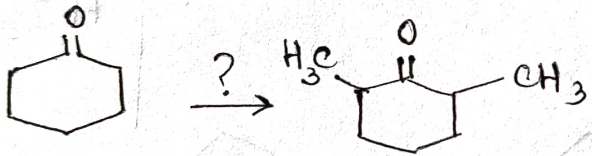
β - keto ester

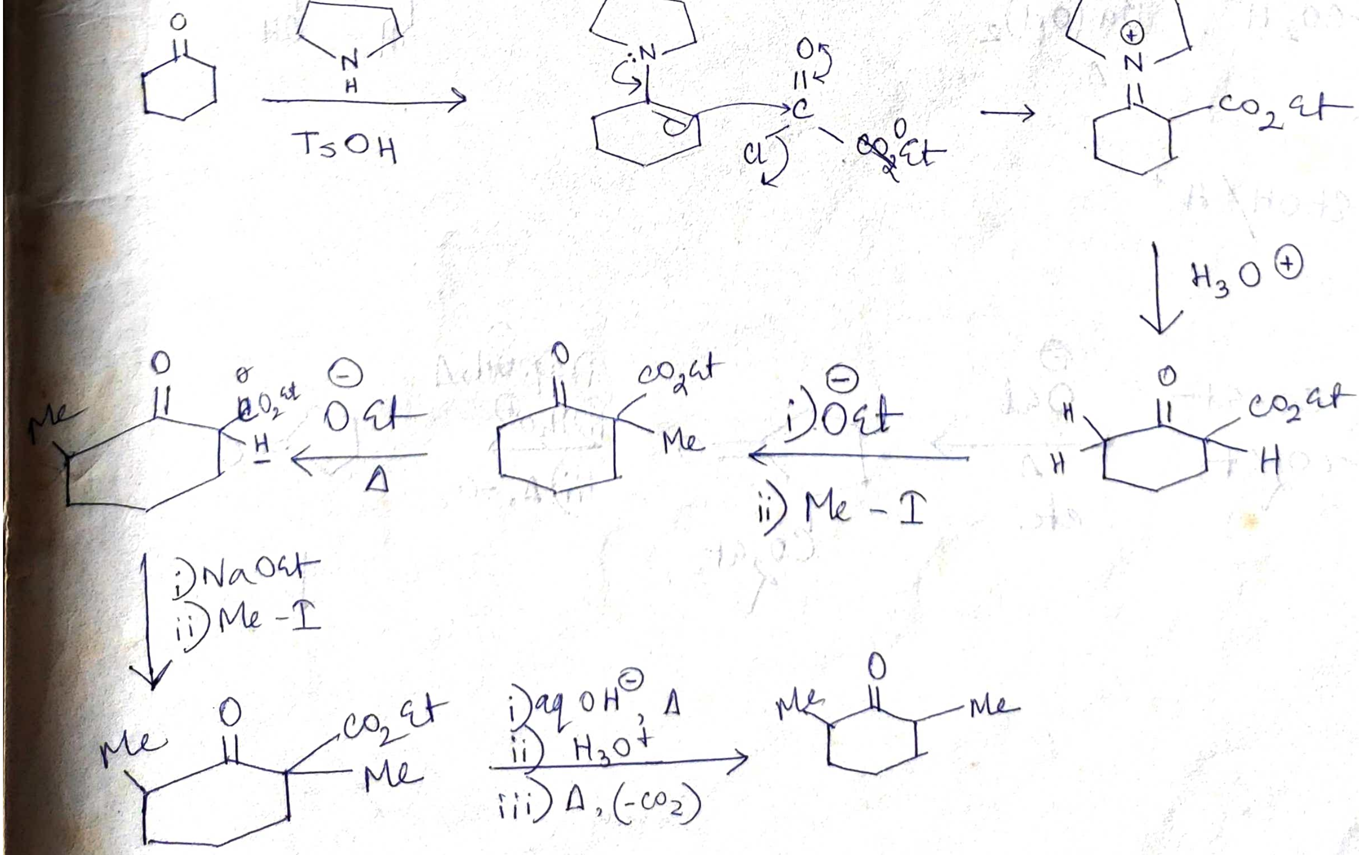


$Ⓑ \xrightarrow[\Delta]{\overset{\ominus}{O}Et} Ⓐ$

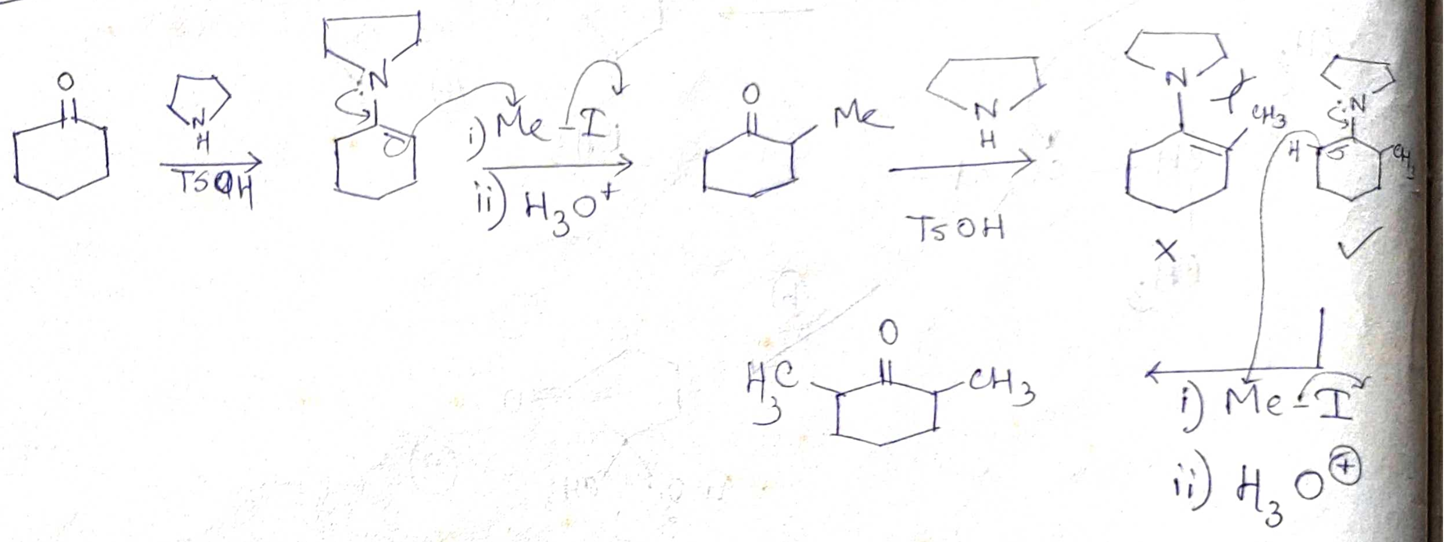
following reverse claisen cond., forward claisen in a different orientation.

✱

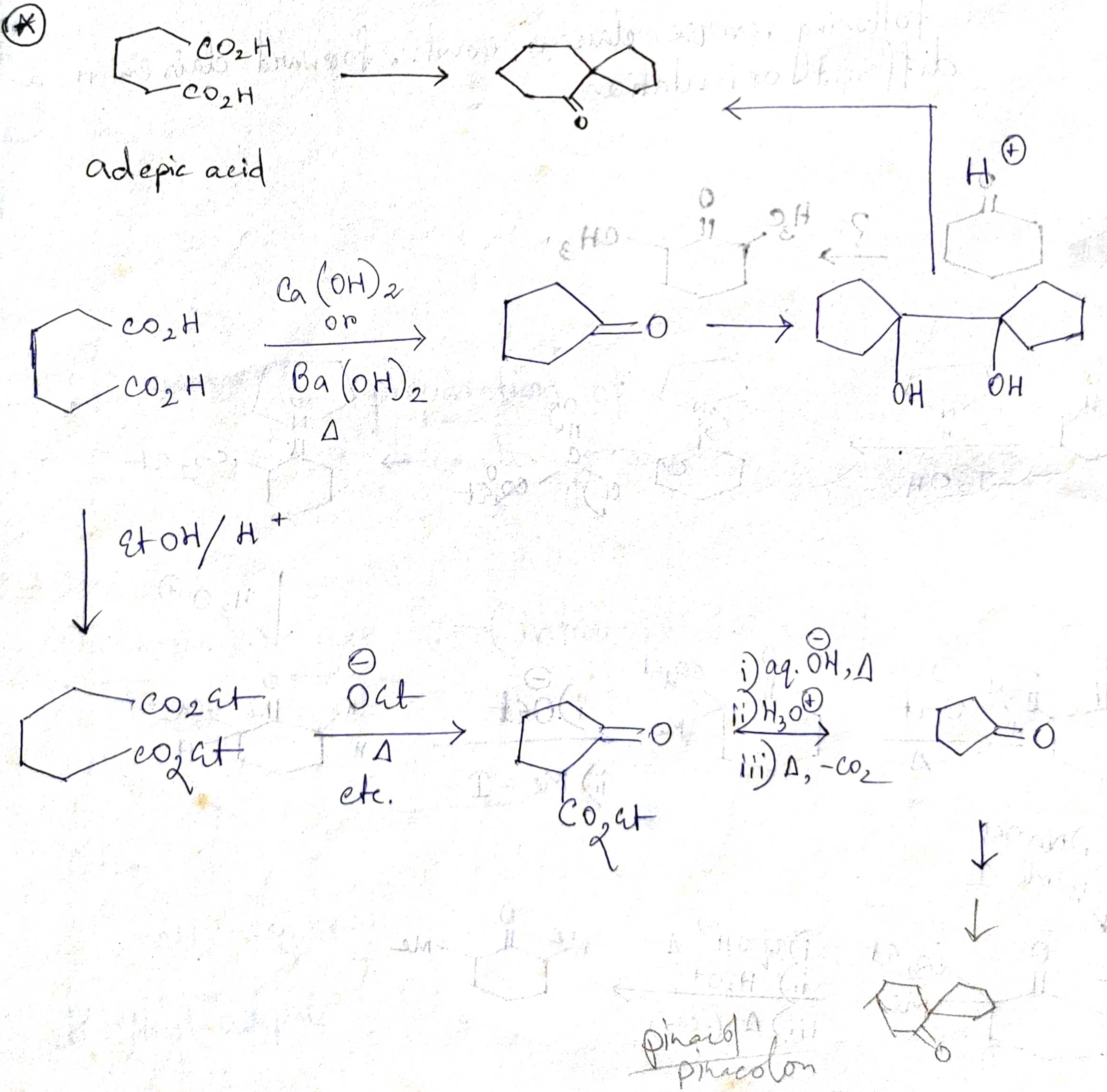




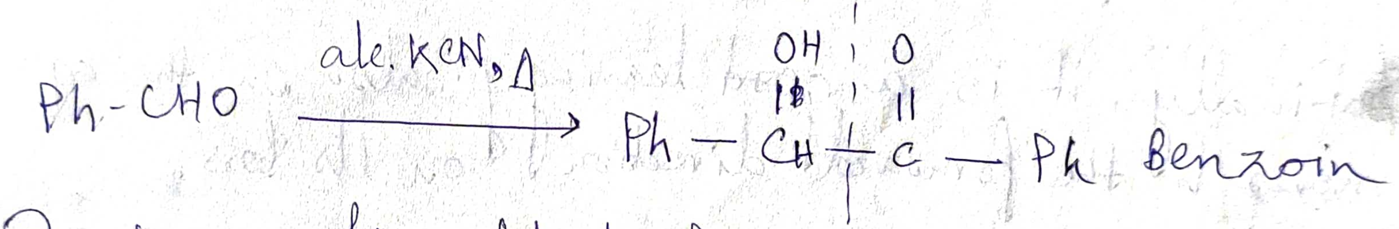
Alternative :



(★)



Benzoin cond : (only for aro. aldehyde)

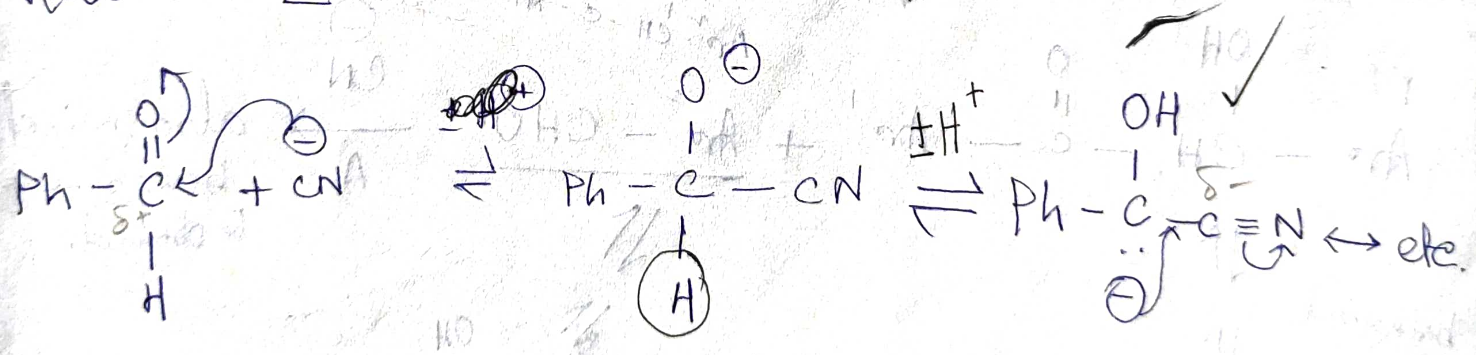


$$\mathrm{Ph{-}CHO} \xrightarrow{\text{alc. KCN}, \Delta} \mathrm{Ph-\overset{OH}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-Ph}$$

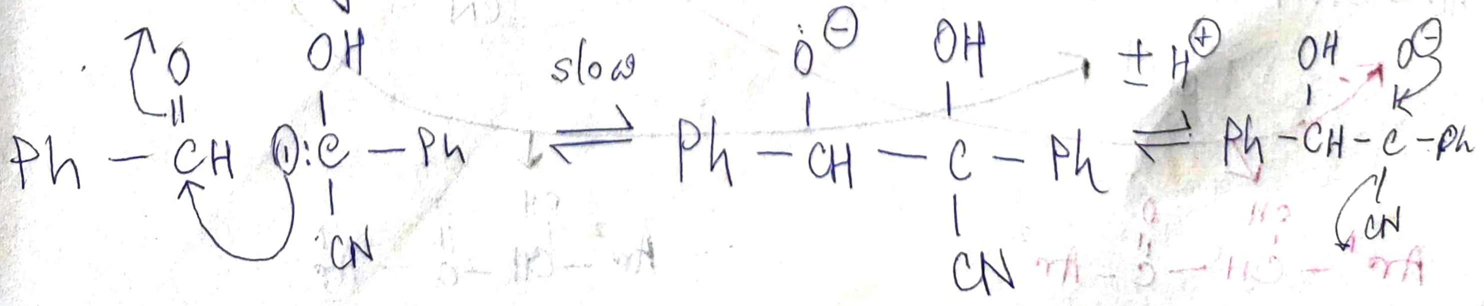
Benzoin

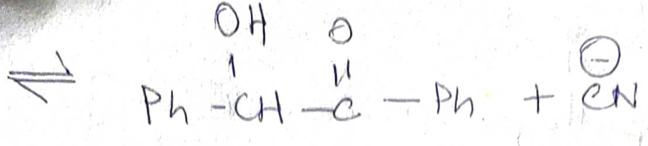
$\overset{\ominus}{CN}$ is a specific catalyst for this rxn.

Rate ∝ $[\mathrm{PhCHO}]^2\,[\overset{\ominus}{CN}]$



Umpoling





$$\rightleftharpoons Ph-\overset{OH}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-Ph + \overset{\ominus}{C}N$$

Role of $\overset{\ominus}{CN}$:

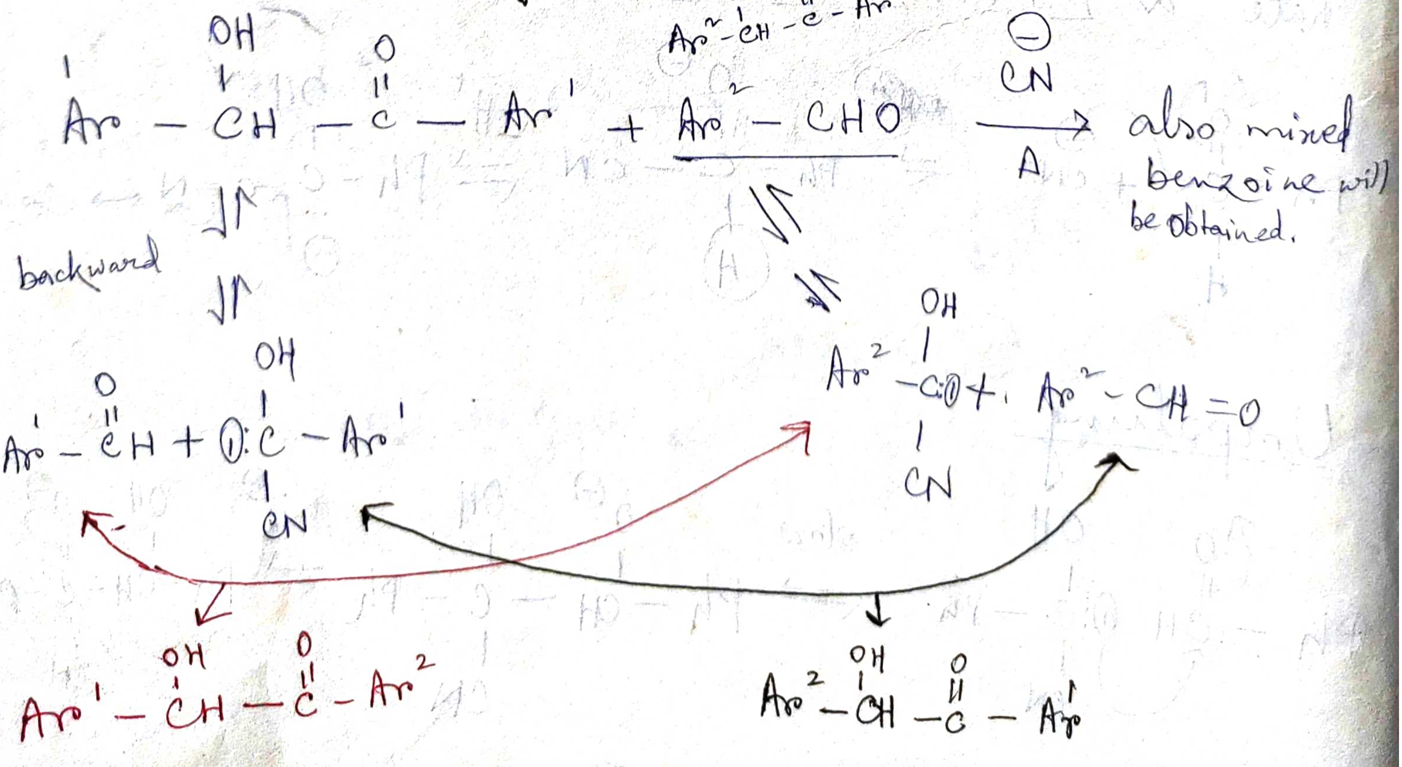
i) acts as $\overset{\ominus}{nu}$

ii) Due to it's strong electron withdrawing effect, the Carbon bound H becomes more acidic and it transfers to Oxygen causing reversal of polarity of the carbonyl C, which then can couple with another carbonyl C.

iii) Again due to it's $e^{\ominus}$ withdrawing effect necessary $H^{\oplus}$ transfer can occur from one O to other.

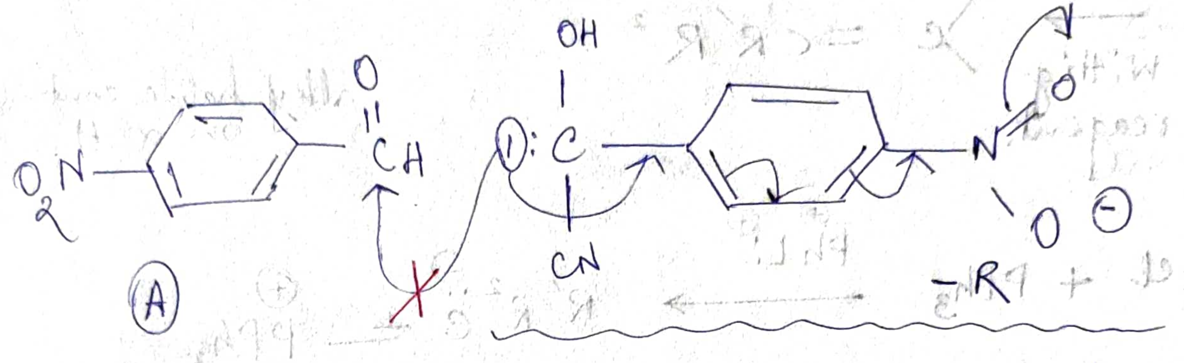
iv) Finally, it is a good leaving gr. also on the eq^n moves to the forward direction on its loss.

Proof of reversibility :

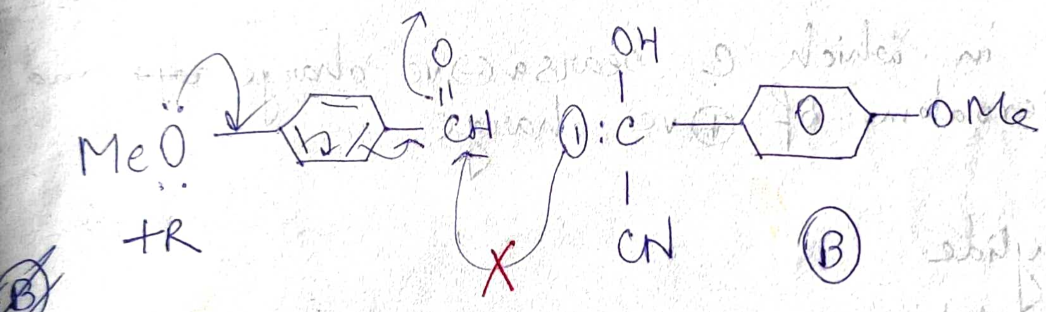


also mixed benzoine will be obtained.

Both p-nitro benzaldehyde and p-anisal dehyde fail to undergo benzoine cond. :



highly deactivated due to highly $e^{\ominus}$ withdrawing $-NO_2$ group



highly deactivated due to ~~highly~~ $e^{\ominus}$ +R effect.

mixture নিলে A acts as electrophile and B acts as $\overset{\ominus}{nu}$.

Wittig rxn :-

$$>C=O \xrightarrow[\text{reagent}]{\text{Wittig}} >C=CR'R^2$$

alkyl halide containing one α H.

$$R'R^2CH-Cl + PPh_3 \xrightarrow{Ph^{\ominus}Li^{\oplus}} R'R^2\ddot{C}^{\ominus}-\overset{\oplus}{P}Ph_3$$

ylide.

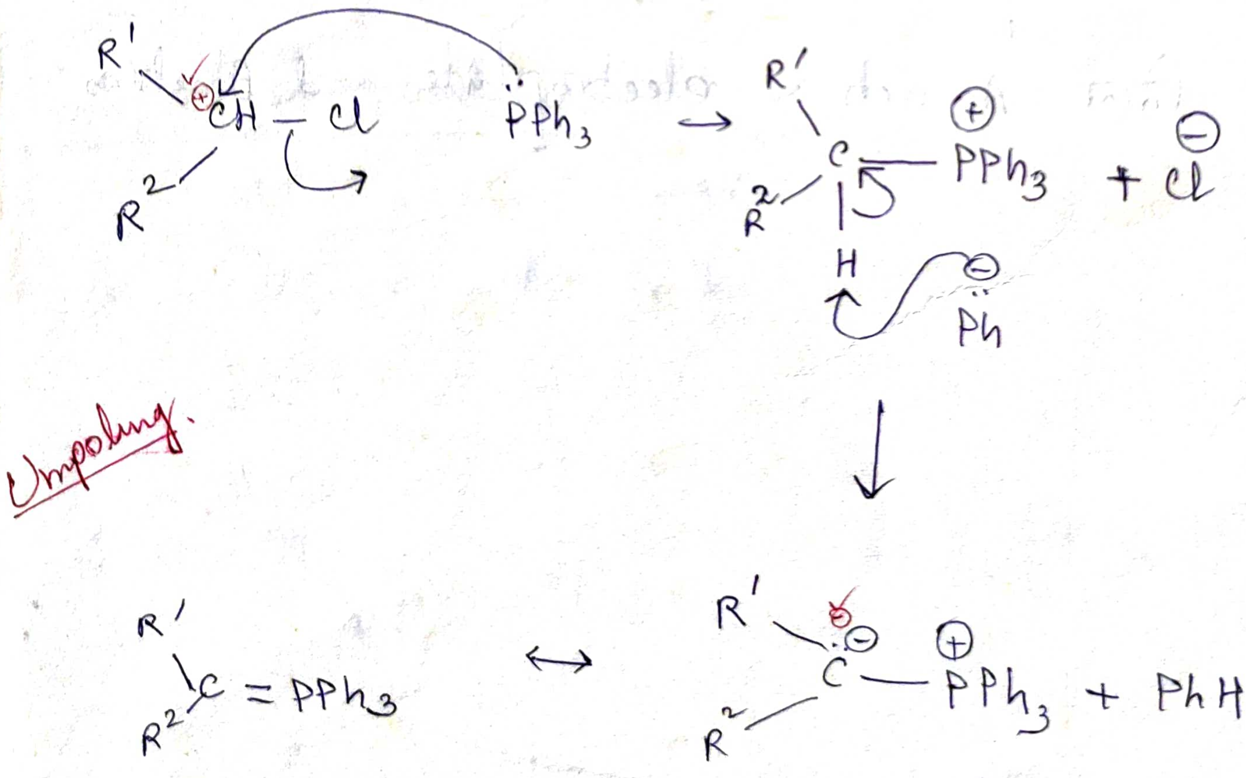
$Ph_3\ddot{C}^{\ominus}$ (triphenyl methyde ion)

Ylide is a species in which C bears a ⊖ve charge ~~adjo~~ and adjousent to a heteroatom of ⊕ve charge.

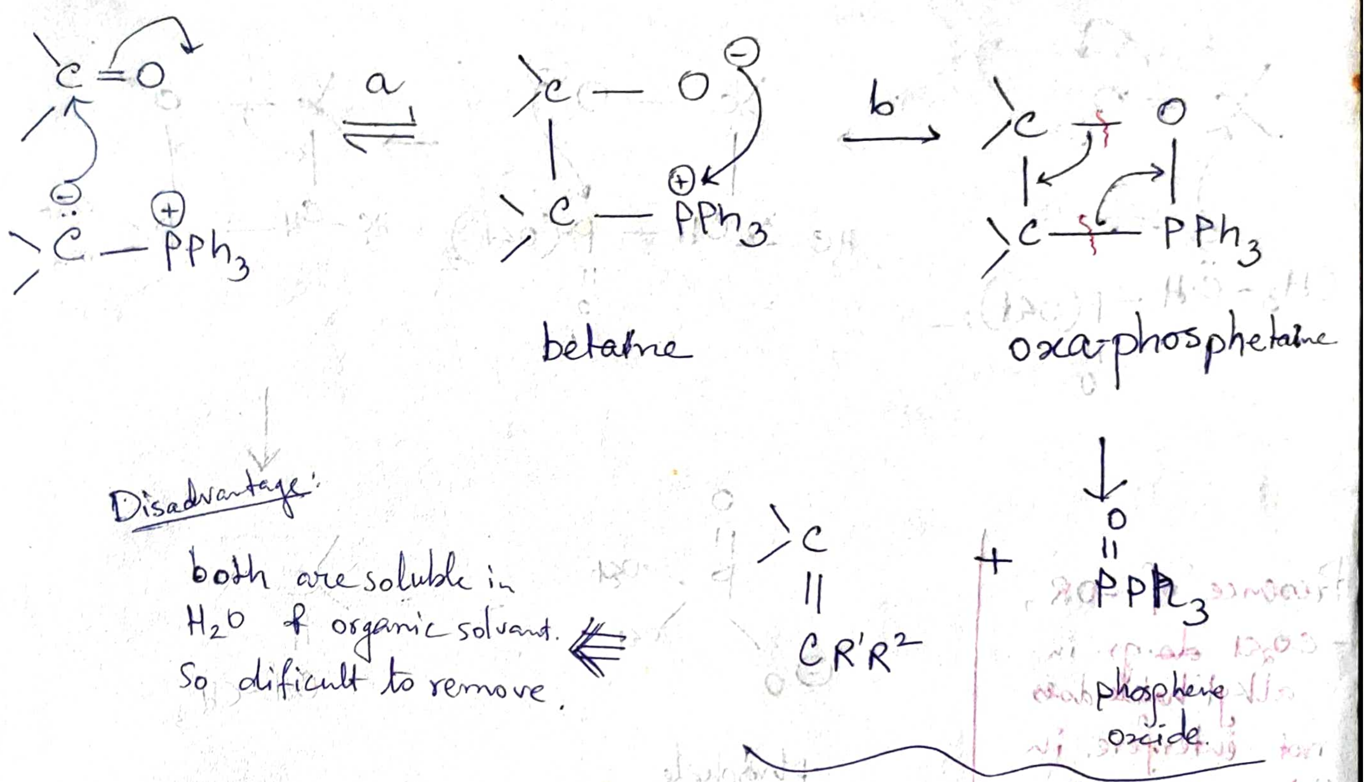
$Ph_3\ddot{S}^{\ominus}$ (sulphonium ylide

$Ph_3\ddot{P}^{\ominus}$ phosphorane ylide

$Ph_3\ddot{N}^{\ominus}$ Azomethyine ylide



P=O very strong bond due to pπ-dπ overlap.



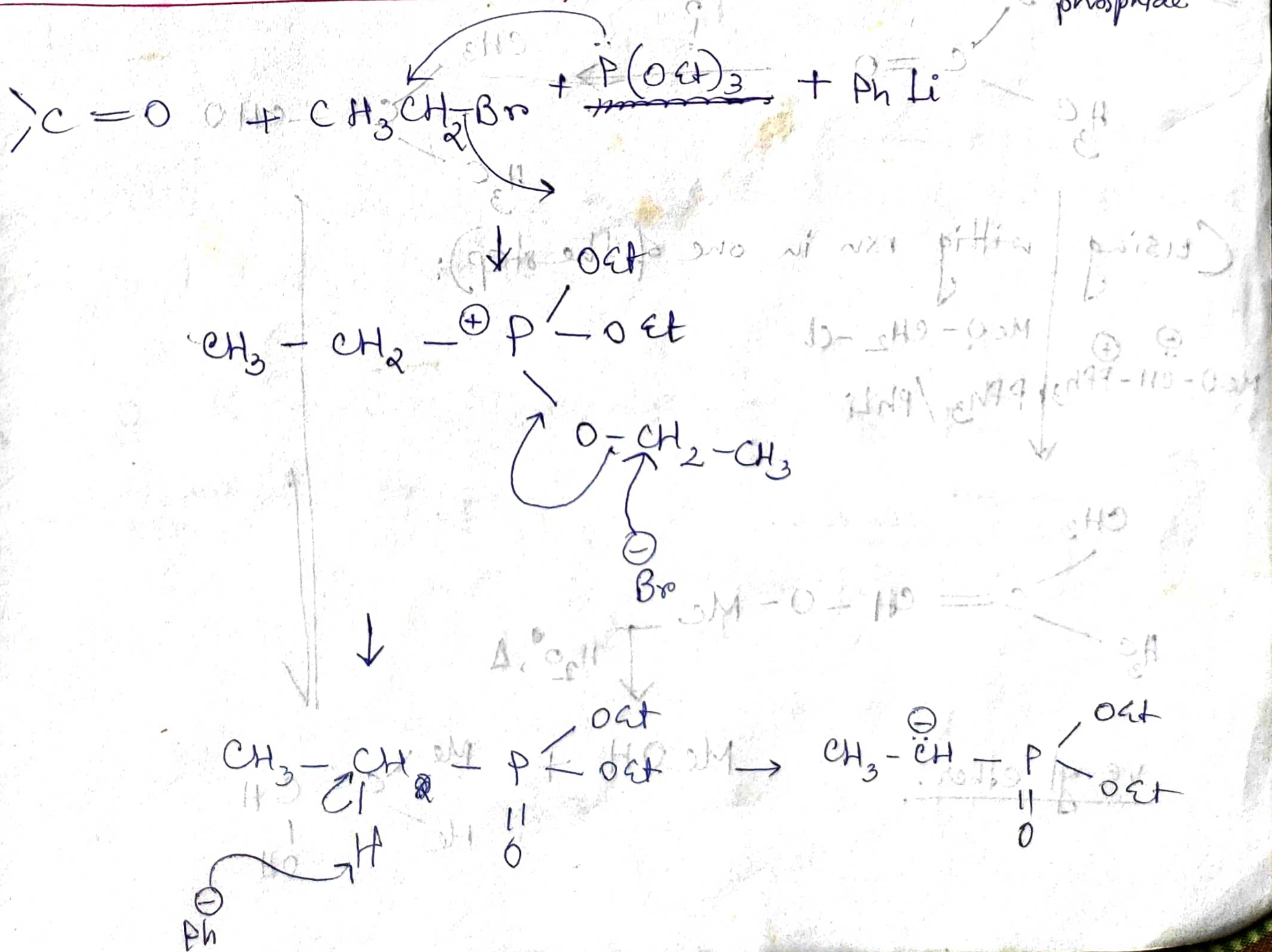
Disadvantage:

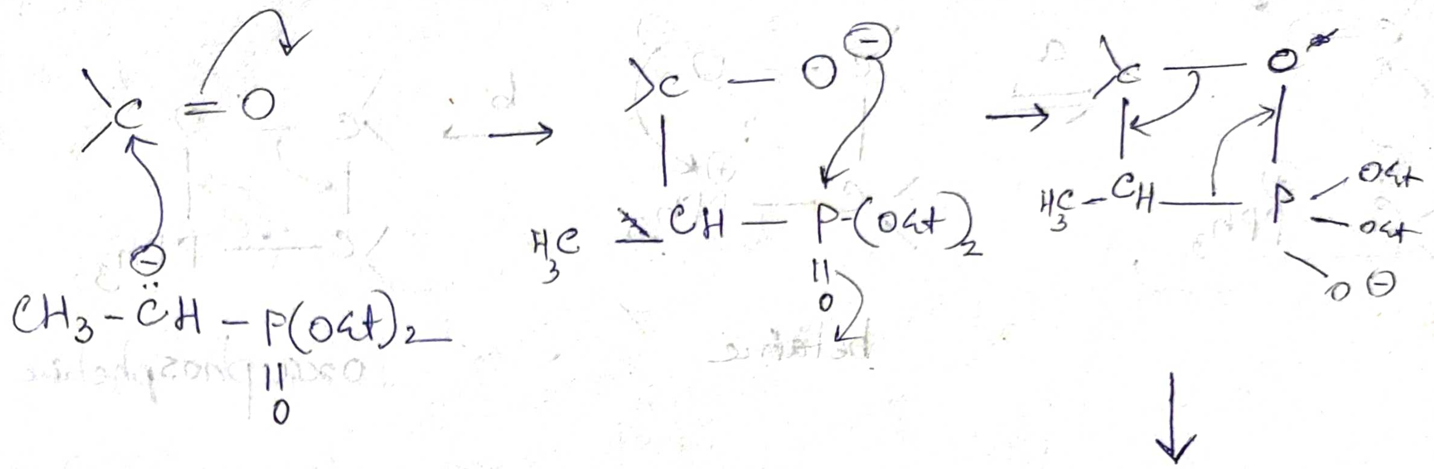
both are soluble in H_2O & organic solvant. So dificult to remove.

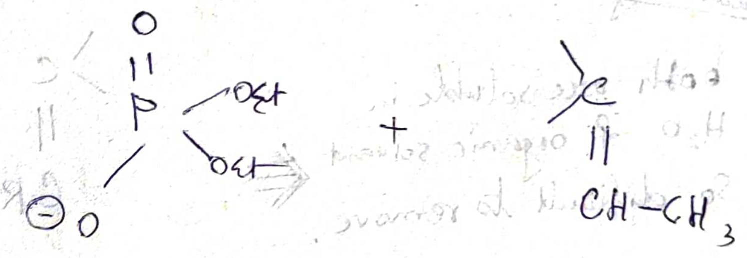
If a chiral phosphene is taken, retension of configuration ~~is tak~~ occur.

Horner-Wordswarth-Emmon's Modification :-

$P(OEt)_3$ = triethyl phosphide



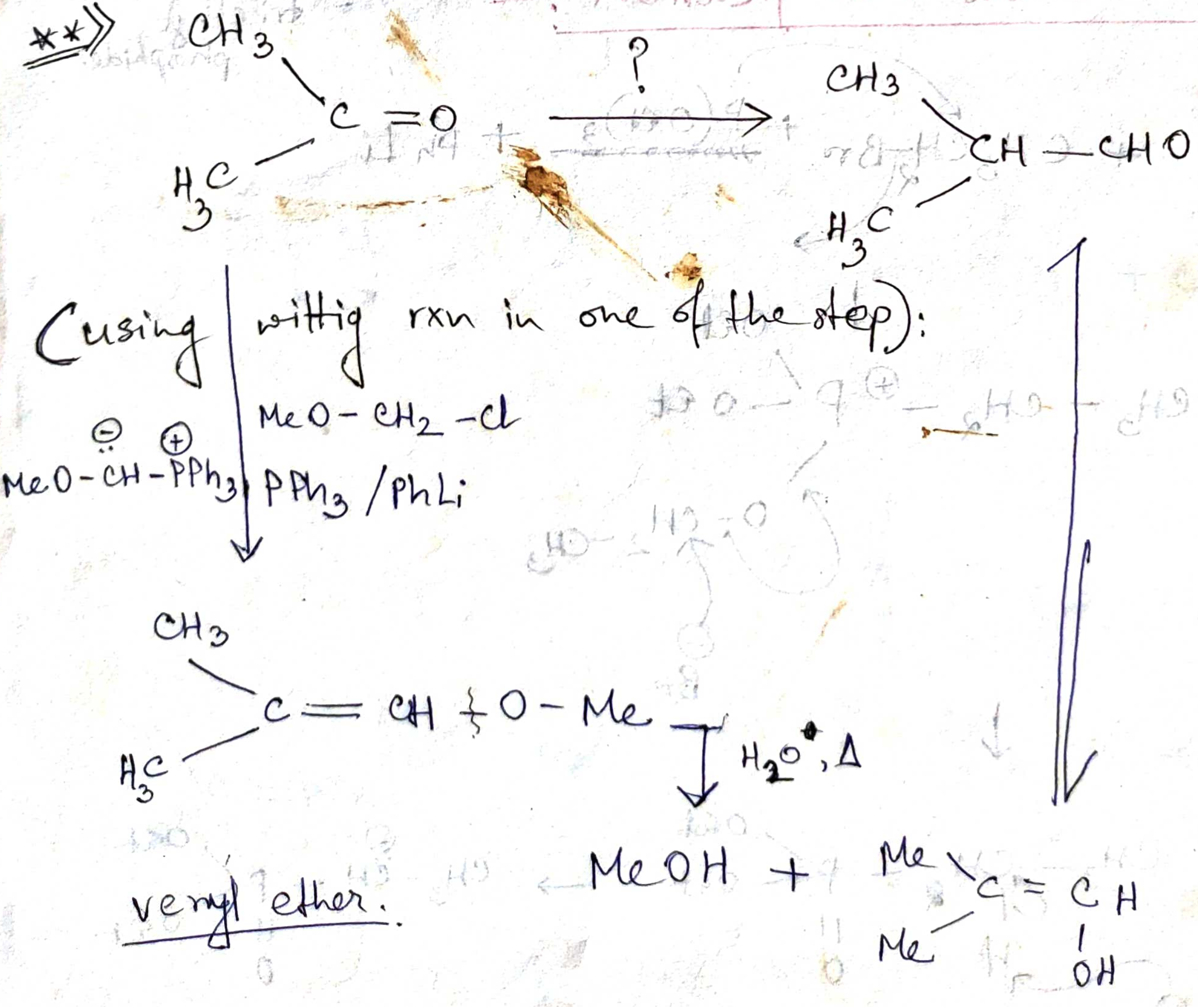




Presence of –OR, –CO_2Et ~~do~~ gr. in alkyl halide does not interfere in this rxn.

phosphate salt

(Soluble in water and easily removed).



(using wittig rxn in one of the step):

$MeO-\overset{\ominus}{C}H-\overset{\oplus}{P}Ph_3$

veryl ether.