

Subject: Aldehydes and ketones

\* Carbonyl group is the most important functional group in organic chemistry.

\* resonance  $\text{>C=O} \leftrightarrow \text{>C}^+ \text{---} \text{O}^-$  The carbonyl carbon is  $sp^2$  hybridized with the three atoms attached to it lie on the same plane (triangle planar)

Physical properties:-

1) They don't form H-bonds, so their b.p alcohol > aldehyde > ether > hydrocarbon

2) They form polar-polar bonds, where  $C^+$  is binded electrostatically with  $O^-$ .

3) They form H-bonds with water  $\rightarrow$  soluble, large chains are insoluble.

Arrange benzaldehyde, benzyl alcohol and p-xylene according to boiling points  
benzyl alcohol > benzaldehyde > p-xylene

$\text{O}=\text{CH}_2$   $\text{O}=\text{CHCH}_3$   $\text{O}=\text{CHCH}_2\text{CH}_2\text{CH}_3$   $\rightarrow$  all of these are aliphatic.

methanal (formaldehyde) ethanal (acetaldehyde) butanal (n-butyraldehyde)  $\text{CH}_3=\text{CHCH}_2\text{CH}$  (3-butenal)

is usually gas (formalin), is used in solutions to preserve biological samples.  $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO}$  (glyceraldehyde)

$\text{CH}_3\text{C}(=\text{O})\text{CH}_3$  (acetone)  $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{CH}_3$  (diethyl ketone) benzaldehyde (benzene ring with CHO) cyclopentanecarbaldehyde (cyclopentane ring with CHO)

Propanone (acetone) 3-pentanone (diethyl ketone) benzaldehyde (benzene ring with CHO) (formylcyclopentane) (cyclopentane ring with CHO)

$\text{Cyclopentane ring with } \text{CH}_3$  (2-methylcyclopentanone)  $\text{CH}_3=\text{CHC}(=\text{O})\text{CH}_3$  (3-buten-2-one)  $\text{Benzene ring with } \text{CHO}$  (2-hydroxybenzene carbaldehyde)  $\text{Cyclopentane ring with } \text{CHO}$  (3-bromo-1-formylcyclopentane or 3-bromo-1-cyclopentanecarbaldehyde)

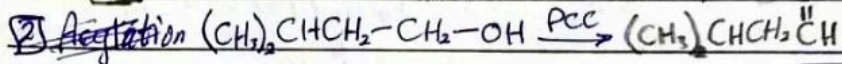
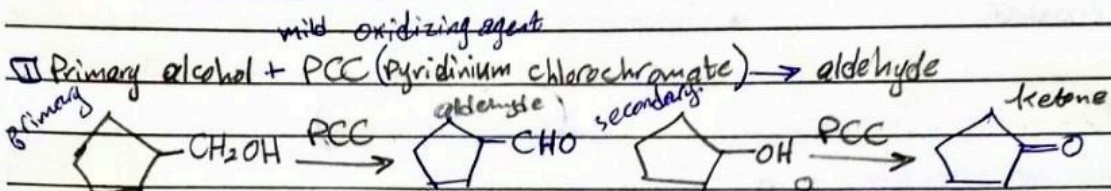
$\text{Benzene ring with } \text{CHO}$  (2-hydroxybenzene carbaldehyde) (methyl vinyl ketone)  $\text{Benzene ring with } \text{CHO}$  (Formyl-2-hydroxybenzene)

$\text{Benzene ring with } \text{C}(=\text{O})\text{CH}_3$  (methyl phenyl ketone)  $\text{Cyclopropane ring with } \text{C}(=\text{O})$  (dicyclopropyl ketone)  $\text{Benzene ring with } \text{C}(=\text{O})\text{C}_6\text{H}_5$  (diphenyl ketone)

(acetophenone) dicyclopropyl ketone diphenyl ketone (benzophenone)

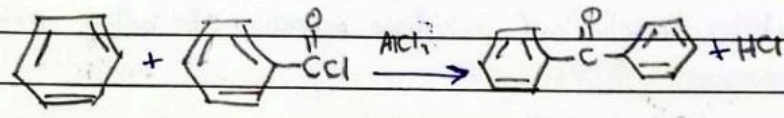


Synthesis of aldehydes and ketones:-



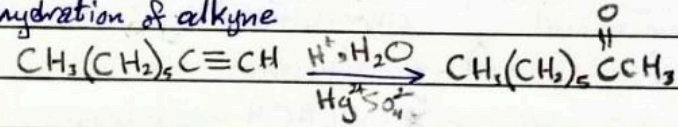
2 Acylation of aromatic ketones:-

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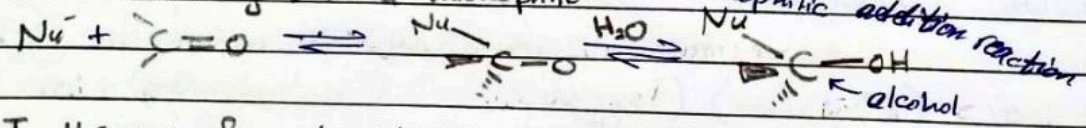
note:- Generally, acylation produces ketones especially aromatic ketones

3 hydration of alkyne

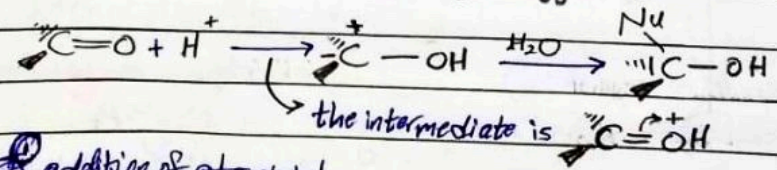


Reactions of aldehydes and ketones:-

\* As the carbon chain of aldehydes and ketones is positively charged, it can interact easily with a nucleophile.

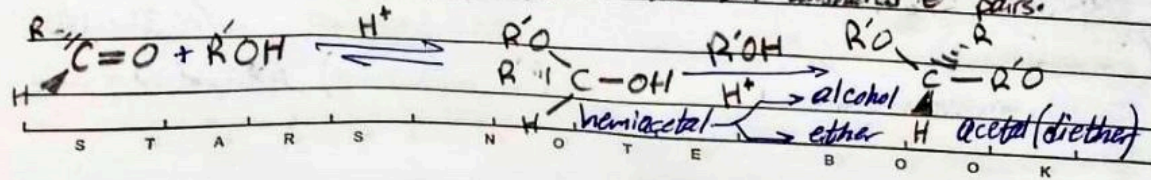


\* In the case of weak nucleophiles, such as H<sub>2</sub>O, we use acid catalyst in order to protonate the carbonyl oxygen.



addition of alcohols

\* Alcohols are weak nucleophiles, as O has two unshared e<sup>-</sup> pairs.

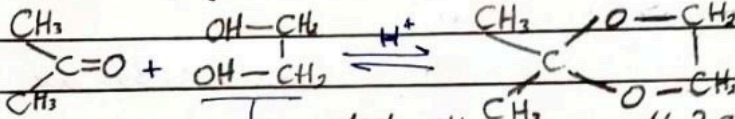




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\* The cyclic form of glucose is actually hemiacetal.

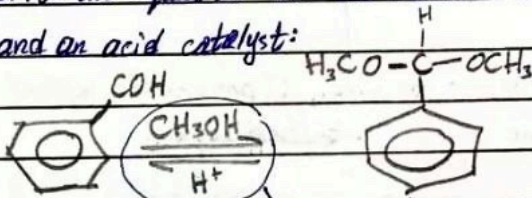
Ketones + glycol  $\xrightarrow{H^+}$  cyclic acetal



we deal with it as we add 2 equivalence of alcohols.

aldehyde or ketone  $\xrightarrow{ROH}$  hemiacetal  $\xrightarrow{ROH}$  acetal

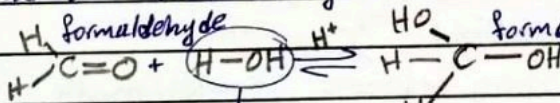
write the equation for the reaction of benzaldehyde with excess methanol and an acid catalyst:



it means more than one equivalence of alcohols.

equilibrium means that heating the product in the presence of excess acid produces substrates.

② addition of water: hydration

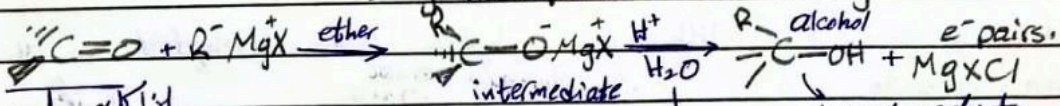


weak nucleophile so we need acid catalyst.

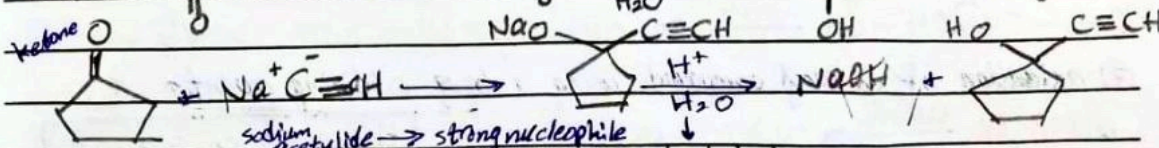
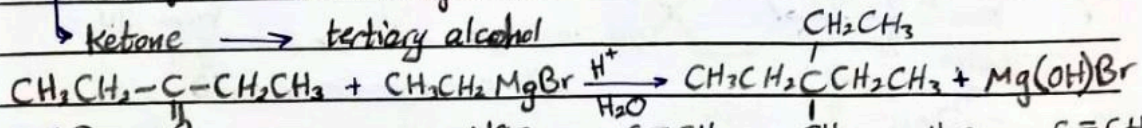
Acetal hydrolysis: is the reverse of acetal formation by the reaction with  $\text{H}_2\text{O}$  or  $\text{H}^+$

③ addition of grignard reagents and acetylides:

strong nucleophile because it is charged without unshared



- Formaldehyde  $\rightarrow$  primary alcohol
- aldehyde  $\rightarrow$  secondary alcohol
- ketone  $\rightarrow$  tertiary alcohol



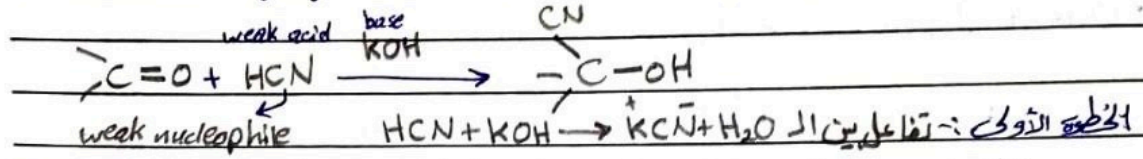
grignard reagent

S T A R S N O T E B O O K



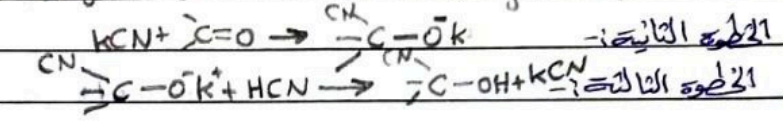
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④ addition of hydrogen cyanide (cyanohydrin) → cyanohydrins



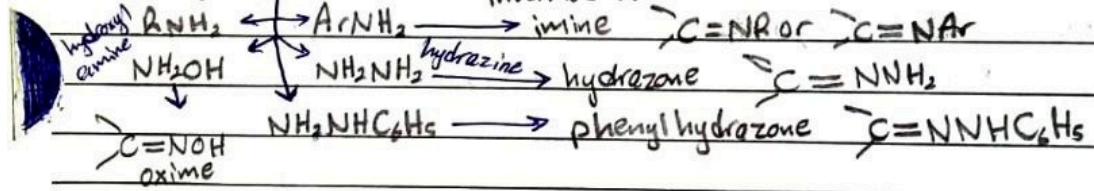
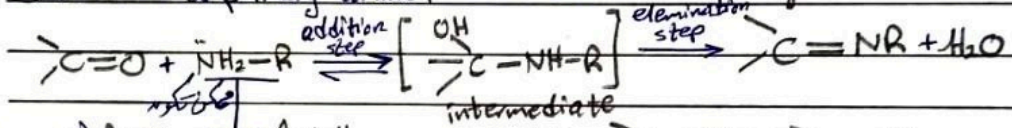
\* The aim of using KOH catalyst is to make CN a strong nucleophile.

cyanohydrin has a C atom that contain OH and C≡N groups



→ is the only reactions in which C preserve its sp<sup>2</sup> hybridization.

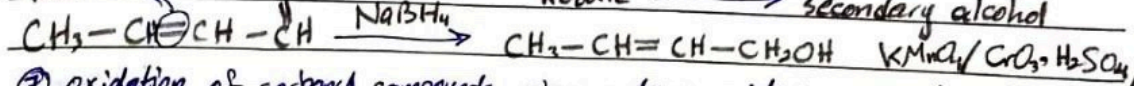
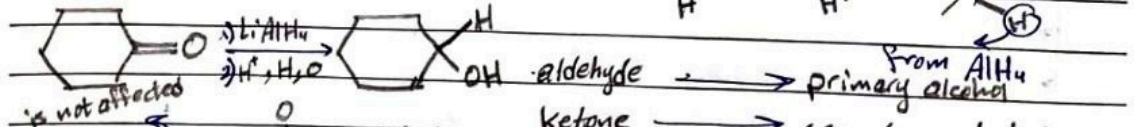
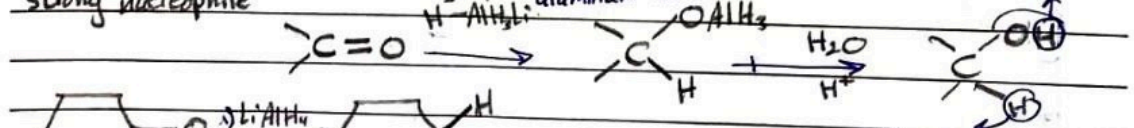
⑤ addition of primary amine: → imine



⑥ reduction of carbonyl compounds: adding H<sup>-</sup> → alcohols

\* We need reducing reagent: LiAlH<sub>4</sub> stronger than NaBH<sub>4</sub>

\* Added hydrogen is a strong nucleophile



⑦ oxidation of carbonyl compounds using a strong oxidizing agent: Ag<sub>2</sub>O

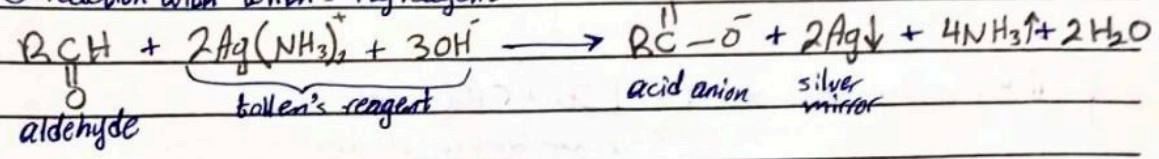
aldehyde  $\xrightarrow{KMnO_4}$  carboxylic acid

ketone  $\xrightarrow{KMnO_4}$  no rxn

this reaction can be used to separate aldehydes from ketones

Subject: .....

③ reaction with Tollen's reagent (silver mirror test).



\* Tollen's test can distinguish aldehydes from ketones as Tollen's reagent doesn't react with ketones.

\* Each mole of  $\text{LiAlH}_4$  or  $\text{NaBH}_4$  can reduce 4 moles of  $\text{C}=\text{O}$

oxidizing agents for aldehydes are:-

$\text{KMnO}_4$        $\text{CrO}_3$        $\text{Ag}_2\text{O}$        $\text{K}_2\text{Cr}_2\text{O}_7$        $\text{PCC} \rightarrow \text{mild}$

