

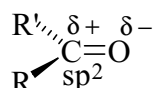
Chapter 18

RCHO : aldehyde \Rightarrow easily oxidized.

aldehyde is more reactive than ketone toward nucleophilic addition.

RCOR' : ketone \Rightarrow difficult to be oxidized.

\Downarrow
C=O carbonyl group

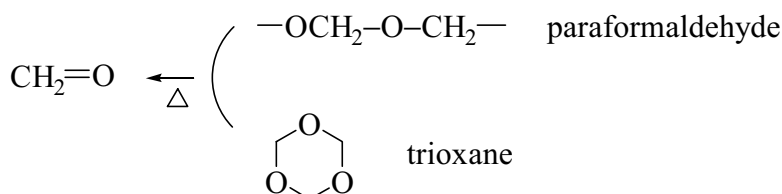


nomenclature : aldehyde - al

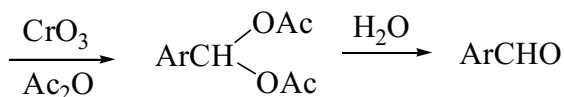
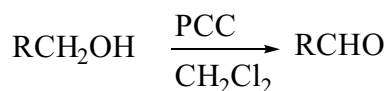
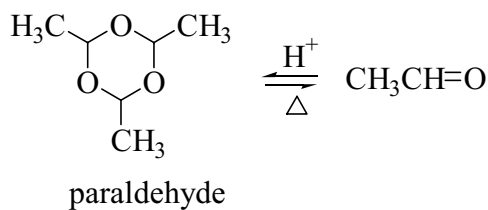
ketone - one (p659 & p660)

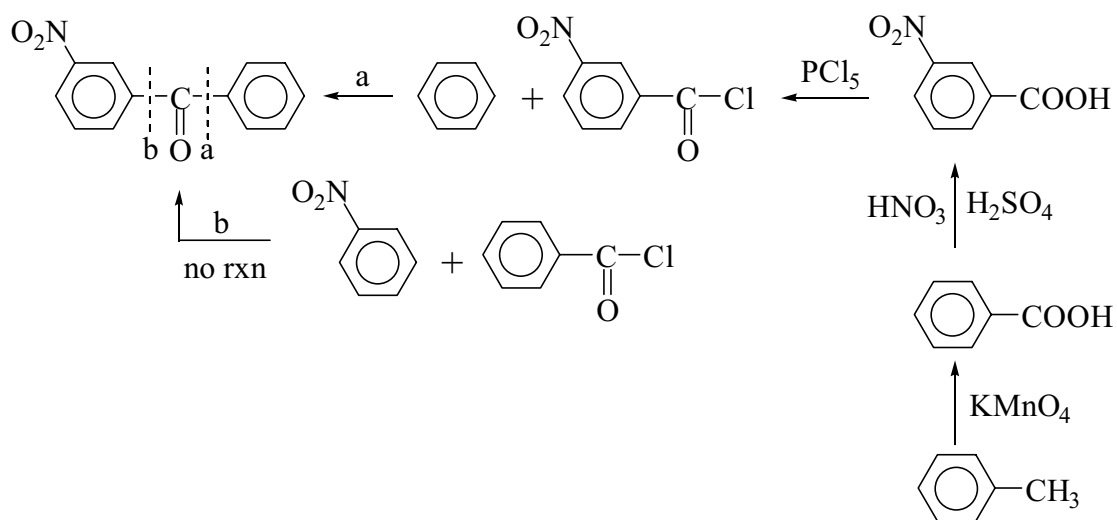
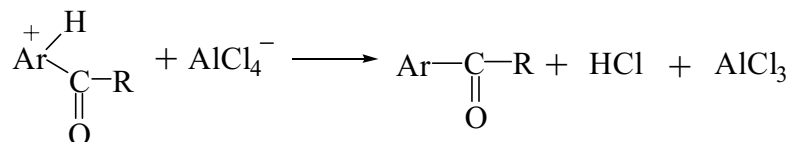
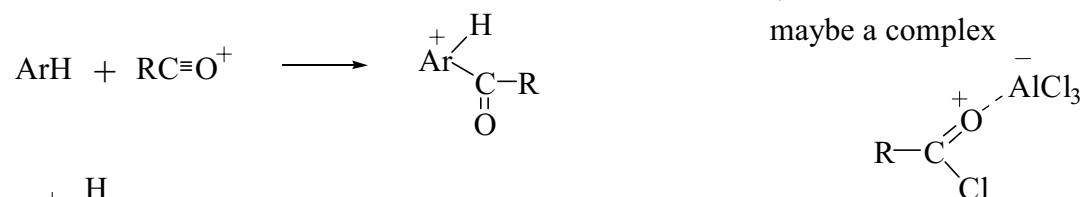
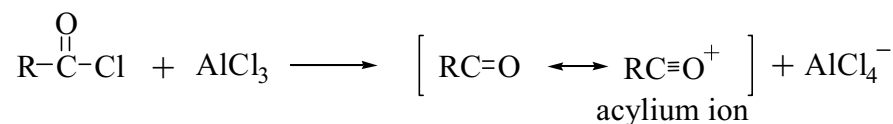
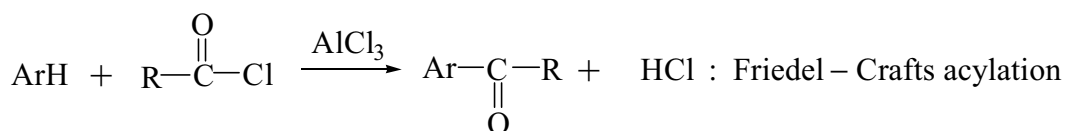
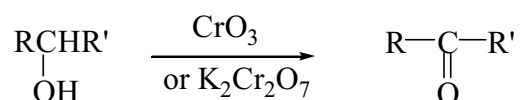
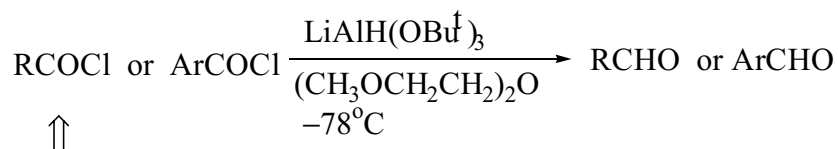
aldehyde) \Rightarrow polar, no hydrogen-bonding
ketone) lower aldehydes and ketones are soluble in H₂O
(presumably due to hydrogen-bonding)

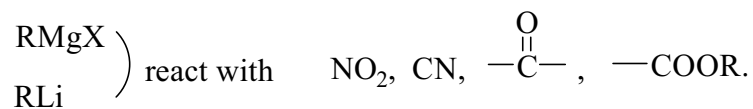
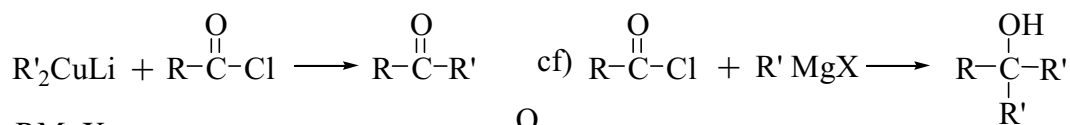
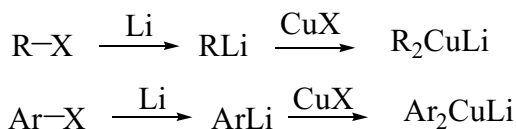
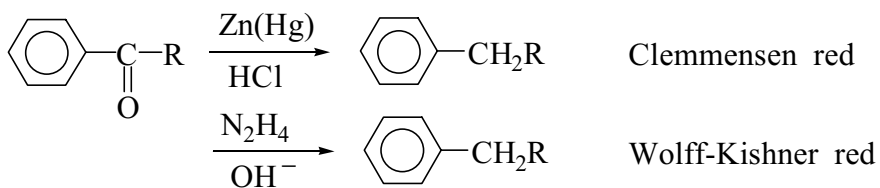
formaldehyde (CH₂O, bp -21°) : formalin (aq soln)
solid polymers



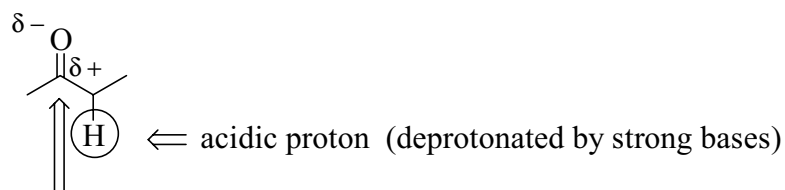
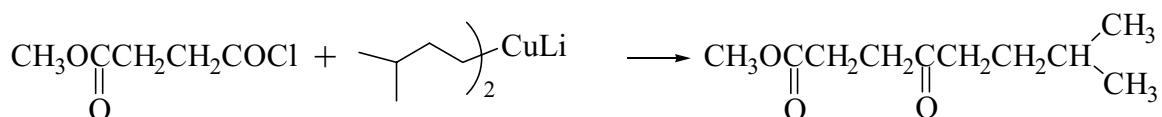
acetaldehyde (CH₃CHO, bp 20°) :



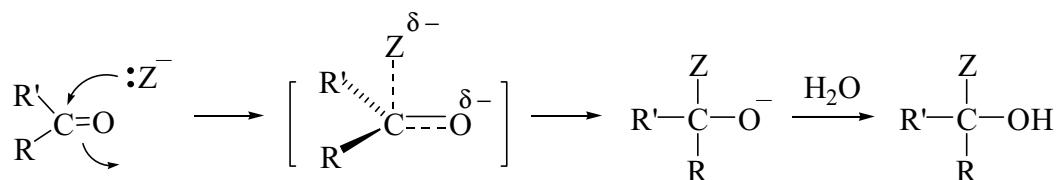




R_2CuLi does not. cf) halide



nucleophilic addition

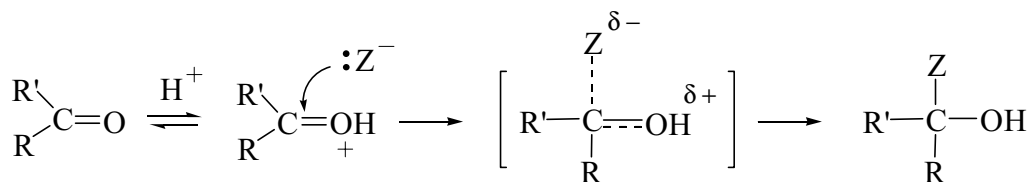
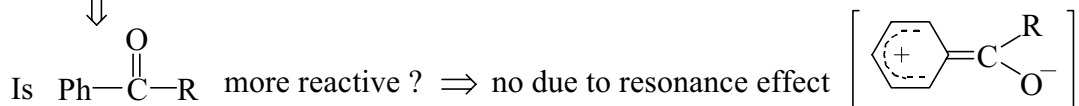
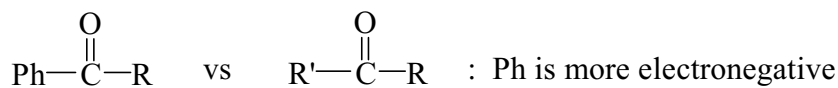


trigonal

tetrahedral

(sterically relatively unhindered)

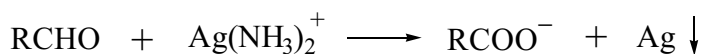
aldehyde is more reactive than ketone due to electronic and steric factors.



lower E_a



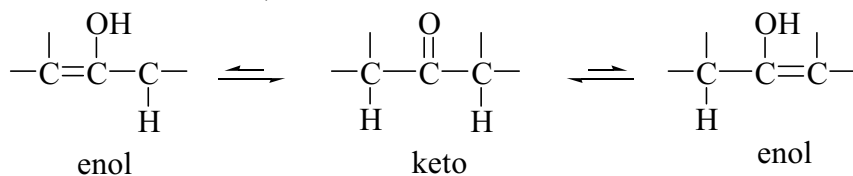
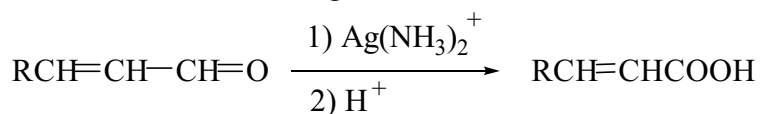
catalyzed by acids (protic or Lewis acid)



to prevent precipitation (Ag_2O) silver mirror
in basic conditions,

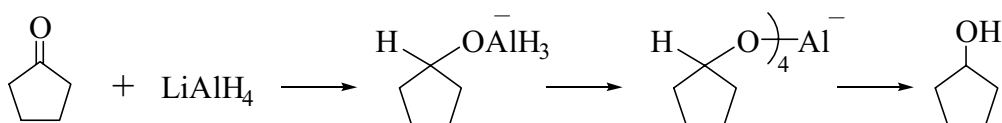
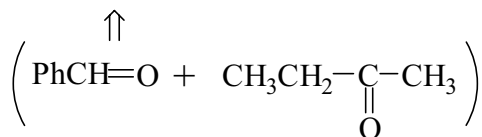
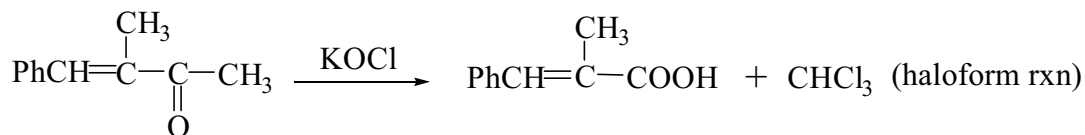
NH_3 is added.

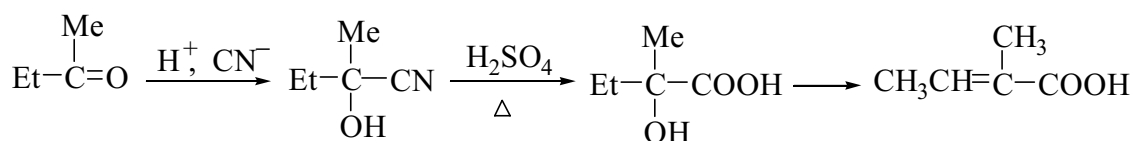
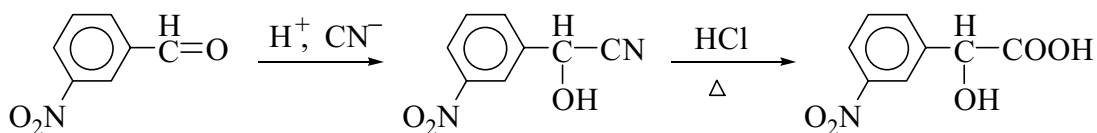
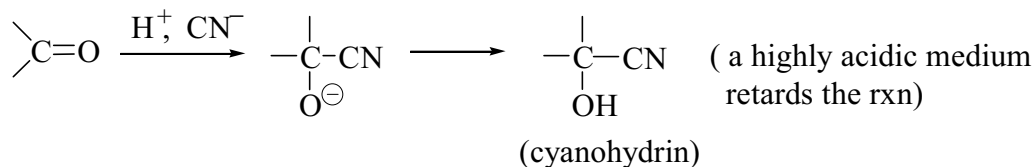
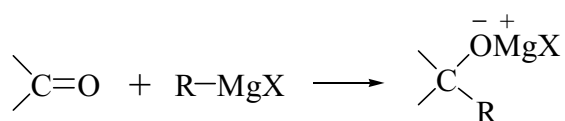
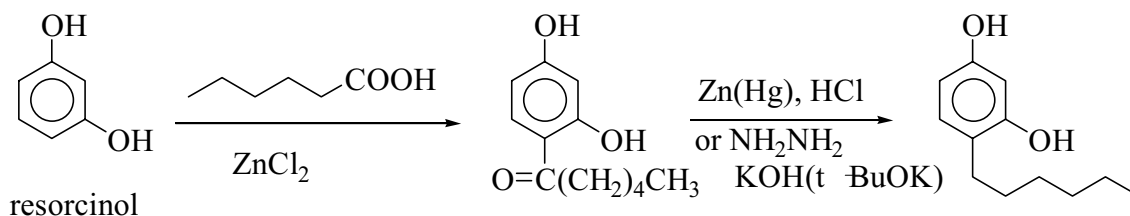
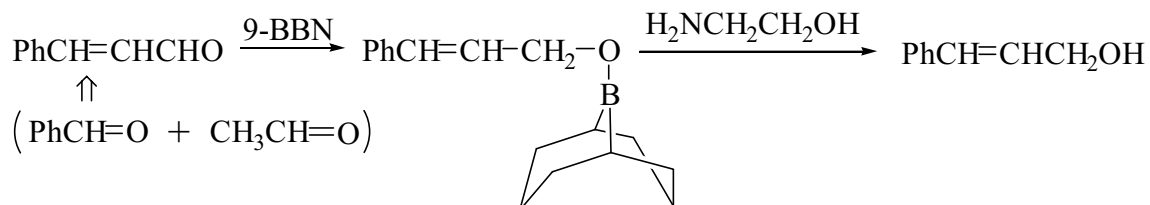
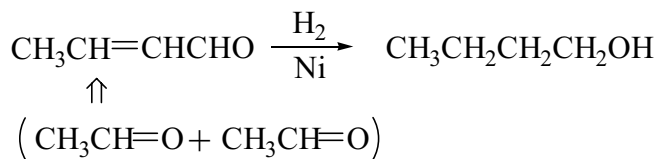
Tollens' reagent

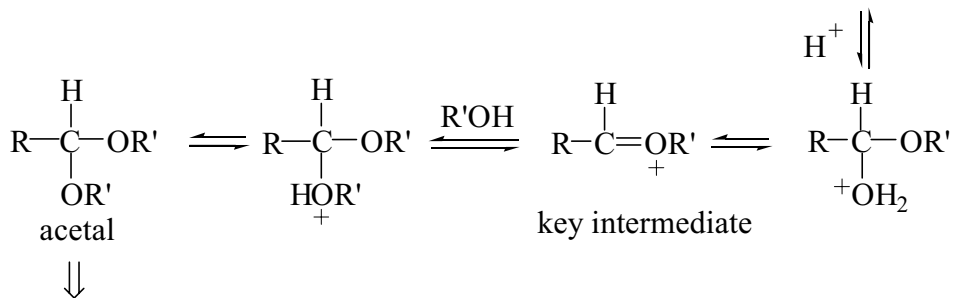
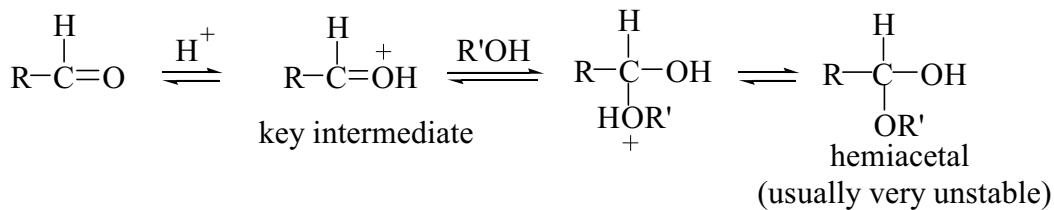


difficult to oxidize it.

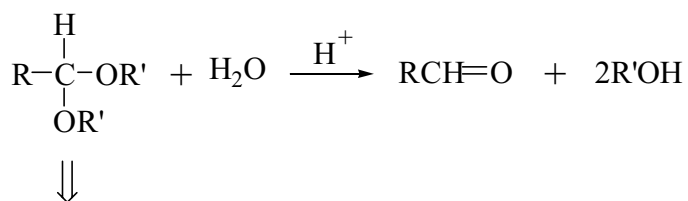
the double bond of the enol form is cleaved in vigorous oxidation condition.



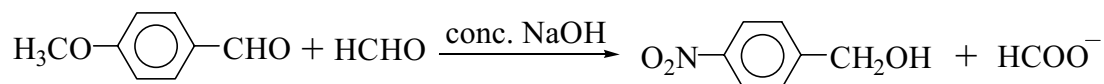
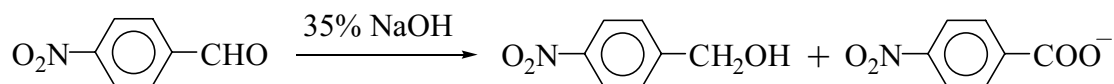
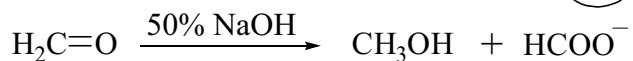
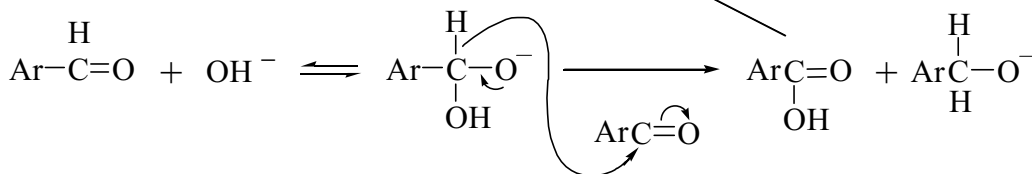




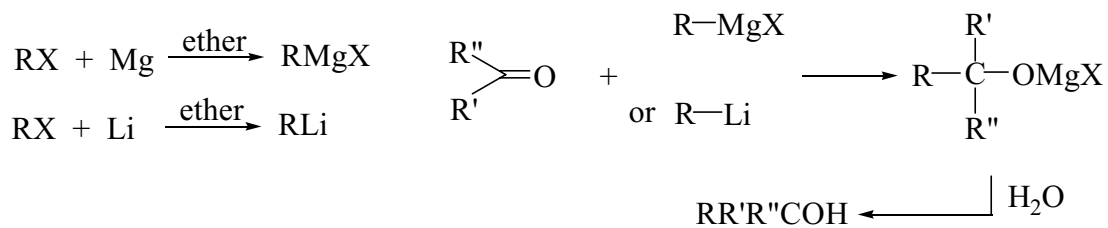
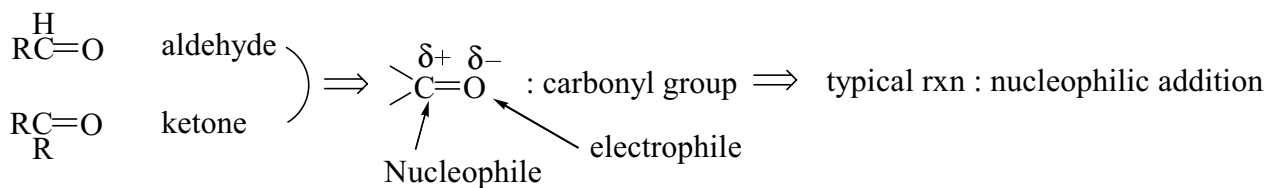
necessary to remove H₂O ⇒ use benzene, toluene or xylene as a solvent to form azeotrope.



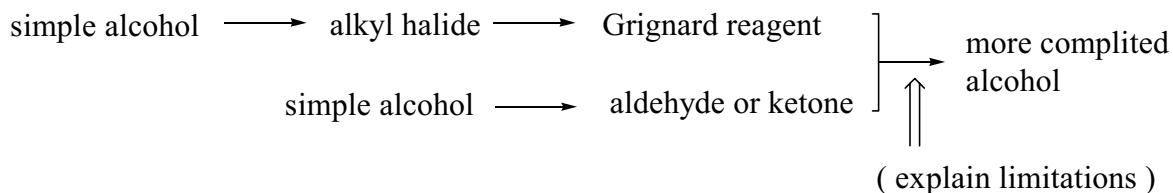
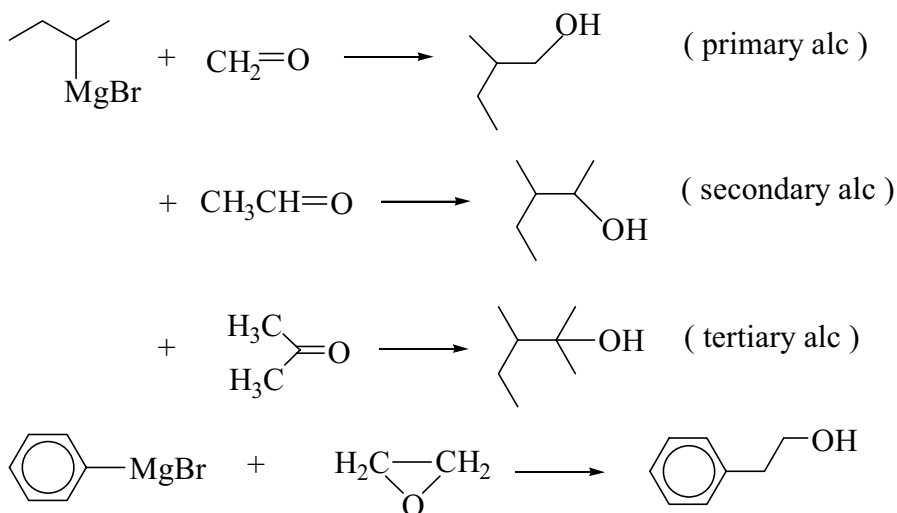
very stable toward bases

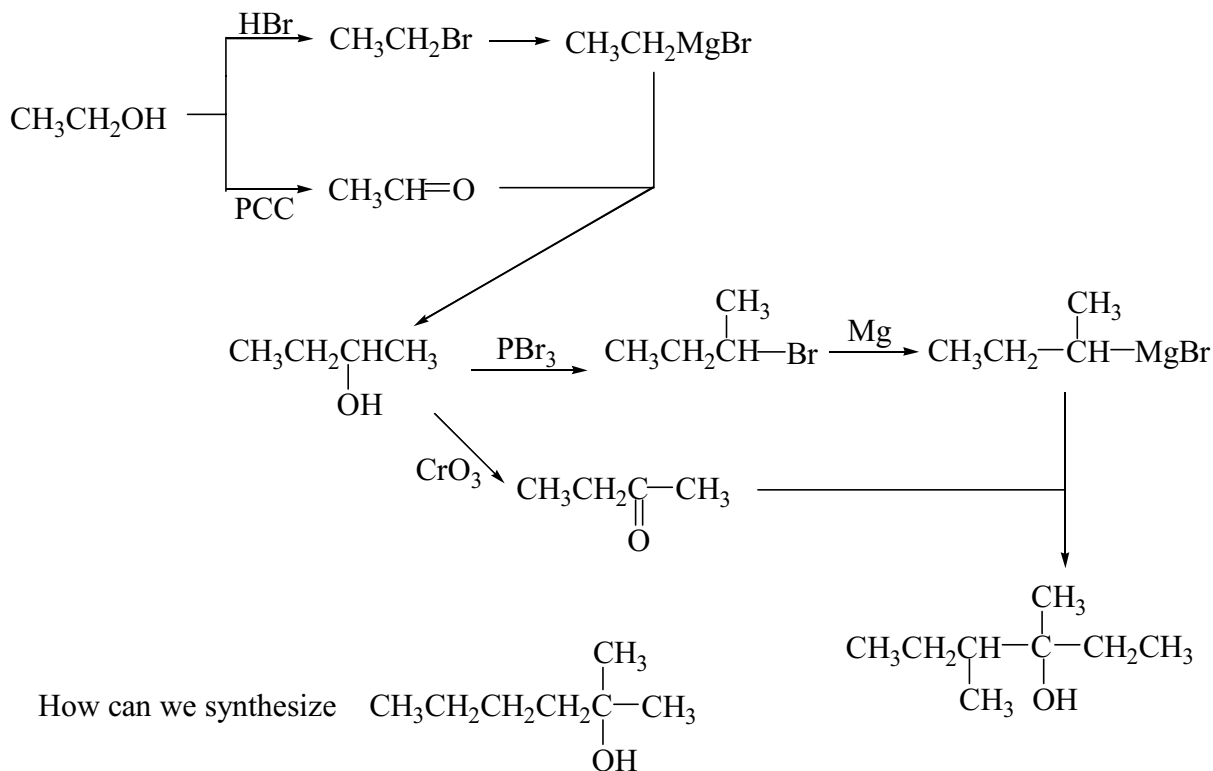


(crossed Cannizzaro rxn)
(others are possible but not formed when an aldehyde is HCHO)



generally RLi is more reactive than RMgX due to more electropositive Li.

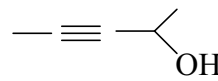
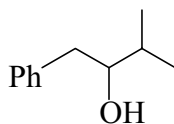
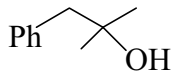
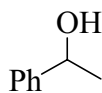
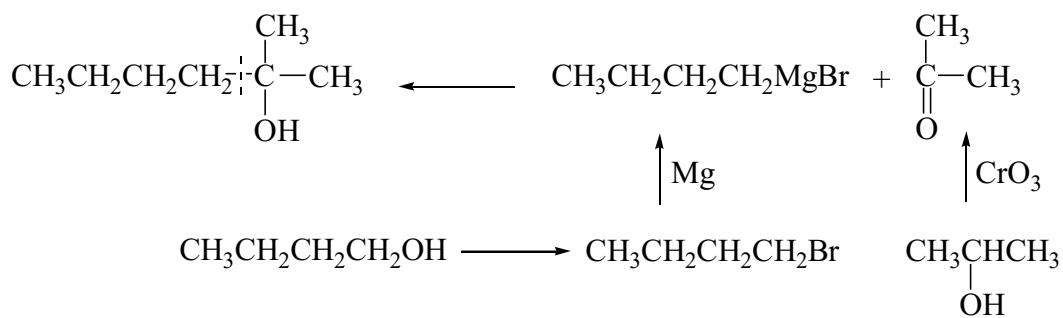




when all alcohols of four carbons or fewer are available ?



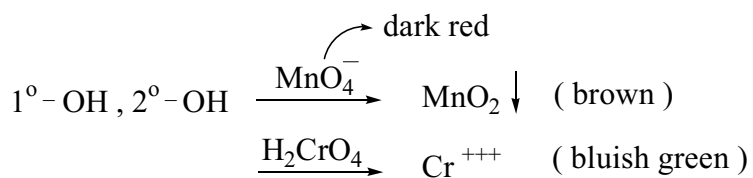
retrosynthetic analysis



limitations

THP protecting group

tests for alc



Lucas test : conc. HCl + ZnCl₂

3°-OH : react immediately (cloudy soln) \implies allyl alc reacts immediately

2°-OH : react within 5 min

1°-OH : no rxn at RT

