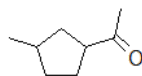


14.13: SOLUTIONS TO ADDITIONAL EXERCISES

14-1

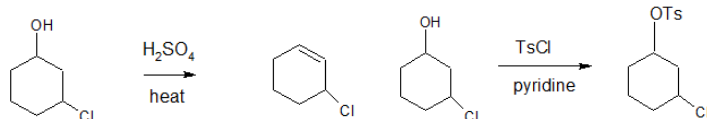
C.



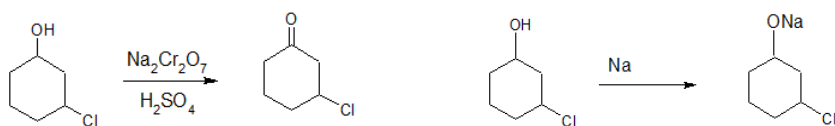
1-(3-methylcyclopentyl)ethan-1-one

14-2

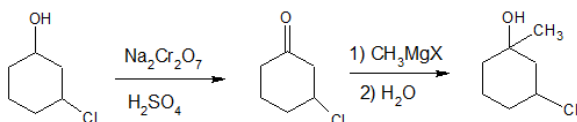
(a) (b)



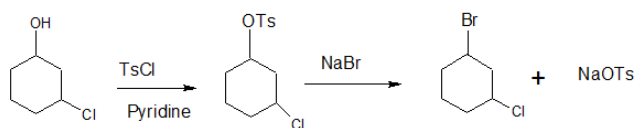
(c) (d)



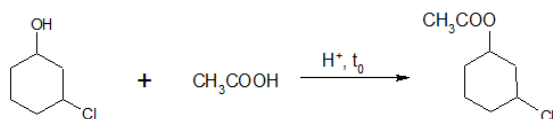
(e)



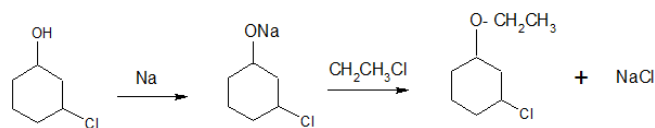
(f)



(g)

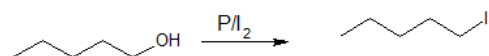
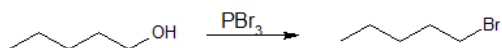
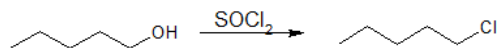


(h)

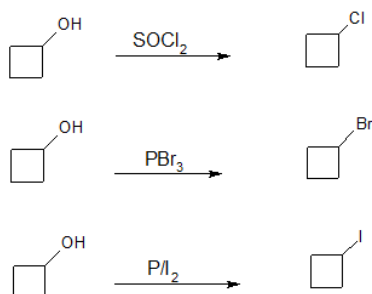


14-3

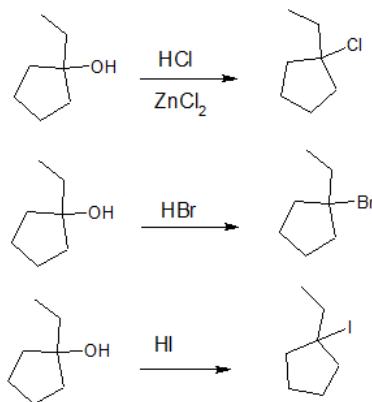
(a)



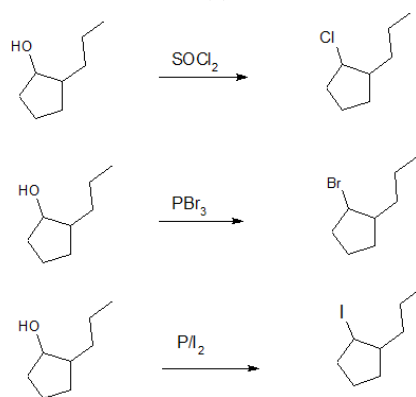
(b)



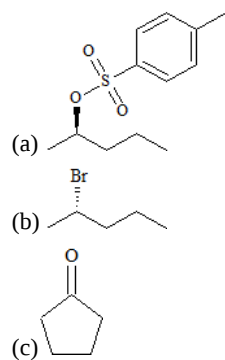
(c)

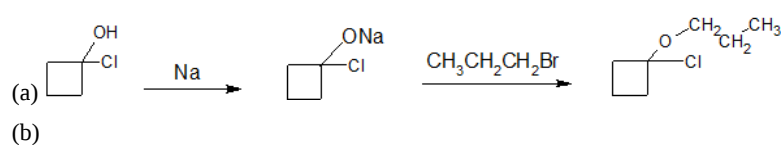
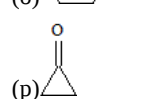
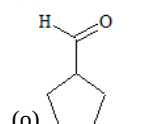
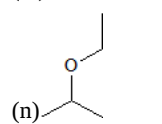
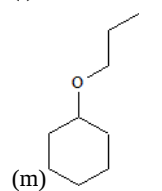
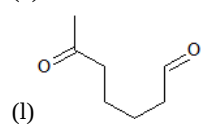
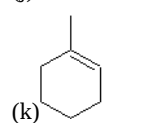
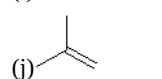
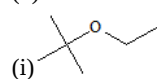
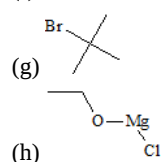
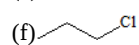
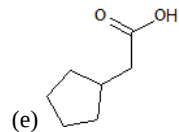
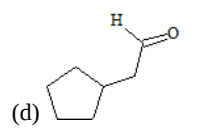


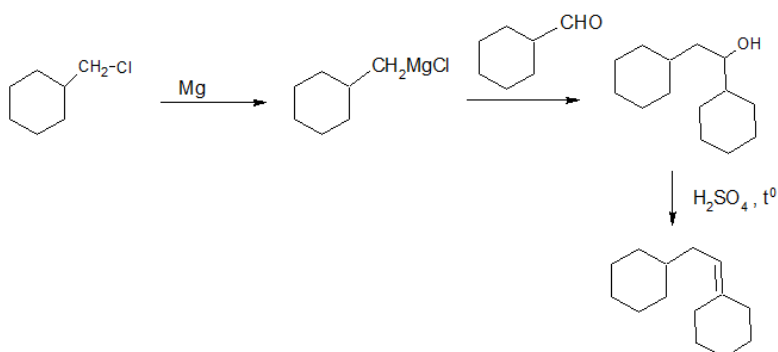
(d)



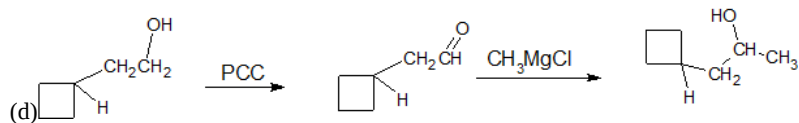
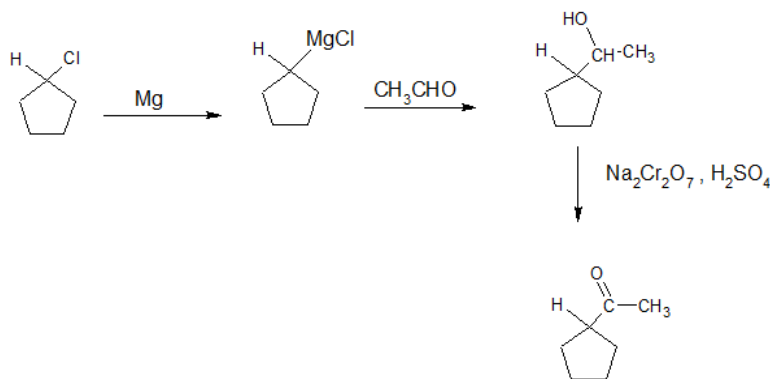
14-4



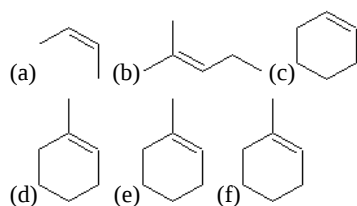




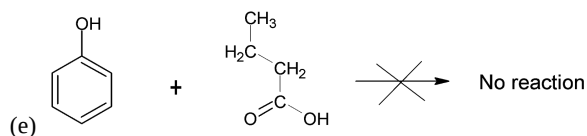
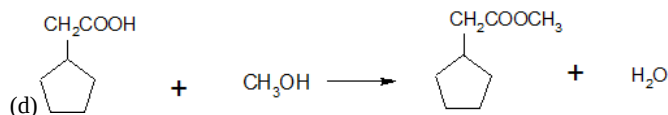
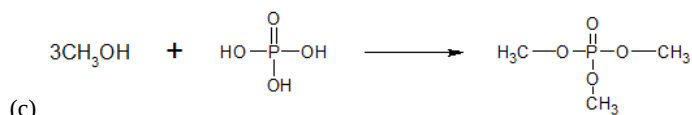
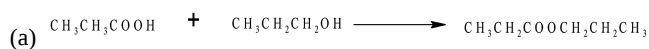
(c)



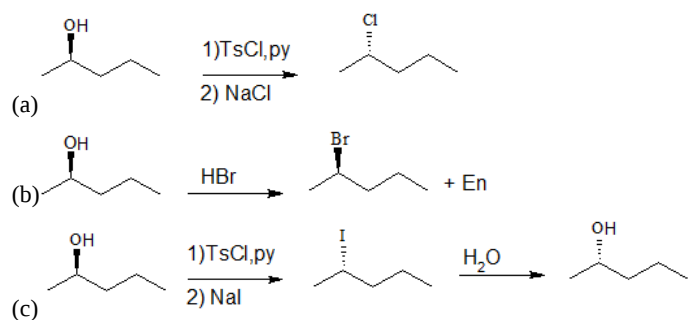
14-6



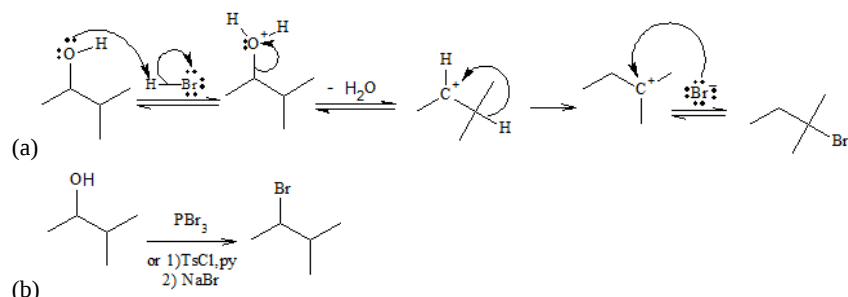
14-7



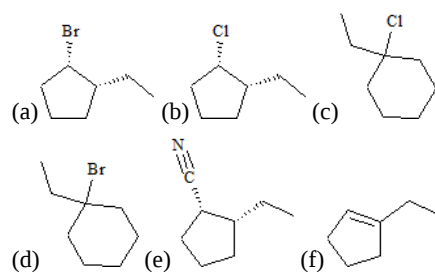
14-8



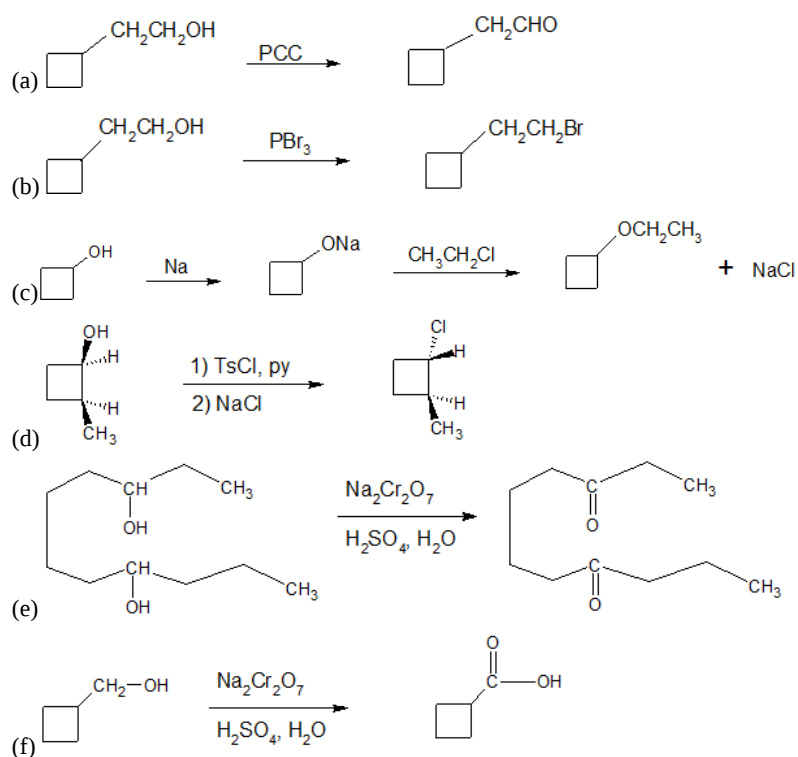
14-9

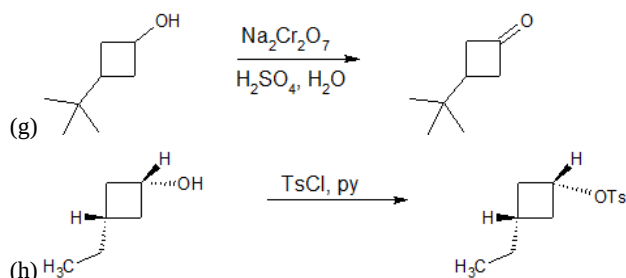


14-10



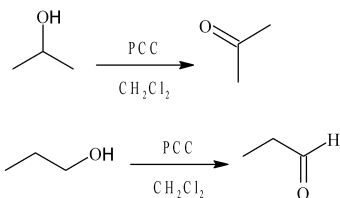
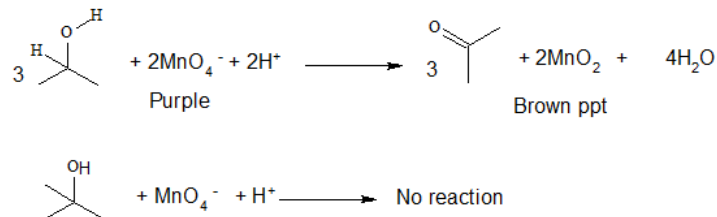
14-11





14-12

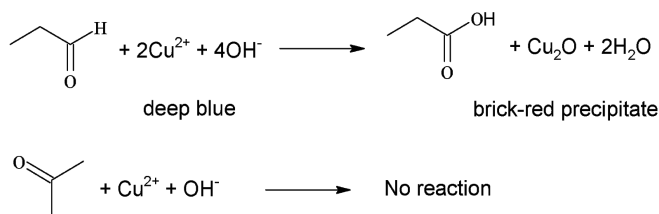
(a) We can use potassium permanganate solution to distinguish between 2-propanol and 2-methyl-2-propanol. In acidic condition, KMnO_4 oxidizes 2-propanol into acetone which forms the MnO_2 brown precipitate and vanishes KMnO_4 purple. As tertiary alcohol cannot be oxidized, 2-methyl-2-propanol remains purple.



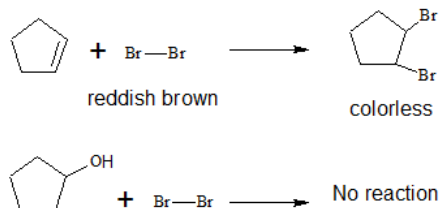
(b) 1-propanol and 2-propanol first need to be oxidized into propanal and acetone respectively.

Note: we use pyridinium chlorochromate (PCC) in methylene chloride CH_2Cl_2 to produce aldehyde without further oxidation.

Fehling's test then can be used to determine the presence of an aldehyde. Propanal reacts with Fehling's reagent (Cu^{2+} in basic solution), forming a brick-red precipitate Cu_2O , while acetone cannot react to Fehling's solution, remaining a deep transparent blue color.

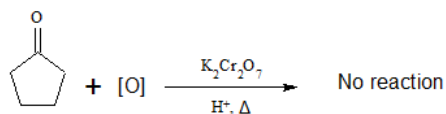
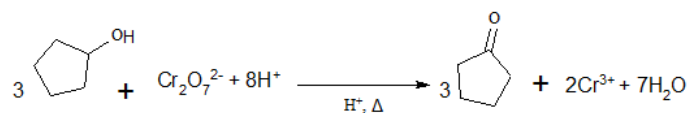


(c) We can use Bromine test to distinguished between cyclopentanol and cyclopentene. Bromine reacts rapidly with cyclopentene, in which the reddish brown color disappears quickly without forming HBr gas bubble. Cyclopentanol does not react with bromine.

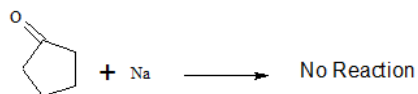
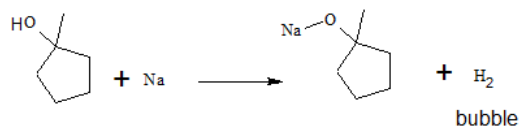


(d) Besides KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic condition is another oxidizing agent that can be used to distinguish between cyclopentanol and cyclopentanone. Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ oxidizes cyclopentanol into cyclopentanone. Evidence for the reaction is the orange solution ($\text{Cr}_2\text{O}_7^{2-}$) turns green solution (Cr^{3+}).

1-cyclopentylethanone cannot be oxidized, remaining the orange solution.

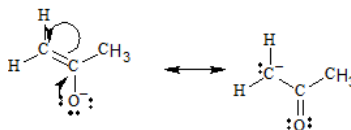


(e) Sodium metal can be used to distinguish between cyclopentanone and 1-methylcyclopentanol. 1-methylcyclopentanol reacts with Na, forming sodium 1-methylcyclopentanolate and releasing H₂ bubbles. Cyclopentanone does not react with sodium metal.

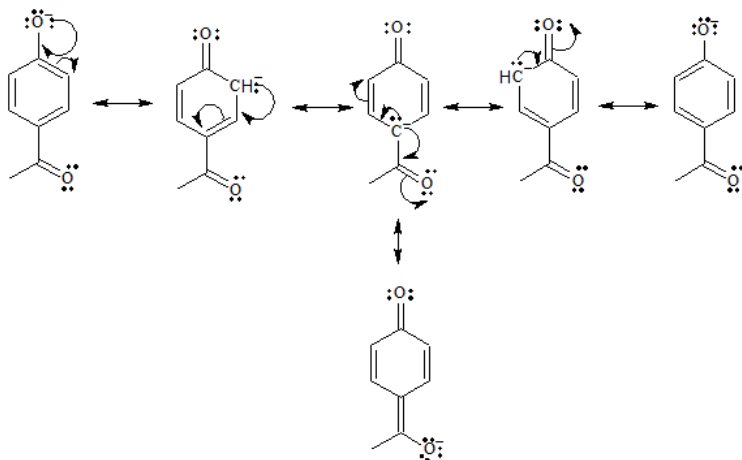


14-13

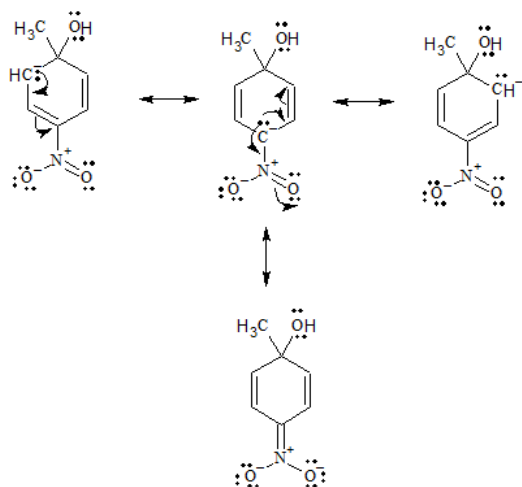
(a)



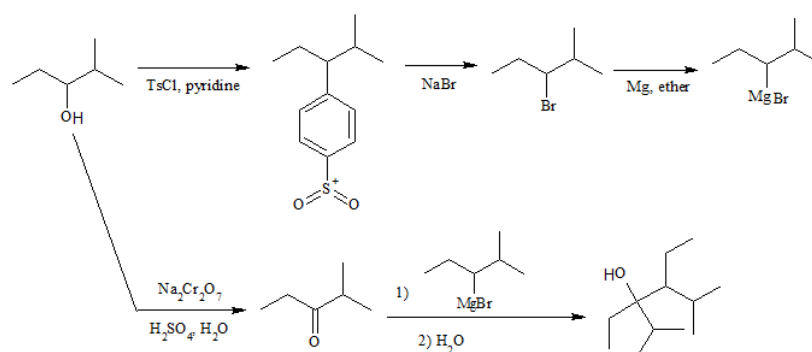
(b)



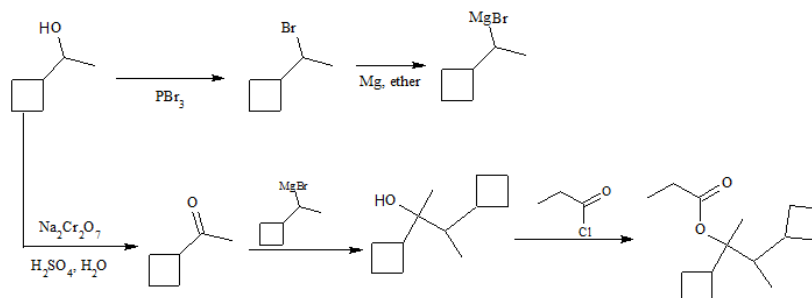
(c)



14-14

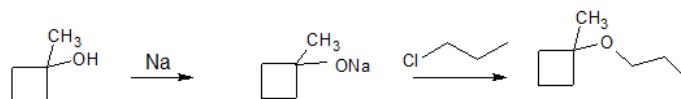


14-15

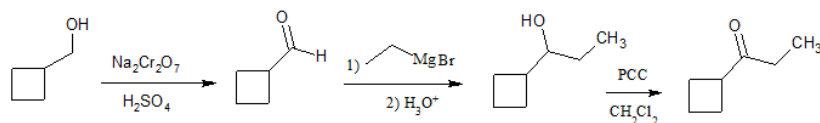


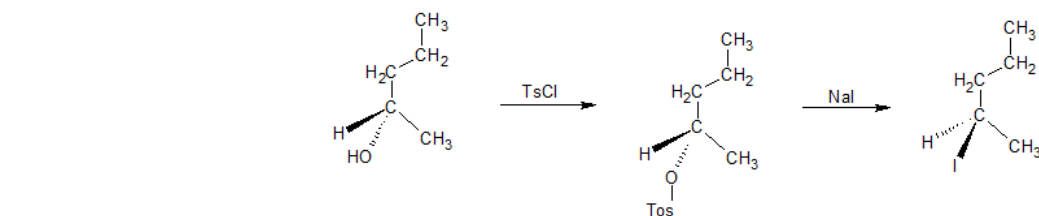
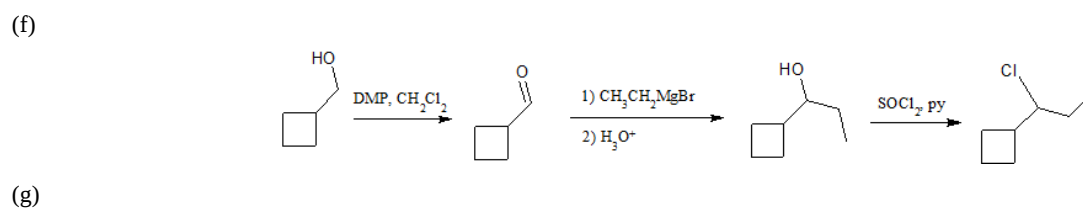
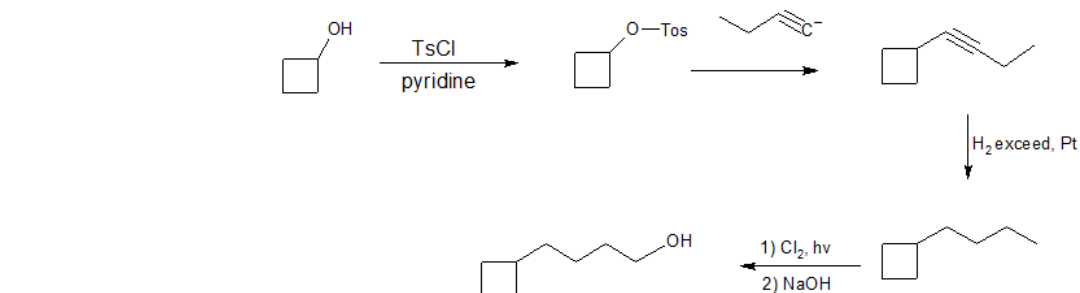
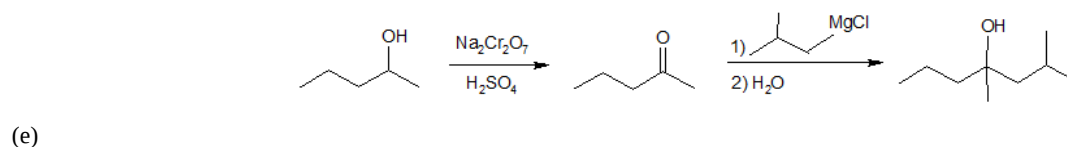
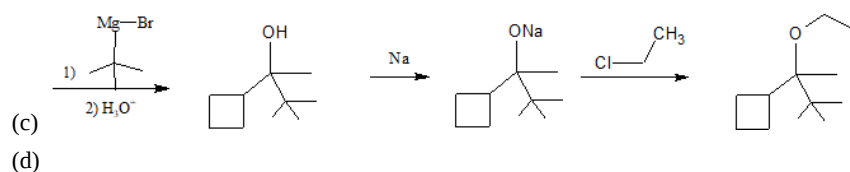
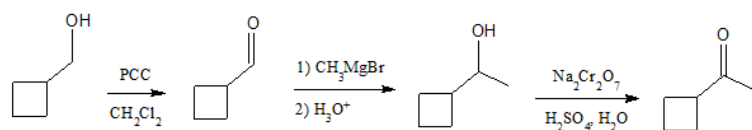
14-16

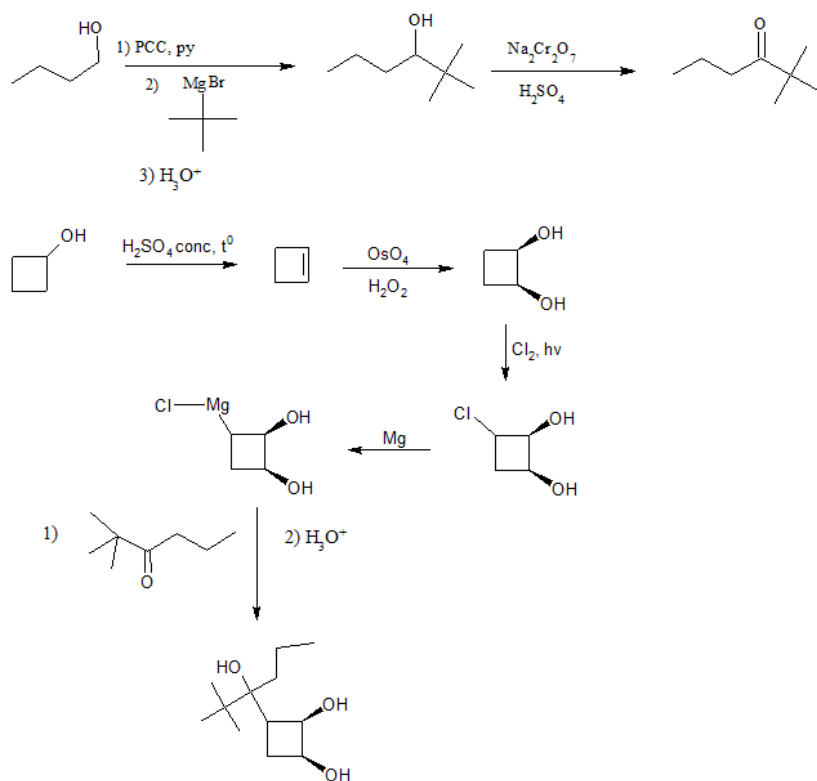
(a)



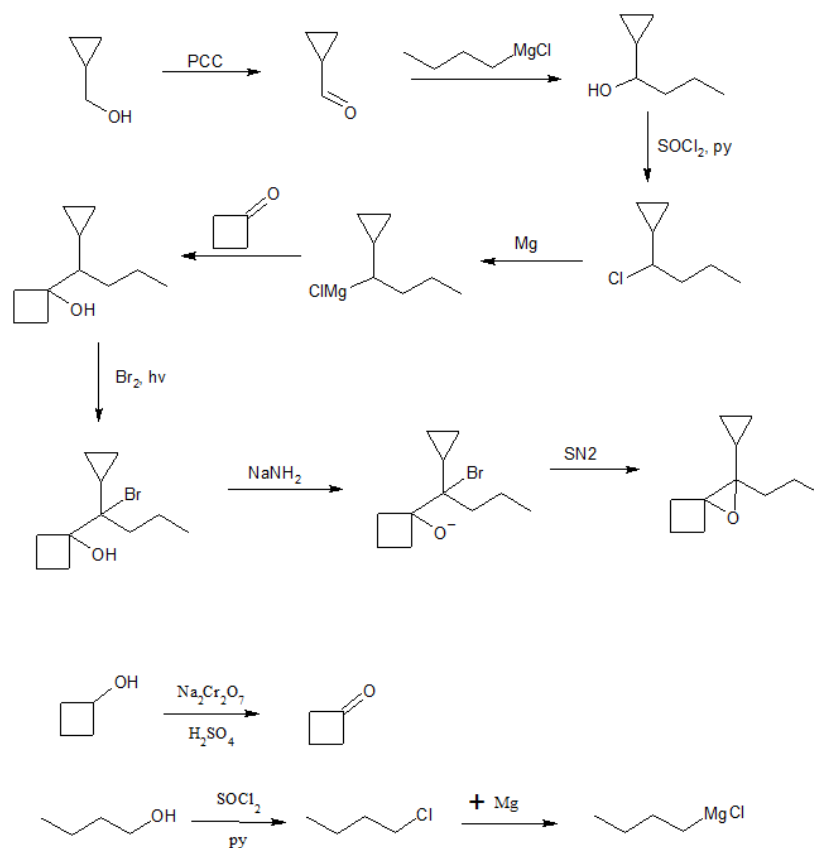
(b)







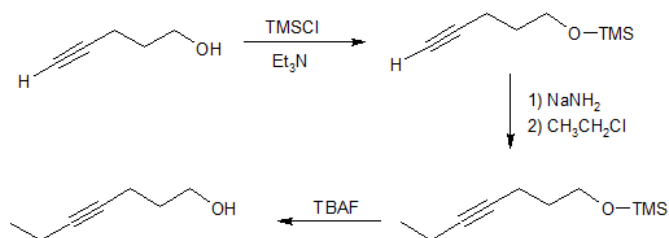
14-17



14-18

a) Alcohol functional group typically has pKa of 16 while the pKa of a terminal alkyne is usually about 25. The strong base NaNH_2 would deprotonate the stronger acid, which in this case is the terminal alkyne. The resulting alkoxide then react with the alkyl halide $\text{CH}_3\text{CH}_2\text{Cl}$

b)



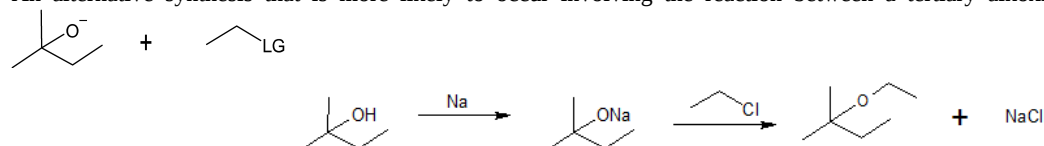
14-19



14-20

Williamson ether synthesis is an S_N2 reaction, which favors strong nucleophile and a primary substrate for back-side attack. Since a tertiary alcohol is given, the resulting alkyl halide is also tertiary, which is sterically hindered for S_N2 reaction to occur. The alkoxide then would function as a base, and an elimination reaction would happen instead of S_N2 reaction.

An alternative synthesis that is more likely to occur involving the reaction between a tertiary alkoxide and a primary alkyl halide:



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