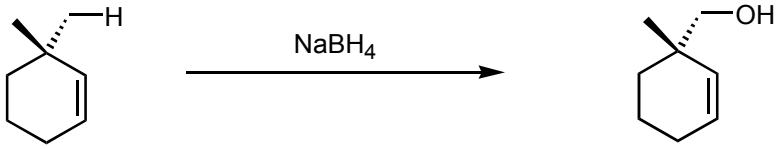
CHEMISTRY 249S 2005: Examination 2 Answer Guide

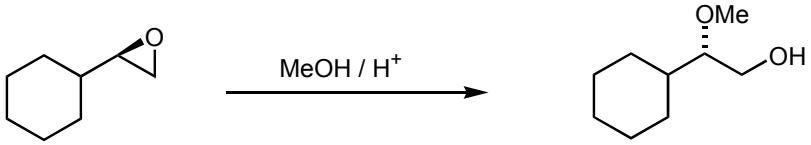
1.

(a)



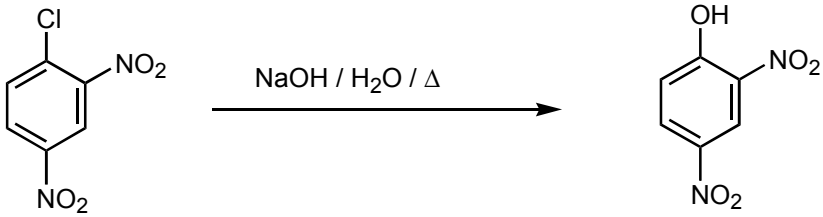
reduction of aldehyde to primary alcohol

(b)



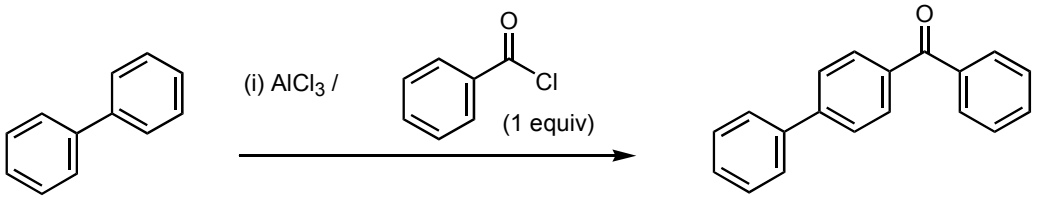
ring-opening of epoxide under acidic catalysis

(c)



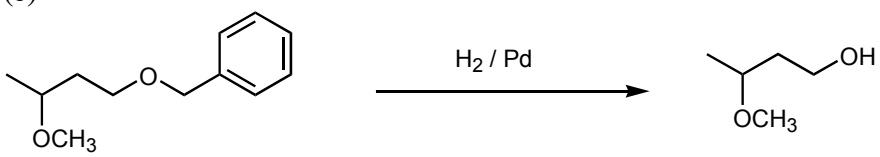
S_NAr substitution by hydroxide

(d)



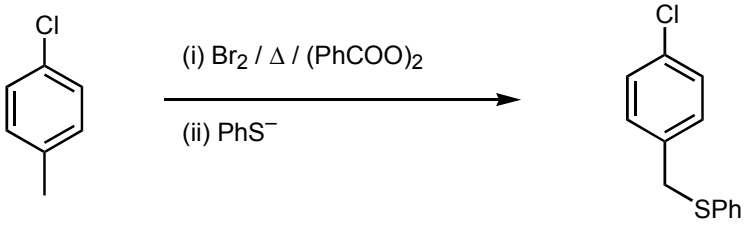
Friedel-Crafts acylation (the phenyl group directs o/p since it can stabilize +ve charge by resonance - the ortho postion is disfavoured on steric grounds)

(e)



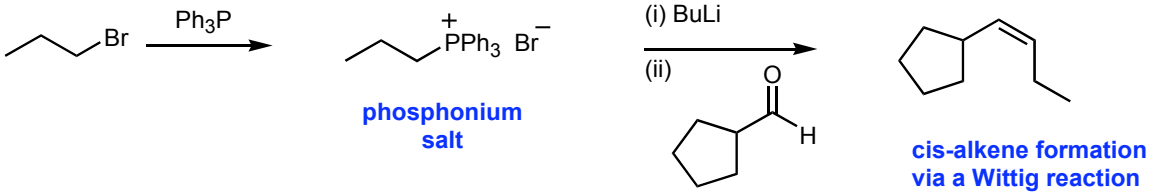
hydrogenolysis of a benzylic ether

(f)



Benzylic bromination (free-radical conditions) followed by S_N2 displacement (much faster than S_NAr)

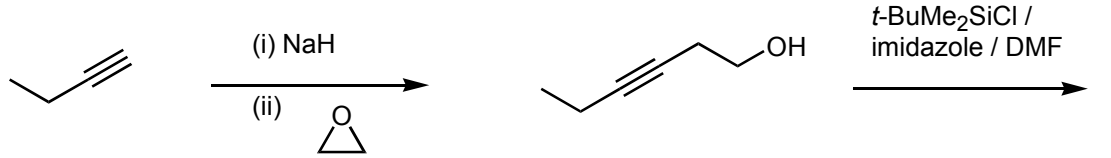
(g)

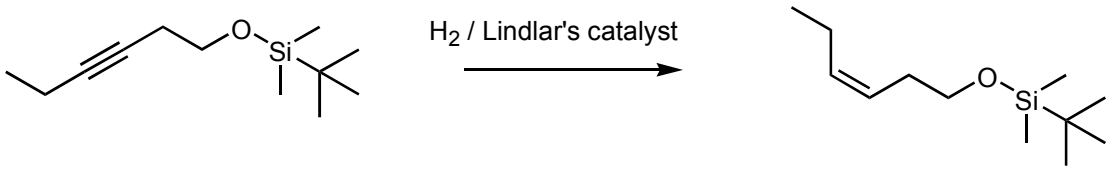


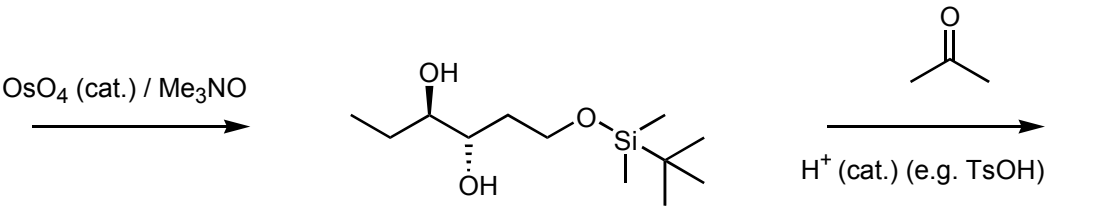
phosphonium salt

cis-alkene formation via a Wittig reaction

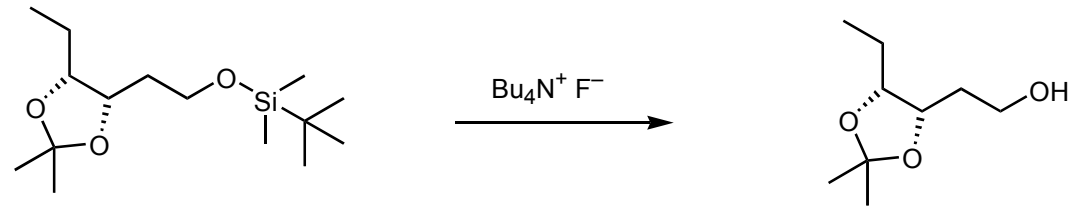
2.

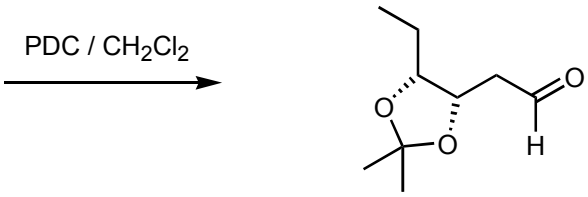






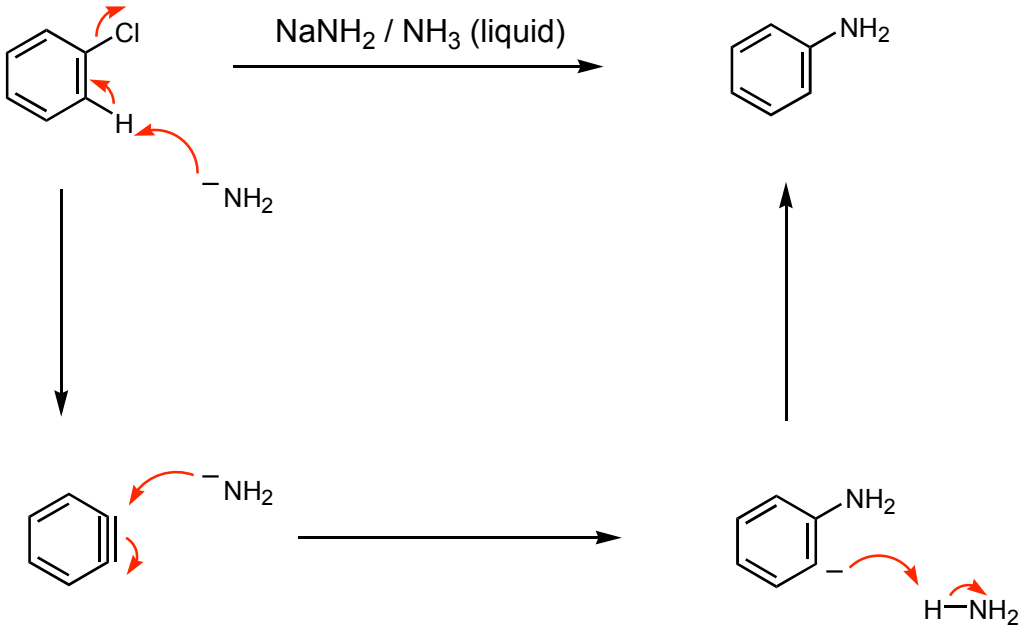
"A"





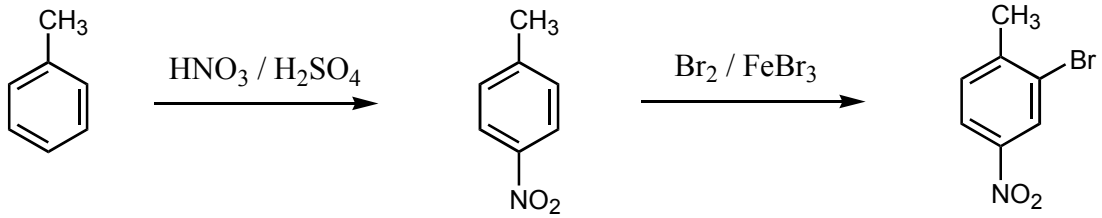
TARGET MOLECULE

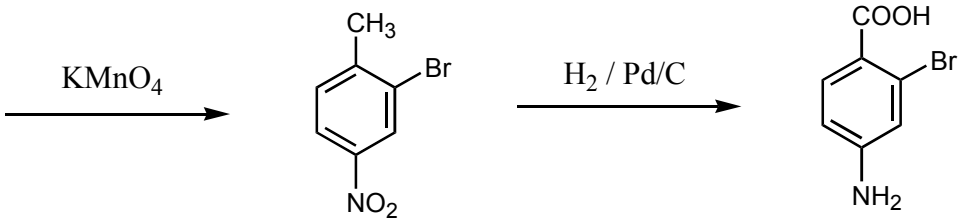
3.



benzyne (very unstable intermediate)

4.
(a)

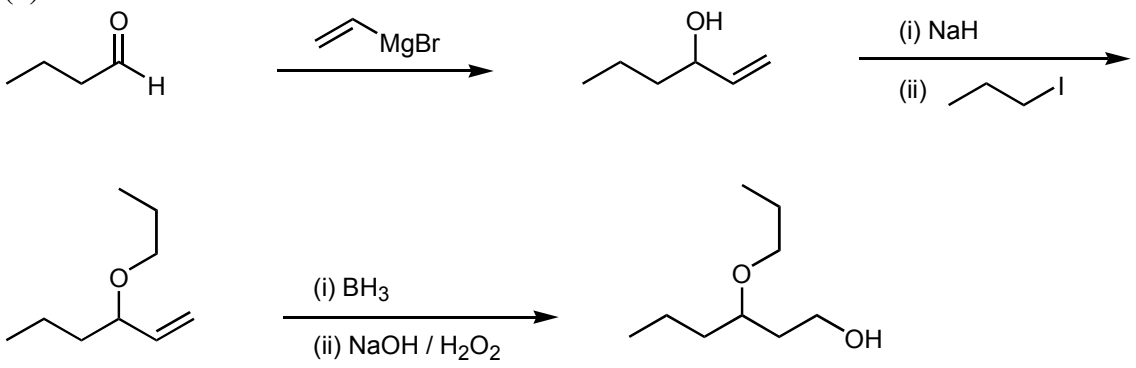


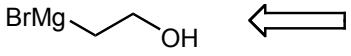


The order of steps is very imnportant in this synthesis!

Nitration must occur before bromination, because a Br substituent is more strongly o/p directing than a methyl group, and would lead to an incorrect substitution pattern
Side-chain oxidation by $KMnO_4$ must occur before nitro group reduction, since the NH_2 functional group is senstive to oxidation

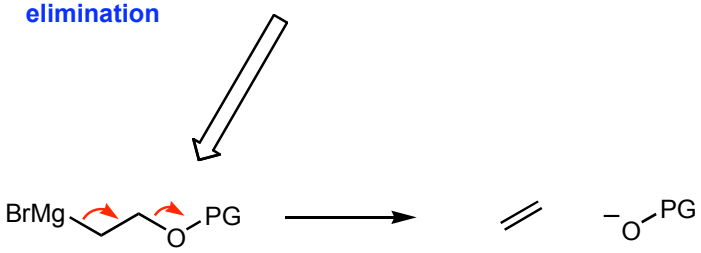
(b)





you cannot use this because of the acidic OH functionality

nor can you use a protected version because it will undergo elimination



PG = Protecting group