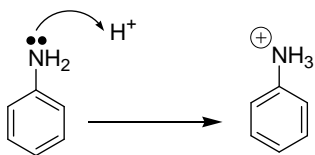
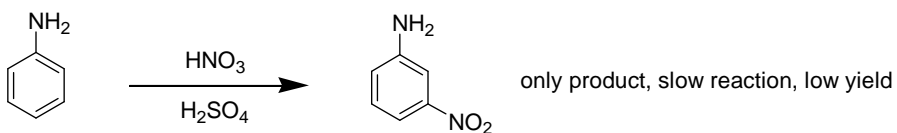


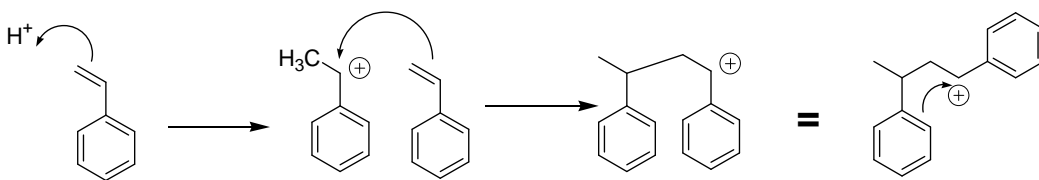
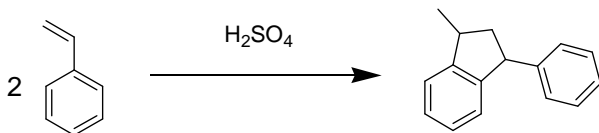


Explain the following reactions with detailed mechanisms.

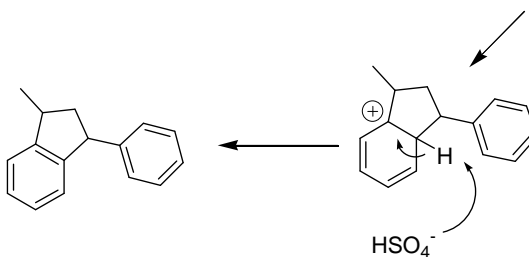


Direct attachment of positive charge to ring gives inductive electron-withdrawing effect, and thereby 1) deactivates the ring and 2) gives the meta-substituted product. Draw the resonance structures of the possible intermediates to check this out.

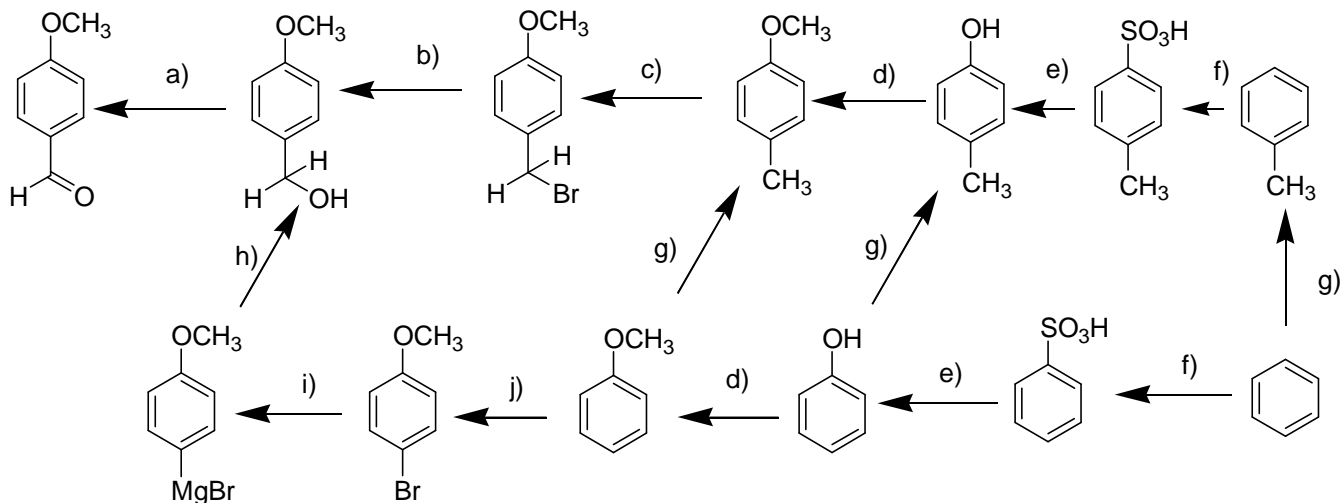
When chemists need to nitrate aminobenzenes, they usually use other non-acidic nitrating reagents like  $\text{CH}_3\text{CH}_2\text{ONO}_2$  (but you don't need to know this) or they first convert the amine to an amide by reaction with an acid chloride or an anhydride (you don't need to know this yet).



Two electrophilic addition steps followed by one electrophilic aromatic substitution step. Redrawing the intermediate helps you see where the last substitution occurs.

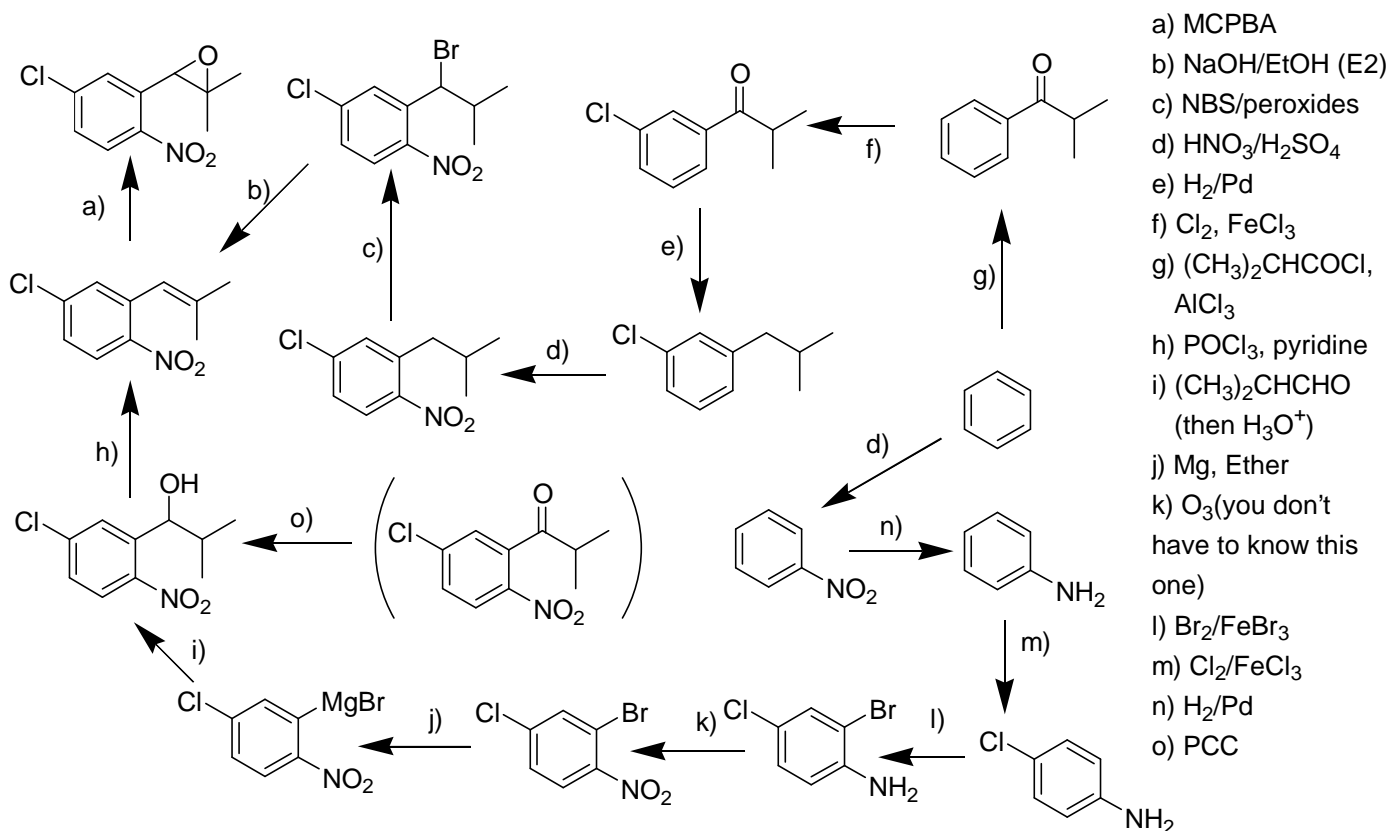


Prepare the following compounds from benzene, inorganic reagents, and organic compounds with 4 or fewer carbons.



a) PCC; b)  $\text{PBr}_3$ ; c) NBS,  $(\text{PhCO}_2)_2$ ; d) NaH, MeBr; e) NaOH, heat; f)  $\text{H}_2\text{SO}_4/\text{SO}_3$ ; g)  $\text{CH}_3\text{Cl}$ ,  $\text{AlCl}_3$ ;  
 h)  $\text{H}_2\text{C}=\text{O}$ ; i) Mg, Ether; j)  $\text{Br}_2$ ,  $\text{FeBr}_3$

Any way you go about it, it looks like seven steps. If you make the ether at an early stage of the procedure, you avoid problems with using NaH in the presence of the aldehyde or the alkyl bromide. Addition of formaldehyde to a grignard reagent is a nice way to make a primary alcohol with an extra carbon. Remember that the  $\text{ArSO}_3\text{H}$  to  $\text{ArOH}$  conversion can only tolerate alkyl substituents on the aryl ring



a) MCPBA  
 b) NaOH/EtOH (E2)  
 c) NBS/peroxides  
 d)  $\text{HNO}_3/\text{H}_2\text{SO}_4$   
 e)  $\text{H}_2/\text{Pd}$   
 f)  $\text{Cl}_2$ ,  $\text{FeCl}_3$   
 g)  $(\text{CH}_3)_2\text{CHCOCl}$ ,  $\text{AlCl}_3$   
 h)  $\text{POCl}_3$ , pyridine  
 i)  $(\text{CH}_3)_2\text{CHCHO}$  (then  $\text{H}_3\text{O}^+$ )  
 j) Mg, Ether  
 k)  $\text{O}_3$  (you don't have to know this one)  
 l)  $\text{Br}_2/\text{FeBr}_3$   
 m)  $\text{Cl}_2/\text{FeCl}_3$   
 n)  $\text{H}_2/\text{Pd}$   
 o) PCC

Figure out the epoxide group and the side chain first (i.e., as the first precursor to the product). Remember that epoxides open easily under acidic conditions and that most of the electrophilic aromatic subst. steps we know use strong Lewis acids. Note that the branching on the side chain rules out simple Friedel-Crafts alkylation. The top route takes seven steps and looks pretty good. The bottom route is longer, and steps l) and m) will probably give mixtures. Step j) might also give problems with competing formation of the  $\text{ArMgCl}$  Grignard. Step o) probably takes us to a dead end.