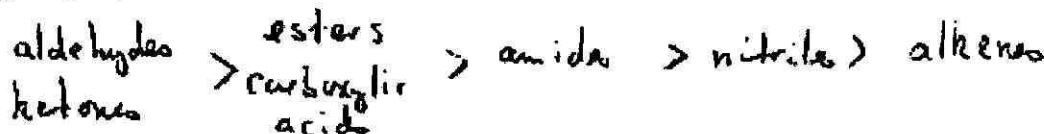


# Problem Set #9

P9.1


In the table below one sees that with  $\text{LiAlH}_4$  as the source of  $\text{H}^-$  ions that ease of hydrolysis proceeds in the order outlined below.



Use the  $\pi$ -M.O. theory derived in class to account for the above facts.

TABLE 19.3 The ease of reduction of various functional groups with  $\text{LiAlH}_4$  in ether

However,  $\text{LiAlH}_4$  is a very powerful reagent, and much less chemoselectivity is possible here than with most of the other metal hydrides

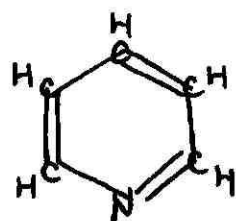
Reaction	Substrate	Product	
6-25	$\text{RCHO}$	$\text{RCH}_2\text{OH}$	Easiest
6-25	$\text{RCOR}$	$\text{RCHOHR}$	
9-45	$\text{RCOCl}$	$\text{RCH}_2\text{OH}$	
7-42	Lactone	Diol	
8-89	$\text{RCH}=\text{CHR}$ 	$\text{RCH}_2\text{CHOHR}$	
9-42	$\text{RCOOR}'$	$\text{RCH}_2\text{OH} + \text{R}'\text{OH}$	
9-38	$\text{RCOOH}$	$\text{RCH}_2\text{OH}$	
9-38	$\text{RCOO}^-$	$\text{RCH}_2\text{OH}$	
9-39	$\text{RCO NR}'$	$\text{RCH}_2\text{NR}'$	
6-27	$\text{RCON}$	$\text{RCH}_2\text{NH}_2$	
9-47	$\text{RNO}_2$	$\text{RNE}_2$	
9-67	$\text{ArNO}_2$	$\text{ArN}=\text{NAr}$	Most difficult
5-9	$\text{RCH}=\text{CHR}$		Inert

2. Consider electrophilic aromatic substitution (EAS) for the molecule benzylaldehyde.



As discussed in class the  $\pi$ -M.O. diagram for the carbonyl group involves only 2 orbitals - one mainly on carbon and the other mainly on oxygen. As it is the carbon end of this molecule which is closest to the benzene ring, it is the carbon based carbonyl M.O. which interacts most with the benzene ring. Using therefore just the 6  $\pi$ -orbitals of benzene and the single most pertinent of the  $\text{C}=\text{O}$   $\pi$  orbitals, construct an M.O. diagram for benzylaldehyde. Does the aldehyde group activate or deactivate the EAS reaction? Is the aldehyde group ortho, meta or para directing? Base your answers on the molecular orbital diagram you created for the benzylaldehyde molecule.

③ Consider the molecule pyridine :



N is more electronegative than C. Pyridine, like benzene, also undergoes electrophilic aromatic substitution.

(i) Starting with the benzene  $\pi$ -MO diagram, by pair-wise mixing derive the form of the HOMO of pyridine.

(ii) Where does EAS occur in pyridine; ortho, meta or para to the N site? Does EAS occur more easily or harder than for benzene?