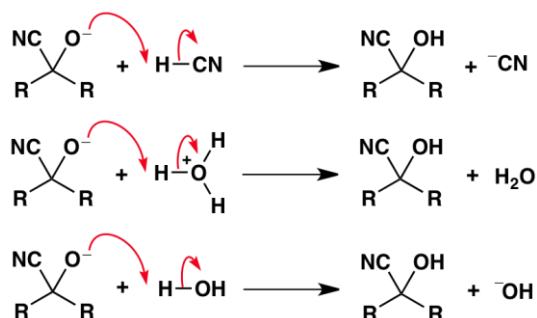


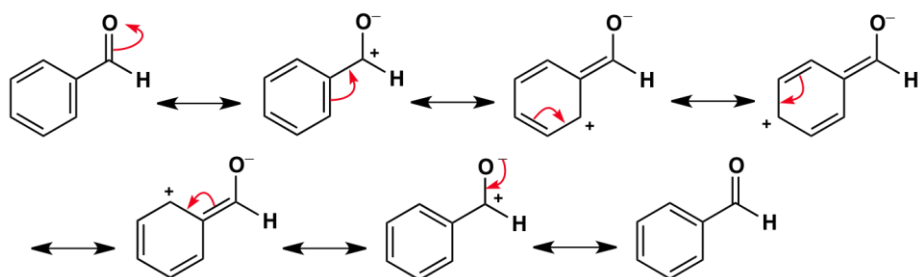
Solutions to Exercises, Chapter 8

8.1

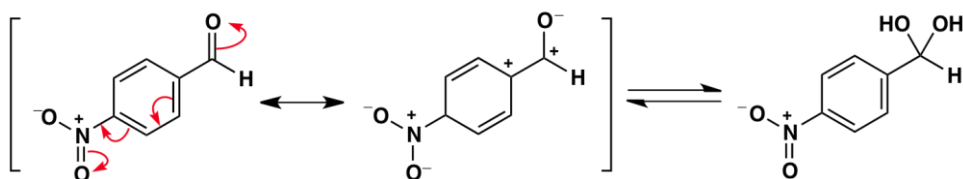


- 8.2 There is an increase in steric strain when an aldehyde or ketone is converted into a cyanohydrin and, as the bulk of the alkyl residues bonded to the carbonyl group increases, this increase in strain becomes larger. Consequently, the equilibrium constant for cyanohydrin formation for these three compounds decreases as H is replaced by CH_3 and then by $\text{CH}(\text{CH}_3)_2$.

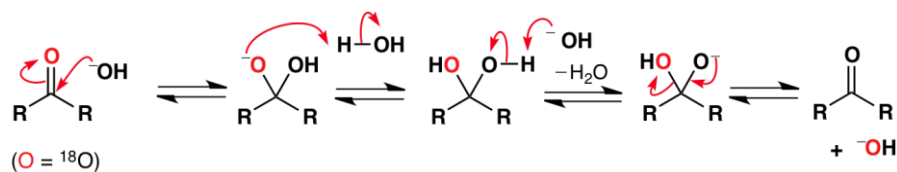
8.3



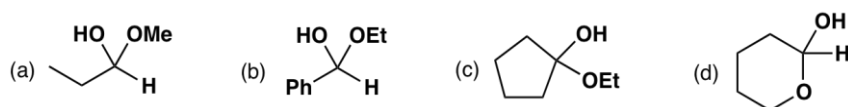
- 8.4 (a) The *t*-butyl group is bulkier than methyl so the increase in steric strain upon nucleophilic attack by CN^- is greater for the *t*-butyl compound.
- (b) In *p*-nitrobenzaldehyde, the alternative resonance forms with electron delocalization into the NO_2 show unfavourable proximity of formal positive charges. Consequently, these contribute less and there will be a smaller resonance stabilization than in the unsubstituted benzaldehyde. This destabilization is smaller in the transition structure for nucleophilic addition.



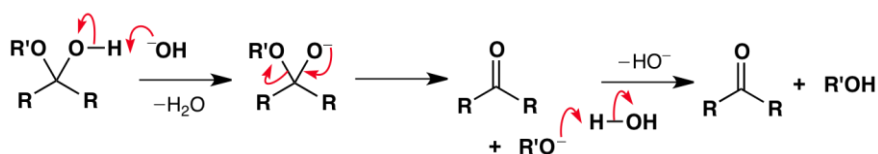
8.5



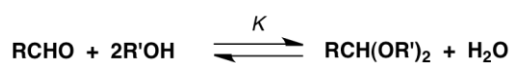
8.6



8.7



8.8 The equilibrium constant for acetal formation:

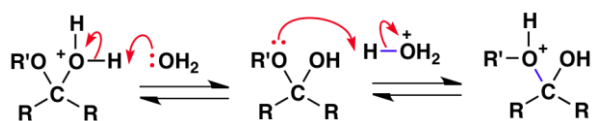


may be written on this occasion as $K = [\text{RCH(OR')}_2][\text{H}_2\text{O}]/[\text{RCHO}][\text{R}'\text{OH}]^2$

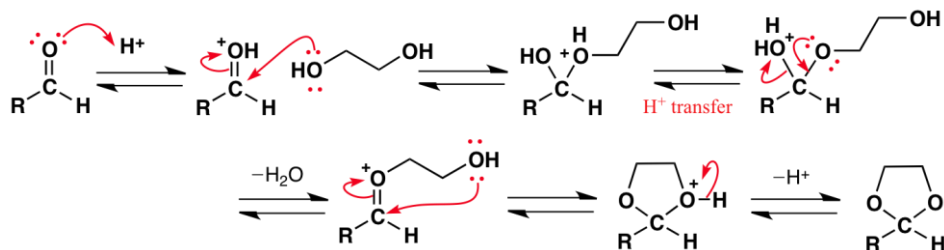
(when a compound is the solvent as well as a reactant, it is not usually included in the expression for K).

In mostly alcoholic solution (high value of $[\text{R}'\text{OH}]^2$), equilibrium favours the formation of acetal, while in mostly aqueous solution (high value of $[\text{H}_2\text{O}]$), equilibrium favours the hydrolysis of acetal to give aldehyde.

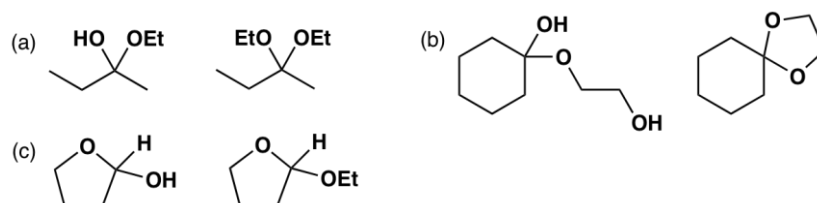
8.9



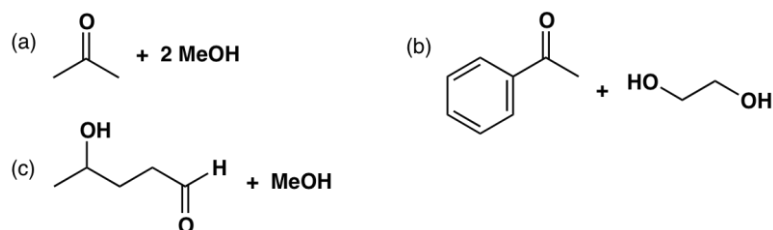
8.10



8.11

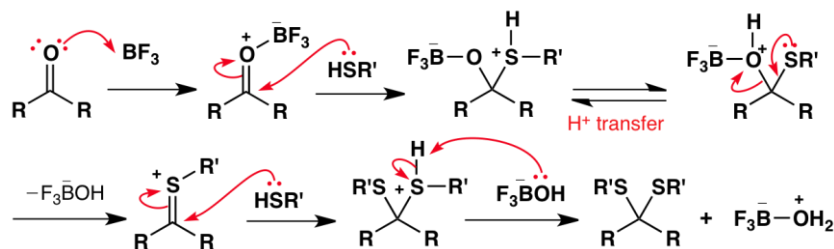


8.12



8.13 The only way for hydrolysis of an acetal to occur under basic conditions is via initial heterolysis to give of an alkoxide and an alkoxy-carbenium which could then give the aldehyde via the hemiacetal. However, alkoxide is a very poor nucleofuge so the first step does not occur.

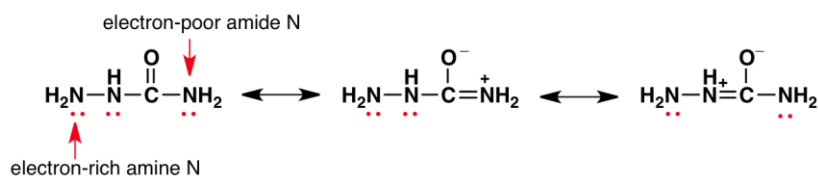
8.14



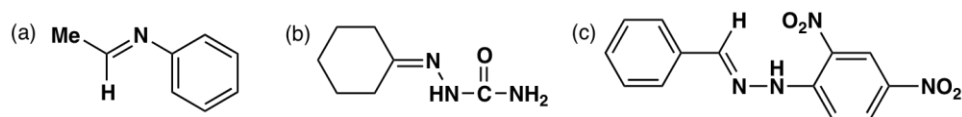
8.15



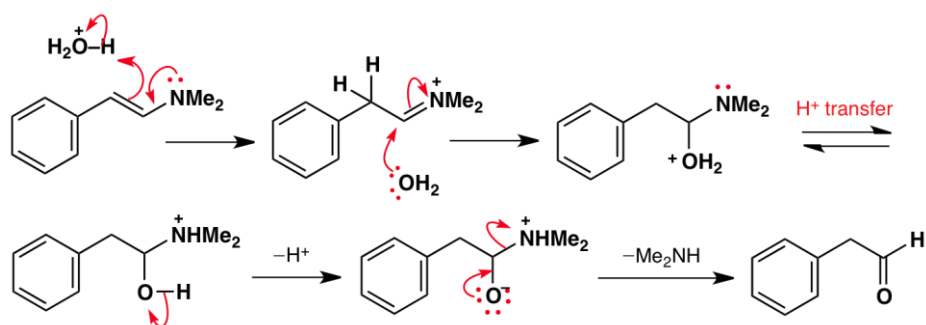
8.16 As the resonance structures show, the nucleophilicity of the lone pairs on the nitrogens which flank the carbonyl group is reduced by resonance interactions (these are amide N atoms). Only the amine N can react.



8.17



8.18



Under acidic aqueous conditions, the enamine will undergo rapid reversible protonation of the N atom, but this leads nowhere so is not given.