

Chapter 19 Information

1. Reducing agent is oxidized; oxidizing agent is reduced. Redox always happens in a pair.
2. Counting oxidation states on carbon: # of heteroatoms + # of pi bonds
3. Reduction reactions.
 - a. Catalytic hydrogenation – adds two H's at once.
 - i. Reduce alkenes: use Pd, Pt, or Ni as a catalyst.
 - ii. Reduce alkyne to *cis* alkene: use Lindlar's catalyst
 - iii. Reduce aldehyde or ketone to alcohol: use H₂ with Raney nickel
 - iv. Reduce acid chloride to aldehyde: use a partially deactivated Pd catalyst (this is the Rosenmund reduction)
 - v. Cannot use catalytic hydrogenation to reduce other acid derivatives.
 - b. "Dissolving metal" reductions – use metallic Na or Li. Electron transfer mechanism.
 - i. Reduce alkyne to *trans* alkene: Na⁰/NH₃
 - ii. Reduce benzene to 1,4-cyclohexadiene (this is the Birch reduction):
Na⁰/NH₃/EtOH
 - c. Hydride reductions.
 - i. NaBH₄ will reduce an aldehyde, ketone, or acid chloride to the corresponding alcohol. It will not reduce an acid or an ester.
 - ii. LiAlH₄ will reduce an aldehyde, ketone, acid, or ester to the corresponding alcohol.
 - iii. LiAlH(OtBu)₃ will reduce an acid chloride to an aldehyde.
 - iv. DIBAL will reduce an ester to an aldehyde.
 - v. DIBAL will reduce a nitrile to an aldehyde (via the imine).
 - vi. LiAlH₄ will reduce an amide to the corresponding amine (complete removal of the carbonyl; goes via an imine which is then further reduced).
 - vii. Neither NaBH₄ nor LiAlH₄ will react with an alkene or an alkyne (there is no partial positive charge for the hydride to attack).
4. Oxidation of alcohols.
 - a. Chromic acid (H₂CrO₄) will oxidize a primary alcohol to a carboxylic acid and a secondary alcohol to a ketone. Note that tertiary alcohols cannot be oxidized.
 - b. Swern oxidation: uses DMSO, oxalyl chloride, triethylamine. Primary alcohols become aldehydes; secondary alcohols become ketones.
 - c. PCC (pyridinium chlorochromate) does the same thing as the Swern.

5. Oxidation of aldehydes and ketones.
 - a. Aldehydes to carboxylic acids.
 - i. Any of the Cr^{VI} or Mn^{VII} reagents will work.
 - ii. Ag_2O
 - iii. Tollens reagent: $\text{Ag}(\text{NH}_3)_2^+$
 - iv. Baeyer-Villiger oxidation: mCPBA or other peracids
 - b. Ketones
 - i. Haloform reaction: $\text{NaOH}/\text{excess I}_2$ gives the carboxylate
 - ii. Baeyer-Villiger oxidation gives an ester. Note migratory aptitudes.
6. Sharpless epoxidation – an enantioselective way of converting allylic alcohols into epoxides using chiral diethyltartrate. Which enantiomer of the epoxide is formed depends on which enantiomer of diethyltartrate is used. We won't cover this one.
7. Hydroxylation of alkenes (adding two OHs)
 - a. Cold, dilute KMnO_4 with NaOH gives the vicinal diol. Syn addition.
 - b. OsO_4 /peroxide also gives the vicinal diol. Also a syn addition.
 - c. Form the epoxide with mCPBA, then open it with either acid or base. Anti addition.
8. Oxidative cleavages
 - a. Of vicinal diols – use periodic acid (HIO_4). Produces aldehydes and ketones.
 - b. Of alkenes – ozonolysis. This is a syn addition of ozone to the alkene, giving a molozonide. It then rearranges to form an ozonide (two O's on one side, one O on the other, in a five-membered ring).
 - i. Oxidative workup (peroxide) gives ketones and carboxylic acids.
 - ii. Reductive workup ($\text{Zn}^0/\text{H}_2\text{O}$ or Me_2S) gives aldehydes and ketones.
 - c. Of alkenes – permanganate cleavage. Dilute, low temperature gives vicinal diols; concentrated, high temperature gives ketones and carboxylic acids. If it's a terminal alkene, one end becomes carbon dioxide.
 - d. Of alkynes
 - i. Ozone, low temperature, aqueous workup gives carboxylic acids. If it's a terminal alkyne, one end becomes carbon dioxide.
 - ii. Permanganate, base, room temperature gives a vicinal diketone.