Review: Chapters 24, 25, sulfonation from 26, and 27 through Monday the 11th

Mechanism:

nucleophilic substitution: Gabriel synthesis, α-halocarbonyl or carboxyl + nucleophile

nucleophilic addition and addition/elimination: lithium enolate of ketone or ester + aldehyde or ketone, Claisen & Dieckmann, aldol, HCN addition, lactone formation

decarboxylation: β-ketoacids and β-dicarboxylic acids

E_2 elimination: Hoffmann elimination, exhaustive methylation of amine followed by Ag_2O

rearrangments: Hoffmann, Curtius, and Schmidt degradations; benzidine, Wolff and Baeyer-Villiger rearrangements

synthesis of aryl diazonium ions: aryl amine + $NaNO_2$ (sodium nitrite) + acid

syn additions: peracid epoxidation (note opening of epoxide gives trans diol), OsO_4 (cis diol), Sharpless epoxidation

oxidative cleavage: HIO_4; forms a cyclic intermediate and requires cis stereochemistry for diol substrate

free radical reactions: acyloin condensation, metallic sodium + diester; Gomberg-Bachman, biphenyls

Wittig Reaction: alpha-bromoester + Ph_3P + methoxide, then react with ketone or aldehyde

Acid/base chemistry

amines are weak bases; resonance effects on basicity

difunctional compounds: nitroalkanes, dicarboxylic acids, β-ketoesters and β-diketones; review earlier acid/base chemistry

Resolution of enantiomeric carboxylic acids by making diastereomeric salts with optically active amines followed by recrystallization

Phase transfer catalysis

Nomenclature: amines, difuctional compounds

Reactions:

carbon-carbon bond forming reactions:
Mannich reaction: aldehyde or ketone + HCHO + amine hydrochloride
benzidine rearrangement to make biphenyls
Henry reaction: nitroalkane + aldehyde + hydroxide to make nitro alkenes
Wolff rearrangement: acid chloride + CH_2N_2 followed by rearrangement of alpha-diazoketone to ketene
Sandmeyer reaction with CuCN to make arylnitriles
acyloin condensation (can also make 8-20 membered ring compounds)
aldol condensation
Claisen and Dieckmann condensations (make 5 and 6 membered ring compounds)
Wittig reaction with α-bromoester and Ph_3P to make alpha beta unsaturated esters

rearrangement reactions:
Hoffmann, Curtius, Schmidt, Wolff, benzidine, Baeyer-Villiger
degradation reactions:
Hoffmann, Curtius, Schmidt: carboxylic acid to amine with loss of carboxyl carbon
substitution reactions
Gabriel synthesis, sulfonation of aromatic ring (H_2SO_4 + SO_3), substitution of diazonium group of aryldiazonium salt for OH, OR, I, Br, Cl, CN, F, NO_2, or H, α-bromoketone or ester + hydroxide
eliminations: Hoffmann (exhaustive methylation, Ag_2O, anti stereochemistry, least substituted alkene); Cope (amine oxide, syn stereochemistry): both convert amines to alkenes
oxidations:
Sharpless epoxidation of allylic alcohol (t-BuOOH + $Ti(O\text{-}iPr)_4$ + DET) followed by LAH reduction
peracid epoxidation of alkene (metachloroperbenzoic acid) followed by hydrolytic ring opening
Osmium tetroxide + N-methylmorpholine N-oxide, potassium permanganate (alkenes to syn-diols)
selenium dioxide, SeO_2 (ketones to α-diketones)
periodic acid, HIO_4 (syn-diols to two aldehydes, α-ketols to aldehyde+carboxylic acid)
Baeyer-Villiger: ketone plus CF_3CO_3H (trifluoroperacetic acid) to make ester or lactone

reductions:
reduction of nitrogen compounds: catalytic reduction with H_2, $LiAlH_4$, $NaBH_4$, NaH_3BCN