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

Mechanism:

**nucleophilic substitution**: Gabriel synthesis, $\alpha$-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**: $\beta$-ketoacids and $\beta$-dicarboxylic acids

**E₂ elimination**: Hoffmann elimination, exhaustive methylation of amine followed by $\text{Ag}_2\text{O}$

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

**synthesis of aryl diazonium ions**: aryl amine + $\text{NaNO}_2$ (sodium nitrite) + acid

**syn additions**: peracid epoxidation (note opening of epoxide gives trans diol), $\text{OsO}_4$ (cis diol), Sharpless epoxidation

**oxidative cleavage**: $\text{HIO}_4$; 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 + $\text{Ph}_3\text{P}$ + 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, difunctional 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 + CH₂N₂ 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 Ph₃P 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 (H₂SO₄ + SO₃), substitution of diazonium group of
- Aryldiazonium salt for OH, OR, I, Br, Cl, CN, F, NO₂, or H, α-bromoketone or ester + hydroxide

Eliminations:
- Hoffmann (exhaustive methylation, Ag₂O, 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-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, SeO₂ (ketones to α-diketones)
- Periodic acid, HIO₄ (syn-diols to two aldehydes, α-ketols to aldehyde+carboxylic acid)
- Baeyer-Villiger: ketone plus CF₃CO₃H (trifluoroperacetic acid) to make ester or lactone

Reductions:
- Reduction of nitrogen compounds: catalytic reduction with H₂, LiAlH₄, NaBH₄, NaH₃BCN