Chem 302, S12 Exam 2 Review Sheet

- Chapter 11: simple alcohol and ether nomenclature
  - <u>preparation of alcohols</u> (these are review, you are welcome use these during synthesis, but I will not explicitly test these review reactions): (a) hydration of alkenes, (b) hydroboration oxidation, (c) S<sub>N</sub>1 or S<sub>N</sub>2
  - <u>reactions of alcohols</u>: (a) conversion to alkyl halides via HX or use of PBr<sub>3</sub> or SOCl<sub>2</sub>, (b) conversion to a good leaving group like OTs or OMs or OTf; (you are not responsible for PBr<sub>3</sub>/SOCl<sub>2</sub> mechanisms)
  - preparation of ethers: (a) Williamson ether synthesis using S<sub>N</sub>2 reaction of RO<sup>-</sup> plus RX, intramolecular to form cyclic ethers; (b) peroxyacid plus alkene (syn addition) to form epoxides
  - <u>reactions of ethers</u>: (a) cleavage using strong acid HX; (b) ring-opening reactions of epoxides, mechanisms for acid vs base conditions, understand which C-O bond is cleaved in an unsymmetrical ether, predict stereochemistry of epoxide ring-opening reactions (anti); basic structure and properties of crown ethers
- Chapter 12: recognize oxidation/reduction reactions among alcohols, aldehyde/ketones, and carboxylic acids/esters
  - oxidation of alcohols: (a) 1° alcohols are oxidized to aldehydes by PCC and are oxidized to carboxylic acids by strong oxidizing agents like H<sub>2</sub>CrO<sub>4</sub>; 2° alcohols are oxidized to ketones by PCC or H<sub>2</sub>CrO<sub>4</sub> or KMnO<sub>4</sub>; 3° alcohols are not oxidized
  - <u>reduction to form alcohols:</u> (a) NaBH<sub>4</sub>/ROH reduces ketones and aldehydes to the corresponding 2° or 1° alcohols; (b) LiAlH<sub>4</sub> reduces ketones to 2° alcohols and it reduces aldehyes/carboxylic acids/esters to 1° alcohols, two equivalents of hydride are added in the reduction of carboxylic acids or esters
  - organometallic reagents: Grignard reagents or organolithium reagents acts as "carbon" nucleophiles; dry conditions (why?) and will react with aldehydes, ketones, epoxides, or esters to produce alcohols as products

## **Chapter 16:** simple ketone/aldehyde nomenclature

- preparation of aldehydes and ketones: (a) oxidation of alcohols; (b) F-C acylation; (c) ozonolysis (review); (d) reduction of esters or acyl chlorides with specialized hydride reagents LiAlH(OtBu)<sub>3</sub> or DIBAL-H to form aldehydes
  - five nucleophilic reactions of aldehyde/ketone: relative reactivity of aldehydes versus ketones; reactions 1-4 are reversible; (1) hydrate formation; acid or base catalysis; (2) cyanohydrin formation, base catalysis only; (3) hemiacetal formation, acid or base catalysis; acetal formation, only acid catalysis works!, use acetals as protecting groups; thioacetals, reduction of thioacetals; (4) imine formation, (1<sup>°</sup> amine, acid catalysis); enamine formation (2<sup>°</sup> amine and carbonyl compound must have α-H for removal in last step; acid catalysis); (5) Wittig reaction, preparation of Wittig reagent, no control over E/Z stereochemistry in alkene product

## Chapter 17: acidity of various carboxylic acids; use/interpret/analyze pKa values

- preparation of carboxylic acids: (a) oxidation of 1° alcohols or aldehydes; (b) Grignard reagent + CO<sub>2</sub> (c) hydrolysis of acid derivatives
- <u>reactions of carboxylic acids</u>: to acyl chlorides, to acid anhydrides, to esters/lactones (mechanism for Fischer esterification); to amides: direct addition of carboxylic acid plus amine is usually unproductive;
- <u>relative reactivity of carboxylic acid derivatives</u>: acid chloride > anhydride > ester > amide; reactivity determined by leaving group ability and reactant stability, IR gives information about the nature of the CO bond; all acid derivatives react by addition/elimination mechanisms
- <u>reactions of acid derivatives</u>: reagents and mechanisms for interconversion of various derivatives; hydrolysis always produces the corresponding carboxylic acid/carboxylate anion

## A couple more comments:

We did not cover 11.11ACDE, 11.14A, 12.8D, 16.10B, 16.12, 16.13, 17.9-17.12

One important goal in studying the above material is to combine these reactions in multi-step syntheses of organic molecules. You will want to be comfortable figuring out how to convert one functional group into another. A retrosynthesis is often quite helpful in picking a molecule apart...