List of Objectives for Chem52

For chapters 16-24, you should be able to

- provide electron-pushing mechanisms for most of the reactions we cover. This includes using isotopes such as D, ^{14}C, and ^{18}O to show explicitly where bond changes occur.
- predict products of reactions or provide missing reagents if given one or more starting materials and the final product.
- fill in missing reagents in a reaction sequence.
- convert a given starting material to a given product, showing any intermediate compounds, in a small number of specified steps (often 2 or 3).
- synthesize a given target from small organic molecules and any inorganic reagents you need. (Any organometallic reagents you wish to use would need to be synthesized.)
- interpret and predict IR, ^{1}H NMR, and ^{13}C NMR spectra of organic molecules.

Things you should be able to do from Ch. 15 (which relates directly to Ch. 16):

1	Name aromatic compounds (and their derivatives) by their IUPAC-accepted common names. You should know the structures of benzene, toluene, the xylenes, phenol, aniline, benzaldehyde, and benzoic acid. (See Table 15.1.) You should also know the structure of pyridine, pyrrole, and furan. (See section 15.5.)
2	Use ortho, meta, and para nomenclature to name disubstituted benzene rings.
3	Use heats of hydrogenation to calculate resonance energies.
4	Draw the resonance (Kekule) structures of benzene.
5	Classify hydrocarbons as aliphatic or aromatic.
6	Determine if a compound, including ions and compounds that contain heteroatoms, should display the special stabilization associated with aromaticity. (Huckel's rule)
7	Combine reactions you have learned to provide a multi-step synthesis of a target molecule.
8	Predict the relative Bronsted-Lowry acid/base strengths with consideration of aromaticity.
9	Explain why cyclobutadiene and cyclooctatetraene are not aromatic. (They are actually antiaromatic with 4n π-electrons.)
10	All recommended and/or required problems and problems similar to them.

Things you should be able to do from Ch. 16:

1	Show/explain mechanistically why aromatic compounds undergo substitution and not addition reactions.
2	*Draw the products and mechanisms (including all electron-pushing arrows, intermediates, and by-products) of electrophilic aromatic substitution reactions. We have covered brominations, chlorinations, nitrations, Friedel-Crafts alkylations and acylations, and sulfonations.
3	Draw resonance contributors for arenium and acylium ions.
4	Predict the products of desulfonation reactions.
5	Predict if a substituent is ring-activating or ring-deactivating.
6	Predict relative rates of electrophilic aromatic substitution reactions due to the presence of ring activating and/or deactivating groups.
7	Provide a reaction energy diagram for an electrophilic aromatic substitution reaction.

8	Predict where an electrophile will add to a ring. You should be able to determine whether a substituent that is already on the ring directs incoming electrophiles o/p or m. You should also be able to predict where an electrophile will add if more than one substituent is already on the ring.
9	Determine where an electrophile will add to an aromatic ring that already has multiple substituents on the ring.
10	Reduce the reactivity of anilines ~~or phenols~~ by protecting the N ~~or O~~ as an acetate, then carry out an electrophilic aromatic substitution, then deprotect the N ~~or O. (I don't think protecting the O as a methyl ether is really very effective.)~~
11	*Draw the products and mechanisms (including all electron-pushing arrows, intermediates, and by-products) of nucleophilic aromatic substitution reactions, both through the elimination/ addition mechanism through benzyne and the addition/elimination mechanism (S_NAr).
12	Prepare benzyne intermediates through the alternate routes mentioned in lecture and provide products or a mechanism of the reaction of benzyne with dienes in a Diels-Alder reaction.
13	Synthesize compounds from benzene, any organic molecules of 3 carbons or less, and any inorganic reagents you need. You may be asked to add more than one substituent to the aromatic ring or to combine previous addition, substitution, and/or elimination reactions with the electrophilic aromatic substitution reactions.
14	Provide products of the reactions of $KMnO_4$ or $Na_2Cr_2O_7/H_2SO_4$ with alkyl benzenes.
15	Provide products and a mechanism for free-radical halogenation of benzylic carbons using either Br_2/hv or NBS/benzoyl peroxide.
16	Provide products and/or reaction conditions for catalytic hydrogenation of aromatic rings.
17	Provide products and/or reaction conditions for catalytic hydrogenation of an aryl alkyl ketone. Recognize that the same reaction conditions also reduce a nitro group to an NH_2.
18	Provide products and/or reaction conditions for the reduction of an NO_2 group by Fe/H_3O^+.
19	Draw products or provide missing reagents for the oxidation of an $–NH_2$ group to an $–NO_2$ group. (CF_3CO_3H). Reaction works for all classes of primary amines.
20	Provide products or missing reagents (but not a mechanism) for the Clemmensen reduction [Zn(Hg) or $SnCl_2$ + HCl)] of aldehydes and ketones to the corresponding CH_2 groups.
21	Provide products, missing reagents (or a mechanism after Ch. 19) for the Wolff-Kishner reduction (H_2NNH_2, NaOH, heat).
22	All recommended and/or required problems and problems similar to them.

Things you should be able to do from Ch. 10 sections 6 and 7 and Ch. 9 sections 7-9:

1	Recognize and name simple organometallic (organomagnesium, organolithium, and diorganocopper) compounds.
2	Prepare organomagnesium (Grignard), organolithium, and diorganocopper (Gilman) reagents from alkyl, aryl, or vinyl halides.
3	Prepare organocuprates (Gilman reagents) from organolithium reagents.
4	Prepare organosodium reagents from terminal alkynes. (8.7)
5	Provide products of reactions that involve Bronsted-Lowry acid-base chemistry of organometallic reagents. (Organometallic reagents are VERY basic.)
6	Provide products of reactions of organocuprates with alkyl, aryl, or vinyl halides.
7	Propose a synthesis of a given compound that incorporates reactions covered in organic I or to date in organic II. In particular, propose an appropriate synthetic pathway to obtain a given alcohol from organometallic reagents and carbonyl compounds.

8	All recommended and/or required problems and problems similar to them.

Things you should be able to do from Ch. 17:

1	Provide IUPAC names for alcohols and phenols.
2	Provide the products of alcohols (and phenols) acting as either acids or bases.
3	Provide products, or missing reagents if given one starting material and the products, for the deprotonation of alcohols/phenols to form alkoxides/phenoxides. (17.2)
4	Draw resonance structures of phenol and the phenoxide ion that involve delocalization of O lone pairs into the aromatic ring.
5	Explain why phenols are more acidic than alcohols. (The conjugate base of a phenol is resonance stabilized. You should be able to draw the resonance contributors.)
6	Draw products of acid/base reactions, label the acid and base on each side of the reaction, and determine the predominant direction of equilibrium without pK_a tables.
7	Provide a detailed description of how you could separate a mixture that contains a carboxylic acid, a phenol, a neutral organic molecule (which doesn't do any acid/base chemistry) and an amine using acid/base reactions and solubility differences. Include in your description that each organic layer would need to be dried, drying agent filtered or decanted, and organic solvent evaporated to isolate the pure organic compounds. It is outlined online at http://www.wfu.edu/chemistry/courses/organic/extract/extscheme.htm
8	Rank alcohols (alkoxides) and phenols (phenoxides) in order of increasing acidity (basicity.)
9	Use resonance structures to explain why some phenols are more acidic than others.
10	Predict the products or provide missing reagents for the hydration of alkenes with either a) Markovnikov or b) anti-Markovnikov regiochemistry. (17.3)
11	Predict the products or provide missing reagents for the synthesis cis- or trans-diols from alkenes. (17.3) To obtain the cis-diol from an alkene, add OsO_4 in pyridine followed by $NaHSO_3$. To obtain a trans-diol from an alkene, add a peroxyacid (RCO_3H) followed by aqueous acid.
12	Use simple metal hydrides (NaH or KH) as bases and complex metal hydrides ($NaBH_4$ or $LiAlH_4$) as reducing agents.
13	Provide products and mechanism of $NaBH_4$/ROH or $LiAlH_4$ (then H_2O) reduction of aldehydes and ketones. (17.4)
14	Provide products and mechanism for $LiAlH_4$ reduction of esters (yielding two alcohols.)
15	Provide products for the $LiAlH_4$ reduction of carboxylic acids.
16	Provide products and a mechanism for the reaction of organomagnesium or organolithium reagents with aldehydes, ketones, esters, or carboxylic acids. (17.5)
17	Provide products of Grignard or organolithium reagents that are allowed to react with epoxides. (See also 18.6)
18	Provide products and a mechanism for the conversion of alcohols to alkyl halides using PBr_3 or $SOCl_2$.
19	Provide products and a mechanism for the conversion of alcohols to alkyl halides using HX.
20	Provide products and a mechanism for the conversion of alcohols to sulfonate esters such as a tosylate. (See also 11.1)
21	Provide products and a mechanism for the dehydration of alcohols under acidic (H_3O^+) or basic ($POCl_3$/pyridine) conditions.
22	Provide products and a mechanism for the conversion of carboxylic acids to esters via an acid chloride after we cover the material in Ch. 21.

23	Provide products (but not a mechanism) for the oxidation of alcohols with Dess-Martin periodinane, pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), $Na_2Cr_2O_7/H_2SO_4$, or CrO_3, or $KMnO_4/NaOH/H_2O$. (Dess-Martin periodinane, PCC and PDC will oxidize primary alcohols to aldehydes and secondary alcohols to ketones. Chromic acid, chromium trioxide, and permanganate will oxidize primary alcohols to carboxylic acids and will oxidize secondary alcohols to ketones.) (17.7)
24	Provide the products and a mechanism for the reaction of alcohols with chlorotrimethylsilane in triethylamine. (for protection of the alcohol)
25	Provide products of and a mechanism for the reaction of a trimethylsilyl ether with H_3O^+ to obtain an alcohol. (to deprotect the alcohol)
26	Use protecting groups, such as the trimethylsilyl ether, to temporarily hide an alcohol so that a reaction can be carried out on another portion of the molecule.
27	Recognize that phenols can be oxidized to quinones and that benzoquinones can be reduced to hydroquinones. (This type of reaction has significant biological consequences.)
28	Provide oxidation products of 1,2-benzenediol (yielding ortho-benzoquinone) and 1,4-benzenediol (yielding para-benzoquinone.)
29	Provide structures for the hydroquinone – semiquinone – benzoquinone oxidation/reduction reactions. (Each step involves one proton, H^+, and one electron transfer.)
30	Recognize the quinone structure found within ubiquinone (coenzyme Q) and other biological compounds such as Vitamin K.
31	Identify alcohols and assign spectral peaks using IR and ^1H NMR spectroscopy.
32	All recommended and/or required problems and problems similar to them.

Things you should be able to do from Ch. 18:

1	Provide IUPAC names for thiols (mercaptans), ethers and sulfides. Provide names/structures for ethylene oxide, tetrahydrofuran, tetrahydropyran, and 1,4-dioxane.
2	Provide products and mechanism for the acid-catalyzed condensation of alcohols to form ethers.
3	Prepare ethers by adding alkoxides to primary or methyl alkyl halides. (Williamson ether synthesis – an S_N2 reaction)
4	Provide products for the alkoxymercuration/demercuration reaction. (overall Markovnikov addition of ROH to an alkene.)
5	Provide a mechanism for the alkoxymercuration step. (You will not be asked to provide a mechanism for the $NaBH_4$ demercuration.)
5	Provide products and mechanism for acid-catalyzed cleavage of ethers by excess HBr or HI to form 2 alkyl halides or 1 eq. of HBr or HI to form an alcohol and an alkyl halide. (18.3) For an unsymmetrical ether, regiochemistry of nucleophilic attack must be taken under consideration.
6	Provide products, missing reagents, or a mechanism for the Claisen Rearrangement of allyl aryl ethers.
7	Define concerted, pericyclic, and sigmatropic reactions.
8	Provide products for the reaction of an alkene with a peroxyacid (mCBPA). See 7.8.
9	Provide products and mechanism for the reaction of vicinal halohydrins in base to form epoxides. (another S_N2 reaction) (18.5)
10	Provide products for nucleophilic ring-opening reactions of epoxides involving either anionic nucleophiles or acid-catalyzed reactions of neutral nucleophiles. (Regiochemistry of nucleophilic attack varies – see 18.6.)

11	Recognize that crown ethers bind metal cations.
12	Recognize that thiols are rather acidic (pKa ~ 10) and can be easily deprotonated.
13	Provide products of the reaction between an alkane thiolate and an alkyl halide. (S_N2)
14	Identify ethers and assign spectral peaks using IR and ^1H NMR spectroscopy.
15	All recommended and/or required problems and problems similar to them.

Cutoff for Exam 1 material.

Things you should be able to do from Ch. 19:

1	Provide IUPAC names for aldehydes and ketones.
2	Synthesize aldehydes from primary alcohols (using PCC or PDC), from alkenes (using ozone followed by a reductive workup), or from esters (using DIBAL, after Ch. 21).
3	Synthesize ketones by oxidation of secondary alcohols, from the ozonation of alkenes, by addition of water to an alkyne (9.4), or from the reaction of an acid chloride and a cuprate (21.4).
4	Provide products or missing reagents (but not a mechanism) for the oxidation of aldehydes to carboxylic acids. (18.3)
5	Provide structures for molecules from the new functional groups (cyanohydrins, imines, enamines, hydrates, hemiacetals, acetals, hydrazones, oximes, or phosphorus ylides) or classify a given molecule as belonging to one of the new functional groups.
6	Identify the electrophile and nucleophile in reactions involving aldehydes and ketones. (19.4)
7	Provide products and mechanism for hydration of aldehydes and ketones under either acidic or basic conditions. (19.5)
8	Provide products and a mechanism for the addition of HCN to an aldehyde or ketone to form a cyanohydrin. (19.6)
9	Provide products for the reduction of a cyanohydrin to yield a vicinal aminoalcohol.
10	Provide products and mechanism for the formation of imines from aldehyde or ketone plus primary amine.
11	Provide product and mechanism for the formation of enamines from aldehyde or ketone plus secondary amine.
12	Provide products and mechanisms for the reactions of aldehydes and ketones with hydroxylamine, hydrazine, phenylhydrazine, or semicarbazide. (Nitrogen behaves as nucleophile to C=O in every case.)
13	Provide products and mechanism for the Wolff-Kishner reduction of aldehydes and ketones.
14	Provide products and mechanism for the acid-catalyzed formation of acetals (from aldehydes or ketones.)
15	Provide products and mechanisms for the conversion of acetals to aldehydes or ketones.
16	Use acetals as protecting groups for synthetic schemes. (Make acetal, do chemistry elsewhere in the molecule, then regenerate the aldehyde or ketone.)
17	Synthesize phosphorus ylides from alkyl halides.
18	Synthesize alkenes using the Wittig reaction of a phosphorus ylide with an aldehyde or ketone.
19	Provide a mechanism for the Wittig reaction.
20	Provide products for 1,2- or 1,4-addition of nucleophiles to α,β-unsaturated aldehydes and ketones. Organolithium, Grignard reagents, organosodium, and $LiAlH_4$ add to the C=O (in a 1,2-

	addition.) Less basic nucleophiles, including 1^o and 2^o amines, enolates, CN^-, and RS^-, add to the β-carbon in a conjugate or Michael or 1,4-addition.
21	Identify aldehydes and ketone and assign spectral peaks using IR and ^1H NMR spectroscopy.
22	All recommended and/or required problems and problems similar to them.

Things you should be able to do from Ch. 20:

1	Provide IUPAC names for carboxylic acids and nitriles. (You may see the common names listed in Table 20.1 in other courses you take.)
2	Arrange chemical species in order of increasing acidity or basicity by recognizing and weighing the importance of factors that influence acidity, especially inductive and resonance effects. (See the online acid/base handout for other chemical attributes that affect acidity: electronegativity, bond energy, inductive and field effects, hybridization, and RESONANCE).
3	Draw products of acid/base reactions, label the acid and base on each side of the reaction, and determine the predominant direction of equilibrium without pK_a tables.
4	Recognize that by the Henderson-Hasselbalch equation that carboxylic acids will exist almost exclusively in their deprotonated form at physiological pH. (Section 20.3)
5	Synthesize carboxylic acids by: 1) oxidation of primary alcohols 2) oxidation of aldehydes 3) oxidation of a benzylic C-H containing group 4) reaction of Grignard, organolithium, or organosodium reagents with CO_2 5) acid catalyzed hydrolysis of a nitrile
6	Provide a full electron-pushing mechanism for the organometallic reactions mentioned in step 5 (all S_N2 reactions), hydrolysis of a nitrile under acidic or basic conditions, acid-catalyzed esterification including lactone formation, and decarboxylation of carboxylic acids that have a C=O on the β carbon. (Decarboxylation will be covered with Ch. 22 material.)
7	Provide a synthesis and mechanism (S_N2) for nitriles from methyl or primary alkyl halides + KCN.
8	Provide products or missing reagents for the dehydration of amides to nitriles upon addition of P_4O_{10} or $POCl_3$.
9	Provide products, missing reagents, or a mechanism for the dehydration of primary amides to nitriles upon addition of $SOCl_2$.
10	Provide products and a mechanism for the reaction of a nitrile with a Grignard followed by an aqueous acidic workup to yield a ketone.
11	Provide products and a mechanism for the reduction of nitriles to primary amines by the addition of $LiAlH_4$.
12	Identify carboxylic acids and nitriles and assign spectral peaks using IR and ^1H NMR spectroscopy.
13	All recommended and/or required problems and problems similar to them.

Things you should be able to do from Ch. 21:

1	Provide IUPAC names for acyl (or acid) halides, carboxylic acid anhydrides, carboxylate salts, esters, thioesters, and amides.
2	Rank relative stability (or reactivity) of various carboxylic acid derivative functional groups toward nucleophilic acyl substitution.
3	Synthesize acyl chlorides from carboxylic acids and $SOCl_2$ or PCl_3. (21.3)

4	**Interconvert between the carboxylic acid derivatives. (See handout.)**
5	Provide products and a mechanism for the conversion of carboxylic acids + amines to amides using DCC.
6	Provide complete electron-pushing mechanisms for any of the carboxylic acid derivative conversions.
7	Recognize or provide molecules representative of new functional groups (lactones, lactams, imides, thioesters, triglycerides/fats, fatty acids, and α-amino acids).
8	Apply the carboxylic acid derivative chemistry to biological molecules (like fats, peptides, acetyl CoA.)
9	Understand how isotopes (D or ^{18}O) can be used to follow/discover reaction mechanisms.
10	**Recognize hydrophilic and lipophilic (or hydrophobic) portions of molecules.**
11	Explain what micelles are and how detergents clean by micellar action.
12	Provide products or missing reagents for the reduction of carboxylic acids to primary alcohols upon addition of BH_3.
13	Recognize that BH_3 reduces carboxylic acids (to primary alcohols) faster than any other functional group and use that fact to selectively reduce carboxylic acids in the presence of other functional groups that are typically susceptible to reduction. (21.3)
14	Provide products and a mechanism for the reaction of 2 equivalents of organolithium, organosodium, or Grignard reagents to an acid chloride to yield a tertiary alcohol upon acidic workup.
15	Provide the products of the reaction of 1 eq. DIBAL (= DIBAH), cold, with an ester to give an aldehyde and a primary alcohol after acidic workup. Amides are also partially reduced to aldehydes when 1 eq. of DIBAL is used under cold reaction conditions.
16	Provide the products of the reaction of DIBAL with a nitrile to give an aldehyde (and NH_4^+) after acidic workup.
17	Provide products and a mechanism for the reduction of amides to amines by $LiAlH_4$. (C=O becomes CH_2.)
18	If given a polymer, identify the starting materials that could be used to make it.
19	Provide the repeating unit for reactions that create polymer products.
20	Determine the starting materials necessary to synthesize a given polymer.
21	Provide the products (but not a mechanism) for the addition of an organocuprate to acid chloride to yield a ketone.
22	Identify carboxylic acid derivatives and assign spectral peaks using IR and ^1H NMR spectroscopy.
23	All recommended and/or required problems and problems similar to them.

Cutoff for Exam 2 material.

Things you should be able to do from Ch. 22:

1	See the big picture! In this chapter the carbonyl compound will behave as a nucleophile and the product will substitute an α-hydrogen for an electrophile.
2	Define and draw compounds that are related as tautomers.
3	Draw enols and enolate anions of a given carbonyl compound, especially aldehydes and ketones..
4	Form ester enolates from the Bronsted-Lowry acid/base reaction of esters with lithium dialkylamides. (You often need a stronger N^- base if there aren't two C=O's beta to each other.)

5	Rank acidities of various carbonyl containing functional groups. See Table 22.1.
6	Predict relative stabilities of enols and enolate anions (based on the relative acidities of the corresponding carbonyl compounds.)
7	Provide products and mechanisms for α-halogenation of aldehydes and ketones under acidic (monohalogenation of more substituted side) or neutral conditions or the haloform reaction (basic conditions, exhaustive halogenation of the less substituted side.) (22.3 and 22.6)
8	Provide products and a mechanism for the dehydrobromination of α-bromoketones. (22.3)
9	Provide products, mechanism, or missing reagents for the Hell-Vollhard-Zelinskii reaction. (22.4)
10	Distinguish between kinetic and thermodynamic enolates and know the conditions to form each. (Strong, irreversible base, such as LDA, and low temp. favor kinetic enolate formation. Weak, reversible base, such as OH^- or an amine, and high temp. favor thermodynamic enolate.)
11	Provide products and mechanisms for the various α-alkylation reactions, including alkylation of a ketone, ester, nitrile, the malonic ester synthesis, and the acetoaceitc ester synthesis. (22.7)
12	Provide products and mechanisms for converting an aldehyde or ketone to its enamine, alkylating the enamine, and hydrolyzing the resulting iminium salt back to an aldehyde or ketone.
13	Provide products and mechanism for the malonic ester synthesis. Followed by ester hydrolysis and decarboxylation, the reaction is used to synthesize carboxylic acids.
14	Provide products and mechanism for the decarboxylation of β-diesters. The product will be a carboxylic acid (and CO_2 and two alcohols.) (This represents a continuation of the malonic ester synthesis.)
15	Provide products and a mechanism (S_N2) for the reaction of an enolate with an alkyl halide, such as the acetoacetic ester synthesis. Followed by ester hydrolysis and decarboxylation, the reaction is used to synthesize methyl ketones
16	Provide products and mechanism for the decarboxylation of β-keto esters. The product will be a ketone (and CO_2.) (This represents a continuation of the acetoacetic ester synthesis.)
17	Use the reactions we have learned to date to provide a multi-step synthesis of a given target compound.
18	All recommended and/or required problems and problems similar to them.

Things you should be able to do from Ch. 23:

1	See the big picture! Use a base to form an enolate. Use the enolate as a nucleophile toward another C=O.
2	Provide products and mechanism for the aldol and mixed aldol reaction (to give a β-hydroxycarbonyl compound) and condensation (to give an α,β-unsaturated carbonyl compound.) (23.2, 23.3, 23.5, and 23.6)
3	Recognize and use the different conditions for self-condensation of a carbonyl compound with its own enolate versus forming the enolate and using it to react with another electrophile. (23.2)
4	Provide products and mechanism for the Claisen condensation. (One ester molecule forms enolate and then the enolate reacts with another identical ester molecule forming a β-keto ester.)
5	Provide products and mechanism for the mixed Claisen condensation. (Use two different ester molecules for the Claisen condensation. The reaction is only useful if one of the esters has an α-hydrogen and can form an enolate while the other ester cannot form an enolate and thus can only behave as an electrophile.)
6	Provide products and mechanism for the Dieckmann condensation. (Simply an intramolecular

	Claisen condensation. You need two esters in the same molecule to get a cyclic β-keto ester. 5-, and 6- membered rings are formed easily. Sometimes 4- and 7-membered rings are formed, but not usually.)
	~~Provide products for ester enolates reacting with α,β-unsaturated ketones in a Michael addition. (See also 19.13.)~~
7	Provide products and mechanism for the Michael Reaction. (Product is often ~~will be~~ a 1,5-dicarbonyl compound.) Stabilized enolates, such as those of a β-dicarbonyl compound, are required. (Enolates formed from monoketones won't do Michael additions.) Anions of Michael donors listed in Table 23.1 will do conjugate additions. (See also 19.13.)
8	Provide products and a mechanism for the Stork reaction, which involves a conjugate addition of an enamine to a Michael-type acceptor. (The product of the addition is typically hydrolyzed to yield a 1,5-dicarbonyl compound.)
9	Provide products and mechanism for the Robinson annulation (a Michael addition followed by an intramolecular aldol.)
10	Provide products and mechanism for the mixed Claisen type reaction that involves an enolate of a ketone reacting with a nonenolizable ester. Product is β-keto ester if a dialkyl carbonate is the ester and the product is a β-diketone if a "normal" ester is used.
11	All recommended and/or required problems and problems similar to them.

Things you should be able to do from Ch. 24:

1	Classify amines as primary, secondary, or tertiary or as quaternary ammonium salts.
2	Name amines by the alkylamine or alkanamine IUPAC system or provide a structure if given the name.
3	Arrange chemical species in order of increasing acidity or basicity. (24.3-5)
4	~~Use the Henderson-Hasselbalch equation to calculate concentrations of acid and conjugate base forms of a compound if given the pK_a and the pH.~~
5	Understand how the Henderson-Hasselbalch equation is used to predict predominant forms of acids and bases at physiological pH, 7.3 (and do it.)
6	Draw products of acid/base reactions, label the acid and base on each side of the reaction, and determine the predominant direction of equilibrium without pK_a tables.
7	Draw resonance contributors, especially those that involve the N lone pair.
8	Prepare amines by reduction of azide, nitrile, nitro, or amide. (You do not need to know mechanisms for azide, nitrile or nitro reduction. You should know the mechanism of the $LiAlH_4$ reduction of amides.)
9	Provide products and a mechanism for the acylation of ammonia, primary amines, or secondary amines.
10	Provide products and a mechanism for the Hofmann elimination.
11	Provide products and a mechanism for the Gabriel synthesis of primary amines. You may use either $NaOH/H_2O$, as in the book, or H_2NNH_2, as in the notes, for the workup step. $H_2O/H_3O^+/\Delta$ will also work.
12	Prepare amines by the reductive amination of aldehydes or ketones. As presented in the text, you may use $NaBH_3CN$ as the reducing agent if you wish.
13	Prepare primary amines by the Hofmann and Curtius rearrangements. You should also know the mechanisms for these reactions.

14	Provide products and a mechanism for the alkylation of ammonia or amines. Over alkylation can be a problem. (Over alkylation can be minimized if excess amine is used.)
15	Synthesize aryl amines by the addition an $-NO_2$ group to the ring (by electrophilic aromatic substitution) followed by reduction to an $-NH_2$ group. (24.8 See also 16.2.)
16	Provide reagents and a mechanism for the synthesis of the nitrosyl cation (NO^+).
17	Form aryl diazonium salts from a variety of aromatic rings. (Ar-H to $ArNO_2$ to $ArNH_2$ to Ar-$^+$NN)
18	Provide a full electron pushing mechanism for the conversion of a primary aryl amine to an aryl diazonium ion.
19	Convert aryl diazonium ions into phenols, aryl halides, aryl cyanides, or back to Ar-H. (You do not need to know mechanisms for these conversions.)
20	Combine the aryl diazonium chemistry with the reactions learned in Ch. 16 (electrophilic aromatic substitution) to produce substituted benzenes. (Review the Ch. 16 reactions and o,p versus m-directing! Recall that $-NO_2$ is meta-directing while $-NH_2$ is o,p-directing.)
21	Provide products and a mechanism for the azo coupling reaction. (An aryl diazonium ion is the electrophile for an electrophilic aromatic substitution.)
22	Be able to draw the structures of pyridine or a generic heterocyclic compound, pyrimidine, and purine. (Covered on final exam.)
23	Identify amines and assign spectral peaks using IR and ^{1}H NMR spectroscopy.
24	All recommended and/or required problems and problems similar to them.

Cutoff for Exam 3 material.

Things you should be able to do from Ch. 26:

1	Draw the structure of all 20 of the common amino acids in proteins from the name, the 3 letter abbreviation, or the 1 letter abbreviation. (See Table 26.1.)
2	Classify the amino acid side chain as neutral, acidic, or basic.
3	Define isoelectric point or isoelectric pH.
4	Calculate the isoelectric pH if given the various pK_a's of the amino acid.
5	Determine whether an amino acid or small peptide would migrate toward the anode (-) or cathode (+) on an electrophoretic gel if buffered to physiological pH.
6	Draw the predominant amino acid structure at a given pH if given pK_a1, pK_a2, and pK_a3 (as appropriate.)
7	Draw the structures of an amino acid as a solution goes from extremely acidic to extremely basic.
8	Approximate pK_a values for the amino acids and their side chains. ($-CO_2H$ is ~ 2. $-NH_3^+$ is ~ 9. Some AA's have a 3rd pKa due to the reactivity of the side chain. See Table 26.1.) You should be able to predict the order of protonation or deprotonation.
9	Draw peptides from the name (i.e. Alanylglycine or Ala-Gly or AG.) Peptides are named N-terminus to C-terminus. (Amino acid R groups should be appropriate for given pH.)
10	Recognize the N-terminus and C-terminus of a peptide or protein.
11	Prepare amino acids using the Hell-Volhard-Zelinskii method, the amidomalonate synthesis, or the reductive amination of α-ketoacids. The Gabriel synthesis (of primary amines) could also be adapted for amino acid synthesis. Though not explicitly spelled out in your lecture notes, it would be reasonable for me to ask about some mechanistic aspects of these reactions.
12	Provide products and a mechanism for the hydrolysis of peptide bonds (6 M HCl, 110 °C, 24 hrs.)

13	Sequence a small peptide by overlapping pieces of peptide chains obtained by partial hydrolysis. (See problem 26.15 as an example.)
14	Describe the process by which amino acid residues are identified and quantified using the reaction with ninhydrin after separation by chromatography.
15	Provide a reasonable mechanism for any of the steps in the ninhydrin to Ruhemann's purple pathway for primary amino acids. The mechanistic steps have been covered throughout the term and must be combined in a reasonable manner.
16	Provide products and a mechanism for the reaction of the N-terminal amino acid of a peptide with phenyl isothiocyanate followed by anhydrous HCl. (Edman Degradation)
17	Draw the N-terminal amino acid (PTH derivative) that results from the Edman Degradation of a peptide.
18	Explain the strategy of peptide synthesis using protecting groups. (i.e. form amide bond between N-protected amino acid 1 and carboxyl-protected amino acid 2, then deprotect to get dipeptide AA1-AA2)
19	Predict products and provide a mechanism for protection of the amino group of an amino acid using the N-benzyloxycarbonyl (Z) or t-butoxycarbonyl (Boc) groups.
20	Provide products, missing reagents, or a mechanism for the deprotection of Z- and Boc-protected amino acids.
21	Protect carboxyl groups of amino acids and peptides by converting the C-terminus to an ester (Fischer esterification.)
22	Provide products and a mechanism for cleavage/deprotection of the C-terminus ester using NaOH, water, and heat.
23	Provide products for the cleavage/deprotection of the C-terminus benzyl ester using H_2/Pd.
24	Provide products and an electron-pushing mechanism for the DCC method of amide formation from DCC, a carboxylic acid, and an amine.
25	Explain the process of the Merrifield method of solid state peptide synthesis: 1) Add N-protected amino acid that will be C-terminal amino acid to resin then wash 2) Deprotect N then wash. 3) Add next N-protected amino acid and DCC then wash. 4) Repeat steps 2 and 3 until desired peptide is obtained. 5) Remove peptide from resin. The above wording is a general outline. You should also be able to show the specific chemicals necessary for each step.
26	Provide a mechanism for step 1 (above) in the Merrifield method. (You already know the mech for step 3.)
27	Define primary, secondary, tertiary, and quaternary structure of proteins.
28	Recognize how hydrogen bonding between amino acids determines the geometry (α-helix, β-sheet, etc) of the protein. Be able to draw the hydrogen bonds.
29	Recognize and explain why antiparallel pleated β-sheets are lower in energy than parallel sheets.
30	Identify amino acids that are likely to be found in a β-sheet (those with small side chains), the interior of a protein (hydrophobic side chains), or the exterior of a protein (hydrophilic side chains.
31	Determine what reactions require coenzymes by looking at the changes to the organic substrate of interest.
32	Briefly explain how/why enzymes work. (See first sentence of section 26.11.)

33	Provide a complete electron-pushing mechanism for the reaction of carboxypeptidase A with a peptide, including the amino acids and co-enzyme that are important in the active site.
34	All recommended and/or required problems and problems similar to them.

Things you should be able to do from Ch. 25:

1	Classify a carbohydrate as a monosaccharide, disaccharides (etc.), oligosaccharide, or polysaccharide.
2	Designate carbohydrates as D or L.
3	Draw an L sugar if given the D sugar and vice versa. (D-glucose and L-glucose are related as enantiomers.)
4	Classify a carbohydrate as an aldose or ketose.
5	Classify a carbohydrate as a triose, tetrose, pentose, hexose, heptose, or octose.
6	Classify a cyclic carbohydrate as a furanose or pyranose.
7	Identify the anomeric carbon of a carbohydrate.
8	Determine if a cyclic carbohydrate is in its α- or β- anomeric form.*
9	If given the name of a particular sugar (i.e. D-glucose), then provide a name for a given cyclic form of the sugar (i.e. α-D-glucofuranose) or provide a structure if given the name.
10	Define/illustrate mutarotation.
11	***Interconvert Fischer projections, Haworth formulas, and chair conformations for carbohydrates.***
12	Recognize deoxy sugars, especially deoxyribose.
13	Recognize aminosugars. (One O of the carbohydrate is replaced by an N.)
14	Provide products and mechanism for the formation of glycosides ~~either by the addition of H^+/ROH, or~~ by the Koenigs-Knorr reaction.
15	Classify carbohydrate linkages (glycosidic bonds) as α or β and by number such as α(1,4).
16	Provide products of reactions that involve carbohydrates reacting as alcohols. (acetylation and alkylation, and the reverse reactions, deacetylation and dealkylation)
17	Provide products and a mechanism of the reaction of CH_3I/Ag_2O to a carbohydrate.
18	Recognize whether or not a sugar will act as a reducing sugar. (It will if there is a free aldehyde or ketone in the molecule. It will not if the carbonyl carbon is tied up as an acetal.)
19	Provide products of the reaction of $NaBH_4$ or H_2/catalyst with an aldose or ketose.
20	Calculate the oxidation state of carbons in a molecule and thereby recognize whether oxidation or reduction has occurred.
21	Use Cu^{2+} salts (from Fehling's reagent or Benedict's reagent) or Ag_2O (Tollin's reagent) to oxidize aldehydes to carboxylic acids.
22	Provide a mechanism or draw the products of the keto-enol tautomerizations that convert one carbohydrate to another (through enediols.) Ex. D-glucose to D-fructose.
23	Provide the products (but not a mechanism) for the oxidation of aldoses to aldonic acids with aqueous bromine buffered to pH 6. (Ketoses do not react.)
24	Provide the products (but not a mechanism) for the oxidation of both the aldehyde and the primary alcohol to form aldaric acids using warm aqueous nitric acid.
25	Provide the products (but not a mechanism) for the enzymatic oxidation of only the primary alcohol to a uronic acid.
26	Provide products and a mechanism for the Kiliani-Fischer chain lengthening reaction.

27	Provide products a a mechanism for the Wohl degradation.
28	Provide or recognize structures of sugar alcohols, aldonic acids, aldaric acids, and uronic acids.
29	Deduce the various structures of carbohydrates if given information about reactivity and optical rotation.
30	Define epimers or provide an epimer of a given compound.
31	Provide a mechanism for an epimerization. Ex: D-glucose to D-mannose.
32	If given the structures of fructose-1,6-bisphosphate, glyceraldehydes-3-phosphate, and dihydroxyacetone phosphate, draw a schematic of the mechanism of Class 1 aldolase, showing the important amino acid side chains of the active site and their reactivity with the appropriate carbohydrate structure. Basically, be able to draw the mechanism of the Class I aldolase.
33	All recommended and/or required problems and problems similar to them.

*Determination of α versus β anomers: for the cyclic form of a D-sugar, drawn with the O of the ring back *and* the anomeric C on the right side of the molecule, if the anomeric OH is up, it's the beta form. If the anomeric OH is down, it's the alpha form.

You do NOT need to memorize the names of the carbohydrates.