GRANDE PRAIRIE REGIONAL COLLEGE DEPARTMENT OF SCIENCE: CHEMISTRY

FORTY-THIRD SESSION 2008 – 2009

COURSE OUTLINE: ORGANIC CHEMISTRY

CH2630 A3

CHEMISTRY 2630 A3: Organic Chemistry II

PREREQUISITE: CH1610 or CH2610

INSTRUCTOR: Dr. John P. Sloan

Office # J207 Phone # 539-2004

E-mail SLOAN@GPRC.AB.CA

LECTURE: CH2630 A2 M,W 8:30 – 9:50 in J229

ALBERTA TRANSFER CREDIT

(Ref: 2008-2009 Guide to Transfer Credit at Alberta Post-Secondary Institutions)

GPRC:	CH 2610 (3)	CH 2630	(3)
U of Alberta:	CHEM 261 (3)	CHEM 263	(3) or AUCHE 252 3
U of Calgary:	CHEM 351 (3)	CHEM 353	(3)
U of Lethbridge:	CHEM 2500 (3)	CHEM 2600	(3)
Athabasca U:	CHEM 350 (3)	CHEM 360	(3)
Canadian UC:	CHEM 241 (4)	CHEM 242	(4)
Concordia UC:	CHEM 261 (3)	CHEM 263	(3)
King's UC:		CHEM 351	(3)

COURSE OUTLINE:

Lecture Component:

A continuation of the study of the fundamental principles of the chemistry of carbon compounds as commenced in Chemistry 2610. The study is based on a reaction mechanism approach to the functional group chemistry of arenes, aldehydes, ketones, carboxylic acids, esters, amides, amino acids and carbohydrates. Topics include: structure and bonding; physical properties; acidity and basicity; conformations of molecules; stereochemistry; addition, elimination and substitution reactions; structure-reactivity relationships; aromaticity and aromatic substitution; and spectroscopic methods for structure determination.

A representative selection of molecules found in agricultural, biological, environmental, industrial, medical, and pharmatheutical applications of organic chemistry will be discussed, e.g., molecules found in agrochemicals, fibres, food additives, perfumes, polymers, and prescription drugs.

Laboratory Component:

Techniques in organic chemistry; preparation of some organic compounds, and; methods of qualitative organic analysis.

Tutorial Component:

Problem solving and discussion sessions with weekly problem sets. Regular assignments will be given and marked.

Notes:

- 1. Lectures: Days, Time and Place CH2630 A3 M,W 8:30 – 9:50 in J229
- 2. Laboratory Component: Day, Time and Place CH2630 L1 T 14:30 17:20 in J119
- 3. Tutorial Component: Day, Time and Place CH2630 S1 F 11:30 12:20 in J229

TEXT BOOKS AND LABORATORY ITEMS:

The following books are required:

Either,

1.1 Wade, L.G.(Jr), Organic Chemistry, 6th Edition, Pearson Prentice-Hall, 2006.

Or.

- 1.2 Solomons, T.W.G., and C.B. Fryhle, Organic Chemistry, 9th Edition, Wiley, 2008
- 2. A Three Ring Binder to Hold: Sloan, J.P., Organic Chemistry Experiments Chemistry 2610/2630, Grande Prairie Regional College, 2008/2009.

Molecular Models are highly recommended, namely:

3. Molecular Model Set for Organic Chemistry, Prentice Hall.

Studiy Guides and Solutions Manuals are supplementary items, namely:

- 4.1 Fernandez, J.E., and Solomons, T.W.G., Study Guide and Solutions Manual to Organic Chemistry, 8th Edition, 2004;
- 4.2 Simek, J.W., Wade L.G.(Jr), Solutions Manual to Organic Chemistry, 6th Edition,

Note:

1. All required and supplementary books, molecular structure model sets, safety glasses, and lab coats are available at the College Bookstore. Organic Chemistry Experiments, by J.P. Sloan, will be given as handouts in advance of each lab period. These are to be inserted in a three ring binder.

EVALUATION:

Examination Schedule and Composition of the Final Grade:

1.	Midterm Exam # 1, Friday February 13	15%
2.	Midterm Exam # 2, Friday March 20	20%
2.	Final Exam to be scheduled between April 16 – 27	30%
3.	Laboratory	25%
4.	Tutorial Grading Component	10%
	5 .	100%

The Grades are based on the alpha grading system. The Registrar's Office will convert alpha grades to four-point equivalence for the calculation of grade point averages. Alpha grades, 4-point equivalence, and grade descriptors are as follows:

Alpha	4-Point Equivalence	Descriptor
Grade		
A+	4.0	Excellent
A	4.0	
A-	3.7	First Class Standing
B+	3.3	
В	3.0	Good
B-	2.7	
C+	2.3	Satisfactory
С	2.0	
C-	1.7	
D+	1.3	Poor
D	1.0	Minimal Pass
F	0.0	Failure

^{*} Other post secondary institutions may not award transfer credit for grades of D and D+.

Notes:

- 1. The Mid-Term exams will be of 1.5 hours duration and the Final Exam will be of 3 hours duration. Between 5 and 15% of exam content will be taken directly from weekly assignments.
- 3. A pass grade is essential for the Laboratory Component.
- 4. The Tutorial Grading Component consists of assignments and will contribute towards 10% of the final grade. A 10 question assignment will normally be given each week during the tutorial hour. To encourage general discussion and active student participation, assignment questions may be answered within "paired teams/study groups". Assignments not completed during the tutorial period are due within 24 hours without penalty, or later at the discretion of the Instructor.

The marking scheme is:

- 4.1 1 mark per correct answer with full details;
- 4.2 ½ mark per correct answer with incomplete details;
- 4.3 20% may be deducted from the mark for each college business day that an assignment is overdue.
- 5. Regular attendance in Lecture, Laboratory, and Tutorial Components is a Course Requirement.

Grande Prairie Regional College Calendar 2008 - 2009: Course Description (page 178).

CH 2630 3(3-1-3)UT 105 Hours Organic Chemistry II

Continuation of the study of structural and chemical properties of the basic functional groups of organic compounds including aromatic compounds, aldehydes, ketones, carboxylic acids and their derivatives and amines. Illustration of these functional groups in natural products such as carbohydrates, amino acids and proteins, nucleic acids and lipids and discussion of the application of spectroscopic methods for structure determination in simple organic molecules.

Prerequisites: CH1610 or CH 2610

CHEMISTRY 2630 A3 READING, STUDYING, AND PRACTICE PROBLEMS

All references are to T.W.G. Solomons and C.B. Fryhle, Organic Chemistry, 9th Edition, Wiley, 2008.

WINTER SEMESTER

Weeks of Jan 5 & 12: SPECTROSCOPIC METHODS OF STRUCTURE DETERMINATION. NUCLEAR MAGNETIC RESONANCE (NMR) and MASS SPECTROSCOPY (MS): Tools for Structure Determination

Sect # Page # Read and Study Chapter 9.

	2-1	
9.1	364	Introduction;
9.2	364	Nuclear Magnetic Resonance (NMR) Spectroscopy;
9.2A	365	Chemical Shift (δ in parts per million, ppm);
	366	Table 9.1: Approximate proton Chemical Shifts;
9.2B	367	Integration of Signal Areas: Integral Step Heights;
9.2C	368	Coupling (Signal Splitting);
9.3	369	Interpreting Proton, ¹ H, NMR Spectra;
9.4	371	Nuclear Spin: The Origin of the Signal;
9.5	373	Detecting the Signal: Fourier Transform NMR Spectrometers;
9.6	374	Shielding and Deshielding of Protons;
	375	Deshielding by Electronegative Groups;
	376	Shielding and Deshielding by Circulation of π Electrons;
9.7	376	The Chemical Shift;
9.7A	377	PPM and the δ Scale;
9.8	377	Chemical Shift Equivalent and Nonequivalent Protons;
9.8A	377	Homotopic Hydrogen Atoms;
9.8B	378	Enantiotopic and Diastereotopic Hydrogen Atoms;
9.9	379	Signal Splitting: Spin-Spin Coupling;
9.9A	380	Vicinal Coupling
9.9B	380	Splitting Tree Dagrams and the Origin of Signal Splitting;
	381	Splitting Analysis for the Doublet
	381	Splitting Analysis fort he Triplet;
	382	Splitting Analysis for the Quartet;
9.9C	385	Coupling Constants – Recognizing Splitting Paterns;
9.9D	385	The Dependence of Coupling Constants on Dihedral Angle;
9.9E	386	Complicating Features;
9.9F	387	Analysis of Complex Interactions;
9.10	388	Proton NMR Spectra and Rate processes
	388	Conformational Chages;
	389	Chemical Exchange Causes Spin Decoupling;
9.11	390	Carbon-13, ¹³ C, NMR Spectroscopy;
9.11A	390	Interpretation of ¹³ C NMR Spectra;
9.11B		One Peak for each Unique carbon Atom;
9.11C	391	¹³ C Chemical Shifts;
	391	Figure 9.19: Approximate ¹³ C Chemical Shifts;
	392	Table 9.2: Approximate ¹³ C Chemical Shifts;
9.11D		Off-Resonance Decoupled Spectra;

DEPT ¹³C Spectra; 9.11E 394 Two-Dimensional (2D) NMR Techniques; 9.12 396 COSY Cross-Peak Correlations; 9.12A 396 **HETCOR Cross-Peak Correlations**; 9.12B 398 399 The Chemistry of Magnetic Resonance Imaging in Medicine; An Introduction to Mass Spectroscopy; 9.13 399 Formation of Ions: Electron Impact Ionization; 9.14 400 9.15 400 Depicting a Molecular Ion; 9.16 401 Fragmentation; Fragmentation by Cleavage at a Single Bond; 9.16A 402 9.16B 403 Fragmentation of Longer Chain and Branched Alkanes; Fragmentation to Form Resonance-Stabilized Cations; 9.16C 404 Fragmentation by Cleavage of Two Bonds; 9.16D 406 Determination of Molecular Formulas and Molecular Weights; 9.17 407 Isotopic Peaks and the Molecular Ion; 9.17A 407 Table 9.4: Principal Stable Isotopes of Common Elements; 408 9.17B 411 High-Resolution Mass Spectroscopy; Table 9.6: Exact Masses of Nuclides; 412 9.18 412 Mass Spectrometer Instrument Designs; 9.18A 412 Ionization Techniques: Electron Impact, Electrospray, and MALDI; Electron Impact Ionization; 412 Electrospray Ionization- A Technique Especially Useful for Biomolecules; 413 MALDI- A Technique Useful for Both Biomolecules and Synthetic Polymers; 414 Mass Analysis: Ion Sorting and Detection; 9.18B 414 Magnetic Focusing; 414 Quadrupole, Ion Trap, and Time-of-Floght (TOF) Mass Analyzers; 414 GC/MS (Gas Chromatography/Mass Spectrometry) Analysis; 9.19 415 Mass Sprectometry of Biomolecules: 9.20 416 Key Terms and Concepts. 416 Concept Map ¹H NMR Spectroscopy Concept Map ¹³C NMR Spectroscopy 417 418 Concept Map Mass Spectroscopy 419 In-Chapter 9.1 to 9.23 Problems: End of Chapter 9.24 to 9.44 420

Week of Jan 19: AROMATIC COMPOUNDS.

425

Learning Group Problems.

Read and Study Chapter 14: Aromatic Compounds: Why the Name? 14.1 596 Nomenclature of Benzene Derivatives; 14.2 597 14.3 599 Reactions of Benzene: 14.4 The Kekulé Structure for Benzene; 600 The Stability of Benzene; 14.5 601 14.6 602 Modern Theories of the Structure of Benzene; The Resonance Explanation of the Structure of Benzene; 14.6A 603 The Molecular Orbital Explanation of the Structure of Benzene; 14.6B 604 14.7 Hückel's Rule, the $4n + 2\pi$ Electron Rule: 605 14.7A 606 The Annulenes:

14.7B 608 NMR Spectroscopy: Evidence of Electron Delocalization in Aromatic Compounds; 14.7C 609 Aromatic Ions: 14.7D 611 Aromatic, Antiaromatic, and Nonaromatic Compounds; Other Aromatic Compounds; 14.8 613 14.8A 613 Benzenoid Aromatic Compounds; Nonbenzenoid Aromatic Compounds: 14.8B 615 14.8C 615 Fullerenes: The Chemistry of Nanotubes; 616 14.9 617 Heterocyclic Aromatic Compounds; Aromatic Compounds in Biochemistry; 14.10 618 Spectroscopy of Aromatic Compounds; 14.11 620 ¹H NMR Spectra; 14.11A620 ¹³C NMR Spectra; 14.11B621 Infrared Spectra of Substituted Benzenes; 14.11C623 Table 14.1; Infrared Absorptions in the 680-860 cm⁻¹ Regions; 623 Visible-Ultraviolet Spectra of Aromatic Compounds; 14.11D624 The Chemistry of Sunscreens (Catching the Sun's Rays and What Happens to Them); 624 14.11E 625 Mass Spectra of Aromatic Compounds; 625 Key Terms and Concepts; Concept Map Aromatic Compounds 626 In-Chapter 14.1 to 14.16 Problems: End of Chapter 14.17 to 14.39 627 Learning Group Problems. 634 Weeks of Jan 26: REACTIONS OF AROMATIC COMPOUNDS. Read and Study Chapter 15. 15.1 Electrophilic Aromatic Substitution Reactions; 637 E+ Ar Subn., a General Mechanism, Arenium Ions; 15.2 637 Halogenation of Benzene; 15.3 640 A Mechanism for the Reaction of Electrophilic Aromatic Bromination; 640 15.4 641 Nitration of Benzene: A Mechanism for the Reaction of Nitration of Benzene: 641 15.5 642 Sulfonation of Benzene; A Mechanism for the Sulfonation of Benzene; 642 Friedel-Crafts Alkylation; 15.6 643 A mechanism for the Reaction of Friedel-Crafts Alkylation; 644 Friedel-Crafts Acylation; 15.7 645 A Mechanism for the Reaction of Friedel-Crafts Acylation; 646 Limitations of Friedel-Crafts Reactions: 15.8 647 Synthetic Applications of Friedel-Crafts Acylations, the Clemmensen Reduction; 15.9 649 Effect of Substituents on Reactivity and Orientation; 15.10 650 Activating Groups: Ortho-Para Directors; 15.10A651 Deactivating Groups: Meta Directors; 15.10B652 Halo Substituents: Deactivating Ortho-Para Directors; 15.10C653 Table 15.1: Electrophilic Substitutions of Chlorobenzne 653 Classification of Substituents; 15.10D653 653 Table 15.2: Effect of Substituents on Electrophilic Aromatic Substitution; Theory of Substituent Effects on Electrophilic Aromatic Substitution; 15.11 653

15.11A653	Reactivity: The Effect of Electron-Releasing and Electron-Withdrawing Groups;
15.11B655	Inductive and Resonance Effects: Theory of Orientation;
15.11C656	Meta-Directing Groups;
15.11D658	Ortho-Para-Directing Groups;
15.11E 661	Ortho-Para Directing and Reactivity of Alkylbenzenes;
662	The Chemistry of Iodine Incorporation in Thyroxine Biosynthesis
15.11F 663	
15.12 664	Reactionss of the Side Chain of Alkyl Benzenes;
15.12A664	Benzylic Radicals and Cations;
665	The Chemistry of Industrial Styrene Synthesis;
15.12B 665	Halogenation of the Side Chain - Benzylic Radicals;
666	A mechanism for the Reaction of Benzylic Halogenation;
15.13 668	Alkenyl Benzenes;
15.13A668	Stability of Conjugated Alkenylbenzenes;
15.13B669	Additions to the Double Bond of Alkenylbenzenes;
15.13C669	Oxidation of the Side Chain;
15.13D670	Oxidation of the Benzene Ring;
15.14 670	Synthetic Applications;
15.14A672	Use of Protecting and Blocking Groups;
15.14B673	Orientation in Disubstituted Benzenes;
15.15 674	Allylic and Benzylic Halides in Nucleophilic Substitution Reactions;
674	Table 15.3: A Summary of Alkyl, Allylic, and Benzylic Halides in S _N 2 and S _N 1 Reactions,
15.16 676	Reduction of Aromatic Compounds;
676	A mechanism for the Reaction of Birch Reduction;
677	Key Terms and Concepts;
678	Concept Map: Summary of Mechanisms;
679	Concept Map: Some Synthetic Connections of Benzene and Aryl Derivatives.
Problems	In-Chapter 15.1 to 15.25
680	End of Chapter 15.26 to 15.56
685	Learning Group Problems.
XV1 £ E-	L. A. DEHVDES AND RETONES I. NILIOI FORIULIS A DDITION TO THE

Week of Feb 2: ALDEHYDES AND KETONES I: NUCLEOPHILIC ADDITION TO THE CARBONYL GROUP.

Read and Study Chapter 16.

16.1	687	Introduction;
16.2	687	Nomenclature of Aldehydes and Ketones;
16.3	689	Physical Properties;
	689	Table 16.1: Physical Properties of Aldehydes and Ketones;
	690	The Chemistry of Aldehydes and Ketones in Perfumes;
16.4	690	Synthesis of Aldehydes;
16.4A	690	Aldehydes by Oxidation of Primary Alcohols;
16.4B	691	Aldehydes by reduction of Acyl Chlorides, Esters and Nitriles;
	692	A Mechanism for the Reaction of Reduction of an Acyl Chloride to an Aldehyde;
	693	A Mechanism for the Reaction of Reduction of an Ester to an Aldehyde;
	693	A mechanism for the Reaction off Reduction of a Nitrile to an Aldehyde
16.5	694	Synthesis of Ketones;
16.5A	694	Ketones from Alkenes, Arenes, and Secondary Alcohols;
16.5B	694	Ketones from Nitriles;

- 16.6 696 Nucleophilic Addition to the Carbon-Oxygen Double Bond;
 - A Mechanism for the Reaction of Addition of a Strong Nucleophile to an Aldehyde or Ketone;
 - A Mechanism for the Reaction of Acid-Catalyzed Nucleophilic Addition to an Aldehyde or Ketone;
- 16.6A 698 Reversibility of Nucleophilic Additions to Carbon-Oxygen Double Bond;
- 16.6B 698 Relative Reactivity: Aldehydes versus Ketones;
- 16.6C 698 Subsequent Reactions of Addition Products;
- 16.7 699 Addition of Alcohols: Hemiacetals and Acetals;
- 16.7A 699 Hemiacetals;
 - 699 A Mechanism for the Reaction of Hemiacetal Formation;
 - A Mechanism for the Reaction of Acid-Catalyzed Hemiacetal Formation;
 - A Mechanism for the Reaction of Base-Catalyzed Hemiacetal Formation;
 - 701 Aldehyde Hydrates: gem-Diols;
 - A mechanism for the Reaction of Hydrate Formation;
- 16.7B 702 Acetals;
 - A mechanism for the Reaction of Acid-Catalyzed Acetal Formation;
- 16.7C 704 Acetals as Protecting Groups;
- 16.7D 705 Thioacetals;
- 16.8 706 The Addition of Derivatives of Ammonia, Primary and Secondary Amines;
- 16.8A 706 Imines;
 - A Mechanism for the Reaction of Imine Formation;
- 16.8B 707 Oximes, Hydrazones and Semicarbazones;
 - 707 Table 16.2: Reactions of Aldehydes and Ketones with Derivatives of Ammonia;
 - 708 The Chemistry of Pyridoxal Phosphate;
- 16.8C 709 Enamines;
 - A mechanism for the Reaction of Enamine Formation;
- 16.9 710 The Addition of Hydrogen Cyanide;
 - A mechanism for the Reaction of Cyanohydrin Formation;
- 16.10 711 The Addition of Ylides: the Wittig Reaction;
 - A mechanism for the Reaction of The Wittig Reaction;
- 16.11 715 Oxidation of Aldehydes;
- 16.12 717 Chemical Analyses of Aldehydes and Ketones;
- 16.12A 715 Derivatives of Aldehydes and ketones:
- 16.12B 715 Tollen's Tset (Silver Mirror Test);
- 16.13 716 Spectroscopic Properties of Aldehydes and Ketones;
- 16.13A716 IR Spectra of Aldehydes and Ketones;
 - 716 Table 16.3: IR Carbonyl Stretching Bands of Aldehydes and Ketones
- 16.13B717 NMR Spectra of Aldehydes and Ketones
 - 717 ¹³C NMR Spectra;
 - 717 ¹H NMR Spectra;
- 16.13C718 Mass Spectra of Aldehydes and Ketones;
- 16.13D718 UV Spectra;
- 16.14 719 Summary of Aldehyde and Ketone Addition Reactions;
 - Nucleophilic Addition Reactions of Aldehydes and ketones;
 - 720 Key Terms and Concepts;
 - 721 Summary of the Mechanisms Acetals, Imines, and Enamines: Common Mechanistic Themes in their Acid-catalyzed Formation from Aldehydes and ketones for Addition Reactions to Aldehydes and Ketones;
 - Summary of Mechanisms: Nucleophilic Addition to Aldehydes and Ketones under Basic Conditions;

- 723 Summary of Mechanisms: Nucleophilic Addition to Aldehydes and Ketones under Basic Conditions:
- 724 Synthetic Connections: Some Synthetic Connections of Aldehydes, Ketones, and Other Functional Groups:
- Problems: In-Chapter 16.1 to 16.18
 - End of Chapter 725 16.19 to 16.46
 - 730 Learning Group Problems.

Weeks of Feb 9 & 23: ALDEHYDES AND KETONES II: ENOLS AND ENOLATES.

Read and Study Chapter 17.

- 17.1 The Acidity of the $\Box \alpha$ Hydrogens of Carbonyl Compounds, Enolate Anions; 733 17.2 735 Keto and Enol Tautomers; 17.3 Reactions via Enols and Enolate Ions: 736 17.3A 736 Racemization; 737 A Mechanism for the Reaction of Base-Catalyzed Enolization 737 A Mechanism for the Reaction of Acid-Catalyzed Enolization 17.3B 738 Halogenation of Aldehydes and Ketones; A Mechanism for the Reaction of Base-Promoted Halogenation of Aldehydes and Ketones; 738 A Mechanism for the Acid-Catalyzed Halogenation of Aldehydes and Ketones; 739 17.3C 739 The Haloform reaction: 740 A Mechanism for the Reaction of Halogenation Steps of the Haloform Reaction; A Mechanism for the Reaction of Cleavage Step of the Haloform Reaction; 741 17.3D 741 Environmental Concerns; 17.4 742 The Aldol Reaction, the Addition of Enolate Anions to Aldehydes and Ketones; 742 A Mechanism for the Reaction of The Aldol Reaction; 17.4A 743 Dehydration of the Aldol Addition Product; A Mechanism for the Reaction of Dehydration of the Aldol Addition Product; 743 17.4B 743 Synthetic Applications of the Aldol Reaction; The Chemistry of A Retro-Aldol Reaction in Glycolysis – Dividing Assets to Double the ATP 745 Yield: 17.4C 746
- The Reversibility of Aldol Additions;
- Acid-Catalyzed Aldol Condensations: 17.4D 746

A Mechanism for the Reaction of The Acid-Catalyzed Aldol Reaction;

- 17.5 747 Crossed Aldol Reactions:
- 17.5A 748 Practical Crossed Aldol Reactions;
 - 749 Table 17.1: Crossed Aldol Reactions;
- 17.5B 749 Claisen-Schmidt Reactions;
 - A mechanism for the Reaction of The Claisen-Schmidt Reaction; 750
- 17.5C 751 Condensations with Nitroalkanes:
- 17.5D 752 Condensations with Nitriles:
- 17.6 752 Cyclization via Aldol Condensations;
 - A Mechanism for the Reaction of The Aldol Cyclyzation; 753
- 17.7 754 Lithium Enolates:
- Regioselective Formation of Enolates; 17.7A 754
- 17.7B 755 Lithium Enolates in Directed Aldol Reactions;
- 17.7C 757 Direct Alkylation of Ketones via Lithium Enolates;
 - 758 The Chemistry of Silyl Enol Ethers;

- 17.8 α -Selenation: A Synthesis of $\alpha\square$, \(\beta\) Unsaturated Carbonyl Compounds; 759 17.9 Additions to $\alpha \square$, β unsaturated Aldehydes and Ketones; 760 A mechanism for the Reaction of The Conjugate Addition to HCN: 761 A Mechanism for the Reaction of The Conjugate Addition of an Amine; 762 17.9A 762 Michael Additions: The Chemistry of Calicheamicin γ_1^{I} Activation for Cleavage of DNA; 763 Summary of Enolate Chemistry; 17.10 764 Key Terms and Concepts. 766 Summary of Mechanisms: Enolates: Formation and Reaction with Electrophiles by 767 Substitution or Addition; Synthetic Connections: Some Synthetic Connections Involving Enolates; 768 In-Chapter 17.1 to 17.27 Problems: End of Chapter 17.28 to 17.44 769 Learning Group Problems. 774 Week of Feb 16: Family Day & Winter Semester Break: No Classes. CARBOXYLIC ACIDS AND THEIR DERIVATIVES: Week of March 2: NUCLEOPHILIC ADDITION-ELIMINATION AT THE ACYL CARBON. Read and Study Chapter 18, and Special Topic B. 18.1 779 Introduction: 779 Table 18.1: Carboxylic Acid Derivatives 779 Nomenclature and Physical Properties; 18.2 18.2A 779 Carboxylic Acids; Table 18.2: Carboxylic Acids; 780 18.2B 781 Carboxylic Salts; 18.2C 781 Acidity of Carboxylic Acids; Dicarboxylic Acids; 18.2D 783 Table 18.3: Dicarboxylic Acids; 783 18.2E 784 Esters: 784 Table 18.4: Carboxylic Esters Carboxylic Anhydrides; 18.2F 785 Acyl Chlorides; 18.2G 785 Amides; 18.2H 785 Nitriles: 18.2I 786 Spectroscopic Properties of Acyl Compounds; 18.2J 786 786 IR Spectra; ¹H NMR Spectra; 788
- Preparation of Carboxylic Acids; 18.3 823 By Oxidation of Alkenes; 789 1. By Oxidation of Aldehydes and Primary Alcohols; 789 2. 789 3. By Oxidation of Alkyl Benzenes;

¹³C NMR Spectra;

788

- By Oxidation of the Benxene Ring: 789 4.
- By Oxidation of Methyl Ketones; 789 5.
- 790 6. By Hydrolysis of Cyanohydrins and Other Nitriles;
- By Carbonation of Grignard Reagents; 790 7.
- Nucleophilic Addition-Elimination at the Acyl Carbon; 18.4 791

- 792 A Mechanism for the Reaction of Acyl Transfer by Nucleophilic Addition-Elimination; 18.4A 793 Relative Reactivity of Acyl Compounds; Synthesis of Acid Derivatives; 18.4B 793 Acyl Chlorides; 18.5 794 18.5A 794 Synthesis of Acyl Chlorides; A Mechanism for the Reaction of Synthesis of Acyl Chlorides Using Thionyl Chloride. 794 18.5B 795 Reactions of Acyl Chlorides; 795 Carboxylic Acid Anhydrides; 18.6 18.6A 795 Synthesis of Carboxylic Acid Anhydrides; Reactions of Carboxylic Acid Anhydrides; 18.6B 796 18.7 797 Esters: 18.7A 797 Synthesis of Esters: Esterification; 798 A Mechanism for the Reaction of Acid-Catalyzed Esterification; 798 Esters from Acyl Chlorides 799 Esters from Carboxylic Acid Anhydrides; Base-Promoted Hydrolysis of Esters: Saponification; 18.7B 800 A Mechanism for the Reaction of Base-Promoted Hydrolysis of an Ester; 800 18.7C 801 Lactones; 18.8 802 Amides; 18.8A 802 Synthesis of Amides; Amides from Acyl Chlorides; 18.8B 803 Amides from Carboxylic Anhydrides; 18.8C 803 Amides from Esters; 18.8D 804 18.8E 804 Amides from Carboxylic Acids and Ammonium Carboxylates; A Mechanism for the Reaction of DCC-Promoted Amide Synthesis 805 Hydrolysis of Amides; 18.8F 805 A Mechanism for the Reaction of Acidic Hydrolysis of an Amide; 806 A Mechanism for the Reaction of Basic Hydrolysis of an Amide; 806 Nitriles from Dehydration of Amides; 18.8G 807 18.8H 807 Hydrolysis of Nitriles; A Mechanism for the Reaction of Acidic Hydrolysis of a Nitrile; 808 A Mechanism for the Reaction of Basic Hydrolysis of a Nitrile; 808 18.8I 809 Lactams; The Chemistry of Penicillins; 809 810 Derivatives of Carbonic Acid; 18.9 Alkyl Chloroformates and Carbamates (Urethanes); 18.9A 810 Decarboxylation of Carboxylic Acids; 18.10 812 The Chemistry of Thiamine; 813 18.10A814 Decarboxylation of Carboxyl Radicals; Chemical Tests for Acyl Compounds; 18.11 815 Summary of the Reactions of Carboxylic Acids and Their Derivatives; 815 Reactions of Carboxylic Acids: 815 1. As Acids: 2. Reduction; Conversion to Acyl Chlorides; 3. 4. Conversion to Esters: 5. Conversion to Amides:
 - 816 Reactions of Acyl Chlorides; Conversion to Acids;

Decarboxylation;

6.

1.

- 2. Conversion to Anhydrides;
- 3. Conversion to Esters:
- 4. Conversion to Amides:
- 5. Conversion to Ketones;
- 6. Conversion to Aldehydes;
- 817 Reactions of Acid Anhydrides;
 - 1. Conversion to Acids:
 - 2. Conversion to Esters:
 - 3. Conversion to Amides;
 - 4. Conversion to Aryl Ketones;
- 817 Reactions of Esters;
 - 1. Hydrolysis;
 - 2. Conversion to Other Esters: Transesterification;
 - 3. Conversion to Amides;
 - 4. Reaction with Grignard Reagents;
 - 5. Reduction:
- 818 Reactions of Amides;
 - 1. Hydrolysis;
 - 2. Conversion to Nitriles;
- 808 Reactions of Nitriles:
 - 1. Hydrolysis to Carboxylic Acid or Carboxylate Anion;
 - 2. Reduction to an Aldehyde with (*i*-Bu)₂AlH (DIBAL-H);
 - 3. Conversion to a Ketone by a Grignard or Organolithium Reagent;
- Summary and Review Tools: Synthetic Connections of Carboxylic Acids and Related Functional Groups: A 3-D Array of Linked Functional Groups.
- 821 Key Terms and Concepts.
- Problems: In-Chapter 18.1 to 18.18
 - 821 End of Chapter 18.19 to 18.55
 - 829 Learning Group Problems.
 - 830 Special Topic B: Step Growth Polymers;
- B.1 830 Polyamides;
 - The Chemistry of a Green Feedstock for Nylon;
- B.2 833 Polyesters;
 - The Chemistry of a PET Green Recycling Method
- B.3 835 Polyurethanes;
- B.4 836 Phenol-Formaldehyde Polymers;
- B.5 837 Cascade Polymers.

Week of March 9: SYNTHESIS AND REACTIONS OF β-DICARBONYL COMPOUNDS: MORE CHEMISTRY OF ENOLATE IONS.

Read and Study Chapter 19, and Special Topics C and D.

- 19.1 841 Introduction;
- 19.2 842 The Claisen Condensation: The Synthesis of β-Keto Esters;
 - A Mechanism fort he Reaction of The Claisen Condensation;
 - 845 The Dieckmann Condensation;
 - A Mechanism for the Reaction of The Dieckmann Condensation;
- 19.2A 846 Crossed Claisen Condensation:

19.2B 847 Acylation of Other Carbanions; 19.3 847 The Acetoacetic Ester Synthesis: Synthesis of Methyl Ketones (Substituted Acetones); 19.3A 847 Alkylation; 19.3B 851 Acylation; 19.3C 852 Acetoacetic Ester Dianion: Alkylation at the Terminal Carbon; 19.4 853 The Malonic Ester Synthesis: Synthesis of Substituted Acetic Acids; A Mechanism for the Reaction of The Malonic Ester Synthesis of Substituted Acetic Acids; 853 857 Further Reactions of Active Hydrogen Compounds; 19.5 19.6 858 Direct Alkylation of Esters and Nitriles; Alkylation of 1,3- Dithianes; 19.7 858 19.8 860 The Knoevenagel Condensation; Michael Additions; 19.9 860 A Mechanism for the Reaction of Michael Addition of an Active Hydrogen Compound; 861 19.10 862 The Mannich Reaction; A Mechanism for the Reaction of The Mannich Reaction; 862 The Chemistry of A Suicide Enzyme Substrate; 863 19.11 Synthesis of Enamines: Stork Enamine Reactions; 864 866 The Chemistry of Antibody-Catalyzed Aldol Condensations; 19.12 867 Barbiturates; 19.13 869 Summary of Important Reactions; Claisen Condensation; 1. 2. Crossed Claisen Condensation; 3. Aceetoacetic Ester Synthesis: 4. Malonic ester Synthesis; 5. Direct Alkylation of Esters; Alkylation of Dithianes; 6. Knoevenahel Condensation; 7. 8. Michael Addition; 9. Mannich Reaction: Strok Enamine Reaction; Summary of Mechanisms: Some Synthetic Connections Involving \(\beta \)-Dicarbonyl Compounds; 871 872 Key Terms and Concepts; In-Chapter 19.1 to 19.24; Problems: End of Chapter 19.25 to 19.51 872 Learning Group Problems. 878 Special Topic C: Thiols, Sulfur Ylides and Disulfides. 881 C.1 882 Preparation of Thiols; C.2 Physical Properties of Thiols; 883 C.3 884 The Addition of Sulfur Ylides to Aldehydes and Ketones; Thiols and Disulfides in Biochemistry; C.4 884 Special Topic D: Thiol Esters and Lipid Biosynthesis; 886 Thiol Esters; D.1 886 D.2 888 Biosynthesis of Fatty Acids; D.3 892 Biosynthesis of Isoprenoid Compounds; 894 Biosynthesis of Steroids; D.4

D.5

898

Cholesterol and Heart Disease.

Week of March 16: AMINES.

```
Read and Study Chapter 2., and Special Topic E.
             Nomenclature:
20.1
       900
20.1A 901
             Arylamines;
             Heterocyclic Amines;
20.1B 901
             Physical Properties and Structure of Amines;
20.2
      902
             Physical Properties;
20.2A 902
             Table 20.1: Physical Properties of Amines;
       902
             Structure of Amines;
20.2B 902
             Basicity of Amines, Amine Salts;
20.3
      903
             Basicity of Aryl Amines;
20.3A 904
             Basicity of Heterocyclic Amines;
20.3B 906
20.3C 906
              Amines versus Amides;
20.3D 907
              Aminium Salts and Quaternary Ammonium Salts;
             Solubility of Amines in Aqueous Acids;
20.3E 908
             Amines as Resolving Agents;
20.3F 908
             The Chemistry of HPLC Resolution of Enantiomers;
       910
             The Chemistry of Biologically Important Amines;
       910
                     2-Phenylethylamines;
              1.
                     Vitamins and Antihistamines;
             2.
                     Tranquilizers;
       912
              3.
                     Neurotransmitters;
20.4
      912
             Preparation of Amines;
             Through Nucleophilic Substitution Reactions;
20.4A 912
                     Alkylation of Ammonia;
                     A Mechanism for the Reaction of Alkylation of NH<sub>3</sub>;
       913
                     Alkylation of Azide Ion and Reduction;
       913
              2.
                     The Gabriel Synthesis;
             Alkylation of Tertiary Amines
       914
             Preparation of Aromatic Amines through Reduction of Nitro Compounds;
20.4B 914
             Preparation of Primary, Secondary, or Tertiary Amines through Reductive Amination;
20.4C 914
             A Mechanism for the Reaction of Reductive Amination;
       915
             Preparation of Primary, Secondary, or Tertiary Amines through Reduction of Nitriles,
20.4D 916
              Oximes and Amides;
             Preparation of Primary Amines through the Hofmann and Curtius Rearrangements;
20.4E 917
              A Mechanism for the Reaction of The Hofmann Rearrangement;
       918
             Reactions of Amines:
      919
20.5
       919
                     Acid-Base Reactions;
              1.
       920
             2.
                     Alkylation;
              3.
                     Acylation;
                     Electrophilic Aromatic Substitution;
             Oxidation of Amines:
20.5A 920
             Reactions of Amines with Nitrous Acid;
20.6 921
             Reactions of Primary Aliphatic Amines with Nitrous Acid;
20.6A 921
             Reactions of Primary Arylamines with Nitrous Acid;
20.6B 921
             A mechanism for the Reaction of Diazotization:
      922
             The Chemistry of N-Nitrosoamines;
       922
20.6C 923
             Reactions of Secondary Amines with Nitrous Acid;
             Reactions of Tertiary Amines with Nitrous Acid;
20.6D 923
```

```
20.7
      923
              Replacement Reactions of Arenediazonium Salts;
20.7A 924
              Synthesis Using Diazonium Salts;
20.7B 924
              The Sandmeyer Reaction: Replacement of the Diazonium Group by -Cl, -Br, -CN;
              Replacement by -I;
20.7C 925
20.7D 925
              Replacement by -F;
              Replacement by -OH;
20.7E 925
              Replacement by Hydrogen: Deamination by Diazotization;
20.7F 925
              Arene Diazonium Salts, Coupling Reactions;
20.8
       926
20.9
      929
              Reactions of Amines with Sulfonyl Chlorides;
20.9A 929
              The Hinsberg Test;
       930
              The Chemistry of Chemotherapy and Sulfa Drugs;
       931
                     Chemotherapy;
              1.
       931
              2.
                     Sulfa Drugs;
       932
                     Essential Nutrients and Antimetabolites:
              3.
20.10 933
              Synthesis of Sulfa Drugs;
              Analysis of Amines;
20.11 934
              Chemical Analysis;
20.11A934
20.11B934
              Spectroscopic Analysis;
                     Infrared Spectra;
              1.
                     <sup>1</sup>H NMR Spectra;
       935
              2.
                     <sup>13</sup>C NMR Spectra;
              3.
                     Mass Spectra of Amines;
              4.
              Eliminations Involving Ammonium Compounds;
20.12 935
20.12A935
              The Hofmann Elimination;
              The Cope Elimination;
20.12B936
              Summary of Preparations and Reactions of Amines;
       937
              Preparation of Amines;
       937
              1.
                     Gabriel Synthesis:
                     By Reduction of Alkyl Azides;
              2.
              3.
                     By Amination of Alkyl Halides;
                     By Reduction of Nitroarenes;
              4.
                     By Reductive Amination;
              5.
       938
                     By Reduction of Nitriles, Oximes, and Amides:
              6.
                     Through the Hofmann and Curtius Rearrangements;
              7.
       938
              Reactions of Amines:
              1.
                     As bases:
       939
              2.
                     Diazatoization of Primary Aryl Amines and Replacement of, or Coupling with, the
                     Diazonium Group;
              3.
                     Conversion to Sulfonamides;
              4.
                     Conversion to Amides:
                     Hofmann and Cope Eliminations;
              Key Terms and Concepts;
       940
              In-Chapter
Problems:
                                   20.1 to 20.20;
              End of Chapter
                                   20.21 to 20.53;
       940
              Learning Group Problems;
       947
       949
              Special Topic E: Alkaloids;
              Alkaloids Containing a Pyridine or Reduced Pyridine Ring;
E.1
      949
              Alkaloids Containing an Isoquinoline or Reduced Isoquinoline Ring;
E.2
      952
```

Alkaloids Containing Indole or Reduced Indole Rings.

E.3

953

Week of March 23: PHENOLS AND ARYL HALIDES: NUCLEOPHILIC AROMATIC SUBSTITUTION.

Read and Study Chapter 21.

Read Special Topics F, G, and H, pages 992-1019.

- 21.1 955 Structure and Nomenclature of Phenols;
- 21.A 955 Nomenclature of Phenols;
- 21.2 956 Naturally Occurring Phenols;
- 21.3 957 Physical Properties of Phenols;
 - 957 Table 21.1: Physical Properties of Phenols;
- 21.4 957 Synthesis of Phenols;
- 21.4A 957 Laboratory Synthesis;
 - 958 The Chemistry of Polyketide Anticancer Antibiotic Biosynthesis;
- 21.4B 959 Industrial Synthesis;
 - 1. Hydrolysis of Chlorobenzene (Dow Process).
 - 2. Alkali Fusion of Sodium Benzenesulfonate.
 - 3, From Cumene Hydroperoxide.
- 21.5 961 Reactions of Phenols as Acids:
- 21.5A 961 Strengths of Phenols as Acids;
 - Table 21.2: Acidity Constants of Phenols;
- 21.5B 962 Distinguishing and Separating Phenols from Alcohols and Carboxylic Acids;
- 21.6 963 Other Reactions of the O-H Group of Phenols;
- 21.6A 963 Phenols in the Williamson Synthesis;
- 21.7 964 Cleavage of Alkyl Aryl Ethers;
- 21.8 964 Reactions of the Benzene Ring of Phenols;
 - 964 1. Bromination;
 - 965 2. Nitration;
 - 3. Sulfonation:
 - 4. Kolbe Reaction;
 - 966 A Mechanism for the Kolbe Reaction;
- 21.9 967 The Claisen Rearrangement;
- 21.10 968 Ouinones;
- 21.11 969 Aryl Halides and Nucleophilic Aromatic Substitution;
 - 970 The Chemistry of The Bombardier Beetle's Noxious Spray;
- 21.11A971 Nucleophilic Aromatic Substitution by Addition-Elimination: The S_NAr Mechanism;
 - 971 A Mechanism for the Reaction of The S_NAr Mechanism;
 - 972 The Chemistry of Bacterial Dehalogenation of a PCB Derivative;
- 21.11B973 Nucleophilic Aromatic Substitution through an Elimination-Addition Mechanism, The Benzyne Mechanism;
 - A Mechanism for the Reaction of The Benzyne Elimination-Addition Mechanism;
- 21.11C976 Phenylation;
- 21.12 977 Spectroscopic Analysis of Phenols and Aryl Halides;
 - 1. Infrared Spectra;
 - 2. 1H NMR Spectra;
 - 3. 13C NMR Spectra;
 - 4. Mass spectra;
 - 978 Concept Map: Some Synthetic Connections of Phenols and Related Aromatic Compounds;
 - 979 Key Terms and Concepts.

Problems:		In-Chapter 21.1 to 21.12		
979		End of Chapter 21.13 to 21.38		
984		Learning Group Problems		
	986	Second Review Problem Set 1 to 24.		
	992	Special Topic F: Aryl Halides: Their Uses;		
F.1	992	Aryl Halides as Insecticides;		
F.2	993	Organic halides as Heerbicides;		
F.3	994	Polychlorinated Biphenyls (PBCBs);		
	995	Special Topic G: Electrocyclic and Cycloaddition Reactions.		
G.1	995	Introduction;		
G.2	995	Electrocyclic Reactions;		
G.2A	997	Electrocyclic Reactions of 4n π-Electron Systems;		
G.2B	1001	Electrocyclic Reactions of $(4n + 2)$ π -Electron Systems;		
	1001	Table G.1: Woodward-Hoffmann Rules for Electrocyclic Reactions;		
G.3	1004	Cycloaddition Reactions;		
	1005	[2 + 2] Cycloadditions;		
G.3B	1007	[4 + 2] Cycloadditions.		
	1008	Special Topic H: Transition Metal Organometallic Compounds;		
H.1	1008	Introduction		
H.2	1009	Electron Counting in Metal Complexes;		
	1010	Table H.1: Common Ligands in Transition Metal Complexes;		
H.3	1011	Metallocenes: Organometallic Sandwich Compounds;		
H.4	1012	Reactions of Transition Metal Complexes;		
H.5	1014	Homogeneous Hydrogenation;		
H.6	1015	Carbon-Carbon Bond-Forming Reactions;		
H.6A	1016	Coupling Reactions;		
		1. The Heck Reaction;		
		2. The Suzuki Reaction;		
		3. The Stille Coupling;		
		4. The Sonogashira Reaction;		
H.6B	1017	Ruthenium Alkylidene (Ruthenium Carbene) Complexes:		
		Olefin Metathesis and Grubbs' Catalysts;		
H.7	1019	Vitamin B ₁₂ : A Transition Metal Biomolecule;		
Week	of Marc	ch 30: CARBOHYDRATES AND LIPIDS (OPTIONAL).		
		Read Chapters 22 & 23.		
	1020	Carbohydrate Recognition in Healing and Disease;		
22.1	1021	Introduction to Carbohydrates;		
22.1A	1021	Classification of Carbohydrates;		
22.1B	1022	Photosynthesis and Carbohydrate Metabolism;		
22.2	1023	Monosaccharides;		
22.2A	1023	Classification of Monosaccharides;		
22.2B	1024	D and L Designation of Monosaccharides;		
22.2C	1025	Structural Formulas of Monosaccharides;		
22.3 1028		Mutarotation;		

22.4 1029 Glycoside Formation; 1030 A Mechanism for the Reaction of Formation of a Glycoside; 1031 A Mechanism for the Reaction of Hydrolysis of a Glycoside; 22.5 Other Reactions of Monosaccharides; 1032 22.5A 1032 Enolization, Tautomerization, and Isomerization; 22.5B 1032 Use of Protecting Groups in Carbohydrate Synthesis; 22.5C 1033 Formation of Ethers; 22.5D 1034 Conversion to Esters: 22.5E 1035 Conversion to Cyclic Acetals 22.6 1035 Oxidation Reactions of Monosaccharides; 22.6A 1035 Benedict's or Tollens' Reagents: Reducing Sugars; 22.6B 1036 Bromine Water: The Synthesis of Aldonic Acids; 22.6C 1037 Nitric Acid Oxidation: Aldaric Acids; Periodate Oxidations: Oxidative Cleavage of Polyhydroxy Compounds; 22.6D 1038 22.7 1040 Reduction of Monosaccharides: Alditols; Reactions of Monosaccharides with Phenylhydrazine: Osazones; 22.8 1041 A Mechanism fofr the Reaction of Phenylosazone Formation; 1041 22.9 1042 Synthesis and Degradation of Monosaccharides; 22.9A 1042 Kiliani-Fischer Synthesis; 22.9B 1043 The Ruff Degradation; The D family of Aldoses; 22.10 1044 Fischer's Proof of the Configuration of D-(+)-Glucose; 22.11 1044 1045 Fig 22.7: The D Family of Aldohexoses; 1047 The Chemistry of Stereoselective Synthesis of All the L-Aldohexoses; 22.12 1049 Disaccharides; 22.12A1049 Sucrose: 22.12B 1050 Maltose; 22.12C1050 Cellobiose: The Chemistry of Artificial Sweeteners 9How Sweet It Is); 1052 22.12D1053 Lactose; Polysaccharides; 22.13 1053 Starch; 22.13A1053 22.13B 1054 Glycogen; 22.13C1055 Cellulose: 22.13D1056 Cellulose Derivatives; 1057 The Chemistry of the Oligosaccharide Synthesis on a Solid Support - The Glycal Assembly Approach; Other Biologically Important Sugars; 22.14 1059 Sugars That Contain Nitrogen; 22.15 1059 22.15A1059 Glycosylamines; Amino Sugars: 22.15B 1060 Glycolipids and Glycoproteins of the Cell Surface: Cell Recognition and the Immune System; 22.16 1061 1063 The Chemistry of Vaccines Against Cancer; Carbohydrate Antibiotics. 22.17 1064 Summary of Reactions of Carbohydrates; 1065 1066 Summary and Review Tools: A Summary of Reactions Involving Monosaccharides; 1067 Key Terms and Concepts. **Problems:** In-Chapter 22.1 to 22.19 End of Chapter 22.20 to 21.45 1067

Learning Group Problems

1071

1073 LIPIDS (Chapter 23) 1073 Insulation for Nerves: 23.1 1074 Introduction to Lipids; 23.2 Fatty Acids and Triacylglycerols; 1075 1076 Table 23.1: Common Fatty Acids; Table 23.2: Fatty Acid Composition Obtained by Hydrolysis of Common Fats and Oils; 1077 23.2A 1077 Hydrogenation of Triacylglycerols; 23.2B 1077 Biological Functions of Triacylglycerols; The Chemistry of Olestra and Other Fat Substitutes; 1078 23.2C 1079 Saponification of Triacylglycerols; 23.2D 1081 Reactions of Carboxyl Groups of Fatty Acids; Reactions of the Alkenyl Chain of Unsaturated Fatty Acids; 23.2E 1081 1082 The Chemistry of Self-Assembled Monolayers - Lipids in Materials Science and Bioengineering; Terpenes and Terpenoids; 23.3 1083 23.3A 1086 Natural Rubber; 23.4 1087 Steroids; 23.4A 1087 Structure and Systematic Nomenclature of Steroids; 23.4B 1089 Cholesterol; 23.4C 1090 Sex Hormones; 23.4D 1092 Ardrenocortical Hormones; 23.4E 1092 **D** Vitamins 23.4F 1093 Other Steroids; 23.4G 1094 Reactions of Steroids; 23.5 1095 Prostaglandins; 23.6 1097 Phospholipids and Cell Membranes; Phosphatides; 23.6A 1097 The Chemistry of STEALTH Liposomes for Drug Delivery; 1099 Derivatives of Sphingosine; 23.6B 1100 23.7 1100 Waxes; Summary of the Reactions of Lipids; 1101 Key Terms and Concepts. 1101 Problems: In-Chapter 23.1 to 23.11 1101 End of Chapter 23.12 to 23.26 Learning Group Problems. 1107 Week of March 31: AMINO ACIDS AND PROTEINS (OPTIONAL). Read Chapter 24. 1107 Catalytic Antibodies: Designer Catalysts 24.1 1108 Introduction: 24.2 1109 Amino Acids: 24.2A 1109 Structures and Names: 24.2B 1109 Essential Amino Acids: 1110 Table 24.1: L-Amino Acids Found in Proteins; 24.2C 1112 Amino Acids as Dipolar Ions;

24.3

1115

Synthesis of $\Box \alpha$ -Amino Acids;

24.3A	1115	From Potassium Phthalimide;
24.3B	1116	The Strecker Synthesis;
	1116	A Mechanism for the Reaction of Formation of:
		an α-Aminonitrile During the Strecker Synthesis;
24.3C	1116	Resolution of DL-Amino Acids;
24.3D	1117	Asymetric Syntheses of Amino Acids;
24.4	1119	Polypeptides and Proteins;
24.4A	1120	Hydrolysis;
24.5	1122	Primary Structure of Polypeptides and Proteins;
24.5A	1122	Edman Degradation;
24.5B	1123	Sanger N-Terminal Analysis;
24.5C	1124	C-Terminal Analysis;
24.5D	1124	Complete Sequence Analysis;
24.5E	1125	Peptide Sequencing Using Mass Spectroscopy and Sequence Databases
	1126	Examples of Polypeptides and Proteins Primary Structure;
24.6A	1126	Oxytocin and Vasopressin;
24.6B	1127	Insulin;
	1128	The Chemistry of Sickle-Cell Anemia
24.6C		Other Polypeptides and Proteins
24.7		Polypeptide and Protein Synthesis;
24.7A		Protecting Groups;
	1131	Activation of Carboxyl Group;
	1132	Peptide Synthesis;
24.7D		Automated Peptide Synthesis;
24.8		Secondary, Tertiary, and Quaternary Structures of Proteins;
24.8A		Secondary Structure;
	1139	Tertiary Structure;
24.8C		Quaternary Structure;
24.9		Introduction to Enzymes;
24.10		Lysozyme: Mode of Action of an Enzyme;
24.11		Serine Proteases;
	1148	Haemoglobin, a Conjugated Protein;
	1148	The Chemistry of Some Catalytic Antibodies;
24.13	1150	Purification and Analysis of Polypeptides and Proteins
		Purification;
		Analysis;
		Proteomics;
		Key Terms and Concepts.
Proble		In-Chapter 24.1 to 24.16
110010		End of Chapter 24.17 to 24.27
	1157	Learning Group Problems
	1157	Dearning Group Problems
Week	of April	6: NUCLEIC ACIDS AND PROTEIN SYNTHESIS
	1158	Read Chapter 25
	1158	Tools for Finding Families;
25.1	1159	Introduction;
25.2	1160	Nucleotides and Nucleosides;

1163 Laboratory Synthesis of Nucleosides and Nucleotides;

25.3

25.3A	1166	Medical Applications;
25.4A	1166	Primary Structure;
25.4B	1167	Secondary Structure;
25.4C	1171	Replication of DNA;
25.5	1173	RNA and Protein Synthesis;
25.5A	1173	Messenger RNA Synthesis;
25.5A	1173	Messenger RNA Synthesis-Transcription;
25.5B	1174	Ribosomes-rRNA
25.5C	1176	Transfer RNA;
25.5D	1177	The Genetic Code;
25.5E	1178	Translation;
25.6	1180	Determining the Base Sequence of DNA:
		The Chain-Terminating (Dideoxynucleotide) Method;
25.6A	1181	DNA Sequencing by the Chain-Terminating (Dideoxynucleotide) Method;

CHEMISTRY 2630 A3: READING, STUDYING, AND PRACTICE PROBLEMS

All references are to Wade, L.G.(Jr), Organic Chemistry, 6th Edition, Pearson Prentice-Hall, 2006.

WINTER SEMESTER

Weeks of Jan 5 & 12: SPECTROSCOPIC METHODS OF STRUCTURE DETERMINATION, Chapters 12/13.

Chapter 12: INFRARED SPECTROSCOPY AND MASS SPECTROSCOPY

Sect # Page # Read and Study Chapter12.

12-1 508	Introduction
12-2 509	The Electromagnetic Spectrum
12-3 510	The Infrared Region
12-4 511	Molecular Vibrations
12-5 513	IR-Active and IR-Inactive Vibrations
12-6 514	Measurement of the IR Spectrum
12-7 517	Infrared Spectroscopy of Hydrocarbons
12-7A 517	Carbon-Carbon Bond Stretching
12-7B 518	Carbon-Hydrogen Bond Stretching
12-7C 518	Interpretation of the IR Spectra of Hydrocarbons
12-8 522	Characteristic Absorptions of Alcohols and Amines
12-9 523	Characteristic Absorptions of Carbonyl Compounds
12-9A 523	Simple Ketones, Aldehydes and Acids
12-9B 527	Resonance Lowering of Carbonyl Frequencies
12-9C 528	Carbonyl Absorptions Above 1710 cm-1
12-10 529	Characteristic Absorptions of C-N Bonds
12-11 530	Simplified Summary of IR Stretching Frequencies
12-12 532	Reading and Interpreting IR Spectra (Solved Problems)
12-13 537	Introduction to Mass Spectroscopy
12-13A	538 The Mass Spectrometer
12-13B	The Mass Spectrum
12-13C	Mass Spectrometry of Mixtures: The GC-MS
12-14 541	Determination of the Molecular Formula by Mass Spectrometry
12-14A	541 High Resolution Mass Spectrometry
12-14B	541 Use of Heavier Isotope Peaks
12-15 544	Fragmentation Patterns in Mass Spectroscopy
12-15A	544 Mass Spectra of Alkanes
12-15B	Fragmentation Giving Resonance Stabilized cations
12-15C	Fragmentation Splitting Out a Small Molecule; Mass Spectra of Alcohols
549	Summary; Common Fragmentation Paterns
551	Chapter 12 Glossary
552	Essential Problem-Solving Skills in Chapter 12
552	Study Problems: In Chapter, 12-1 to 12-11; End of Chapter, 12-12 to 12-28

Chapter 13: NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Read and Study Chapter 13.

- 13-1 559 Introduction;
- 13.2 559 Theory of Nuclear Magnetic Resonance;
- Magnetic Shielding by Electrons; 13.3 562
- 13.4 The NMR Spectrometer; 564
- 13.5 565 The Chemical Shift;
- 13.5A 565 Measurement of Chemical Shifts;
 - Table 13.1: Variation of Chemical Shift with Electronegativity; 567
 - Table 13.2: Chemical Shifts of the Chloromethanes: 567
- 13.5B 567 Characteristic Values of Chemical Shifts;
 - Table 13.3: Typical values of Chemical Shifts; 568
 - 568 Vinyl and Aromatic Protons;
 - Acetylenic Hydrogens; 570
 - 570 Aldehyde Protons;
 - Hydrogen-Bonded protons; 571
 - 571 Carboxylic Acid protons;
- 572 The Number of Signals; 13.6
- Areas of the Peaks; 13.7 573
- Spin-Spin Splitting; 13.8 576
- Theory of Spin-Spin Splitting; 13.8A 576
- The N + 1 Rule; 13.8B 578
 - Relative peak Intensities of Symmetric Multiplets Pascal's Triangle; 578
- The Range of Magnetic Coupling; 13.8C 578
 - Problem-Solving Strategy; Drawing an NMR Spectrum; 581
- Coupling Constants; 13.8D 582
- Complex Splitting; 13.9 585
- 13.10 588 Stereochemical Nonequivalence of protons;
- Time Dependence of NMR Spectroscopy; 13.11 591
- Conformational Changes; 13.11A591
- 13.11B591 Fast Proton Transfers: Hydroxyl Protons and N-H Protons;
 - Problem Solving Strategy; Interpreting Proton NMR Spectra; 594
- 13.12 599 Carbon-13 NMR Spectroscopy;
- 13.12A599 Sensitivity of Carbon NMR;
- Fourier Transform NMR Spectroscopy; 13.12B600
- Carbon Chemical Shifts; 13.12C601
- Inportant Differences Between ¹H and ¹³C Techniques; Operating Frequency and Peak Areas; 13.12D602
- Spin-Spin Splitting; 13.12E 603
 - 603
 - Proton Spin Decoupling: Each Carbon Atom Appears as a Singlet; Off-Resonance Decoupling: Splits the ¹³C Nuclei According to the N + 1 Rule; 603
- DEPT ¹³C NMR: Distortionless Enhanced Polarization Transfer; 13.12F 604
 - Table 13.4: Summary of DEPT Spectra; 605
- Interpreting Carbon NMR Spectra; 13.13 607
- Nuclear Magnetic Resonance Imaging; 13.14 609
 - Problem-Solving Strategy: Spectroscopy Problems; 610
 - Chapter 13 Glossary; 614
 - 615 Essential Problem-Solving Skills in Chapter 13;

616 Study Problems: In Chapter 13.1 – 13.32; End of Chapter 13.33 – 13.52.

Week of Jan 19: AROMATIC COMPOUNDS.

		Read and Study Chapter 14.
14.1	623	Introduction;
14.2	624	Nomenclature of Benzene Derivatives;
14.3	626	Reactions of Benzene;
14.4	627	The Kekulé Structure for Benzene:

- 14.4 627 The Kekulé Structure for Benzene:
- 14.5 628 The Stability of Benzene;
- 14.6 629 Modern Theories of the Structure of Benzene;
- 14.6A 630 The Resonance Explanation of the Structure of Benzene;
- 14.6B 631 The Molecular Orbital Explanation of the Structure of Benzene;
- 14.7 632 Hückel's Rule, the (4n+2) □ Electron Rule;
- 14.7A 633 The Annulenes:
- 14.7B 635 NMR Spectroscopy Evidence of Electron Delocalization in Aromatic Compounds;
- 14.7C 636 Aromatic Ions;
- 14.7D 638 Aromatic, Antiaromatic, and Nonaromatic Compounds;
- 14.8 640 Other Aromatic Compounds;
- 14.8A 640 Benzenoid Aromatic Compounds;
- 14.8B 642 Nonbenzenoid Aromatic Compounds;
- 14.8C 642 Fullerenes;
- 14.9 644 Heterocyclic Aromatic Compounds;
- 14.10 645 Aromatic Compounds in Biochemistry;
- 14.11 648 Spectroscopy of Aromatic Compounds;
- 14.11A648 H-1 NMR Spectra;
- 14.11B648 C-13 NMR Spectra;
- 14.11C651 Infrared Spectra of Substituted Benzenes;
- 14.11D652 Visible-Ultraviolet Spectra of Aromatic Compounds;
- 14.11E 653 Mass Spectra of Aromatic Compounds;
 - Key Terms and Concepts;
 - 654 Concept Map Aromatic Compounds
 - 655 Study Problems: In-Chapter 14.1 14.15; End of Chapter 14.16 14.38
 - 662 Learning Group Problems.

Weeks of Jan 26: REACTIONS OF AROMATIC COMPOUNDS.

Read and Study Chapter 15.

- 15.1 665 Electrophilic Aromatic Substitution Reactions;
- 15.2 666 E+ Ar Subn., a General Mechanism, Arenium Ions;
- 15.3 668 Halogenation of Benzene;
- 15.4 669 Nitration of Benzene:
- 15.5 670 Sulfonation of Benzene;
- 15.6 671 Friedel-Crafts Alkylation;
- 15.7 673 Friedel-Crafts Acylation;
- 15.8 675 Limitations of Friedel-Crafts Reactions;
- 15.9 677 Synthetic Applications of Friedel-Crafts Acylations, the Clemmensen Reduction;
- 15.10 679 Effect of Substituents on Reactivity and Orientation;

15.10A679	Activating Groups: Ortho-Para Directors;
15.10B680	Deactivating Groups: Meta Directors;
15.10C681	Halo Substituents: Deactivating Ortho-Para Directors;
15.10D681	Classification of Substituents;
15.11 681	Theory of Substituent Effects on Electrophilic Aromatic Substitution;
15.11A681	Reactivity: The Effect of Electron-Releasing and Electron-Withdrawing Groups;
15.11B684	Inductive and Resonance Effects: Theory of Orientation;
15.11C685	Meta-Directing Groups;
15.11D686	Ortho-Para-Directing Groups;
15.11E 690	Ortho-Para Directing and Reactivity of Alkylbenzenes;
15.11F 692	Summary of Substituent Effects on Orientation and Reactivity;
15.12 693	Alkyl Benzenes, Side Chain Reactions;
15.12A693	Benzylic Radicals and Cations;
15.12B694	Halogenation of the Side Chain - Benzylic Radicals;
15.13 697	Alkenyl Benzenes;
15.13A697	Stability of Conjugated Alkenylbenzenes;
15.13B698	Additions to the Double Bond of Alkenylbenzenes;
15.13C699	Oxidation of the Side Chain;
15.13D698	Oxidation of the Benzene Ring;
15.14 699	Synthetic Applications;
15.14A701	Use of Protecting and Blocking Groups;
15.14B702	Orientation in Disubstituted Benzenes;
15.15 703	Allylic and Benzylic Halides in Nucleophilic Substitution Reactions;
15.16 705	Reduction of Aromatic Compounds;
15.16A706	The Birch Reduction;
707	Key Terms and Concepts;
708	Concept Map: Summary of Mechanisms;
709	Concept Map: Some Synthetic Connections of Benzene and Aryl Derivatives.
710	Study Problems: In-Chapter 15.1 - 15.25; End of Chapter 15.26 - 15.56
715	Learning Group Problems.

Week of Feb 2: ALDEHYDES AND KETONES I: NUCLEOPHILIC ADDITION TO THE CARBONYL GROUP.

Read and Study Chapter 16.

16.1	717	Introduction;
16.2	717	Nomenclature of Aldehydes and Ketones;
16.3	719	Physical Properties;
16.4	720	Synthesis of Aldehydes;
16.4A	720	Aldehydes by Oxidation of Primary Alcohols;
16.4B	721	Aldehydes by reduction of Acyl Chlorides, Esters and Nitriles;
16.5	724	Synthesis of Ketones;
16.5A	724	Ketones from Alkenes, Arenes, and Secondary Alcohols;
16.5B	725	Ketones from Alkynes;
16.5C	726	Ketones from Lithium Dialkyl Cuprates;
16.5D	727	Ketones from Nitriles;
16.6	728	Nucleophilic Addition to the Carbon-Oxygen Double Bond;
16.6A	730	Reversibility of Nucleophilic Additions to Carbon-Oxygen Double Bond;
16.6B	730	Relative Reactivity: Aldehydes versus Ketones;

- 16.6C 731 Subsequent Reactions of Addition Products;
- 16.7 731 Addition of Water, Alcohols & Thiols: Hydrates, Hemiacetals, Acetals & Thioacetals;
- 16.7A 731 Hydrates and Hemiacetals;
- 16.7B 734 Acetals;
- 16.7C 736 Acetals as Protecting Groups;
- 16.7D 738 Thioacetals;
- 16.8 738 The Addition of Derivatives of Ammonia, Primary and Secondary Amines;
- 16.8A 739 Imines:
- 16.8B 740 Oximes, Hydrazones and Semicarbazones;
- 16.8C 740 Enamines:
 - 743 Table 16.2: Reactions of Aldehydes and Ketones with Derivatives of Ammonia;
- 16.9 743 The Addition of Hydrogen Cyanide;
- 16.10 745 The Addition of Ylides: the Wittig Reaction;
- 16.11 749 The Addition of Organometallic Reagents, the Reformatsky Reaction;
- 16.12 751 Oxidation of Aldehydes and Ketones;
- 16.12A751 The Baeyer-Villiger Oxidation of Aldehydes and Ketones;
- 16.13 753 Chemical Analyses of Aldehydes and Ketones;
- 16.13A753 Derivatives of Aldehydes and Ketones;
- 16.13B753 Tollen's Test (The Silver Mirror test);
- 16.14 754 Spectroscopic Properties of Aldehydes and Ketones;
- 16.14A754 IR Spectra of Aldehydes and Ketones;
- 16.14B754 NMR Spectra of Aldehydes and Ketones;
- 16.14C756 Mass Spectra of Aldehydes and Ketones;
- 16.14D756 Ultraviolet Spectra of Aldehydes and Ketones;
 - 757 Summary of the Mechanisms Acetals, Imines, and Enamines: Common Mechanistic Themes in their Acid-catalyzed Formation from Aldehydes and ketones for Addition Reactions to Aldehydes and Ketones;
 - 758 Summary of Mechanisms: Nucleophilic Addition to Aldehydes and Ketones under Basic Conditions;
 - 759 Summary of Mechanisms: Nucleophilic Addition to Aldehydes and Ketones under Basic Conditions;
 - 761 Key Terms and Concepts.
 - 761 Study Problems: In-Chapter; 16.1 16.22; End of Chapter 16.23 16.53
 - 767 Learning Group Problems.

Weeks of Feb 9 & 23: ALDEHYDES AND KETONES II: ALDOL REACTIONS.

Read and Study Chapter 17.

- 17.1 770 The Acidity of the □-Hydrogens of Carbonyl Compounds, Enolate Ions;
- 17.2 772 Keto and Enol Tautomers;
- 17.3 773 Reactions via Enols and Enolate Ions:
- 17.3A 773 Racemization;
- 17.3B 775 Halogenation of Ketones;
- 17.3C 776 The Haloform reaction;
- 17.4 779 The Aldol Reaction, the Addition of Enolate Ions to Aldehydes and Ketones;
- 17.4A 779 Dehydration of the Aldol Addition Product;
- 17.4B 780 Synthetic Applications;
- 17.4C 781 The Reversibility of Aldol Additions;
- 17.4D 783 Acid-Catalyzed Aldol Condensations;

Crossed Aldol Reactions; 17.5 784 17.5A 785 Practical Crossed Aldol Reactions: 17.5B 786 Claisen-Schmidt Reactions: Condensations with Nitroalkanes; 17.5C 788 17.5D 789 Condensations with Nitriles; 789 17.6 Cyclization via Aldol Condensations; Lithium Enolates; 17.7 791 17.7A 791 Regioselective Formation of Enolate Anions; 17.7B 792 Lithium Enolates in Directed Aldol Reactions; Direct Alkylation of Ketones via Lithium Enolates; 17.7C 794 17.8 796 \Box -Selenation: A Synthesis of \Box , β Unsaturated Carbonyl Compounds; Additions to □ , βunsaturated Aldehydes and Ketones; 797 17.9 Conjugate Addition of Organocopper Reagents; 17.9A 799 17.9B 800 Michael Additions; Summary of Mechanisms – Enolates: Formation and Reaction of Electrophiles by Substitution 802 or Addition; Synthetic Connections: Some Synthetic Connections Involving Enolates; 803 804 Key Terms and Concepts. 804 Study Problems: In-Chapter 17.1 - 17.27; End of Chapter 17.28 - 17.45 Learning Group Problems. 809 Week of Feb 16: Family Day & Winter Semester Break: No Classes. Week of March 2: CARBOXYLIC ACIDS AND THEIR DERIVATIVES: NUCLEOPHILIC ADDITION-ELIMINATION AT THE ACYL CARBON. Read and Study Chapter 18. 814 18.1 Introduction; 18.2 Nomenclature and Physical Properties; 814 18.2A 814 Carboxylic Acids; Carboxylic Salts; 18.2B 816 18.2C 816 Acidity of Carboxylic Acids; Dicarboxylic Acids; 18.2D 818 18.2E 819 Esters; Carboxylic Anhydrides; 18.2F 820 Acyl Chlorides; 18.2G 820 Amides: 18.2H 820 Nitriles; 18.2I 821 18.2J 821 Spectroscopic Properties of Acyl Compounds; Preparation of Carboxylic Acids: 18.3 823 Nucleophilic Addition-Elimination at the Acyl Carbon; 826 18.4 Relative Reactivity of Acyl Compounds; 18.4A 828 Synthesis of Acid Derivatives; 18.4B 828 Acyl Chlorides; 18.5 828 18.5A 828 Synthesis of Acyl Chlorides; Reactions of Acyl Chlorides; 18.5B 829 Carboxylic Acid Anhydrides; 18.6 830 18.6A 830 Synthesis of Carboxylic Acid Anhydrides; Reactions of Carboxylic Acid Anhydrides;

18.6B 831

```
18.7 832
             Esters:
18.7A 832
             Synthesis of Esters: Esterification;
18.7B 835
             Base-Promoted Hydrolysis of esters: Saponification;
18.7C 837
             Lactones;
18.8 838
             Amides;
             Synthesis of Amides;
18.8A 838
18.8B 838
             Amides from Acyl Chlorides;
             Amides from Carboxylic Anhydrides;
18.8C 839
18.8D 840
             Amides from Esters;
             Amides from Carboxylic Acids and Ammonium Carboxylates;
18.8E 840
             Hydrolysis of Amides;
18.8F 841
             Nitriles from Dehydration of Amides;
18.8G 843
18.8H 843
             Hydrolysis of Nitriles;
18.8I 845
             Lactams;
18.9
             Derivatives of Carbonic Acid
      846
             Alkyl Chloroformates and Carbamates (Urethanes);
18.9A 846
             Decarboxylation of Carboxylic Acids;
18.10 848
18.10A850
             Decarboxylation of Carboxyl Radicals;
18.11 851
             Chemical Tests for Acyl Compounds;
             Summary of the Reactions of Carboxylic Acids and Their Derivatives;
      851
             Summary and Review Tools: Synthetic Connections of Carboxylic Acids and Related
      856
             Functional Groups: A 3-D Array of Linked Functional Groups.
             Key Terms and Concepts.
      857
             Study Problems: In-Chapter 18.1 - 18.18; End of Chapter 18.19 - 18.55
      858
             Learning Group Problems.
      866
             Special Topic B: Step Growth Polymers;
      867
B.1
      868
             Polyamides;
B.2
      870
             Polyesters:
             Polyurethanes;
B.3
      872
B.4
      873
             Phenol-Formaldehyde Polymers;
B.5
      874
             Cascade Polymers.
```

Week of Mar 9: SYNTHESIS AND REACTIONS OF β-DICARBONYL COMPOUNDS: MORE CHEMISTRY OF ENOLATE IONS.

Read and Study Chapter 19.

19.1	879	Introduction;
19.2	880	The Claisen Condensation: The Synthesis of β-keto Esters;
19.2A	883	Crossed Claisen Condensation;
19.2B	885	Acylation of Other Carbanions;
19.3	885	The Acetoacetic Ester Synthesis: Synthesis of Methyl Ketones (Substituted Acetones);
19.3A	885	Alkylation;
19.3B	889	Acylation;
19.3C	890	Acetoacetic Ester Dianion: Alkylation at the Terminal Carbon
19.4	891	The Malonic Ester Synthesis: Synthesis of Substituted Acetic Acids;
19.5	895	Further Reactions of Active Hydrogen Compounds;
19.6	896	Direct Alkylation of Esters and Nitriles;
19.7	897	Alkylation of 1,3- Dithianes;

- 19.8 898 The Knoevenagel Condensation;

19.9 898 Michael Additions: 19.10 900 The Mannich Reaction: 19.11 902 Synthesis of Enamines: Stork Enamine Reactions; 19.12 907 Barbiturates; 19.13 908 Summary of Important Reactions; Summary of Mechanisms: Some Synthetic Connections Involving β-Dicarbonyl Compounds; 911 912 Key Terms and Concepts. 912 Study Problems: In-Chapter 19.1 - 19.24; End of Chapter 19.25 - 19.51 919 Learning Group Problems. 922 Special Topic C: Thiols, Sulfur Ylides and Disulfides. C.1923 Preparation of Thiols; Physical Properties of Thiols; C.2 924 The Addition of Sulfur Ylides to Aldehydes and Ketones; C.3925 C.4 925 Thiols and Disulfides in Biochemistry; 927 Thiol Esters and Lipid Biosynthesis; Thiol Esters: 927 D.1 D.2 929 Biosynthesis of Fatty Acids; Biosynthesis of Isoprenoid Compounds; D.3 933 D.4 935 Biosynthesis of Steroids; D.5 939 Cholesterol and heart Disease.

Week of Mar 16: AMINES.

20.1

20.7A 963

941

Read and Study Chapter 20.

```
Nomenclature:
20.1A 942
             Arylamines;
20.1B 942
             Heterocyclic Amines;
             Physical Properties and Structure of Amines;
20.2 943
20.2A 943
             Physical Properties;
             Structure of Amines:
20.2B 944
             Basicity of Amines, Amine Salts;
20.3 945
20.3A 946
             Basicity of Aryl Amines;
             Basicity of Heterocyclic Amines;
20.3B 947
             Amines versus Amides;
20.3C 947
             Aminium Salts and Quaternary Ammonium Salts;
20.3D 948
             Solubility of Amines in Aqueous Acids;
20.3E 949
             Amines as Resolving Agents;
20.3F 950
             Some Biologically Important Amines;
20.4
      952
             Preparation of Amines;
20.5
      954
             Through Nucleophilic Substitution Reactions;
20.5A 954
             Preparation of Aromatic Amines through Reduction of Nitro Compounds;
20.5B 956
             Preparation of Primary, Secondary, or Tertiary Amines through Reductive Amination;
20.5C 957
             Preparation of Primary, Secondary, or Tertiary Amines through Reduction of Nitriles, Oximes
20.5D 958
             and Amides:
20.5E 960
             Preparation of Primary Amines through the Hofmann and Curtius Rearrangements;
             Reactions of Amines:
20.6
      962
             Oxidation of Amines;
20.6A 963
             Reactions of Amines with Nitrous Acid;
20.7
      963
```

Reactions of Primary Aliphatic Amines with Nitrous Acid;

```
Reactions of Primary Arylamines with Nitrous Acid;
20.7B 964
20.7C 965
             Reactions of Secondary Amines with Nitrous Acid;
             Reactions of Tertiary Amines with Nitrous Acid;
20.7D 966
             Arene Diazonium Salts, Replacement Reactions;
20.8
      966
20.8A 966
             Synthesis Using Diazonium Salts;
             The Sandmeyer Reaction: Replacement of the Diazonium Group by -Cl, -Br, -CN;
20.8B 967
             Replacement by -I;
20.8C 968
             Replacement by -F;
20.8D 968
20.8E 968
             Replacement by -OH;
             Replacement by Hydrogen: Deamination by Diazotization;
20.8F 968
20.9
      969
             Arene Diazonium Salts, Coupling Reactions;
             Reactions of Amines with Sulfonyl Chlorides;
20.10 972
             The Hinsberg Test;
20.10A972
20.11 974
             The Sulfa Drugs, Sulfanilamide;
             Chemotherapy;
20.11A974
             Sulfa Drugs;
20.11B974
             Essential Nutrients and Antimetabolites;
20.11C975
20.11D976
             Synthesis of Sulfa Drugs;
20.12 977
             Analysis of Amines;
             Chemical Analysis;
20.12A977
             Spectroscopic Analysis;
20.12B978
             Eliminations Involving Ammonium Compounds;
20.13 979
             The Hofmann Elimination;
20.13A979
20.13B980
             The Cope Elimination:
             Summary of Preparations and Reactions of Amines;
      981
             Key Terms and Concepts;
      984
             Study Problems: In-Chapter 20.1 - 20.20; End of Chapter 20.21 - 20.53
      895
             Learning Group Problems.
      992
      994
             Special Topic E: Alkaloids;
E.1
      994
             Alkaloids Containing a Pyridine or Reduced Pyridine Ring;
             Alkaloids Containing an Isoquinoline or Reduced Isoquinoline Ring;
E.2
      997
```

Week of Mar 23: PHENOLS AND ARYL HALIDES: NUCLEOPHILIC AROMATIC SUBSTITUTION. ORGANIC HALIDES AND ORGANOMETALLIC COMPOUNDS IN THE ENVIRONMENT.

Read and Study Chapter 21.

E.3

998

Read Special Topics F, G, and H, pages 1041-1071.

Alkaloids Containing Indole or Reduced Indole Rings.

- 21.1 1001 Structure and Nomenclature of Phenols; 21.A 1001 Nomenclature of Phenols: 21.2 1002 Naturally Occurring Phenols; Physical Properties of Phenols; 21.3 1003 Synthesis of Phenols; 21.4 1003 Laboratory Synthesis; 21.4A 1003 Industrial Synthesis; 21.4B 1005
 - 1. Hydrolysis of Chlorobenzene (Dow Process).
 - 2. Alkali Fusion of Sodium Benzenesulfonate.

3, From Cumene Hydroperoxide. 21.5 1008 Reactions of Phenols as Acids: 21.5A 1008 Strengths of Phenols as Acids; Distinguishing and Separating Phenols from Alcohols and Carboxylic Acids; 21.5B 1010 21.6 1010 Other Reactions of the O-H Group of Phenols; 21.6A 1011 Phenols in the Williamson Synthesis; 21.7 1011 Cleavage of Alkyl Aryl Ethers; 1012 Reactions of the Benzene Ring of Phenols; 21.8 21.9 1014 The Claisen Rearrangement; 21.10 1015 Quinones; 21.11 1016 Aryl Halides and Nucleophilic Aromatic Substitution; 21.11A1018 Nucleophilic Aromatic Substitution by Addition-Elimination: The SNAr Mechanism; 21.11B1019 Nucleophilic Aromatic Substitution through an Elimination-Addition Mechanism The Benzyne Mechanism; 21.11C1024 Phenylation; Spectroscopic Analysis of Phenols and Aryl Halides; 21.12 1025 Concept Map: Some Synthetic Connections of Phenols and Related Aromatic Compounds; 1026 Key Terms and Concepts. 1027 1027 Study Problems: In-Chapter 21.1 - 21.12; End of Chapter 21.13 - 21.38; 1032 Learning Group Problems 1035 Second Review Problem Set 1 to 24. 1041 Special Topic F: Electrocyclic and Cycloaddition Reactions. F.1 1041 Introduction; F.2 1041 Electrocyclic Reactions; F.2A 1043 Electrocyclic Reactions of 4n pi-Electron Systems; F.2B 1047 Electrocyclic Reactions of (4n + 2) pi-Electron Systems; F.3 1050 Cycloaddition Reactions; F.3A 1051 [2+2] Cycloadditions; F.3B 1053 [4+2] Cycloadditions. 1055 Special Topic G: Transition Metal Organometallic Compounds; G.1 1055 Introduction G.2 1056 Electron Counting: the 18-Electron Rule; G.3 1058 Metallocenes: Organometallic Sandwich Compounds; G.4 1059 Reactions of Transition Metal Complexex; G.5 Homogeneous Hydrogenation; 1061 G.6 1062 Carbon-Carbon Bond-Formation Using Rhodium Complexes Vitamin B12: A Transition Metal Biomolecule; G.7 1064 1066 Special Topic H: Organic Halides and Organometallic Compounds in the Environment; H.1 1066 Organic Halides as Insecticides; H.2 1068 Organic Halides as Herbicides; H.3 1069 Germicides; H.4 1069 Polychlorinated Biphenyls (PCBs); H.5 1070 Polybromobiphenyls (PBBs);

Week of Mar 30: CARBOHYDRATES AND LIPIDS (OPTIONAL).

Organometallic Compounds;

H.6

1070

- 1072 Carbohydrate recognition in Healing and Disease; 22.1 1073 Introduction to Carbohydrates; 22.1A 1073 Classification of Carbohydrates; 22.1B 1074 Photosynthesis and Carbohydrate Metabolism; Monosaccharides: 22.2 1076 22.2A 1076 Classification of Monosaccharides; D and L Designation of Monosaccharides; 22.2B 1076 22.2C 1077 Structural Formulas of Monosaccharides; 22.3 1081 Mutarotation: 22.4 1082 Glycoside Formation; 22.5 1085 Other Reactions of Monosaccharides; 22.5A 1085 Enolization, Tautomerization, and Isomerization; 22.5B 1085 Use of Protecting Groups in Carbohydrate Synthesis; 22.5C 1086 Formation of Ethers; 22.5D 1087 Conversion to Esters: Conversion to Cyclic Acetals 22.5E 1088 22.6 1088 Oxidation Reactions of Monosaccharides; 22.6A 1088 Benedict's or Tollens' Reagents: Reducing Sugars; 22.6B 1089 Bromine water: The Synthesis of Aldonic Acids; 22.6C 1090 Nitric Acid Oxidation: Aldaric Acids; 22.6D 1091 Periodate Oxidations: Oxidative Cleavage of Polyhydroxy Compounds; 22.7 1093 Reduction of Monosaccharides: Alditols; 22.8 1094 Reactions of Monosaccharides with Phenylhydrazine: Osazones; 22.9 1095 Synthesis and Degradation of Monosaccharides; 22.9A 1095 Kiliani-Fischer Synthesis; 22.9B 1097 The Ruff Degradation; 22.10 1097 The D family of Aldoses; Fischer's Proof of the Configuration of D-(+)-Glucose; 22.11 1099 22.12 1102 Disaccharides: 22.12A1102 Sucrose: 22.12B 1103 Maltose; Cellobiose; 22.12C1104 22.12D1107 Lactose; 22.13 1107 Polysaccharides; 22.13A1107 Starch; 22.13B 1109 Glycogen; Cellulose: 22.13C1110 22.13D1111 Celluose Derivatives; 22.14 1113 Other Biologically Important Sugars;
- Sugars That Contain Nitrogen; Glycosylamines; 22.15A1114
- 22.15B1115 Amino Sugars;

22.15 1114

- Glycolipids and Glycoproteins of the Cell Surface: Cell Recognition and the Immune System; 22.16 1116
- 22.17 1119 Carbohydrate Antibiotics.
 - 1120 Summary of Reactions of Carbohydrates;
 - Summary and Review Tools: A Summary of Reactions Involving Monosaccharides;
 - 1122 Key Terms and Concepts.
 - 1122 Study Problems: In-Chapter 22.1 - 22.19; End of Chapter 22.20 - 21.45;
 - **Learning Group Problems** 1127

1142 LIPIDS (Chapter 23) 1129 Insulation for Nerves: 23.1 1130 Introduction to Lipids; 23.2 1131 Fatty Acids and Triacylglycerols; 23.2A 1133 Hydrogenation of Triacylglycerols; 23.2B 1134 Biological Functions of Triglycerols; 23.2C 1135 Saponification of Triglycerols; 23.2D 1138 Reactions of Carboxyl Groups of Fatty Acids; 23.2E 1139 Reactions of the Alkenyl Chain of Unsaturated Fatty Acids; 23.3 1139 Terpenes and Terpenoids; 23.3A 1143 Natural Rubber; 23.4 1143 Steroids: 23.4A 1143 Structure and Systematic Nomenclature of Steroids; 23.4B 1145 Cholesterol; 23.4C 1147 Sex Hormones; 23.4D 1149 Ardrenocortical Hormones: 23.4E 1150 **D** Vitamins 23.4F 1150 Other Steroids: 23.4G 1151 Reactions of Steroids; 23.5 1153 Prostaglandins; 23.6 1154 Phospholipids and Cell Membranes; 23.6A 1155 Phosphatides; Derivatives of Sphingosine; 23.6B 1157 23.7 1158 Waxes; 1159 Summary of the Reactions of Lipids; 1159 Key Terms and Concepts. Study Problems: In-Chapter 23.1 - 23.11; End of Chapter 23.12 - 23.26; 1160 1164 Learning Group Problems. Week of April 6: AMINO ACIDS AND PROTEINS (OPTIONAL). Read Chapter 24. Catalytic Antibodies: Designer Catalysts 1166

```
24.1
      1167
             Introduction:
24.2
      1168
             Amino Acids:
24.2A 1168
             Structures and Names:
24.2B 1168
             Essential Amino Acids;
24.2C 1170
             Amino Acids as Dipolar Ions;
24.3 1173
             Laboratory Synthesis of □-Amino Acids;
             Direct Ammonolysis of an □-Halo Acid;
24.3A 1173
             From Potassium Phthalimide;
24.3B 1173
24.3C 1174
             The Strecker Synthesis;
24.3D 1175
             Resolution of DL-Amino Acids;
24.3E 1175
             Asymetric Syntheses of Amino Acids;
24.4 1177
             Analysis of Polypeptides and Proteins;
24.4A 1179
             Hydrolysis;
             Primary Structure of Polypeptides and Proteins;
24.5
      1181
```

- 24.5A 1181 Edman Degradation;
- 24.5B 1182 Sanger N-Terminal Analysis;
- 24.5C 1183 C-Terminal Analysis;
- 24.5D 1183 Complete Sequence Analysis;
- 24.5E 1184 Peptide Sequencing Using Mass Spectroscopy and Sequence Databases;
- 24.6 1185 Examples of Polypeptides and Proteins Primary Structure;
- 24.6A 1187 Oxytocin and Vasopressin;
- 24.6B 1187 Insulin;
- 24.6C 1188 Other Polypeptides and Proteins
- 24.7 1189 Polypeptide and Protein Synthesis;
- 24.7A 1190 Protecting Groups;
- 24.7B 1191 Activation of Carboxyl Group;
- 24.7C 1192 Peptide Synthesis;
- 24.7D 1193 Automated Peptide Synthesis;
- 24.8 1195 Secondary, Tertiary, and Quaternary Structures of Proteins;
- 24.8A 1195 Secondary Structure;
- 24.8B 1199 Tertiary Structure;
- 24.8C 1199 Quaternary Structure;
- 24.9 1200 Introduction to Enzymes;
- 24.10 1202 Lysozyme: Mode of Action of an Enzyme;
- 24.11 1203 Serine Proteases;
- 24.12 1210 Haemoglobin, a Conjugated Protein;
- 24.13 1211 Purification and Analysis of Polypeptides and Proteins
- 24.13A1211 Purification;
- 24.13B1211 Analysis;
- 24.14 1213 Proteomics;
 - 1216 Key Terms and Concepts.
 - 1217 Study Problems: In-Chapter 24.1 24.16; End of Chapter 24.17 24.27.
 - 1219 Learning Group Problems

Week of April 7: REVIEW.

REFERENCES TO ORGANIC LECTURE AND LABORATORY TEXTS

Solomons, T.W.G., and Fryhle, C.B., Organic Chemistry, 8th Edition, Wiley, 2002. ISBN 0-471-41799-8, QD253.2.S65 2003

Solomons, T.W.G., Organic Chemistry, 5th/6th/7th Editions, Wiley, 1992/95/2000/02. QD251.2.S66.

Solomons, T.W.G., Study Guide and Solutions Manual to Organic Chemistry, 5th/6th/7th Editions, Wiley, 1992/95/2000/02. ISBN 0-471-83661-3.

Solomons, T.W.G., Fundamentals of Organic Chemistry, 3rd/4th/5th Editions, Wiley, 1990/94/97, ISBN 0-471-14649-8 QD251.2.S657 1997.

Wade, L.G.(Jr), Organic Chemistry, 1st/2nd/3rd/4th/5th/6th Editions, Pearson/Prentice-Hall, 1987/91/95/99/2003/06ISBN 0-13-147871-0, QD 251.3.W 33 2006.

Simek, J.W., Solutions Manual to Organic Chemistry by Wade, Prentice-Hall, 1991/95.

Morrison, R.T., and Boyd, R.N., Organic Chemistry, Allyn and Bacon, 1973, 1983, and 1987 Editions, QD 251.2.M 67.

Bailey, P.S., Jr, Bailey, C.A., Organic Chemistry: A brief Survey of Concepts and Applications, 6th Edition, Prentice Hall, 2000, ISBN 0-13-924119-1, QD251.2.B34 2000 547-dc21

Baker, A.D., Engel, R., Organic Chemistry, West, 1992, QD251.2.B345.

Boxer, R., Essential of Organic Chemistry, Wm. C. Brown, 1997, ISBN 0-697-14060-1.

Brown, W.H., Introduction to Organic Chemistry, Saunders College Publishing/Harcourt Brace College Publishers, 1997, ISBN 0-03-016914-3.

Brown, W.H., Foote, C.S., B.L. Iverson, Organic Chemistry, 4th Edition, Thomson/Brooks /Cole, 1998, ISBN 0-534-46773-3.

Bruice, P.Y., Organic Chemistry, 1st/2nd/3rd/4th/5th Editions, 1995/98/2001/04/07, Pearson/Prentice Hall.

Carey, F.A., Organic Chemistry, 1st/2nd/3rd/4th/5th Editions, 1987/92/96/2000/03 McGraw-Hill, ISBN 0-07-242458-3, QD 251.3.C37 2003.

Carroll, F.A., Perspectives on Structure and Mechanism in Organic Chemistry, Brooks/Cole, 1998, ISBN 0-534-24948-5, QD476.C375 1998 547-dc20.

Clayden, J., Greeves, N., Warren, S., Wothers, P., Organic Chemistry, Oxford University Press, 2001, ISBN 0198503466

Ege, S.N., Organic Chemistry, 2nd/5th Editions, Heath/Houghton Mifflin1989/2004, ISBN 0-618-31809-7.

Fessenden, R.J., and Fessenden, J.S., Organic Chemistry, 3rd/4th/5th/6th Editions, 1986/90/94/98, Brooks/Cole, QD 251.2.F 49.

Fox, M.A., Whitesell, J.K., Organic Chemistry, 2nd/3rd Editions, Jones and Barlett, 1997/2003, ISBN 0-7637-0178-5, QD251.2.F69 1997 & ISBN 0-7637-2197-2, QD251.3.F69 2003.

Hornback, J.M., Organic Chemistry, 1998, Brooks/Cole, QD 253.H66 1998. ISBN 0-534-35254-5

Loudon, G.M., Organic Chemistry, 4th Edition, Oxford University Press, 2002, ISBN 0-19-511999-1, QD 252.3.L68 2001.

Lowry, T.H., and Richardson, K.S., Mechanism and Theory in Organic Chemistry, 3rd Edition, Harper & Row, 1987, QD471.L68, ISBN 0-06-044084-8.

March, J., Advanced Organic Chemistry, 4th Edition, Wiley, 1992, QD251.2.M37, ISBN 0-471-60180-2

Miller, B., Advanced Organic Chemistry: Reactions and Mechanisms, Prentice Hall, 1998, ISBN O-13-373275-4

Millam, M.J., Reaction Guide for the Brief Organic Chemistry Course, Heath, 1988, ISBN 0-669-13247-0

Mackie, R.K., Smith, D.M., and Aitken, R.A., Guide Book to Organic Synthesis, 2nd Edition, Longman Scientific and Technical, 1990, ISBN 0-582-03375-6.

McMurray, J., Organic Chemistry, 1984/88/92/96/2004/08 (7th Edition), Thomson/Brooks/Cole.

McMurray, J., Fundamentals of Organic Chemistry, 1990, 1998 (4th Edition), 2000 (5th Edition), Brooks/Cole, ISBN 0-534-37366-6, QD 251.2.M4.

McMurray, J., Castellion, M.E., Fundamentals of General, Organic and Biological Chemistry, 3rd Edition., ISBN 0-13-918517-3.

Ouellette, R.J., and Rawn, J.D., Organic Chemistry, Prentice Hall, 1996, QD 251.2.094.

Raber, D.J., and Raber, N.K., Organic Chemistry, West, 1988, QD251.2.R33.

Streitwieser, A.(Jr), and Heathcock, C.H., Introduction to Organic Chemistry, 3rd Edition, MacMillan, 1985, QD 251.2S 76.

Pine, S.H., Organic Chemistry, McGraw-Hill, 5th ed., 1987.

Vollhardt, K.P.C., Shore, N.E., Organic Chemistry, 2nd Edn. Freeman, 1994. QD 251.2.V 65.

Vollhardt, K.P.C., Organic Chemistry, Freeman, 1987. QD 251.2.V 65.

Sykes, A Guidebook to Mechanisms in Organic Chemistry, Longmans, 6th ed., 1987.

Pavia, D.L., Lampman, G.M., Kriz, G.S., and Engel, R.G. Introduction to Organic Laboratory Techniques: a Microscale Approach, 1st/2nd Editions, Saunders, 1990/95, ISBN 0-03-025418-3/0-03-006232-2.

Pavia, D.L., Lampman, G.M., and Kriz, G.S., Introduction to Organic Laboratory Techniques, Saunders, 3rd ed., 1988, QD 261.

Fessenden, R.J., and Fessenden, J.S., Organic Laboratory Techniques, 2nd Edition, 1993, Brooks/Cole, QD 261.F466 1993.

Mayo, D.W., Pike R.M., and Trumper, P.K., Microscale Organic Laboratory: with Multistep and Multistep Syntheses, 3rd Edition, Wiley, 1994, QD 261.M38.

Mayo, D.W., Pike R.M., and Butcher, S.S., Microscale Organic Laboratory, Wiley, 1986, QD 261.M38.

Mayo, D.W., Pike R.M., Butcher, S.S., and Trumper, P.K., Microscale Techniques for the Organic Laboratory, Wiley, 1991, ISBN 0471-62192-7 (pbk).

Most, C.F.(Jr), Experimental Organic Chemistry, Wiley, 1988, QD261.M78.

Wilcox, C.F.(Jr), Experimental Organic Chemistry: a Small-Scale Approach, 1st/2nd Editions, MacMillan, 1988/95, QD261.W497./QD261.W497, ISBN 0-02-427691-X.

Fieser, L.F., and Williamson, K.L., Organic Experiments, 7th edition, Heath, 1992, ISBN 0-669-24344-2.

Rappoport, Z., CRC Handbook of Tables for Organic Compound Identification, 3rd edition, CRC Press Inc, 1973, ISBN 0-8493-0303-6.

Svoronos, P., and Sarlo, E., Organic Chemistry Laboratory Manual, Wm. C. Brown, 1994, ISBN 0-697-14799-1.

Williamson, K.L., Microscale Organic Experiments, Heath, 1987.

Williamson, K.L., Macroscale and Microscale Organic Experiments, 4th Edition, Houghton Mifflin, 2003, ISBN 0-618-19702-8.

Zanger, M., and McKee, J.R., Small Scale Synthesis: A Laboratory Textbook of Organic Chemistry, Wm. C. Brown, 1995, ISBN 0-697-20957-1.

Zubrick, J.W., The Organic Chem Lab Survival Manual: A Student's Guide to Techniques, 4th Edition, Wiley, 1997, ISBN 0-471-12948-8.

Rappoport, Z., CRC Handbook of Tables for Organic Compound Identification, 3rd Edition, CRC Press, 1964, ISBN 0-8493-0303-6.

Weast, R.C. (Editor), CRC Handbook of Chemistry and Physics, Annual Editions, CRC Press.

The Aldrich Catalog/Handbook of Fine Chemicals, Aldrich Chemical Company.

Note: Many of these books are located in Room J207. Some of the texts are also located in the College Library. Additional items are located in J207, J211, the Chemistry Laboratories and the College Library, e.g.

- 55. Encyclopaedia's on Chemistry, Science and Technology;
- 56. Pouchert, C.J., The Aldrich Library of Infrared Spectra, 3rd Edition, Aldrich Chemical Co, 1981;
- 57. Pouchert, C.J., The Aldrich Library of FT-IR Spectra, Aldrich Chemical Co, 1985;
- 58. Pouchert, C.J., The Aldrich Library of NMR Spectra, Aldrich Chemical Co, 1983;
- 59. Pouchert, C.J., The Aldrich Library C-13 and H-1 FT- NMR Spectra, Aldrich Chemical Co, 1992;
- 60. Chemical and Engineering News, Jacobs M. (Editor), Published Weekly by the American Chemical Society (available on-line in J.P. Sloan's office);
- 61. Journal of Agricultural and Food Chemistry, Seiber, J.N., (Editor), Published Monthly by the American Chemical Society (available on-line in J.P. Sloan's office).

Document Reference: H\CH2630\CH2630A3 08-09out.doc