

THE COLLEGE OF THE BAHAMAS
SCHOOL OF NATURAL SCIENCES & ENVIRONMENTAL STUDIES
CHEMISTRY DEPARTMENT

CHEM 330 – ORGANIC CHEMISTRY II

COURSE DESCRIPTION:

This course explores the major groups of organic chemicals. It guides the student through an in-depth investigation of functional group reactions, structures and properties. Also, it seeks to encourage students to consider the roles of organic chemicals in the world around us and to explore environmental and industrial effects and applications.

OBJECTIVES:

After successful completion of this course, students will be able to:

1. List eight major groups of organic compounds
2. Describe the structure of major organic compounds
3. State the formal IUPAC names for selected compounds
4. Describe substitution, addition, oxidation, dehydration and hydrolysis reactions
5. Discuss the effects of reaction conditions on reaction rates
6. Predict the chemical reactivity of an organic compound by analyzing its structure
7. Explain why different compounds use different reaction mechanisms
8. Differentiate between electrophilic and nucleophilic mechanisms
9. Synthesize selected organic compounds
10. Analyze and identify organic chemicals through experimentation
11. Evaluate the effect of organic compounds on the environment.

COURSE CONTENT:

1. **Structure and Properties** [Review of some important concepts]

The Chemical bond. Quantum mechanics. Atomic orbitals. Electronic configuration. Pauli exclusion principle. Molecular orbitals. The covalent bond. Hybrid orbitals- sp , sp^2 , sp^3 . Unshared pairs of electrons. Intramolecular forces. Bond dissociation energy. Homolysis and heterolysis. Polarity of bonds. Polarity of molecules. Structure and physical properties. Melting point. Intermolecular forces. Boiling point. Solubility. Acids and bases.

2. **Methane**

Structure of methane. Physical properties. Source. Reactions Oxidation. Heat of combustion. Chlorination: a substitution reaction. Control of chlorination. Reaction with other halogens: halogenation. Relative reactivity. Reaction mechanisms. Mechanism of chlorination. Free radicals. Chain reactions. Inhibitors. Heat of reaction. Energy of activation. Progress of reaction: energy changes. Rate of reaction. Relative rates of reaction. Relative reactivities of halogens toward methane. An alternative mechanism for halogenation. Structure of the methyl radical. Sp^2 Hybridization. Transition state. Reactivity and development of the transition state. Chlorofluorocarbons and the ozone shield. Molecular formula: its fundamental importance.

3. **Alkanes Free-Radical Substitution**

Classification by structure: the family. Structure of ethane Free rotation about the carbon-carbon single bond. Conformations. Torsional strain. Propane and butanes. Conformations of n-butane. Van der Waals repulsion. Higher alkanes. The homologous series. Nomenclature. Alkyl groups. Common names of alkanes. IUPAC names of alkanes. Classes of carbon atoms and hydrogen atoms. Physical properties. Industrial source. Industrial source vs. laboratory preparation. Preparation-

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The Grignaud reagent: an organometallic compound. Coupling of alkyl halides with organometallic compounds. Reactions-Hydrogenation Mechanism of halogenation. Orientation of halogenation. Relative reactivities of alkanes toward halogenation. Ease of abstraction of hydrogen atoms. Energy of activation. Stability of free radicals. Ease of formation of free radicals. Transition state for halogenation. Orientation and reactivity. Reactivity and selectivity. Non-rearrangement of free radicals. Isotopic tracers. Combustion. The greenhouse effect.
Pyrolysis: cracking
Determination of structure. Analysis of alkanes

4. Stereochemistry I Stereoisomers

Stereochemistry and stereoisomerism. Isomer number and tetrahedral carbon. Optical activity. Plane-polarized light The polarimeter. Specific rotation. Enantiomerism: the discovery. Enantiomerism and tetrahedral carbon. Enantiomerism and optical activity. Prediction of Enantiomerism. Chirality. The chiral center. Enantiomers. The racemic modification. Optical activity: a closer look. Configuration. Specification of configuration: *R* and *S* Sequence rules. Diastereomers. *Meso* structures. Specification of configuration: more than one chiral center. Conformational isomers. Reactions involving stereoisomers. Generation of a chiral center. Synthesis and optical activity. Reactions of chiral molecules with optically active reagents. Resolution. Reactions of chiral molecules. Mechanism of free-radical chlorination

5. Alkyl Halides Nucleophilic Aliphatic Substitution

Homolytic and heterolytic chemistry. Relative rates of competing reactions. Structure. The functional group. Classification and nomenclature. Physical properties. Preparation. Reactions-Nucleophilic aliphatic substitution. Nucleophiles and leaving groups. Rate of reaction: effect of concentration. Kinetics. Kinetics of nucleophilic aliphatic substitution. Second-order and first-order reactions. Nucleophilic aliphatic substitution: duality of mechanisms. The S_N2 reaction: mechanism and kinetics. The S_N2 reaction: Stereochemistry. Inversion of configuration. The S_N2 reaction: reactivity. Steric hindrance. The S_N1 reaction: mechanism and kinetics. Rate-determining step. Carbocations. Structure of carbocations. Stabilization of carbocations. Accommodation of charge. Polar effects. The S_N1 reaction: reactivity. Ease of formation of carbocations. Rearrangement of carbocations. S_N2 vs S_N1 . Analysis of alkyl halides

6. Alcohols and Ethers

ALCOHOLS

Introduction. Structure of alcohols. Classification of alcohols. Nomenclature of alcohols. Physical properties of alcohols. Industry source. Fermentation of carbohydrates. Fuel from carbohydrates. Carbon dioxide balance. Ethanol. Preparation of alcohols. Reactions of alcohols. Alcohols as acids and bases. Reaction of alcohols with hydrogen halides. Acid catalysis. Formation of alkyl sulfonates. Oxidation of alcohols. Analysis of alcohols.

ETHERS

Structure and nomenclature of ethers. Physical properties of ethers. Industrial sources of ethers. Dehydration of alcohols. Preparation of ethers – Williamson synthesis. Reactions of ethers. Cleavage by acids.

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CHEM 330 – ORGANIC CHEMISTRY II

7. Role of the Solvent *Secondary Bonding*

Role of the solvent. Secondary bonding. Solubility: non-ionic solutes, Protic and aprotic solvents. Ion pairs. The S_N1 reaction: role of the solvent. Ion-dipole bonds. The S_N2 reaction: role of the solvent: Protic and aprotic solvents. The S_N2 vs S_N1 : effect of the solvent. Solvolysis. Nucleophilic assistance by the solvent.

8. Alkenes 1. Structure and preparation. Elimination

Unsaturated hydrocarbons. Structure of ethylene. The carbon-carbon double bond. Propylene. Hybridization and orbital size. The butylenes. Geometric isomerism. Higher alkenes. Names of alkenes. Physical properties. The organic chemistry of vision. Industrial source. Preparation - Dehydrohalogenation. of alkyl halides: 1, 2 elimination. Kinetics of Dehydrohalogenation Duality of mechanism. The E_2 mechanism. Evidence for the E_2 , mechanism-Kinetics and absence of rearrangements, Isotope effects. Absence of hydrogen exchange. The element effect. The E_2 reaction: orientation and reactivity. The $E1$ mechanism. Evidence for the E_1 mechanism. Evidence for the E mechanism. The E_1 reaction: orientation. Elimination E_2 vs E_1 . Elimination vs substitution. Dehydration of alcohols.

9. Alkenes 11. Reactions of the carbon-carbon Double Bond *Electrophilic and Free-Radical Addition*

Reactions of alkenes

Reactions at the carbon-carbon double bond. Addition

Hydrogenation. Heat of hydrogenation

Addition of hydrogen halides. Markovnikov's rule. Regioselective reactions

Addition of hydrogen bromide. Peroxide effect. Addition of sulfuric acid. Addition of water.

Hydration

Electrophilic addition: mechanism rearrangements, orientation and reactivity.

Addition of halogens. Mechanism of addition of halogens

Halohydrin formation: addition of the elements of hypohalous. Acids

Addition of alkenes. Dimerization. Addition of alkenes. Alkylation. Oxymercuration-demercuration. Hydroboration-oxidation.

Orientation of hydroboration. Mechanism of hydroboration

Free-radical addition. Mechanism of the peroxide-initiated addition of HBr.

Orientation of free-radical addition. Other free-radical additions.

Free-radical polymerization of alkenes

Hydroxylation. Formation of 1,2 diols.

Cleavage: determination of structure by degradation. Ozonolysis. Analysis of alkenes

10. Stereochemistry II. Stereoselective and Stereospecific Reactions

Organic chemistry in three dimensions. Stereochemistry of addition of halogens to alkenes.

Syn- and *anti*addition. Mechanism of addition of halogens to alkenes. Stereochemistry of the $E2$ reaction. *Syn*-and *anti*-elimination. Stereospecific reactions. Stereoselectivity vs. stereospecificity. A look ahead

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11. Conjugation and Resonance Dienes

The carbon-carbon double bond as a substituent
Free-radical halogenation of alkenes: substitution vs. addition
Free-radical substitution in alkenes: allylic rearrangement. Symmetry of the allyl radical. The theory of resonance. The allyl radical as a resonance hybrid. Stability of the allyl radical. Orbital picture of the allyl radical. Using the resonance theory. Resonance stabilization of alkyl radicals. Hyperconjugation. The allyl cation as a resonance hybrid. Nucleophilic substitution in allylic substrates: S_N1 Reactivity, Allylic rearrangement Stabilization of carbocations: the resonance effect. Nucleophilic substitution in allylic substrates: S_N2 . Nucleophilic substitution in vinylic substrates. Vinylic cations. Dienes: structure & properties. Stability of conjugated dienes. Resonance in conjugated dienes. Resonance in alkenes, Hyperconjugation. Ease of formation of conjugated dienes: orientation of elimination. Electrophilic addition of conjugated dienes. 1,4-Addition, 1,2-vs. 1,4-Addition. Rate of Equilibrium. Free-radical polymerization of dienes. Rubber and rubber substitutes. Isoprene and the isoprene rule.
Analysis of dienes.

12. Alkynes

Structure of ethyne. The carbon-carbon triple bond. Higher alkynes. Nomenclature. Physical properties of alkynes. Reactions of alkynes. Industrial source of acetylene. Preparation of alkynes. Reactions of alkynes. Reduction of alkynes. Electrophilic addition of alkynes. Hydration of alkynes. Tautomerism. Acidity of alkynes. Very weak acids. Reactions of metal acetylides. Synthesis of alkynes.
Formation of carbon-carbon bonds. Role-played by organometallic compounds. Analysis of alkynes.

13. Cyclic Aliphatic Compounds

Open-chain and cyclic compounds. Nomenclature.
Industrial source. Preparation
Reactions-reactions of small-ring compounds. Cyclopropane and cyclobutane.
Baeyer strain theory.
Heats of combustion and relative stabilities of the cycloalkanes. Orbital picture of angle strain. Factors affecting stability of conformations. Conformations of cycloalkanes.
Equatorial and axial bonds in cyclohexane.
Stereoisomerism of cyclic compounds. *Cis and trans isomers*
Stereoisomerism of cyclic compounds. Conformational analysis
Stereochemistry of elimination from alicyclic compounds
Carbenes. Methylene. Cycloaddition.
Addition of substituted carbenes. 1,1-Elimination
Cyclic ethers. Crown ethers. Host-guest relationship.
Epoxides. Structure and preparation.
Reactions of epoxides.
Acid-catalyzed cleavage of epoxides. Anti-Hydroxylation
Base-catalyzed Cleavage of epoxides. Orientation of cleavage of epoxides
Analysis of alicyclic compounds.

14. Aromaticity Benzene

Aliphatic and aromatic compounds. Structure of benzene
Molecular formula. Isomer number. Kekulé structure
Stability of the benzene ring. Reactions of benzene.

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CHEM 330 – ORGANIC CHEMISTRY II

Stability of the benzene ring. Heats of hydrogenation and combustion. Carbon-carbon bond lengths in benzene. Resonance structure of benzene. Orbital picture of benzene. Representation of the benzene ring. Aromatic character. The Hückel $4n+2$ rule. Nomenclature of benzene derivatives. Polynuclear aromatic hydrocarbons. Naphthalene. Quantitative elemental analysis: Nitrogen and sulfur.

15. Electrophilic Aromatic Substitution

Effect of substituent groups. Determination of orientation. Determination of relative reactivity. Classification of substituent groups. Orientation in disubstituted benzenes. Orientation and synthesis. Mechanism of nitration, sulfonation, Friedel-Crafts alkylation, halogenation. Desulfonation, Mechanism of protonation. Mechanism of electrophilic aromatic substitution: a summary. Mechanism of electrophilic aromatic substitution: the two steps. Reactivity and orientation. Theory of reactivity. Theory of orientation. Electron release via resonance. Effect of halogen on electrophilic aromatic substitution. Relation to other carbonation reactions. Electrophilic substitution in naphthalene.

16. Aromatic-aliphatic Compounds *Arenes and Their Derivatives*

The aromatic ring as a substituent. Aromatic-aliphatic hydrocarbons: arenes. Structure and nomenclature of arenes and their derivatives. Physical properties. Industrial source of alkylbenzenes. Preparation of alkylbenzenes. Friedel-Crafts alkylation. Mechanism of Friedel-Crafts alkylation. Limitations of Friedel-Crafts alkylation. Reactions of alkylbenzenes. Oxidation of alkylbenzenes. Electrophilic aromatic substitution in alkylbenzenes. Halogenation of alkylbenzenes: ring *vs.* side chain. Side-chain halogenation of alkylbenzenes. Resonance stabilization of the benzyl radical. Triphenylmethyl: a stable free radical. Stability of the benzyl cation. Nucleophilic substitution in benzylic substrates. Preparation of alkenylbenzenes. Conjugation with the ring. Reactions of alkenylbenzenes. Addition to conjugated alkenylbenzenes. Analysis of arenes.

ASSESSMENT:

3 Class Tests	30%
1 assignment/Project	10%
Mid Term Examination	20%
Final Examination	40%

TEXTBOOK:

Morson, Robert T., Boyd Robert N., Organic Chemistry. Allyn Bacon Publishers, 7th Edition. ISBN 0132678160

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Supplementary Text:

Hornback, Joseph M., Organic Chemistry. Brooks/Cole Publishing company, 1998,
ISBN 0-534-35254-5

Iverson, B.L. and Iverson, S.A., Student Study Guide and Problems Book for Organic Chemistry,
Volumes 1 and 2. Saunders College Publishing Co., 1995

Bruice, Paula Yurkanis. Organic Chemistry, 2nd Edition. Prentice Hall, 1999
Wade Jr., L.G. Organic Chemistry, 4th Edition. Prentice Hall, 1999

**Scientific American; Scientific American In. 1995-1991: ISSN 0036-8733

**Educational in Chemistry; The Royal Society of Chemistry 1999; ISSN 0013-7613

**Journal of research in Science Teaching; John Wiley and sons Inc. 1999; ISSN 0022-4308

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RATIONALE:

Much of the new medicinal and industrial chemicals are based on organic compounds. These compounds can have a profound effect on our lifestyles, industrial productions and our environment. Thus the study of organic chemistry is an important endeavor for a science major.

Organic chemistry is of particular importance and relevance to individuals pursuing careers in Medicine, Environmental Science, Biochemical/Biomedical Research and Analysis. Presently, all of these are areas in which there is a national need for qualified personnel.

It should be recognized that organic chemistry is a very broad area to cover. In Chemistry 230, students are introduced to the basic backbone of organic chemistry. The need for additional details and further understanding of essential organic chemistry can be satisfied by Organic Chemistry II, Chemistry 330.