

Analytcs

Explain the Lambert-Beer law. What types of molecular vibrations exist?

Explain the physical effect underlying NMR spectroscopy. What information can be obtained from an NMR spectrum?

What are diastereotopic and homotopic protons (give one example) and how do they differ in ^1H NMR?

What is the anisotropy effect?

Explain the physical principles of mass spectrometry. Name three ionization methods used in mass spectrometry and briefly explain each.

Calculate the isotopic distribution of the molecular peak for a compound, for instance with:

a) 2 bromine atoms and 1 chlorine atom

b) 1 bromine atom and 2 chlorine atoms ($^{35}\text{Cl}:^{37}\text{Cl}\approx 3:1$; $^{79}\text{Br}:^{81}\text{Br}\approx 1:1$)

Explain the difference between fluorescence and phosphorescence using the Jablonski term diagram.

Explain the basic concepts of column chromatography and mention different methods.

Stereochemistry

Explain the terms *constitution*, *configuration*, and *conformation*, and give an example for each.

Explain the terms enantiomers and diastereomers using suitable examples. How can these be separated?

What does *ee* or *de* mean? What analytical methods can be used to determine these values?

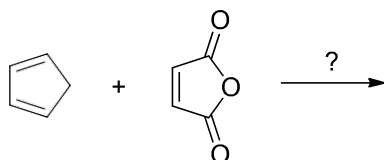
Determine the absolute configuration of chemical compounds using the CIP rules.

Explain the terms *retention*, *inversion*, and *racemization* using an example, and describe the difference between $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ in terms of stereochemistry.

Describe *E/Z* and *cis/trans* isomers with appropriate examples.

What is the difference between chemo-, regio-, and enantioselectivity?

Explain the terms *exo* and *endo* based on the following reaction:



Nucleophilic Substitution / Elimination / Addition

Compare S_N1 and S_N2 using energy diagrams. What is the fundamental difference between the two reactions in terms of reaction kinetics and the stereochemistry of the products formed?

Describe the influence of the following factors on the mechanism of nucleophilic substitution: nucleophile strength; leaving group; solvent; substrate structure (degree of substitution).

Explain the mechanisms of the different substitution reactions (S_Ni , S_N1 , and S_N2) and their stereochemistry. Explain the factors influencing whether a nucleophilic aliphatic substitution proceeds via S_N1 or S_N2 and discuss their energy diagrams. What is the effect of the solvent?

What are ambident nucleophiles? Give examples of different ambident nucleophiles and explain under which reaction conditions which products are formed by which mechanism.

Explain the principle of the Finkelstein reaction and give an example.

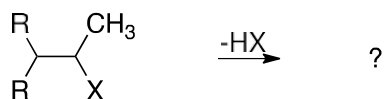
What is the difference between Hofmann alkylation, Hofmann elimination, and Gabriel synthesis?

What properties characterize a good leaving group and a good nucleophile? Provide an example for each. Define the terms nucleophilicity and basicity. Give an example of a non-nucleophilic base. Why does the compound act as a base but not as a nucleophile?

Describe all the elementary steps (mechanism) as well as the energy diagram of an E1 and E2 reaction using appropriate examples.

Discuss the structural factors (with respect to both reactants) for E1 vs. E2 vs. E1cb using appropriate examples.

Explain using the following example why Hofmann and Saytzeff eliminations of comparable substrates yield different products.

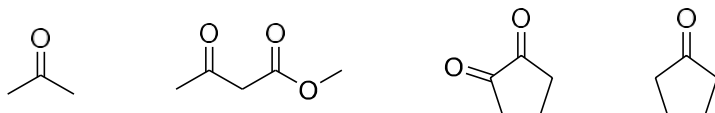


Carbonyl Compounds

Explain the different reactivities of aldehydes and ketones, as well as in comparison to carboxylic esters and amides, during reactions with nucleophiles.

Give an example of how to convert an aldehyde into a ketone (including the mechanism and reagents).

Arrange the following products in order of increasing enol character, including justification.



Describe all the elementary steps of a Wittig reaction using an appropriate example, including the mechanism. How does the stability of the phosphonium ylide affect the configuration of the product (stereochemistry)?

Explain the difference between aldol addition and aldol condensation. Provide a specific reaction for each, including the mechanism.

Describe a Stork reaction (enamine alkylation) using an appropriate example. What is the advantage of synthesizing an enamine followed by alkylation compared to a direct base-catalyzed alkylation of the C-H acidic starting material?

Explain the mechanism of the Knoevenagel reaction using an example.

How can a carbonyl group be reduced to an alcohol? Provide two different reagents and discuss the different mechanisms.

Describe the Wolff-Kishner and Clemmensen reductions of ketones to alkanes. Discuss the relevant differences between these two methods.

Explain the mechanism of the haloform reaction. What are the reactants and products?

Explain the mechanism of the Mannich reaction. What are the reactants and products?

Describe the different reactivities of NaBH₄ and LiAlH₄ in the reduction of aldehydes, ketones, and esters. Discuss the different mechanisms of reducing an aldehyde with NaBH₄ in methanol and LiAlH₄ in THF.

Carboxylic Acid Derivatives

Name 5 carboxylic acid derivatives and rank their reactivity (including justification) in reactions with nucleophiles.

Explain the differences between S_N2 and S_N2t using specific examples.

Describe the synthesis of esters starting from an acid and a primary or tertiary alcohol (including reagents, intermediates, and mechanism).

Explain the mechanism of the Claisen condensation using a specific example. What compounds are obtained in the intramolecular variant (Dieckmann condensation)? Also, describe the mechanism of the final hydrolysis and decarboxylation.

Explain the mechanisms of the Curtius, Schmidt, Hofmann, and Lossen degradations.

Describe the Arndt-Eistert homologation, including the mechanism.

Explain the production of acyl chlorides by reacting $R-COOH$ with thionyl chloride. Discuss the different mechanisms of this reaction, both with and without the addition of a catalytic amount of DMF.

Explain the activation of a carboxylic acid using carbodiimide reagents (including the mechanism).

Aromatics

What conditions must be met for a compound to be classified as aromatic? Explain the Hückel rule and provide an example for each $n=0$ to $n=3$.

Provide the general mechanism and the energy profile of an S_EAr (electrophilic aromatic substitution), including σ - and π -complexes.

To which position does the nitro group direct an electrophilic substitution on benzene, and to which position does the methoxy group direct it? Explain both cases using resonance structures.

Describe the Friedel-Crafts alkylation and acylation. How do these two reactions differ (incl. the required equivalents of the Lewis acid)?

Describe the mechanism of nucleophilic aromatic substitution using a specific example (including the energy profile).

Explain the effects of the following substituents on reaction kinetics (activating vs. deactivating in comparison to benzene) and the regioselectivity (ortho, meta, para) of the second substitution during electrophilic aromatic substitution: toluene, bromobenzene, acetanilide, anisole, methyl benzoate.

Explain the mechanism of the Vilsmeier-Haack synthesis using the reaction of anisole to *p*-methoxybenzaldehyde.

Rank the following compounds according to their basicity and provide justification: NH_3 , triethylamine, aniline, 4-nitroaniline, 4-methoxyaniline.

Describe the preparation of a diazonium salt starting from aniline, including the mechanism.

Provide the mechanism of the Sandmeyer reaction using the synthesis of chlorobenzene as an example.

Heteroaromatics

Explain the differences between π -electron-deficient and π -electron-rich heteroaromatics. Also, discuss the electrophilic first substitution on thiophene and pyridine using resonance structures.

Discuss the different aromaticity and its impact on the reactivity (S_E and cycloadditions) of furan, pyrrole, and thiophene. What should be considered during electrophilic substitution on furan and pyrrole (mineral acids)?

Sketch the mechanism of a nucleophilic aromatic substitution on an appropriate pyridine derivative and explain why it proceeds faster or slower than on an analogous benzene derivative.

Provide 3 different methods for synthesizing thiophenes (with mechanisms).

Describe the mechanism of pyridine synthesis according to Hantzsch.

Explain the mechanism and process of the Skraup quinoline synthesis.

Explain the mechanism and process of the Fischer indole synthesis.

Describe the synthesis of the following heteroaromatics: 1,3-oxazole, imidazole, 1,3-thiazole, 1,2,3-triazole, pyrimidine.

Natural Products

Explain the terms *anomeric effect* and *mutarotation* using specific examples. Draw the different anomers of D-glucose in the chair form. What is meant by epimeric sugars?

Explain the classification of terpenes according to the number of their subunits. Provide one concrete example for three different classes.

In which configuration (according to Fischer) do α -amino acids occur in nature? Draw this for alanine and name the configuration according to Cahn-Ingold-Prelog priority rules.

What is meant by the isoelectric point?

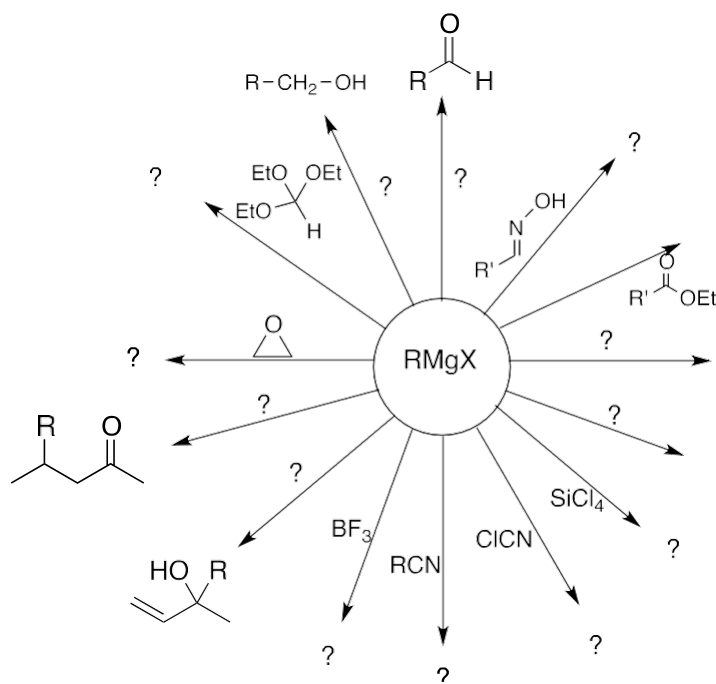
What is meant by the primary, secondary, tertiary, and quaternary structure of a protein? By which types of bonds are these structures stabilized?

Explain the terms *nucleoside* and *nucleotide* and name three differences between DNA and RNA.

Organometallics

Discuss the different reactivities of Grignard and Reformatsky reagents and provide specific examples.

Complete and formulate the reaction mechanism for the following reactions (selected examples will be given in the exam):



Organolithium reagents: How is the Li-C bond characterized? What solvents are used for Li-organyls and why? Why must the reaction be carried out under anhydrous conditions?

Compare the structures and bonding characteristics of lithium organyls, copper organyls, lithium organocuprates, and zinc organyls, and name the most important applications of these substance classes in organic synthesis.

Draw the general catalytic cycle for palladium-catalyzed cross-couplings and name the individual steps.

Complete the following:

Name	$\text{R}^1\text{-X}$	$\text{R}^2\text{-M}$ (organometallic cpd.)	Product
Kumada			
		$\text{R}^2\text{-ZnX}$	
Stille			
		$\text{R}^2\text{-SiR}_3$	
Sonogashira			
		$\text{R}^2\text{-BX}_2$	
Heck			

Electrocyclic Reactions

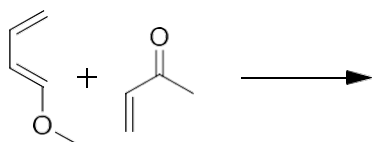
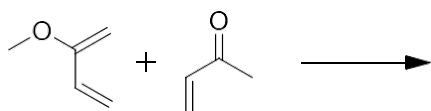
What is meant by an electrocyclic reaction?

Describe the π -MO orbitals in terms of phase, energy level, and occupancy for butadiene and cyclopentadiene.

Explain the Woodward-Hoffmann rule. In doing so, address the terms conrotatory/disrotatory and suprafacial/antarafacial.

Provide examples of [2+2], [2+4], and 1,3-dipolar cycloadditions.

What are the main products of the following reactions and why?



Explain the terms endo/exo and the endo rule using the Diels-Alder reaction between maleic anhydride and cyclopentadiene as an example!