

Summary Sheet: Two Key Concepts for Nucleophilic Substitution on Carbonyls

plus a third bonus concept.

Predicting the rate of reaction at a carbonyl and the fate of the resulting tetrahedral intermediate depend on understanding two key concepts: 1. The electronic nature of the atoms adjoining the carbonyl; 2. Steric bulk around the carbonyl.

Key Concept #1: The importance of electronic factors

Take the simplest carbonyl, formaldehyde.

It undergoes one type of reaction: nucleophilic addition.



What happens when you substitute one of the hydrogens on formaldehyde for a different functional group?



The rate of the reaction will depend on two key factors:

1) Electronegative functional groups make the carbonyl carbon more electrophilic, which increases the rate of reaction with nucleophiles.



2) Donation of π -electrons by the R group makes the carbonyl carbon less electrophilic, which decreases the rate of reaction with nucleophiles.



Does this discussion seem familiar from electrophilic aromatic substitution? It should! It's the same principle!

Recall from electrophilic aromatic substitution:

Strongly activating: NH_2 , NHR , NR_2 , OH , O^-

Moderately deactivating: COOH , CO_2R , CH , CHO , COR

Moderately activating: HCOOH , HCOOR , COCH_3 , OR

Strongly Deactivating: CF_3 , CCl_3

Weakly activating: CH_3 , C_2H_5 , R , C_6H_5

Weakly Deactivating: F , Cl , Br , I
deactivating due to electronegativity but are π -donors

Look: look at the position of OH and O^- . They are extremely strong π -donors. This is why carbonyl groups are resistant to attack under basic conditions, strong π -donation by O^- into the carbonyl makes it extremely resistant toward nucleophilic attack.

Just like with electrophilic aromatic substitution, π -donation trumps electronegativity. The stronger the π -donor, the more resistant the carbonyl will be towards nucleophilic attack.

The presence of donating groups makes the carbonyl carbon less electrophilic and the carbonyl oxygen more nucleophilic. Recall these resonance forms:



The carbonyl is the most nucleophilic (and Lewis basic) site. Therefore, it is protonated first.

A good proxy for donating ability is pK_a , especially when the atom attached to the carbonyl is the same.



The tetrahedral intermediate can undergo further reaction.



How can you predict what will happen?

Leaving group ability is directly related to the pK_a of the conjugate acid.



pK_a of conjugate acid

*remember, however, that under basic conditions OH will be O^- , which means it would have to leave as O^- , an extremely bad leaving group.

Advice: Know your pK_a 's cold. They are a great measure of leaving group ability and also of the electron donating ability of the conjugate base, which comes up *again and again* when discussing chemical reactivity.

Aldehydes and ketones

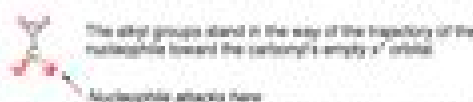


Key concept #2: The importance of steric factors

Formaldehyde again, as the hydrogens are replaced with progressively bulkier groups, the reaction rate goes down.



Why? Recall the antibonding (π^*) orbitals of the carbonyl group.



The same concept applies for the rate of reaction of nucleophiles with esters and amides.



A final important concept: Lewis acids make carbonyls more electrophilic.



For example, in the Fischer esterification, the first step is protonation of the carbonyl, and



The protonated carbonyl, which is now more electrophilic, reacts with the relatively weak nucleophile, the alcohol.



Note in this example that the reaction between the Lewis acid (HCl) and nucleophile (EtOH) is reversible under the reaction conditions, whereas using, say, a Grignard reagent would result in irreversible protonation of the nucleophile (i.e. no reaction). Compatibility between Lewis acids and nucleophiles is treated with more detail in advanced level organic chemistry courses.

In general: more nucleophilic = less electrophilic = faster rate of reaction with electrophiles = higher electron density = more Lewis basic (= less Lewis acidic) = more electron rich = less electrophilic
more electrophilic = less nucleophilic = faster rate of reaction with nucleophiles = lower electron density = less Lewis basic (= more Lewis acidic) = less electron rich = more electrophilic

* Recall: acylfluorides are the result of a thermodynamic equilibrium, while nucleophilicity is measured by reaction rate

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Atta-ur- Rahman



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and from oxidation reduction mechanisms to named reactions we cover both fundamental and advanced topics to cater to students at all levels Real world examples have been integrated throughout the chapters to show how organic reactions play essential roles in pharmaceuticals biochemistry agriculture and environmental science This approach bridges the gap between theory and practical applications helping readers appreciate the relevance of organic chemistry in daily life

Advanced Organic Chemistry-Reactions & Mechanics Prasad Pinnoju,2025-03-21 Advanced Organic Chemistry Reactions Mechanisms is a comprehensive textbook aimed at students and researchers with a strong foundation in organic chemistry The book delves into the intricacies of reaction mechanisms which are at the heart of understanding how organic molecules interact and transform under different conditions The chapters cover a range of topics including fundamental principles of reaction mechanisms the role of intermediates types of organic reactions and various strategies for predicting reaction outcomes Designed for advanced learners this book emphasizes a deep understanding of organic reactions beyond basic descriptions focusing on the electron movement stereochemistry and kinetics that influence reactions in organic synthesis The content is meticulously structured starting with introductory concepts and gradually progressing to more complex mechanisms such as pericyclic reactions aromatic substitution and oxidation reduction processes The book provides practical insights into how reaction mechanisms are applied in synthetic organic chemistry and industrial processes With its clear explanations diagrams and problem solving strategies this book is an indispensable resource for anyone looking to deepen their understanding of organic chemistry whether in academia research or industry

Study Guide and Solutions Manual for Organic Chemistry Susan McMurry,1996 This revision of the best selling organic chemistry textbook today has been fully updated and revised to offer more applications a completely new chapter and dozens of new problems and examples McMurryUs text is currently in use at hundreds of colleges and universities throughout the United States and Canada and is an international bestseller from the United Kingdom to the Pacific Rim In this edition McMurry continues to do what he does best focus on the important material of the course and explain it in a concise clear way

Chemical Literacy and Writing Chemical Reactions Nikolay Gerasimchuk,2022-09-12 Writing chemical reactions in general and inorganic chemistry is not a trivial task However writing reactions for chemical processes correctly is a clear indicator of proficiency and competence in a subject Unfortunately very few students grasp the concept of the correct writing of chemical reactions quickly and so are unable to move through topics of general analytical and inorganic chemistry freely Because the ability to write and balance different types of chemical reactions is a fundamental issue this becomes a key question of chemical literacy The successful writing of chemical reactions includes two components the prediction of products of these reactions and their possible variations and balancing these reactions providing a material balance between starting compounds and reactions products This book explores that element of the teaching of the fundamentals of chemical literacy writing complete equations of chemical reactions and balancing them It contains 49 figures 22 schemes and 12 tables and 93 problems with answers This

book will be very useful for high school students interested in chemical sciences higher education teachers students in colleges and universities majoring in chemistry and biochemistry and chemistry professional working in industry It also contains information about properties of the most common elements and applications of a variety of their chemical compounds

Organic Chemistry Philip S. Bailey, Jr., Christina A. Bailey, 1989

Electron Flow in Organic Chemistry Paul H. Scudder, 2013-02-19 Sets forth the analytical tools needed to solve key problems in organic chemistry With its acclaimed decision based approach *Electron Flow in Organic Chemistry* enables readers to develop the essential critical thinking skills needed to analyze and solve problems in organic chemistry from the simple to complex The author breaks down common mechanistic organic processes into their basic units to explain the core electron flow pathways that underlie these processes Moreover the text stresses the use of analytical tools such as flow charts correlation matrices and energy surfaces to enable readers new to organic chemistry to grasp the fundamentals at a much deeper level This Second Edition of *Electron Flow in Organic Chemistry* has been thoroughly revised reorganized and streamlined in response to feedback from both students and instructors Readers will find more flowcharts correlation matrices and algorithms that illustrate key decision making processes step by step There are new examples from the field of biochemistry making the text more relevant to a broader range of readers in chemistry biology and medicine This edition also offers three new chapters Proton transfer and the principles of stability Important reaction archetypes Qualitative molecular orbital theory and pericyclic reactions The text s appendix features a variety of helpful tools including a general bibliography quick reference charts and tables pathway summaries and a major decisions guide With its emphasis on logical processes rather than memorization to solve mechanistic problems this text gives readers a solid foundation to approach and solve any problem in organic chemistry

Guide to Medical and Dental Schools Saul Wischnitzer, Edith Wischnitzer, 2006 Updated with the latest facts and figures this school directory and guidance manual presents profiles of all accredited medical dental and osteopathic schools in the United States and Canada Here is information on tuition and fees application procedures and much more The book also includes the latest available full length model Medical College Admission Test MCAT with answers and selected questions with answers from recent Dental College Admission Tests DAT The authors offer advice on when and where to apply to dental and medical schools information on assessing one s chances for acceptance at the schools and all important test taking tips for students preparing to take the MCAT or DAT This new edition includes sample essays for medical school applications and a special section dedicated to high school students who are making long term plans for a medical or dental career

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Fundamentals of Organic Chemistry John McMurry, 1986 Written for the short course where content must be thorough but to the point FUNDAMENTALS OF ORGANIC CHEMISTRY Fifth Edition provides an effective clear and readable introduction to the beauty and logic of organic chemistry McMurry presents only those subjects needed for a brief course while maintaining the important pedagogical tools commonly found in larger books With clear explanations thought provoking examples and an innovative vertical format for explaining reaction mechanisms FUNDAMENTALS takes a modern approach primary organization is by functional group beginning with the simple alkanes and progressing to the more complex Within the primary organization there is also an emphasis on explaining the fundamental mechanistic similarities of reactions Through this approach memorization is minimized and understanding is maximized This new edition represents a major revision The text has been revised at the sentence level to further improve clarity and readability many new examples and topics of biological relevance have been added and many new features have been introduced *Organic Chemistry* G. Marc Loudon, 2009 Introduces organic chemistry through a mechanistic approach within a functional group framework Contains 1 668 exercises many of which are taken directly from the scientific literature that encourage readers to analyze and synthesize chemical concepts Includes modern topics such as alkene metathesis Suzuki and Stille cross coupling reactions and examples drawn from contemporary medical practice Provided by the publisher **A Foundation Course for College Organic Chemistry** B. S. Balaji, 2024-08-22 To understand and improve the underlying principles that govern how organic reactions occur A Foundation Course for College Organic Chemistry follows a brick by brick building approach Emphasis is given to interrelating experimental facts and findings with predictions mechanism and inferences results Discussions focus on clarifying how complex organic reactions occur which is based on electronegativity differences movement of electrons through framework or bonds and addition or removal of atoms hydrogen halogens or groups hydroxy amino The book begins with simple rules governing the deconstruction of reactions and applies them to explain how esterification amide and cyanide hydrolysis reactions proceed The importance of stereochemistry used in drug development biology and medicine aromatic electrophilic and nucleophilic substitutions reaction kinetics and dynamics is explained with suitable examples Features A systematic and structured approach is used to study all aspects of reactive intermediates

generation structure geometry and reactions of carbocations carbanions and carbon free radicals This book incorporates scientific methods to deduce reaction mechanisms with simple and relevant explanations and limitations A proper explanation is given to understand the influence of functional groups on the stability and reactivity of intermediates pKa HSAB principles structure activity relations and how these can be exploited in organic chemistry Information is presented in an accessible way for students teachers researchers and scientists

Organic Chemistry II For Dummies John T.

Moore, Richard H. Langley, 2010-06-10 A plain English guide to one of the toughest courses around So you survived the first semester of Organic Chemistry maybe even by the skin of your teeth and now it's time to get back to the classroom and lab Organic Chemistry II For Dummies is an easy to understand reference to this often challenging subject Thanks to this book you'll get friendly and comprehensible guidance on everything you can expect to encounter in your Organic Chemistry II course An extension of the successful Organic Chemistry I For Dummies Covers topics in a straightforward and effective manner Explains concepts and terms in a fast and easy to understand way Whether you're confused by composites baffled by biomolecules or anything in between Organic Chemistry II For Dummies gives you the help you need in plain English

The Chemistry Companion Vandana Jangde, Reenu Mishra, Danuj Kumar Markam, Anshu Priti Kujur, Gurudev Choudhary, 2025-06-13 The Chemistry Companion is a thoughtfully designed resource tailored to meet the academic needs of engineering students This book provides a comprehensive collection of questions and answers based on the chemistry syllabus commonly followed in engineering courses across various institutions Structured to support both learning and revision the book covers essential topics in physical organic and inorganic chemistry offering clear explanations and concise answers to help students strengthen their conceptual understanding

Basic Inorganic and Organic Chemistry Jagdish

Krishanlal Arora, 2023-08-21 Basic Inorganic and Organic Chemistry is a comprehensive textbook that serves as an essential introduction to the fundamental concepts of both inorganic and organic chemistry The book covers a wide range of topics starting from the atomic structure and periodic trends to the principles of chemical bonding molecular shapes and reactivity In the inorganic chemistry section it explores the properties and behaviors of main group elements transition metals coordination compounds and their applications In the organic chemistry section the book delves into the structure properties and reactions of carbon based compounds offering insights into functional groups reaction mechanisms and stereochemistry Throughout the text readers will find a balanced blend of theoretical concepts and practical applications making it an invaluable resource for students and enthusiasts looking to develop a strong foundation in chemistry

In-Depth Advanced

Organic Chemistry Rajeev Khatri, 2025-02-20 In Depth Advanced Organic Chemistry is a comprehensive guide to the study of carbon containing compounds often referred to as the chemistry of life We cover a wide range of topics from the synthesis of complex molecules to the study of reaction mechanisms and catalysis making this book an authoritative resource for students researchers and professionals We begin with an introduction to organic chemistry principles including molecular structure

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A Textbook of Organic Chemistry, 22e Arun Bahl & B S Bahl, 2019 With an increased focus on fundamentals this new edition of A Textbook of Organic Chemistry continues to present the time tested functional group approach to the subject This examination oriented book breaks the intricacies of Organic Chemistry into easy to understand steps which gives the student the necessary foundation to build upon learn and understand Organic Chemistry in a way that is efficient as well as long lasting

Organic Chemistry T. W. Graham Solomons, Craig B. Fryhle, Scott A. Snyder, 2016-01-19 The 12th edition of Organic Chemistry continues Solomons Fryhle Snyder's tradition of excellence in teaching and preparing students for success in the organic classroom and beyond A central theme of the authors approach to organic chemistry is to emphasize the relationship between structure and reactivity To accomplish this the content is organized in a way that combines the most useful features of a functional group approach with one largely based on reaction mechanisms The authors philosophy is to emphasize mechanisms and their common aspects as often as possible and at the same time use the unifying features of functional groups as the basis for most chapters The structural aspects of the authors approach show students what organic chemistry is Mechanistic aspects of their approach show students how it works And wherever an opportunity arises the authors show students what it does in living systems and the physical world around us

Advances in Organic Synthesis Atta-ur- Rahman, 2018-09-25 Advances in Organic Synthesis is a book series devoted to the latest advances in synthetic approaches towards challenging structures The series presents comprehensive reviews written by eminent authorities on different synthetic approaches to selected target molecules and new methods developed to achieve specific synthetic transformations or optimal product yields Advances in Organic Synthesis is essential for all organic chemists in academia and the industry who wish to keep abreast of rapid and important developments in the field

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