

ADDITION REACTIONS EXAMPLES

EMBARCKING ON A JOURNEY THROUGH THE FASCINATING WORLD OF ORGANIC CHEMISTRY REVEALS THE PIVOTAL ROLE OF ADDITION REACTIONS. THESE FUNDAMENTAL TRANSFORMATIONS ARE THE BUILDING BLOCKS FOR SYNTHESIZING A VAST ARRAY OF ORGANIC COMPOUNDS, FROM EVERYDAY PLASTICS TO LIFE-SAVING PHARMACEUTICALS. UNDERSTANDING ADDITION REACTIONS, AND SPECIFICALLY DELVING INTO ADDITION REACTIONS EXAMPLES, IS CRUCIAL FOR ANY STUDENT OR PROFESSIONAL IN CHEMISTRY. THIS ARTICLE WILL COMPREHENSIVELY EXPLORE VARIOUS TYPES OF ADDITION REACTIONS, ILLUSTRATING THEM WITH CLEAR EXAMPLES AND EXPLAINING THEIR SIGNIFICANCE IN SYNTHETIC CHEMISTRY. WE WILL COVER NUCLEOPHILIC ADDITION TO CARBONYLS, ELECTROPHILIC ADDITION TO ALKENES AND ALKYNES, AND THE VITAL DIELS-ALDER REACTION, AMONG OTHERS. PREPARE TO GAIN A DEEP APPRECIATION FOR HOW MOLECULES ARE BUILT AND MODIFIED THROUGH THESE ESSENTIAL CHEMICAL PROCESSES.

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THE ESSENCE OF ADDITION REACTIONS: BUILDING MOLECULAR COMPLEXITY

IN THE VAST LANDSCAPE OF ORGANIC CHEMISTRY, ADDITION REACTIONS STAND OUT AS FUNDAMENTAL PROCESSES THAT DRIVE THE CREATION AND TRANSFORMATION OF MOLECULES. AT THEIR CORE, ADDITION REACTIONS INVOLVE THE JOINING OF TWO OR MORE MOLECULES TO FORM A LARGER, SINGLE PRODUCT. THIS OFTEN OCCURS WHEN A MOLECULE CONTAINING A MULTIPLE BOND, SUCH AS A DOUBLE OR TRIPLE BOND, REACTS WITH ANOTHER MOLECULE THAT ADDS ACROSS THIS UNSATURATION. THE BEAUTY OF ADDITION REACTIONS LIES IN THEIR ABILITY TO INCREASE MOLECULAR COMPLEXITY AND INTRODUCE NEW FUNCTIONAL GROUPS, PAVING THE WAY FOR THE SYNTHESIS OF A STAGGERING VARIETY OF ORGANIC COMPOUNDS. UNDERSTANDING SPECIFIC ADDITION REACTIONS EXAMPLES IS KEY TO UNLOCKING THE SYNTHETIC POTENTIAL OF ORGANIC CHEMISTRY.

WHAT ARE ADDITION REACTIONS?

AN ADDITION REACTION IS A CHEMICAL REACTION IN WHICH TWO OR MORE MOLECULES COMBINE TO FORM A SINGLE PRODUCT MOLECULE. IN THE CONTEXT OF ORGANIC CHEMISTRY, THIS TYPICALLY INVOLVES THE BREAKING OF A PI BOND (π BOND) IN AN UNSATURATED COMPOUND (CONTAINING DOUBLE OR TRIPLE BONDS) AND THE FORMATION OF TWO NEW SIGMA BONDS (σ BONDS) AS ATOMS FROM ANOTHER MOLECULE ARE ADDED. THESE REACTIONS ARE CHARACTERIZED BY AN INCREASE IN THE DEGREE OF SATURATION OF THE ORGANIC MOLECULE. FOR INSTANCE, AN ALKENE, WITH ITS $C=C$ DOUBLE BOND, CAN UNDERGO ADDITION REACTIONS TO BECOME AN ALKANE, WITH A $C-C$ SINGLE BOND, THUS BECOMING MORE SATURATED.

KEY CHARACTERISTICS OF ADDITION REACTIONS

SEVERAL KEY CHARACTERISTICS DEFINE ADDITION REACTIONS:

- **FORMATION OF A SINGLE PRODUCT:** THE DEFINING FEATURE IS THAT MULTIPLE REACTANTS COMBINE TO FORM ONE PRODUCT MOLECULE.
- **BREAKING OF PI BONDS:** USUALLY, A PI BOND IN A MULTIPLE BOND SYSTEM (LIKE $C=C$ OR $C\equiv C$) IS BROKEN, WHICH IS WEAKER THAN A SIGMA BOND.
- **FORMATION OF SIGMA BONDS:** TWO NEW SIGMA BONDS ARE FORMED, CONNECTING THE ADDED ATOMS TO THE PARENT MOLECULE.
- **INCREASE IN SATURATION:** THE MOLECULE BECOMES MORE SATURATED AS THE MULTIPLE BOND IS CONVERTED TO A SINGLE BOND.
- **ATOM ECONOMY:** ADDITION REACTIONS OFTEN EXHIBIT HIGH ATOM ECONOMY, MEANING MOST OR ALL OF THE ATOMS FROM THE REACTANTS ARE INCORPORATED INTO THE PRODUCT, MINIMIZING WASTE.

TYPES OF ADDITION REACTIONS

ADDITION REACTIONS CAN BE BROADLY CLASSIFIED BASED ON THE NATURE OF THE ATTACKING SPECIES AND THE TYPE OF SUBSTRATE. THE MOST COMMON CLASSIFICATIONS INCLUDE ELECTROPHILIC ADDITION, NUCLEOPHILIC ADDITION, CONJUGATE ADDITION, CYCLOADDITION, AND RADICAL ADDITION REACTIONS. EACH TYPE INVOLVES A DISTINCT MECHANISM AND IS RELEVANT TO DIFFERENT CLASSES OF ORGANIC COMPOUNDS.

ELECTROPHILIC ADDITION REACTIONS: ATTACKING THE PI BOND

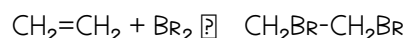
ELECTROPHILIC ADDITION REACTIONS ARE PERHAPS THE MOST COMMONLY ENCOUNTERED TYPE OF ADDITION REACTION, PARTICULARLY WITH UNSATURATED HYDROCARBONS LIKE ALKENES AND ALKYNES. THESE REACTIONS ARE INITIATED BY AN ELECTROPHILE, A SPECIES THAT IS ELECTRON-DEFICIENT AND SEEKS ELECTRON-RICH SITES. IN ALKENES AND ALKYNES, THE PI ELECTRONS IN THE MULTIPLE BOND SERVE AS THE ELECTRON-RICH TARGET FOR THE ELECTROPHILE. THE PROCESS TYPICALLY INVOLVES THE FORMATION OF A CARBOCATION INTERMEDIATE OR A CYCLIC INTERMEDIATE, WHICH IS THEN ATTACKED BY A NUCLEOPHILE TO COMPLETE THE ADDITION.

ELECTROPHILIC ADDITION TO ALKENES

ALKENES, WITH THEIR CARBON-CARBON DOUBLE BONDS, ARE HIGHLY REACTIVE TOWARDS ELECTROPHILES DUE TO THE PRESENCE OF THE RELATIVELY LOOSELY HELD PI ELECTRONS. THE GENERAL MECHANISM INVOLVES THE ATTACK OF THE PI BOND ON AN ELECTROPHILE, FORMING A CARBOCATION (OR A SIMILAR INTERMEDIATE), WHICH IS SUBSEQUENTLY ATTACKED BY A NUCLEOPHILE.

HALOGENATION OF ALKENES: ADDING HALOGENS ACROSS THE DOUBLE BOND

THE ADDITION OF HALOGENS LIKE BROMINE (Br_2) OR CHLORINE (Cl_2) TO ALKENES IS A CLASSIC EXAMPLE OF ELECTROPHILIC ADDITION. THE HALOGEN MOLECULE BECOMES POLARIZED AS IT APPROACHES THE ELECTRON-RICH PI BOND. THE INITIAL STEP INVOLVES THE FORMATION OF A CYCLIC HALONIUM ION INTERMEDIATE, WHERE THE HALOGEN ATOM BRIDGES THE TWO CARBON ATOMS OF THE DOUBLE BOND. THIS CYCLIC STRUCTURE THEN UNDERGOES NUCLEOPHILIC ATTACK BY A HALIDE ION (X^-) FROM THE OPPOSITE SIDE, LEADING TO THE FORMATION OF A VICINAL DIHALIDE (A COMPOUND WITH TWO HALOGEN ATOMS ON ADJACENT CARBONS). FOR EXAMPLE, THE REACTION OF ETHENE WITH BROMINE YIELDS 1,2-DIBROMOETHANE.



HYDROHALOGENATION OF ALKENES: MARKOVNIKOV'S RULE IN ACTION

HYDROHALOGENATION INVOLVES THE ADDITION OF HYDROGEN HALIDES (HX), SUCH AS HCl , HBr , OR HI , ACROSS THE DOUBLE BOND OF AN ALKENE. THIS REACTION FOLLOWS MARKOVNIKOV'S RULE, WHICH STATES THAT IN THE ADDITION OF A PROTIC ACID HX TO AN UNSYMMETRICAL ALKENE, THE HYDROGEN ATOM ADDS TO THE CARBON ATOM THAT ALREADY HAS THE GREATER NUMBER OF HYDROGEN ATOMS, AND THE HALIDE ION ADDS TO THE MORE SUBSTITUTED CARBON ATOM. THIS REGIOSELECTIVITY IS EXPLAINED BY THE FORMATION OF THE MORE STABLE CARBOCATION INTERMEDIATE. FOR INSTANCE, THE ADDITION OF HCl TO PROPENE RESULTS IN THE FORMATION OF 2-CHLOROPROPANE AS THE MAJOR PRODUCT.



HYDRATION OF ALKENES: ADDING WATER TO FORM ALCOHOLS

THE HYDRATION OF ALKENES, THE ADDITION OF WATER ACROSS THE DOUBLE BOND, IS A CRUCIAL METHOD FOR SYNTHESIZING ALCOHOLS. THIS REACTION IS TYPICALLY CATALYZED BY A STRONG ACID, SUCH AS SULFURIC ACID (H_2SO_4). THE MECHANISM INVOLVES THE PROTONATION OF THE ALKENE TO FORM A CARBOCATION, WHICH IS THEN ATTACKED BY WATER. SUBSEQUENT DEPROTONATION YIELDS THE ALCOHOL. LIKE HYDROHALOGENATION, HYDRATION OF UNSYMMETRICAL ALKENES FOLLOWS MARKOVNIKOV'S RULE. THE ACID CATALYST PLAYS A VITAL ROLE IN INITIATING THE REACTION BY PROTONATING THE ALKENE.



OXYMERCURATION-DEMERCURATION: A HYDRATION ALTERNATIVE

OXYMERCURATION-DEMERCURATION IS A TWO-STEP PROCESS THAT PROVIDES A RELIABLE METHOD FOR HYDRATING ALKENES,

OFTEN YIELDING ALCOHOLS WITH MARKOVNIKOV REGIOSELECTIVITY AND AVOIDING CARBOCATION REARRANGEMENTS THAT CAN OCCUR WITH DIRECT ACID-CATALYZED HYDRATION. IN THE FIRST STEP, THE ALKENE REACTS WITH MERCURY(II) ACETATE ($\text{Hg}(\text{OAc})_2$) IN THE PRESENCE OF WATER AND AN ALCOHOL SOLVENT, FORMING A MERCURINIUM ION INTERMEDIATE, FOLLOWED BY ATTACK BY WATER. THE RESULTING ORGANOMERCURIAL COMPOUND IS THEN TREATED WITH SODIUM BOROHYDRIDE (NaBH_4) IN THE SECOND STEP TO REMOVE THE MERCURY, YIELDING THE ALCOHOL. THIS METHOD IS PARTICULARLY USEFUL FOR SYNTHESIZING TERTIARY ALCOHOLS FROM HIGHLY SUBSTITUTED ALKENES.

HYDROBORATION-OXIDATION: ANTI-MARKOVNIKOV HYDRATION

HYDROBORATION-OXIDATION IS A POWERFUL TWO-STEP REACTION THAT ACHIEVES THE SYN-ADDITION OF WATER TO ALKENES WITH ANTI-MARKOVNIKOV REGIOSELECTIVITY AND SYN STEREOCHEMISTRY. IN THE HYDROBORATION STEP, BORANE (BH_3) OR A SUBSTITUTED BORANE ADDS ACROSS THE DOUBLE BOND IN A CONCERTED FASHION, WITH BORON ATTACHING TO THE LESS SUBSTITUTED CARBON AND HYDROGEN TO THE MORE SUBSTITUTED CARBON. THIS PROCESS IS THEN FOLLOWED BY OXIDATION WITH HYDROGEN PEROXIDE (H_2O_2) IN BASIC CONDITIONS, WHICH REPLACES THE BORON-CONTAINING GROUP WITH A HYDROXYL GROUP, RESULTING IN AN ALCOHOL WITH THE HYDROXYL GROUP ON THE LESS SUBSTITUTED CARBON OF THE ORIGINAL DOUBLE BOND.

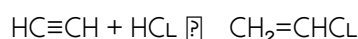
EXAMPLE: $\text{CH}_3\text{-CH=CH}_2 + \text{BH}_3$ FOLLOWED BY $\text{H}_2\text{O}_2/\text{OH}^- \rightarrow \text{CH}_3\text{-CH}_2\text{-CH}_2\text{OH}$

ELECTROPHILIC ADDITION TO ALKYNES

ALKYNES, WITH THEIR CARBON-CARBON TRIPLE BONDS, ARE ALSO SUSCEPTIBLE TO ELECTROPHILIC ADDITION REACTIONS, BUT THEY ARE GENERALLY LESS REACTIVE THAN ALKENES. THE TRIPLE BOND CONTAINS TWO π BONDS, ALLOWING FOR THE ADDITION OF TWO MOLES OF THE ELECTROPHILIC REAGENT. SIMILAR MECHANISMS TO THOSE OBSERVED WITH ALKENES ARE INVOLVED, INCLUDING THE FORMATION OF VINYL CARBOCATIONS OR CYCLIC INTERMEDIATES.

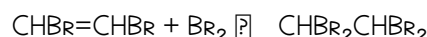
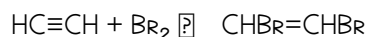
HYDROHALOGENATION OF ALKYNES

THE ADDITION OF HYDROGEN HALIDES (HX) TO ALKYNES CAN OCCUR TWICE. THE FIRST ADDITION FOLLOWS MARKOVNIKOV'S RULE, FORMING A VINYL HALIDE. UNDER APPROPRIATE CONDITIONS, A SECOND ADDITION OF HX CAN OCCUR ACROSS THE RESULTING DOUBLE BOND, ALSO FOLLOWING MARKOVNIKOV'S RULE, TO YIELD A GEMINAL DIHALIDE (BOTH HALOGENS ON THE SAME CARBON). FOR EXAMPLE, THE REACTION OF ETHYNE WITH EXCESS HCl YIELDS 1,1-DICHLOROETHANE.



HALOGENATION OF ALKYNES

SIMILAR TO ALKENES, ALKYNES REACT WITH HALOGENS (X_2) TO FORM DIHALOALKENES WITH THE FIRST ADDITION. FURTHER ADDITION OF HALOGEN CAN LEAD TO TETRAHALOALKANES. THE INITIAL ADDITION OFTEN PROCEEDS VIA A CYCLIC HALONIUM ION INTERMEDIATE. THE REACTION OF ETHYNE WITH EXCESS BROMINE YIELDS 1,1,2,2-TETRABROMOETHANE.



HYDRATION OF ALKYNES: FORMATION OF ENOLS AND KETONES

THE HYDRATION OF ALKYNES, TYPICALLY CATALYZED BY MERCURY(II) SALTS AND A STRONG ACID, RESULTS IN THE FORMATION OF ENOLS, WHICH THEN TAUTOMERIZE TO CARBONYL COMPOUNDS (ALDEHYDES OR KETONES). TERMINAL ALKYNES (LIKE ETHYNE) FORM ALDEHYDES, WHILE INTERNAL ALKYNES FORM KETONES. THE INITIAL PRODUCT OF HYDRATION IS A VINYL ALCOHOL (ENOL), WHICH IS UNSTABLE AND QUICKLY REARRANGES TO THE MORE STABLE KETO FORM. FOR EXAMPLE, THE HYDRATION OF ETHYNE

PRODUCES ACETALDEHYDE, AND THE HYDRATION OF PROPYNE YIELDS ACETONE.



NUCLEOPHILIC ADDITION REACTIONS: ATTACKING THE ELECTROPHILIC CENTER

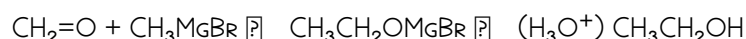
NUCLEOPHILIC ADDITION REACTIONS ARE CHARACTERISTIC OF COMPOUNDS CONTAINING POLAR MULTIPLE BONDS, MOST NOTABLY CARBONYL GROUPS ($\text{C}=\text{O}$) FOUND IN ALDEHYDES AND KETONES. IN THESE REACTIONS, A NUCLEOPHILE, AN ELECTRON-RICH SPECIES, ATTACKS THE ELECTROPHILIC CARBON ATOM OF THE CARBONYL GROUP. THE π ELECTRONS OF THE CARBONYL BOND MOVE TO THE ELECTRONEGATIVE OXYGEN ATOM, FORMING AN ALKOXIDE INTERMEDIATE, WHICH IS THEN PROTONATED TO YIELD THE FINAL PRODUCT, OFTEN AN ALCOHOL OR A RELATED DERIVATIVE.

NUCLEOPHILIC ADDITION TO CARBONYL COMPOUNDS

THE CARBON ATOM IN A CARBONYL GROUP IS ELECTROPHILIC DUE TO THE ELECTRONEGATIVITY OF THE OXYGEN ATOM, WHICH PULLS ELECTRON DENSITY AWAY FROM THE CARBON. THIS MAKES THE CARBONYL CARBON SUSCEPTIBLE TO ATTACK BY NUCLEOPHILES. THE OXYGEN ATOM, BEING ELECTRONEGATIVE, CARRIES A PARTIAL NEGATIVE CHARGE AND CAN ACCEPT A PROTON OR ANOTHER ELECTROPHILE IN A LATER STEP.

ADDITION OF GRIGNARD REAGENTS TO ALDEHYDES AND KETONES

GRIGNARD REAGENTS (R-MgX) ARE POWERFUL NUCLEOPHILES AND STRONG BASES. THEY READILY ADD TO THE CARBONYL CARBON OF ALDEHYDES AND KETONES, FORMING ALKOXIDES. UPON ACIDIC WORKUP, THESE ALKOXIDES ARE PROTONATED TO YIELD ALCOHOLS. THE TYPE OF ALCOHOL FORMED DEPENDS ON THE CARBONYL COMPOUND: ADDITION TO FORMALDEHYDE YIELDS PRIMARY ALCOHOLS, TO OTHER ALDEHYDES YIELDS SECONDARY ALCOHOLS, AND TO KETONES YIELDS TERTIARY ALCOHOLS. FOR EXAMPLE, THE REACTION OF METHYLMAGNESIUM BROMIDE WITH FORMALDEHYDE PRODUCES ETHANOL.

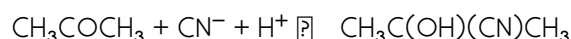


ADDITION OF ORGANOLITHIUM REAGENTS

ORGANOLITHIUM REAGENTS (R-Li) ARE SIMILAR TO GRIGNARD REAGENTS IN THEIR REACTIVITY AND ARE ALSO EXCELLENT NUCLEOPHILES. THEY ADD TO CARBONYL GROUPS IN ALDEHYDES AND KETONES VIA THE SAME GENERAL MECHANISM, LEADING TO THE FORMATION OF ALCOHOLS AFTER ACIDIC WORKUP. THEIR REACTIVITY CAN SOMETIMES BE MORE VIGOROUS THAN GRIGNARD REAGENTS.

ADDITION OF CYANIDE IONS: CYANOHYDRIN FORMATION

THE ADDITION OF CYANIDE IONS (CN^-) TO ALDEHYDES AND KETONES FORMS CYANOHYDRINS. THE CYANIDE ION IS A GOOD NUCLEOPHILE THAT ATTACKS THE CARBONYL CARBON. THE RESULTING ALKOXIDE INTERMEDIATE IS THEN PROTONATED BY THE SOLVENT (OFTEN DILUTE ACID). CYANOHYDRINS ARE VERSATILE SYNTHETIC INTERMEDIATES, AS THE NITRILE GROUP CAN BE HYDROLYZED TO A CARBOXYLIC ACID OR REDUCED TO AN AMINE. FOR INSTANCE, THE REACTION OF ACETONE WITH CYANIDE AND ACID YIELDS ACETONE CYANOHYDRIN.



ADDITION OF ALCOHOLS: ACETAL AND HEMIACETAL FORMATION

IN THE PRESENCE OF AN ACID CATALYST, ALCOHOLS CAN ADD TO ALDEHYDES AND KETONES TO FORM HEMIACETALS (OR HEMIKETALS) AND ACETALS (OR KETALS). THE FIRST STEP INVOLVES THE NUCLEOPHILIC ATTACK OF THE ALCOHOL ON THE PROTONATED CARBONYL GROUP, FORMING A HEMIACETAL. IF A SECOND MOLECULE OF ALCOHOL ADDS TO THE HEMIACETAL (AFTER PROTONATION OF THE HYDROXYL GROUP AND LOSS OF WATER), AN ACETAL IS FORMED. ACETALS ARE STABLE IN BASIC CONDITIONS BUT CAN BE HYDROLYZED BACK TO THE CARBONYL COMPOUND AND ALCOHOL IN ACIDIC CONDITIONS, MAKING THEM USEFUL AS PROTECTING GROUPS FOR CARBONYLS.

ADDITION OF AMINES: IMINE AND ENAMINE FORMATION

PRIMARY AMINES REACT WITH ALDEHYDES AND KETONES IN THE PRESENCE OF AN ACID CATALYST TO FORM IMINES (SCHIFF BASES), WHICH CONTAIN A $C=N$ DOUBLE BOND. THE MECHANISM INVOLVES NUCLEOPHILIC ADDITION OF THE AMINE TO THE CARBONYL GROUP, FOLLOWED BY DEHYDRATION. SECONDARY AMINES REACT WITH CARBONYL COMPOUNDS TO FORM ENAMINES, WHICH ARE CHARACTERIZED BY A $C=C$ DOUBLE BOND ADJACENT TO A NITROGEN ATOM.

REDUCTION OF CARBONYLS: USING HYDRIDES

REDUCING AGENTS LIKE LITHIUM ALUMINUM HYDRIDE ($LiAlH_4$) AND SODIUM BOROHYDRIDE ($NaBH_4$) ARE EXCELLENT SOURCES OF HYDRIDE IONS (H^-), WHICH ACT AS NUCLEOPHILES. THEY ADD TO THE CARBONYL CARBON, REDUCING THE CARBONYL GROUP TO AN ALCOHOL. $LiAlH_4$ IS A STRONGER REDUCING AGENT AND CAN REDUCE ALDEHYDES, KETONES, ESTERS, AND CARBOXYLIC ACIDS TO ALCOHOLS. $NaBH_4$ IS Milder AND IS TYPICALLY USED FOR THE REDUCTION OF ALDEHYDES AND KETONES TO ALCOHOLS.

CONJUGATE ADDITION (1,4-ADDITION): EXPANDING THE SCOPE

CONJUGATE ADDITION, ALSO KNOWN AS 1,4-ADDITION, IS A TYPE OF NUCLEOPHILIC ADDITION REACTION THAT OCCURS WITH α,β -UNSATURATED CARBONYL COMPOUNDS AND OTHER CONJUGATED SYSTEMS. IN THESE REACTIONS, THE NUCLEOPHILE ATTACKS THE β -CARBON (THE CARBON ATOM TWO POSITIONS AWAY FROM THE CARBONYL CARBON) OF THE CONJUGATED SYSTEM, RATHER THAN THE CARBONYL CARBON ITSELF (1,2-ADDITION). THIS IS OFTEN FAVORED WITH SOFTER NUCLEOPHILES AND UNDER SPECIFIC REACTION CONDITIONS.

MICHAEL ADDITION: A CLASSIC CONJUGATE ADDITION

THE MICHAEL ADDITION IS A PRIME EXAMPLE OF CONJUGATE ADDITION. IT INVOLVES THE ADDITION OF A CARBANION (GENERATED FROM A COMPOUND WITH AN ACIDIC α -HYDROGEN, SUCH AS A β -DICARBONYL COMPOUND OR A MALONATE ESTER) TO AN α,β -UNSATURATED CARBONYL COMPOUND. THE REACTION IS TYPICALLY CATALYZED BY A BASE. THE INITIAL ATTACK IS AT THE β -CARBON, FORMING AN ENOLATE INTERMEDIATE, WHICH IS THEN PROTONATED TO YIELD A PRODUCT WITH THE NUCLEOPHILE ADDED TO THE β -POSITION.

CONJUGATE ADDITION TO α,β -UNSATURATED CARBONYLS

α,β -UNSATURATED CARBONYL COMPOUNDS, LIKE ENONES AND ENALS, POSSESS A CONJUGATED SYSTEM WHERE THE π ELECTRONS ARE DELOCALIZED. THIS DELOCALIZATION ALLOWS FOR NUCLEOPHILIC ATTACK AT BOTH THE CARBONYL CARBON (1,2-ADDITION) AND THE β -CARBON (1,4-ADDITION OR CONJUGATE ADDITION). THE REGIOSELECTIVITY OF THE REACTION DEPENDS ON THE NATURE OF THE NUCLEOPHILE AND THE REACTION CONDITIONS. SOFTER NUCLEOPHILES, SUCH AS ORGANOCUPRATES (GILMAN REAGENTS), TEND TO FAVOR 1,4-ADDITION, WHILE HARDER NUCLEOPHILES, LIKE GRIGNARD REAGENTS, CAN LEAD TO A MIXTURE OF 1,2- AND 1,4-ADDITION PRODUCTS, WITH 1,2-ADDITION OFTEN PREDOMINATING.

CYCLOADDITION REACTIONS: FORMING RINGS

CYCLOADDITION REACTIONS ARE A CLASS OF PERICYCLIC REACTIONS WHERE TWO OR MORE UNSATURATED MOLECULES REACT TO FORM A CYCLIC PRODUCT. IN THESE REACTIONS, NEW SIGMA BONDS ARE FORMED, AND PI BONDS ARE CONSUMED. THE MOST FAMOUS AND SYNTHETICALLY USEFUL CYCLOADDITION REACTION IS THE DIELS-ALDER REACTION.

DIELS-ALDER REACTION: A [4+2] CYCLOADDITION

THE DIELS-ALDER REACTION IS A [4+2] CYCLOADDITION REACTION BETWEEN A CONJUGATED DIENE (A MOLECULE WITH TWO CONJUGATED DOUBLE BONDS) AND A DIENOPHILE (A MOLECULE WITH A DOUBLE OR TRIPLE BOND). THIS REACTION FORMS A SIX-MEMBERED RING, TYPICALLY A CYCLOHEXENE OR A CYCLOHEXADIENE DERIVATIVE. IT IS A CONCERTED REACTION, MEANING ALL BOND BREAKING AND FORMING OCCURS IN A SINGLE STEP, PROCEEDING THROUGH A CYCLIC TRANSITION STATE.

MECHANISM OF THE DIELS-ALDER REACTION

THE DIELS-ALDER REACTION INVOLVES THE OVERLAP OF THE FRONTIER MOLECULAR ORBITALS (THE HIGHEST OCCUPIED MOLECULAR ORBITAL, HOMO, OF ONE REACTANT AND THE LOWEST UNOCCUPIED MOLECULAR ORBITAL, LUMO, OF THE OTHER). TYPICALLY, THE HOMO OF THE DIENE INTERACTS WITH THE LUMO OF THE DIENOPHILE. THE REACTION RESULTS IN THE FORMATION OF TWO NEW SIGMA BONDS AND THE REARRANGEMENT OF PI BONDS, LEADING TO A CYCLIC PRODUCT. THE STEREOCHEMISTRY OF THE REACTANTS IS GENERALLY PRESERVED IN THE PRODUCT.

FACTORS AFFECTING DIELS-ALDER REACTIVITY

SEVERAL FACTORS INFLUENCE THE RATE AND SUCCESS OF THE DIELS-ALDER REACTION. ELECTRON-WITHDRAWING GROUPS ON THE DIENOPHILE AND ELECTRON-DONATING GROUPS ON THE DIENE GENERALLY ENHANCE REACTIVITY. STERIC HINDRANCE CAN ALSO PLAY A ROLE, AFFECTING THE APPROACH OF THE REACTANTS. TEMPERATURE AND SOLVENT CAN ALSO INFLUENCE THE REACTION RATE AND SELECTIVITY.

APPLICATIONS OF THE DIELS-ALDER REACTION

THE DIELS-ALDER REACTION IS A CORNERSTONE OF ORGANIC SYNTHESIS, ALLOWING FOR THE EFFICIENT CONSTRUCTION OF COMPLEX SIX-MEMBERED RING SYSTEMS, WHICH ARE PREVALENT IN MANY NATURAL PRODUCTS AND PHARMACEUTICALS. IT IS WIDELY USED IN THE SYNTHESIS OF STEROIDS, ALKALOIDS, AND OTHER BIOLOGICALLY ACTIVE MOLECULES.

OTHER CYCLOADDITION REACTIONS

WHILE THE DIELS-ALDER REACTION IS THE MOST PROMINENT, OTHER CYCLOADDITION REACTIONS EXIST, SUCH AS THE [2+2] CYCLOADDITION, [3+2] CYCLOADDITION (E.G., 1,3-DIPOLAR CYCLOADDITIONS), AND [2+2+2] CYCLOADDITIONS, EACH LEADING TO DIFFERENT RING SIZES AND TYPES OF CYCLIC PRODUCTS.

RADICAL ADDITION REACTIONS: UNPAIRED ELECTRONS AT PLAY

RADICAL ADDITION REACTIONS ARE INITIATED BY SPECIES WITH UNPAIRED ELECTRONS, KNOWN AS RADICALS. THESE REACTIONS TYPICALLY INVOLVE A CHAIN MECHANISM, CONSISTING OF INITIATION, PROPAGATION, AND TERMINATION STEPS. RADICAL ADDITIONS ARE OFTEN OBSERVED WHEN REACTIONS ARE CARRIED OUT IN THE PRESENCE OF RADICAL INITIATORS OR UNDER UV

IRRADIATION.

RADICAL ADDITION OF HBr TO ALKENES (ANTI-MARKOVNIKOV)

THE ADDITION OF HBr TO ALKENES IN THE PRESENCE OF PEROXIDES PROCEEDS VIA A RADICAL MECHANISM AND RESULTS IN ANTI-MARKOVNIKOV ADDITION. THE PEROXIDE INITIATES THE FORMATION OF BROMINE RADICALS ($\text{Br}^\bullet$). THESE RADICALS ADD TO THE ALKENE TO FORM A CARBON RADICAL. THE CARBON RADICAL THEN ABSTRACTS A HYDROGEN ATOM FROM HBr, REGENERATING A BROMINE RADICAL AND FORMING THE ANTI-MARKOVNIKOV ADDITION PRODUCT. THIS IS A KEY CONTRAST TO THE IONIC HYDROHALOGENATION, WHICH FOLLOWS MARKOVNIKOV'S RULE.

EXAMPLE: $\text{CH}_3\text{-CH=CH}_2 + \text{HBr (PEROXIDE)} \rightarrow \text{CH}_3\text{-CH}_2\text{-CH}_2\text{Br}$

RADICAL POLYMERIZATION: A KEY APPLICATION

RADICAL ADDITION IS THE FUNDAMENTAL PROCESS IN RADICAL POLYMERIZATION, A MAJOR METHOD FOR PRODUCING PLASTICS. INITIATORS LIKE BENZOYL PEROXIDE GENERATE RADICALS, WHICH THEN ADD TO MONOMER UNITS (E.G., ETHENE, STYRENE, VINYL CHLORIDE). THE GROWING POLYMER CHAIN ACTS AS A RADICAL AND CONTINUES TO ADD MORE MONOMER UNITS, LEADING TO THE FORMATION OF LONG POLYMER CHAINS. THE TERMINATION OF THE GROWING CHAINS OCCURS THROUGH RADICAL COMBINATION OR DISPROPORTIONATION.

CATALYSIS IN ADDITION REACTIONS: ENHANCING EFFICIENCY

CATALYSIS PLAYS A CRUCIAL ROLE IN MANY ADDITION REACTIONS, SIGNIFICANTLY INCREASING REACTION RATES AND OFTEN IMPROVING SELECTIVITY. CATALYSTS ARE SUBSTANCES THAT INCREASE THE SPEED OF A CHEMICAL REACTION WITHOUT BEING CONSUMED IN THE PROCESS. VARIOUS TYPES OF CATALYSTS ARE EMPLOYED IN DIFFERENT ADDITION REACTIONS.

ACID CATALYSIS IN HYDRATION

AS DISCUSSED EARLIER, ACID CATALYSTS, SUCH AS SULFURIC ACID, ARE ESSENTIAL FOR THE HYDRATION OF ALKENES. THE ACID PROTONATES THE ALKENE, INITIATING THE FORMATION OF A CARBOCATION INTERMEDIATE, WHICH IS THEN ATTACKED BY WATER. THE ACID IS REGENERATED AT THE END OF THE REACTION.

METAL CATALYSIS IN HYDROGENATION

METAL CATALYSTS LIKE PLATINUM (Pt), PALLADIUM (Pd), AND NICKEL (Ni) ARE WIDELY USED IN THE HYDROGENATION OF ALKENES AND ALKYNES, WHERE HYDROGEN GAS (H_2) IS ADDED ACROSS THE MULTIPLE BOND TO FORM SATURATED COMPOUNDS. THESE HETEROGENEOUS CATALYSTS PROVIDE A SURFACE FOR THE ADSORPTION AND ACTIVATION OF BOTH THE HYDROGEN AND THE UNSATURATED SUBSTRATE, FACILITATING THE ADDITION REACTION.

BASE CATALYSIS IN CONJUGATE ADDITION

BASE CATALYSTS ARE OFTEN EMPLOYED IN CONJUGATE ADDITION REACTIONS, SUCH AS THE MICHAEL ADDITION. THE BASE ABSTRACTS AN ACIDIC PROTON FROM A CARBON ADJACENT TO ELECTRON-WITHDRAWING GROUPS, GENERATING A NUCLEOPHILIC ENOLATE OR CARBANION SPECIES THAT CAN THEN PARTICIPATE IN THE ADDITION REACTION.

CONCLUSION: THE ENDURING IMPORTANCE OF ADDITION REACTIONS

ADDITION REACTIONS REPRESENT A CORNERSTONE OF ORGANIC SYNTHESIS, PROVIDING EFFICIENT PATHWAYS FOR MOLECULAR TRANSFORMATION AND THE CONSTRUCTION OF COMPLEX ORGANIC MOLECULES. FROM THE ELECTROPHILIC ADDITION TO SIMPLE ALKENES TO THE INTRICATE CYCLOADDITIONS LIKE THE DIELS-ALDER REACTION, THESE PROCESSES ARE VITAL FOR CREATING THE DIVERSE RANGE OF COMPOUNDS THAT UNDERPIN OUR MODERN WORLD. UNDERSTANDING THE MECHANISMS AND NUANCES OF VARIOUS ADDITION REACTIONS EXAMPLES ALLOWS CHEMISTS TO DESIGN AND EXECUTE SOPHISTICATED SYNTHETIC STRATEGIES, LEADING TO NEW MATERIALS, MEDICINES, AND TECHNOLOGIES. THE ABILITY TO ADD ATOMS AND FUNCTIONAL GROUPS ACROSS MULTIPLE BONDS, OFTEN WITH HIGH CONTROL OVER REGIOSELECTIVITY AND STEREOCHEMISTRY, MAKES ADDITION REACTIONS AN INDISPENSABLE TOOL IN THE ORGANIC CHEMIST'S ARSENAL. AS WE CONTINUE TO EXPLORE THE FRONTIERS OF CHEMISTRY, THE FUNDAMENTAL PRINCIPLES OF ADDITION REACTIONS WILL UNDOUBTEDLY REMAIN CENTRAL TO INNOVATION AND DISCOVERY.

FREQUENTLY ASKED QUESTIONS

WHAT IS THE MOST COMMON TYPE OF ADDITION REACTION WITH ALKENES?

ELECTROPHILIC ADDITION IS THE MOST COMMON TYPE OF ADDITION REACTION WITH ALKENES, WHERE AN ELECTROPHILE ATTACKS THE ELECTRON-RICH PI BOND.

CAN ALKYNES UNDERGO ADDITION REACTIONS?

YES, ALKYNES, WITH THEIR TRIPLE BONDS, CAN ALSO UNDERGO ADDITION REACTIONS. THEY CAN ADD TWO EQUIVALENTS OF A REAGENT, UNLIKE ALKENES WHICH TYPICALLY ADD ONE.

GIVE AN EXAMPLE OF ADDITION OF HYDROGEN HALIDES TO ALKENES.

THE ADDITION OF HBr TO ETHENE ($\text{CH}_2=\text{CH}_2$) FORMS BROMOETHANE ($\text{CH}_3\text{CH}_2\text{Br}$). IF THE ALKENE IS UNSYMMETRICAL, MARKOVNIKOV'S RULE DICTATES THE REGIOCHEMISTRY OF THE ADDITION.

WHAT IS CATALYTIC HYDROGENATION OF ALKENES?

CATALYTIC HYDROGENATION IS AN ADDITION REACTION WHERE HYDROGEN GAS (H_2) IS ADDED ACROSS THE DOUBLE BOND OF AN ALKENE IN THE PRESENCE OF A METAL CATALYST LIKE PLATINUM, PALLADIUM, OR NICKEL, CONVERTING THE ALKENE TO AN ALKANE.

WHAT IS HYDRATION OF ALKENES AND WHAT ARE THE CONDITIONS?

HYDRATION OF ALKENES IS THE ADDITION OF WATER (H_2O) ACROSS THE DOUBLE BOND TO FORM AN ALCOHOL. THIS TYPICALLY REQUIRES AN ACID CATALYST, SUCH AS SULFURIC ACID (H_2SO_4).

WHAT IS HALOGENATION OF ALKENES AND WHAT ARE THE PRODUCTS?

HALOGENATION OF ALKENES INVOLVES THE ADDITION OF A HALOGEN, LIKE BROMINE (Br_2) OR CHLORINE (Cl_2), ACROSS THE DOUBLE BOND. IT TYPICALLY FORMS A VICINAL DIHALIDE, MEANING THE TWO HALOGEN ATOMS ARE ON ADJACENT CARBON ATOMS.

CAN CARBONYL COMPOUNDS UNDERGO ADDITION REACTIONS?

YES, CARBONYL COMPOUNDS, LIKE ALDEHYDES AND KETONES, UNDERGO NUCLEOPHILIC ADDITION REACTIONS WHERE A NUCLEOPHILE ATTACKS THE ELECTROPHILIC CARBONYL CARBON.

PROVIDE AN EXAMPLE OF NUCLEOPHILIC ADDITION TO A CARBONYL COMPOUND.

THE REACTION OF A GRIGNARD REAGENT ($R-MgX$) WITH AN ALDEHYDE OR KETONE IS A CLASSIC EXAMPLE OF NUCLEOPHILIC ADDITION. THE NUCLEOPHILIC CARBON OF THE GRIGNARD REAGENT ATTACKS THE CARBONYL CARBON, LEADING TO THE FORMATION OF AN ALKOXIDE INTERMEDIATE WHICH IS THEN PROTONATED.

ADDITIONAL RESOURCES

HERE ARE 9 BOOK TITLES RELATED TO ADDITION REACTIONS, WITH SHORT DESCRIPTIONS:

1. ORGANIC CHEMISTRY: THE ART OF FUNCTIONAL GROUP TRANSFORMATIONS

THIS COMPREHENSIVE TEXTBOOK DELVES INTO THE FUNDAMENTAL PRINCIPLES OF ORGANIC CHEMISTRY, WITH A SIGNIFICANT PORTION DEDICATED TO UNDERSTANDING HOW MOLECULES CHANGE THROUGH VARIOUS REACTION TYPES. IT PROVIDES DETAILED EXPLANATIONS AND NUMEROUS EXAMPLES OF ADDITION REACTIONS, COVERING MECHANISMS, REGIOSELECTIVITY, AND STEREOCHEMISTRY. STUDENTS WILL FIND THIS AN INVALUABLE RESOURCE FOR MASTERING THE CONSTRUCTION OF NEW CARBON-CARBON AND CARBON-HETEROATOM BONDS.

2. MECHANISMS IN ORGANIC CHEMISTRY: A VISUAL APPROACH

FOCUSING ON THE "WHY" BEHIND CHEMICAL TRANSFORMATIONS, THIS BOOK USES CLEAR, STEP-BY-STEP DIAGRAMS TO ILLUSTRATE THE ELECTRON MOVEMENTS IN VARIOUS ORGANIC REACTIONS. IT OFFERS AN IN-DEPTH EXPLORATION OF ADDITION REACTIONS, BREAKING DOWN COMPLEX MECHANISMS INTO DIGESTIBLE STEPS. THE VISUAL FORMAT MAKES IT PARTICULARLY EFFECTIVE FOR STUDENTS SEEKING TO GRASP THE INTRICACIES OF ELECTROPHILIC, NUCLEOPHILIC, AND RADICAL ADDITIONS.

3. STEREOCHEMISTRY OF ORGANIC REACTIONS: CONTROL AND PREDICTABILITY

THIS SPECIALIZED VOLUME EXAMINES THE CRITICAL ROLE OF STEREOCHEMISTRY IN ORGANIC SYNTHESIS. IT THOROUGHLY DISCUSSES HOW ADDITION REACTIONS CAN BE CONTROLLED TO PRODUCE SPECIFIC STEREOISOMERS, A CRUCIAL ASPECT FOR PHARMACEUTICAL AND FINE CHEMICAL INDUSTRIES. THE BOOK PROVIDES NUMEROUS CASE STUDIES AND EXAMPLES OF STEREOSELECTIVE ADDITION REACTIONS, HIGHLIGHTING IMPORTANT REAGENTS AND CONDITIONS.

4. ADVANCED TOPICS IN CATALYSIS FOR ORGANIC SYNTHESIS

THIS BOOK EXPLORES THE CUTTING-EDGE OF CATALYTIC METHODS USED TO FACILITATE ORGANIC REACTIONS. IT FEATURES EXTENSIVE COVERAGE OF TRANSITION METAL CATALYSIS AND ORGANOCATALYSIS AS APPLIED TO VARIOUS ADDITION REACTIONS. READERS WILL LEARN HOW CATALYSTS CAN SIGNIFICANTLY IMPROVE THE EFFICIENCY, SELECTIVITY, AND SUSTAINABILITY OF FORMING NEW BONDS THROUGH ADDITION PROCESSES.

5. NAME REACTIONS IN ORGANIC SYNTHESIS: A PRACTICAL GUIDE

THIS PRACTICAL HANDBOOK SERVES AS A COMPREHENSIVE REFERENCE FOR IMPORTANT NAMED REACTIONS IN ORGANIC CHEMISTRY. IT DEDICATES SUBSTANTIAL SECTIONS TO KEY ADDITION REACTIONS LIKE THE DIELS-ALDER, MICHAEL, AND GRIGNARD REACTIONS, EXPLAINING THEIR HISTORICAL CONTEXT AND SYNTHETIC UTILITY. THE BOOK OFFERS CLEAR REACTION SCHEMES AND EXAMPLES OF THEIR APPLICATION IN BUILDING COMPLEX MOLECULES.

6. PERICYCLIC REACTIONS AND CONCERTED MECHANISMS

THIS TEXT FOCUSES ON REACTIONS THAT OCCUR IN A SINGLE, CONTINUOUS STEP WITHOUT THE FORMATION OF DISCRETE INTERMEDIATES. IT PROVIDES A THOROUGH TREATMENT OF PERICYCLIC REACTIONS, INCLUDING CYCLOADDITION REACTIONS WHICH ARE A PROMINENT EXAMPLE OF ADDITION PROCESSES. UNDERSTANDING THESE CONCERTED PATHWAYS OFFERS A DEEPER INSIGHT INTO THE ELECTRONIC FACTORS GOVERNING REACTIVITY.

7. ORGANOMETALLIC CHEMISTRY AND CATALYSIS IN ORGANIC TRANSFORMATIONS

BRIDGING THE GAP BETWEEN INORGANIC AND ORGANIC CHEMISTRY, THIS BOOK EXPLORES THE ROLE OF ORGANOMETALLIC COMPOUNDS AND THEIR CATALYTIC APPLICATIONS. IT EXTENSIVELY COVERS TRANSITION METAL-CATALYZED ADDITION REACTIONS, SUCH AS HYDROBORATION, HYDROSILYLATION, AND HYDROFORMYLATION. THE BOOK HIGHLIGHTS HOW THESE CATALYSTS ENABLE HIGHLY EFFICIENT AND SELECTIVE BOND FORMATIONS.

8. GREEN CHEMISTRY IN MODERN SYNTHESIS: SUSTAINABLE ADDITION REACTIONS

THIS BOOK CHAMPIONS ENVIRONMENTALLY FRIENDLY APPROACHES TO ORGANIC SYNTHESIS, EMPHASIZING THE DEVELOPMENT OF SUSTAINABLE CHEMICAL PROCESSES. IT SHOWCASES EXAMPLES OF ADDITION REACTIONS THAT UTILIZE LESS HAZARDOUS REAGENTS, GENERATE LESS WASTE, AND REQUIRE LESS ENERGY. READERS WILL DISCOVER HOW PRINCIPLES OF GREEN CHEMISTRY ARE BEING APPLIED TO IMPROVE THE EFFICIENCY AND ENVIRONMENTAL IMPACT OF ADDITION REACTIONS.

9. THE ALKENES: SYNTHESIS AND REACTIVITY

AS A CORNERSTONE OF ORGANIC CHEMISTRY, ALKENES ARE CENTRAL TO UNDERSTANDING ADDITION REACTIONS. THIS BOOK PROVIDES A DETAILED EXPLORATION OF THE SYNTHESIS, STRUCTURE, AND EXTENSIVE REACTIVITY OF ALKENES. IT OFFERS A DEEP DIVE INTO THE VARIOUS TYPES OF ADDITION REACTIONS THAT ALKENES UNDERGO, INCLUDING ELECTROPHILIC ADDITIONS, RADICAL ADDITIONS, AND CYCLOADDITIONS, WITH ABUNDANT EXAMPLES.

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