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CHEMISTRY II

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Hydrocarbon Compounds:

Alkanes, Alkenes, Alkynes, and Aromatic Hydrocarbons



1. ALKANES

Alkanes are a class of organic compounds consisting solely of carbon and hydrogen atoms bonded by single bonds, with no other functional groups present. They follow the general formula C_nH_{2n+2} and can be categorized into three main groups: linear straight-chain alkanes, branched alkanes, and cycloalkanes. Alkanes are classified as saturated hydrocarbons due to their lack of unsaturation, meaning they have no double or triple bonds, which are highly reactive in organic chemistry. Although not entirely unreactive, alkanes could be more interesting under most laboratory conditions. Nonetheless, they hold great significance in organic chemistry and industry, as they are a primary component of gasoline and lubricating oils, as well as being extensively utilized in various organic processes.

In the nomenclature of *branched-chain alkanes*, the longest continuous chain of carbon atoms is called the parent chain. Any side branches are known as substituent groups because they appear to replace hydrogen atoms in the straight chain. Naming involves identifying the largest hydrocarbon chain, its branches, functional groups, and their relative priority. If you envision removing a hydrogen atom from an alkane, the resulting partial structure is called an alkyl group. Alkyl groups are not independent stable compounds; they are components of larger compounds. The naming of alkyl groups involves replacing the **-ane** ending of the parent alkane with an -**yl** ending.

When it comes to generating alkyl groups, straight-chain alkyl groups are formed by removing a hydrogen atom from an end carbon of an alkane molecule. On the other hand, branched alkyl groups are created by removing a hydrogen atom from an internal carbon. There are two possible 3-carbon alkyl groups and four possible 4-carbon alkyl groups. In the accompanying illustration, alkyl groups derived from straight-chain alkanes are shown (Figure 1). It's worth mentioning that when naming alkyl groups, the prefixes "sec-" (for secondary) and "tert-" (for tertiary) are used for the 4-carbon alkyl groups in the figure. These prefixes indicate the number of other carbon atoms attached to the branching carbon atom, and there are four possibilities: primary (1°), secondary (2°), tertiary (3°), and quaternary (4°).



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Figure 1. Ways that carbon and hydrogen might combine to make alkanes.

Organic compounds display a remarkable variety due to the ability of carbon atoms to form ring structures. Organic compounds containing hydrocarbon rings are referred to as *cyclic hydrocarbons*. To indicate the presence of a ring structure in a hydrocarbon, the prefix "**cyclo**-" is added to the hydrocarbon's name. Therefore, cyclic hydrocarbons that consist exclusively of single bonds are known as cycloalkanes. Cycloalkanes can possess rings with three, four, five, six, or even more carbon atoms. For example, the name for the six-carbon cycloalkane is "cyclohexane." It's important to note that cyclohexane (C₆H₁₂) has two fewer hydrogen atoms than straight-chain hexane (C₆H₁₄). This difference arises because, in cyclohexane, a valence electron from each of two carbon atoms forms a carbon-carbon bond instead of a carbon-hydrogen bond.

When naming substituted cycloalkanes, the same International Union of Pure and Applied Chemistry (IUPAC) rules used for straight-chain alkanes are generally followed, but with a few adjustments. With cycloalkanes, there's no need to identify the longest chain because the ring is always considered the parent chain. Since cyclic structures lack ends, numbering starts from the carbon atom bonded to the substituent group. When there are two or more substituents, the carbons are numbered around the ring to give the lowest possible set of numbers for the substituents. If only one group is attached to the ring, no numbering is necessary. An example in Figure 2 can illustrate the naming process for cycloalkanes.



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Figure 2. Examples of cycloalkanes.

1.1. Physical properties of Alkanes

The physical properties of alkanes, such as their boiling and melting points, are influenced by several factors. One of the primary contributors to these properties is the presence of weak dispersion forces (also known as London dispersion forces or Van der Waals forces) between molecules. As the molecular weight of alkanes increases, there is a regular and predictable increase in both boiling and melting points. This effect results from the stronger dispersion forces that occur in larger molecules. Dispersion forces arise from temporary fluctuations in electron distribution within molecules, leading to the creation of temporary dipoles. Larger molecules have more electrons and larger electron clouds, meaning these temporary dipoles are more significant. As a result, it takes more energy to break these forces and convert a solid into a liquid or a liquid into a gas. This explains why larger alkanes have higher melting and boiling points.

Conversely, increased branching in alkane molecules tends to lower their boiling points. This effect can be explained by considering the shape and surface area of the molecules. Branched-chain alkanes are more nearly spherical compared to straight-chain alkanes, and they have smaller surface areas. Smaller surface areas lead to weaker dispersion forces between molecules, making it easier to overcome these forces and change from a liquid to a gas (boil). Consequently, the presence of branches in the alkane molecule results in lower boiling points.

For example, consider the alkanes pentane, isopentane (2-methylbutane), and neopentane (2,2dimethylpropane). Pentane has no branches and boils at 36.1 °C. Isopentane has one branch and boils at 27.85 °C, and neopentane has two branches and boils at 9.5 °C. The increasing degree of branching in these molecules leads to progressively lower boiling points. Similarly, straight-chain octane boils at 125.7 °C, whereas isooctane (2,2,4-trimethylpentane) with more branching boils at 99.3 °C due to reduced dispersion forces resulting from its increased spherical shape and reduced surface area.

In the context of solubility, the general guideline is "like dissolves like." This means that polar substances are soluble in polar solvents, nonpolar substances are soluble in nonpolar solvents, but polar and nonpolar substances do not readily mix. Alkanes, being nonpolar molecules, are insoluble in water, which is a polar solvent. Because they are less dense than water, alkanes tend to float on water surfaces, as is the case with oil slicks. Alkanes, as well as other substances that do not dissolve in water, are often described as hydrophobic, meaning they have an aversion to water. Liquid alkanes with high molecular weight are used as emollients to replace natural oils that may be washed away during bathing or swimming. For example, Vaseline is a semisolid mixture of alkanes used for this purpose.

Alkanes are characterized by their low reactivity and limited biological activity. They are colorless and odorless, nonpolar compounds. The relatively weak London dispersion forces between alkane molecules lead to varying physical states based on molecular size and shape. Short carbon chains result in gaseous substances, while moderate carbon chains yield volatile liquids with densities around 0.7 g/mL. Longer carbon chains result in solids. This relationship between molecular size, shape, and intermolecular forces explains the differences in physical states.

Because alkanes have relatively predictable physical properties and undergo few chemical reactions beyond combustion, they are frequently used as a basis for comparing the properties of other organic compound families. This is particularly evident when examining their physical properties, including boiling points. Cycloalkanes, structurally related to alkanes but have a ring structure, exhibit slightly higher boiling points (about 20 K higher) than their corresponding straight-chain alkanes. This modest increase in boiling points for cycloalkanes is attributed to the tidier and less "wriggly" arrangement of molecules due to the ring structure, allowing them to get closer together.

1.2. Chemical properties of Alkanes

Alkanes, often referred to as paraffins, get their name from the Latin term "parum affinis," which means "little affinity." This name is fitting because alkanes exhibit little chemical affinity for other substances and are generally chemically inert to most laboratory reagents. They are also relatively biologically inert and are not frequently involved in the chemistry of living organisms. Alkanes are known for their low reactivity compared to other chemical species.

This low reactivity is primarily due to the fact that the carbon atoms in alkane molecules have achieved their octet of electrons by forming four covalent bonds. This is the maximum number of bonds allowed under the octet rule, explaining carbon's valence number of 4. These four bonds formed by carbon in alkanes are sigma bonds, which are highly stable due to the extensive overlap of carbon's atomic orbitals with those of neighboring atoms. To initiate reactions in alkanes, additional energy input is required, often heat or radiation. Alkanes can react with oxygen, halogens, and other substances under suitable conditions. For example, combustion in an engine or furnace involves the reaction of an alkane with oxygen when the alkane is used as fuel, resulting in the formation of carbon dioxide and water along with the release of a significant amount of heat. Alkanes can also react with chlorine (Cl₂) through chlorination. When a mixture of alkane and chlorine is irradiated with ultraviolet light, a sequential substitution of hydrogen atoms in the alkane by chlorine atoms occurs, producing a combination of chlorinated products. For instance, methane can react with Cl₂ to yield a mixture of CH₃Cl, CH₂Cl₂, CHCl₃, and CCl₄.

Alkanes are non-polar solvents because they consist solely of carbon and hydrogen atoms. They are immiscible in water but readily mixed with other non-polar solvents. Due to the weak dipole-dipole forces present in alkanes, they cannot break the strong hydrogen bonds between water molecules, explaining their immiscibility in water.

Moreover, they exhibit a range of physical states, with methane through butane being flammable gases at standard temperature and pressure. For example, pentane is an extremely flammable liquid, with boiling and melting points increasing as the chain length grows. Longer alkanes are waxy solids, and

examples include candle wax, which contains chains typically ranging from C20 to C25. As the chain length increases, you eventually reach polyethylene, consisting of carbon chains of indefinite length, and it is generally a hard, white solid.

1.3. Haloalkanes

Haloalkanes, which are organic compounds containing halogen substituents, are less commonly encountered in biochemical pathways of terrestrial organisms compared to their oxygen-containing counterparts. However, the reactions that haloalkanes undergo, particularly nucleophilic substitutions and eliminations, are important and serve as relatively simple models for many mechanistically similar but structurally more complex reactions found in biomolecules. Therefore, a detailed study of the substitution and elimination reactions of alkyl halides, two fundamental reaction types in organic chemistry, is essential.

The physical properties of haloalkanes differ from those of their corresponding alkanes, and these differences can be understood by considering the size of the halogen substituent and the polarity of the carbon-halogen (C-X) bond. The bond strength of C-X decreases as the size of the halogen (X) increases. Halogens increase in size going down the periodic table, which results in longer carbon-halogen bond lengths. Additionally, the bond strengths decrease in the same direction in the periodic table. In the context of halomethanes (CH₃X), the C-X bond-dissociation energies decrease along the series F > Cl > Br > I while the C-X bond lengths increase. This trend results from the larger size of halogens as we move from fluorine to iodine. The C-X bond is polarized, as halogens are more electronegative than carbon. This polarization results in a polar C-X bond, with the carbon atom carrying a slight positive charge (δ +) and the halogen bearing a slight negative charge (δ -). This polarity leads to a substantial dipole moment in halomethanes. It implies that the carbon atom bonded to the halogen can act as an electrophile in polar reactions, making it susceptible to attack by nucleophilic species.

Haloalkanes typically have higher boiling points than their corresponding alkanes. This is mainly due to the coulombic attraction between the δ + and δ - ends of C-X bond dipoles in the liquid state, a type of dipole-dipole interaction. The boiling points also increase with the size of the halogen (X) because of more significant London interactions. London forces arise from the mutual correlation of electrons among molecules and are more effective when the outer electrons are not tightly bound to the nucleus, as is the case with larger atoms. The polarizability of an atom or group, which indicates the degree to which its electron cloud can be deformed under the influence of an external electric field, plays a crucial role in determining the strength of London interactions and, consequently, boiling points.

Haloalkanes, which contain an electrophilic carbon atom bonded to a halogen, can undergo nucleophilic substitution reactions. In these reactions, the electrophilic carbon atom reacts with nucleophiles, which are substances that possess an unshared pair of electrons. Nucleophiles can be either anions (negatively charged species) like hydroxide (OH-) or neutral species such as ammonia (:NH₃). In a nucleophilic substitution reaction, the nucleophile attacks the haloalkane and replaces the halide ion (X⁻) (Figure 3).



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Figure 3. Nucleophilic substitution mechanism: a) negative nucleophile gives neutral product; b) neutral nucleophile gives positively charged product (as a salt).

- Nucleophilic Substitution with a negatively charged nucleophile: In this case, a negatively charged nucleophile, such as hydroxide (OH⁻), reacts with a haloalkane. The result is a neutral substitution product, where the nucleophile replaces the halide ion.
- Nucleophilic Substitution with an uncharged nucleophile: Here, an uncharged nucleophile (Nu) reacts with a haloalkane. The outcome is a positively charged product, along with a counterion, which forms a salt.

The term "leaving group" refers to the halide ion (X⁻) that is displaced during the reaction. It is called the leaving group because it departs from the molecule, making space for the incoming nucleophile.

1.3.1. The $S_N 2$ reaction

The name S_N2 provides insight into the nature of this mechanism: "S" stands for substitution; "N" stands for Nucleophilic; and "2" indicates that it is a bimolecular reaction because the haloalkane (substrate) and the nucleophile are involved in the rate-determining step. The S_N2 mechanism is a type of reaction mechanism that involves two fundamental processes: i) the reaction of an electrophile (the substrate) and a nucleophile to form a new covalent bond, and ii) the breaking of a bond in the substrate to form a stable ion or molecule, which results in the departure of a leaving group.

A crucial characteristic of the S_N2 mechanism is its single-step nature, occurring without intermediates. In this process, the incoming nucleophile reacts with the alkyl halide (the substrate) from the opposite side to the leaving group. This leads to the inversion of the stereochemical configuration, as the nucleophile bonds to the carbon atom on one side of the substrate. At the same time, the halide ion departs from the other side. The transition state exhibits a planar arrangement of the remaining three bonds to carbon. Figure 4 shows the mechanism of the S_N2 reaction.





The nucleophile (in this case, OH⁻) attacks the electrophilic carbon from the backside, which is the side opposite to the direction in which the leaving group (Br⁻) departs. As the nucleophile approaches the carbon, the leaving group (Br-) begins to leave. The formation of the new C-OH bond and the breaking of the old C-Br bond occur simultaneously. During this process, there is a very short transient moment when the carbon atom is partially bonded with both OH and Br, leading to a high-energy transition state. In the transition state of the S_N2 reaction, there are five groups around the carbon (sp² hybridization), and it can be described as "pentacoordinated." Eventually, the new bond is completely formed, and the old bond is entirely broken. As the reaction forms products, the inversion motion is completed, and the carbon returns to the tetrahedral sp³ configuration. This orbital description helps explain the stereochemical inversion in S_N2 reactions.

1.3.2. The S_N 1 reaction

The S_N1 mechanism ("1" indicates that it is an unimolecular reaction, as only the haloalkane is involved in the rate-determining step) is another substitution reaction mechanism In these reactions, bond breaking between the carbon and the leaving group occurs before bond formation with the nucleophile begins.

The haloalkane spontaneously dissociates into a carbocation (positively charged carbon) and the leaving group X- in a slow, rate-limiting step. The intermediate carbocation is immediately trapped by the nucleophile (e.g., water) in a faster second step. Water is not considered a reactant in the step whose rate is measured. Due to the involvement of a carbocation intermediate, the stereochemical outcome of S_N1 reactions is different from that of S_N2 reactions. Carbocations are planar, sp^2 -hybridized, and achiral (lacking a chiral center). As a result, if an S_N1 reaction is carried out on one enantiomer of a chiral reactant

and goes through an achiral carbocation intermediate, the product loses its optical activity. This leads to a racemic mixture, meaning a 50:50 mixture of enantiomers is formed (Figure 5).



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Figure 5. Stereochemistry of the $S_N 1$ mechanism.

1.3.3. Factors that determine $S_N 1$ or $S_N 2$ predominance

a. Structure of the nucleophile. In an S_N2 reaction, the nucleophile plays a crucial role in the ratedetermining step. Hence, the effectiveness of the nucleophile directly influences the likelihood of the reaction proceeding via this mechanism. Conversely, in an S_N1 reaction, the nucleophile's involvement in the rate-determining step is minimal. Consequently, an S_N1 reaction can, in principle, occur at a similar rate with various common nucleophiles, irrespective of their relative nucleophilic strengths.

Nucleophilicity is a kinetic attribute gauged through relative reaction rates. To determine the relative nucleophilicities of different nucleophiles, we assess their ability to displace a leaving group from a haloalkane. A key trend is that the more basic a species is, the more potent its nucleophilicity. This trend reflects the influence of nucleophiles' basicity on their nucleophilic reactivity. For instance, negatively charged nucleophiles like hydroxide ions (OH⁻) and alkoxide ions (RO⁻) typically exhibit stronger nucleophilic properties and greater basicity than neutral nucleophiles.

b. Structure of the haloalkane. S_N1 reactions are primarily influenced by electronic considerations, particularly the relative stabilities of carbocation intermediates. The stability of carbocations is a critical factor. Tertiary (3°) carbocations are the most stable and require the least energy to form, while primary (1°) carbocations are the least stable and necessitate the highest energy for their formation. In fact, 1° carbocations are so unstable that they have never been observed in solution. Consequently, 3° haloalkanes are most prone to undergo reactions involving carbocation formation, 2° haloalkanes are less inclined toward this mode of reaction, and methyl and 1° haloalkanes never engage in such reactions.



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In contrast, S_N2 reactions are governed by steric factors, and their transition states are highly sensitive to the degree of congestion at the reaction site. This distinction can be summarized as follows: The success of a substitution reaction depends on the nucleophile's ability to approach the substitution center and initiate the formation of a new covalent bond with it. A comparison of the ease of nucleophilic approach to the substitution center in a 1° haloalkane versus a 3° haloalkane reveals that the former offers a significantly more accessible approach. In the case of a 1° haloalkane, the backside of the substitution center is shielded by two hydrogen atoms and one alkyl group. Conversely, a 3° haloalkane features three alkyl groups crowding the backside of the substitution center.



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When electronic and steric factors are pitted against each other, it becomes evident that 3° haloalkanes predominantly undergo S_N1 reactions. This is because 3° carbocation intermediates exhibit remarkable stability, and the backside approach of a nucleophile to the substitution center in a 3° haloalkane is impeded by the presence of three surrounding groups. In contrast, 3° haloalkanes do not participate in S_N2 reactions. Halomethanes and 1° haloalkanes, on the other hand, are not hindered by crowding around the substitution center and consequently follow the S_N2 mechanism, never involving the S_N1 mechanism due to the extreme instability of methyl and primary carbocations.

c. The leaving group. In both S_N1 and S_N2 reactions, the transition state for nucleophilic substitution on a haloalkane leads to a partial negative charge on the halogen leaving group. The suitability of halogens like Cl⁻, Br⁻, and I⁻ as leaving groups arises from their favorable combination of size and electronegativity, effectively stabilizing the resulting negative charge. Consequently, the ability of a group to serve as a leaving group hinges on its stability as an anion. The most stable anions, found in the conjugate bases of strong acids, make the best leaving groups. Within this group, the optimal leaving groups are the halogens I⁻, Br⁻, and Cl⁻. In contrast, hydroxide ion (OH⁻), methoxide ion (CH₃O⁻), and amide ion (NH₂⁻) are considered exceptionally poor leaving groups and are rarely, if ever, displaced in nucleophilic aliphatic substitution reactions. Given that the leaving group departs with a negative charge in most S_N2 reactions, the superior leaving groups can most effectively stabilize this negative charge within the transition state. Enhanced charge stabilization by the leaving group results in a lower energy transition state, consequently accelerating the reaction rate. However, it's essential to note that the groups providing the most effective charge stabilization also happen to be the weakest bases. As a result, weak bases like Cl⁻, Br⁻, and tosylate ion serve as good leaving groups, while strong bases like OH⁻ and NH₂⁻ are unsuited for this role.

d. Solvent. Solvents play a crucial role in providing the medium for reactants to dissolve and facilitating nucleophilic substitution reactions. Typically, the solvents used in these reactions fall into two categories: protic and aprotic. The impact of solvents on S_N2 and S_N1 reactions differs significantly. Protic solvents are characterized by the presence of -OH groups and their ability to act as hydrogenbond donors. Examples of protic solvents for nucleophilic substitution reactions include water, low-molecular-weight alcohols, and low-molecular-weight carboxylic acids. These solvents can effectively solvate both anionic and cationic components through electrostatic interactions between their partially negatively charged oxygen(s) and the cation, as well as between their partially positively charged hydrogen(s) and the anion. This property benefits ionizing C-X bonds to produce an X⁻ anion and a carbocation, making protic solvents ideal for carrying out S_N1 reactions.



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The solvent choice significantly affects $S_N 2$ reaction rates. Protic solvents containing -OH or -NH groups are generally less favorable for $S_N 2$ reactions, while polar aprotic solvents, which are polar but lack -OH or -NH groups, are more conducive. Protic solvents, such as methanol and ethanol, tend to slow down $S_N 2$ reactions by solvating the reactant nucleophile. Solvent molecules form a cage around the nucleophile via hydrogen bonding, effectively reducing its energy and reactivity.



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Aprotic solvents lack -OH groups and cannot function as hydrogen bond donors. They are unsuitable for facilitating carbocation formation as they would leave the departing group unsolvated, making them unsuitable for S_N1 reactions. Polar aprotic solvents such as dimethyl sulfoxide and acetone, along with less polar aprotic solvents like dichloromethane and diethyl ether, are particularly suitable for S_N2 reactions. These solvents can solvate cations but not anions, making them compatible with "naked" and highly reactive anions as nucleophiles when ionic nucleophiles like Na⁺CN⁻ and Na⁺OH⁻ are used. Consequently, they enable nucleophilic anions to retain their high reactivity and lead to increased rates of S_N2 reactions. For example, switching from methanol to HMPA has resulted in a notable rate increase of 200,000 for the reaction of azide ion with 1-bromobutane.

It's important to emphasize that both S_N1 and S_N2 reactions exhibit solvent effects, but these effects stem from different mechanisms. S_N2 reactions are hindered in protic solvents because solvation lowers the ground-state energy of the nucleophile. In contrast, S_N1 reactions benefit from protic solvents as solvation reduces the transition state energy, leading to the formation of a carbocation intermediate.

1.3.4. Elimination Reactions.

Elimination reactions have greater complexity compared to substitution reactions for a variety of reasons. Firstly, they present a challenge in terms of regiochemistry. When an unsymmetrical halide undergoes elimination (removal of HX), it typically yields a mixture of alkene products, and our ability to predict the major product is limited. Zaitsev's rule, established by Russian chemist Alexander Zaitsev in 1875, provides some guidance; it suggests that base-induced elimination reactions usually, though not always, result in the formation of the most stable alkene product. This corresponds to the alkene with a higher number of alkyl substituents on the carbon atoms, forming the double bond. Additionally, the study of elimination reactions is further complicated by the existence of various mechanisms through which they can occur, just like substitution reactions.

The E2 Mechanism

The E2 (bimolecular elimination) reaction is initiated by treating an alkyl halide with a strong base, such as a hydroxide ion or alkoxide ion (RO⁻). This pathway represents the most frequently observed type of elimination reaction. Much like the S_N2 reaction, the E2 reaction unfolds in a single step without intermediate stages. When the base initiates the removal of an H⁺ atom from a carbon adjacent to the leaving group, several concurrent processes occur: the breaking of the C-H bond, the formation of a C=C bond, and the departure of the leaving group, carrying with it the electron pair from the C-X bond (Figure 6). This mechanism is substantiated by various pieces of evidence, including the observation that E2 reactions exhibit second-order kinetics and adhere to the rate law: rate = k [RX] [Base]. In this scenario, the base and the alkyl halide participate in the rate-determining step.



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Figure 6. E2 elimination reaction mechanism.

Stereochemistry in E2 eliminations reveals that these reactions occur with a periplanar geometry, where all four critical atoms—the hydrogen, the two carbons, and the leaving group—are aligned in the same plane. There are two possible orientations for this periplanar geometry: *syn periplanar*, where the H and the X are on the same side of the molecule (Figure 7a), and *anti periplanar*, where the H and the X are on opposite sides of the molecule (Figure 7b). Between the two, the anti periplanar geometry is energetically favored because it permits the substituents on the two carbons to assume a staggered conformation. In contrast, the syn geometry necessitates their alignment in an eclipsed manner.



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Figure 7. Stereoselectivity of E2 elimination: a) syn periplanar geometry, eclipsed and higher energy; b) anti periplanar geometry, staggered and lower energy.

The significance of periplanar geometry lies in the requirement for overlap between the sp³ and s orbitals in the initial C-H and C-X bonds, which must transform into p orbitals in the alkene product. Such orbital overlap is most easily achieved if all the orbitals are inherently situated in the same plane from the outset—hence the term "periplanar".

The E1 mechanism

Similar to the relationship between the E2 and S_N2 reactions, the S_N1 reaction has a counterpart known as the E1 reaction (unimolecular elimination). Substantial evidence supports the E1 mechanism. E1 reactions exhibit first-order kinetics, aligning with a rate-determining, unimolecular dissociation process.

In contrast to the E2 reaction, which necessitates anti periplanar geometry, the E1 reaction lacks specific geometric prerequisites since the halide and the hydrogen depart in separate steps. Consequently, we anticipate obtaining a more stable (in accordance with Zaitsev's rule) product from the E1 reaction, and this expectation holds. E1 eliminations commence with the same unimolecular dissociation, leading to the formation of a carbocation, as seen in the SN1 reaction. However, in E1 reactions, this dissociation is followed by the loss of H⁺ from the adjacent carbon instead of a substitution process (Figure 8).



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rigure 8. ET eminiation reaction mechanism.

In fact, E1 and S_N1 reactions typically occur together when an alkyl halide is treated with a non-basic nucleophile in a protic solvent. Consequently, substrates that are well-suited for E1 reactions are also ideal for S_N1 reactions, resulting in mixtures of both substitution and elimination products. For instance, when 2-chloro-2-methylpropane is heated to 65° C in an 80% aqueous ethanol solution, it yields a mixture of 2-methyl-2-propanol (S_N1) and 2-methylpropene (E1) in a 64:36 ratio.

2. ALKENES

Alkenes, due to their double bond, possess a lower hydrogen count compared to alkanes with the same number of carbon atoms. Specifically, the formula for alkenes is C_nH_{2n} , in contrast to C_nH_{2n+2} for alkanes. This difference reflects their unsaturated nature. For example, ethylene exhibits the formula C_2H_4 , while ethane has the formula C_2H_6 . Similar to other organic compounds, a few alkenes are still recognized by common names. In these cases, the -**ene** ending of the corresponding alkane is replaced by -**ylene**, and additional substituent names are introduced as prefixes.

Cycloalkenes follow a naming convention that bears similarities to their open-chain counterparts. However, because there's no clear chain end in a cyclic structure, numbering is initiated in a manner that situates the double bond between C1 and C2 while simultaneously ensuring the first substituent is assigned the lowest possible number. It's worth noting that indicating the position of the double bond in the name is optional, as it's always positioned between C1 and C2. In the case of dienes, more recent naming rules, although not universally adopted, recommend placing the locant immediately before the suffix.

For historical reasons, a handful of alkenes have names firmly ingrained in common usage that don't strictly adhere to established rules. For instance, the alkene derived from ethane is ideally named "ethene."

Still, the term "ethylene" has been circulating for so long that it is recognized by the IUPAC. Additionally, it's worth mentioning that a = CH_2 substituent is referred to as a "methylene group", a H₂C=CH substituent is termed a "vinyl group," and an H₂C=CHCH₂- substituent is designated an "allyl group".

The carbon-carbon double bond in alkenes exhibits distinctive electronic and structural characteristics. The double bond comprises sigma (σ) and pi (π) components (Figure 9). In the case of ethene, it adopts a planar configuration featuring two trigonal carbon atoms with bond angles approximating 120°. Consequently, both carbon atoms are best described as sp² hybridized. On each carbon atom, two sp2 hybrids overlap with hydrogen 1s orbitals, forming the four C-H σ bonds. The remaining sp² orbitals, one on each carbon, combine through the overlap to create the carbon-carbon σ bond. Additionally, each carbon atom possesses a 2p orbital, oriented in a parallel fashion and positioned closely enough to overlap, thereby generating the π bond. In a π bond, electron density is distributed across both carbon atoms, encompassing regions above and below the molecular plane.



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2.1. Cis-Trans Isomerism in Alkenes

Rotation around the double bond in alkenes entails the disruption of the π bond. While unrestricted rotation typically occurs around single bonds, the same does not apply to double bonds. To enable rotation around a double bond, the π bond must be broken and reformed. Consequently, the barrier to rotation around a double bond must be at least as substantial as the strength of the π bond itself, estimated at approximately 350 kJ/mol (84 kcal/mol). This stands in stark contrast to the minimal 12 kJ/mol barrier to bond rotation in ethane.

Nevertheless, alkenes can assume *cis* and *trans* configurations, resulting in isomerism. Since bond rotation is prohibited, two 2-butenes cannot spontaneously interconvert, making them distinct and isolable compounds. Analogous to disubstituted cycloalkanes, these compounds are referred to as *cis-trans* stereoisomers. The variant with substituents situated on the same side of the double bond is labeled as cis-2-butene, while the isomer with substituents on opposing sides is designated as trans-2-butene.



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The *cis-trans* naming convention employed earlier applies exclusively to disubstituted alkenes, compounds possessing two substituents other than hydrogen on the double bond. For trisubstituted and tetrasubstituted double bonds, a more comprehensive method is necessary to describe the double-bond geometry.

2.2. Stability of Alkenes

The previous *cis*- and *trans*-2-butene isomers exhibit different degrees of stability. When the alkene is subjected to treatment with a potent acid catalyst, *cis*-2-butene transforms *trans*-2-butene. However, when they reach an equilibrium state, their stabilities are not equal. The *trans* isomer surpasses the *cis* isomer in stability by 2.8 kJ/mol (0.66 kcal/mol) at room temperature, establishing a ratio of 76:24. The decreased stability of *cis* alkenes in comparison to their *trans* counterparts arises from steric strain between the two larger substituents situated on the same side of the double bond.

The stability assessment of alkenes involves the hydrogenation process, where alkenes are converted into their corresponding alkanes. The stability procedure takes places by the treatment of alkenes with H₂ gas in the presence of a catalyst, such as palladium or platinum. Energy diagrams illustrating the hydrogenation reactions of *cis*- and *trans*-2-butane are depicted in the figure (Figure 10). Due to the 2.8 kJ/mol lower stability of *cis*-2-butene compared to *trans*-2-butane, the energy diagram positions the cis alkene at a higher energy level. Post-reaction, however, both curves reach an equivalent energy level (butane). Consequently, it can be deduced that ΔG° for the reaction of the cis isomer must exceed ΔG° for the reaction of the trans isomer by 2.8 kJ/mol. In simpler terms, more energy is released during the hydrogenation of the cis isomer, as it initially possesses higher energy.



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2.3. Physical Properties of Alkenes

For alkanes, the melting point tends to rise with an increase in the number of carbon atoms (e.g., butane, pentane, and hexane). In case of alkenes, they exhibit a different pattern. Cis disubstituted alkenes generally have lower melting points compared to their corresponding alkanes (Table 1).

The melting points are also influenced by the molecular shape and packing within the crystal lattice. The presence of a double bond in cis-disubstituted alkenes causes a U-shaped distortion in the molecule, disrupting the packing and leading to lower melting points. These are usually lower than those of both the corresponding alkanes and their isomeric trans alkenes. Notably, the sub-room-temperature melting point of vegetable oil can be attributed to a cis double bond.

Compound	Melting point (°C)		
Butane	-138		
trans-2-Butene	-106		
cis-2-Butene	-139		
Pentane	-130		
trans-2-Pentene	-135		
cis-2-Pentene	-180		
Hexane	-95		
trans-2-Hexene	-133		
cis-2-Hexene	-141		
trans-3-Hexene	-115		
cis-3-Hexene	-138		

Table 1. Comparison of melting points of alkanes and alkenes.

2.4. Synthesis of alkenes

Alkenes can be derived from alcohols through elimination reactions. The process involves treating alcohols with mineral acids at elevated temperatures, leading to the formation of alkenes by eliminating water, a procedure known as dehydration. This dehydration can occur through either the E1 or E2 pathways. Typically, alcohols are dehydrated by heating them in the presence of sulfuric or phosphoric acid at relatively high temperatures, within the range of 120-170°C. It's important to note that the ease of water elimination from alcohols increases with the substitution level on the carbon atom bearing the hydroxy group (Figure 11).



Source: Image made by the authors.



2.5. Reactivity of Alkenes

In the process of adding HX to an alkene, the hydrogen atom attaches to the carbon atom that has fewer alkyl substituents, while the halogen (X) atom attaches to the carbon atom with more alkyl substituents. When both carbon atoms in the double bond have the same degree of substitution, a mixture of addition products is formed. For instance, when HX is added to 2-methylpropene, it results in the formation of the more stable tertiary carbocation intermediate rather than the less stable primary carbocation (Figure 12).



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Figure 12. Addition of HCI (HX) to a 2-methylpropene (alkene).

This phenomenon can be explained by the Hammond Postulate, which states:

- Electrophilic addition to an unsymmetrically substituted alkene yields the more highly substituted carbocation intermediate. A more highly substituted carbocation forms faster than a less highly substituted one and proceeds to give the final product.
- A more highly substituted carbocation is more stable than a less highly substituted one. Carbocation stability follows the order: tertiary > secondary > primary > methyl.

In essence, the Hammond Postulate helps explain why a more stable carbocation intermediate forms faster – the higher stability reduces the activation energy required for its formation, allowing it to dominate the reaction pathway and produce the more substituted product. The connection between stability and reaction rate is a fundamental concept in understanding the outcome of addition reactions to alkenes.

2.5.1. Halogenation of Alkenes: Addition of X₂

In the context of halogenating alkenes, both bromine and chlorine readily undergo addition reactions with alkenes, resulting in the formation of 1,2-dihalides. This chemical process is referred to as *halogenation*. To illustrate, let's examine the reaction between ethylene and bromine, leading to the production of haloalkanes (Figure 13). From our prior observations, one conceivable mechanism for the reaction of alkenes with bromine might involve electrophilic addition, with Br1 attaching to the alkene to generate a carbocation intermediate. This intermediate could then proceed to react with Br2, ultimately yielding the dibromo addition product.



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Figure 13. Halogenation of ethylene with bromine.

However, this mechanism, while plausible, only partially accounts for some known aspects of the reaction. In particular, it fails to explain the stereochemistry of the addition reaction, meaning it does not clarify which stereoisomer product is formed. An explanation for the observed stereochemistry in the addition reaction was put forth in 1937 by George Kimball and Irving Roberts. They proposed that the reaction intermediate is not a carbocation but rather a bromonium ion (R₂Br1) created through the electrophilic addition of Br1 to the alkene (Figure 14). The formation of the bromonium ion occurs in a single step involving the interaction of the alkene with Br1, accompanied by the simultaneous loss of Br2.



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Figure 14. Formation of the bromonium ion.

2.5.2. Halohydrins form Alkenes: Addition of XOH

An additional example of electrophilic addition is when alkenes react with hypohalous acids like HOCl or HOBr, resulting in the formation of 1,2-halo alcohols, commonly known as *halohydrins*. It's important to note that halohydrin formation doesn't occur through the direct interaction of an alkene with HOBr or HOCl.

As previously demonstrated in the preceding section, when Br_2 reacts with an alkene, the cyclic bromonium ion intermediate interacts with the sole nucleophile available, the bromide ion. However, when the reaction takes place in the presence of an additional nucleophile, this intermediate bromonium ion can be intercepted by the introduced nucleophile, leading to the formation of an alternative product (Figure 15). For instance, when a high water concentration is present, water competes with the bromide ion as the nucleophile. Water utilizes its lone pair of electrons to break open the bromonium ion ring, forming a carbon-oxygen bond. As a result of this step, oxygen becomes positively charged. Following this, a proton (H⁺) is released from oxygen, resulting in the formation of H₃O⁺ and the neutral bromohydrin addition product.



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Figure 15. Mechanism of bromohydrin formation.

2.5.3. Hydration of Alkenes: Addition of H₂O by Oxymercuration

Oxymercuration entails the electrophilic addition of mercury (Hg) to the alkene through a reaction with mercury(II) acetate, often denoted as Hg(OAc)₂, within an aqueous tetrahydrofuran (THF) solvent. Subsequently, when the intermediate organomercury compound is treated with sodium borohydride (NaBH₄), the process of demercuration unfolds, ultimately resulting in the formation of an alcohol.

The oxymercuration of alkenes closely parallels the formation of halohydrins (Figure 16). The sequence of reactions commences with the electrophilic addition of mercuric (Hg) ions to the alkene, forming an intermediate mercurinium ion that bears structural similarity to a bromonium ion. Like in the halohydrin formation, nucleophilic water addition occurs, followed by proton elimination, yielding a stable organomercury product. The final step, demercuration of the organomercury compound through its reaction with sodium borohydride, is a multifaceted process that involves radicals.



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Figure 16. Mechanism of oxymercuration of an alkene.

It is worth noting that the regiochemistry of this reaction adheres to Markovnikov's rule for water addition. This means that the hydroxyl (OH) group attaches to the more highly substituted carbon atom, while the hydrogen (H) replaces mercury, and its attachment may occur from either side of the molecule, depending on specific circumstances.

2.5.4. Reduction of Alkenes: Hydrogenation

Alkenes can undergo *hydrogenation* by reacting with molecular hydrogen (H₂) in the presence of a metal catalyst like palladium or platinum. This reaction results in the formation of saturated alkane products. Palladium is often employed as a finely powdered catalyst "supported" on an inert substance such as charcoal (Pd/C) to enhance the surface area for the reaction. Platinum, on the other hand, is typically used as PtO₂ and is known as Adams' catalyst, named after its discoverer, Roger Adams.

Catalytic hydrogenation differs from most other organic reactions in that it's a heterogeneous process rather than a homogeneous one. In other words, the hydrogenation reaction doesn't occur in a uniform solution but takes place on the surface of solid catalyst particles. Importantly, hydrogenation typically results in syn stereochemistry, meaning both hydrogen atoms are added to the double bond from the same side.

Hydrogenation commences with the adsorption of H₂ onto the catalyst surface, where it dissociates into hydrogen atoms. The alkene then adsorbs to the catalyst surface, forming a complex with the metal atoms via its π bond. A hydrogen atom is transferred from the metal to one of the alkene carbon atoms, forming a partially reduced intermediate with a C-H bond and a carbon-metal bond. A second hydrogen atom is transferred from the alkane product and regenerating the catalyst. The syn stereochemistry is retained, as both hydrogens are added to the same face of the alkene.

3. ALKYNES

An alkyne is a type of hydrocarbon characterized by the presence of a carbon-carbon triple bond. The simplest alkyne, acetylene (C_2H_2), consists of two carbon atoms connected by a triple bond. In the past, acetylene had wide industrial applications, serving as a primary raw material for producing substances like acetaldehyde, acetic acid, vinyl chloride, and other high-volume chemicals. However, more efficient methods utilizing ethylene as a starting material have now largely replaced these processes. Acetylene is still employed in synthesizing acrylic polymers and is most notably recognized for its use in high-temperature oxy-acetylene welding torches.

Alkyne nomenclature adheres to the general principles applied to hydrocarbons. The suffix -**yne** is used to denote alkyne compounds, and the location of the triple bond is indicated by specifying the number of the initial carbon atom within the alkyne chain. To establish the primary carbon numbering, the chain's origin begins at the end nearest the triple bond, ensuring that the triple bond receives the lowest possible numerical position. Compounds featuring more than one triple bond are categorized as diynes, triynes, and so forth, while compounds with double and triple bonds are known as enynes (not ynenes). When numbering an enyne chain, the count starts from the end closer to the first multiple bond, whether it's a double or a triple bond. In cases with a choice in numbering, double bonds are assigned lower numbers than triple bonds. Similar to alkyl and alkenyl substituents derived from alkanes and alkenes, respectively, alkynyl groups are also a possibility in alkyne compounds.

In an alkyne, each of the two carbon atoms is characterized by sp hybridization (Figure 17). One of the hybrid orbitals on each carbon atom undergoes overlap with a hydrogen atom, forming a σ bond between the two carbon atoms due to the mutual overlap of the remaining sp hybrid orbitals. Moreover, each carbon atom possesses two perpendicular p orbitals, each housing a single electron. These two sets of p orbitals overlap to generate two perpendicular π bonds. Due to the diffuse nature of π bonds, the distribution of electrons within the triple bond takes on the appearance of a cylindrical cloud. Given that both carbon atoms in an alkyne adopt sp hybridization, the molecule takes on a linear structure. The carbon-carbon bond length is shorter than that of a double bond, measuring 1.20 Å, as opposed to the 1.33 Å typical for a double bond.



Source: Chem 12A: Organic Chemistry Fall 2022. Andy Wells, Chabot College, Open Education Resource (OER) LibreTexts Project, https://chem.libretexts.org/Courses/Chabot_College/Chem_12A: Organic Chemistry Fall 2022.

Figure 17. Hybridization of ethyne.

3.1. Physical Properties of Alkynes

The boiling points of alkynes closely resemble those of their corresponding alkenes and alkanes. Ethyne, however, is an exception because it does not possess a boiling point under atmospheric pressure; instead, it sublimes at -84°C. Propyne (with a boiling point of -23.2°C) and 1-butyne (boiling point of 8.1°C) exist as gases, while 2-butyne is only slightly liquid (boiling point of 27°C) at room temperature. Alkynes of medium size are typically distillable liquids.

Alkynes are characterized as high-energy compounds, primarily due to the presence of a triple bond, housing four π electrons within a relatively confined space. This concentration of electrons results in electron-electron repulsion, contributing to the relative weakness of the two π bonds and the high energy content of the alkyne molecule itself. Because of this property, alkynes often undergo reactions that release substantial amounts of energy and must be handled with care. They are susceptible to polymerization and can undergo explosive decomposition. For example, ethyne can be transported in pressurized cylinders containing acetone and porous stabilizers like pumice.

Terminal alkynes exhibit remarkable acidity. The strength of an acid (H-A) increases with the electronegativity or electron-attracting capacity of atom A. Notably, the electronegativity of an atom varies with its structural environment. Electronegativity is influenced by the hybridization of the atom's orbitals. Electrons in s orbitals are more strongly attracted to the atomic nucleus than those in p orbitals. Consequently, an atom with hybrid orbitals having a higher s character (e.g., sp, with 50% s and 50% p character) exhibits slightly greater electronegativity compared to the same atom with hybrid orbitals possessing less s character (sp³, with 25% s and 75% p character. The relatively high s character in the carbon hybrid orbitals of terminal alkynes contributes to their enhanced acidity compared to alkanes and alkenes (Figure 18). For instance, the pKa of ethyne is notably low at 25, especially when contrasted with ethene and ethane.

Acidity of Simple Hydrocarbons					
Family	Example	Κα	p <i>K</i> α		
Alkyne	HC≡CH	10 ⁻²⁵	25	Stronger acid	
Alkene	H ₂ C=CH ₂	10 ⁻⁴⁴	44		
Alkane	CH ₄	10 ⁻⁶⁰	60	Weaker acid	

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Figure 18. Compared acidity of hydrocarbons.

3.2. Synthesis of Alkynes

Synthesis of alkynes involves treating a 1,2-dihaloalkane, often referred to as a vicinal dihalide, with an excess of a robust base, such as KOH or NaNH₂. As a result, HX is eliminated twice, leading to the formation of an alkyne. This elimination process resembles the way HX is removed to generate an alkene.

The initial vicinal dihalides can be readily obtained by adding Br₂ or Cl₂ to alkenes. Consequently, the combined halogenation and dehydrohalogenation sequence provides a means to transform an alkene into an alkyne. For instance, converting diphenylethylene into diphenylacetylene can be accomplished by reacting it with Br2 and subsequently treating it with a base (Figure 19).



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Figure 19. Synthesis of the alkyne diphenylacetylene.

3.3. Reactivity of Alkynes. Addition of HX and X₂

As a general principle, electrophiles engage in addition reactions with alkynes in a manner similar to their interactions with alkenes. In the case of electrophilic addition to an alkene, such as HBr, the reaction typically proceeds in two steps and includes the formation of an alkyl carbocation intermediate (Figure 20). If we were to consider HBr adding to an alkyne via a comparable mechanism, it would lead to the formation of an analogous vinylic carbocation as an intermediate step. The regiochemistry of this addition adheres to Markovnikov's rule, with the halogen attaching to the more highly substituted side of the alkyne bond and hydrogen bonding to the less highly substituted side. Generally, the resulting product exhibits trans stereochemistry between H and X, although exceptions may occur.



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Figure 20. Comparable mechanism of addition of HBr to an alkene and alkyne.

3.4. Mercury (II)-catalyzed Hydration of Alkynes

The direct addition of water, catalyzed by mercury(II) ions, results in the Markovnikov product, while an indirect approach involving a hydroboration-oxidation sequence leads to the formation of the non-Markovnikov product. Notably, alkynes do not readily react with aqueous acid, but they can readily undergo hydration when in the presence of mercury(II) sulfate acting as a Lewis acid catalyst. This reaction exhibits Markovnikov regiochemistry, with the OH group attaching to the more highly substituted carbon atom and the H bonding to the less highly substituted one.

The mechanism behind the mercury(II)-catalyzed alkyne hydration is analogous to the oxymercuration reaction observed with alkenes (Figure 21). Initially, electrophilic addition of mercury(II) ions to the alkyne generates a vinylic cation, which subsequently interacts with water, leading to the loss of a proton and creating a mercury-containing enol intermediate. Unlike alkene oxymercuration, removing mercury does not require treatment with NaBH₄; the reaction's acidic conditions are adequate to replace mercury with hydrogen. This is followed by tautomerization, ultimately resulting in the formation of a ketone.





3.5. Reduction and Oxidation of Alkynes

Alkynes can be converted into alkanes through hydrogenation using H₂ over a metal catalyst. This reaction transpires in two steps, with an alkene intermediate involved. A complete reduction to the alkane can be achieved when utilizing palladium on carbon (Pd/C) as the catalyst. However, the hydrogenation can be arrested at the alkene stage if the less active Lindlar catalyst is employed. The Lindlar catalyst consists of finely divided palladium metal precipitated onto a calcium carbonate support and subsequently deactivated through treatment with lead acetate and quinoline, which is an aromatic amine. The hydrogenation follows a syn stereochemistry, resulting in a cis alkene product.

Similarly to alkenes, alkynes can be cleaved through a reaction with potent oxidizing agents such as ozone or KMnO₄ (Figure 22). It is worth noting, though, that this reaction has limited practical utility, and we mention it primarily for completeness. Triple bonds are generally less reactive than double bonds, and the yields of cleavage products are, at times, low. In cases where internal alkynes are cleaved, carboxylic

acids are among the products obtained, whereas cleaving terminal alkyne results in the formation of CO₂ as one of the products.



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Figure 22. Oxidation of internal and terminal alkynes to carboxylic acids.

4. AROMATIC COMPOUNDS

In the early days of organic chemistry, the term "aromatic" was initially employed to describe compounds known for their pleasant fragrances, such as benzaldehyde (found in cherries, peaches, and almonds), toluene (derived from Tolu balsam), and benzene (derived from coal distillation). However, it was soon recognized that substances categorized as aromatic exhibited distinct chemical behaviors compared to most other organic compounds. Today, we use the term "aromatic" to denote a class of compounds characterized by six-membered benzene-like rings containing three double bonds.

Aromatic compounds have garnered many informal names more than any other group of organic compounds. While IUPAC guidelines discourage the use of most of these non-systematic names, they do permit some of the more extensively employed ones to persist. As a result, methylbenzene is commonly recognized as toluene, hydroxybenzene as phenol, aminobenzene as aniline, and so forth.

Monosubstituted benzenes are systematically named in a manner consistent with other hydrocarbons, with the parent name being "-**benzene**." Hence, C_6H_5Br is recognized as bromobenzene, $C_6H_5NO_2$ as nitrobenzene, and $C_6H_5CH_2CH_2CH_3$ as propylbenzene. Alkyl-substituted benzenes are sometimes referred to as arenes and are named differently depending on the size of the alkyl group. If the alkyl substituent contains fewer carbon atoms than the benzene ring (six or fewer), the compound is named an alkyl-substituted benzene. If the alkyl substituent is larger than the ring (comprising seven or more carbons), it is designated phenyl-substituted alkane. The term "**phenyl**" signifies the $-C_6H_5$ unit when considering the benzene ring as a substituent

Disubstituted benzenes are denoted using one of the prefixes: **ortho** (o), **meta** (m), or **para** (p). In an ortho-disubstituted benzene, both substituents are located in a 1,2 arrangement on the ring. A metadisubstituted benzene has its substituents in a 1,3 relationship, while a para-disubstituted benzene positions its substituents in a 1,4 relationship. In cases where benzenes have more than two substituents, the nomenclature involves selecting a carbon atom as number 1 and numbering the substituents on the ring to minimize the second substituent's number. If any ambiguity persists, the numbering ensures that the third or fourth substituent receives the lowest possible number until a distinction is achieved. When listing the substituents alphabetically in the name, refer to the second and third examples where the parent names are designated as -phenol and - toluene instead of -benzene.

Benzene (C₆H₆) differs from the corresponding six-carbon cycloalkane (C₆H₁₂) by having six fewer hydrogens, making it unsaturated. It is often depicted as a six-membered ring with alternating double and single bonds. However, since the mid-1800s, it has been well-established that benzene is significantly less reactive than typical alkenes and does not readily undergo typical alkene addition reactions. A quantitative assessment of benzene's stability can be obtained through the heats of hydrogenation. Cyclohexene, an isolated alkene, has a $\Delta H^{\circ}_{hydrog}$ value of 2118 kJ/mol (228.2 kcal/mol), and 1,3-cyclohexadiene, a conjugated diene, has a $\Delta H^{\circ}_{hydrog}$ of 2230 kJ/mol (255.0 kcal/mol). If we extrapolate this process to "cyclohexatriene" (benzene), we might anticipate a $\Delta H^{\circ}_{hydrog}$ value slightly below 2356 kJ/mol, roughly three times the value of cyclohexene. However, the actual value is 2206 kJ/mol, which is approximately 150 kJ/mol (36 kcal/mol) lower than expected. This means that during the hydrogenation of benzene, 150 kJ/mol less heat is released than expected, signifying that benzene is inherently 150 kJ/mol more stable than anticipated.

Further evidence of benzene's uniqueness is that all its carbon-carbon bonds share the same length, measuring 139 pm, which falls between the typical single (154 pm) and double (134 pm) bonds. Moreover, an electrostatic potential map reveals that the electron density in all six C-C bonds is uniform (Figure 23). Consequently, benzene takes on a planar configuration resembling a regular hexagon. All C-C-C bond angles are 120°, all six carbon atoms exhibit sp² hybridization, and each carbon features a perpendicular p orbital outside the plane of the six-membered ring.



Source: Organic Chemistry. A tenth Edition. John McMurry, Cornell University (Emeritus), CC BY-SA 4.0, https://openstax.org/details/books/organic-chemistry. *Figure 23.* Electrostatic potential map of benzene.

Since all six carbon atoms and their respective p orbitals in benzene are indistinguishable, it is impossible to define three localized p bonds where a given p orbital overlaps exclusively with a single neighboring p orbital. Instead, each p orbital interacts equally well with both adjacent p orbitals, resulting in a depiction of benzene where all six p electrons are free to move throughout the entire ring. In resonance terms, benzene is a hybrid of two equivalent forms, with neither form being accurate by itself. The actual structure of benzene lies somewhere in between the two resonance forms but cannot be adequately represented using conventional conventions. To illustrate the equivalence of the carbon-carbon bonds in

benzene, chemists occasionally employ a circle within the ring. Nevertheless, this representation must be used cautiously, as it does not convey the number of p electrons within the ring.

4.1. Electrophilic Aromatic Substitution

Electrophilic aromatic substitution is the most prevalent reaction involving aromatic compounds. In this reaction, an electrophile (E1) interacts with an aromatic ring, displacing one of the hydrogen atoms. It's important to note that this reaction is not exclusive to benzene or its derivatives; it is a defining feature of all aromatic rings. Electrophilic substitution reactions offer a versatile means of introducing various substituents onto an aromatic ring. There are numerous possibilities, including the substitution of an aromatic ring with halogens (such as Cl, Br, or I), a nitro group (NO₂), a sulfonic acid group (SO₃H), a hydroxyl group (OH), an alkyl group (R), or an acyl group (COR). With just a few basic starting materials, it becomes feasible to synthesize an extensive array of substituted aromatic compounds, numbering in the thousands.

Substituted aromatic compounds exhibit distinct behavior when subjected to electrophilic substitution reactions. The presence of a substituent on the aromatic ring has a twofold impact:

Reactivity: Substituents can either activate or deactivate the aromatic ring, influencing its reactivity. Activating substituents make the ring more reactive than benzene, while deactivating substituents reduce its reactivity compared to benzene. For example, an -OH substituent enhances the reactivity of the ring, making it approximately 1000 times more reactive than benzene. In contrast, an -NO₂ substituent severely diminishes the reactivity, making the ring over 10 million times less reactive.



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Orientation: The orientation of the electrophilic substitution reaction is also influenced by substituents. Different substituents on the benzene ring determine the position of the second substitution, leading to the formation of ortho, meta, or para-disubstituted products. For instance, an -OH group favors ortho and para substitution, while a carbonyl group such as -CHO predominantly directs substitution to the meta position. These effects on orientation are grouped into three categories: ortho- and para-directing activators, ortho- and para-directing deactivators, and meta-directing deactivators. Notably, there are no meta-directing activators.



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Classifying a substituent as activating or deactivating depends on its impact on the electron density of the ring. Activating groups donate electrons to the ring, making it more electron-rich, thus stabilizing the carbocation intermediate and reducing the activation energy. Deactivating groups withdraw electrons from the ring, making it more electron-poor, destabilizing the carbocation intermediate, and increasing the activation energy. A combination of inductive and resonance effects influences this electron donation or withdrawal:

- Inductive Effects: Substituents either inductively withdraw or donate electrons through a σ bond due to differences in electronegativity. For example, halogens, hydroxyl groups, carbonyl groups, cyano groups, and nitro groups inductively withdraw electrons from the ring. In contrast, alkyl groups inductively donate electrons.
- Resonance Effects: The interaction of a substituent's p orbital with the aromatic ring's p orbital can lead to electron withdrawal or donation. For example, carbonyl, cyano, and nitro substituents withdraw electrons from the ring through resonance, resulting in a positive charge within the ring. Conversely, halogen, hydroxyl, alkoxyl (OR), and amino substituents donate electrons to the ring through resonance, producing a negative charge in the ring. Notably, the resonance effects of electron-donating substituents (e.g., hydroxyl, alkoxyl, and amino groups) outweigh their inductive effects, enhancing their activating character.

These factors collectively determine the reactivity and orientation of electrophilic aromatic substitutions in the presence of substituents. For instance, alkyl groups are electron-donating inductively and are ortho and para directors, while halogens are electron-withdrawing inductively but ortho and para directors due to weak electron-donating resonance effects. Understanding the impact of various substituents on reactivity and orientation is essential for predicting the outcomes of electrophilic aromatic substitution reactions.

4.2. Alkylation and Acylation of Aromatic Rings: The Friedel-Crafts Reaction

One of the most valuable electrophilic aromatic substitution reactions employed in laboratories is alkylation, which involves adding an alkyl group to a benzene ring (Figure 24). This reaction, known as the Friedel-Crafts reaction in honor of its discoverers, proceeds by treating the aromatic compound with an alkyl chloride, denoted as RCl, in the presence of aluminum chloride (AlCl₃). An electron pair originating from the aromatic ring attacks the carbocation, resulting in the formation of a carbon-carbon (C–C) bond

and giving rise to a novel carbocation intermediate. The role of aluminum chloride is to catalyze the reaction by facilitating the dissociation of the alkyl halide. Subsequently, the elimination of a hydrogen atom concludes the reaction, leading to the formation of the neutral alkylated substitution product.



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Figure 24. Mechanism of reaction of benzene with 2-chloropropane.

Despite its practicality, the Friedel-Crafts alkylation reaction exhibits several limitations. Firstly, it exclusively accommodates alkyl halides as reactants. Aromatic (aryl) halides and vinylic halides do not participate in the reaction because the formation of aryl and vinylic carbocations is energetically unfavorable under Friedel-Crafts reaction conditions. A second constraint involves the unsuitability of Friedel-Crafts reactions for aromatic rings bearing certain substitutions. Specifically, rings substituted with strongly electron-withdrawing groups such as carbonyl (C=O) or basic amino groups that can be protonated are unresponsive to this reaction. Furthermore, a third limitation arises in controlling the extent of the Friedel-Crafts alkylation reaction, making it challenging to halt the reaction after a single substitution. This often results in polyalkylation, where the reaction yields multiple alkyl groups attached to the ring. For instance, when benzene reacts with one mole equivalent of 2-chloro-2-methylpropane, the major product is p-di-tert-butylbenzene, accompanied by minor quantities of tert-butylbenzene and unreacted benzene. A high yield of monoalkylation product can only be achieved when a large excess of benzene is employed.

In a manner analogous to the alkylation of an aromatic ring, acylation can be achieved by reacting the aromatic compound with a carboxylic acid chloride, denoted as RCOCl, in the presence of AlCl₃. This process entails substituting an acyl group (-COR) onto the aromatic ring (Figure 25). The mechanism underlying the Friedel-Crafts acylation reaction closely resembles that of Friedel-Crafts alkylation. Furthermore, the same limitations applicable to the aromatic substrate, as previously discussed for alkylation, also hold true for acylation. The electrophilic reactant, in this case, is a resonance-stabilized acyl cation, which is generated through the interaction between the acyl chloride and AlCl₃.



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Figure 25. Mechanism of acylation of benzene.

4.3. Oxidation and Reduction of Aromatic Rings

Despite its unsaturation, the benzene ring displays remarkable inertness towards strong oxidizing agents, such as KMnO₄ and Na₂Cr₂O₇, which are reagents capable of cleaving carbon-carbon bonds in alkenes. However, the presence of an aromatic ring exerts a profound influence on the behavior of alkyl side chains. Alkyl side chains readily react with oxidizing agents and undergo conversion into carboxyl groups, denoted as -CO₂H. The overall consequence of this transformation is the conversion of an alkylbenzene into benzoic acid. For example, the oxidation of butylbenzene using aqueous KMnO₄ leads to the formation of benzoic acid (Figure 26).



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Figure 26. Oxidation of butylbenzene with KMnO₄.

Just as aromatic rings are generally resistant to oxidation, they also remain unresponsive to catalytic hydrogenation conditions that would typically reduce alkene double bonds. Consequently, it is possible to selectively reduce an alkene double bond in the presence of an aromatic ring. To hydrogenate an aromatic ring, it becomes necessary to use a platinum catalyst in conjunction with hydrogen gas at pressures in the range of several hundred atmospheres or to employ a more potent catalyst, such as rhodium on carbon. Under these conditions, aromatic rings are transformed into cyclohexanes. For example, o-xylene can be converted into 1,2-dimethylcyclohexane in Figure 27.



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Figure 27. Reduction of *o*-xylene with H₂.