Alkenes: Structure, Naming, and Reactivity — Study Guide

This guide covers everything you need to know about alkenes before diving into their reactions. We start with what an alkene actually is at the electronic level, build up to IUPAC naming including E/Z stereoisomerism, and finish with why the structure of alkenes makes them so reactive. This is the foundation for every alkene reaction you will encounter in organic chemistry. Drawing on Clayden's Organic Chemistry, Wade's Organic Chemistry, McMurry's Organic Chemistry, and Chemistry LibreTexts.

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2	The π Bond as a Source of Electron Density
3	Why is the π Bond Weaker Than the σ Bond?
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1. What is an Alkene? Structure of the C=C Double Bond

An alkene is any organic molecule containing at least one carbon-carbon double bond (C=C). The double bond is not simply two single bonds stacked together — it is composed of two fundamentally different types of bonding with very different properties and locations in space.

Bond Type	Description
σ (sigma) bond	Formed by direct, head-on overlap of sp^2 hybrid orbitals on each carbon. Lies along the internuclear axis between the two carbons. Strong and cylindrically symmetric — free rotation is possible around a pure σ bond, but restricted in a double bond because rotation would break the π bond.
π (pi) bond	Formed by sideways (lateral) overlap of unhybridized p-orbitals on each carbon. The electron density sits above AND below the plane of the molecule — NOT along the internuclear axis. Weaker than the σ bond (~65 kcal/mol vs ~83 kcal/mol). This is the reactive component in all addition reactions.

Each alkene carbon is sp^2 hybridized. This means:

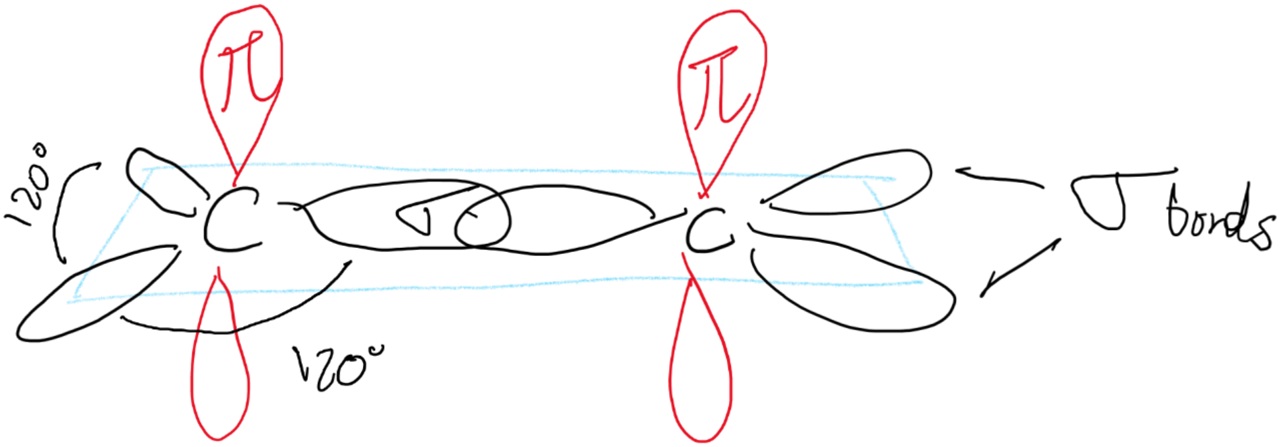
- Three sp^2 hybrid orbitals form, pointing toward the corners of an equilateral triangle (120° apart). These form the σ bonds to other atoms (the other alkene carbon and any H or substituent groups).
- One unhybridized p-orbital remains on each alkene carbon, pointing perpendicular to the plane of the three sp^2 orbitals.
- When the p-orbitals on the two adjacent alkene carbons align parallel to each other, they overlap sideways to form the π bond.

> Key geometry: All six atoms directly attached to a C=C double bond lie in the same plane (the molecular plane). This planarity is enforced by the π bond — rotating around the C=C axis would destroy the sideways p-orbital overlap and break the π bond entirely.

This planarity has a critical consequence for naming: the two substituents on each end of the double bond can be either on the same side (Z, or cis) or opposite sides (E, or trans) of the double bond, and these are distinct, non-interconvertible compounds at room temperature. This is covered in Section 7.

Hybridization Comparison

Hybridization	Bond Angles
sp^3 (alkane)	109.5°
sp^2 (alkene)	120°
sp (alkyne)	180°



2. The π Bond as a Source of Electron Density

The π bond is the key to understanding why alkenes undergo addition reactions. To understand this, you need to think about where the π electrons actually are in space — and compare that to where the electrons in a C–H or C–C σ bond are.

Where Are the π Electrons?

- The π electrons occupy a region of space above AND below the plane of the molecule — the two lobes of the π bond, one on each face.
- This electron cloud is exposed and accessible to the outside world. It protrudes out from the molecule, away from the carbon nuclei.
- In contrast, σ-bonding electrons are buried between the two nuclei they connect, tightly held along the internuclear axis and much harder for an outside reagent to reach.
- The exposed π electrons make the alkene electron-rich relative to its environment — and electron-rich regions attract electron-poor species (electrophiles).

> *The π bond is the nucleophilic site of the alkene. Its exposed electron density above and below the molecular plane is what electrophiles attack. Remove the π bond, and the alkene loses its defining reactivity.*

Why Alkenes Are More Reactive Than Alkanes

Alkanes (σ-bonds only) have no exposed electron cloud of this kind. Every electron in an alkane is locked in C–H or C–C σ bonds along internuclear axes, inaccessible to electrophiles under normal conditions. This is why alkanes are famously unreactive — they require extreme conditions (combustion, radical halogenation with UV light) for most reactions.

Alkenes, by contrast, present an accessible, electron-rich π cloud to any approaching electrophile. The reaction begins the moment an electrophile comes close enough for the π electrons to reach out and bond to it.

Feature	Alkane (C–C σ only)
Electron exposure	Electrons buried along C–C axis
Nucleophilicity	Very low
Typical reaction	Substitution (radical, harsh)
Reactivity	Low

3. Why is the π Bond Weaker Than the σ Bond?

The π bond is weaker than the σ bond for a fundamental geometric reason: sideways (lateral) overlap of p-orbitals is inherently less efficient than head-on overlap of sp^2 orbitals.

In a σ bond, the two orbitals point directly at each other along the internuclear axis. Maximum overlap occurs when the orbitals are aligned end-to-end — this gives a strong, stable bond. In a π bond, the two p-orbitals point perpendicular to the internuclear axis. They overlap sideways, with the electron density above and below the plane. This sideways overlap is less efficient: the orbitals are not pointing directly at each other, so the overlap integral is smaller and the bond is weaker.

Bond	Approximate Bond Energy
C–C σ bond (single bond)	~83 kcal/mol
C=C σ component	~83 kcal/mol
C=C π component	~65 kcal/mol
Full C=C double bond (total)	~146 kcal/mol

Notice that the total C=C bond energy (~146 kcal/mol) is less than twice the C–C single bond energy (~83 kcal/mol). This confirms that the π component contributes only ~65 kcal/mol — weaker than the σ component. The π bond is the weak link in the double bond.

Why This Matters for Addition Reactions

In every alkene addition reaction, only the π bond breaks — the σ bond stays intact throughout. The two new bonds that form in the addition product are both σ bonds (e.g., a new C–H and a new C–X bond in hydrohalogenation). Since σ bonds are typically ~83 kcal/mol each, forming two new σ bonds releases ~166 kcal/mol, while breaking the π bond costs only ~65 kcal/mol. The net energy balance is strongly favorable.

> Addition reactions are generally thermodynamically favorable: two new strong σ bonds form at the expense of one weaker π bond. The net release of ~100 kcal/mol of energy drives the reaction forward. This is why alkenes react readily with so many reagents under mild conditions.

The π Bond and Restricted Rotation

The weakness and geometry of the π bond also explains why C=C double bonds cannot rotate freely. To rotate around the C=C axis, the two p-orbitals (which are currently parallel and overlapping sideways) would have to twist out of alignment. At 90° rotation, the p-orbitals would be perpendicular to each other — zero overlap, zero π bond. Completing a full 180° rotation and then allowing the π bond to reform would interconvert E and Z isomers.

The energy barrier to C=C rotation is approximately 65 kcal/mol (the energy of the π bond that must be broken). This is far too high for thermal rotation at room temperature (compare to C–C σ bond rotation, which costs only ~3 kcal/mol). This is why E and Z alkenes are stable, isolable compounds that do not interconvert at room temperature.

4. Electrophilic Addition: The Core Mechanism

All alkene addition reactions — regardless of the specific reagent — follow the same underlying logic called electrophilic addition. Understanding this general mechanism means you can reason through any addition reaction you encounter, even one you have never seen before.

The Four-Step Pattern

1. An electrophile (electron-poor species) approaches the alkene. The exposed π electrons above and below the molecular plane are attracted to the electrophile's electron deficiency.
2. The π electrons of the alkene act as a nucleophile and attack the electrophile, donating two electrons to form a new bond. The π bond breaks — the two electrons that were shared as the π bond now become a new σ bond to the electrophile.
3. One carbon of the former double bond gains a bond to the electrophile and becomes more electron-rich. The other carbon loses its share of the π electrons and becomes electron-deficient. It typically becomes a carbocation (positive charge, sp^2, planar) or is stabilized by an adjacent bridging atom in a cyclic intermediate (as in halogenation or oxymercuration).
4. A nucleophile — either the departing partner of the electrophile or a solvent molecule — attacks the electron-deficient carbon, forming the second new σ bond and completing the addition.

> *In every alkene addition: the π bond breaks, two new σ bonds form, and the product is more saturated than the starting material. Atoms are added to the molecule — nothing is lost. This is why these are called addition reactions.*

What Makes a Good Electrophile for an Alkene?

Any species with a region of electron deficiency can act as an electrophile toward the alkene π system. Common examples:

Electrophile	Source
H^+ (proton)	HX (HCl, HBr, HI) or H_3O^+
$Br^{\delta+}$ or $Cl^{\delta+}$	Br_2 or Cl_2 (polarized by π electrons)
Hg^{2+}	$Hg(OAc)_2$ (mercuric acetate)
BH_3 (Lewis acid)	Borane or $BH_3\cdot THF$

Carbocation vs Bridged Intermediates: Why It Matters

The nature of the intermediate formed in Step 3 has profound consequences for the product:

- Carbocation (flat, sp^2): The positive charge sits entirely on carbon. The empty p-orbital can be attacked from either face — giving a racemic mixture at any new chiral center. Carbocations are also susceptible to rearrangements (hydride and alkyl shifts). Formed in hydrohalogenation and acid-catalyzed hydration.
- Cyclic bridged intermediate (bromonium, mercurinium): The electrophile bridges both carbons, blocking one face entirely. The nucleophile must attack from the opposite face — enforcing anti addition. No rearrangements occur because there is no discrete carbocation. Formed in halogenation and oxymercuration.
- No intermediate (concerted): In hydroboration, the boron and hydrogen deliver simultaneously in a single step via a four-membered cyclic transition state. Both groups add to the same face (syn addition), and no intermediate exists, so no rearrangements are possible.

> The identity of the intermediate tells you the stereochemistry: carbocation → racemization; cyclic bridged → anti addition; concerted → syn addition. Memorize this pattern and you can predict stereochemistry for any addition reaction.

5. Alkenes as Synthetic Building Blocks

Alkenes are among the most strategically important functional groups in organic synthesis. A single alkene can be transformed into a wide variety of products simply by choosing different reaction conditions. The π bond is a synthetic handle — a controllable point of reactivity that allows chemists to build molecular complexity in a predictable way.

One Alkene, Many Products

Consider propene (CH_2=$CHCH_3$). By choosing different reagents, you can obtain any of the following from the same starting material:

Reagent	Product
HBr	2-bromopropane (Markovnikov)
Br_2 / CH_2Cl_2	1,2-dibromopropane (anti addition)
H_2SO_4 / H_2O	2-propanol (Markovnikov alcohol)
$Hg(OAc)_2$ / H_2O; $NaBH_4$	2-propanol (Markovnikov, no rearrangement)
BH_3; H_2O_2 / NaOH	1-propanol (anti-Markovnikov alcohol)
OsO_4 or $KMnO_4$ (cold)	Propane-1,2-diol (syn diol)
mCPBA	Propylene oxide (epoxide)

Every one of those products comes from the same starting alkene. The π bond is attacked in each case — only the identity of the electrophile, and therefore the intermediate and stereochemical outcome, changes.

The Unifying Theme

> *One alkene. Many reactions. All of them begin with the same step: the π electrons attack an electrophile. Everything else — the product, the regiochemistry, the stereochemistry — flows from the nature of that electrophile and the intermediate it produces.*

This is why mastering alkene structure and the logic of electrophilic addition is so valuable: it gives you a single framework that explains dozens of different reactions. You do not need to memorize each reaction independently — you need to understand the π bond, identify the electrophile, determine what intermediate forms, and the product follows logically.

Quick Reference: Alkene Structure Summary

Property	Detail
Hybridization of C=C carbons	sp^2 (three sp^2 orbitals + one unhybridized p-orbital per carbon)
Geometry	Trigonal planar at each carbon; 120° bond angles; all 6 atoms in one plane
σ bond	Head-on overlap of sp^2 orbitals; along C–C axis; strong (~83 kcal/mol)
π bond	Sideways overlap of p-orbitals; above and below molecular plane; weaker (~65 kcal/mol)
Nucleophilic site	The π bond — exposed electron density above and below the plane
Reaction type	Electrophilic addition — electrophile attacks π electrons first
Overall outcome	π bond broken + 2 new σ bonds formed → more saturated product
Rotation?	Restricted — rotation around C=C requires breaking the π bond (~65 kcal/mol barrier)
E/Z isomers?	Yes — because rotation is restricted, substituents are locked in space

6. IUPAC Nomenclature of Alkenes

Naming alkenes follows directly from alkane nomenclature but adds rules for the position and geometry of the double bond. Mastering this section is essential both for exams and for reading any organic chemistry text or paper.

The Parent Chain Rules

IUPAC naming of alkenes uses a 6-step process:

1. Find the longest carbon chain that contains the C=C double bond. This is the parent chain. Use the alkene suffix: methene (1C), ethene (2C), propene (3C), butene (4C), pentene (5C), hexene (6C), etc.
2. Number the chain from the end closest to the double bond, giving the double bond the lowest possible locant.
3. Identify the position of the double bond using the lower-numbered carbon of the C=C pair (e.g., but-1-ene, but-2-ene).
4. Identify all substituents (methyl, ethyl, chloro, etc.) and their positions.
5. Alphabetize substituents and place them as prefixes before the parent name.
6. If E/Z geometry applies, add the E or Z descriptor in parentheses at the front (covered in Section 7).

> Key rule: The double bond always takes priority over substituents when numbering the chain. The double bond gets the lowest possible number even if this gives substituents higher numbers.

Common Parent Chain Names

Carbons in chain	Alkane name
2	Ethane
3	Propane
4	Butane
5	Pentane
6	Hexane

Worked Naming Examples

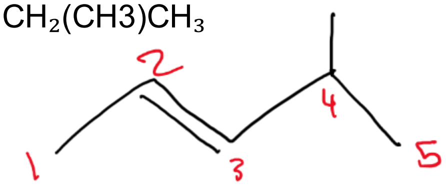
Example A — Simple alkene

Structure: $CH_2=CHCH_2CH_3$

1. Longest chain containing C=C: 4 carbons → parent name: butene.
2. Number from left (C=C starts at C1): double bond at C1.
3. No substituents.
4. Name: but-1-ene.

Example B — Substituted alkene

Structure: $CH_3CH=ChCH_2(CH3)CH_3$



1. Longest chain containing C=C: 5 carbons → parent: pentene.
2. Number from left (gives C=C the lower number, C2): double bond at C2.
3. Methyl substituent at C3.
4. Name: 4-methylpent-2-ene.

Example C — Cycloalkene

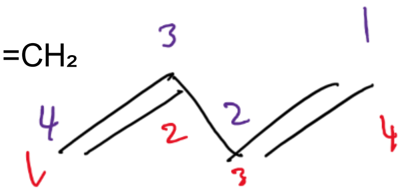
For cyclic alkenes, the ring carbons bearing the double bond are automatically C1 and C2; no locant is needed for the double bond itself.

1. A 6-membered ring with one double bond: cyclohexene.
2. A 6-membered ring with a methyl group on the carbon adjacent to the double bond: 3-methylcyclohexene (C1 and C2 have the double bond; the methyl is at C3, the next carbon).

Multiple Double Bonds

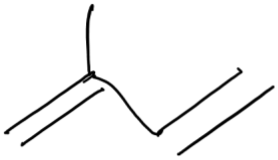
When a molecule has two or more double bonds, use the multiplying prefixes diene (2), triene (3), tetraene (4), etc., and list both positions:

- $CH_2=CH-CH=CH_2$



→ buta-1,3-diene (two double bonds at C1 and C3)

- $CH_2=C(CH_3)-CH=CH_2$



*Note: If numbering for alkenes is tied, use substituents as tie breakers.

→ 2-methylbuta-1,3-diene (isoprene — the monomer of natural rubber)

Common Trivial Names (Still Used)

Trivial Name	IUPAC Name
Ethylene	Ethene
Propylene	Propene
Isobutylene	2-methylpropene
Isoprene	2-methylbuta-1,3-diene
Styrene	Ethenylbenzene (vinylbenzene)

7. E/Z Stereoisomerism in Alkenes

Because rotation around the C=C double bond is restricted (breaking the π bond would require ~65 kcal/mol), substituents on either end of the double bond are locked in space. When both carbons of the double bond carry two different substituents, two distinct spatial arrangements are possible — these are called E/Z stereoisomers (or geometric isomers).

When Does E/Z Isomerism Exist?

E/Z isomerism exists only when BOTH carbons of the C=C double bond each carry two different substituents. If either carbon has two identical substituents (e.g., $=CH_2$), no E/Z isomerism is possible.

Case	E/Z Isomerism?
$CH_2=CH_2$ (ethene)	No — both substituents on each carbon are identical (H and H)
$CH_2=CHCH_3$ (propene)	No — C1 has two H's (identical substituents)
$CH_3CH=CHCH_3$ (but-2-ene)	Yes — both carbons have two different substituents (H and CH_3)
$CH_3CH=C(CH_3)_2$	No — C2 has two identical CH_3 groups
ClCH=CHBr	Yes — both carbons have two different substituents

The Cahn-Ingold-Prelog (CIP) Priority Rules for E/Z Assignment

Unlike the older cis/trans system (which only works for simple cases), the E/Z system uses Cahn-Ingold-Prelog (CIP) priority rules to handle any alkene unambiguously. The steps are:

1. For each carbon of the double bond, assign priorities to its two substituents based on atomic number. Higher atomic number = higher priority.
2. If two substituents have the same atom directly attached, expand outward: compare the next set of atoms, then the next, until a difference is found.
3. If the two higher-priority groups on each carbon are on the SAME side of the double bond → Z (from German zusammen, 'together').
4. If the two higher-priority groups are on OPPOSITE sides → E (from German entgegen, 'opposite').

> Memory aid: Z = same side (like cis); E = opposite sides (like trans). This works for simple cases. For complex cases with four different substituents, you must use CIP priority rules — don't rely on cis/trans language.

Worked E/Z Examples

Example A — But-2-ene

$CH_3CH{=}CHCH_3$ (but-2-ene): each carbon of the double bond has CH_3 (higher priority) and H (lower priority).

- (Z)-but-2-ene: both CH_3 groups on the same side → same side as each other.

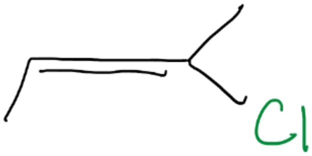
  (Also called cis-but- 2-ene.)

- (E)-but-2-ene: the two CH_3 groups on opposite sides. (Also called trans-but-2-ene.)

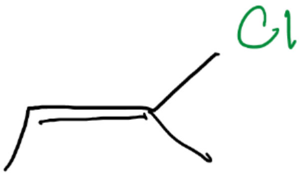
Example B — 2-Chlorobut-2-ene (a more complex case)

$CH_3C(Cl){=}CHCH_3$: C2 has Cl (atomic number 17, higher priority) and CH_3 (C, atomic number 6, lower priority). C3 has CH_3 (higher priority, C with three H's) and H (lower priority).

- If Cl and CH_3 (the higher-priority group on C3) are on the same side → Z.



- If Cl and CH_3 (the higher-priority group on C3) are on opposite sides → E.



Example C — CIP priority when atoms are tied

For (E) or (Z)-pent-2-ene: $CH_3CH{=}CHCH_2CH_3$. On C3, the substituents are H and CH_2CH_3 (ethyl). On C2, H and CH_3 (methyl). Compare CH_2CH_3 vs CH_3: at the first carbon they're tied (both C). Expand: ethyl has (C, H, H) next; methyl has (H, H, H) next. Carbon outranks hydrogen → ethyl has higher priority. The higher-priority groups are CH_2CH_3 (on C3) and CH_3 (on C2). Their spatial relationship determines E or Z.

E/Z Isomers Have Different Physical Properties

Property	(Z)-but-2-ene (cis)
Boiling point	3.7°C
Melting point	–139°C
Dipole moment	Higher (bond dipoles reinforce)
Stability	Slightly less stable

> E isomers (trans) are generally more stable than Z isomers (cis) for alkyl-substituted alkenes because the bulky groups are farther apart, reducing steric strain. However, there are exceptions when electronic effects dominate.

8. Classes and Physical Properties of Alkenes

Just as alkanes are classified by the degree of substitution at a carbon, alkenes are classified by the substitution pattern around the double bond. This classification directly predicts reactivity (more substituted = more reactive toward electrophiles, more stable thermodynamically).

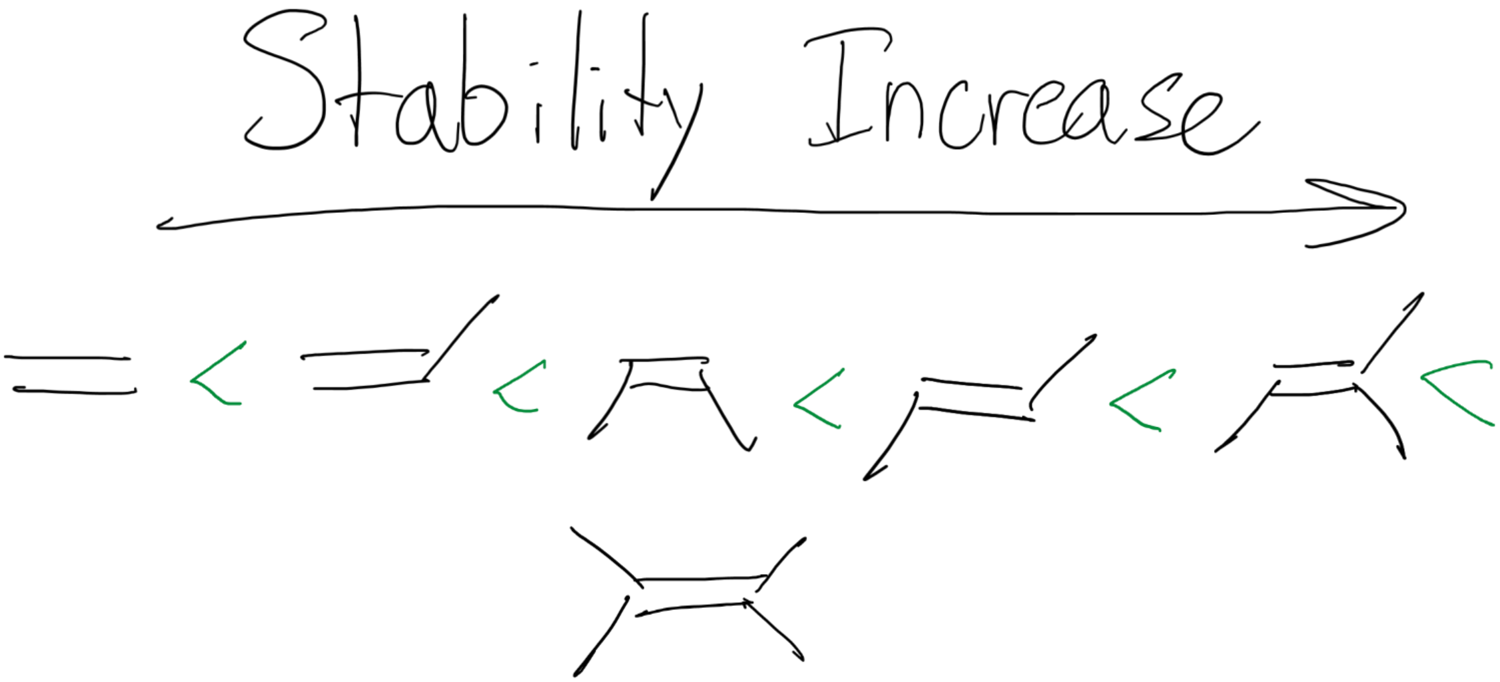
Classification by Substitution

Class	Definition
Monosubstituted	One alkyl group on the C=C
Disubstituted	Two alkyl groups total on the C=C
Trisubstituted	Three alkyl groups on the C=C
Tetrasubstituted	Four alkyl groups on the C=C

Thermodynamic Stability of Alkenes: Hyperconjugation

More highly substituted alkenes are more thermodynamically stable. The reason is hyperconjugation: alkyl groups adjacent to the double bond can donate electron density into the π* (antibonding) orbital of the C=C through partial overlap of their C–H σ bonds with the π system. More alkyl groups = more hyperconjugative stabilization = lower potential energy.

This is the same effect that stabilizes carbocations (which is why tertiary carbocations are more stable than secondary or primary). In the context of alkenes, it means that when two alkenes are in equilibrium, the more substituted alkene predominates. This is Zaitsev's rule applied to alkene stability.



Physical Properties of Alkenes

Property	Trend and Explanation
Boiling point	Increases with molecular weight (chain length). Similar to alkanes — London dispersion forces dominate. Alkenes boil slightly lower than corresponding alkanes of the same MW because the planar C=C reduces surface contact.
Melting point	E (trans) isomers typically have higher melting points than Z (cis) isomers because their more symmetric shape packs into crystals more efficiently.
Polarity	Alkenes are slightly more polar than alkanes due to the π electron cloud, but still essentially nonpolar. Z isomers have a larger dipole moment than E isomers (bond dipoles reinforce in Z; cancel in E).
Solubility	Insoluble in water; soluble in nonpolar organic solvents (hexane, ether, CH_2Cl_2). Like dissolves like.
Density	Less dense than water (all common alkenes float). Densities ~0.6–0.7 g/mL.

Quick Recap — Nomenclature and Properties

- ✓ Longest chain containing C=C → parent alkene name
- ✓ Number from end closest to C=C; double bond gets lowest locant
- ✓ E/Z: assign CIP priorities; same side = Z; opposite = E
- ✓ More substituted alkenes → more stable (hyperconjugation)
- ✓ E (trans) → more stable than Z (cis) for alkyl-substituted alkenes
- ✗ Don't number from the end closest to a substituent if that gives the double bond a higher number
- ✗ Don't use cis/trans for complex alkenes with four different substituents — use E/Z
- ✗ Don't confuse higher priority with larger group: priority is based on atomic number, not size

References & Further Reading

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