BP204T · B.PHARM THEORY

BP204T Pharmaceutical Organic Chemistry

Unit II — Alkenes & Conjugated Dienes

Pills & Python Notes

From-zero teaching standard: every technical term is defined before use.

Syllabus coverage: Unit II (12 hours).

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Chapter 4 — Alkenes: Preparation

Learning Objectives

After studying this chapter you should be able to:

1. Define an alkene and state its general formula (CnH2n).
2. Explain what sp^2 hybridization means and describe the structure of the C=C double bond (one sigma bond + one pi bond).
3. Explain why the pi bond makes alkenes reactive, and why restricted rotation around C=C leads to cis–trans isomerism.
4. Name and write the equations for four preparation methods: dehydration of alcohols, dehydrohalogenation of alkyl halides, dehalogenation of vicinal dihalides, and the Wittig reaction.
5. State Zaitsev's rule and use it to predict the major alkene from an alcohol or alkyl halide.
6. Explain the Wittig reaction, including what a phosphorus ylide is and why the reaction is useful.

4.1 Key Definitions Box

Term	Simple Definition
Alkene	A hydrocarbon (compound of only carbon and hydrogen) that contains at least one carbon–carbon double bond (C=C). Example: ethene, CH2=CH2.
Saturated	A compound in which every carbon–carbon bond is a single bond (no multiple bonds). Alkanes are saturated.
Unsaturated	A compound that contains at least one multiple bond (double or triple bond). Alkenes and alkynes are unsaturated. "Unsaturated" means the molecule can still take up more hydrogen.
General formula CnH2n	Every simple alkene with n carbon atoms has 2n hydrogen atoms (e.g., C3H6 for propene). One double bond removes two hydrogens compared with an alkane (CnH2n+2).
sp^2 hybridization	A way carbon atoms arrange their electron orbitals to form a double bond. In an alkene, each doubly-bonded carbon uses three sp^2 hybrid orbitals (to make sigma bonds) and one unhybridized p orbital (to make the pi bond). Geometry is flat (planar), with bond angles ≈ 120°.
Sigma (σ) bond	A bond formed when two orbitals overlap head-on, along the line joining the two nuclei. Strong; allows free rotation.
Pi (π) bond	A bond formed when two p orbitals overlap side-by-side, above and below the plane of the nuclei. Weaker than sigma; the electron cloud sits exposed above and below the plane. **Does not allow rotation** — twisting would break the sideways overlap.
Restricted rotation	Because the pi bond breaks if twisted, rotation around C=C is locked. This is why cis–trans isomers exist (next section).
cis–trans isomerism	When each carbon of a double bond carries two different groups, two different arrangements are possible: **cis** = two same groups on the same side of the double bond; **trans** = on opposite sides. They are different compounds with different properties.

4.1.1 Terminology Alerts — words students confuse

- **Alkene vs alkane vs alkyne:** –ane = single bonds only (saturated); –ene = at least one C=C; –yne = at least one C≡C. The ending tells you the bond type.
- **Unsaturated vs unstable:** "Unsaturated" does NOT mean "unstable". It means the molecule has a multiple bond and can still add more atoms (e.g., add H2). Alkenes are quite stable compounds — they are just *reactive* toward addition.
- **Sigma vs pi:** sigma = strong, head-on, rotates freely; pi = weaker, sideways, exposed electrons, locks rotation. In addition reactions, it is the **pi bond** that breaks, never the sigma bond.
- **cis vs trans:** both must have two *different* groups on each carbon. CH2=CH–CH3 (propene) has no cis/trans forms because one carbon carries two identical H atoms.

4.2 From-zero: what is an alkene?

Concept. An alkene is a hydrocarbon containing a carbon–carbon double bond.

Simple explanation. Methane (CH4) and ethane (CH3–CH3) are alkanes — every bond is a single bond. Remove two hydrogens from ethane and join the two carbons with a double bond: you get **ethene, CH2=CH2**. That double bond changes everything.

The double bond is **two bonds in one**: a strong sigma (σ) bond plus a weaker pi (π) bond. Think of the sigma bond as two hands gripping directly, and the pi bond as two hands touching sideways, with the electron cloud bulging above and below the molecule like two soft cushions. Those exposed pi electrons are loosely held — easy targets for anything electron-hungry. That is the single most important fact about alkene chemistry: **the pi bond is the reactive part of the molecule.**

The pi bond also **locks rotation**. In ethane the two CH3 groups spin freely; in ethene, twisting would tear apart the sideways p-orbital overlap, so the molecule stays flat and rigid. Consequence: if the two carbons of the double bond each carry two *different* groups, you get **two distinct isomers** — cis (same groups on the same side) and trans (on opposite sides).

Key takeaway: Alkene = C=C = one σ + one π bond. The exposed, weakly-held π electrons make alkenes reactive, and the locked rotation makes cis/trans isomerism possible.

4.3 Preparation of alkenes

There are four syllabus methods. Each follows the same logic: **remove two atoms from two neighbouring carbons → a double bond forms between them.**

4.3.1 Method (a) — Dehydration of alcohols

Concept. Remove water (H2O) from an alcohol to make an alkene.

Reaction with conditions:

CH3–CH2–OH →(conc. H2SO4, heat) CH2=CH2 + H2O

(ethanol → ethene + water)

Conditions: concentrated sulphuric acid (conc. H2SO4) as dehydrating agent, heated to about **170–180 °C**. (Conditions vary slightly across textbooks — some give 180 °C, others a range of 170–180 °C; any value in this range is acceptable in an exam.)

Mechanism (E1 — unimolecular elimination), step-by-step in words:

First, what is **E1**? E = elimination (atoms are removed), 1 = the slow, rate-determining step involves only ONE molecule.

1. **Protonation:** The oxygen of the –OH group grabs a proton (H^+) from the acid, forming –$OH2^+$. Water is a much better leaving group than OH^-, so this step "activates" the leaving group.
2. **Loss of water:** The C–O bond breaks; water (H2O) leaves. This creates a **carbocation** — a carbon with only six electrons and a positive charge — on the carbon that carried the OH. This is the slow step. (Carbocations are electron-deficient; their stability order is 3° > 2° > 1° > methyl, which decides which alkene forms — see Zaitsev's rule below.)
3. **Loss of a proton:** A base in the mixture ($HSO4^-$ or another alcohol molecule) removes a hydrogen from a carbon *next to* the carbocation carbon. The electrons of that C–H bond collapse to form the C=C double bond. The proton taken by the acid in step 1 is returned, so H2SO4 acts as a catalyst.

> **Worked example — which alkene forms from 2-butanol?**

CH3–CH(OH)–CH2–CH3 $\xrightarrow{}$(conc. H2SO4, Δ) ?

After protonation and loss of water, the carbocation is CH3–C^+H–CH2–CH3 (a 2° carbocation). A proton can be removed from C-1 (giving 1-butene, CH2=CH–CH2–CH3) or from C-3 (giving 2-butene, CH3–CH=CH–CH3). **Zaitsev's rule** (below) says the more substituted alkene is major: **2-butene is the major product**, 1-butene the minor product.

Zaitsev's rule (Saytzeff's rule): *When more than one alkene can form in an elimination, the major product is the more substituted alkene — the one with the greater number of alkyl groups attached to the doubly-bonded carbons.* Simple memory: "the double bond goes where the hydrogens are fewest" — the H is removed from the carbon that already has fewer hydrogens, so the double bond ends up between the most substituted carbons. Reason: more alkyl groups donate electron density and stabilize the double bond (hyperconjugation), and the E1 transition state resembles the carbocation/alkene, favouring the more stable one.

Key takeaway: Alcohol + conc. H2SO4 + heat → alkene + H2O, via an E1 carbocation mechanism; Zaitsev's rule picks the major product.

4.3.2 Method (b) — Dehydrohalogenation of alkyl halides

Concept. Remove HX (a hydrogen halide) from an alkyl halide to make an alkene.

Reaction with conditions:

CH3–CH2–CH2–Br + KOH(alc) $\xrightarrow{}$(heat) CH3–CH=CH2 + KBr + H2O

(1-bromopropane → propene)

Conditions: alcoholic KOH (KOH dissolved in ethanol), heated. ⚠️ Terminology alert: **alcoholic KOH causes elimination** (removes HX → alkene), while **aqueous KOH causes substitution** (replaces X with OH → alcohol). Students mix these up constantly — the solvent decides the reaction.

Mechanism (E2 — bimolecular elimination), step-by-step in words:

1. The hydroxide ion (OH^-) acts as a **base** and attacks a hydrogen on a carbon *adjacent* to the carbon carrying the halogen (a β-hydrogen).
2. **In one concerted step** (all at once — that is what E2 means: both molecules involved in the single slow step): the C–H bond electrons form the C=C double bond while the C–X bond breaks, expelling X^-. No carbocation intermediate forms.
3. The elimination prefers the **anti** geometry: the H and the X leave from opposite sides of the molecule (anti-periplanar), which gives the most stable transition state. This is called **anti-elimination**.

> **Worked example — Zaitsev with 2-bromobutane:**

$CH_3–CHBr–CH_2–CH_3 + KOH(alc) \xrightarrow{\Delta} ?$

Removing H from C-1 gives 1-butene (less substituted); removing H from C-3 gives 2-butene (more substituted). **Major product: 2-butene (Zaitsev product).** Note there are more β-hydrogens on C-3's side? No — count: C-1 has 3 H, C-3 has 2 H; Zaitsev is about alkene substitution, not H-count: the product with the more substituted double bond (2-butene) dominates.

Key takeaway: Alkyl halide + alcoholic KOH + heat → alkene + KBr + H2O, by E2 anti-elimination; Zaitsev's rule again picks the major (more substituted) alkene.

4.3.3 Method (c) — Dehalogenation of vicinal dihalides

Concept. Remove two halogen atoms from *adjacent* carbons to make an alkene.

Reaction with conditions:

$CH_2Br–CH_2Br \xrightarrow{(Zn\ dust,\ \Delta)} CH_2=CH_2 + ZnBr_2$

(1,2-dibromoethane → ethene + zinc bromide)

Conditions: zinc dust, heated.

What "vicinal" means: vicinal (from Latin *vicinus* = neighbour) means the two halogen atoms sit on **adjacent (neighbouring) carbon atoms**. A **geminal** dihalide (both halogens on the *same* carbon) does NOT give an alkene by this method — another common confusion.

Mechanism in words (simplified): Zinc metal donates electrons to the C–Br bonds. Both C–Br bonds break, the two bromine atoms leave as ZnBr2, and the two carbons form a C=C double bond between them. This is essentially the reverse of halogen addition to an alkene.

Key takeaway: Vicinal dihalide + Zn dust + heat → alkene + ZnBr2. Halogens must be on neighbouring carbons.

4.3.4 Method (d) — Wittig reaction

Concept. Convert a carbonyl compound (aldehyde or ketone) directly into an alkene with the double bond in an exactly known position.

From-zero: what is a phosphorus ylide? An **ylide** is a neutral molecule that has a positive and a negative charge on *adjacent* atoms. A **phosphorus ylide** has P^+ next to C^-. It is made in two steps:

Step 1 — phosphonium salt formation:

$PPh_3 + R–X \rightarrow [R–P^+Ph_3]\ X^-$

Triphenylphosphine (PPh_3) attacks an alkyl halide (R–X); phosphorus takes the alkyl group and becomes positively charged → an **alkyltriphenylphosphonium salt**.

Step 2 — ylide formation (base removes a proton):

$[R–P^+Ph_3]\ X^- + base \rightarrow Ph_3P^+–C^-HR\ (\leftrightarrow Ph_3P=CHR) + HX$

A strong base removes a proton from the carbon next to phosphorus, giving the **ylide**, often written $Ph_3P=CH–R$ (the double-bond form is a convenient shorthand; the real structure has charge separation, $P^+–C^-$).

Wittig reaction itself:

$R_2C=O + Ph_3P=CH–R' \rightarrow R_2C=CH–R' + Ph_3P=O$

(carbonyl + ylide → alkene + triphenylphosphine oxide)

Mechanism in words (numbered steps):

1. **Nucleophilic attack:** The negatively charged carbon of the ylide attacks the positively polarised carbon of the carbonyl group (C=O). This forms a C–C bond and pushes the carbonyl π electrons onto oxygen, giving a dipolar intermediate called a **betaine** (positive P, negative O, on adjacent atoms).
2. **Ring closure:** The negatively charged oxygen attacks the positively charged phosphorus, forming a four-membered ring intermediate called an **oxaphosphetane** (a ring of P–C–C–O).
3. **Ring breakdown:** The four-membered ring splits apart: the C–C bond pair forms the new C=C double bond (the alkene product), and the P–O pair forms **triphenylphosphine oxide, Ph3P=O** (a very strong P=O bond — forming it is what drives the reaction forward).

> **Worked example:**

CH3–CHO + Ph3P=CH2 → CH3–CH=CH2 + Ph3P=O

(acetaldehyde + methylene ylide → propene + triphenylphosphine oxide)

Advantage / limitation: The great advantage of the Wittig reaction is that **the position of the new double bond is exactly known** — it forms precisely where the carbonyl carbon was, so there is no mixture of isomeric alkenes (no Zaitsev ambiguity). Limitation: it needs the ylide to be prepared from an alkyl halide and PPh3, and it produces a full equivalent of Ph3P=O as by-product.

Key takeaway: Carbonyl + phosphorus ylide → alkene (double bond exactly at the old carbonyl carbon) + Ph3P=O, via betaine → oxaphosphetane → breakdown.

4.4 Summary Table — Preparation of Alkenes

Method	Starting material	Reagent & conditions	Product	Key point
Dehydration	Alcohol (R–OH)	conc. H2SO4, 170–180 °C	Alkene + H2O	E1 via carbocation; Zaitsev's rule
Dehydrohalogenation	Alkyl halide (R–X)	alcoholic KOH, heat	Alkene + KBr + H2O	E2 anti-elimination; Zaitsev's rule
Dehalogenation	Vicinal dihalide	Zn dust, heat	Alkene + ZnBr2	Halogens on adjacent carbons
Wittig	Aldehyde/ketone + ylide	(ylide from PPh3 + R–X, then base)	Alkene + Ph3P=O	Exact double-bond position

4.5 Worked Examples (Chapter 4)

Example 1. Dehydration of ethanol: CH3CH2OH →(conc. H2SO4, 180 °C) CH2=CH2 + H2O. Only one alkene is possible.

Example 2. Dehydration of 2-butanol (Zaitsev): CH3–CH(OH)–CH2–CH3 → major: CH3–CH=CH–CH3 (2-butene) + minor: CH2=CH–CH2–CH3 (1-butene).

Example 3. Dehydrohalogenation of 2-bromobutane: CH3–CHBr–CH2–CH3 + KOH(alc) →(Δ) major CH3–CH=CH–CH3 + minor CH2=CH–CH2–CH3.

Example 4. Dehalogenation: CH2Br–CH2Br →(Zn, Δ) CH2=CH2 + ZnBr2.

Example 5. Wittig: CH3–CHO + Ph3P=CH2 → CH3–CH=CH2 + Ph3P=O.

4.6 Pharmacy Relevance (Chapter 4)

- Alkenes are building blocks in organic synthesis: many drug molecules and intermediates contain C=C bonds that are later converted into alcohols, halides, or epoxides (see Chapter 5 reactions).
- The dehydration and dehydrohalogenation methods are classic laboratory preparations a pharmacy student performs in practical organic chemistry (Vogel's Textbook of Practical Organic Chemistry describes such preparations).
- The Wittig reaction's ability to place a double bond at an exact position is valuable in the synthesis of complex molecules such as vitamins and natural-product-like drug scaffolds, where isomeric mixtures would be unacceptable.

4.7 India Context (Chapter 4)

- Dehydration of ethanol to ethene is historically linked to India's fermentation-based ethanol industry (sugarcane molasses → ethanol), showing how a bulk commodity connects to basic organic transformations taught in every Indian pharmacy college laboratory.
- Zaitsev's rule and E1/E2 mechanisms are standard, high-weightage topics in Indian competitive examinations (GPAT, NIPER JEE) — mastering the alcoholic-KOH-vs-aqueous-KOH distinction alone saves marks every year.

4.8 Common Confusions (Chapter 4)

1. **Alcoholic KOH vs aqueous KOH:** alcoholic KOH → elimination (alkene); aqueous KOH → substitution (alcohol). The *solvent* decides, not the KOH.
2. **Vicinal vs geminal dihalide:** only *vicinal* (adjacent carbons) gives an alkene with Zn. Geminal (same carbon) does not.
3. **E1 vs E2:** E1 = two steps, carbocation intermediate, dehydration of alcohols; E2 = one concerted step, no carbocation, dehydrohalogenation with alcoholic KOH.
4. **Zaitsev vs "most hydrogens removed":** Zaitsev picks the *more substituted alkene*, not the product from removing the most hydrogens.

4.9 Common Mistakes (Chapter 4)

- Writing the dehydration product of 2-butanol as only 1-butene (forgetting Zaitsev's rule — the major product is 2-butene).
- Drawing the Wittig alkene with the double bond in the wrong place — it must be exactly at the former carbonyl carbon.
- Forgetting water (H2O) as a product in dehydration equations.

4.10 Mnemonics (Chapter 4)

- **Zaitsev = "the rich get richer":** the double bond prefers the carbon neighbourhood that is already "rich" in alkyl groups (more substituted alkene wins).
- **"Alcoholic KOH Eliminates, Aqueous KOH Substitutes"** — both start with A: Alcoholic→Alkene, Aqueous→Alcohol.
- **Wittig = "Where the C=O was, the C=C will be"** — exact double-bond position.

4.11 One-Minute Revision (Chapter 4)

- Alkene = C=C = 1σ + 1π; π is reactive, locks rotation → cis/trans.
- Alcohol →(conc. H_2SO_4, 170–180 °C, E1) alkene + H_2O; Zaitsev: more substituted alkene major.
- Alkyl halide →(alc. KOH, Δ, E2 anti) alkene; Zaitsev again.
- Vicinal dihalide →(Zn, Δ) alkene + $ZnBr_2$.
- Carbonyl + P-ylide → alkene + $Ph_3P{=}O$ (Wittig); double bond exactly at old C=O; via betaine → oxaphosphetane.

Practice Questions — Chapter 4

MCQs (10) — answer key at the end of the chapter questions

1. The general formula of an alkene is: (a) C_nH_{2n+2} (b) C_nH_{2n} (c) C_nH_{2n-2} (d) C_nH_n
2. In ethene, each carbon is: (a) sp^3 hybridized (b) sp^2 hybridized (c) sp hybridized (d) unhybridized
3. Dehydration of ethanol with conc. H_2SO_4 is carried out at about: (a) 0 °C (b) 100 °C (c) 170–180 °C (d) 300 °C
4. The dehydration of alcohols proceeds by: (a) E1 mechanism (b) E2 mechanism (c) SN1 mechanism (d) free-radical mechanism
5. Zaitsev's rule states that the major product is: (a) the least substituted alkene (b) the more substituted alkene (c) always the terminal alkene (d) always 1-butene
6. Dehydrohalogenation of alkyl halides requires: (a) aqueous KOH (b) alcoholic KOH (c) conc. H_2SO_4 (d) Zn dust
7. Aqueous KOH with an alkyl halide gives: (a) an alkene (b) an alcohol (c) an alkyne (d) an ether
8. Vicinal dihalide means: (a) both halogens on the same carbon (b) halogens on adjacent carbons (c) halogens on alternate carbons (d) one halogen only
9. $CH_2Br–CH_2Br$ with Zn dust on heating gives: (a) $CH_3–CH_3$ (b) $CH_2{=}CH_2$ (c) $CH{\equiv}CH$ (d) $CH_3–CH_2Br$
10. The by-product of the Wittig reaction (besides the alkene) is: (a) PPh_3 (b) $Ph_3P{=}O$ (c) H_2O (d) KBr

Answer key: 1-b, 2-b, 3-c, 4-a, 5-b, 6-b, 7-b, 8-b, 9-b, 10-b

Short-answer (5)

1. Define sp^2 hybridization and state the geometry and bond angle in ethene.
2. Why is rotation restricted around a C=C double bond?
3. State Zaitsev's rule with one example.
4. Distinguish between alcoholic KOH and aqueous KOH in their action on alkyl halides.
5. What is a phosphorus ylide? How is it prepared?

Long-answer (3)

1. Describe the E1 mechanism of dehydration of alcohols with energy/stability reasoning for Zaitsev's rule.
2. Compare the four methods of alkene preparation with equations, conditions, and one limitation each.
3. Explain the Wittig reaction with the preparation of the ylide and the complete mechanism in words.

Mechanism-writing (2)

1. Write the step-by-step E1 mechanism for the dehydration of 2-butanol, showing the carbocation and both possible alkenes.
2. Write the Wittig mechanism (ylide + acetaldehyde → propene) showing betaine and oxaphosphetane intermediates.

Application-based (2)

1. An alcohol C4H10O on dehydration gives mainly 2-butene. Identify the alcohol and explain using Zaitsev's rule. (Answer: 2-butanol; the 2° carbocation leads preferentially to the more substituted alkene.)
2. You need pure 1-butene free from 2-butene. Which preparation method would you choose — dehydration of 2-butanol or a Wittig route from propanal? Justify. (Answer: Wittig from propanal + Ph3P=CH2 places the double bond exactly at the terminal position with no isomeric mixture.)

Viva (5)

1. What is the hybridization of carbon in an alkene?
2. Why do alkenes show cis–trans isomerism while alkanes do not?
3. Name the intermediate in E1 dehydration.
4. What does "vicinal" mean?
5. Why is the Wittig reaction synthetically valuable?

Chapter 5 — Electrophilic Addition, Markovnikov, Anti-Markovnikov, Ozonolysis

Learning Objectives

After studying this chapter you should be able to:

1. Define electrophile and nucleophile, and describe the general two-step mechanism of electrophilic addition to alkenes.
2. Explain why the more stable carbocation intermediate decides the product (link to Markovnikov's rule).
3. State Markovnikov's rule in your own words and apply it to the addition of HX, X2, and H2O/H^+ to unsymmetrical alkenes.
4. Explain the peroxide (Kharasch) effect: conditions, free-radical mechanism, and why only HBr shows it.
5. Write ozonolysis equations, predict carbonyl products, and work backwards from products to the parent alkene.
6. Use the bromine test to detect a C=C bond.

5.1 Key Definitions Box

Term	Simple Definition
Electrophile	An "electron-lover": a species that is attracted to electrons because it is positively charged or electron-deficient (e.g., H^+, Br^+, carbocations). In alkene reactions, the electrophile attacks the π electrons.
Nucleophile	A "nucleus-lover": an electron-rich species (negative charge or lone pair, e.g., Br^-, OH^-, H2O) that donates electrons to an electron-deficient centre.
Carbocation	A carbon atom with only six valence electrons and a positive charge (e.g., CH3–C⁺H–CH3). Electron-deficient; stability order: tertiary (3°) > secondary (2°) > primary (1°) > methyl. Formed as the intermediate in electrophilic addition.
Electrophilic addition	The characteristic reaction of alkenes: the π bond breaks and two new sigma bonds form as an electrophile (E^+) and then a nucleophile (Nu^-) add across the double bond. General form: C=C + E–Nu → E–C–C–Nu.
Markovnikov's rule	In the addition of HX to an unsymmetrical alkene, the hydrogen (the electrophilic part) adds to the carbon already bearing the greater number of hydrogens, so that the more stable carbocation forms.
Peroxide effect (Kharasch effect)	The reversal of Markovnikov's rule seen ONLY when HBr adds to an alkene in the presence of peroxides (ROOR): Br adds to the less substituted carbon (anti-Markovnikov product) via a free-radical mechanism.
Free radical	A species with one unpaired electron (e.g., Br·). Very reactive. Stability order parallels carbocations: 3° > 2° > 1°.
Ozonolysis	Cleavage of a C=C double bond by ozone (O3) followed by reductive workup (Zn/H2O or (CH3)2S), giving carbonyl compounds (aldehydes/ketones). Used to locate the double bond.
Conjugation	(Preview of Chapter 6) Alternating double and single bonds (C=C–C=C) allowing π-electron delocalisation.
Syn addition	Addition in which both new groups add to the *same face* of the double bond (e.g., catalytic hydrogenation). Its opposite is *anti* addition (opposite faces).

5.1.1 Terminology Alerts

- **Electrophile vs nucleophile:** electrophile = electron-poor, seeks electrons (H^+, Br^+); nucleophile = electron-rich, gives electrons (Br^-, H2O). In the first step of electrophilic addition, the **alkene acts as the nucleophile** (its π electrons attack the electrophile).
- **Markovnikov vs anti-Markovnikov:** Markovnikov = H goes to the carbon with more H (normal, ionic mechanism); anti-Markovnikov = Br goes to the carbon with more H (only HBr + peroxides, radical mechanism).
- **Carbocation vs free radical:** carbocation = positive charge, six electrons; radical = neutral, one unpaired electron (seven electrons). Different species, different mechanisms.
- **Ozonolysis vs oxidation:** ozonolysis *cleaves* the double bond into two carbonyl pieces; ordinary oxidation may only add OH groups. Do not confuse.

5.2 From-zero: electrophilic addition — the master mechanism

Concept. Almost every reaction of an alkene is an **addition across the double bond**: the π bond breaks, and two atoms/groups attach themselves to the two carbons.

Simple explanation. The π electrons sit exposed above and below the molecule, loosely held. Anything electron-hungry — an **electrophile** — is attracted to them. The general mechanism has two steps:

Step 1 — the π electrons attack the electrophile. The C=C π cloud reaches out to the electrophile (E^+). A new bond forms between one carbon and E, and the π bond breaks. The *other* carbon is left with only six electrons → a **carbocation**. Because carbocations have a stability order (3° > 2° > 1°), the π electrons attack in whichever orientation puts the positive charge on the **more substituted carbon**. This single fact explains Markovnikov's rule.

Step 2 — the nucleophile captures the carbocation. A nucleophile (Nu^-), electron-rich, donates its electrons to the positive carbon, forming the second new bond. Product: E–C–C–Nu. The π bond is gone, replaced by two new sigma bonds.

> **Worked example — HBr addition to propene, in words:**

$CH_3–CH=CH_2 + HBr \rightarrow ?$

1. HBr is polar: H is slightly positive (δ^+, the electrophile), Br slightly negative (δ^-).
2. The π electrons of propene attack H^+. Two orientations are possible:

- (a) H^+ bonds to the terminal CH_2 carbon → carbocation on the middle carbon: $CH_3–C^+H–CH_3$, a **2° carbocation** (more stable).
- (b) H^+ bonds to the middle carbon → carbocation on the terminal carbon: $CH_3–CH_2–C^+H_2$, a **1° carbocation** (less stable).

Path (a) wins because the 2° carbocation is more stable.

1. Br^- (nucleophile) attacks the 2° carbocation → **$CH_3–CHBr–CH_3$ (2-bromopropane)**. This is the **Markovnikov product**: H added to the carbon already having more H (the terminal CH_2), Br to the more substituted carbon.

Key takeaway: Electrophilic addition = π attacks electrophile → most stable carbocation → nucleophile captures it. Carbocation stability decides everything.

5.3 Named/standard additions

5.3.1 Addition of HX (hydrohalogenation)

Reagents/conditions: HX (HCl, HBr, HI); no catalyst needed; often at room temperature. Reactivity order: HI > HBr > HCl.

Equation: $CH_3–CH=CH_2 + HBr \rightarrow CH_3–CHBr–CH_3$ (Markovnikov product).

Mechanism: the two-step electrophilic addition described above (π → H^+ → 2° carbocation → Br^- capture).

Limitation: with unsymmetrical alkenes a mixture is possible if the two possible carbocations are close in stability; the rule predicts the *major* product, not the exclusive one.

5.3.2 Addition of X2 — the bromine test

Reagents/conditions: Br_2 in CCl_4 (or bromine water), room temperature, no catalyst.

Equation: $CH_2=CH_2 + Br_2 \rightarrow CH_2Br–CH_2Br$ (1,2-dibromoethane).

Mechanism in words (simplified): the π electrons attack one bromine atom of Br_2, forming a C–Br bond and a **cyclic bromonium ion** (a three-membered ring with positive charge shared over Br and both carbons) plus Br^-. Then Br^- attacks one carbon of the ring from the back side (**anti addition**), opening the ring to give the vicinal dibromide. (Textbooks present the bromonium-ion version; the key exam point is anti addition giving the trans-dibromide from a cis-alkene.)

The bromine test — pharmacy/analytical relevance: the brown-red colour of bromine **disappears** (decolourised) when an alkene is present, because Br_2 is consumed to form the colourless dibromide. This is the classic qualitative test for unsaturation (C=C), used in pharmaceutical analysis to detect double bonds in oils, fats, and drug samples.

5.3.3 Acid-catalysed hydration (addition of H_2O)

Reagents/conditions: H_2O with acid catalyst (H^+, commonly dilute H_2SO_4), heat.

Equation: CH3–CH=CH2 + H2O →(H⁺) CH3–CH(OH)–CH3 (propan-2-ol; Markovnikov product).

Mechanism in words:

1. π electrons attack H^+ → most stable (2°) carbocation: CH3–C⁺H–CH3.
2. Water (nucleophile, via its lone pair) attacks the carbocation → protonated alcohol, CH3–C⁺H2(OH)–CH3… more precisely CH3–CH(OH2⁺)–CH3.
3. Another water molecule removes the extra proton → the alcohol CH3–CH(OH)–CH3, and H^+ is regenerated (catalyst).

Note: this is the exact reverse of the E1 dehydration in Chapter 4 — same carbocation, opposite direction.

5.3.4 Catalytic hydrogenation (brief)

Reagents/conditions: H2 gas with metal catalyst Pt, Pd, or Ni, room temperature/pressure (conditions vary).

Equation: CH2=CH2 + H2 →(Pt) CH3–CH3.

Key points: both H atoms add to the **same face** of the double bond (**syn addition**) because the alkene adsorbs onto the metal surface. Converts unsaturated → saturated. (Detailed surface mechanism is beyond this syllabus; know reagents, syn addition, and the equation.)

5.4 Markovnikov's rule — stated, proved, practised

Rule (memorise this wording): *When HX adds to an unsymmetrical alkene, the hydrogen atom adds to the carbon that already bears the greater number of hydrogen atoms* — equivalently, the electrophile (H^+) adds to the **less substituted** carbon so that the **more stable carbocation** is formed, and the halide ends up on the more substituted carbon.

Mnemonic: "The rich get richer" — the carbon already rich in hydrogens gets the new hydrogen; the carbon rich in alkyl groups gets the halogen.

> **Worked example 1 — propene + HBr:**

CH3–CH=CH2 + HBr → CH3–CHBr–CH3 (2-bromopropane, major). Reason: H^+ adds to C-1 (CH2, more H) giving the 2° carbocation CH3–C⁺H–CH3 rather than the 1° carbocation. Br^- captures it.

> **Worked example 2 — 2-methylpropene + HCl:**

(CH3)2C=CH2 + HCl → (CH3)2CCl–CH3 (tert-butyl chloride; 2-chloro-2-methylpropane). Reason: H^+ adds to the terminal CH2 → **3° carbocation** (CH3)2C⁺–CH3, the most stable possible; Cl^- captures it. No rearrangement needed here since the 3° cation forms directly.

Exceptions/limits: the rule predicts the major product when carbocations differ in stability; if a **carbocation rearrangement** (hydride or methyl shift) can give a more stable cation, the rearranged product may dominate — recognise this as a possible complication, though detailed rearrangements are treated with the reactions where they arise.

Key takeaway: Markovnikov = H to the H-rich carbon, via the most stable carbocation.

5.5 Anti-Markovnikov addition — the peroxide (Kharasch) effect

Concept. Under special conditions, HBr adds to alkenes **backwards** (anti-Markovnikov).

Conditions — memorise exactly: HBr ONLY, in the presence of peroxides (ROOR, e.g., benzoyl peroxide), usually with heat or light to start the radicals. **HCl and HI do NOT show the peroxide effect** — this is one of the most-tested common mistakes.

Why only HBr? The radical chain needs two propagation steps to both be energetically favourable. For HCl, the step RO· + H–Cl → ROH + Cl· is endothermic (the H–Cl bond is too strong); for HI, the radical-addition step is reversible and unproductive. Only HBr fits both steps. (Know the conclusion firmly; the bond-energy argument is the standard textbook explanation.)

Free-radical mechanism in words (numbered steps):

First, what is a **free radical**? A species with one unpaired electron (written with a dot, e.g., Br·). Radicals are extremely reactive and react in **chain reactions**: initiation (radicals created) → propagation (radicals consumed and regenerated) → termination.

1. **Initiation:** the peroxide breaks: RO–OR → 2 RO· (heat/light). Then RO· + HBr → ROH + **Br·** (bromine radical generated).
2. **Propagation step 1:** Br· adds to the alkene. It adds to the **less substituted (terminal) carbon**, because that puts the unpaired electron on the **more substituted carbon** → the **more stable carbon radical** (radical stability: 3° > 2° > 1°, same order as carbocations). For propene: Br· + CH3–CH=CH2 → CH3–C·H–CH2Br (2° radical, more stable than the 1° alternative).
3. **Propagation step 2:** the carbon radical abstracts H from HBr: CH3–C·H–CH2Br + HBr → CH3–CH2–CH2Br + **Br·**. Product = **1-bromopropane** (anti-Markovnikov: Br ended up on the less substituted carbon), and Br· is regenerated to continue the chain.

Equation: CH3–CH=CH2 + HBr →(peroxide) CH3–CH2–CH2Br (1-bromopropane).

⚠️ **Common mistake alert:** writing anti-Markovnikov products for HCl/peroxide or HI/peroxide — wrong. Only HBr. Also: peroxides have NO effect on the ionic (normal) additions of HCl, HBr (without peroxide), HI, H2O, or X2.

Key takeaway: HBr + peroxide → anti-Markovnikov via Br· radical chain; Br adds to the less substituted carbon giving the more stable radical. HCl/HI never do this.

5.6 Ozonolysis

Concept. Ozone (O3) **cuts** the C=C double bond completely, turning each doubly-bonded carbon into a carbonyl compound (C=O).

Reagents/conditions: (1) O3, then (2) **reductive workup**: Zn/H2O or dimethyl sulphide, (CH3)2S. (Oxidative workup with H2O2 would give carboxylic acids instead — the syllabus method is the reductive one giving aldehydes/ketones.)

What "reductive workup" means: after ozone adds to the double bond, a second reagent (Zn/H2O or Me2S) breaks down the ozonide intermediate gently, "reducing" it to carbonyls. Without it you would not get clean aldehydes/ketones.

General pattern — memorise: each carbon of the old C=C becomes a C=O carbon:

- =CH2 → formaldehyde, HCHO
- =CH–R → aldehyde, R–CHO
- =C(R)2 → ketone, R2C=O

> **Worked example 1 — ethene:**

CH2=CH2 →(1. O3; 2. Zn/H2O) 2 HCHO (two molecules of formaldehyde).

Worked example 2 — 2-butene:

CH3–CH=CH–CH3 →(1. O3; 2. Zn/H2O) 2 CH3–CHO (two molecules of acetaldehyde).

Worked example 3 — 2-methyl-2-butene:

(CH3)2C=CH–CH3 →(1. O3; 2. Zn/H2O) (CH3)2C=O (acetone) + CH3–CHO (acetaldehyde). The (CH3)2C= carbon (two alkyl groups) becomes a ketone; the CH–CH3 carbon becomes an aldehyde.

Reverse problem — "find the alkene from ozonolysis products":

Problem: An alkene on ozonolysis gives one molecule of acetone, (CH3)2C=O, and one of acetaldehyde, CH3–CHO. Identify the alkene.

Solution in words: Remove the =O oxygens and join the two carbonyl carbons with a double bond: (CH3)2C=O + O=CH–CH3 → (CH3)2C=CH–CH3. **Answer: 2-methyl-2-butene.** Trick: mentally erase each =O, then connect the carbons with C=C.

Use: ozonolysis **locates the position of the double bond** in an unknown alkene — a classical structure-determination tool.

Key takeaway: O3 then Zn/H2O splits C=C into carbonyls: =CH2→HCHO, =CHR→RCHO, =CR2→R2CO. Reverse it to find the alkene.

5.7 Summary Tables (Chapter 5)

Table A — Electrophilic additions compared

Reaction	Reagent	Product type	Regiochemistry	Key intermediate
HX addition	HX	Alkyl halide	Markovnikov	Most stable carbocation
X2 addition	Br2/CCl4	Vicinal dibromide	Anti addition	Bromonium ion
Hydration	H2O, H^+	Alcohol	Markovnikov	Most stable carbocation
Hydrogenation	H2, Pt/Pd/Ni	Alkane	Syn addition	(surface; no ion)
HBr + peroxide	HBr, ROOR	Alkyl bromide	Anti-Markovnikov	Most stable carbon radical

Table B — Ozonolysis quick reference

Alkene fragment	Carbonyl product
=CH2	HCHO (formaldehyde)
=CH–R	R–CHO (aldehyde)
=C(R)2	R2C=O (ketone)

5.8 Pharmacy Relevance (Chapter 5)

- **Bromine test for unsaturation** is a pharmacopoeial qualitative test: fixed oils and fats are characterised by their iodine value (a quantitative cousin of the bromine test), which measures C=C content — directly relevant to the analysis of oils used in pharmacy.
- Markovnikov hydration is the laboratory route to alcohols (e.g., propan-2-ol, a common pharmaceutical solvent/disinfectant) from alkenes.
- Understanding carbocation stability and regioselectivity trains the mechanistic thinking needed later for drug metabolism (many metabolic oxidations pass through carbocation-like or radical intermediates).

5.9 India Context (Chapter 5)

- The addition reactions of this chapter (HX, Br2, hydration) are performed in undergraduate practical classes across Indian pharmacy colleges and are favourite GPAT/NIPER JEE questions — particularly "which product, Markovnikov or anti-Markovnikov?" traps with HCl/peroxide.
- Catalytic hydrogenation on an industrial scale (vegetable ghee/vanaspati manufacture) is a familiar Indian example of alkene → alkane conversion.

5.10 Common Confusions (Chapter 5)

1. **Who is the electrophile?** In HX addition, H^+ (not X^-) is the electrophile and adds first. The alkene's π electrons are the nucleophile in step 1.
2. **Markovnikov = H to the carbon with MORE hydrogens.** Students often reverse it. "Rich get richer."
3. **Peroxide effect only for HBr.** HCl + peroxide and HI + peroxide give normal Markovnikov products.
4. **Ozonolysis products:** =CH2 gives formaldehyde (HCHO), not "nothing". Count the carbons — both halves of the alkene appear as products.
5. **Syn vs anti:** hydrogenation = syn (same face); Br2 addition = anti (opposite faces, via bromonium ion).

5.11 Common Mistakes (Chapter 5)

- Drawing the carbocation on the wrong carbon in the mechanism (always place + on the more substituted carbon).
- Forgetting the second step (nucleophile capture) — the mechanism has TWO steps, not one.
- Writing anti-Markovnikov products for HCl in presence of peroxide.
- In ozonolysis reverse problems, joining carbonyl carbons with a single bond instead of a double bond.

5.12 Mnemonics (Chapter 5)

- **Markovnikov: "The rich get richer"** — H joins the H-rich carbon.
- **Peroxide effect: "Only HBr plays the peroxide game"** — HCl and HI sit out.
- **Ozonolysis: "Cut at the double, cap with oxygen"** — erase C=C, put =O on each carbon; reverse by erasing =O and rejoining with C=C.
- **E–Nu order: "Electrophile first, Nucleophile next"** — the π bond meets E^+ before Nu^-.

5.13 One-Minute Revision (Chapter 5)

- Electrophilic addition: π attacks E^+ → most stable carbocation → Nu^- captures.
- HX/X2/H2O add Markovnikov (H to H-rich carbon); Br2 test: brown colour disappears.
- HBr + ROOR → anti-Markovnikov (1-bromopropane from propene) via Br· radical chain; HCl/HI never.
- Hydrogenation: H2, Pt/Pd/Ni, syn addition → alkane.
- Ozonolysis: O3; Zn/H2O → carbonyls; =CH2 → HCHO, =CHR → RCHO, =CR2 → R2CO; reverse to find the alkene.

Practice Questions — Chapter 5

MCQs (10)

1. In electrophilic addition, the first species to attack the alkene is the: (a) nucleophile (b) electrophile (c) free radical (d) solvent
2. The intermediate in HX addition to an alkene is a: (a) carbanion (b) carbocation (c) free radical (d) bromonium ion
3. Propene + HBr (no peroxide) gives mainly: (a) 1-bromopropane (b) 2-bromopropane (c) 1,2-dibromopropane (d) propyne
4. 2-methylpropene + HCl gives: (a) 1-chloro-2-methylpropane (b) 2-chloro-2-methylpropane (c) 1,2-dichloro-2-methylpropane (d) 2-methyl-1-propene
5. The peroxide effect is shown by: (a) HCl (b) HBr (c) HI (d) all of these
6. Propene + HBr in presence of peroxide gives: (a) 2-bromopropane (b) 1-bromopropane (c) 1,2-dibromopropane (d) allyl bromide
7. The bromine test for an alkene shows: (a) brown colour appears (b) brown colour disappears (c) white precipitate (d) no change
8. Ozonolysis of ethene (reductive workup) gives: (a) 2 acetaldehyde (b) 2 formaldehyde (c) formic acid (d) $CO_2 + H_2O$
9. Ozonolysis of 2-butene gives: (a) 2 acetaldehyde (b) acetone + formaldehyde (c) 2 acetone (d) propanal only
10. An alkene gives acetone + acetaldehyde on ozonolysis. It is: (a) 2-butene (b) 2-methyl-2-butene (c) 1-butene (d) ethene

Answer key: 1-b, 2-b, 3-b, 4-b, 5-b, 6-b, 7-b, 8-b, 9-a, 10-b

Short-answer (5)

1. Define electrophile and nucleophile with one example each.
2. State Markovnikov's rule.
3. Why does the peroxide effect occur only with HBr?
4. What is reductive workup in ozonolysis? Name two reagents used.
5. Write the equation for the bromine test and state the observation.

Long-answer (3)

1. Describe the general mechanism of electrophilic addition with the HBr + propene example, explaining the role of carbocation stability.
2. Explain the peroxide effect with the complete free-radical mechanism for HBr + propene.
3. Describe ozonolysis with three examples and explain how it locates a double bond (include one reverse problem).

Mechanism-writing (2)

1. Write the two-step mechanism for the acid-catalysed hydration of propene.
2. Write the initiation and propagation steps of the peroxide-effect mechanism for HBr + propene.

Application-based (2)

1. A sample of cooking oil decolourises bromine water but a sample of ghee does not. Explain and name the test. (Answer: the oil contains unsaturated fatty acids (C=C), which consume Br2 — the bromine test for unsaturation; ghee is largely saturated.)
2. An unknown alkene C5H10 on ozonolysis gives CH3CHO + CH3CH2CHO. Deduce the alkene. (Answer: CH3–CH=CH–CH2–CH3, 2-pentene — join the carbonyl carbons: CH3CH=CHCH2CH3.)

Viva (5)

1. What is the order of carbocation stability?
2. Which adds first to the alkene in HX addition — H or X? Why?
3. Name the two peroxides' role: which species starts the radical chain?
4. What is syn addition? Give one example.
5. How will you distinguish an alkene from an alkane in the laboratory?

Chapter 6 — Conjugated Dienes and Diels–Alder

Learning Objectives

After studying this chapter you should be able to:

1. Define a diene and classify dienes as isolated, conjugated, or cumulated, with examples.
2. Explain the extra stability of conjugated dienes using resonance/delocalisation.
3. Draw the resonance forms of the allylic carbocation from 1,3-butadiene + HBr.
4. Distinguish 1,2-addition from 1,4-addition products and explain kinetic vs thermodynamic control.
5. Describe the Diels–Alder reaction: components, concerted mechanism, conditions, stereospecificity (cis principle, endo rule), with the butadiene + maleic anhydride example.
6. State the pharmacy relevance of the Diels–Alder reaction.

6.1 Key Definitions Box

Term	Simple Definition
Diene	A hydrocarbon containing **two** carbon–carbon double bonds. Example: 1,3-butadiene, CH2=CH–CH=CH2.
Isolated diene	The two double bonds are separated by **more than one** single bond (e.g., CH2=CH–CH2–CH=CH2, 1,4-pentadiene). Behaves like two independent alkenes.
Conjugated diene	Double and single bonds **alternate**: C=C–C=C (e.g., CH2=CH–CH=CH2, 1,3-butadiene). The π electrons are delocalised over all four carbons — extra stability and special reactions.
Cumulated diene (allene)	The two double bonds share a **common carbon**: C=C=C (e.g., CH2=C=CH2, allene/propadiene).
Conjugation	Alternating π and σ bonds allowing π electrons to spread (delocalise) over more than two atoms.
Resonance (delocalisation)	When π electrons are spread over several atoms, the true structure is a blend ("hybrid") of two or more Lewis structures (**resonance forms**). Delocalisation lowers energy = extra stability.
Allylic (position/carbocation/radical)	The carbon **next to** a double bond is the allylic carbon (C=C–C·). An **allylic carbocation** (C=C–C$^+$ ↔ $^+$C–C=C) is stabilised by resonance — the positive charge is shared over two carbons.
Kinetic control	The product that forms **fastest** (lowest activation energy) dominates — favoured at **low temperature**.
Thermodynamic control	The **most stable** product dominates — favoured at **higher temperature**, when the reaction is reversible enough to equilibrate.
Dienophile	"Diene-lover": the alkene (2π component, usually electron-poor, e.g., maleic anhydride) that reacts with the diene in the Diels–Alder reaction.
Cycloaddition	A reaction in which two π systems join to form a ring. The Diels–Alder is a [4+2] cycloaddition (4 π electrons of diene + 2 of dienophile).
Concerted	Happening in a **single step** with no intermediate — all bond-breaking and bond-forming occurs together through one transition state.
Stereospecific	A reaction in which the stereochemistry of the starting material decides the stereochemistry of the product (cis stays cis).

6.1.1 Terminology Alerts

- **Conjugated vs isolated vs cumulated:** count the single bonds between the double bonds — zero shared carbon with one single bond between = conjugated (C=C–C=C); more single bonds = isolated; shared carbon = cumulated (C=C=C).
- **Resonance forms are NOT real separate molecules** — they are imaginary drawings; the real molecule is the blend (hybrid). Students often say "the molecule flips between forms" — wrong; it is one delocalised structure.
- **1,2- vs 1,4-addition:** the numbers count atoms from where the electrophile first adds: 1,2 = adds to adjacent carbons; 1,4 = adds to the two ends of the conjugated system.
- **Kinetic vs thermodynamic:** kinetic = fastest formed (low T); thermodynamic = most stable (higher T). They are different products here — do not merge them.

6.2 From-zero: types of dienes

Concept. A diene has two C=C bonds. Their *relative positions* decide the chemistry.

Simple explanation with examples:

1. **Isolated diene** — double bonds far apart: CH2=CH–CH2–CH=CH2 (1,4-pentadiene). The two π systems cannot "talk" to each other. Each double bond reacts like an ordinary alkene.
2. **Conjugated diene** — alternating double–single–double: CH2=CH–CH=CH2 (1,3-butadiene). The four p orbitals line up side-by-side, so the π electrons **delocalise** (spread) over all four carbons. This delocalisation gives **extra stability** and new reaction patterns (1,4-addition).
3. **Cumulated diene (allene)** — double bonds share one carbon: CH2=C=CH2 (propadiene, common name allene). The two π bonds are perpendicular to each other.

Key takeaway: isolated = independent double bonds; conjugated = C=C–C=C with delocalised π electrons (the interesting one); cumulated = C=C=C.

6.3 Stability of conjugated dienes — resonance in words

Concept. A conjugated diene is more stable than an isolated diene with the same formula.

Simple explanation. In 1,3-butadiene, the four p orbitals overlap in a row, so the four π electrons spread over all four carbons instead of staying in two separate double bonds. This spreading (**delocalisation**) lowers the molecule's energy — like spreading a crowd over a larger hall lowers the crowding. Chemists draw this with **resonance forms**:

CH2=CH–CH=CH2 ↔ $^{+}$CH2–CH=CH–C^{-}H2 (and equivalent forms)

— the real molecule is the **hybrid** (blend) of these drawings, with partial double-bond character in the middle bond too.

Heat of hydrogenation — the evidence, in simple words: adding H2 across a double bond releases heat. An isolated diene releases roughly twice the heat of one double bond — but 1,3-butadiene releases **less** than expected, meaning it *started* at a lower energy: extra stability. (Textbooks quote the difference as roughly 15 kJ/mol; values vary slightly between sources, so quote cautiously.) This missing heat is the experimental proof of delocalisation.

Key takeaway: conjugation lets π electrons delocalise over four carbons → lower energy → conjugated dienes are more stable than isolated dienes (proved by lower heat of hydrogenation).

6.4 Electrophilic addition to 1,3-butadiene — 1,2 vs 1,4

Concept. HBr can add to a conjugated diene in two ways because the intermediate is resonance-stabilised.

The allylic carbocation — define first: when the π electrons of CH2=CH–CH=CH2 attack H^{+}, the H^{+} adds to a terminal carbon (C-1), giving:

CH3–C^{+}H–CH=CH2 ↔ CH3–CH=CH–C^{+}H2

This is an **allylic carbocation**: the positive charge sits next to a double bond, so it is shared over two carbons via resonance. Draw it as **two resonance forms**: charge on C-2 (a 2° allylic cation) and charge on C-4 (a 1° allylic cation). The real ion is the hybrid with partial positive charge on both C-2 and C-4.

Two products — mechanism in words:

1. H^{+} adds to C-1 of 1,3-butadiene → allylic carbocation (two resonance forms, + on C-2 and C-4).
2. Br^{-} can attack **either** positively-charged carbon:

- Attack at **C-2** → Br on the carbon next to where H added: CH3–CHBr–CH=CH2, **3-bromo-1-butene** — the **1,2-addition product** (H and Br on adjacent carbons C-1, C-2; one double bond remains).
- Attack at **C-4** → Br at the far end: CH3–CH=CH–CH2Br, **1-bromo-2-butene** — the **1,4-addition product** (H on C-1, Br on C-4; the double bond has "moved" to the middle).

Kinetic vs thermodynamic control — define first, then apply:

- **Kinetic control** = the faster-formed product wins. Attack at C-2 (1,2-product) has the lower activation barrier (the C-2 resonance form carries more of the positive charge and is the more stable contributor), so at **low temperature** the 1,2-product dominates.
- **Thermodynamic control** = the more stable product wins. The 1,4-product has the more substituted (internal) double bond, so it is the more stable alkene. At **higher temperature**, addition becomes partly reversible and the mixture equilibrates toward the 1,4-product.

Commonly quoted conditions (values vary slightly across textbooks — treat as approximate): at about **−80 °C**, the 1,2-product (3-bromo-1-butene) is major (kinetic); at about **40 °C**, the 1,4-product (1-bromo-2-butene) is major (thermodynamic).

Free-radical addition (brief): peroxides + HBr with 1,3-butadiene: Br· adds to a terminal carbon giving an **allylic radical** (CH2Br–C·H–CH=CH2 ↔ CH2Br–CH=CH–C·H2, two resonance forms), which then abstracts H from HBr at either radical carbon → 1,2- and 1,4-products. Same regiochemistry logic as the ionic case, but via radicals.

> **Worked example:** CH2=CH–CH=CH2 + HBr →(low T) CH3–CHBr–CH=CH2 (1,2, major); →(higher T) CH3–CH=CH–CH2Br (1,4, major).

Key takeaway: conjugated diene + HBr → allylic cation (two resonance forms) → 1,2-product (kinetic, low T) vs 1,4-product (thermodynamic, higher T).

6.5 The Diels–Alder reaction

Concept. The most famous reaction of conjugated dienes: diene + alkene → a six-membered ring, in one step.

The components — define first:

- **Diene** = the 4π component: a conjugated diene (C=C–C=C), e.g., 1,3-butadiene. It must be able to adopt the **s-cis** conformation (both double bonds on the same side of the middle single bond) so the two ends can reach the dienophile.
- **Dienophile** = "diene-lover": the 2π component, an alkene — usually one carrying electron-withdrawing groups (e.g., maleic anhydride), which makes it electron-poor and eager to react with the electron-rich diene.

Reaction with conditions:

CH2=CH–CH=CH2 + (maleic anhydride) →(heat) Diels–Alder adduct

Conditions: heat; **no catalyst needed**. The reaction is driven by converting three π bonds into stronger σ bonds.

Mechanism — concerted, in words (numbered steps):

The Diels–Alder has **no intermediate** — it is **concerted** (single step):

1. The diene and dienophile approach in parallel planes, the diene's terminal carbons (C-1 and C-4) lining up with the dienophile's two carbons.
2. They pass through a **six-membered cyclic transition state**: six atoms in a ring-like arrangement, with partial bonds forming and breaking simultaneously.
3. **Three π bonds break** (two of the diene, one of the dienophile) and **three new bonds form**: two new C–C **sigma** bonds (diene ends to dienophile carbons) and **one new π bond** (in the middle of the old diene, now inside the new ring).
4. Product: a **cyclohexene ring** (a six-membered ring with one double bond), with the dienophile's substituents attached to the two new sp^3 carbons.

> **Worked example — 1,3-butadiene + maleic anhydride, structure in words:**

Maleic anhydride is a cis-alkene (cis-butenedioic anhydride): a C=C with the two carbonyl groups of the anhydride on the same side. In the adduct, the butadiene's C-1 and C-4 bond to the two alkene carbons of maleic anhydride, giving a six-membered ring with the new double bond between the middle two carbons, and the anhydride ring hanging off the two new sp^3 ring carbons on the **same face** (cis) — the **cis principle** (below). The product is **tetrahydrophthalic anhydride** (a cyclohexene ring fused to the anhydride ring).

Stereospecificity — two rules, simply stated:

1. **Cis principle:** the stereochemistry of the dienophile is preserved — a *cis*-dienophile gives *cis* substituents in the product; a *trans*-dienophile gives *trans* substituents. Because the reaction is concerted, groups have no time to rotate.
2. **Endo rule:** when the dienophile has π-withdrawing substituents (like the carbonyls of maleic anhydride), they prefer to lie **under** the diene π system in the transition state (**endo** orientation) rather than pointing away (**exo**) — the endo product is the major one, due to favourable secondary orbital interactions. (Know the statement and which is major; the orbital detail is beyond this level.)

Pharmacy relevance (cautious wording): the Diels–Alder reaction builds six-membered rings quickly and stereospecifically, so it is widely used in organic synthesis for preparing **drug intermediates and natural-product frameworks** that contain cyclohexene-type rings. (No specific drug synthesis is claimed here — the value is the general ring-forming ability.)

Limitations: the diene must be conjugated and able to adopt the s-cis conformation; very electron-rich dienophiles react sluggishly (the normal Diels–Alder wants an electron-poor dienophile); the reaction is reversible at very high temperatures (retro-Diels–Alder).

Key takeaway: conjugated diene (4π) + dienophile (2π) → cyclohexene ring, concerted, one step, no catalyst, stereospecific (cis in → cis out; endo preferred).

6.6 Summary Tables (Chapter 6)

Table A — Diene types

Type	Arrangement	Example	Reactivity note
Isolated	C=C–(C)n–C=C, n ≥ 2	CH2=CH–CH2–CH=CH2	Like two separate alkenes
Conjugated	C=C–C=C	CH2=CH–CH=CH2	Delocalised; 1,2/1,4 addition; Diels–Alder
Cumulated (allene)	C=C=C	CH2=C=CH2	Perpendicular π bonds

Table B — 1,2 vs 1,4 addition to 1,3-butadiene

Feature	1,2-addition	1,4-addition
Product (with HBr)	CH3–CHBr–CH=CH2 (3-bromo-1-butene)	CH3–CH=CH–CH2Br (1-bromo-2-butene)
Double bond in product	Terminal (less substituted)	Internal (more substituted)
Control	Kinetic (forms faster)	Thermodynamic (more stable)
Favoured at	Low T (≈ −80 °C)	Higher T (≈ 40 °C)

6.7 Pharmacy Relevance (Chapter 6)

- Conjugated diene systems appear in many natural products (carotenoids, terpenes) and in drug scaffolds; recognising conjugation helps predict stability and UV absorption (conjugated systems absorb at longer wavelengths — the basis of UV assays).
- The Diels–Alder reaction is a workhorse ring-forming step in the synthesis of drug intermediates and natural products, valued because it sets multiple stereocentres in one concerted step.
- The kinetic/thermodynamic control concept recurs throughout pharmaceutical chemistry (e.g., in controlling product distributions in synthesis and in understanding drug–receptor binding pathways).

6.8 India Context (Chapter 6)

- Isoprene (2-methyl-1,3-butadiene), a conjugated diene, is the monomer of natural rubber — historically central to India's rubber industry (Kerala); its polymerisation chemistry begins with the 1,4-addition pattern taught in this chapter.
- Diels–Alder and diene chemistry are standard GPAT/NIPER JEE topics: "1,2 vs 1,4 product at low vs high temperature" is a perennial one-mark question.

6.9 Common Confusions (Chapter 6)

1. **Resonance forms are not isomers** — they are drawings of one delocalised molecule, not molecules flipping back and forth.
2. **1,2 vs 1,4 numbers** count from the carbon where the electrophile adds (C-1), not from either end randomly.
3. **Kinetic (low T) vs thermodynamic (high T)** — students often swap them. Cold = fast product; hot = stable product.
4. **Diels–Alder needs a conjugated diene in s-cis form** — an isolated diene will not react.
5. **Concerted = one step, no intermediate.** Do not draw a carbocation in a Diels–Alder mechanism.

6.10 Common Mistakes (Chapter 6)

- Drawing the allylic carbocation with the + on the wrong carbons (it is shared over C-2 and C-4 of the original diene numbering).
- Assigning the 1,4-product as major at −80 °C (it is the 1,2-product at low temperature).
- Forgetting that the Diels–Alder forms TWO new sigma bonds and ONE new pi bond (three π bonds are consumed).
- Writing the dienophile's cis substituents as trans in the adduct (cis principle violated).

6.11 Mnemonics (Chapter 6)

- **Diene types: "1-2-3"** — 1 single bond between = conjugated; 2+ = isolated; 0 (shared carbon) = cumulated.
- **Kinetic/thermodynamic: "Cold is quick, hot is happy"** — low T gives the quickly-formed product; higher T gives the most stable ("happiest") product.
- **Diels–Alder: "4 + 2 = 6"** — 4 π electrons + 2 π electrons = a 6-membered ring.
- **Endo: "ENDo = uNDer"** — substituents tuck under the diene.

6.12 One-Minute Revision (Chapter 6)

- Dienes: isolated (independent), conjugated C=C–C=C (delocalised, extra stable), cumulated C=C=C.
- Conjugated diene + HBr → allylic cation (resonance, + on C-2/C-4) → 1,2-product (kinetic, ≈ −80 °C) vs 1,4-product (thermodynamic, ≈ 40 °C).
- Diels–Alder: diene (4π, s-cis) + dienophile (2π) →(heat, no catalyst) cyclohexene ring; concerted via 6-membered cyclic TS; 3 π → 2 σ + 1 π; stereospecific: cis stays cis (cis principle), endo preferred (endo rule).
- Example: 1,3-butadiene + maleic anhydride → tetrahydrophthalic anhydride adduct.

Practice Questions — Chapter 6

MCQs (10)

1. 1,3-butadiene is a: (a) isolated diene (b) conjugated diene (c) cumulated diene (d) alkyne
2. CH2=C=CH2 is an example of: (a) isolated diene (b) conjugated diene (c) cumulated diene (allene) (d) alkene
3. Conjugated dienes are extra stable because of: (a) hyperconjugation (b) resonance/delocalisation of π electrons (c) inductive effect (d) hydrogen bonding
4. The intermediate in HBr addition to 1,3-butadiene is: (a) vinylic carbocation (b) allylic carbocation (c) free radical only (d) bromonium ion
5. The 1,2-addition product of HBr to 1,3-butadiene is: (a) 1-bromo-2-butene (b) 3-bromo-1-butene (c) 1,4-dibromo-2-butene (d) 2-bromo-1-butene
6. At low temperature (≈ −80 °C), the major product is the: (a) 1,4-product (thermodynamic) (b) 1,2-product (kinetic) (c) 1,2-product (thermodynamic) (d) polymer
7. At higher temperature (≈ 40 °C), the major product is the: (a) 1,2-product (b) 1,4-product (c) no reaction (d) dibromide
8. The Diels–Alder reaction is a: (a) [2+2] cycloaddition (b) [4+2] cycloaddition (c) electrophilic substitution (d) free-radical addition
9. The Diels–Alder mechanism is: (a) two-step via carbocation (b) concerted single step (c) via free radicals (d) via bromonium ion
10. 1,3-butadiene + maleic anhydride gives: (a) a four-membered ring (b) a cyclohexene-type adduct (c) an open-chain diene (d) benzene

Answer key: 1-b, 2-c, 3-b, 4-b, 5-b, 6-b, 7-b, 8-b, 9-b, 10-b

Short-answer (5)

1. Classify: CH2=CH–CH2–CH=CH2; CH2=CH–CH=CH2; CH2=C=CH2.
2. What is an allylic carbocation? Draw its resonance forms for the HBr + butadiene case.
3. Distinguish kinetic control from thermodynamic control.
4. Define dienophile with one example.
5. State the cis principle and the endo rule.

Long-answer (3)

1. Explain why conjugated dienes are more stable than isolated dienes, using resonance and heat of hydrogenation.
2. Describe 1,2- vs 1,4-addition of HBr to 1,3-butadiene with mechanism, products, and temperature effects.
3. Describe the Diels–Alder reaction with mechanism, conditions, stereospecificity, and the butadiene + maleic anhydride example.

Mechanism-writing (2)

1. Write the mechanism of HBr addition to 1,3-butadiene showing the allylic carbocation resonance forms and both products.
2. Describe the concerted Diels–Alder transition state in words, counting the π bonds broken and the σ/π bonds formed.

Application-based (2)

1. Isoprene (CH2=C(CH3)–CH=CH2) is a conjugated diene used to make rubber. Predict whether HBr at −80 °C gives mainly the 1,2- or 1,4-product, and state the product. (Answer: the 1,2 (kinetic) product — H^+ adds to C-1 giving the allylic cation CH3–C^+(CH3)–CH=CH2 ↔ CH3–C(CH3)=CH–C^+H2; Br^- attack at C-2 gives CH3–CBr(CH3)–CH=CH2, 3-bromo-3-methyl-1-butene.)
2. Explain why cyclopentadiene (a conjugated diene locked in s-cis form) undergoes the Diels–Alder reaction faster than an open-chain diene. (Answer: it is permanently held in the reactive s-cis conformation, so no energy is wasted rotating into it.)

Viva (5)

1. How many π electrons do the diene and dienophile contribute in a Diels–Alder reaction?
2. What is the product ring size in a Diels–Alder reaction?
3. Why is the Diels–Alder called stereospecific?
4. What is the difference between endo and exo?
5. Name the adduct of 1,3-butadiene and maleic anhydride.

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