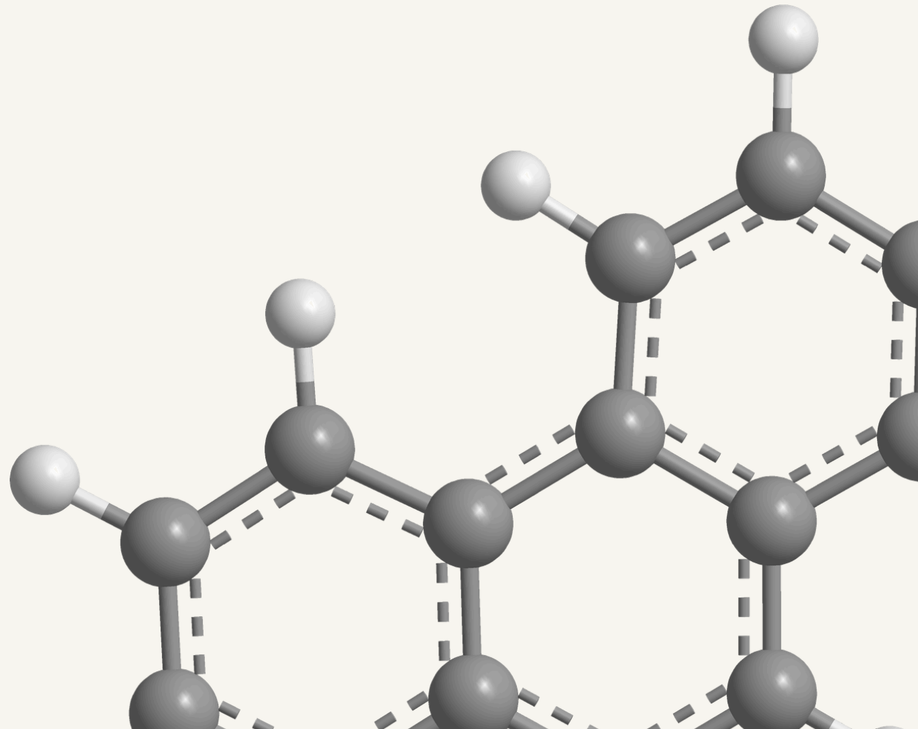
Lecture 10

Alkadienes: double effect, extraction and chemical



Lecture: PhD, acc. professor: Kudaibergenova B.M

Aim and Objectives

Aim

To study the structure, classification, preparation and chemical properties of alkadienes, with attention to the influence of two double bonds and the conjugation effect on reactivity.

Objectives

1. Define alkadienes and their general formula
2. Classify them by double bond position
3. Explain structure and conjugation
4. Identify types of isomerism
5. Study preparation methods
6. Study hydrogenation, halogenation and hydrohalogenation
7. Explain 1,2- and 1,4-addition
8. Examine polymerization and applications

Alkadienes link simple alkenes with polymer chemistry: one conjugated diene, butadiene, is the monomer behind much of the world’s synthetic rubber.

Introduction to Alkadienes

Unsaturated hydrocarbons with two C=C bonds.

$$C_nH_{2n-2} \quad (n \geq 3)$$

- Each C=C is one σ and one π bond
- Undergo electrophilic addition
- May show conjugation between π bonds
- Starting materials for synthetic rubber

Compound	Structure
Propadiene	$CH_2=C=CH_2$
Buta-1,3-diene	$CH_2=CH–CH=CH_2$
Buta-1,2-diene	$CH_2=C=CH–CH_3$
Penta-1,3-diene	$CH_2=CH–CH=CH–CH_3$

> The formula is the same as for alkynes, so dienes and alkynes with equal carbon numbers are isomers. Propadiene is the simplest diene and needs only three carbons.

Classification of Alkadienes

$CH_2=C=CH_2$

Cumulated: share one carbon. Example: propadiene (allene)

$C=C–C=C$

Conjugated: one single bond between. Example: buta-1,3-diene

$C=C–C–C=C$

Isolated: two or more single bonds between. Example: penta-1,4-diene

- Cumulated: central carbon is sp-hybridized
- Conjugated: most stable and most useful
- Isolated: react like two separate alkenes

The class decides the chemistry. Isolated dienes behave as two independent alkenes, while conjugated dienes have unique reactions such as 1,4-addition and the Diels–Alder reaction.

Structure and Conjugation Effect

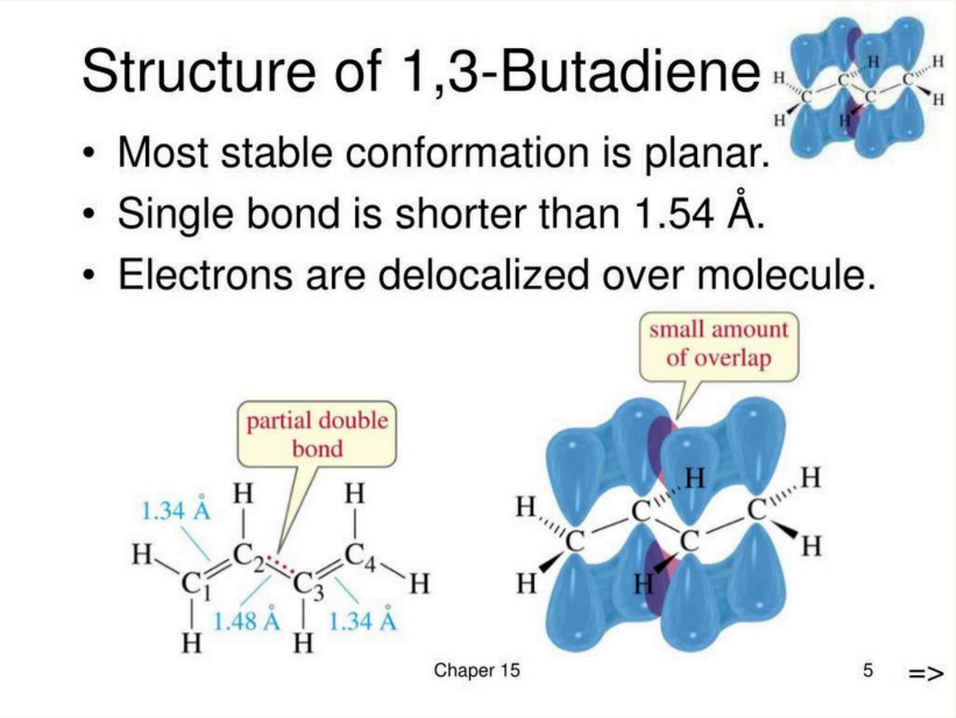
Conjugation: adjacent p orbitals overlap continuously along alternating single and double bonds.

$$CH_2=CH-CH=CH_2$$

All four carbons are sp^2; π electrons are delocalized

- More stable than a nonconjugated analogue
- π density spread over several carbons
- Changes bond lengths and reactivity
- Allows 1,2- and 1,4-addition

> In butadiene the central C–C bond is shorter than a normal single bond, because it has partial double-bond character. Hydrogenation of a conjugated diene releases less heat than for an isolated one, which shows the extra stability.



Isomerism of Alkadienes

Type	Example
Position	Buta-1,2-diene and buta-1,3-diene
Chain	Penta-1,3-diene and 2-methylbuta-1,3-diene (C_5H_8)
Geometrical (E/Z)	Penta-1,3-diene: restricted rotation about C=C

Geometrical isomerism needs two different groups on each carbon of a double bond. Penta-1,3-diene therefore has E and Z forms about its C3=C4 bond. Some cumulated dienes also show axial chirality.

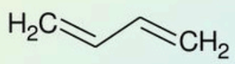
Nomenclature of Alkadienes

1. Longest chain containing both double bonds
2. Lowest locants for the double bonds
3. Replace the alkane ending with -diene
4. Give the position of each double bond
5. Name and number substituents

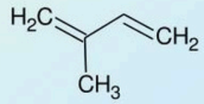
Structure	IUPAC name
$CH_2=C=CH_2$	Propadiene
$CH_2=CH–CH=CH_2$	Buta-1,3-diene
$CH_2=C=CH–CH_3$	Buta-1,2-diene
$CH_2=CH–CH=CH–CH_3$	Penta-1,3-diene
$CH_2=C(CH_3)–CH=CH_2$	2-Methylbuta-1,3-diene

Monomery

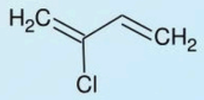
- Największe znaczenie mają:
  - ✓ Butadien (buta-1,3-dien)



  - ✓ Izopren (2-metylobuta-1,3-dien)



  - ✓ Chloropren (2-chlorobuta-1,3-dien)



The locants are written before -diene, and the final -e of the alkane stem is kept: buta-1,3-diene. 2-Methylbuta-1,3-diene is isoprene, the monomer of natural rubber.

Preparation of Alkadienes

$$CH_3CH_2CH_2CH_3 \xrightarrow{(\text{catalyst}, \Delta)} CH_2{=}CH{-}CH{=}CH_2 + 2H_2$$

Dehydrogenation of butane

$$CH_3CH_2CH{=}CH_2 \xrightarrow{(\text{catalyst}, \Delta)} CH_2{=}CH{-}CH{=}CH_2 + H_2$$

Dehydrogenation of but-1-ene

$$2C_2H_5OH \xrightarrow{(\text{catalyst}, \Delta)} CH_2{=}CH{-}CH{=}CH_2 + 2H_2O + H_2$$

Lebedev process from ethanol

Steam cracking: buta-1,3-diene is mainly recovered from the C_4 fraction.

> Dehydrogenation is endothermic and needs high temperature. Today most butadiene is a by-product of ethylene production by steam cracking, while the Lebedev process was historically important for synthetic rubber.

Physical and Chemical Properties

- Small dienes: gases or volatile liquids
- Poorly soluble in water
- Soluble in organic solvents
- Boiling points rise with molecular mass
- Many are flammable

Reaction	Reagents	Products
Hydrogenation	H_2, catalyst	Alkenes, alkanes
Halogenation	Br_2, Cl_2	Halides
Hydrohalogenation	HCl, HBr	Haloalkenes
Polymerization	Initiator	Polymers
Diels–Alder	Dienophile	Cyclohexenes
Combustion	O_2	CO_2, H_2O

All chemical properties arise from the C=C bonds. Conjugated dienes add a special feature: they can react at the 1,2 or 1,4 positions and take part in cycloaddition.

Hydrogenation of Alkadienes

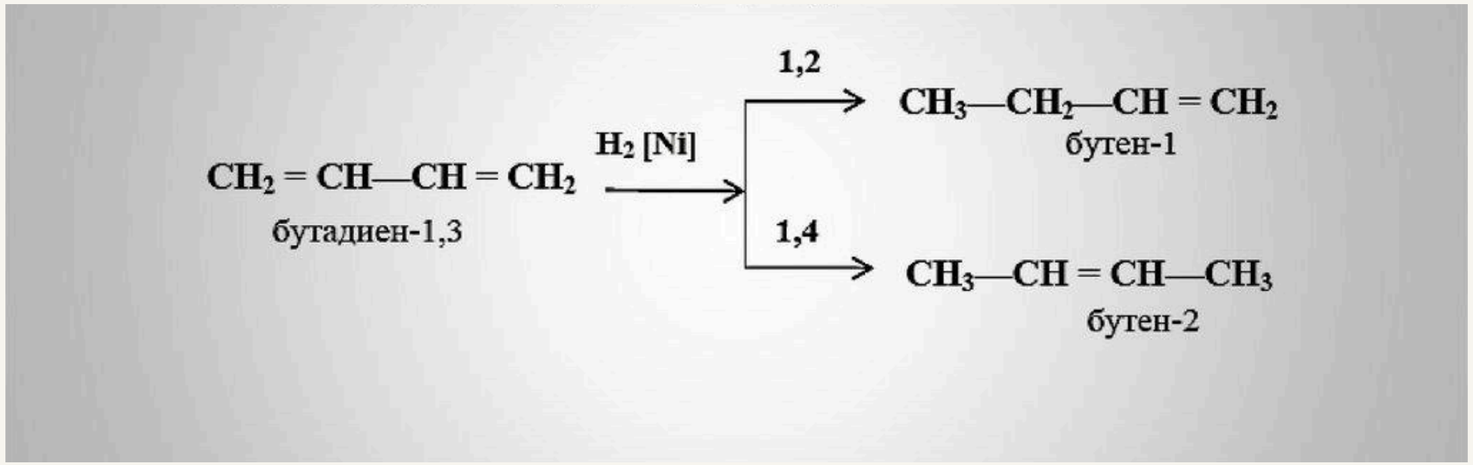
$$CH_2{=}CH{-}CH{=}CH_2 + H_2 \rightarrow C_4H_8$$

Partial: but-1-ene or but-2-ene, depending on catalyst and conditions

$$CH_2{=}CH{-}CH{=}CH_2 + 2H_2 \xrightarrow{(Ni)} CH_3CH_2CH_2CH_3$$

Complete: butane

Hydrogenation is used to make saturated hydrocarbons and to modify unsaturated compounds. Partial hydrogenation of a diene is harder to control than that of an alkyne, because both double bonds are alkene-like.



Electrophilic Addition: 1,2 and 1,4

$CH_3–CHBr–CH=CH_2$

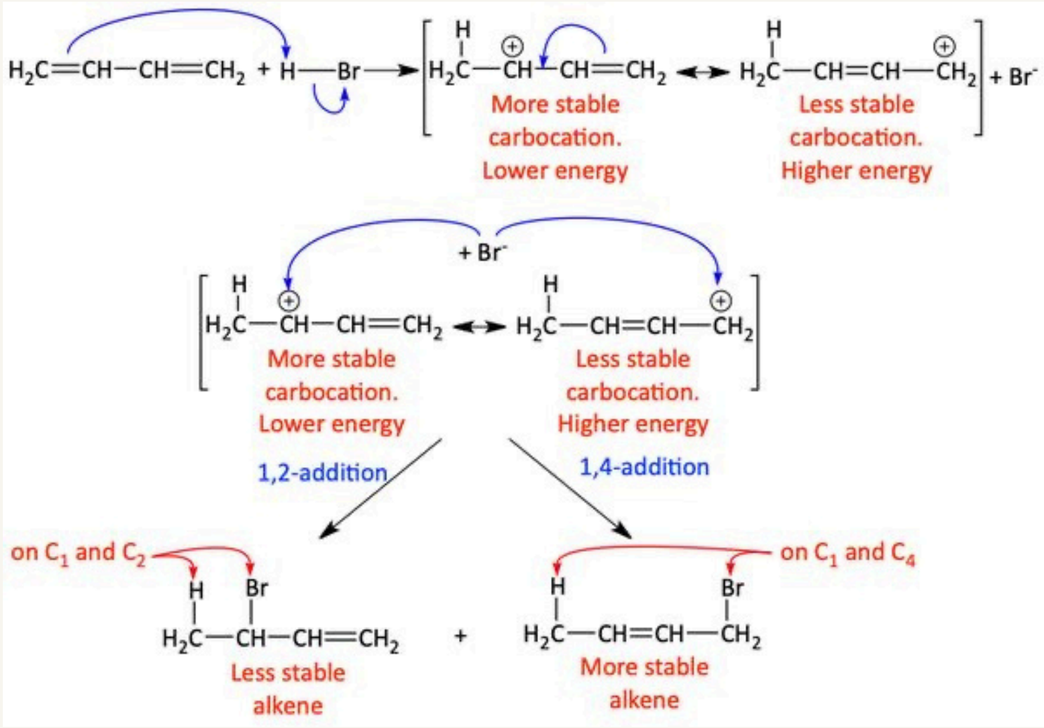
1,2-Addition: 3-bromobut-1-ene

$CH_3–CH=CH–CH_2Br$

1,4-Addition: 1-bromobut-2-ene

1. Electrophile (H^+) attacks the conjugated π system
2. A resonance-stabilized allylic cation forms
3. Br^- attacks at either of two positions
4. Two constitutional isomers result

Reaction: $CH_2=CH–CH=CH_2$ + HBr. Protonation at C1 gives a cation with positive charge shared between C2 and C4. In the 1,4-product the double bond shifts to the middle of the chain.



Kinetic and Thermodynamic Control

Kinetic control

- Favoured at low temperature
- Lower activation energy
- 1,2-Product is the kinetic product

Thermodynamic control

- Dominates at higher temperature
- Reaction is reversible
- 1,4-Product is more stable: more substituted C=C

HBr and butadiene: at 0 °C about 71% is the 1,2-product and 29% the 1,4-product; at 40 °C about 15% and 85% (approximate values reported in OpenStax Organic Chemistry). Temperature changes which product predominates.

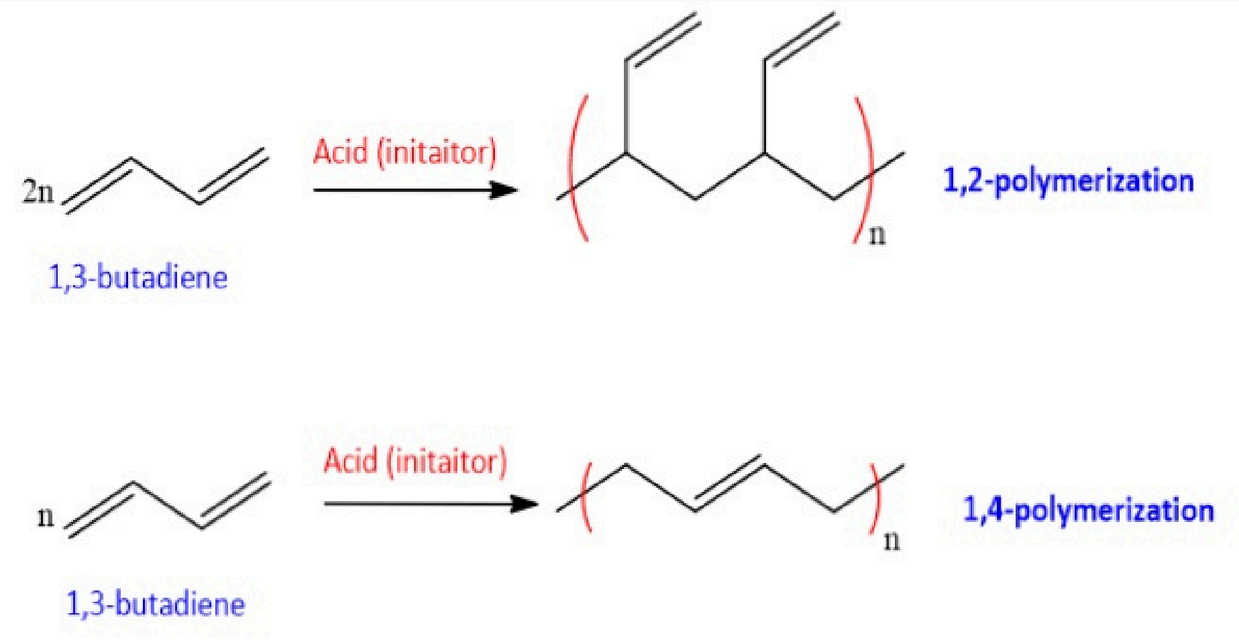
Polymerization of Alkadienes

$$n\ CH_2{=}CH{-}CH{=}CH_2 \rightarrow [{-}CH_2{-}CH{=}CH{-}CH_2{-}]_n$$

Polybutadiene

$$n\ CH_2{=}C(CH_3){-}CH{=}CH_2 \rightarrow [{-}CH_2{-}C(CH_3){=}CH{-}CH_2{-}]_n$$

Polyisoprene: properties depend on stereochemistry



Synthetic rubber uses

- Automotive tires
- Rubber hoses
- Conveyor belts
- Footwear
- Industrial rubber parts

Many monomer molecules join into long chains. Cis-polyisoprene is elastic like natural rubber, while the trans form is hard. After polymerization, remaining C=C bonds allow vulcanization with sulfur.

Diels–Alder Reaction and Applications

$$CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH_2 \rightarrow C_6H_{10}$$

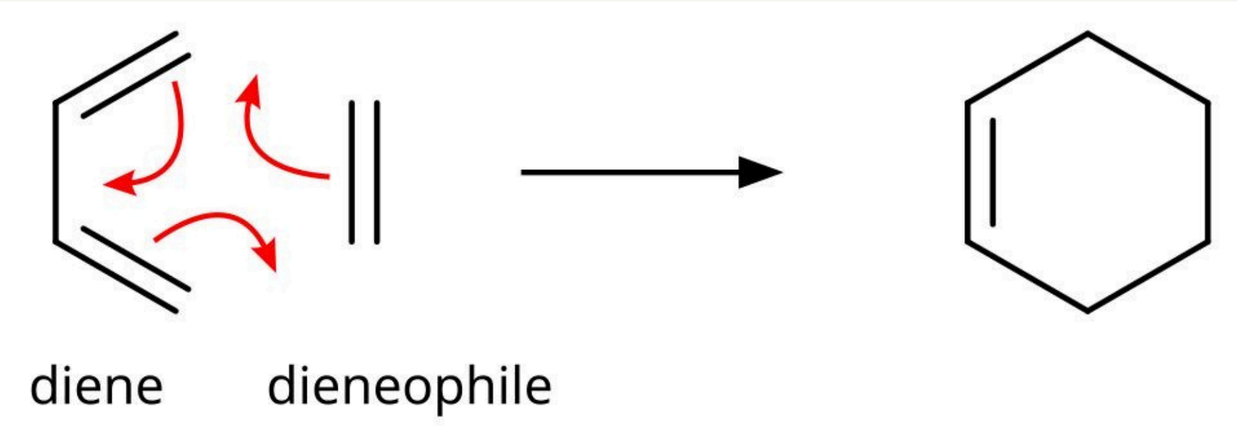
Conjugated diene + dienophile gives cyclohexene

Industrial significance

Synthetic rubber, elastomers, plastics and chemical intermediates.

- Two new C–C σ bonds
- Six-membered ring
- Usually concerted
- Widely used in synthesis

The diene must adopt the s-cis conformation to react. Reactions are fastest when the dienophile carries an electron-withdrawing group, such as C=O or C≡N.



Conclusion

- Cumulated, conjugated or isolated dienes
- Conjugation delocalizes π electrons and adds stability
- Prepared by dehydrogenation and steam cracking
- Addition, oxidation, combustion and polymerization
- Conjugated dienes give 1,2- and 1,4-addition
- Temperature shifts the product distribution
- Essential for synthetic rubber and polymers

References

- McMurry. Organic Chemistry
- Clayden, Greeves, Warren. Organic Chemistry
- Solomons et al. Organic Chemistry
- OpenStax: Kinetic versus Thermodynamic Control
- Ethanol-to-butadiene: The Reaction and Its Catalysts