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REVIEW:

Conjugated = separated by a single bond from a double bond

Examples of Conjugated Systems

- 1. Double bonds (2 or more)
- 2. Allylic Cations



3. Allylic Anions



4. Allylic Radicals



REVIEW: Molecules below at diastereomers (a class of stereoisomers)





E-1,3-pentadiene

Z-1,3-pentadiene

The two molecules below are constitutional (structural) isomers. 1,4-pentadiene is not conjugated. It has double bonds separated by **2** single bonds.

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1,4-pentadiene

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E-1,3-pentadiene
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NOT conjugated

1,2-pentadiene, shown below is not conjugated. It has **cumulated** double bonds. This molecule is an **allene** and is a structural isomer with respect to the above 1,3-pentadienes.





Addition Reactions of Conjugated Systems



These are structural isomers.

The product 3-bromobutene is a **1,2-addition** product, whereas 1-bromo-2-butene is the product of an **1,4-addition** reaction. The numbers (**1,2-** or **1,4-**) indicate the position where the H and Br added to the 1,3-butadiene.

Why does the temperature affect the ratio obtained?



From the 2 resonance forms (connected by the double-headed arrow) of the allylic cation in the above figure, we see that the positive charge is shared between the C2 and C4.

Note: The allylic cation has two electrons delocalized across the three carbons. It was drawn to have two resonance forms, but it is a *single entity*, therefore we cannot differentiate and speak of one form being a primary carbocation (therefore less stable) and the other being a secondary carbocation (therefore more stable).

Answer to the above question:

- 3-bromo-1-butene has a higher yield at the lower temperature because it is formed faster than 1-bromo-2-butene: **kinetic control**
- 3-bromo-1-butene has lower yield than 1-bromo-2-butene at higher temperature due to **thermodynamic control**. The addition of bromine to the allylic cation is reversible at high temperature. 3-Bromo-1-butene can be converted back to the allylic cation, and then form 1-bromo-2-butene which is the thermodynamically more favored product.

To understand thermodynamic and kinetic control, let's look at the reaction's energy diagram.



Reaction Coordinate (Progress of a Reaction)

 ΔG = Free energy of the reaction – this determines ratio of starting material and product ΔH = Enthalpy of the reaction (change in bond energies)

T = Temperature (in degrees Kelvin)

 $\Delta S = Entropy$ (a measure of disorder)

 E_A = Activation energy (the amount of energy needed for reaction to proceed). This is a factor that determines the rate of a reaction. When E_A is small the reaction is fast; when it is large the reaction is slow.

Transition State (TS) = Where bonds are partially made and partially broken

For an exothermic reaction, there is release of heat and ΔG is always negative (depicted in the energy diagram, the product would be lower on the energy diagram than the starting material).

Now let's look at the energy diagram of the HBr addition to butadiene reaction

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Reaction Coordinate

The activation energy barrier to form the 1,2-product, 3-bromo-1-butene is much *smaller* than the 1,4-product, 1-bromo-2-butene (so that it can be formed easier and **faster**. We call this **kinetically favoured**).

However, the energy of 1-bromo-2-butene is lower than 3-bromo-1-butene, so that it is more **stable** than 3-bromo-1-butene (it is **thermodynamically favoured**).

Why is 1-bromo-2-butene more stable?

- The bromine atom is bulky. It likes to stay away from the rest of the molecule to avoid steric clashes.
- Alkene carbons are somewhat electron deficient. More highly substituted alkenes are more stable due to donation of electron density by the substituents (C vs H)



Practical Applications for Conjugated Addition Reaction:

Example: Rubber formation – Formally by a conjugated addition reaction

Rubber is a natural product produced by rubber tree *Hivea brasiliensis* (>2500 lbs per acre). The rubber is collected in the form of syrup (latex) and after concentration as raw rubber it is very sticky (like chewing gum). This is not very useful.

Other sources of rubber but with very minimal yields:

- 1. Sunflower Dandelion (~40 lbs per acre)
- 2. Lettuce



Rubber can be viewed as a polymer of 2-methyl-1,3-butadiene, which is also known as isoprene. Addition of acid will form a resonance-stabilized cation. Note that non-enzymatic polymerization (e.g. in lab synthesis) would give undesirable trans isomer instead of the cis naturally formed in plants by enzymatic processes.

Charles Goodyear

- Add sulfur and heat to rubber resulting to vulcanized rubber – elastic (not plastic (malleable to a new shape) or sticky)

Another example: Styrene Butadiene Rubber (SBR) synthesis (by conjugated cation) SBR is a **copolymer**.



Another representation:



Example: Terpenes or Terpenoids or Isoprenoids

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an isoprene unit, a C5 unit

Nomenclature for multiple C5 units in a terpene:

- a. One C5 unit = hemiterpene
- b. Two C5 units = monoterpene
- c. Three C5 units = sesquiterpene
- d. Four C5 units = diterpene

Examples of Terpenes

1st C5 unit 2nd C5 unit

Limonene = a monoterpene with two C5 units



 α -pinene = a monoterpene with two C5 units



Geraniol = a sesquiterpene with three C5 units

Extra Example:

