



Goes according to Markovnikov's rule; $\ensuremath{\textit{cis}}\xspace$ -addition

eg. H₂SO₄

RECALL: Elimination reactions

OCH₃

δ-



-OH and -OCH₃ are bad leaving groups and so these reactions would not occur spontaneously without an acid catalyst.

To determine whether an elimination can occur, ask yourself three questions:



- 1. Is there a good leaving group present? Eg. Yes, Br is a good leaving group
- 2. Is there a hydrogen on the carbon next to the carbon containing the leaving group? Eg. Yes, on the bridge-heads on either side of the carbon containing the Br.
- Is Bredt's Rule being followed?
 Eg. No, if a double bond was being formed, it would be at a bridge-head and Bredt's rule states that a double bond cannot be formed at a bridge-head if the rings are small and all bridges >0. (double bond too strained)

Substitution would likely not occur either as the electrophilic site is hindered (tertiary carbon).

Addition Reactions



For alternate regiochemistry (addition of Br onto the less substituted carbon) need dialkyl peroxide



Examples of peroxides



Hydrogen peroxide HO-OH

Radical mechanism



O-Br bond is not strong as both atoms are electron withdrawing elements. Therefore, *tert*-butyl alcohol is formed



Propagation -

Radical forms on that carbon with the maximum number of alkyl groups attached: radicals are electron deficient and electron-donating substituents stabilize them



Example without HBr – a polymerization reaction occurs



shorthand notation for polypropylene

Note more stable radical (in this case tetiary) is always formed by addition onto double bond

There is a termination step (not shown) that ends this polymerization. It requires combination of 2 radicals. It could be two growing chain radicals meeting or it could be from peroxide. If less peroxide is used the polymer chain will be longer.

Polymers

Poly = many Meros = parts

Examples of Biopolymers

- Polysaccharides

 polymers of sugars
- Proteins and peptides
 polymers of amino acids
- Nucleic acid polymers (DNA and RNA)
 polymers of nucleotides
- Fats and polyketidespolymers of fatty acids
- 5. Polyisoprenoids/ terpenoids- polymers of isoprene (i. e. natural compound rubber)

Polymer formation

Teflon



Teflon is very unreactive and does not adhere substances

Many polymers degrade into their components if heated enough, and can further decompose.

Polyethylene



Polyacrylonitrile



Polyacrylonitrile can form HCN if it is heated to decomposition.

Polyvinyl chloride



Such polymers containing chloride can form HCl if decomposed.

Copolymers



Copolymers are composed of two different subunits. Lucite



Polystyrene

$$Ph \equiv C_6H_5 \equiv$$

phenyl group is Ph

Example: Mechanism of polystyrene formation





Divinyl benzene can be added as a cross-linker so chains link on both of its double bonds This make the copolymer more solid (as you encounter in many products) – typically about one part in 100 to one part in 6 of divinylbenzene may be added



Conjugated Systems

Definition: Systems that are separated by exactly one single bond from a double bond

Compounds containing conjugated systems:

Polyenes:

Example: **1,3-Butadiene**

Double bonds are separated by one single bond

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Tends to be planar; p orbitals want to be aligned, even though rotation along the sigma bond is not restricted. Transoid conformation is in equilibrium with cisoid conformation. **Aromatic Compounds:** THIS SECTION on AROMATIC COMPOUNDS NOT COVERED in this course

- 1) Cyclic
- 2) Conjugated throughout
- 3) Planar
- 4) 4n + 2 electrons, where n is an integer (n=1,2,3,4...)

Example: 1,2-Dibromobenzene



Benzene:

- 36 kcal/mole more stable than is expected

Aromatic Compounds Are Not Like Alkenes: - Much less reactive

$\begin{array}{c} & \overbrace{C} \\ \\ \hline{C} & \overbrace{C} & \overbrace{C} & \overbrace{C} \\ \\ \\[]] \\[]]] \\[]]] []]$

Aromatic compounds do not undergo simple addition reactions like alkenes do, but rather they require a catalyst (such as AlCl₃ in this case) to produce a highly electrophilic species than can draw out the π electrons. Once the cation (conjugated) forms, elimination is fast to regenerate the aromatic system (does not add the negative species such as chloride)

ABOVE SECTION on AROMATIC COMPOUNDS NOT COVERED in this course

Conjugated Intermediates:

1) Cation:	\odot	\longleftrightarrow	$/ - \oplus$	Conjugation stabilizes the positive charge
	Allyl Cation			
2) Radical:	۰ Allyl Radical	~	<i>/</i> ~•	Conjugation stabilizes the radical
3) Anion:	⊖ Allyl Anion	~	Ø	Conjugation stabilizes the negative charge

- e.g. of reactivity Friedel-Crafts Alkylation - NOT COVERED in this course

Polyenes:



1,3-Pentadiene is planar often so that p-orbitals can overlap as seen below. The partial interaction of orbitals in the middle bond shortens the bond length due to partial double bond character. There is still rapid rotation about the single bond between the two double bonds, but the preferred conformation all pi bonds aligned. (Transoid preferred over ciosoid)



1,3-Pentadiene prefers to be planar so that p-orbitals can overlap

Molecular Orbitals: Example 1: Ethylene



Looking at both sigma and pi bonds

Е

A.O. means atomic orbitals (s, sp², p) M.O. means molecular orbitals (σ , π)

Looking only at the π orbitals:

 $H_2C=CH_2$

Е Lowest Unoccupied π^{*} π^{*} Molecular Orbital (LUMO) hν $\Delta E = hv = hc$ 171nm 1↓ Highest π π Occupied Molecular Orbital (HOMO) - heat

An electron can be excited from the HOMO to the LUMO using light of a precise wavelength dependent on the energy difference between the two orbitals (since the orbitals are quantized). The electron can go back to it's original orbital and heat (or light) is produced in the process.