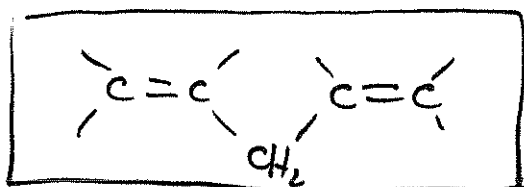
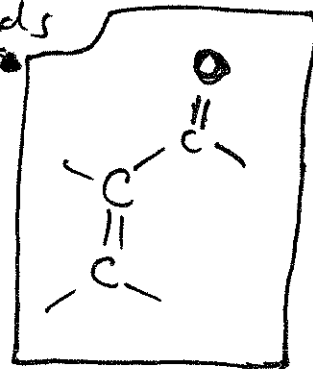
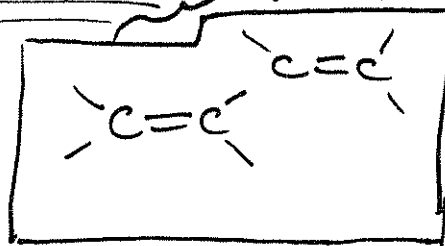


Chapter 18 Polyenes

Double bonds separated by one single bond called CONJUGATED double bonds



isolated double bonds
(2 or more single bonds between double bonds)



Nomenclature of conjugated or isolated double bond or triple bond containing compounds → use suffix

2 double bonds "adiene"

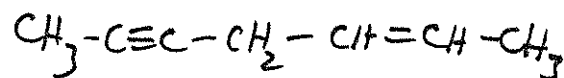
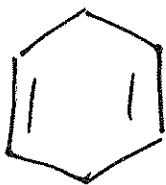
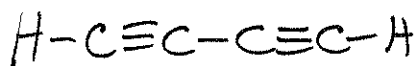
3 double bonds "atriene"

2 triple bonds " " "

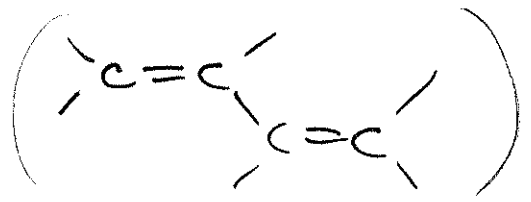
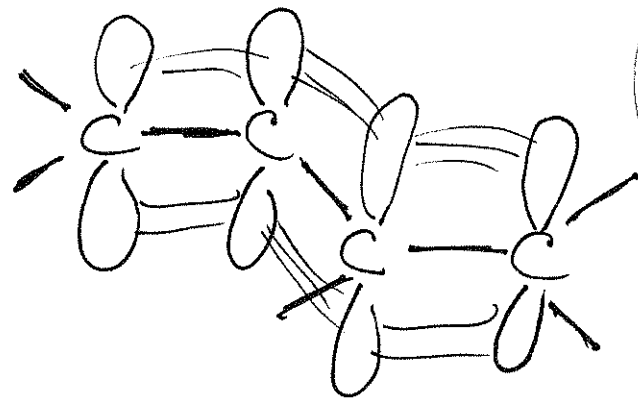
3 triple bonds " " "

and indicate position of double bonds or triple bonds

⊛ (triple bonds take precedence when double + triple bonds present in the same compd)

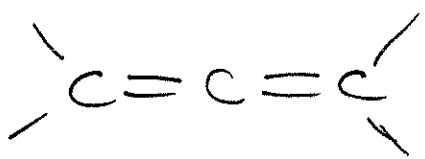


Conjugated systems - π -bonds interact



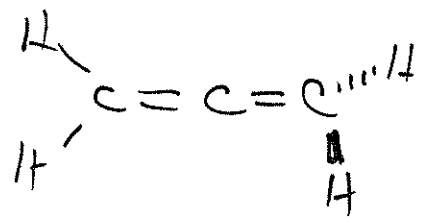
• p-orbitals overlap over all 4-carbon atoms

Cumulenes:



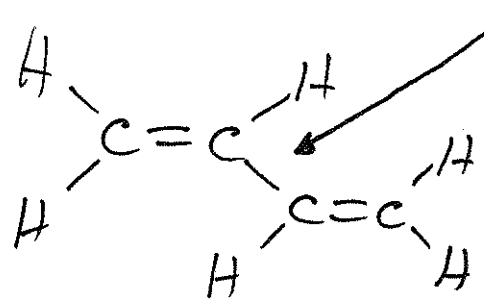
• less stable than isolated double bonds

most common cumulene:

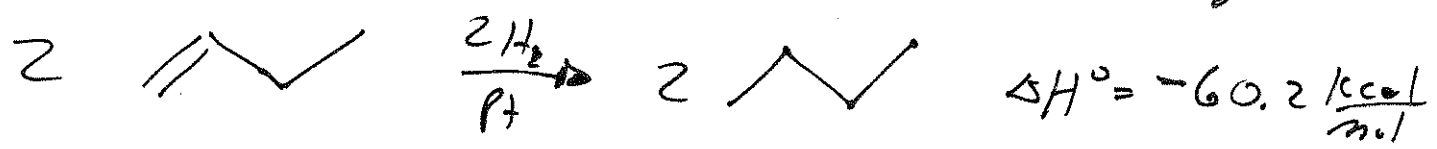


allene (common)
1,2-propadiene (IUPAC)

1,3-Butadiene



- single bond here shorter than in unconjugated system (1.48 vs 1.54 Å)
- planar
- more stable than unconjugated system



• 1,3-butadiene more stable by 3.6 kcal/mole

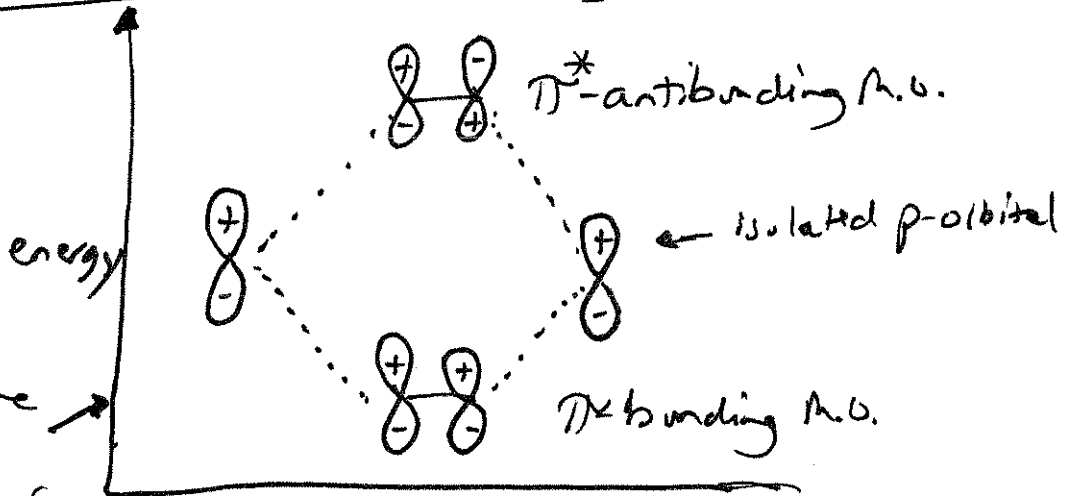
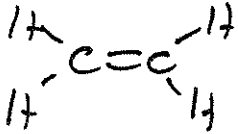
resonance energy $\boxed{3.6 \frac{\text{kcal}}{\text{mol}}}$ **18-2**

What explains the

- stability
- planarity
- bond lengths of conjugated systems?

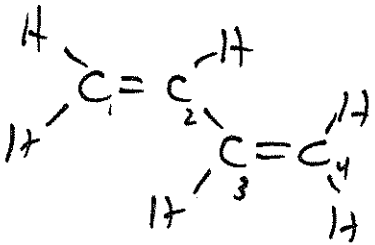
Molecular Orbital Theory

remember ethene

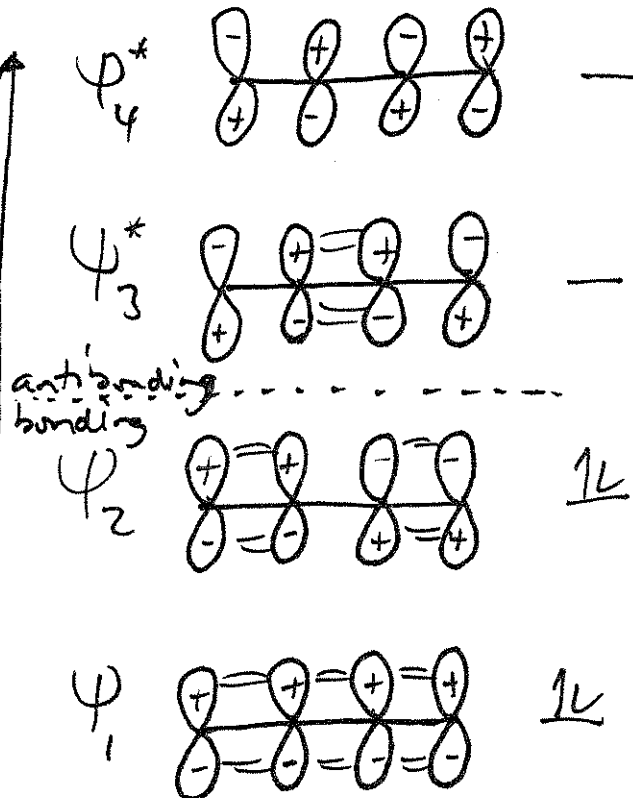


of M.O.'s the same as # of orbitals used to form M.O.'s ($\frac{1}{2}$ bonding, $\frac{1}{2}$ antibonding)

1,3-butadiene



energy



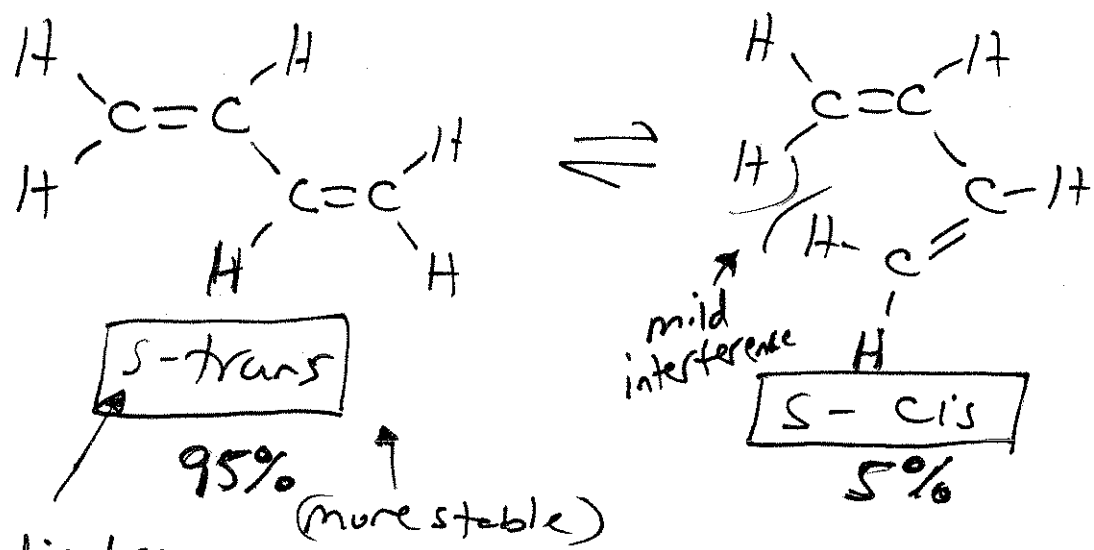
There is db character between C2 + C3 because lowest energy M.O. shortens C2-C3 bond length

planar because to have $2e^-$ delocalized over 4 carbons the system needs to be planar

Conjugated system more stable because $2-\pi$ electrons delocalized over 4-carbons

18-3

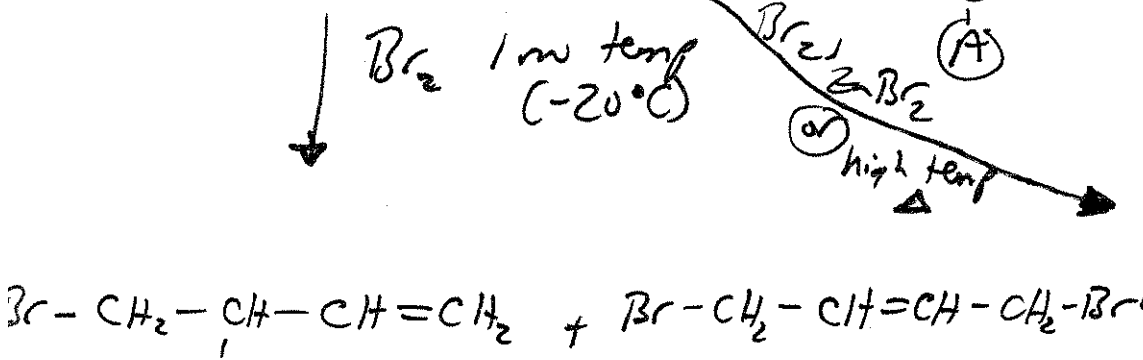
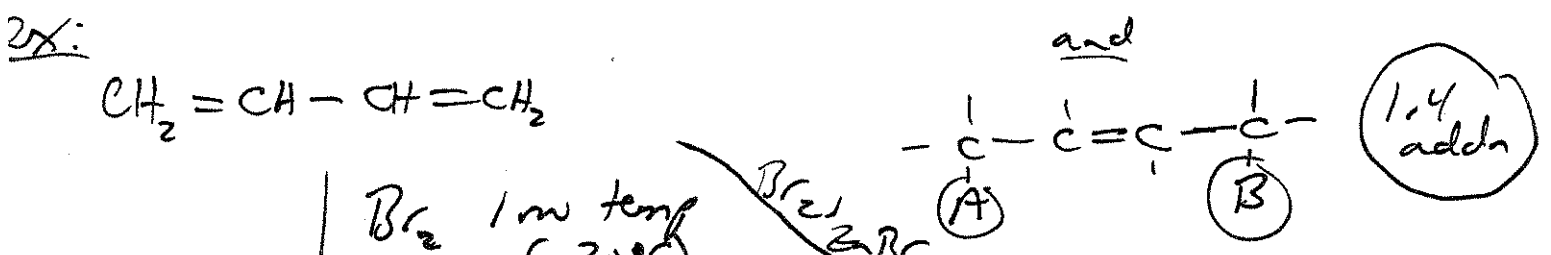
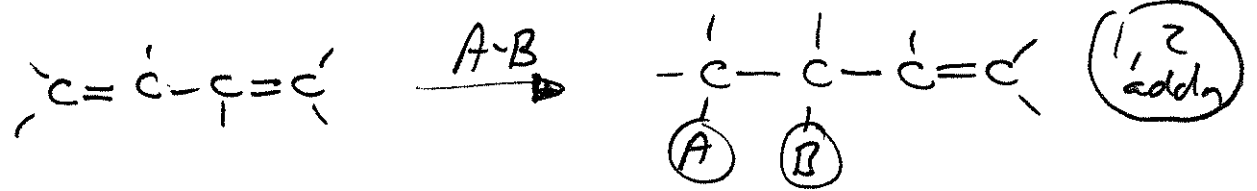
Conformations of 1,3-butadiene



indicates stereochem refers to single bond

Addition Reactions in Conjugated Systems

- 1,2 and 1,4 addition



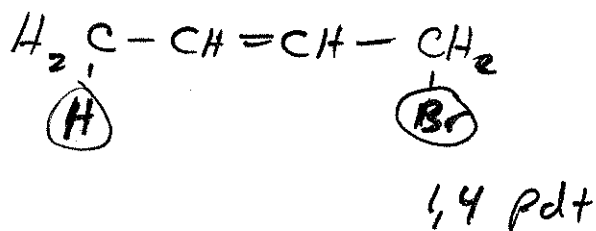
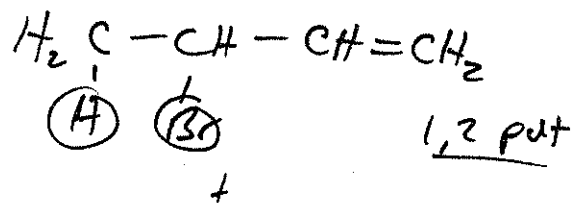
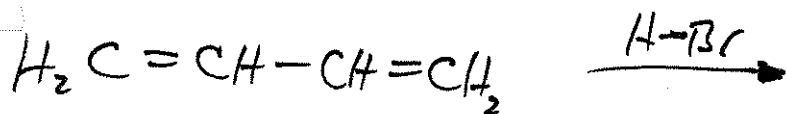
1,2 addn 30%
 1,4 addn 70%

Thermodynamically favored ratio

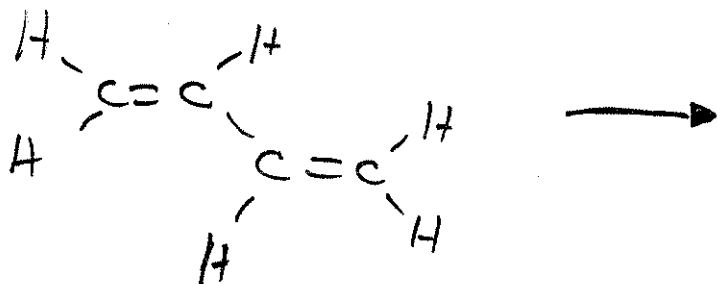
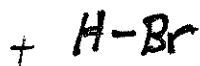
1,2 addn pdt **60%** • kinetically favored ratios
 1,4 addn pdt **40%**

18-4

Another example

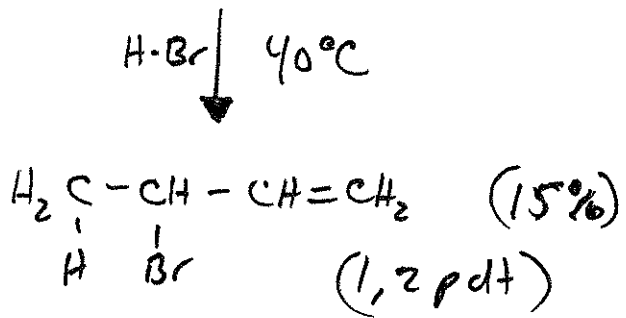
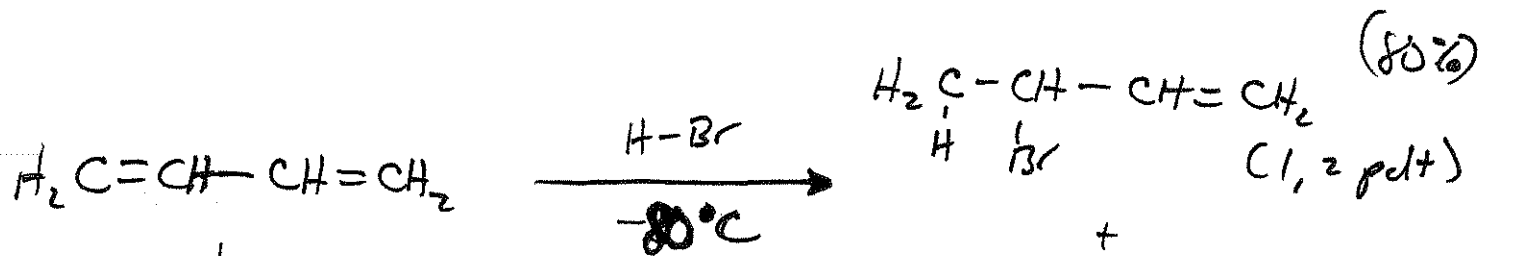


Mechanism



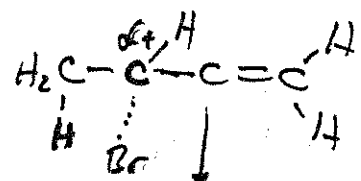
- Trans double bond more stable than cis

- allylic carbocation

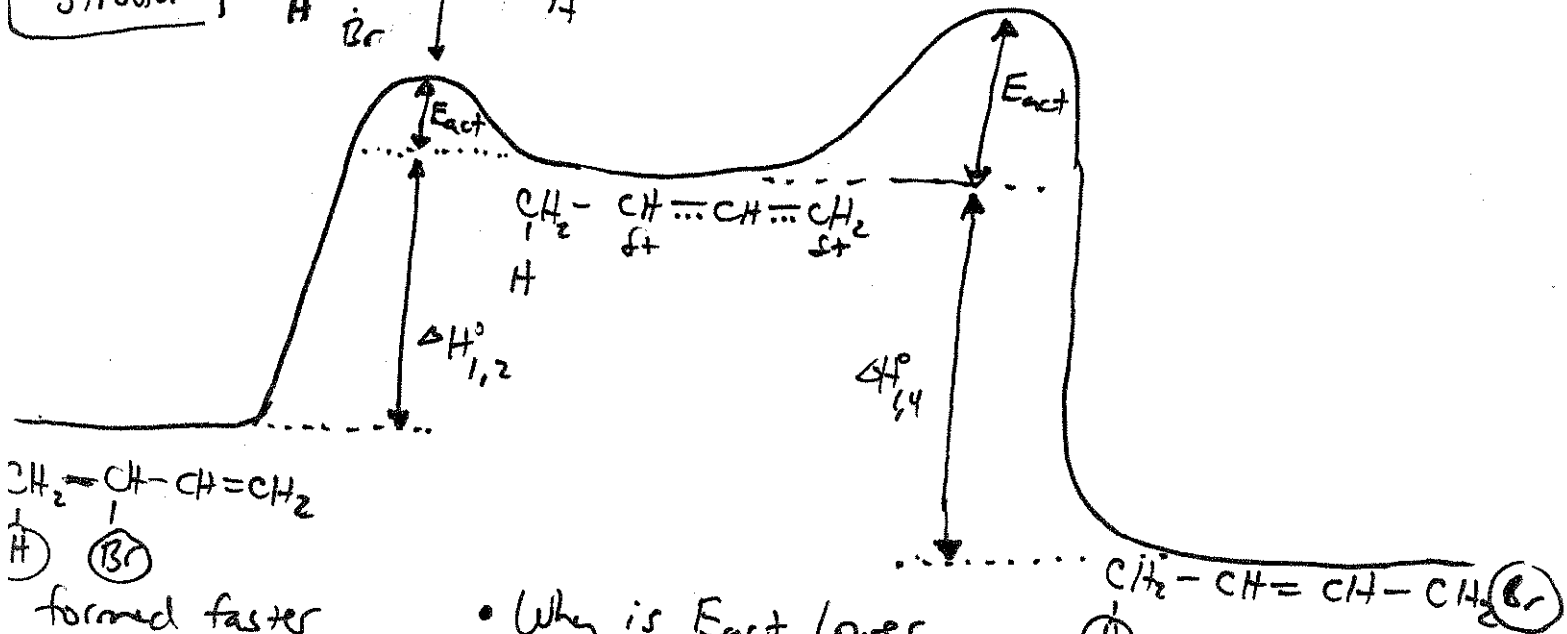
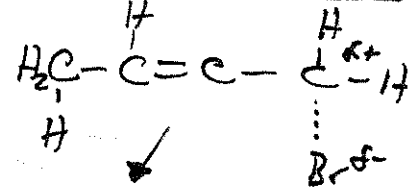


Which is the Thermodynamic product and which is the kinetic product?

1,2-addn
Transition state structure



1,4-addn
Transition state structure

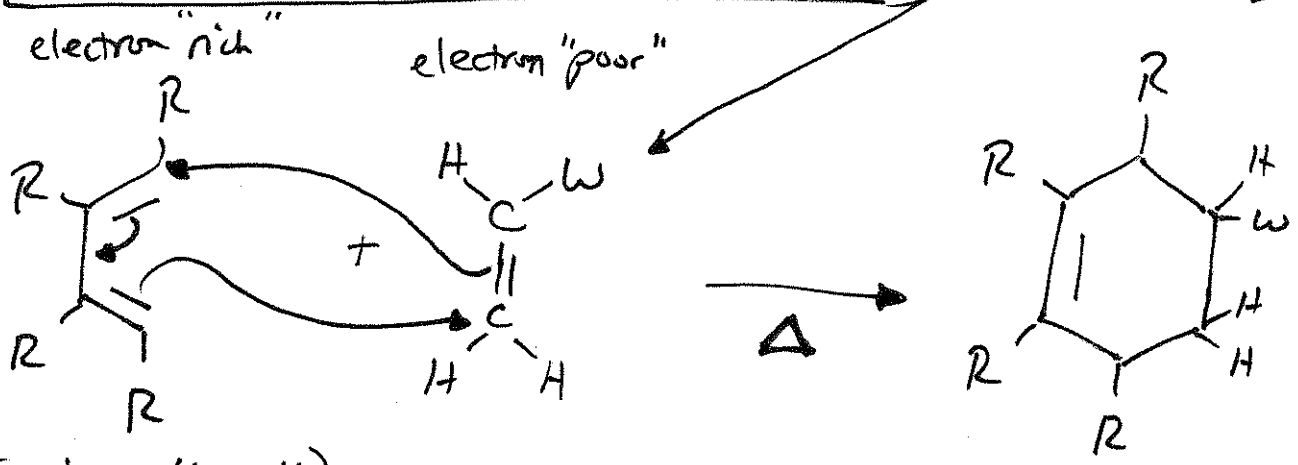


$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
H Br
formed faster
(because lower activation energy)
1,2 addn

- Why is E_{act} lower for 1,2 addn vs 1,4 addn?
→ Because the more highly substituted 2° carbocation T.S. structure is more stable than 1° carbocation T.S. structure
- 1,4 addn
more stable

The Diels-Alder Reaction

dienophile can also be an alkyne



(s-cis configuration)

DIENE

DIENOPHILE

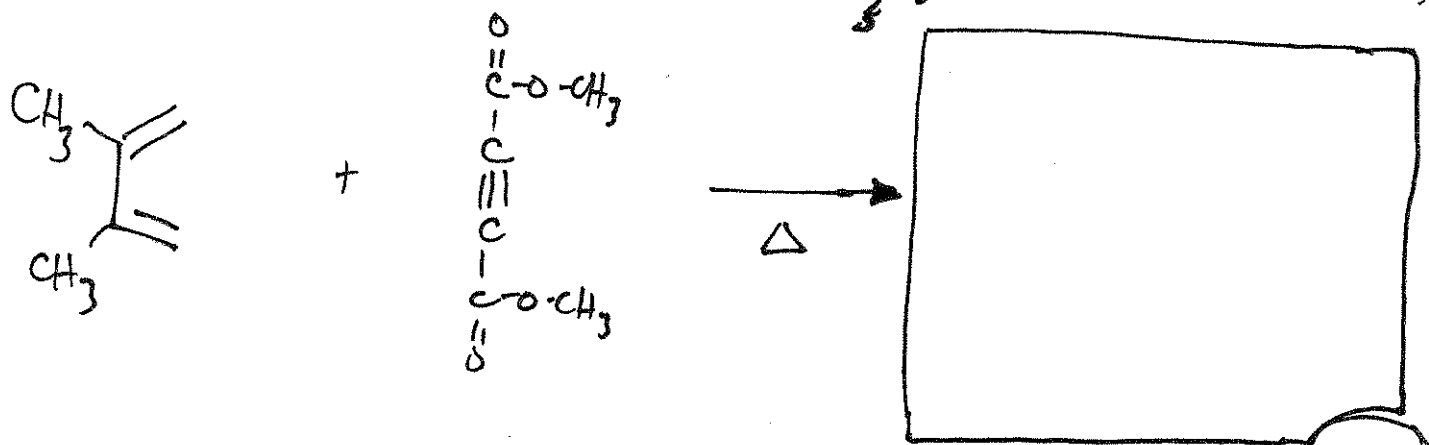
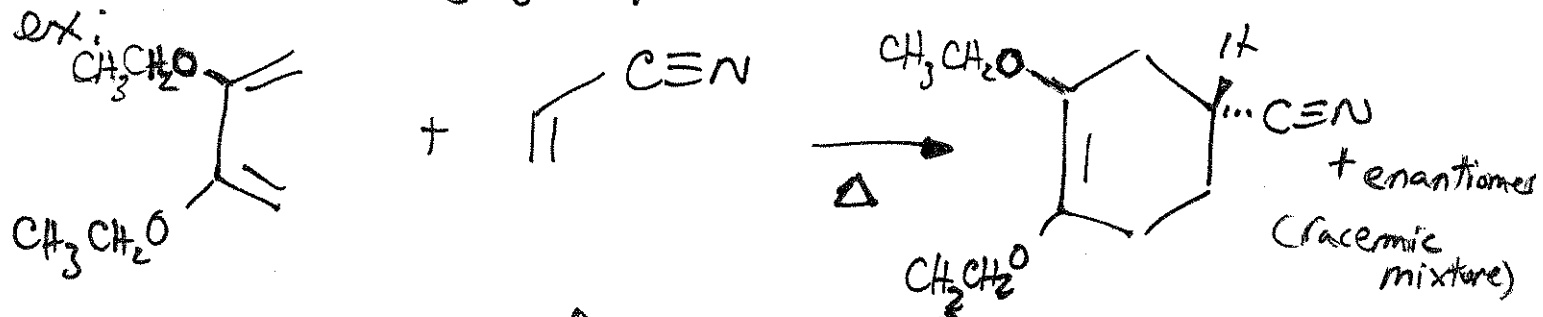
R = alkyl
alkoxy
(H)

W = $\overset{\text{O}}{\parallel}\text{C}$ groups
-CEN
-NO₂
(or H)

• in Diels-Alder rxn 2- π bonds converted to 2 sigma bonds

⊗ Electron movement is CONCERTED - occurs in 1 step simultaneously

- alkyl + alkoxy groups (electron releasing) helps reactivity of diene
- electron withdrawing (w) substituents help reactivity of dienophile



The Diels-Alder Reaction

(from Wade Org. Chem
3rd Ed.)

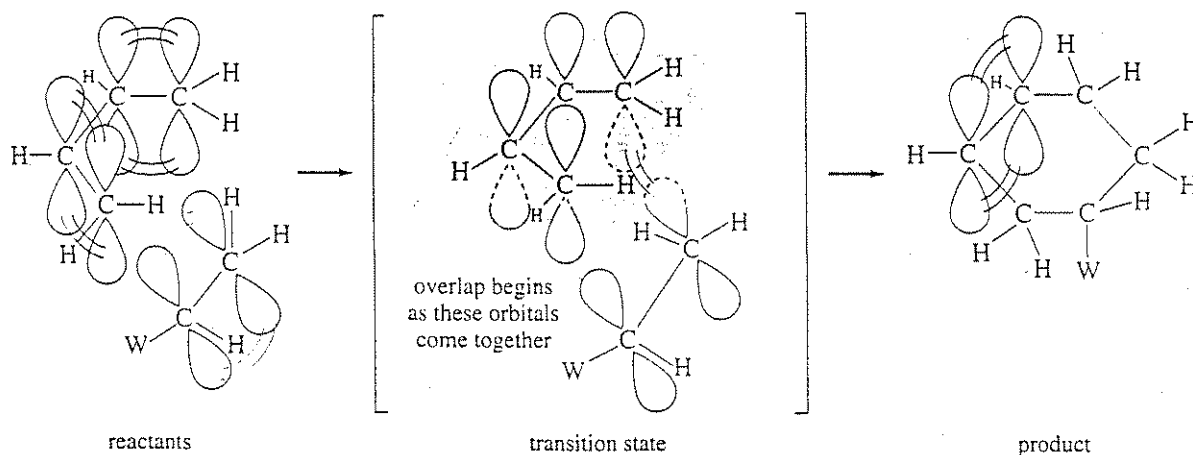


FIGURE 15-15 The Diels-Alder reaction has a concerted mechanism, with all the bond making and bond breaking occurring in a single step. Three pairs of electrons move simultaneously, requiring a transition state with overlap between the end p orbitals of the diene and those of the dienophile.

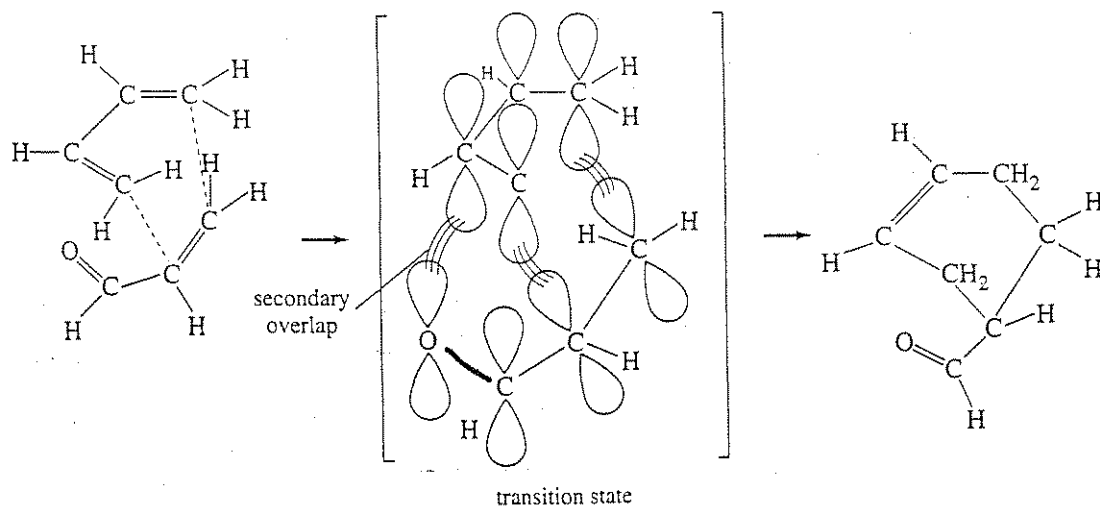


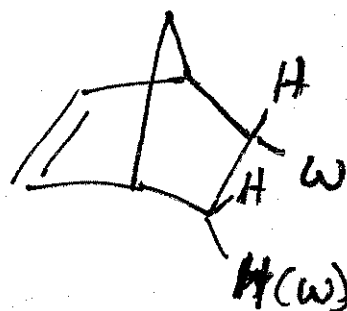
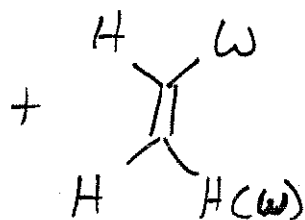
FIGURE 15-17 In most Diels-Alder reactions, there is *secondary overlap* between the p orbitals of the electron-withdrawing group and those of the central carbon atoms of the diene. Secondary overlap stabilizes the transition state, and it favors products having the electron-withdrawing groups in *endo* positions.

Diels-Alder Rxns

→ Electron Rich dienes - act as nucleophiles

→ Electron Poor dienophiles (with electron withdrawing groups) - act as electrophiles

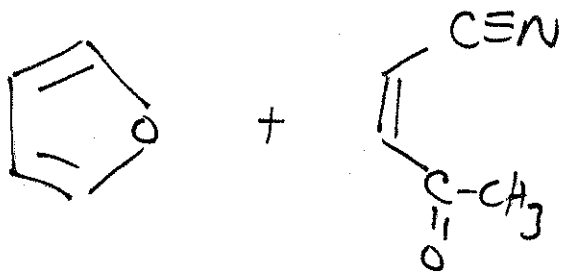
Cyclic Dienes in Diels-Alder Rxns



1-carbon bridge

(Note Stereochem)

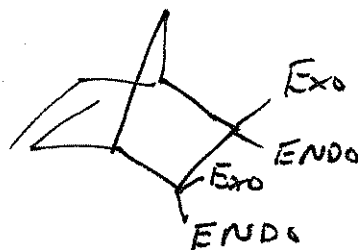
Very reactive diene - always in s-cis configuration



⊗ Stereochemistry of products = ENDO

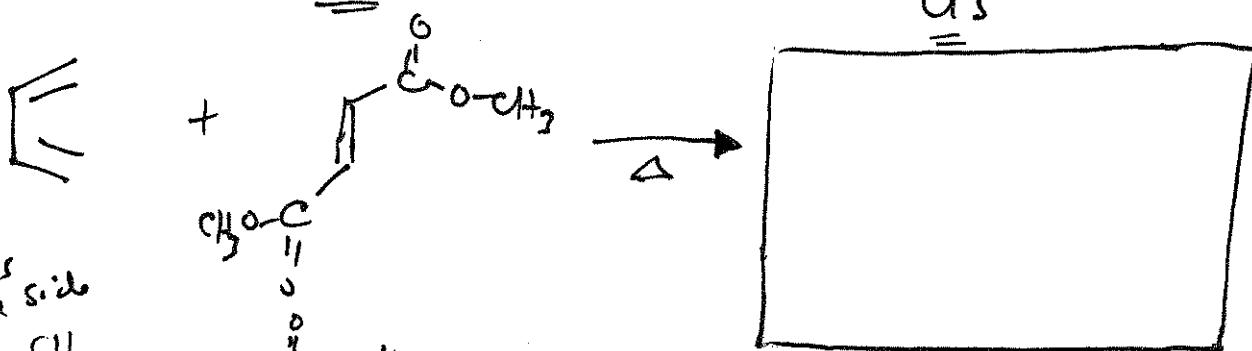
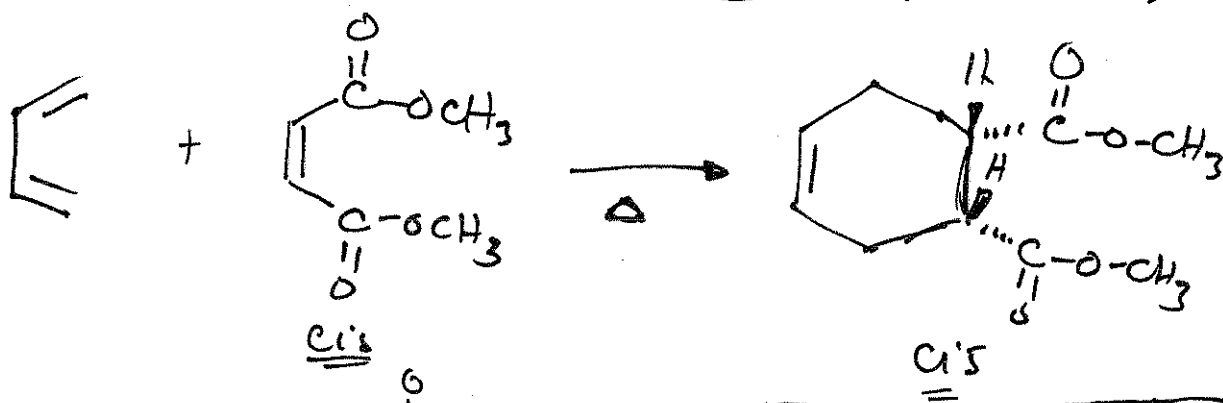
ENDO = substituents from dienophile in product stick away from bridgehead (see Fig 15-17 18-9)

• in contrast, EXO stereochem. substituents from dienophile stick towards bridgehead



Addition Stereochemistry - SYN Addition

- diene adds to one face of the dienophile
- substituents on the same side of the diene or dienophile will be cis in newly formed ring (subst. on opposite sides will be trans in product ring)

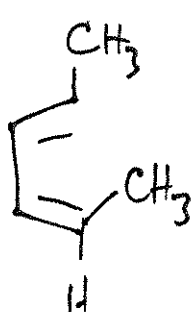
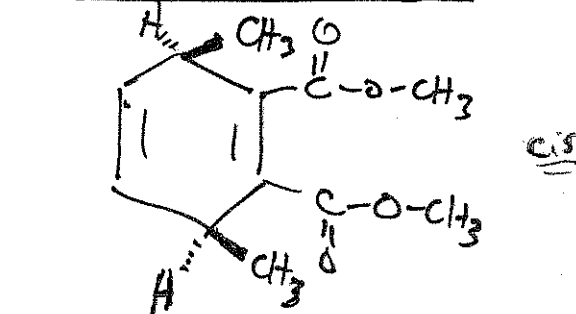
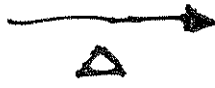
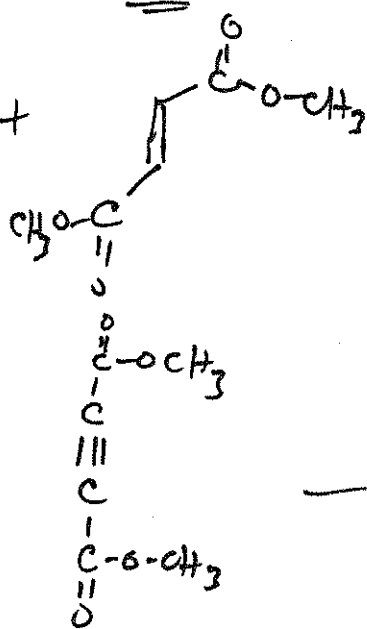


H₂ groups on same side of diene

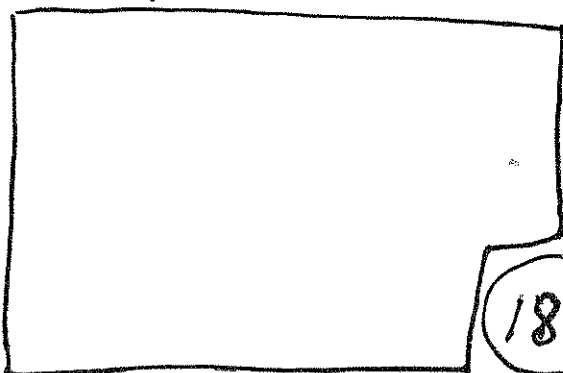
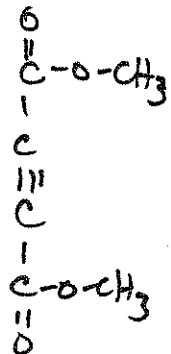
cis



+



+

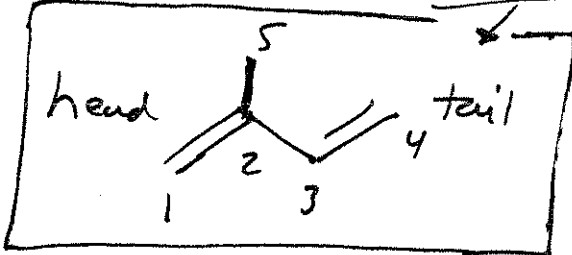


Biological Alkenes + Polyenes

Pheromones - insect sex attractants
 - communication chemicals
 (p 748 in text)

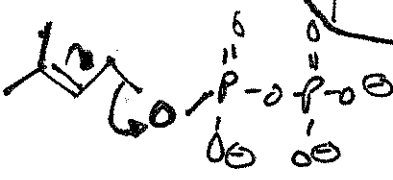
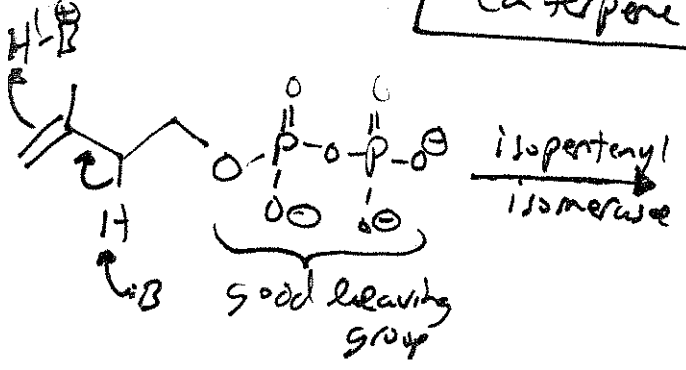
Terpenes → natural products that contain multiples of 5 carbon atoms in their structures
 → see pp 750 + 751 in text for some terpene examples (count # of carbon atoms)

• Terpenes are made from isoprene units



Isoprene Rule - isoprene units are favored to be connected in a head-to-tail manner ↓

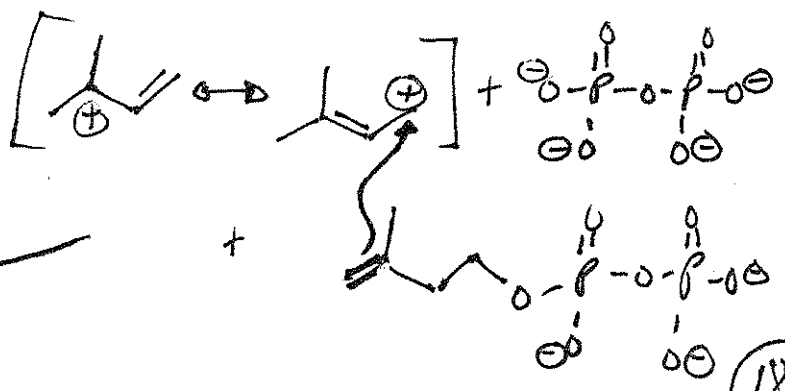
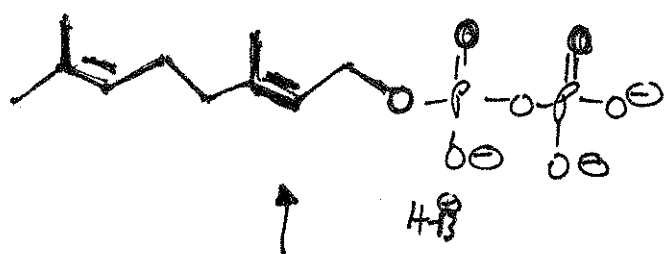
Mechanism to make Geranyl pyrophosphate (a terpene precursor)



ex: geranyl

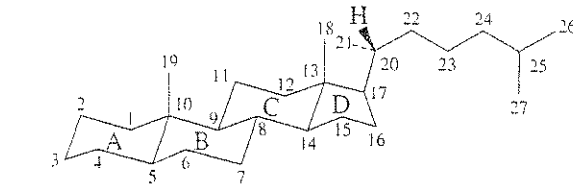
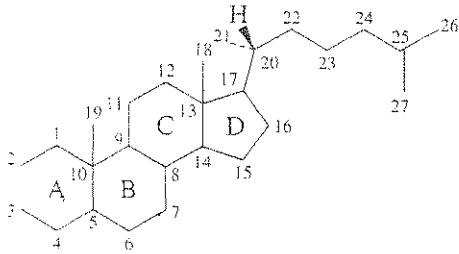
(-)-menthone

dimethylallyl transferase

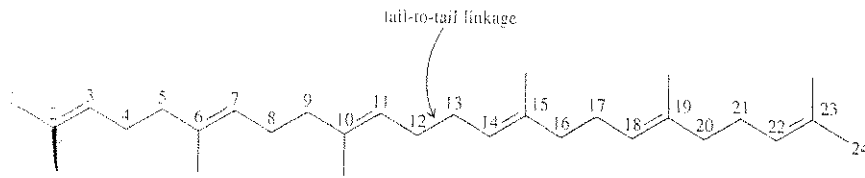


Steroids - triterpenoids (derived from terpenes but don't have a multiple of 5-carbons)

steroid skeleton - rigid because rings fused together



cholestane

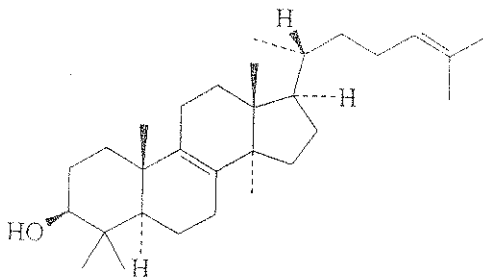


squalene
(6E,10E,14E,18E)-2,6,10,15,19,23-hexamethyl-
2,6,10,14,18,22-tetraicosahexaene

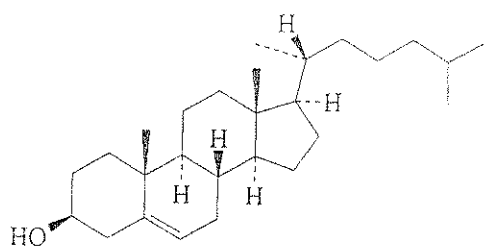
a triterpene

Squalene - used to form steroid skeleton

→ see p 756 in text - Synthesis of Lanosterol (a steroid) from Squalene oxide (mechanism)



lanosterol

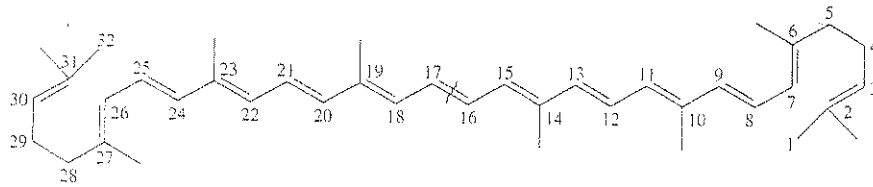


cholesterol

• Lanosterol can be converted biosynthetically to cholesterol (a steroid you've probably heard of)

Carotenoids - have 8-isoprene units

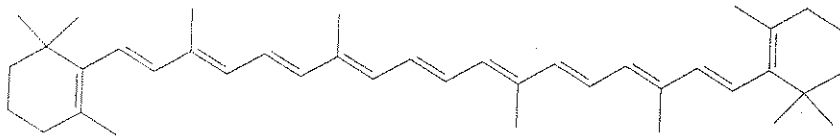
Lycopene - one example of a Carotenoid.



lycopene

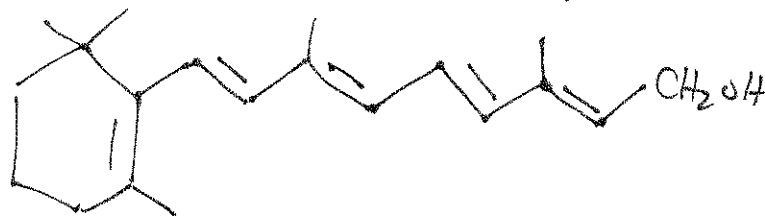
dissected at the point of tail-to-tail
connection of two 20-carbon units

- Carotenoids are highly conjugated → have colors such as red, yellow, orange



β -carotene

$\frac{1}{2}$ molecule of β -carotene → Vitamin A



- See text (p759) → how Vit. A (Retinol) is used in vision