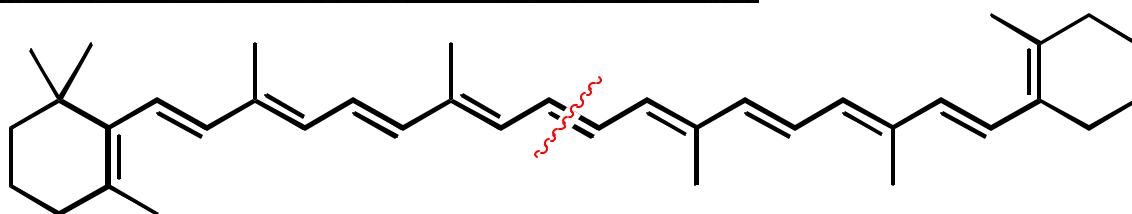
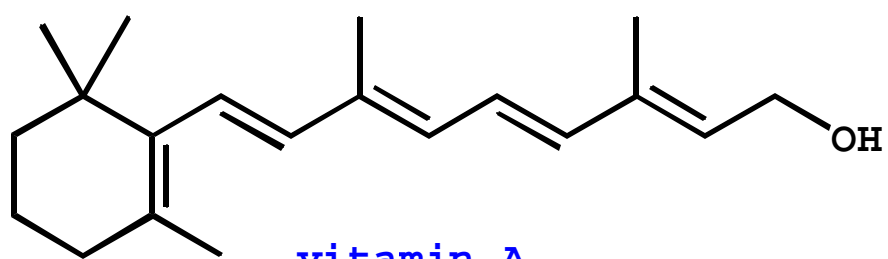


Chapter 14 - Conjugated Dienes and UV Spectroscopy*

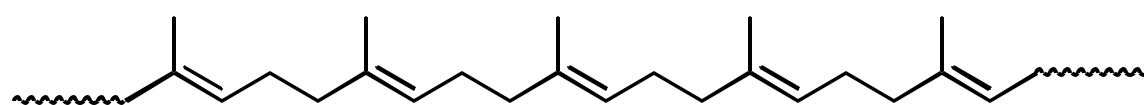
Some examples...



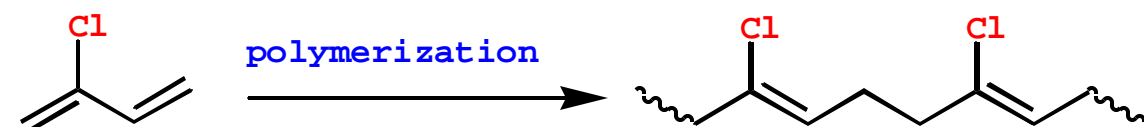
β-carotene



vitamin A



natural rubber

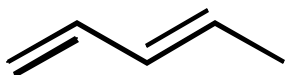


chloroprene

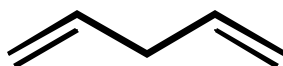
neoprene (Z)

*Conjugated and unconjugated dienes

Conjugated p-system has alternating double and single bonds

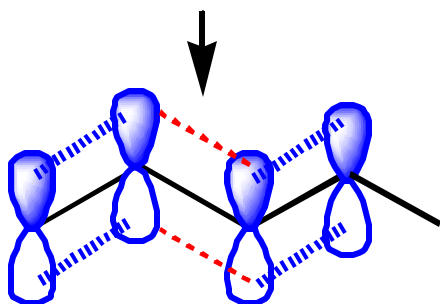


1,3-pentadiene
[conjugated]



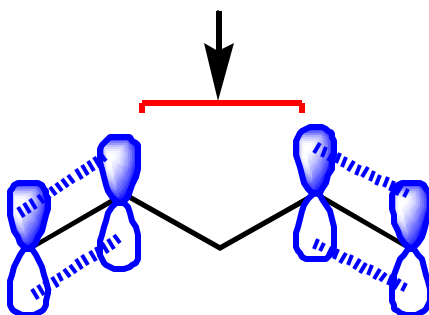
1,4-pentadiene
[unconjugated]

favorable
overlap



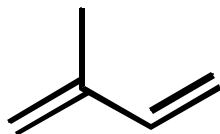
conjugated =
more stable

too far apart
to overlap



unconjugated =
less stable

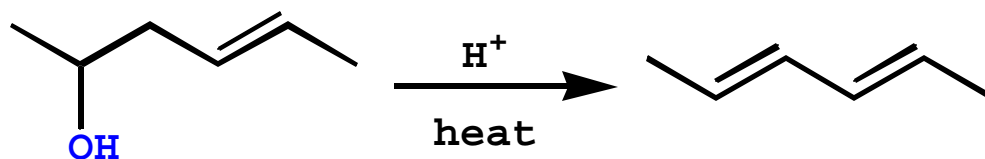
*Nomenclature



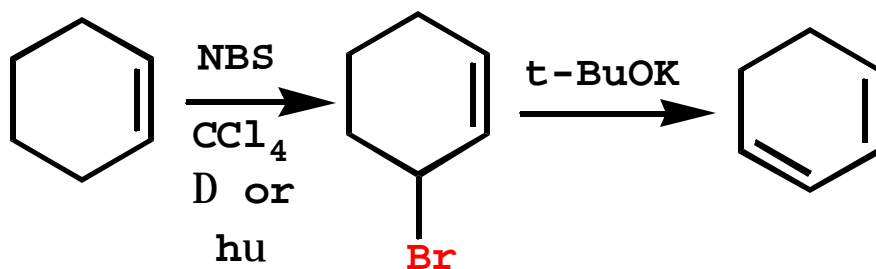
2-methyl-1,3-butadiene (**isoprene**)
natural rubber is a polymer of isoprene

*Preparation of dienes

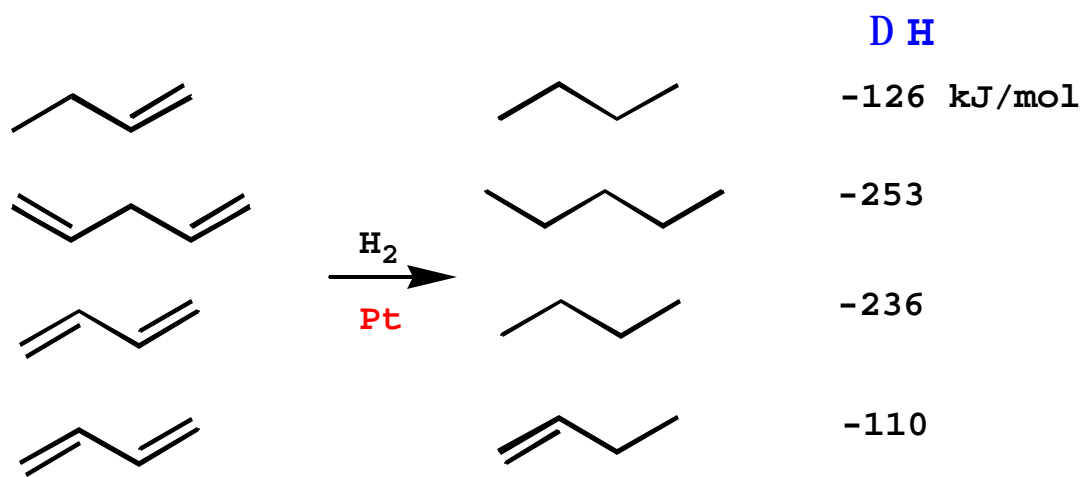
(1) Dehydration...



(2) Dehydrohalogenation...

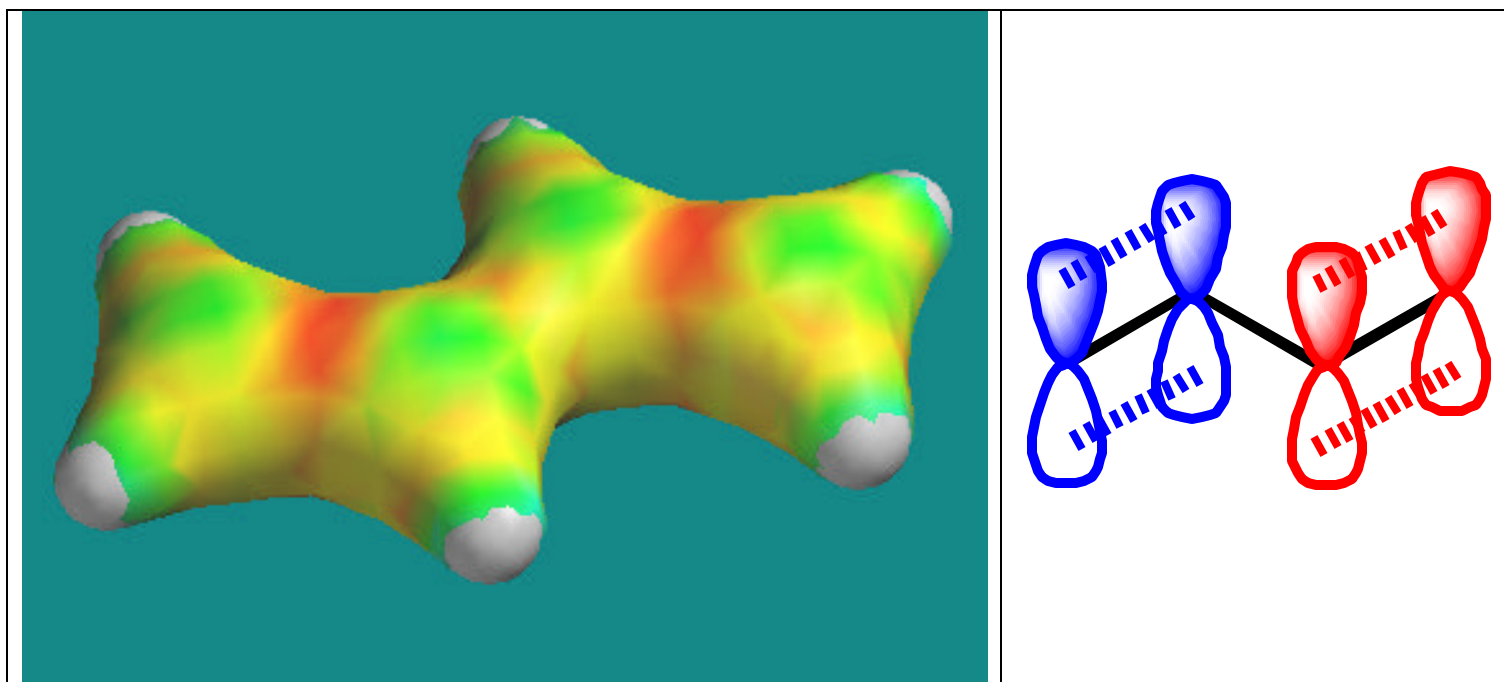


*Stability of dienes



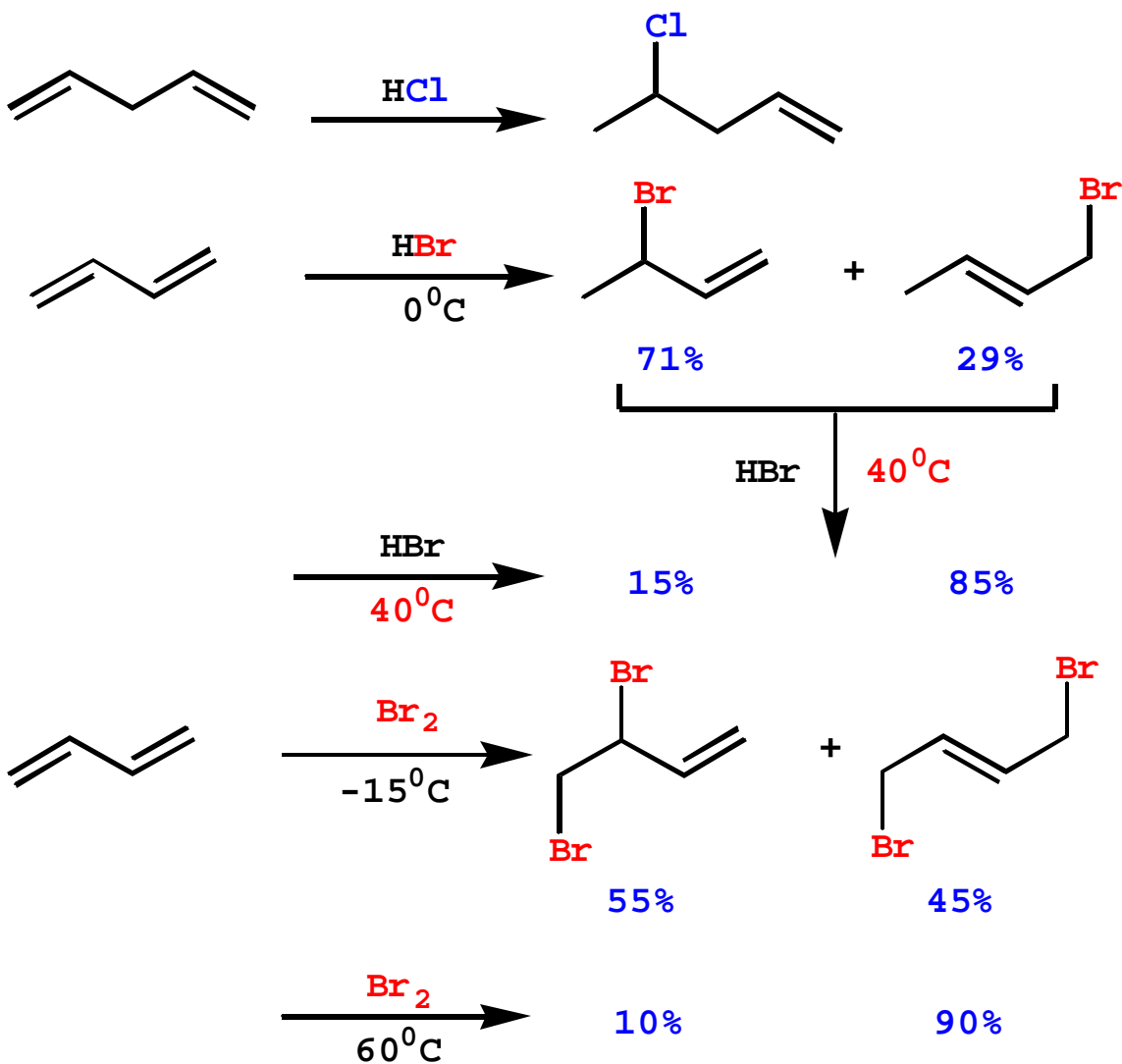
*Structure

	C-C length (Å)	C=C length (Å)
$\text{H}_3\text{C}-\text{CH}_3$	1.54	
$\text{H}_2\text{C}=\text{CH}_2$	-	1.33
$\text{H}_2\text{C}=\text{CH}-\text{CH}_3$	1.51	1.33
$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$	1.48	1.34

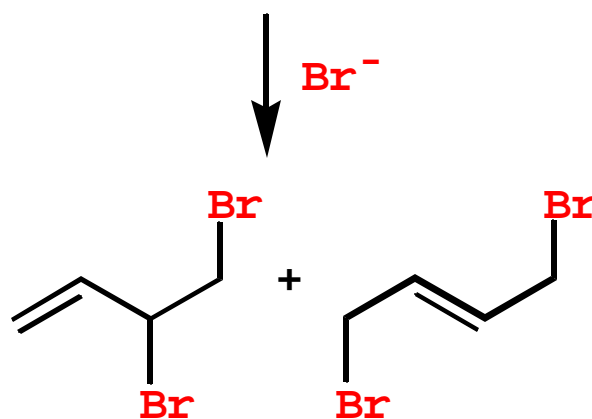
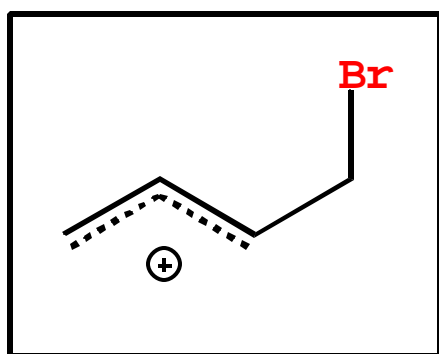
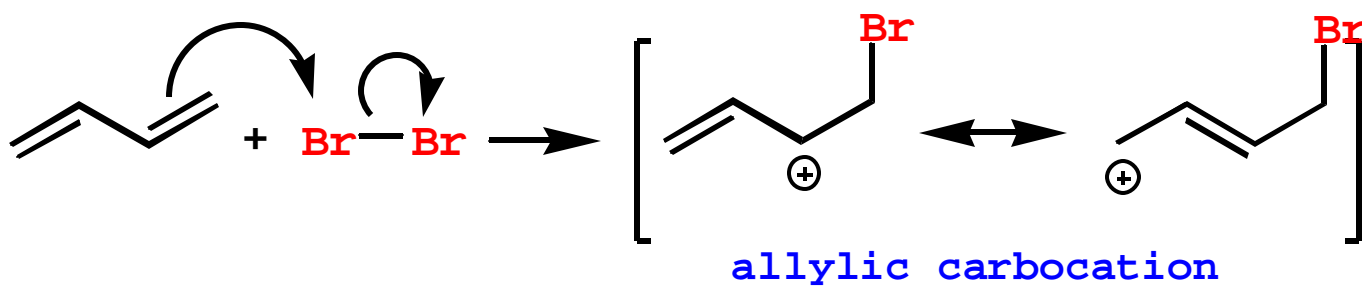


*Reactions of conjugated dienes

**Electrophilic additions -> allylic carbocation intermediate



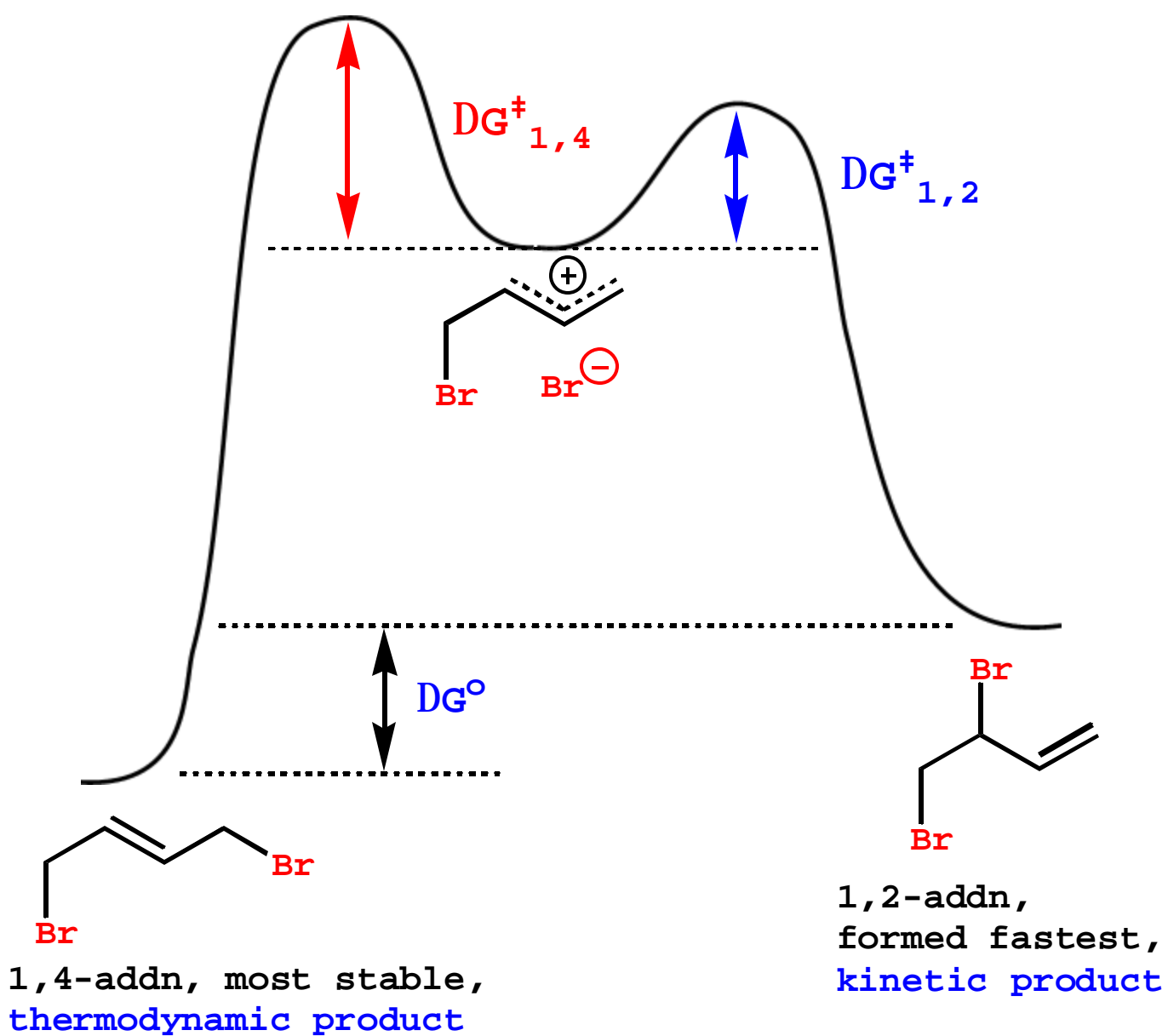
Mechanism...



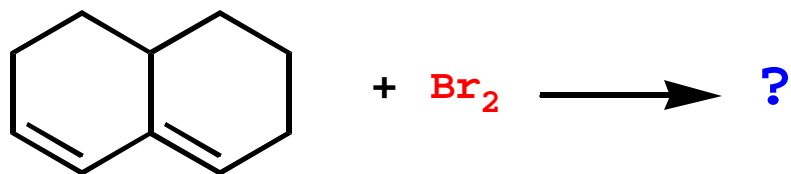
carbocation stability:



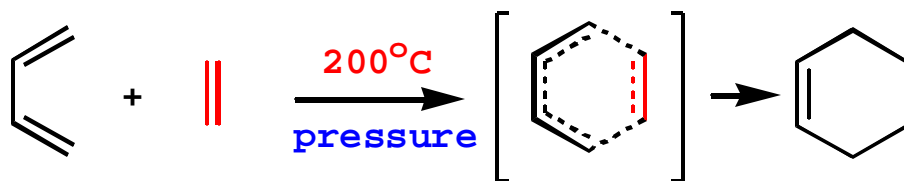
****Energy profile and kinetic vs thermodynamic processes...**



Question: What are the expected kinetic and thermodynamic products in the following reaction?



****Diels-Alder reaction...**

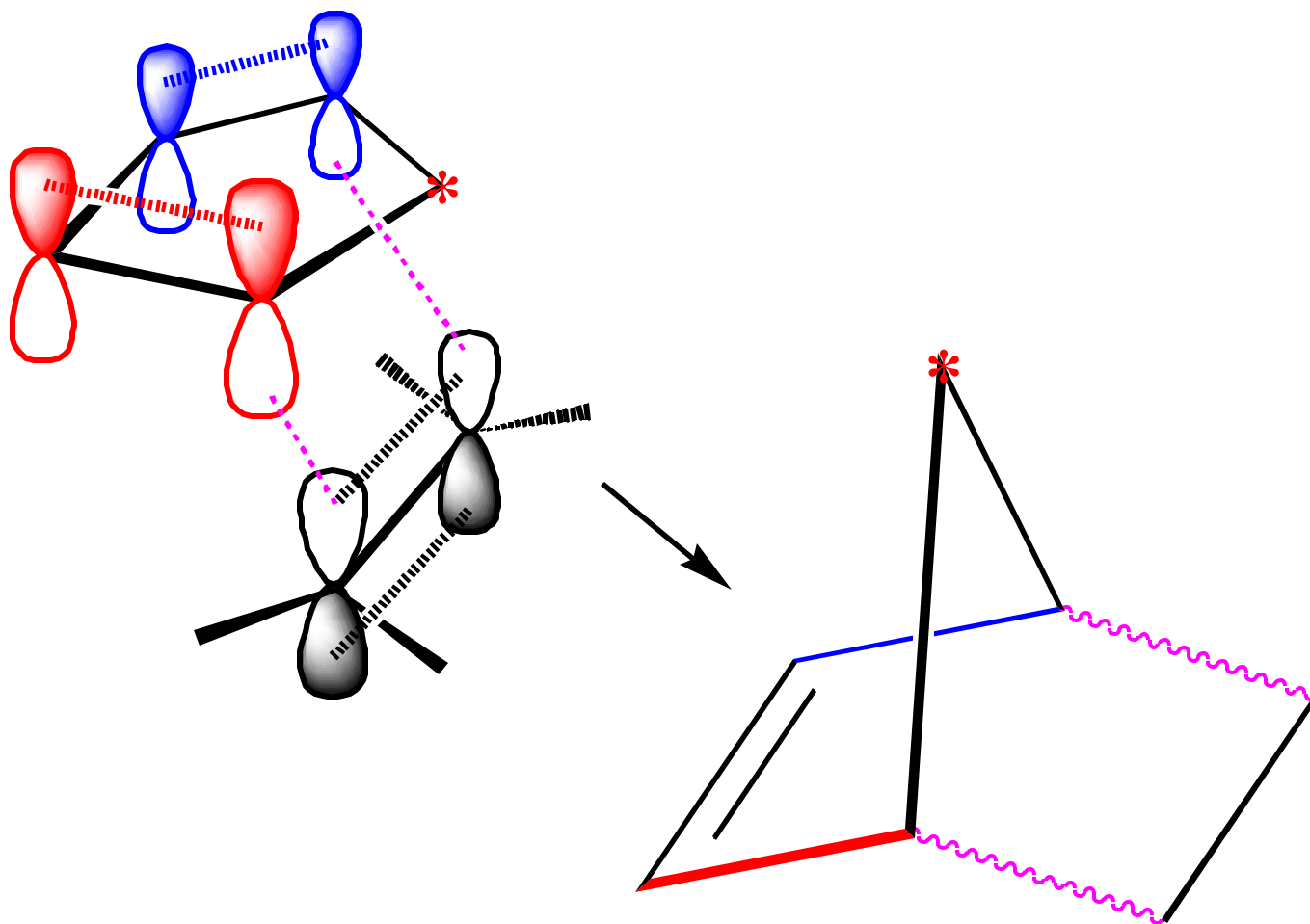


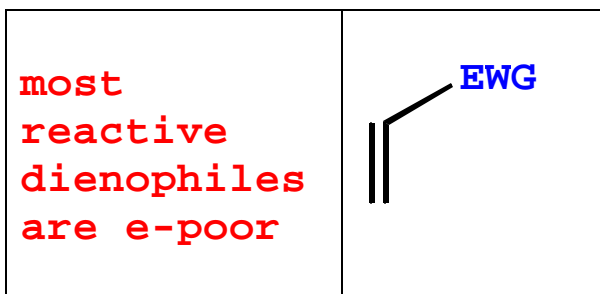
diene

dienophile

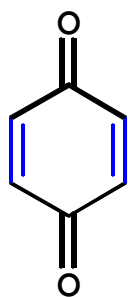
transition
state

cycloadduct

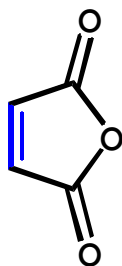




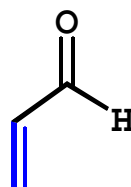
Some typical dienophiles...



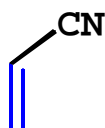
benzoquinone



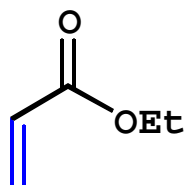
maleic
anhydride



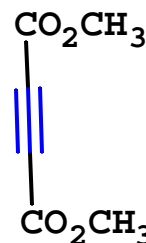
acrolein



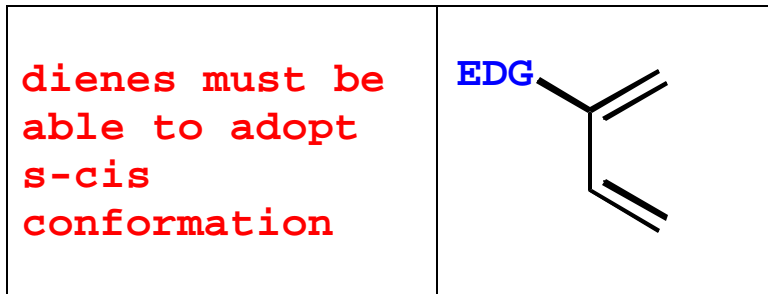
acrylonitrile



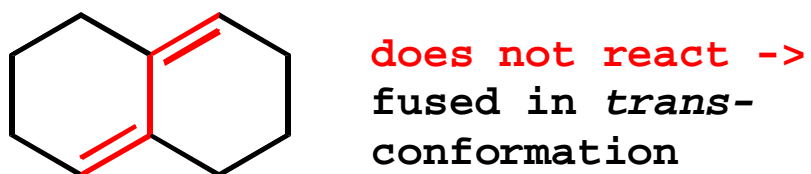
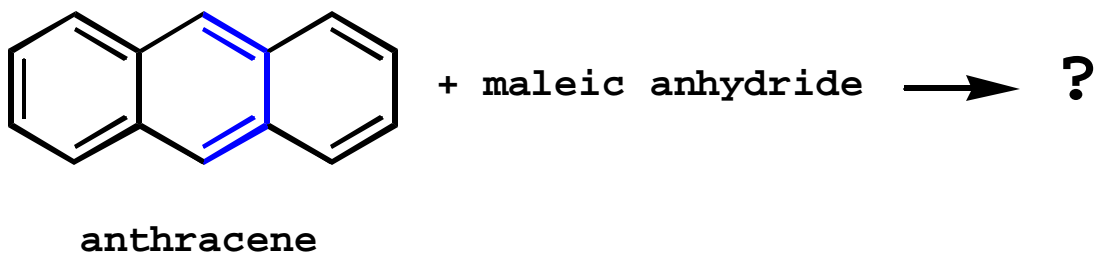
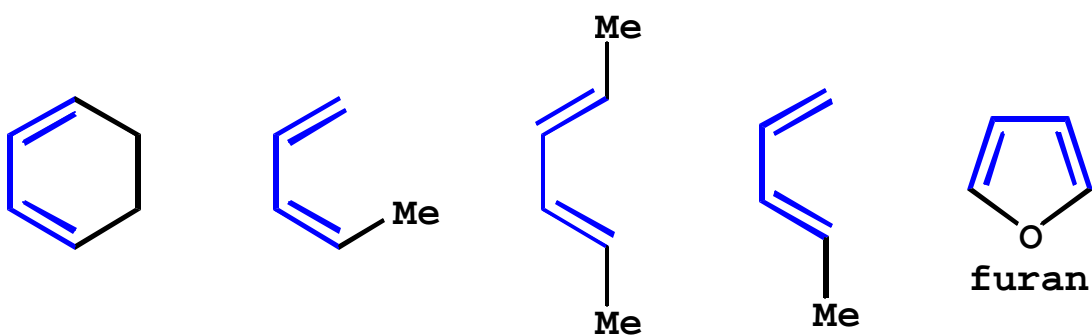
ethyl
acrylate

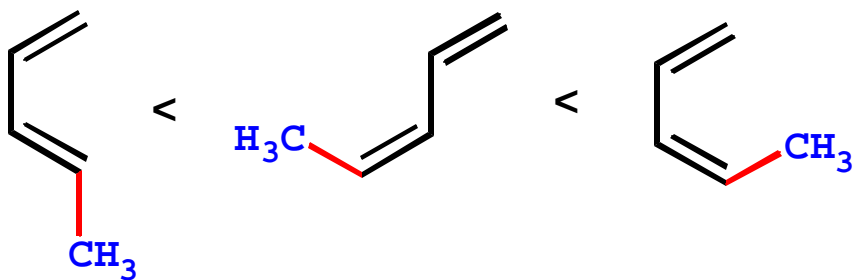
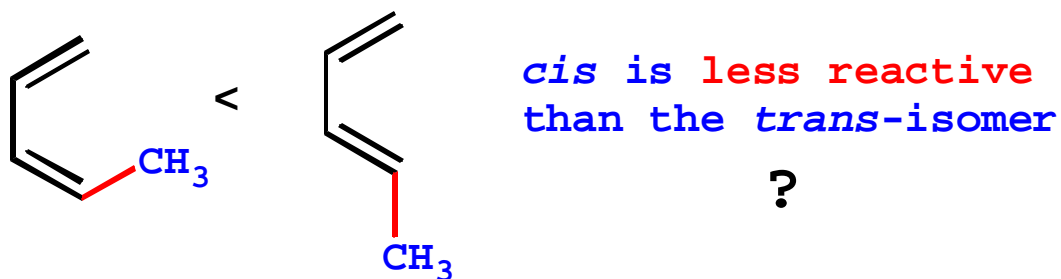


dimethyl
acetylene-
dicarboxylate



Some typical dienes...

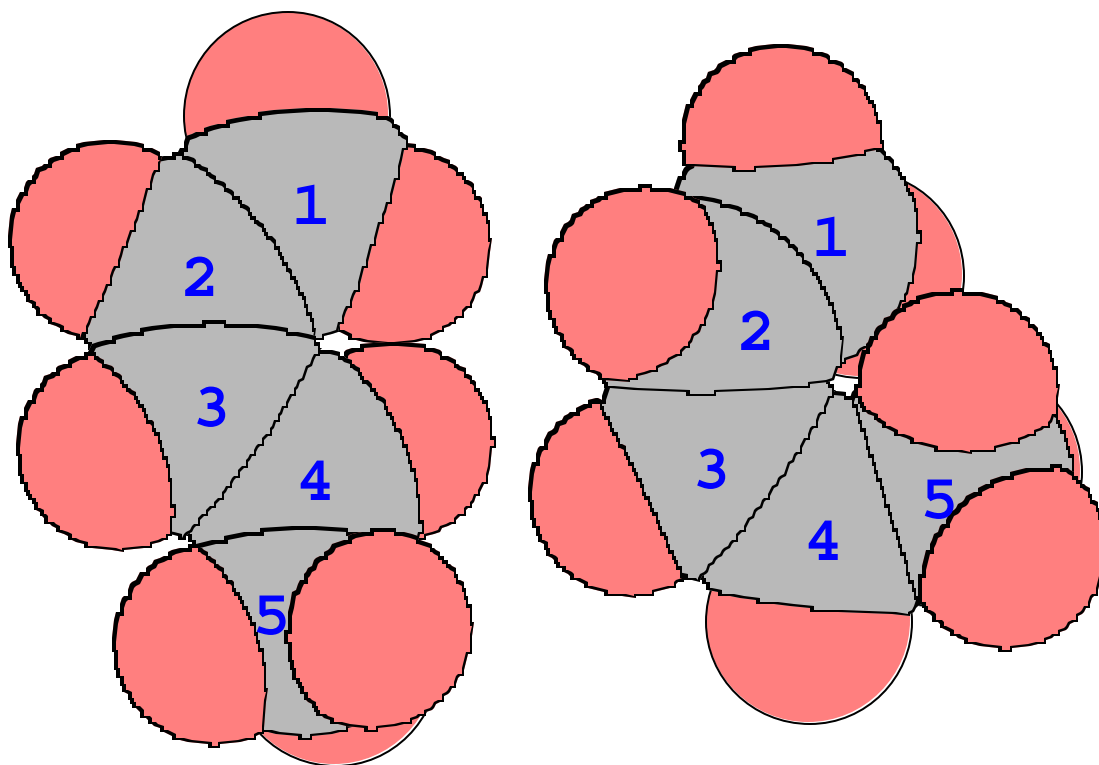




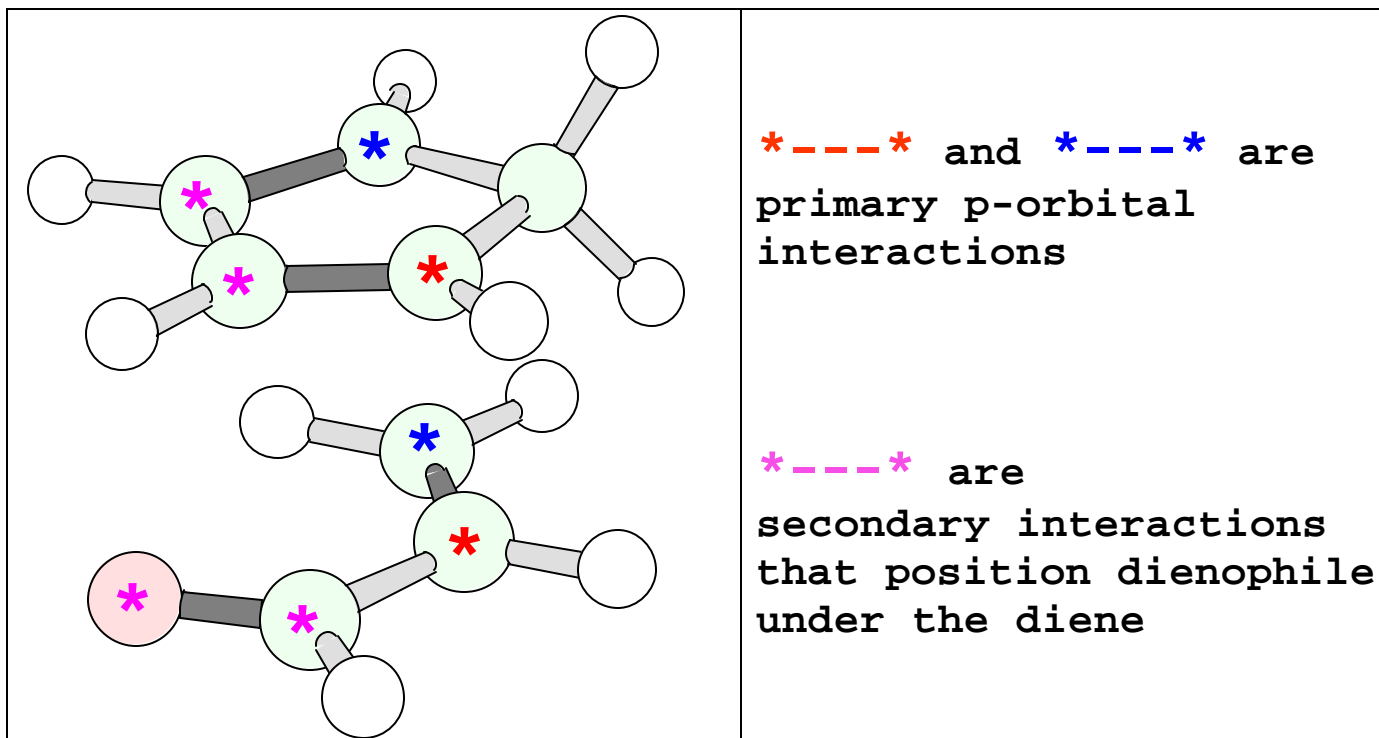
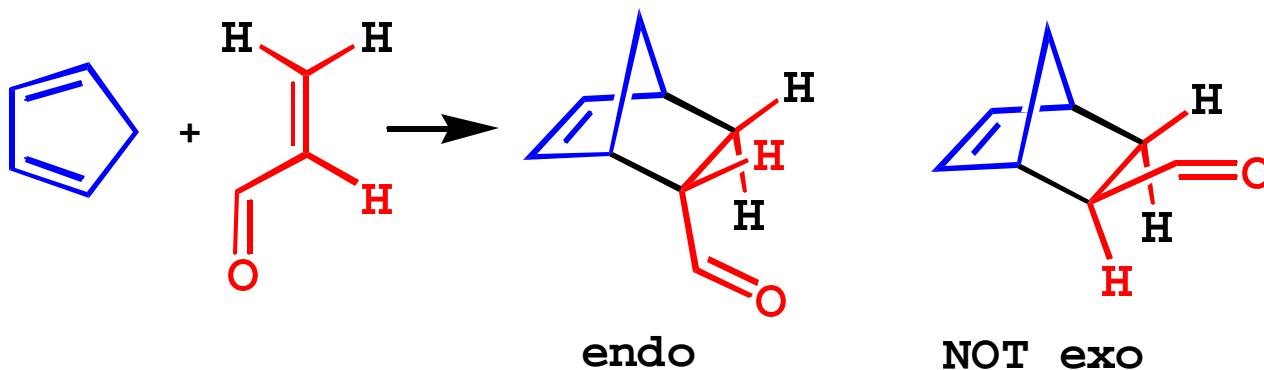
E = 0 kcal/mol

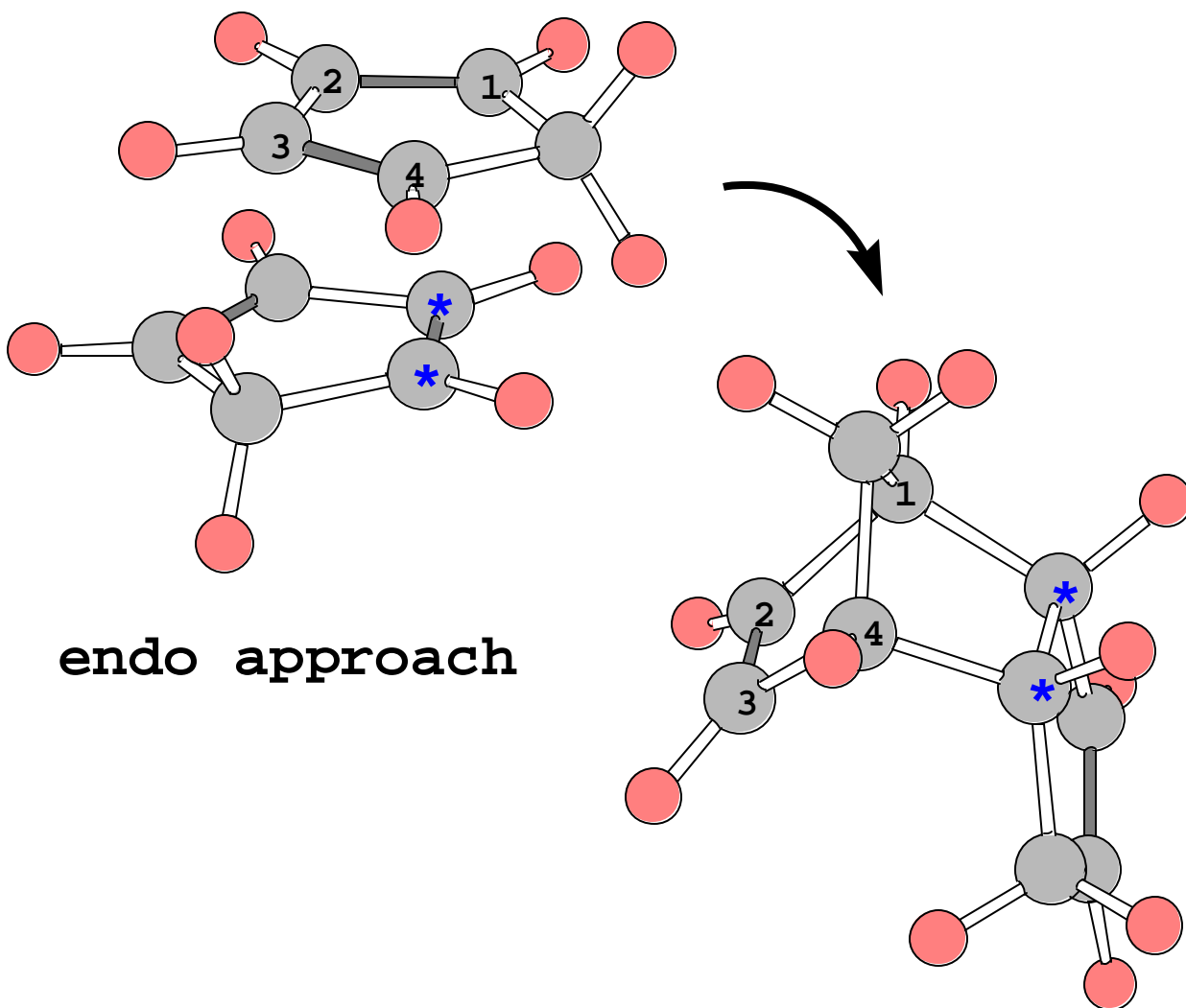
0.37

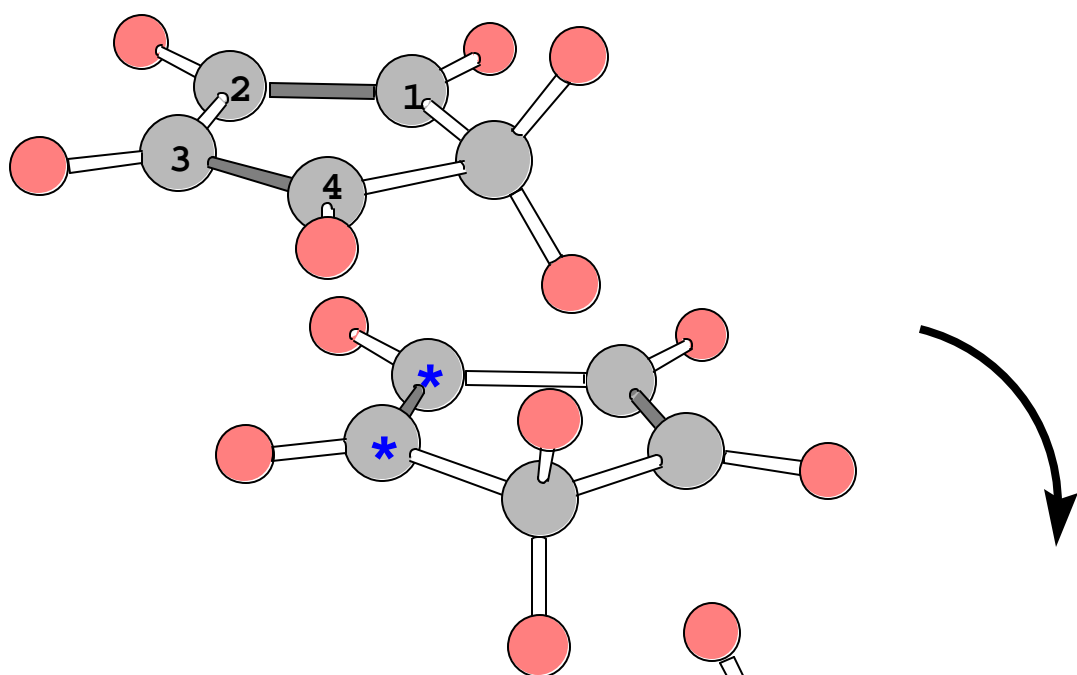
1.45



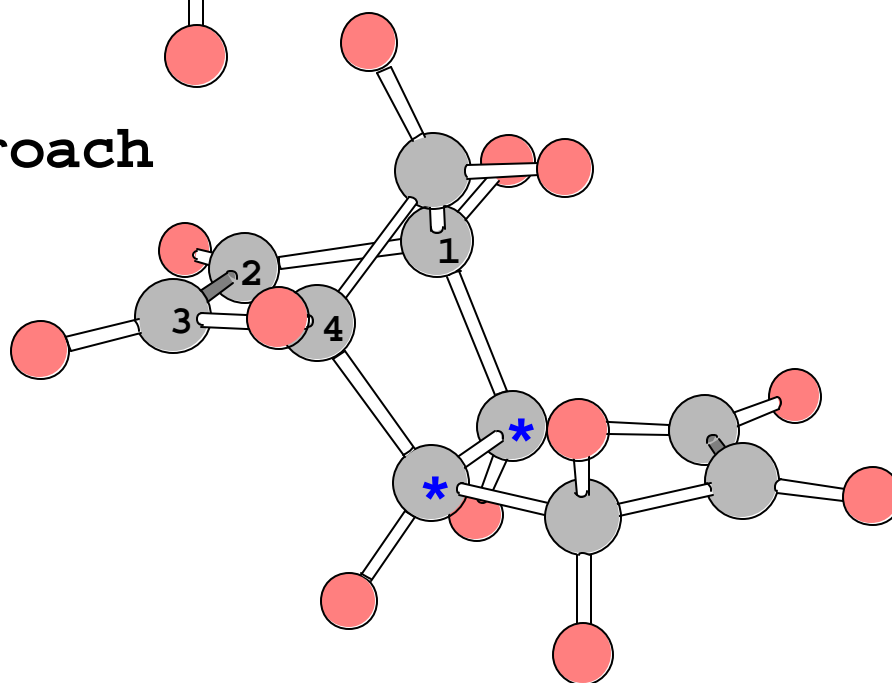
Endo approach -> major product defined by secondary interactions



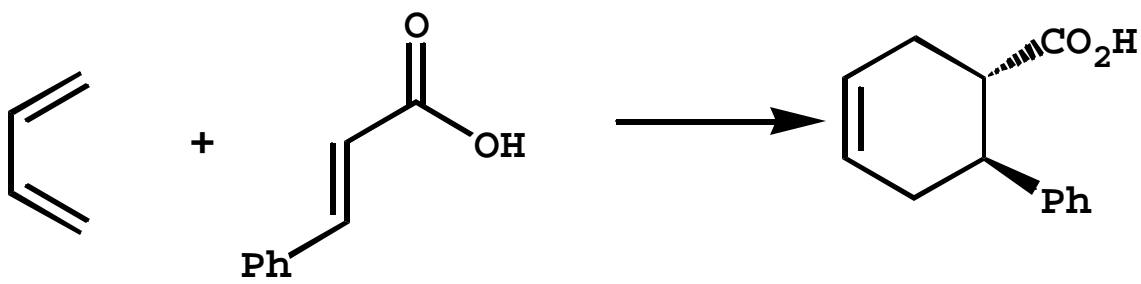
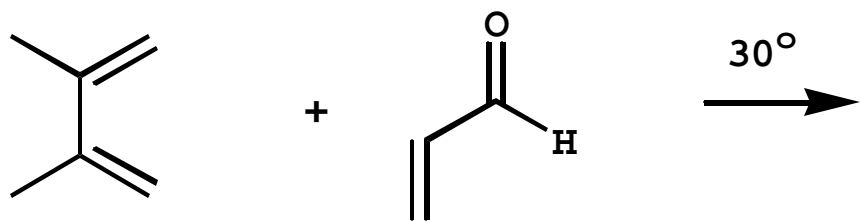
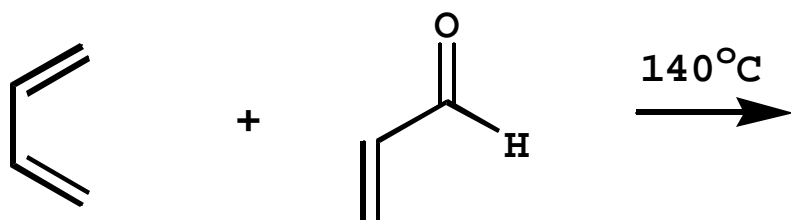




exo approach



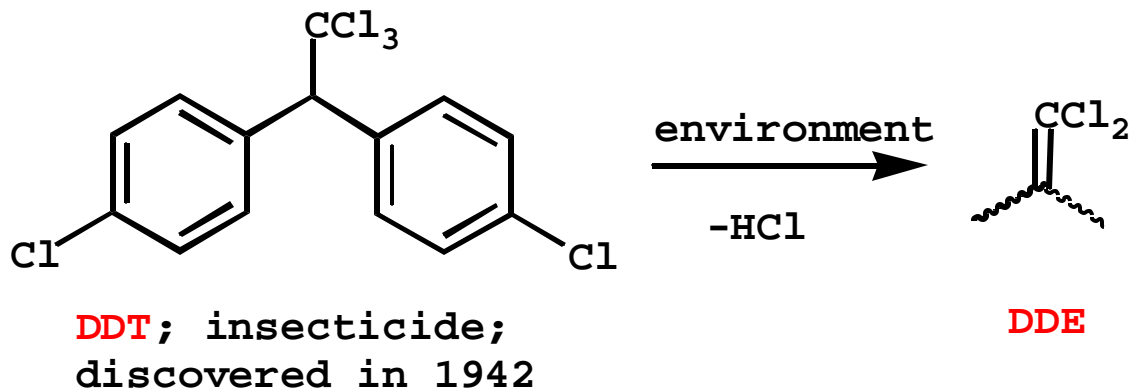
Few final examples...



trans-cinnamic acid

Extra: Chlorocarbon insecticides

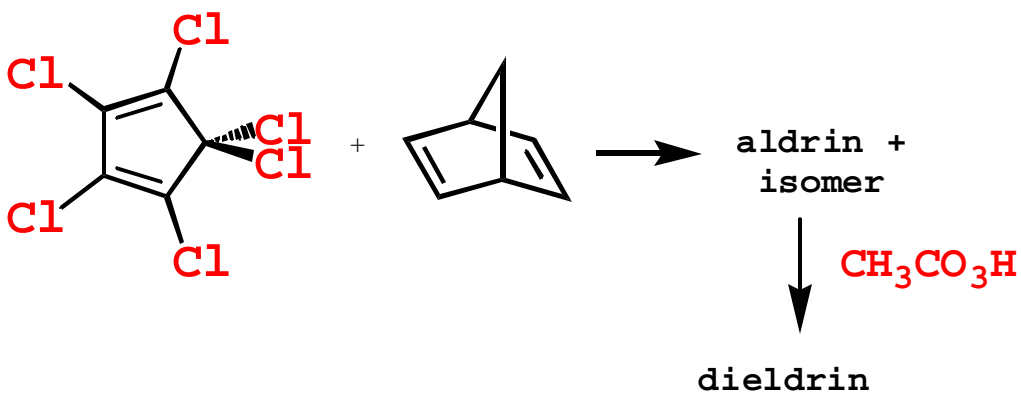
numerous insect carried diseases...typhus, malaria

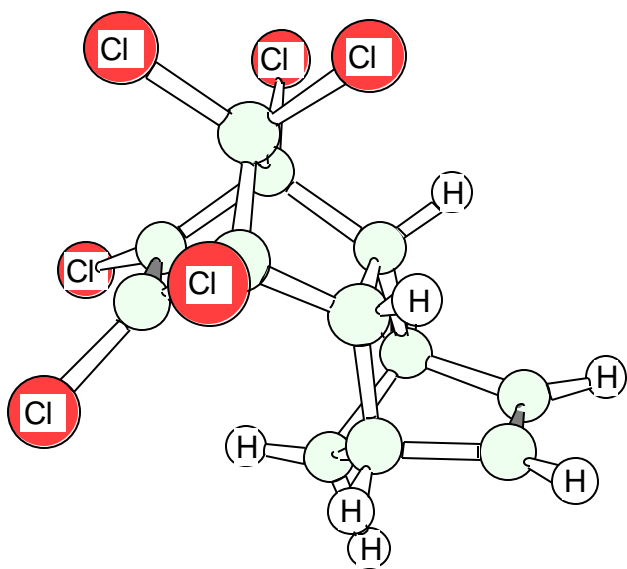


DDE accumulates in fatty tissue of humans; long term effects are unknown

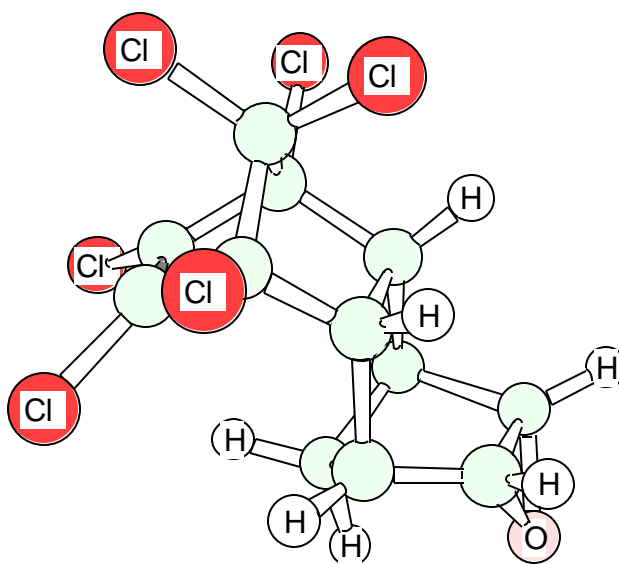
late 1940's populations of hawks, eagles, etc. showed serious declines -> DDE responsible for thin egg shells; inhibits carbonic anhydrase an enzyme that controls Ca supply

DDT and DDE are hard (persistent) insecticides; others are aldrin, dieldrin, chlordane

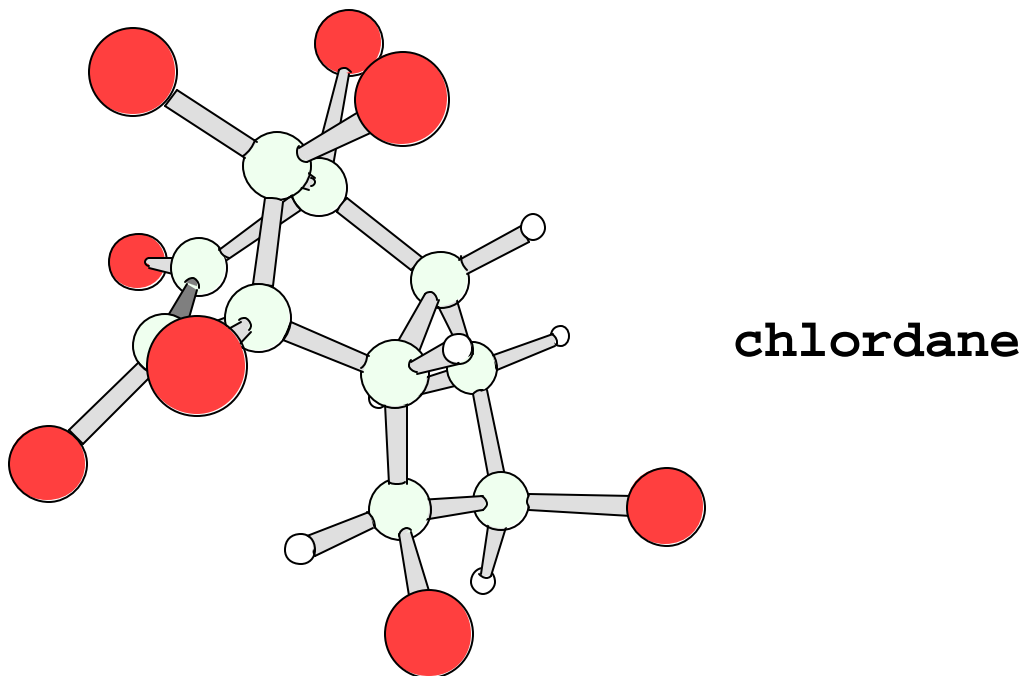
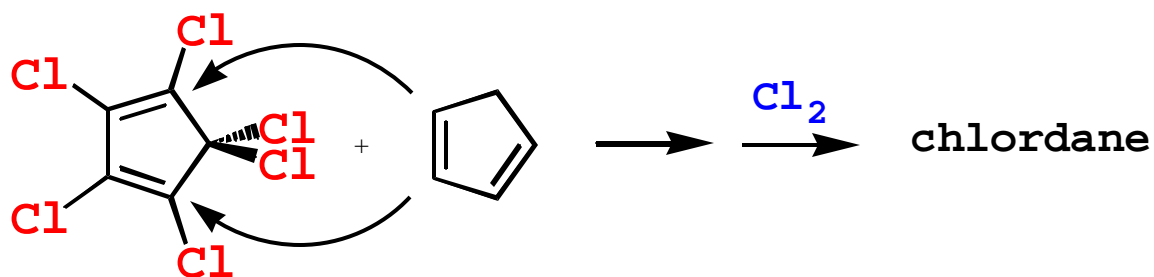




aldrin



dieldrin



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