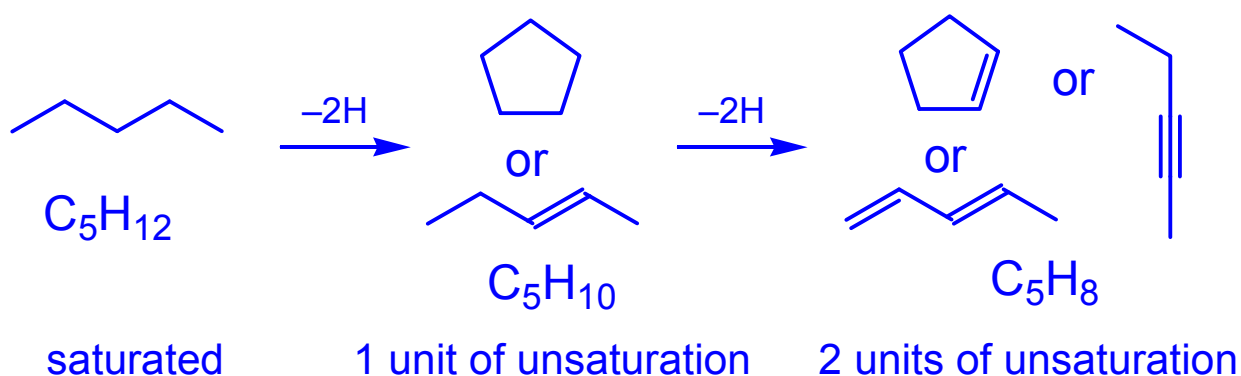


## 4. Alkenes and Alkynes (text 4.1 – 4.5)

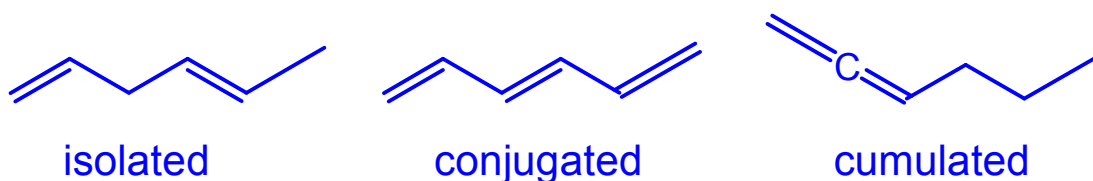
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### A. Structure and Nomenclature

- Alkenes with one C=C bond have the formula  $C_nH_{2n}$ . Alkynes with one C≡C bond have the formula  $C_nH_{2n-2}$ .
- Such compounds are said to be *unsaturated* because they have less than the maximum number of hydrogens.
- Each reduction of *two H* from the general alkane formula represents *one unit* of unsaturation (one index of hydrogen deficiency).

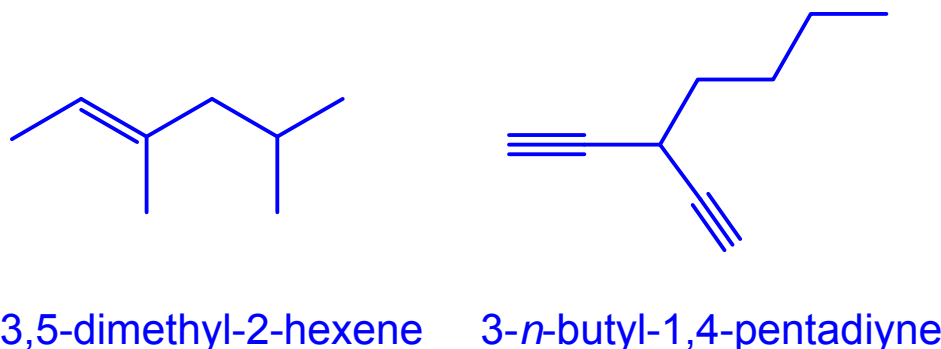


- So, each unit of unsaturation can be a pi-bond or a ring.
- When there are two or more multiple bonds, the arrangements can be as follows:
  1. Isolated, with two or more  $\sigma$  bonds between  $\pi$  bonds
  2. Conjugated, where multiple bonds alternate with a  $\sigma$  bond
  3. Cumulated, e.g. two double bonds on a single carbon.

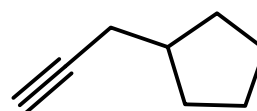


*What can be said about the 2p orbitals of a conjugated system?*

- In systematic nomenclature, the multiple bond (for C=C and C≡C) is given the lowest possible number on the parent chain. This *fixes* the chain numbering, and C=C (alkene) has the suffix *ene*, and C≡C (alkyne) the suffix *yne*.



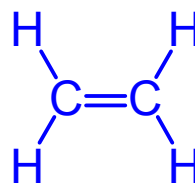
- Many simple compounds are known by common names:
  - $\text{H}_2\text{C}=\text{CH}_2$       ethylene      IUPAC = ethene
  - $\text{HC}\equiv\text{CH}$       acetylene      IUPAC = ethyne
  - $\text{CH}_3\text{CH}=\text{CH}_2$       propylene      IUPAC = propene
- Some substituents are also known by their common names:
  - $\text{H}_2\text{C}=\text{CH}-$       vinyl       $\text{H}_2\text{C}=\text{CH}_2-\text{Cl}$  vinyl chloride
  - $\text{H}_2\text{C}=\text{CHCH}_2-$       allyl       $\text{H}_2\text{C}=\text{CHCH}_2-\text{Br}$  allyl bromide
  - $\text{HC}\equiv\text{CCH}_2-$       propargyl



propargyl cyclopentane

## B. Shapes of Alkenes and Alkynes

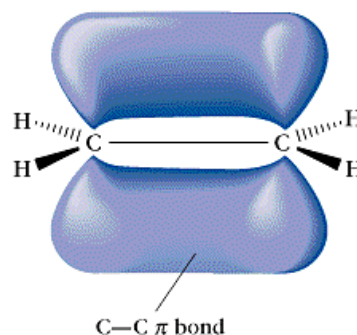
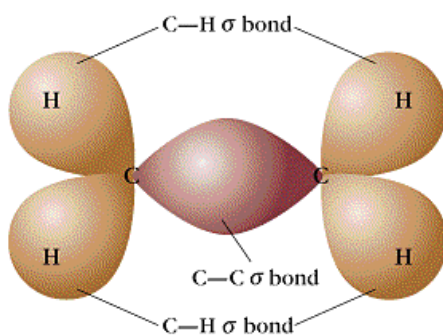
- Alkene: each C is bonded to three groups and is  $sp^2$  (planar) with a bond angle of  $120^\circ$ .



- Alkyne: each C is bonded to two groups and is  $sp$  (linear) with a bond angle of  $180^\circ$ .

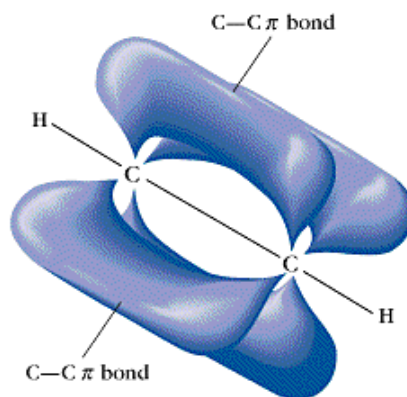
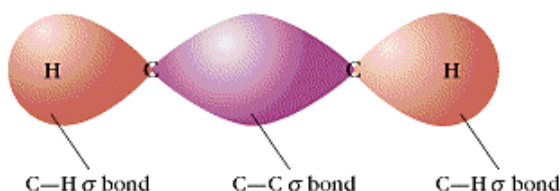


- A double bond (between atoms N, C, O, etc.) consists of two adjacent  $sp^2$ -hybridized atoms.
  - The three  $sp^2$  orbitals are used to form  $\sigma$  bonds to each of the three attached groups.
  - The remaining  $p$  orbital overlaps sideways with the  $p$  from the adjacent atom to form one  $\pi$  bond.
  - This results in a planar structure for all atoms involved, for example ethylene:



- Note that  $\pi$  bonds have electron density both above and below the molecular plane.

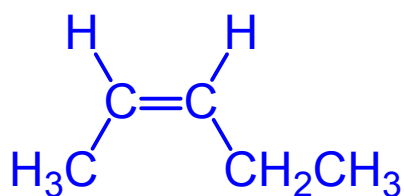
- A triple bond consists of two adjacent  $sp$ -hybridized atoms.
  - The  $sp$  orbitals are for  $\sigma$  bonds. The two  $\pi$  bonds originate from the sideways overlap of two  $p$  orbitals from each of the atoms, e.g. ethyne.



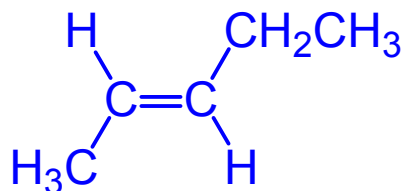
- Linear structure for all atoms involved, and there are two regions of electron density for each of the  $\pi$  bonds.

### C. *Cis-trans Isomerism*

- A multiple bond prevents free rotation about the involved atoms. Such rotation would require breaking the  $\pi$  bond and is not energetically favourable. As a result, *cis-trans* (geometric) isomers can exist for *non-symmetric* alkenes.

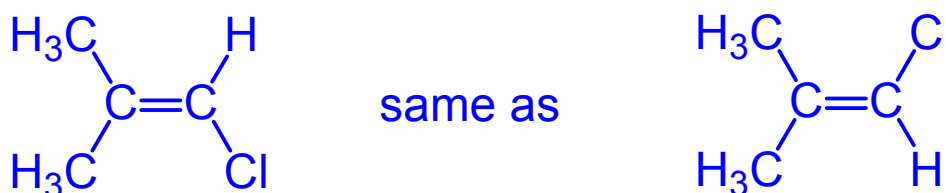


*cis*-2-pentene  
mp =  $-179^{\circ}$ , bp =  $38^{\circ}$

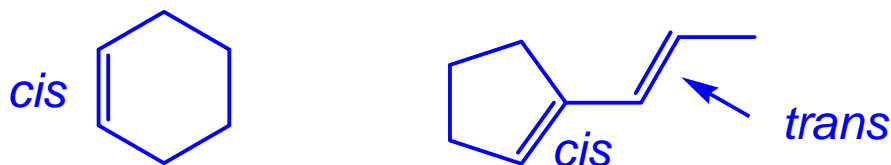


*trans*-2-pentene  
mp =  $-136^{\circ}$ , bp =  $36^{\circ}$

- In this context, the terms *cis-trans* refer to the relative orientation of designated substituents on the C=C bond.
  - Note: *cis-trans* terms are also used to describe the orientations of substituents bonded to a cycloalkane ring. Do not confuse the two different uses.
- Recognize that if any of the two substituents on any one of the two carbons is identical, there cannot be *cis-trans* isomers. The molecule shown below has no stereoisomers.



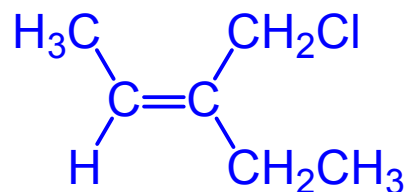
- Also, in ring compounds of 7 carbons or less, the double bond must be *cis* (as defined by the carbon atoms).



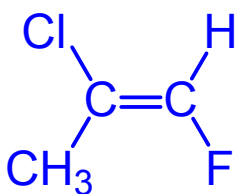
- For every C=C in a molecule, there is a possibility of 2 *cis-trans* isomers. So, for  $n$  C=C's in a molecule, there is a maximum of  $2^n$  possible isomers.
- The actual number of isomers is decreased if one or more of the double bonds is symmetrical (*i.e.* has two identical substituents on one of the C=C atoms).
  - $\text{CH}_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}_2$  has three C=C, but the one on the right does not have *cis-trans* isomers.

## D. E and Z Convention for Stereoisomers

- cis-trans* terms refer to the *relative* positions of the substituents, and they can sometimes be ambiguous.



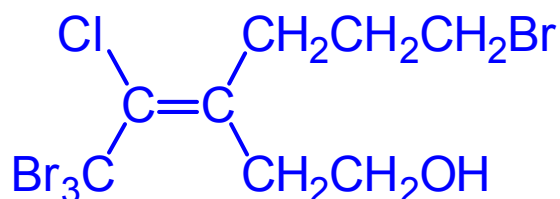
- In this molecule,  $\text{CH}_3$  is *trans* to  $\text{CH}_2\text{CH}_3$ , but *cis* to  $\text{CH}_2\text{Cl}$ .
- The *E-Z* convention for naming *cis-trans isomers* is unambiguous. The convention prioritizes each of the two substituents on each of the two alkene  $\text{C}=\text{C}$  based on rules:
  - Atoms directly attached to a  $\text{C}=\text{C}$  atom are arranged in the order of descending atomic number (nothing else!!!!)
    - e.g.  $\text{Br} > \text{S} > \text{F} > \text{O} > \text{N} > \text{C} > \text{H}$
    - For different isotopes of the same element, atomic mass determines order (e.g.  $\text{H}^2 > \text{H}^1$ ).
    - Example:



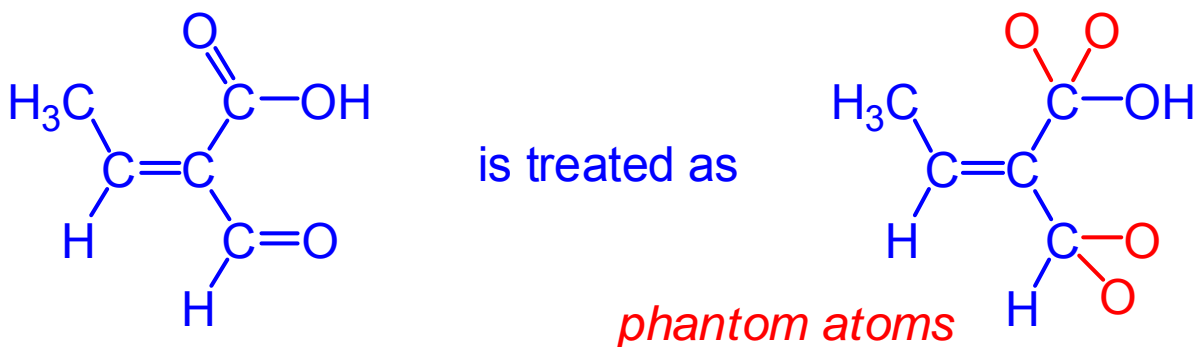
- When rule #1 leads to a “tie” between atoms, continue on to rules #2 and #3.

2. Beginning with atoms involved in a “tie,” proceed along the chain to the **first difference** in bonded atoms. The atomic number at that point determines priority.

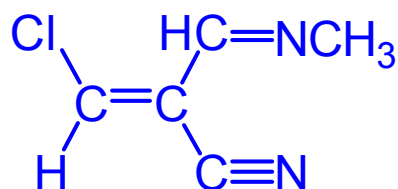
○ Example:



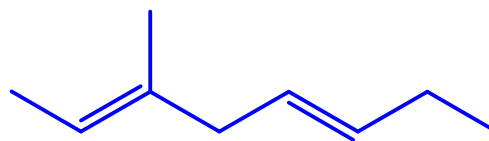
3. For atoms attached by double or triple bonds, they are given single-bond equivalencies so that they can be treated like single-bonded groups. Replace each  $\pi$  bond with two single bonds to “phantom” atoms identical to the real atoms at both ends of the  $\pi$  bond.



○ Example:



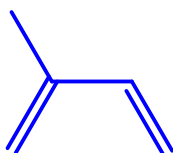
- We then assign a **configuration label** to the isomer: If two groups of higher priority are on the same sides of the double bond, then the alkene is *Z* (*zusammen*). If the two groups of higher priority are on opposite sides of the double bond, the alkene is *E* (*entgegen*).
- In nomenclature, *E* or *Z* is italicized and placed in brackets in front of the compound name. For the *Z* isomer above, we have (*Z*)-3-chloromethylpent-2-ene.
- If there is more than one double bond, give labels to each double bond.



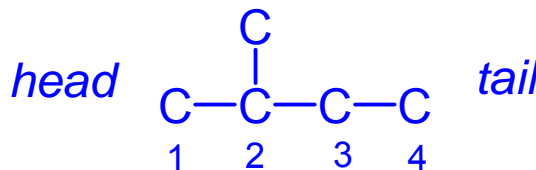
(*2E,5E*)-3-methylocta-2,5-diene

## ***E. Terpenes: Naturally Occurring Alkenes***

- Terpenes are a large family of naturally occurring compounds. Their basic carbon skeleton can be broken down into two or more units that are identical with the five-carbon skeleton of isoprene (building blocks of terpenes).

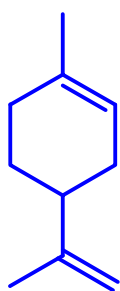


isoprene  
(2-methyl-1,3-butadiene)

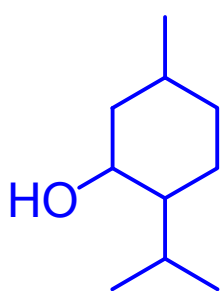




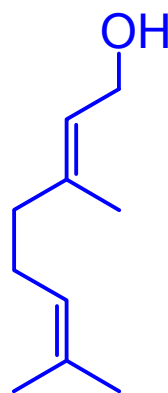
- Terpenes are naturally formed (usually in plants), and in most cases, isoprene units are connected head-to-tail.
- The isoprene unit is only a building block. When assembled into a natural product, enzymes will remove, modify, or add double bonds, substituents, etc. However, the basic framework of the **C<sub>5</sub> skeleton** remains intact.
- The terpenes have familiar characteristic odours such as lemon oil (limonene), peppermint (menthol), roses (geraniol) and ginger (zingiberene). You should be able to identify the isoprene units in these and other terpenes.



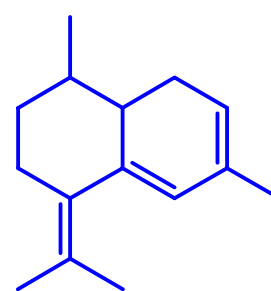
limonene



menthol



geraniol



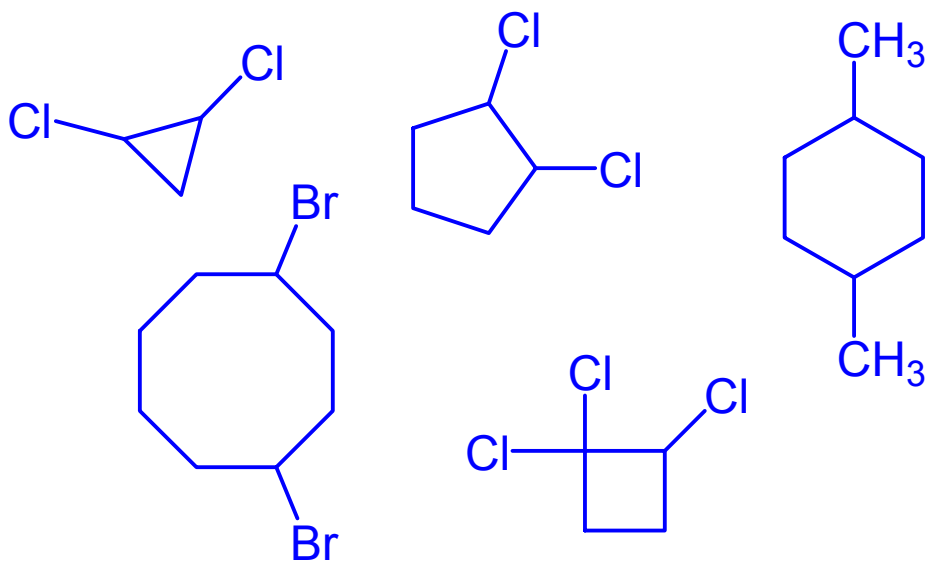
zingiberene

## Summary

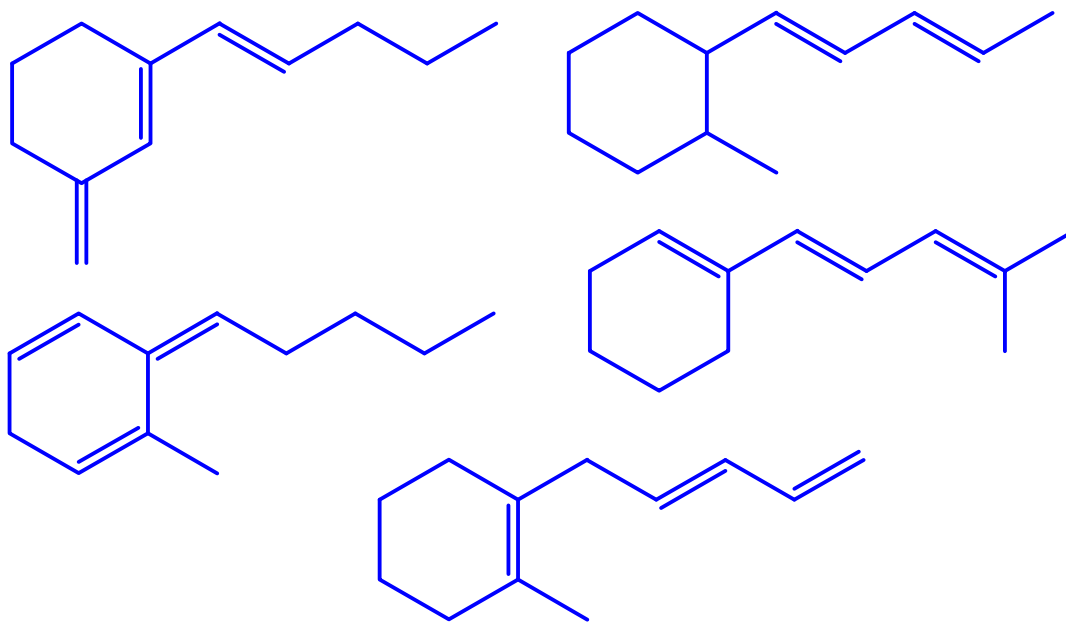
- Chapter 4, pages 98-113.
- Problems: 8, 9, 12, 14, 15, 20, 22, 25, 28, 31, 33, 39, 45.
- Past midterm tests:
  - 2005: 15 – 18
  - 2006: 16 – 19
  - 2007: 15 – 17
  - 2008: 17 – 20

## Past Test Questions

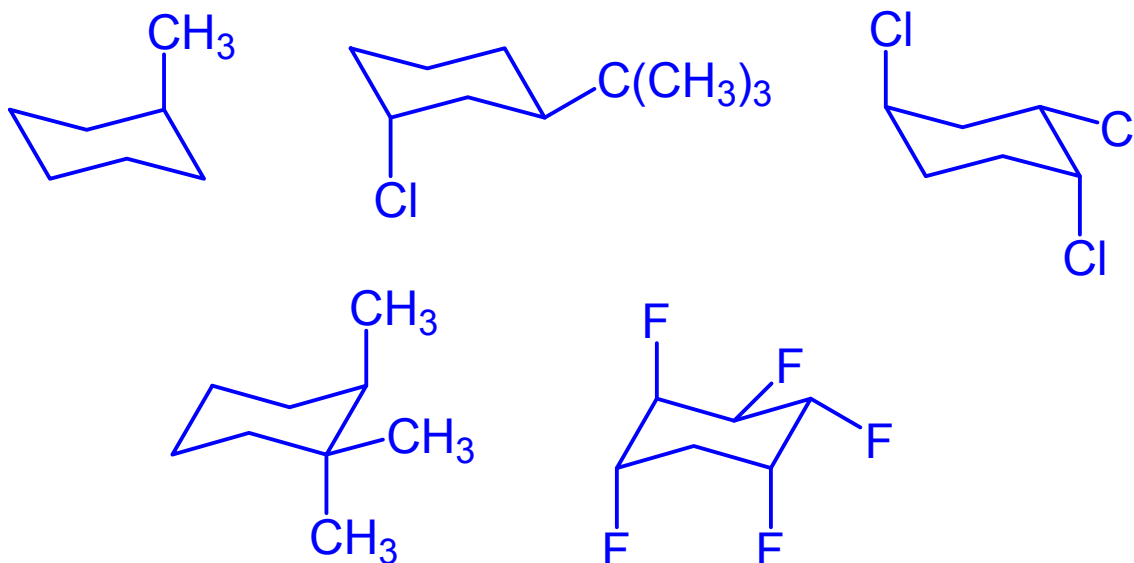
- Which one of the following compounds does NOT show *cis-trans* isomerism?



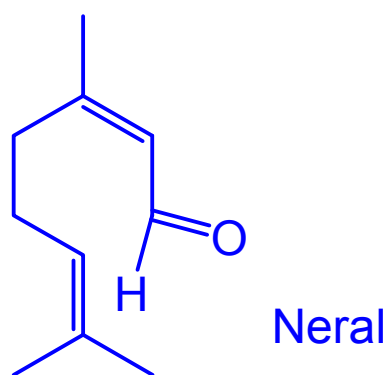
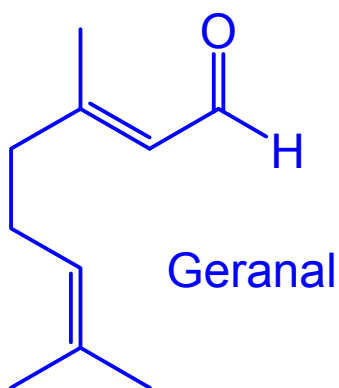
- Which one of the following molecules has the greatest number *cis-trans* isomers?



- Which one of the following molecules is shown in *its* most stable conformation?



- MCAT Question: Geranal and neral are two terpenes that can be isolated from lemon grass. What is the relationship of these two molecules?



- Conformations
- Resonance structures
- Structural isomers
- *cis-trans* isomers