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USNCO Coaching Session National Exam Preparation Tutorial Notes: Organic/Biochemistry

Steven Chen and Susan Park

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Useful References

- https://www.compoundchem.com/2014/05/22/typesofisomerism/
- https://usnco-quizzes.web.app/
- Patrick, Graham. BIOS Instant Notes in Organic Chemistry, CRC Press LLC, 2004. ProQuest Ebook Central

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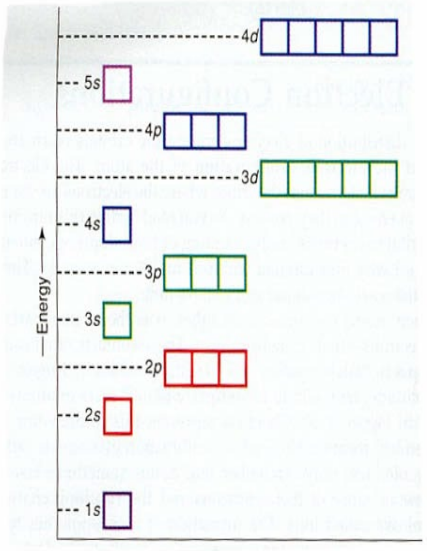
REFRESHER

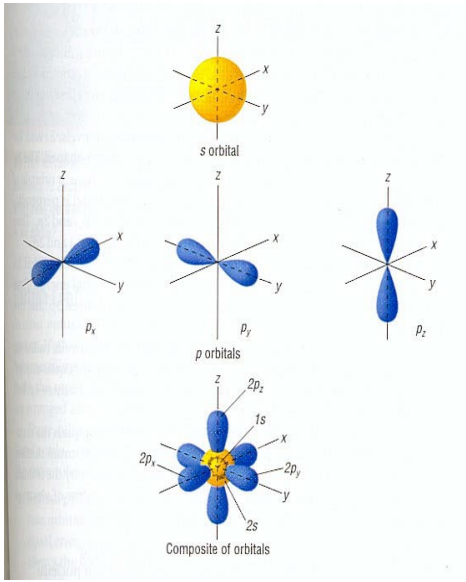
Functional Groups

Functional Group	Type of Compound	Suffix/prefix	Sample	Name
R=R'	Alkene	-ene	$CH_2=CH_2$	Ethene
R=R'	Alkyne	-yne	CH=CH	Ethyne
R-OH	Alcohol	-ol (or –anol), and the carbon to which the -OH is attached must be specified (unless the -OH is at the end).	CH_3CH_2-OH	Ethanol
R-O-R'	Ether	**IUPAC:** -oxy for shorter carbon chain and then –ane for longer carbon chain **Common:** -yl for both carbon chains, then add the word "ether"	CH_3CH_2-O- CH_2CH_3	Ethoxy ethane OR Diethyl ether
O || R-C-H	Aldehyde	-al (or -anal)	O || CH_3-C-H	Ethanal
O || R-C-R'	Ketone	-one (or –anone), and the number of the carbon belonging to the carbonyl group (the carbon to which the doubly-bonded oxygen is attached) must be specified.	O || CH_3-C- CH_3	2-propanone
O || R-C-OH	Carboxylic Acid	-oic acid (or –anoic acid)	O || CH_3-C-OH	Ethanoic acid
O || R-C-O-R'	Ester	-yl for the carbon chain that came from the alcohol (the chain that is single bonded to one oxygen) -oate (or –anoate) for carbon chain that came from the carboxylic acid (the chain that is single bonded to an oxygen and double bonded to another oxygen)	O || CH_3-C-O-CH_2CH_3	Ethyl Ethanoate

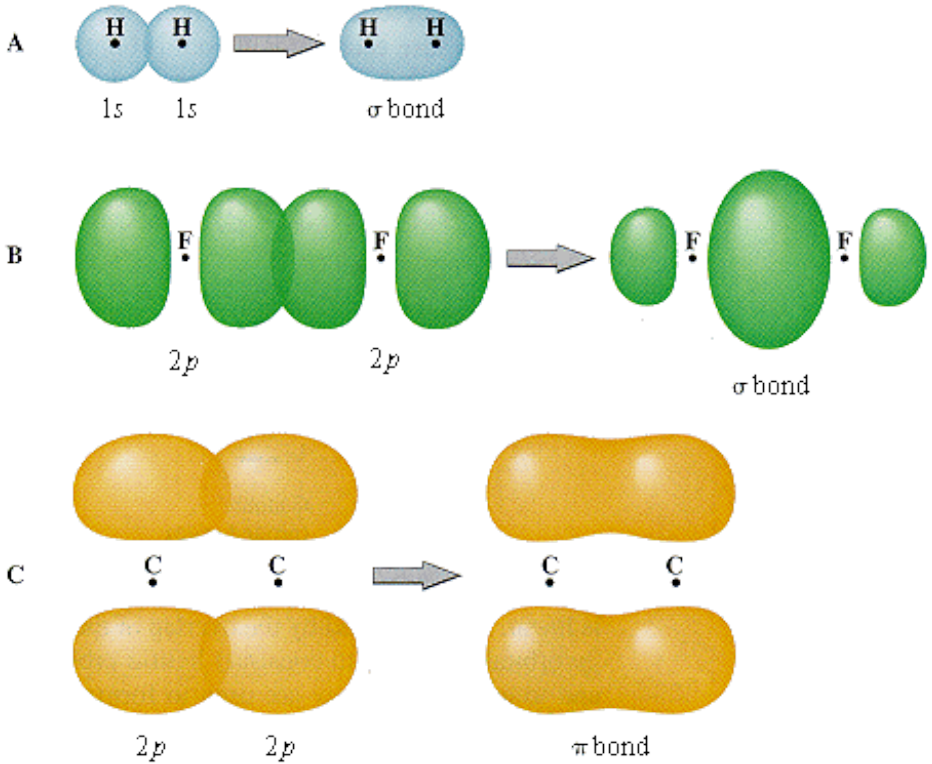
Hybrid Orbitals

- sp^3 hybridization = the 2s orbital mixes with three of the 2p orbitals. FOUR hybrid orbitals
- sp^2 hybridization = the 2s orbital mixes with two of the 2p orbitals. THREE hybrid orbitals
- sp^1 hybridization = the 2s orbital mixes with one of the 2p orbitals. TWO hybrid orbitals



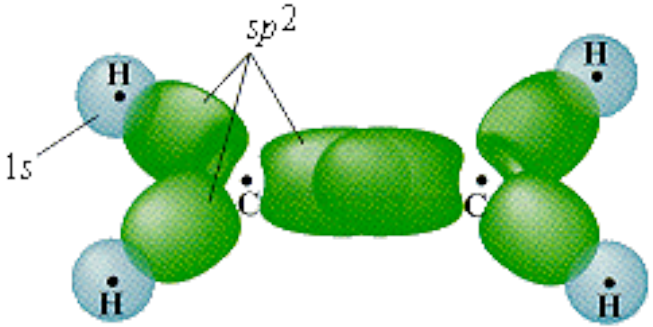


Hybridization



Multiple Bonding

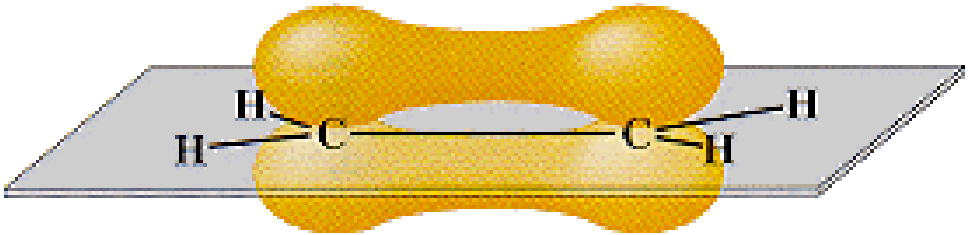
- Now imagine that the atoms of ethene move into position.
- Two of the sp^2 hybrid orbitals of each carbon overlap with the 1s orbitals of the hydrogens.
- The remaining sp^2 hybrid orbital on each carbon overlap to form a σ bond.



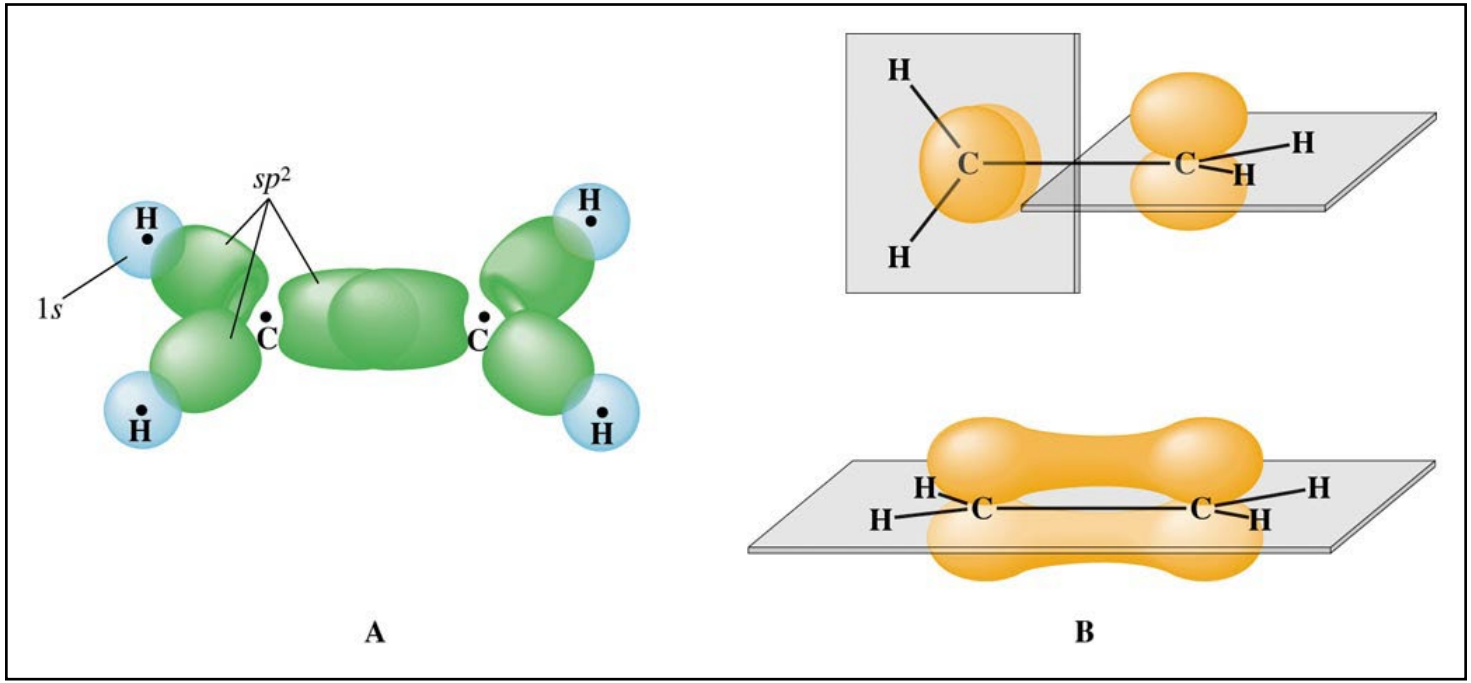
A

Multiple Bonding

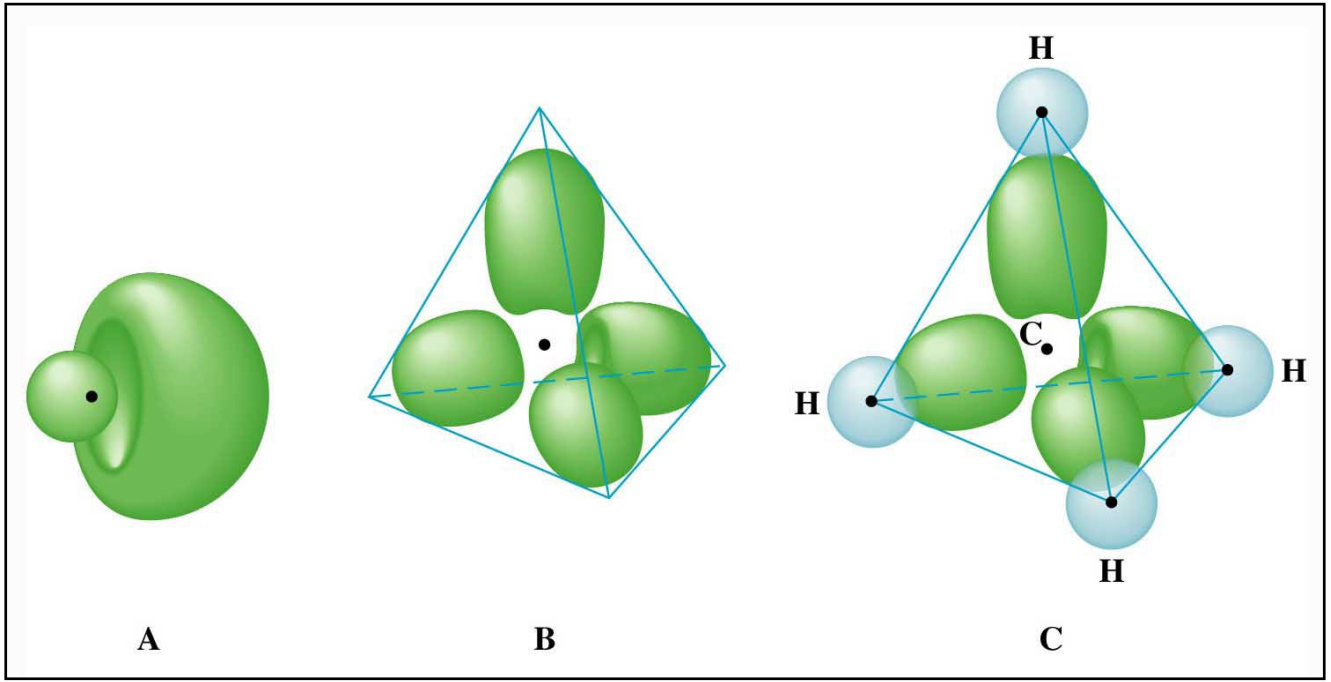
- The remaining “unhybridized” 2p orbitals on each of the carbon atoms overlap side-to-side forming a π **bond**.
- You therefore describe the carbon-carbon double bond as one σ bond and one π bond.



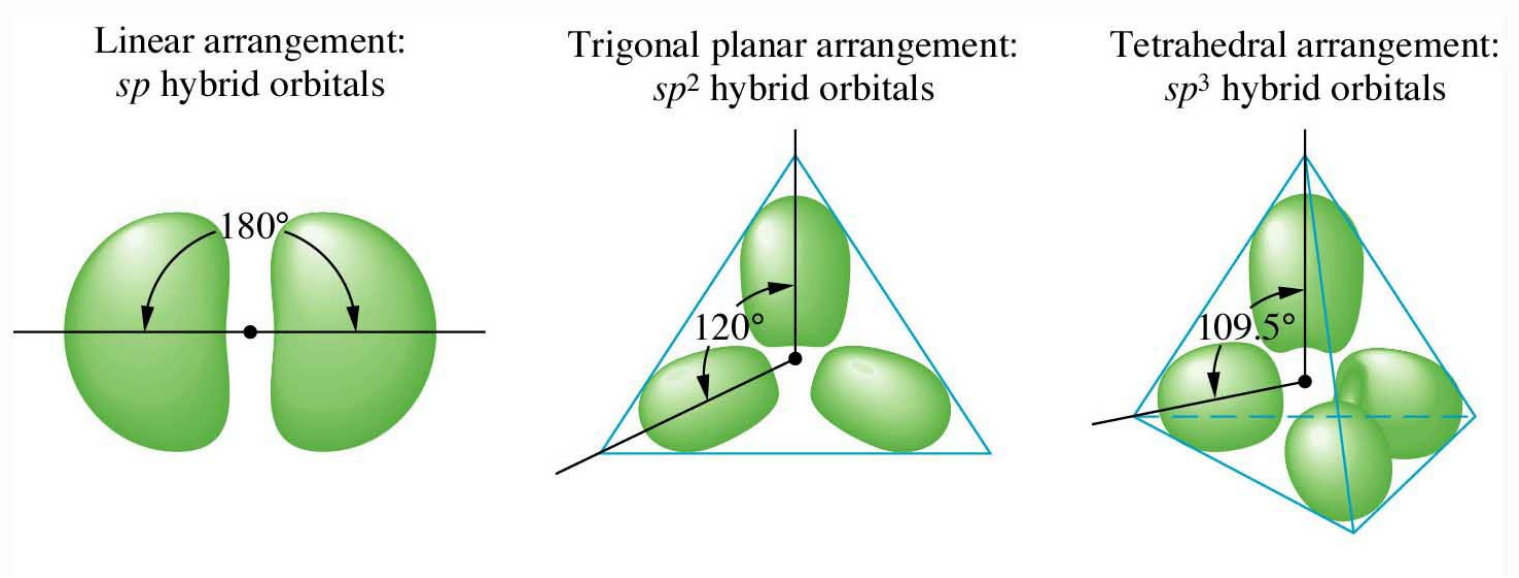
Bonding in Ethylene



Spatial Arrangement of sp^3 Hybrid Orbitals



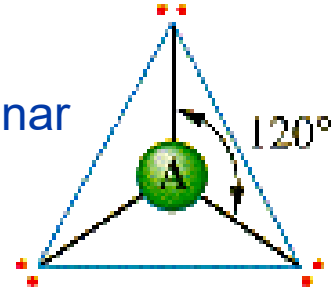
Diagrams of Hybrid Orbitals Showing Their Spatial Arrangements.



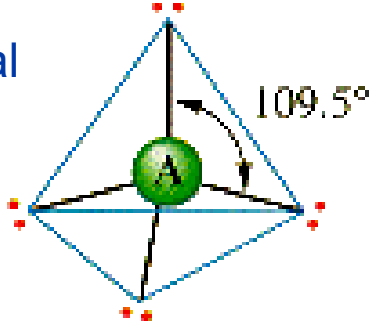
Arrangement of Electron Pairs About an Atom

2 pairs
Linear

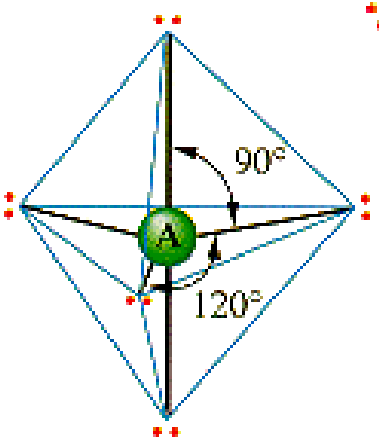
3 pairs
Trigonal planar



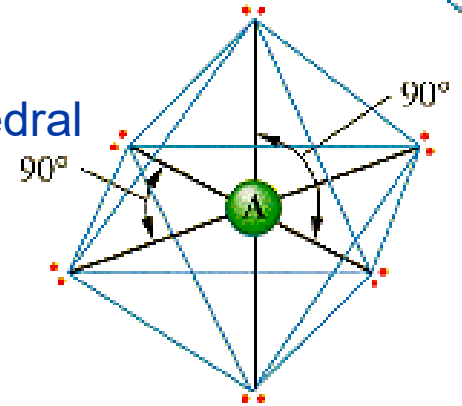
4 pairs
Tetrahedral



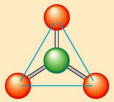
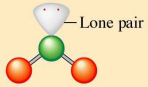
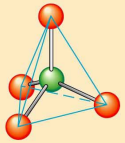
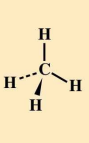
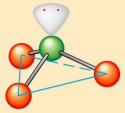
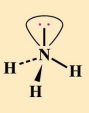
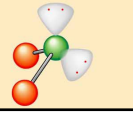
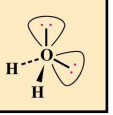
5 pairs
Trigonal bipyramidal



6 pairs
Octahedral



Electron Pairs and Arrangements

ELECTRON PAIRS Total	Bonding	Lone	ARRANGEMENT OF PAIRS	MOLECULAR GEOMETRY		EXAMPLE	
2	2	0	Linear	Linear AX_2		BeF_2	
3	3	0	Trigonal planar	Trigonal planar AX_3		BF_3	
	2	1		Bent (or angular) AX_2		SO_2	
4	4	0	Tetrahedral	Tetrahedral AX_4		CH_4	
	3	1		Trigonal pyramidal AX_3		NH_3	
	2	2		Bent (or angular) AX_2		H_2O	

ELECTRON PAIRS Total	Bonding	Lone	ARRANGEMENT OF PAIRS	MOLECULAR GEOMETRY		EXAMPLE	
5	5	0	Trigonal bipyramidal	Trigonal bipyramidal AX_5		PCl_5	
	4	1		Seesaw (or distorted tetrahedron) AX_4		SF_4	
	3	2		T-shaped AX_3		ClF_3	
	2	3		Linear AX_2		XeF_2	
6	6	0	Octahedral	Octahedral AX_6		SF_6	
	5	1		Square pyramidal AX_5		IF_5	
	4	2		Square planar AX_4		XeF_4	

55. Which of these could have the formula $C_6H_{12}O$?

I. An acyclic ester
II. A cyclic ether

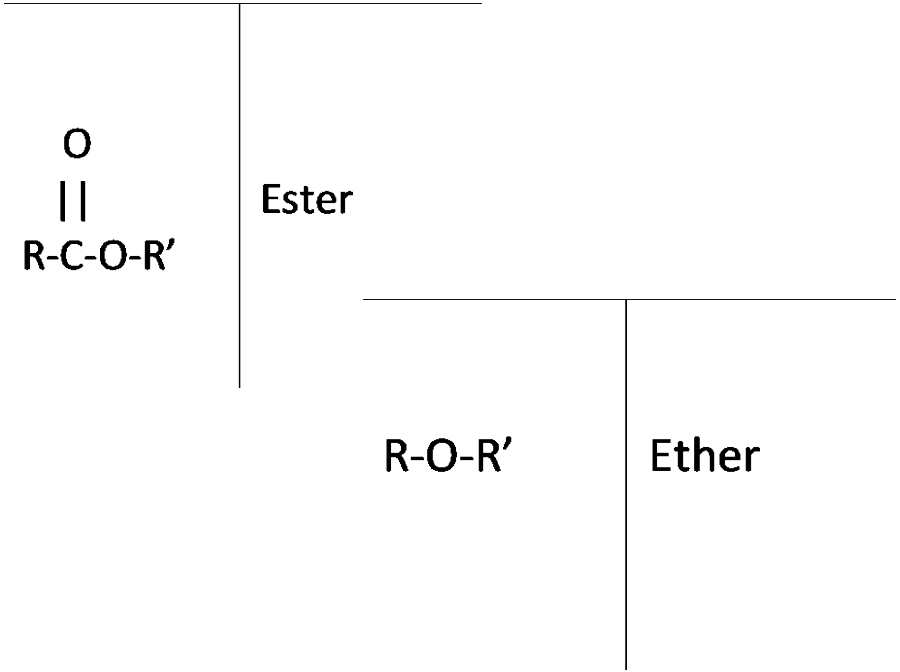
(A) I only

(B) II only

(C) Either I or II

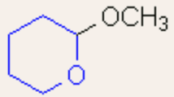
(D) Neither I nor II

Acyclic Ester vs. Cyclic Ether

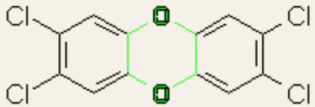
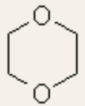


- Cyclic ethers often have specific names that are used as base names:


cis-2,5-dimethyltetrahydrofuran — after — furan




2-methoxytetrahydropyran — after — pyran

2,3,7,8-tetrachlorodibenzodioxin — 1,4-dioxane

https://sites.science.oregonstate.edu/~gablek/CH336/Chapter9/ethernom.htm

2021 National Exam

56. Which is the best explanation for the higher reactivity of conjugated dienes relative to non-conjugated alkenes in electrophilic addition reactions?

(A) Conjugated dienes can form allylic cations on reaction with electrophiles while non-conjugated alkenes cannot.

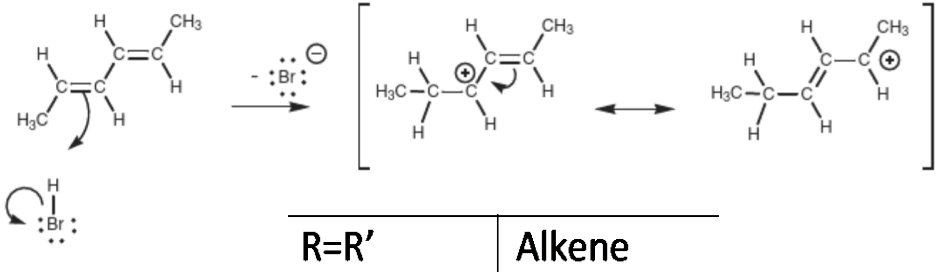
(B) Conjugated dienes have more potentially reactive sites than do non-conjugated alkenes.

(C) The π bonding in conjugated dienes is weaker than the π bonding in non-conjugated alkenes.

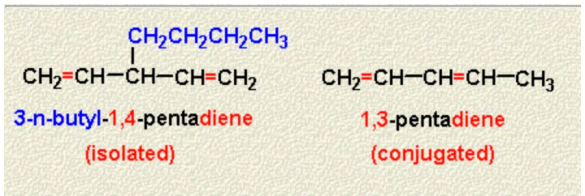
(D) Conjugated dienes are nonplanar while non-conjugated alkenes are planar.

Conjugated Diene

- A conjugated diene consists of two alkene units separated by a single bond– hence ‘conjoined’. Whereas, a non-conjugated diene has ’isolated’ C-double bonds.
- A conjugated system consists of delocalized pi bonds, usually across alternating single and double bonds. Often refers to aromatic molecules that are cyclic and planar with sp^2 hybridizations

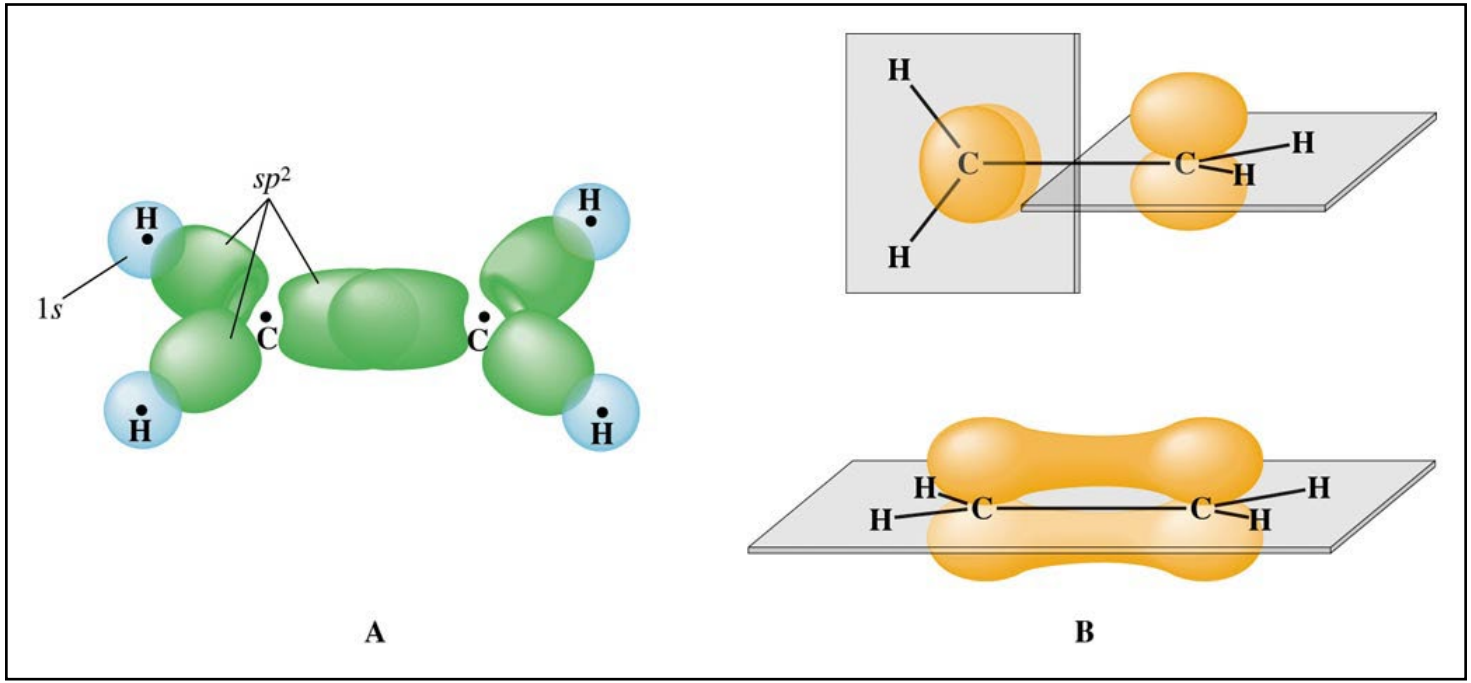


R=R’	Alkene



https://www.chem.ucalgary.ca/courses/350/Carey5th/Ch10/ch10-2.html
http://www.chem.uiuc.edu/organic/Alkenes/Chapter%203/sec3-14/3-14.htm

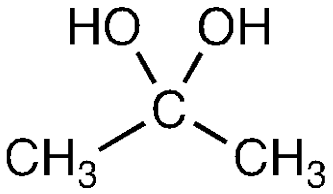
Bonding in Ethylene



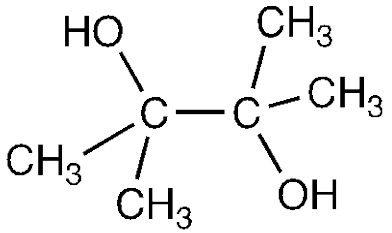
2021 National Exam

57. Which compound will NOT form in the reaction of acetone (propanone) with aqueous base?

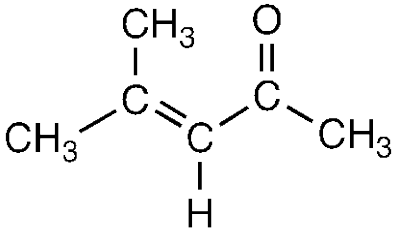
(A)



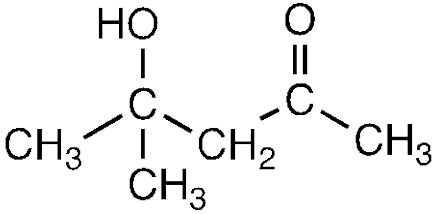
(B)



(C)



(D)



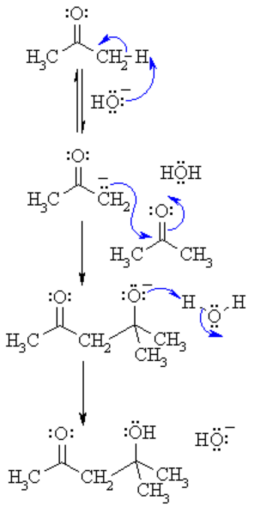
Aldol Condensation of a Ketone

1. MECHANISM OF THE ALDOL REACTION OF A KETONE

Step 1:
First, an acid-base reaction. Hydroxide functions as a base and removes the acidic α-hydrogen giving the reactive enolate.

Step 2:
The nucleophilic enolate attacks the ketone at the electrophilic carbonyl **C** in a nucleophilic addition type process giving an intermediate alkoxide.

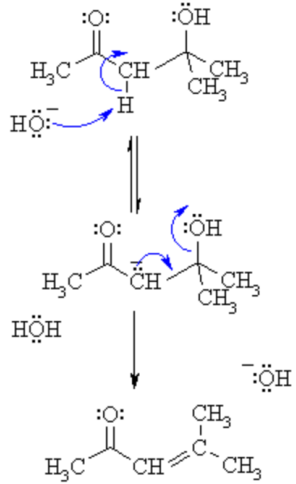
Step 3:
An acid-base reaction. The alkoxide deprotonates a water molecule creating hydroxide and the β-hydroxyketone, the **aldol** product.

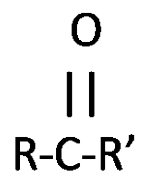


2. MECHANISM OF THE DEHYDRATION OF THE ALDOL PRODUCT

Step 1:
First, an acid-base reaction. Hydroxide functions as a base and removes an acidic α-hydrogen giving the reactive enolate.

Step 2:
The electrons associated with the negative charge of the enolate are used to form the **C=C** and displace the leaving group, regenerating hydroxide giving the conjugated ketone.



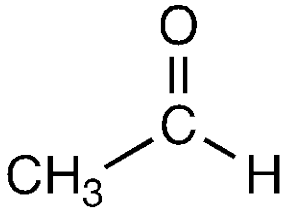


Ketone

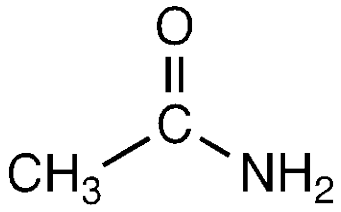
https://www.chem.ucalgary.ca/courses/350/Carey5th/Ch18/ch18-3-5.html

58. Which compound would have the lowest C=O stretching frequency in its infrared spectrum?

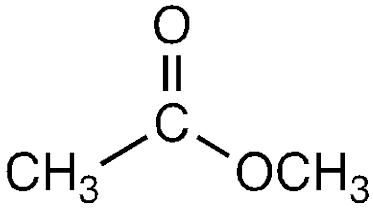
(A)



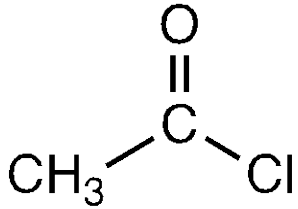
(B)



(C)



(D)

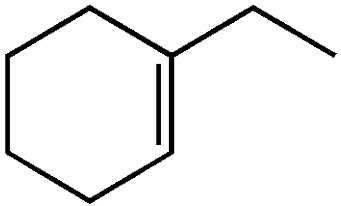


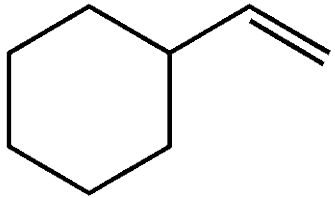
IR Spectrum

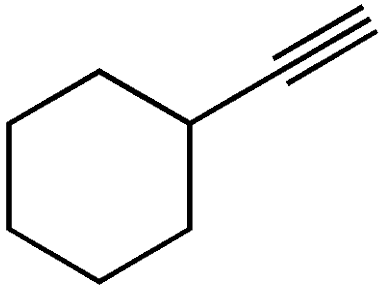
- "Molecules can absorb energy in the infrared region of the electromagnetic spectrum resulting in the increased vibration of covalent bonds. There are two types of vibration resulting in the stretch or the bending of bonds. These vibration occur at specific frequencies (or energies) depending on the bond involved. It is useful to think of the bonds as springs and atoms as weights in order rationalize the energy required for such vibrations."
- "There are two factors affecting the frequency of vibration – the masses of the atoms and the 'stiffness' of the bond.
  - Multiple bonds such as double or triple bonds are stronger and stiffer than single bonds and so their stretching vibrations occur at higher frequency (or energy).
  - The stretching vibration of bonds also depends on the mass of the atoms. The vibration is faster when the bond involves a light atom rather than a heavy when the bond involves a light atom rather than a heavy atom." (i.e. light atoms have higher frequency)
- Diagram of infrared spectrum: https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/infrared/infrared.htm

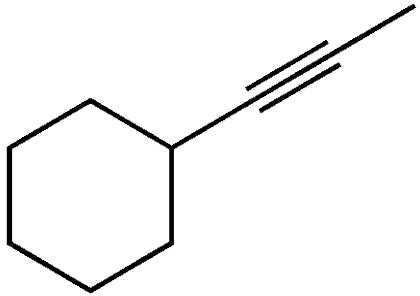
Patrick, Graham. BIOS Instant Notes in Organic Chemistry, CRC Press LLC, 2004. ProQuest Ebook Central

59. Which compound reacts fastest with aqueous acid?

(A) 

(B) 

(C) 

(D) 

2021 National Exam

60. How many possible dipeptides can be formed using the twenty commonly occurring amino acids?

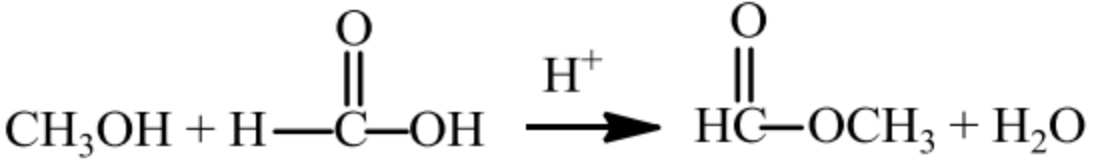
(A) 40 **(B)** 200 **(C)** 210 **(D)** 400

A dipeptide has 2 positions. Each position can be filled by any of the 20 amino acids. So the total combinations are 20 X 20 = 400

PRACTICE QUESTIONS

Past National Exam

58. The reaction below is best classified as



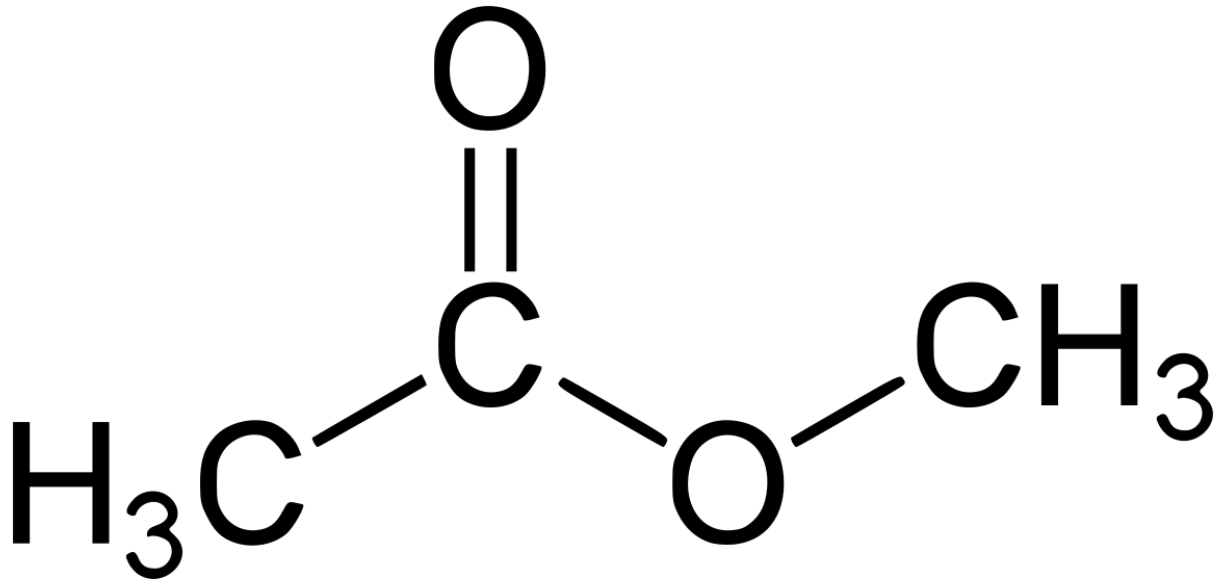
(A) addition.

(B) esterification.

(C) neutralization.

(D) saponification.

Name this Ester



Methyl ethanoate

Past National Exam

58. Which combination of reactants and catalyst will produce methyl propanoate, $CH_3CH_2COOCH_3$, upon heating?

(A) CH_3CH_2OH and CH_3COOH with catalytic NaOH

(B) CH_3CH_2OH and CH_3COOH with catalytic H_2SO_4

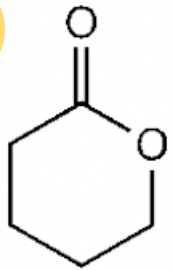
(C) CH_3OH and CH_3CH_2COOH with catalytic NaOH

(D) CH_3OH and CH_3CH_2COOH with catalytic H_2SO_4

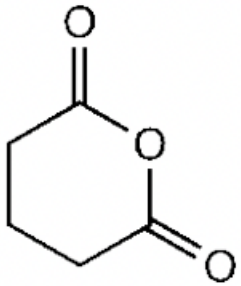
Past National Exam

55. Which compound is an ester?

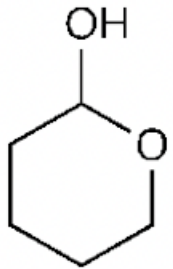
(A)



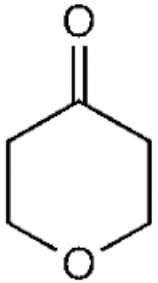
(B)



(C)



(D)



Past National Exam

57. What reaction conditions most effectively convert a carboxylic acid to a methyl ester?

(A) CH_3OH, HCl

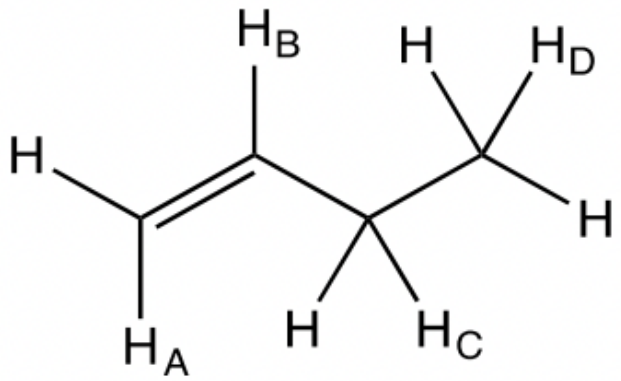
(B) CH_3I, HCl

(C) CH_3OH, NaOH

(D) CH_3I, $SOCl_2$

Past National Exam

57. One hydrogen in 1-butene is replaced by bromine to give a chiral molecule. Which hydrogen is replaced?



(A) H_A **(B)** H_B **(C)** H_C **(D)** H_D

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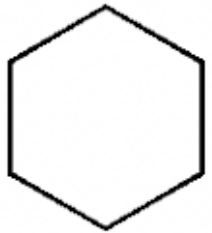
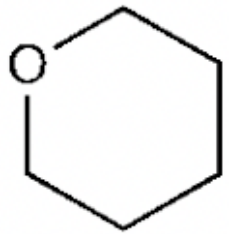
Past National Exam

56. A pure substance is found to rotate the plane of plane-polarized light. Which compound is it?

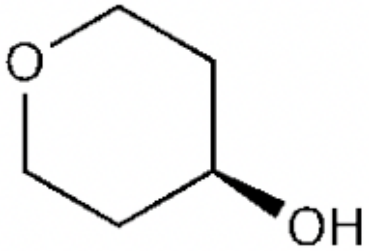
(A)



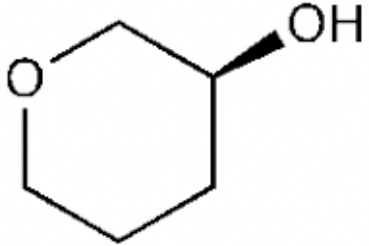
(B)



(C)

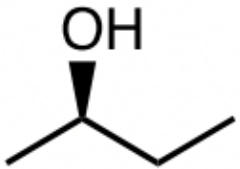


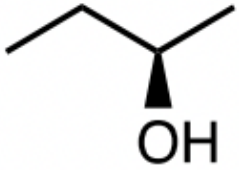
(D)



Past National Exam

55. What is the relationship between the following two molecules?





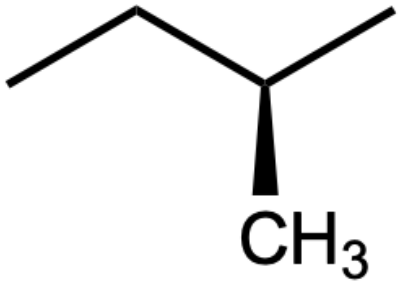
(A) Structural isomers

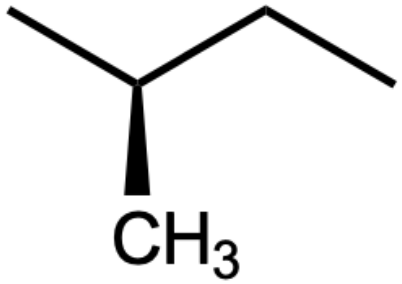
(B) Geometric isomers

(C) Enantiomers

(D) Identical

Also Identical





Past National Exam

55. Which compound can exhibit geometric isomerism?

(A) 1-butene

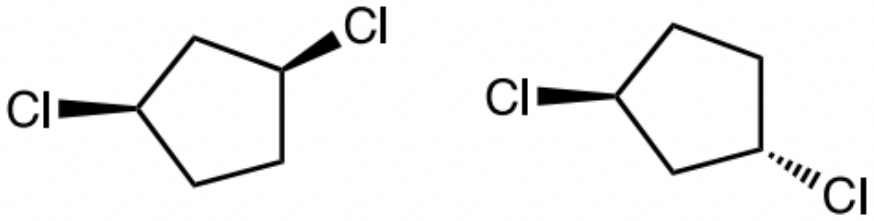
(B) 2-butene

(C) 1-butyne

(D) 2-butyne

Past National Exam

56. What is the relationship between the two compounds shown?



(A) Identical

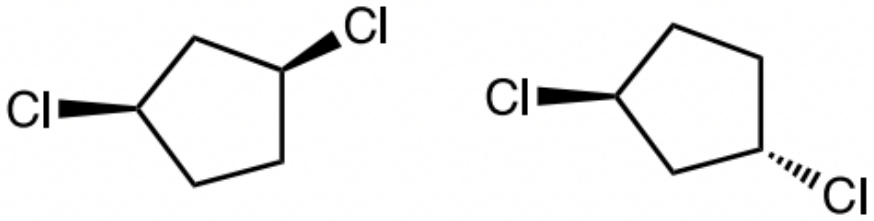
(B) Structural isomers

(C) Geometric isomers

(D) Mirror image isomers

Past National Exam

56. What is the relationship between the two compounds shown?



(A) Identical

(B) Structural isomers

(C) Geometric isomers

(D) Mirror image isomers

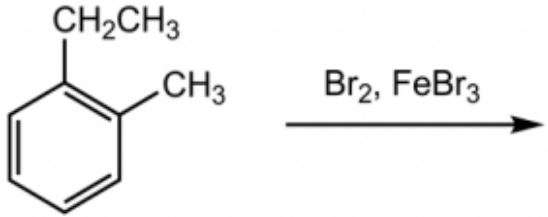
Past National Exam

58. How many distinct compounds have the formula C_5H_{12}?

(A) One **(B)** Two **(C)** Three **(D)** Four

Past National Exam

58. What is the maximum number of monosubstitution products of the aromatic substitution reaction shown?



(A) 1 **(B)** 2 **(C)** 3 **(D)** 4

Past National Exam

56. How many isomers have the formula $C_2H_2Br_2$?

(A) 1 **(B)** 2 **(C)** 3 **(D)** 4