Summer 2018 Org II **Exam 1** **Ch14-17** **(50 points)**

Name: _____

(1-10) are True/False. (10pts)

1) "*Conjugation*" means three or more, consecutive, aligned and interacting p orbitals.

2) Normal ethers are unreactive under neutral and basic conditions.

3) Clemmensen and Birch created the rules that predict whether pericyclic reactions are "allowed" or "forbidden".

4) Fluorobenzene undergoes nitration and bromination reactions *slower* than Toluene.

5) 4-Methyl-1,3-dioxane has ten Hydrogens.

6) In an Electrophilic Aromatic Substitution (EAS) reaction, the rate determining step is the endothermic formation of a non-aromatic carbocation sigma complex.

7) In their Molecular Orbital description, *aromatic* species display a "closed bonding shell" π electron configuration.

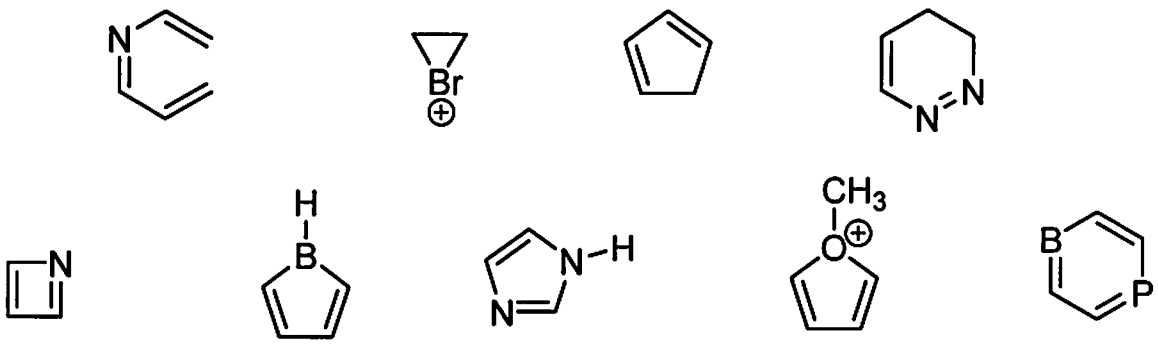
8) Kinetic control is when the speeds of different reactions determines the major product.

9) The *polygon rule* provides a quick way to predict π electron configurations for aromatic (or anti aromatic) systems.

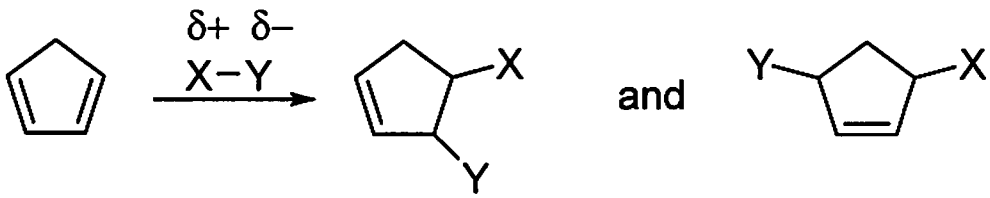
10) Cyclohexa-1,3-diene is more stable than cyclohexa-1,4-diene.

11) Label each diene as either *s-cis* or *s-trans*, and then indicate which is **more stable.** (1+1=2pts)

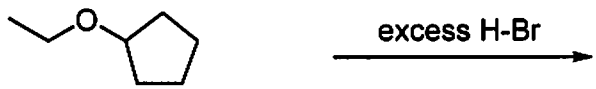
12) Indicate which of the following molecules are aromatic, non-aromatic or anti-aromatic. (Assume all the species are planar). (9pts)

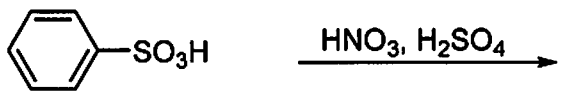


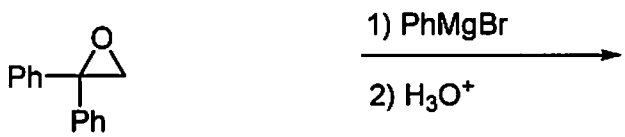
13) (4pts) Draw the mechanism (*i.e. curly arrows*) to show how both products are generated in this electrophilic addition using the polar reagent X-Y.

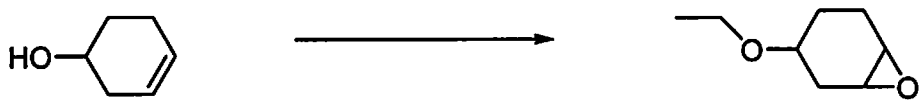


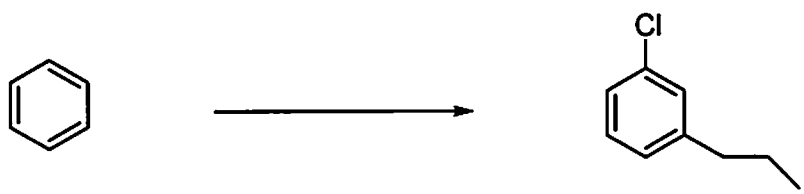
14) Provide the products in the first 3 reactions, and sets of reagents for the last 2 reactions. (5x2=10pts)







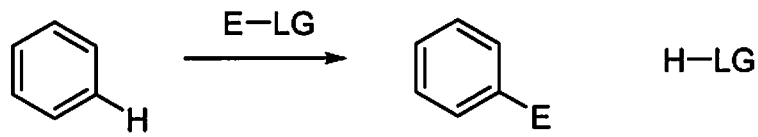




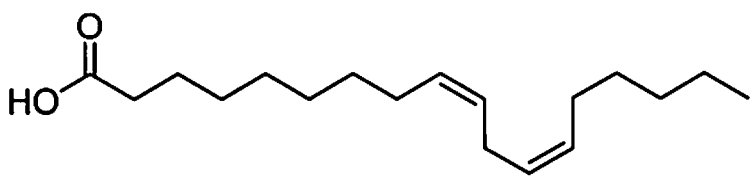
15) (1+1pts) i) State one way that you can distinguish (tell the difference) between "nucleophilic aromatic substitution" and "electrophilic aromatic substitution" processes?

ii) Provide one reason why you are taught about Molecular Orbital theory.

16) Write the mechanism (*i.e. curly arrows*) for the following generic Electrophilic Aromatic Substitution. (*You do **not** need to draw all the resonance structures of the intermediate sigma complex*). (4pts)



17) (4pts) Below is "Linoleic acid" found in nuts and seeds which is an essential fatty acid that must be consumed for proper human health.



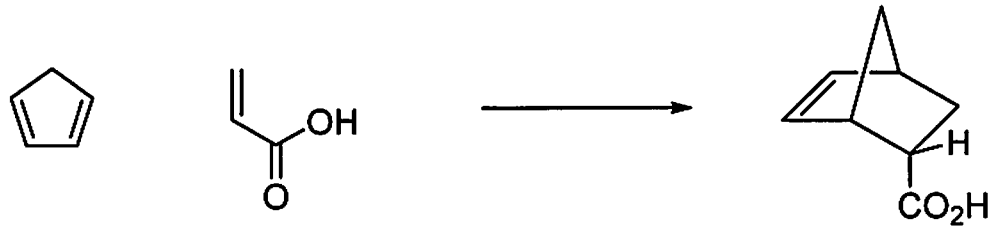
a) How many carbons are in this molecule?

b) How many carbon-carbon π bonds are there?

c) Are the carbon-carbon π bonds *isolated*, *conjugated* or *cumulated*?

d) This molecule has excellent anti-inflammatory and anti-oxidant properties. In "organic chemistry" terms this means it can react to give a *stable* free-radical. Indicate which <u>hydrogen</u> you think would be removed from Linoleic acid to produce the most stable <u>carbon</u> centered radical (i.e. a radical on a carbon).

18) (1+2+2=5pts). The following reaction is an example of a Diels Alder reaction.



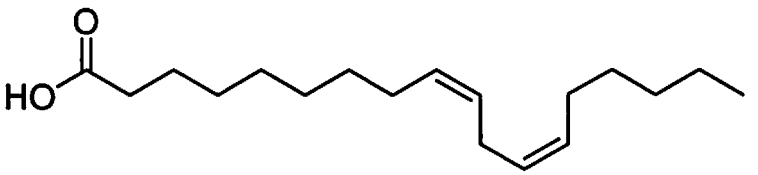
a) Why is this called a [4+2] type of cycloaddition?

b) For Diels Alder reactions, what is the ENDO rule?

c) Draw the mechanism (*i.e. movement of curly arrows*) for this reaction.

****BONUS Points (up to 2 points)****

For Linoleic acid from (Q17) shown again below:



The systematic name of this carboxylic acid is *octadeca-9,12-dienoic acid*, but that is incomplete. The numbers 9 and 12 tell you where the double bonds start, but what is missing from this IUPAC name?

Explain (*guess*) why this fatty acid is also called an *omega-6* (also ω-6, or n-6) version of a fatty acid.

hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
* *Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

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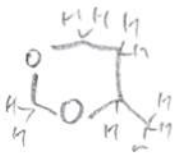
1) "*Conjugation*" means three or more, consecutive, aligned and interacting p orbitals. True

2) Normal ethers are unreactive under neutral and basic conditions. True

3) Clemmensen and Birch created the rules that predict whether pericyclic reactions are "allowed" or "forbidden". f

4) Fluorobenzene undergoes nitration and bromination reactions *slower* than Toluene. True



5) 4-Methyl-1,3-dioxane has ten Hydrogens. True

6) In an Electrophilic Aromatic Substitution (EAS) reaction, the rate determining step is the endothermic formation of a non-aromatic carbocation sigma complex. True

7) In their Molecular Orbital description, *aromatic* species display a "closed bonding shell" π electron configuration. True

8) Kinetic control is when the speeds of different reactions determines the major product. True

9) The *polygon rule* provides a quick way to predict π electron configurations for aromatic (or anti aromatic) systems. True

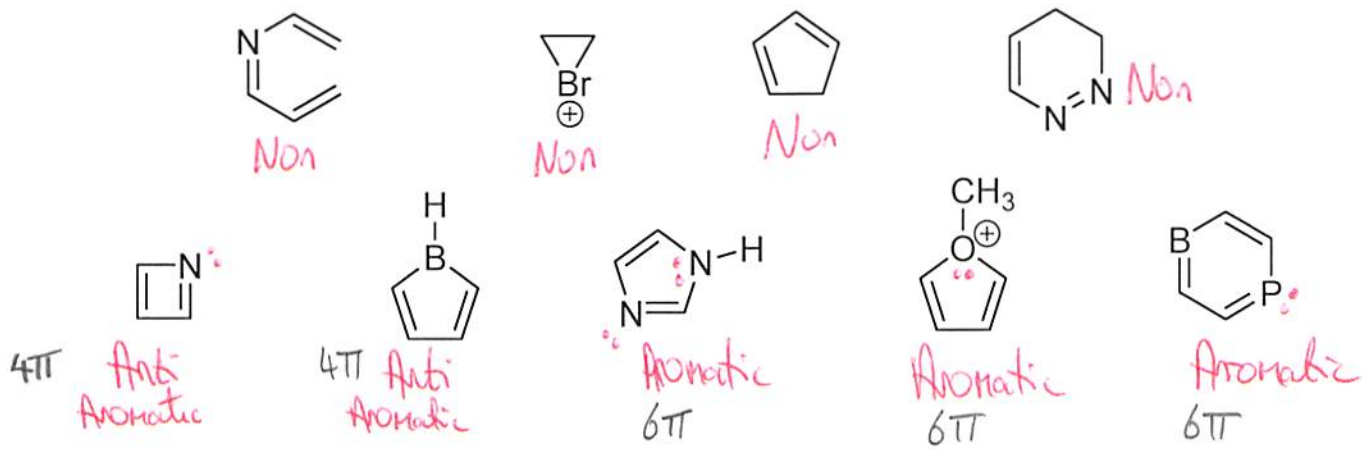
10) Cyclohexa-1,3-diene is more stable than cyclohexa-1,4-diene. True

11) Label each diene as either *s-cis* or *s-trans*, and then indicate which is **more stable**. (1+1=2pts)

More Stable →  S-trans

 S-cis

12) Indicate which of the following molecules are aromatic, non-aromatic or anti-aromatic. (<u>Assume all the species are planar</u>). (9pts)



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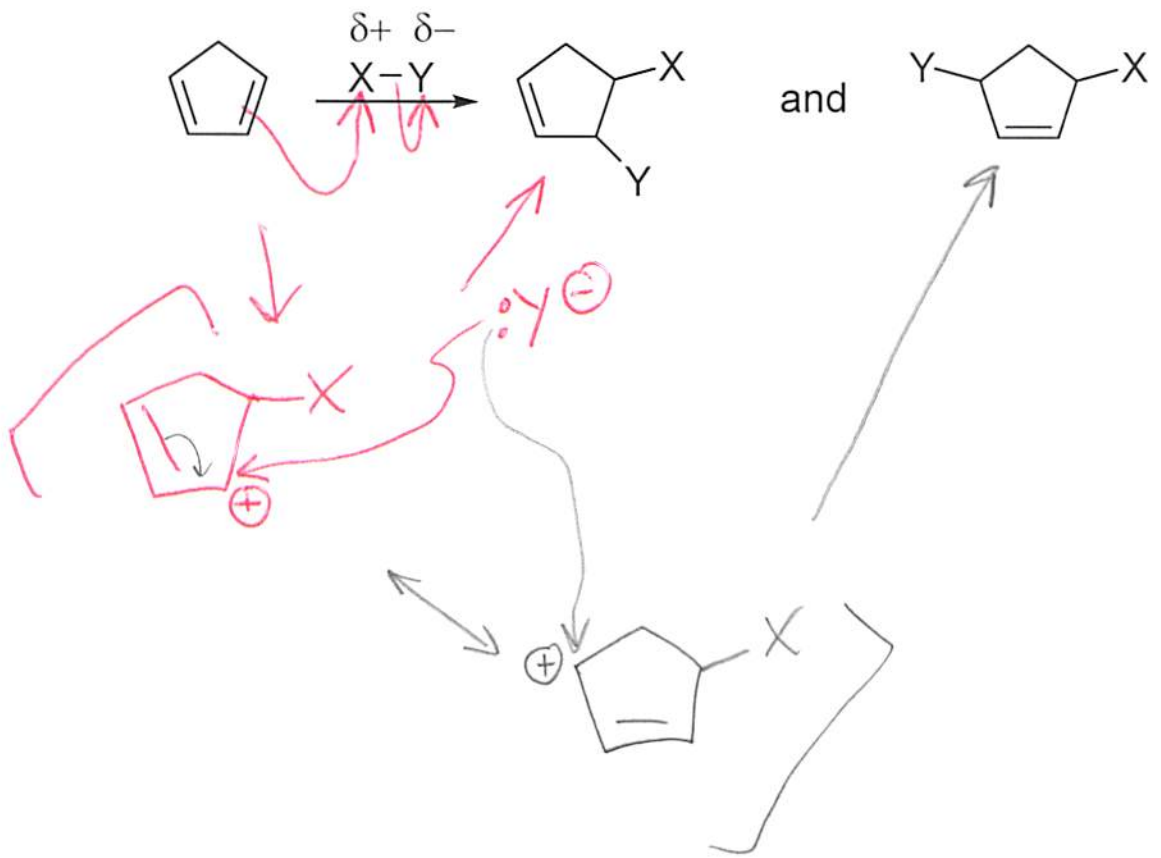

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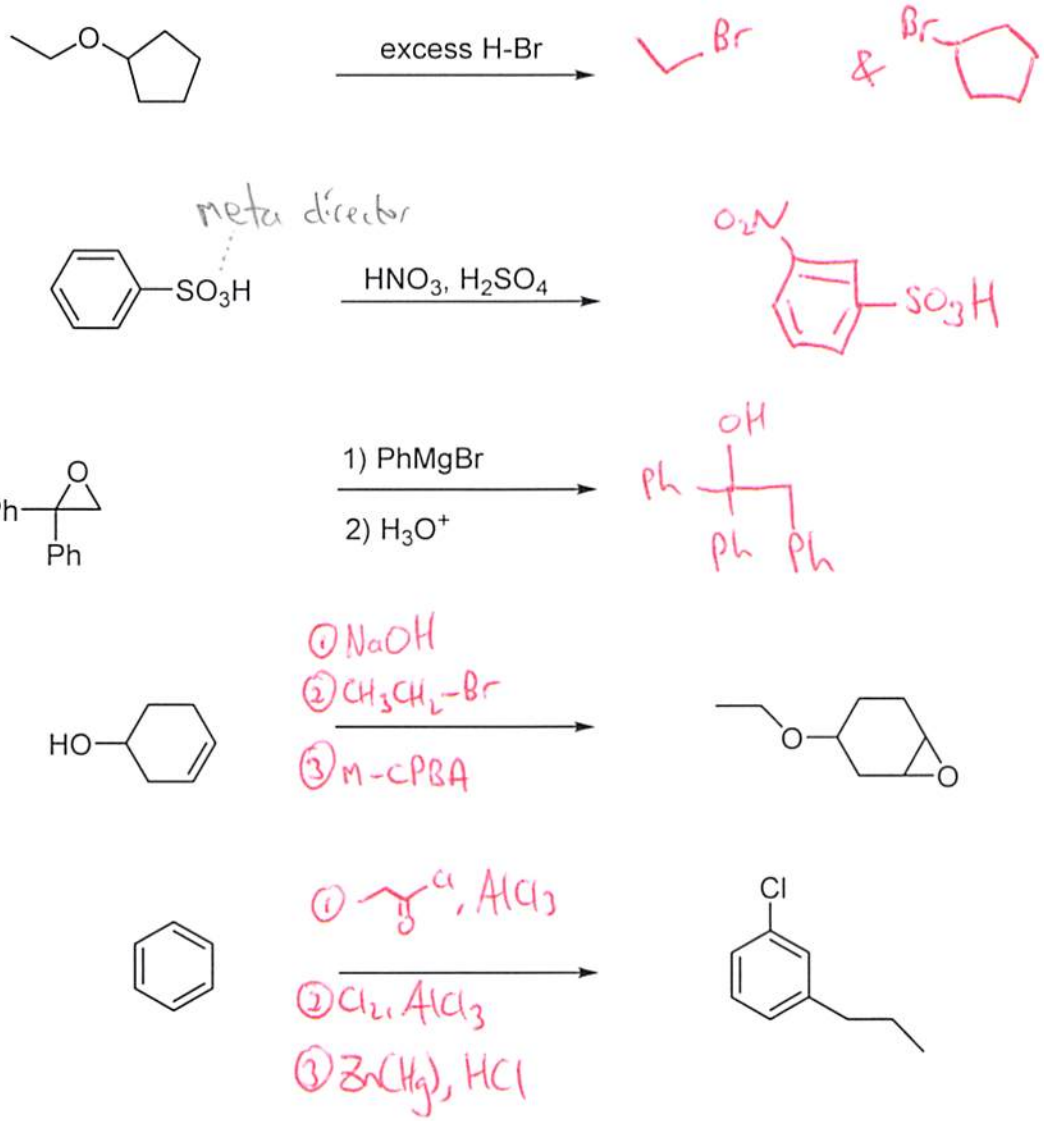


15) (1+1pts) i) State one way that you can distinguish (tell the difference) between "nucleophilic aromatic substitution" and "electrophilic aromatic substitution" processes?

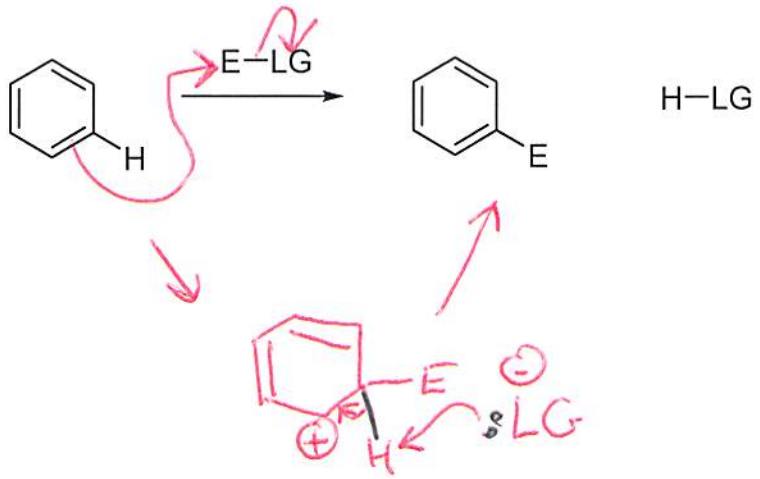
EAS: H gets substituted, NAS: leaving group gets substituted.

EAS: Electrophilic reagent, NAS: Nucleophilic reagent.

ii) Provide one reason why you are taught about Molecular Orbital theory.

- Delocalization of π bonding
- Conjugation stability
- aromaticity
- HOMO/LUMO interactions
- Woodward/Hoffman rules... etc

16) Write the mechanism (*i.e. curly arrows*) for the following generic Electrophilic Aromatic Substitution. (*You do **not** need to draw all the resonance structures of the intermediate sigma complex*). (4pts)



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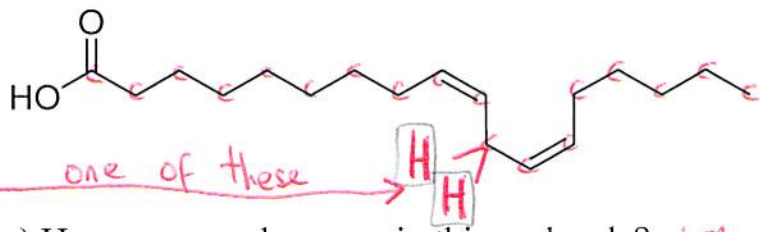


a) How many carbons are in this molecule? 18

b) How many carbon-carbon π bonds are there? 2

c) Are the carbon-carbon π bonds *isolated*, *conjugated* or *cumulated*?

d) This molecule has excellent anti-inflammatory and anti-oxidant properties. In "organic chemistry" terms this means it can react to give a *stable* free-radical. Indicate which <u>hydrogen</u> you think would be removed from Linoleic acid to produce the most stable <u>carbon</u> centered radical (i.e. a radical on a carbon).

This is a radical with the most amount of resonance stabilization (Greatest conjugation).

18) (1+2+2=5pts). The following reaction is an example of a Diels Alder reaction.

diene

dienophile

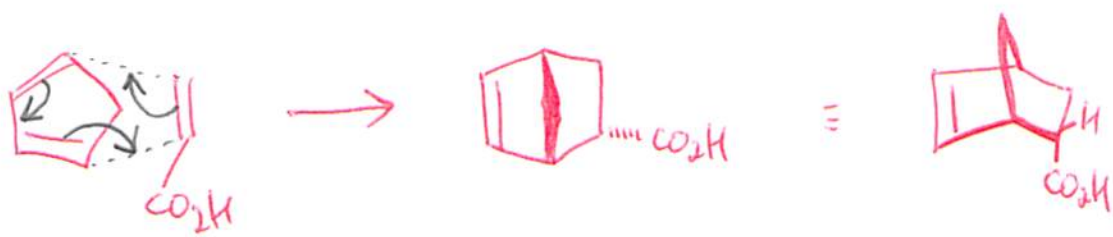
a) Why is this called a [4+2] type of cycloaddition?

Diene provides 4 π electrons, & the dienophile provides 2 π electrons.

b) For Diels Alder reactions, what is the ENDO rule?

If the substituent on the dienophile contains a π bond, there will be a preference for that substituent to go into the Endo position of the product (due to 'secondary orbital overlap').

c) Draw the mechanism (*i.e. movement of curly arrows*) for this reaction.



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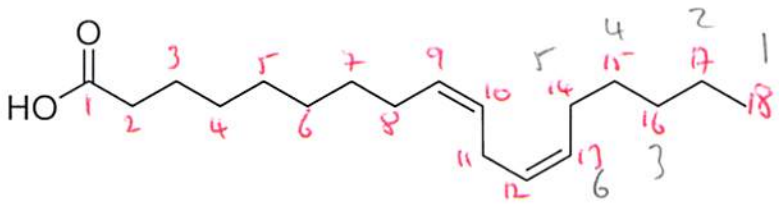

The systematic name of this carboxylic acid is *octadeca-9,12-dienoic acid*, but that is incomplete. The numbers 9 and 12 tell you where the double bonds start, but what is missing from this IUPAC name?

The stereochemistry about the C=C double bonds. (Two different groups on both ends.)

9Z and 12Z. (9Z,12Z)-Octadeca-9,12-dienoic acid

Explain (*guess*) why this fatty acid is also called an *omega-6* (also ω-6, or n-6) version of a fatty acid.

This is a method to describe the position of the last double bond. Omega (ω) means "the end", so "omega minus 6" means 6 carbons from the end of the chain.