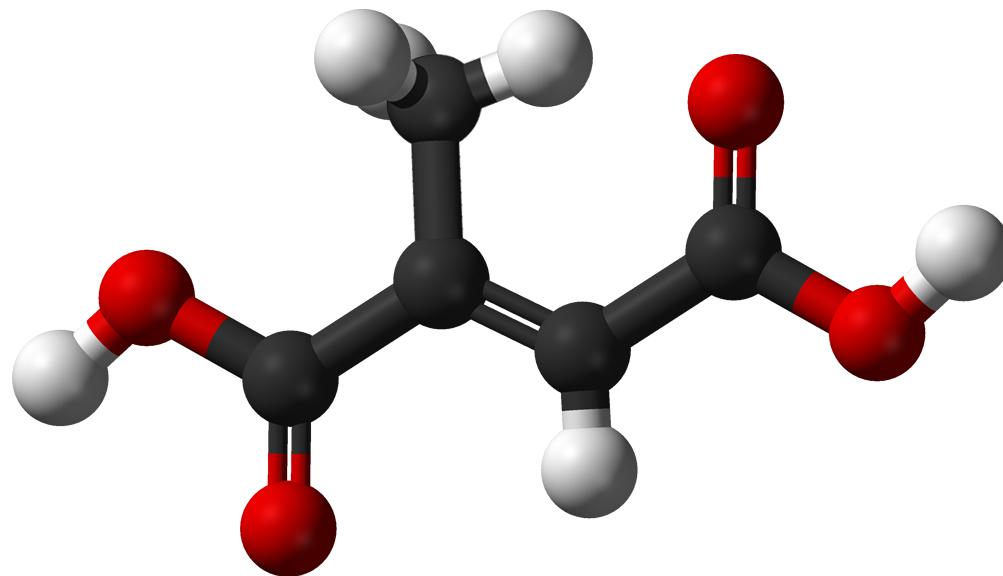


FUNDEMENTALS OF ORGANIC CHEMISTRY



SPLASH 2018
Matthew Yarnall

Periodic Table of the Elements

1 IA 1A	2 IIA 2A	Periodic Table of the Elements												18 VIIIA 8A				
H Hydrogen 1.008		<table border="1"> <tr> <td>Atomic Number</td><td>Symbol</td><td>Name</td><td>Atomic Mass</td></tr> </table>												Atomic Number	Symbol	Name	Atomic Mass	He Helium 4.003
Atomic Number	Symbol	Name	Atomic Mass															
3 Li Lithium 6.941	4 Be Beryllium 9.012	5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180											
11 Na Sodium 22.990	12 Mg Magnesium 24.305	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948											
		3 IIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B							
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 83.798	
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294	
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018	
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]	

5

57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.242	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Alkali Metal

Alkaline
Earth

Trans
Me

10

S

mimetal

Nonmetal

Halogen

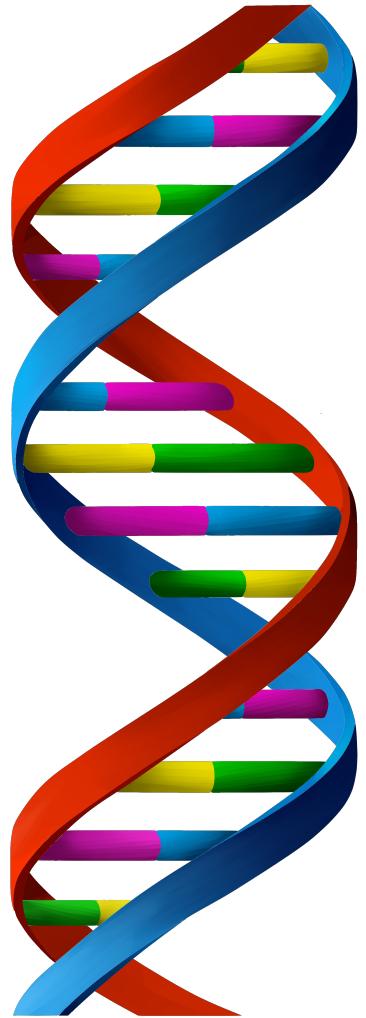
Noble
Gas

Lanthan

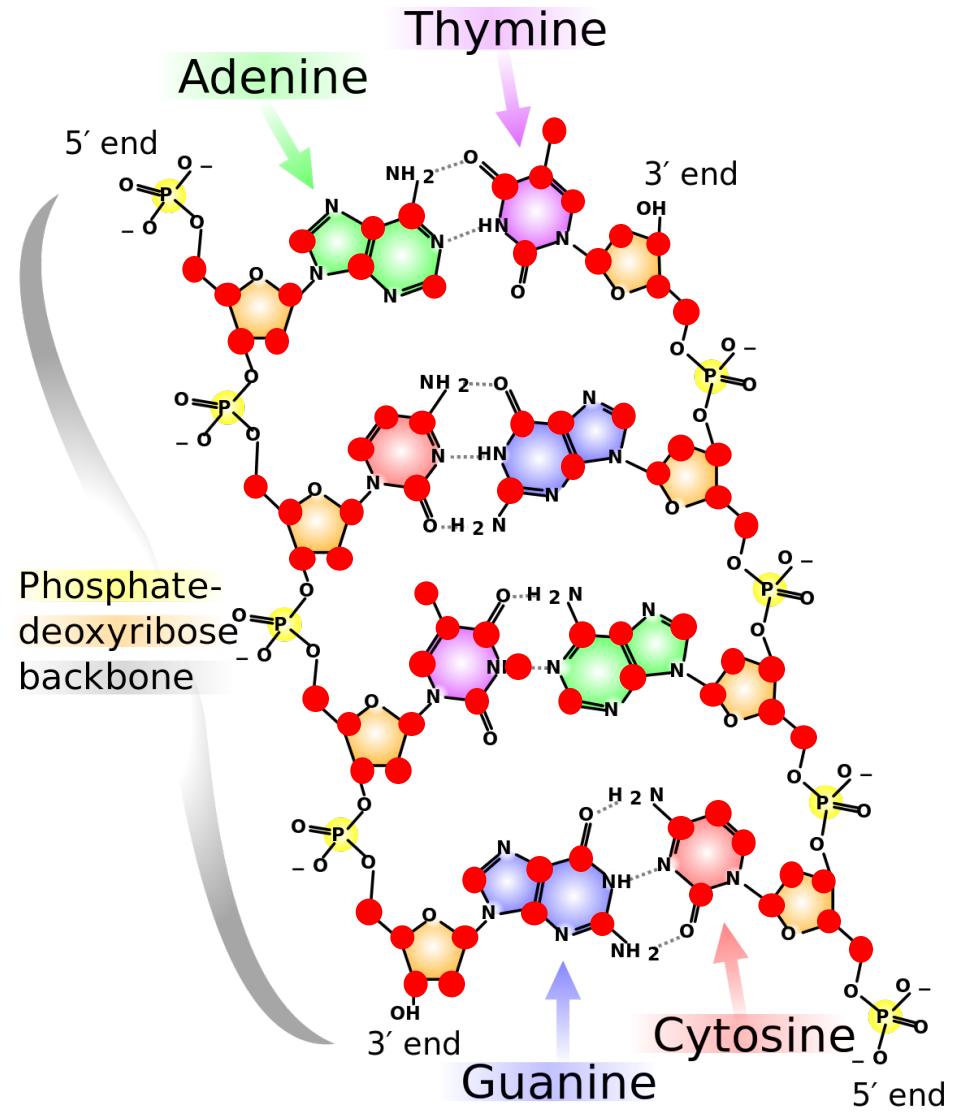
Ac

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Carbon is EVERYWHERE!

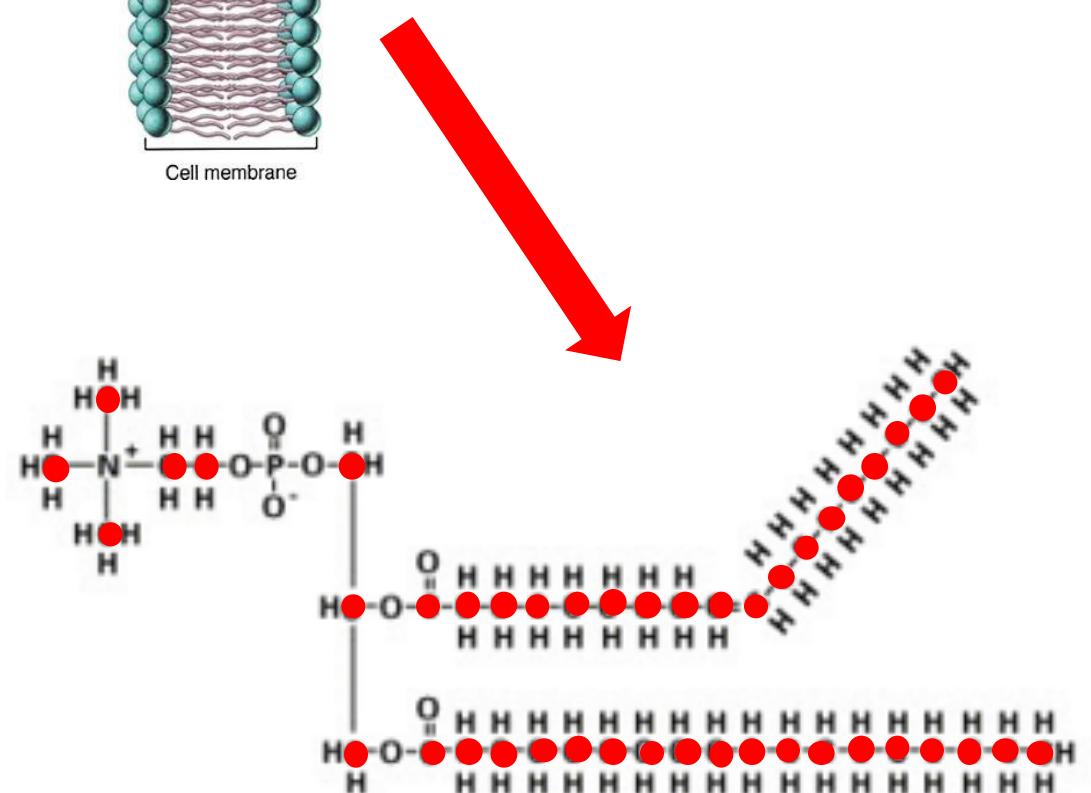
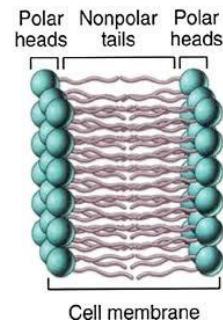
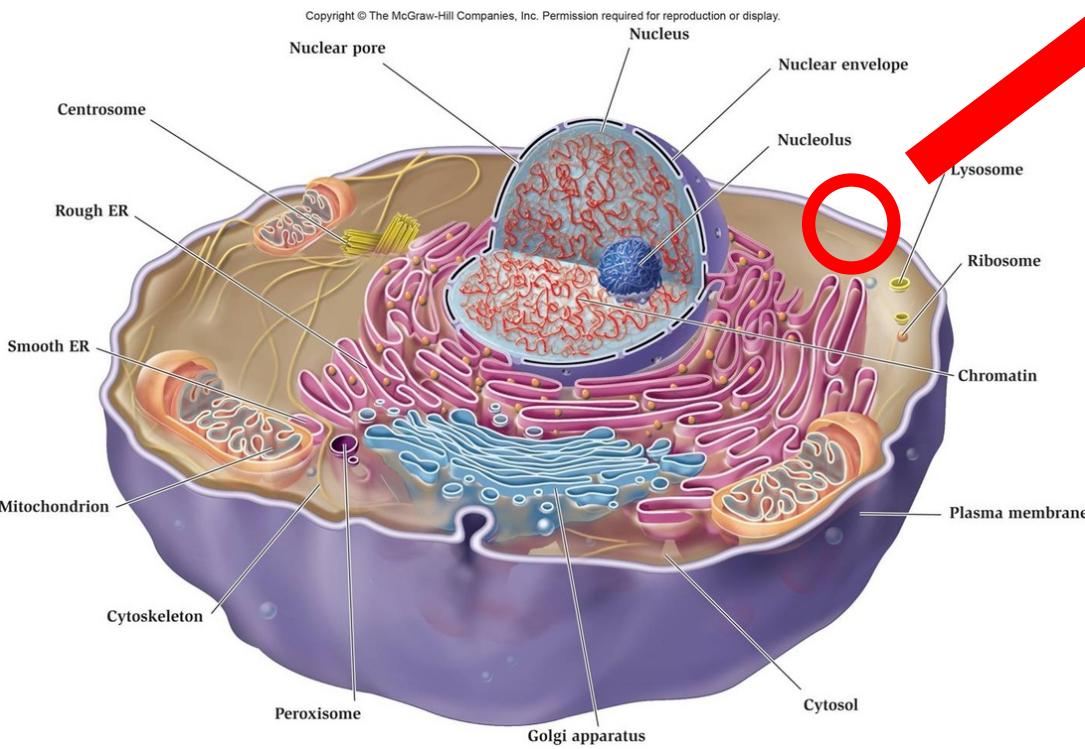


DNA



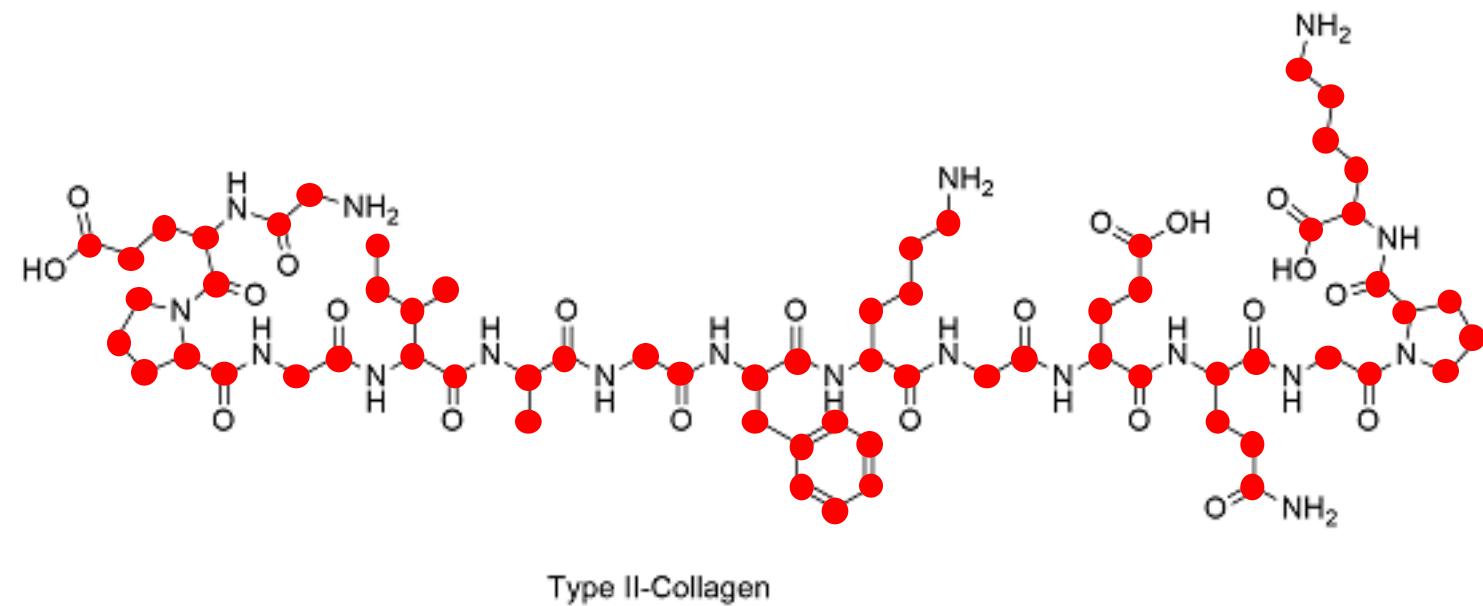
Carbon is EVERYWHERE!

Cell Membranes



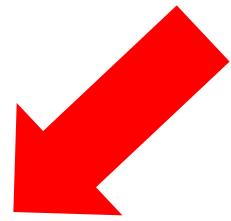
Carbon is EVERYWHERE!

Bones



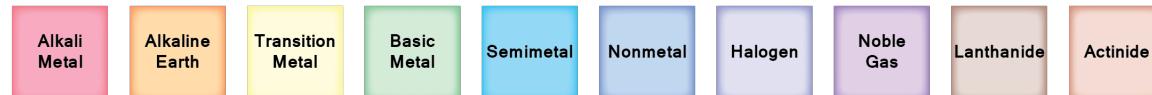
Why Carbon?

The Periodic Table



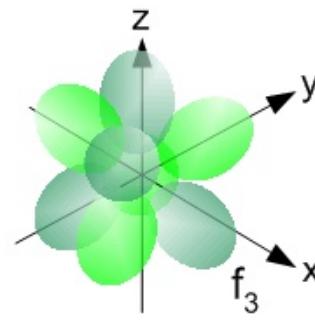
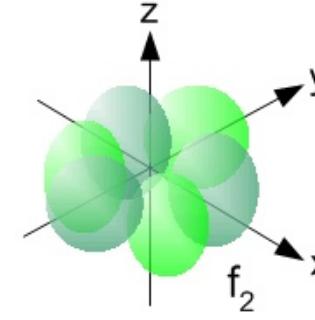
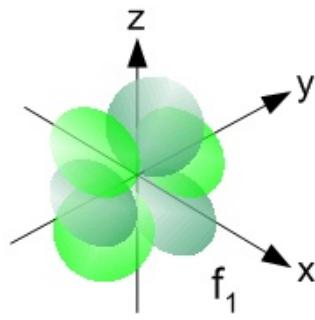
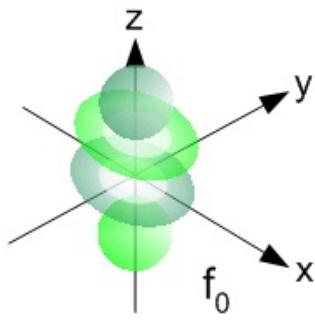
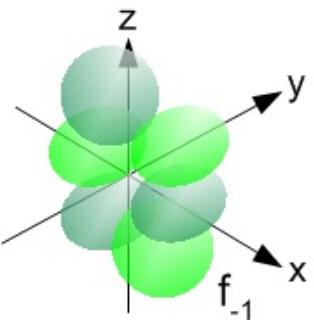
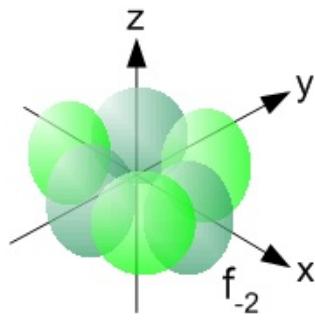
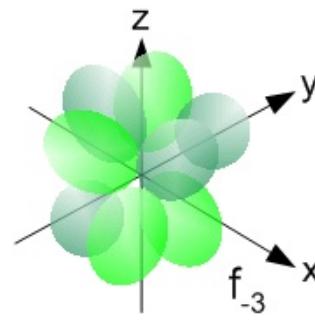
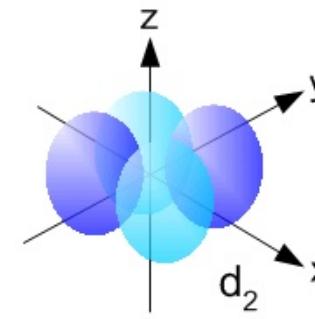
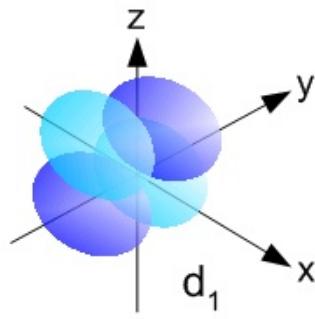
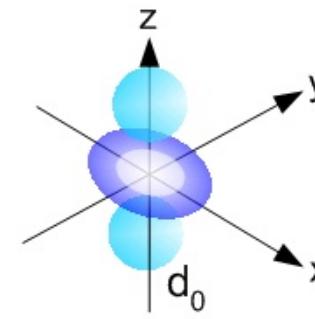
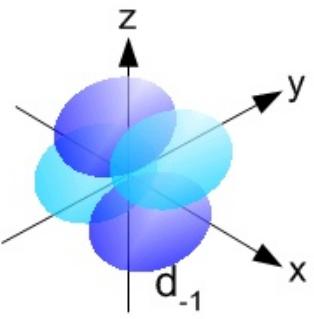
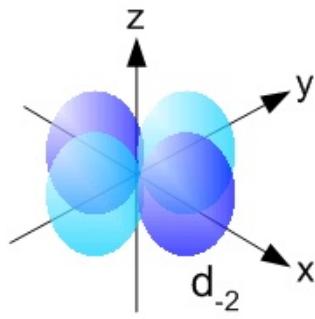
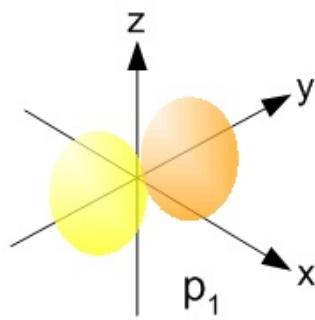
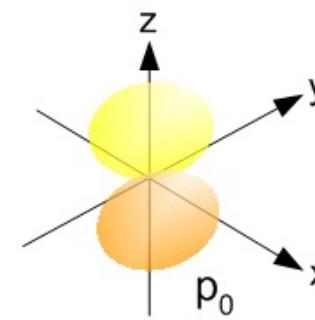
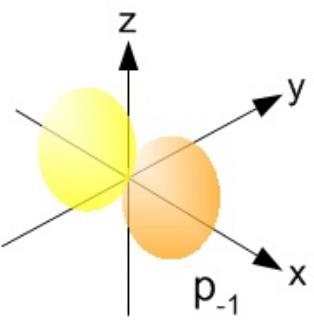
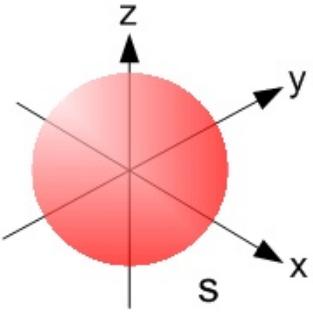
1 IA 1A	H Hydrogen 1.008	2 IIA 2A	Be Beryllium 9.012											18 VIIIA 8A					
3 Li Lithium 6.941	4 Be Beryllium 9.012	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 4.003		
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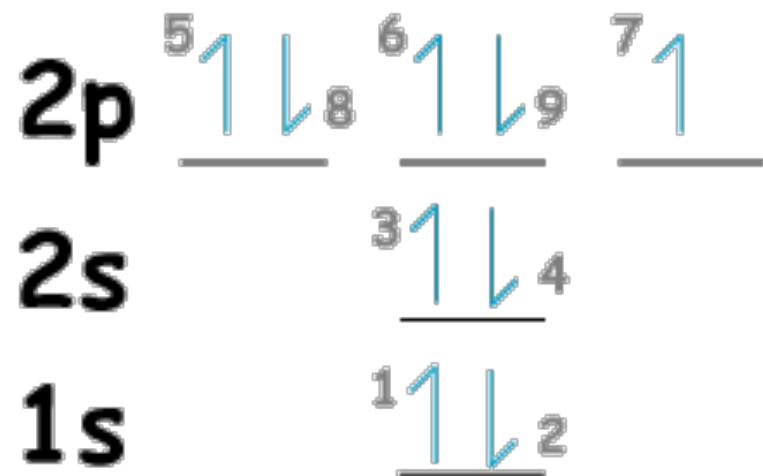


Electron Configurations in the Periodic Table

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
←							4f						→
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
←							5f						→



Orbital diagram for $1s^2 2s^2 2p^5$

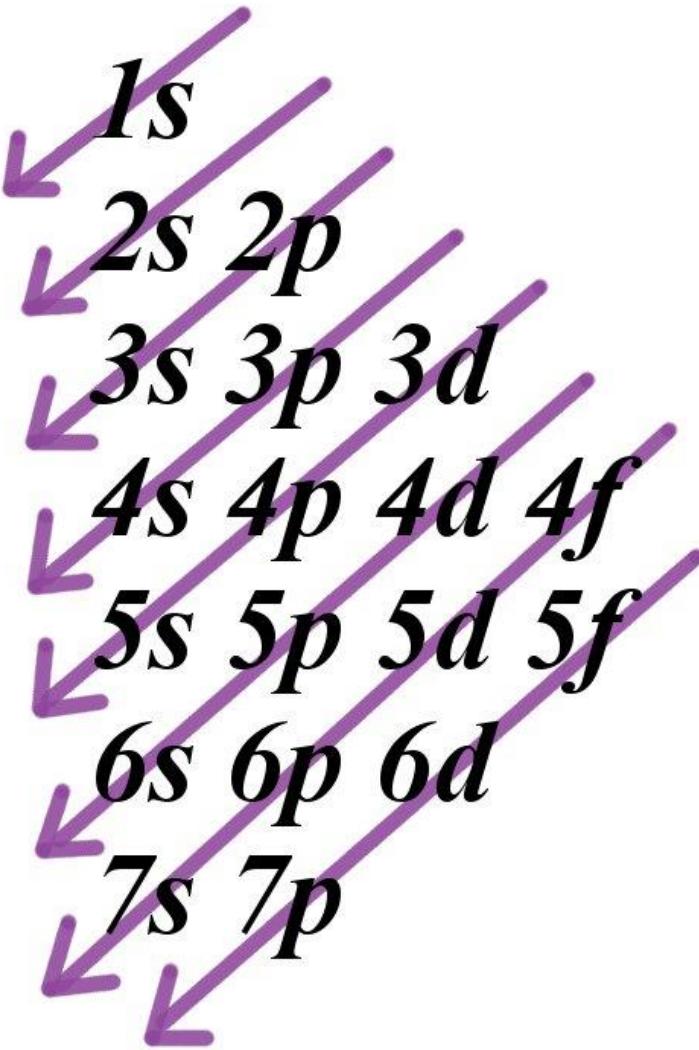


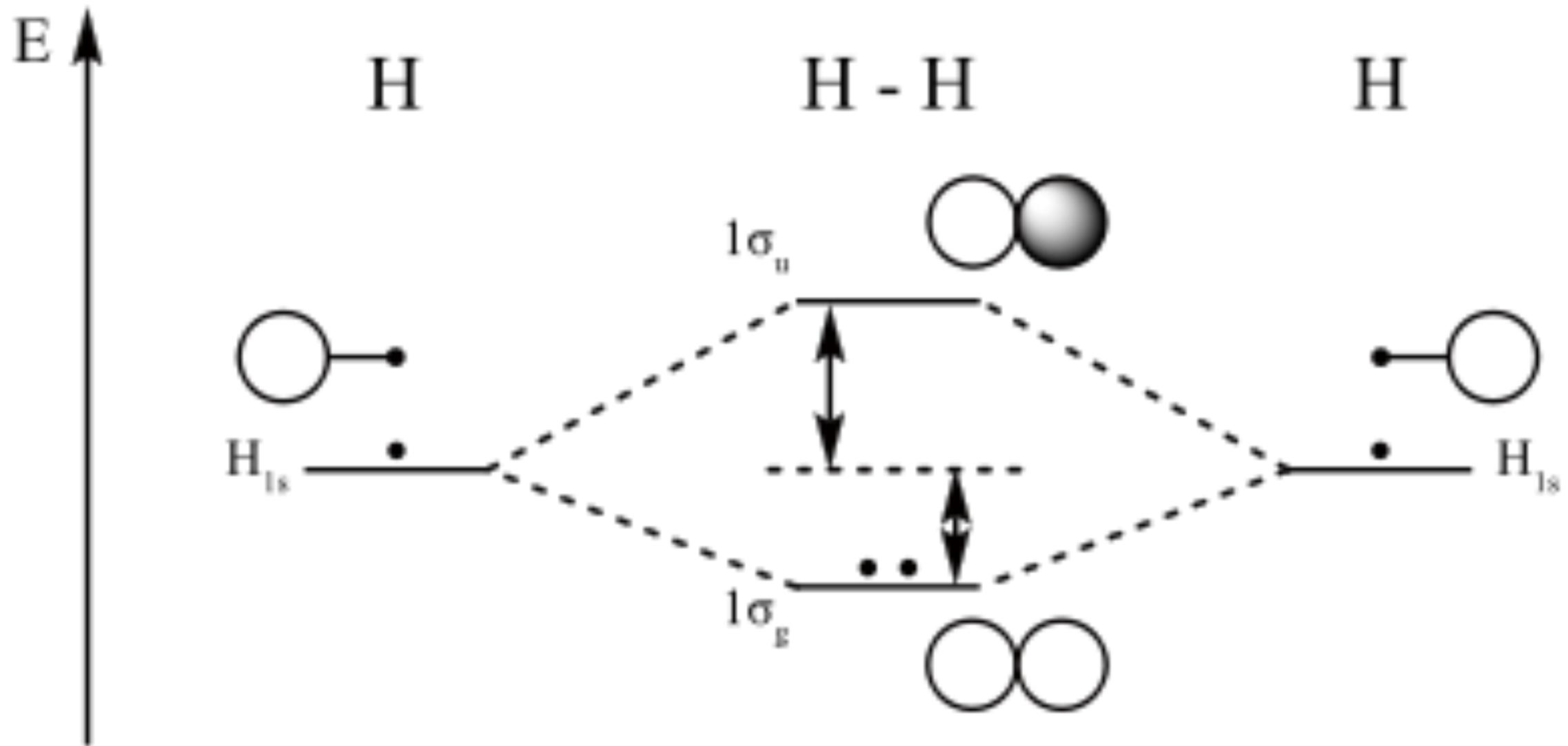
$\begin{array}{c} | \\ \text{1} \end{array}$: e^- with spin = $+1/2$

$\begin{array}{c} \backslash \\ \text{1} \end{array}$: e^- with spin = $-1/2$

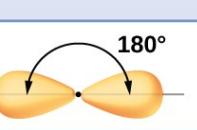
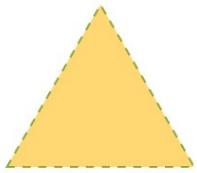
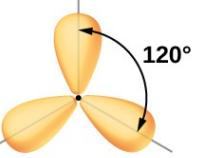
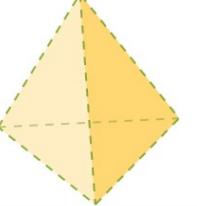
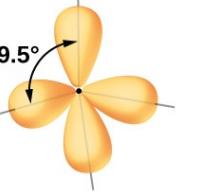
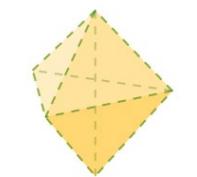
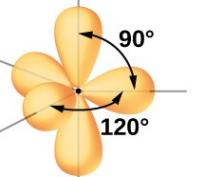
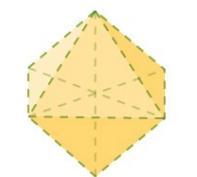
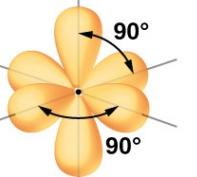
: order e^- is filled

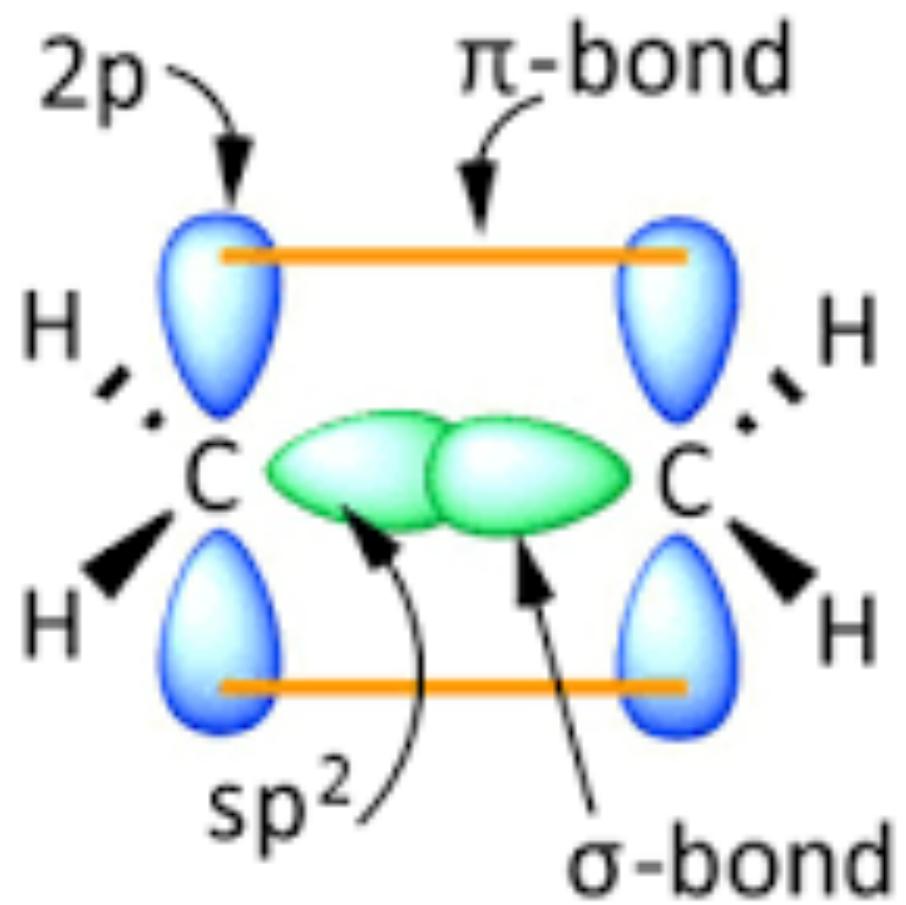
— : orbital



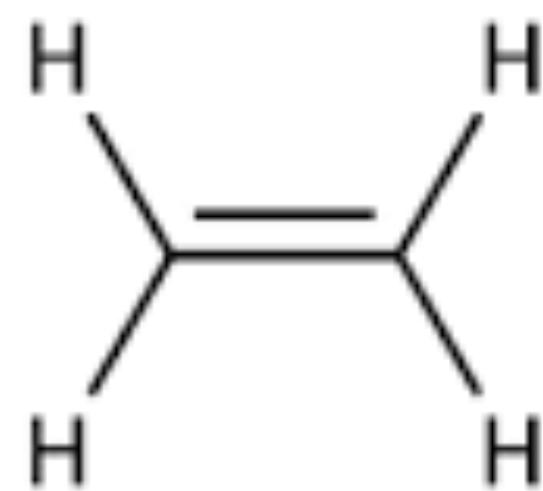


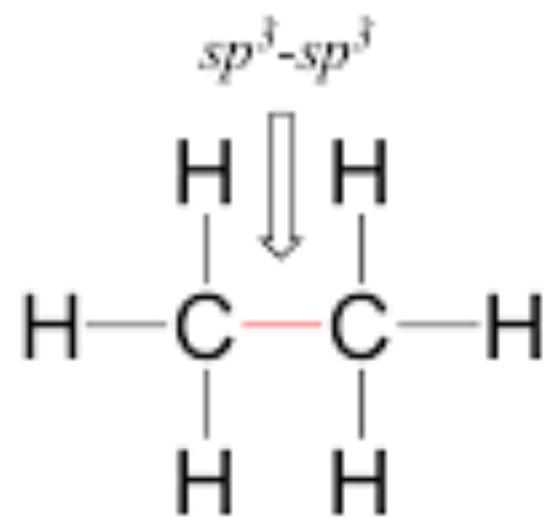
Orbital Hybridization

Regions of Electron Density	Arrangement		Hybridization	
2	-----	linear	sp	 180°
3		trigonal planar	sp^2	 120°
4		tetrahedral	sp^3	 109.5°
5		trigonal bipyramidal	sp^3d	 90° 120°
6		octahedral	sp^3d^2	 90° 90°

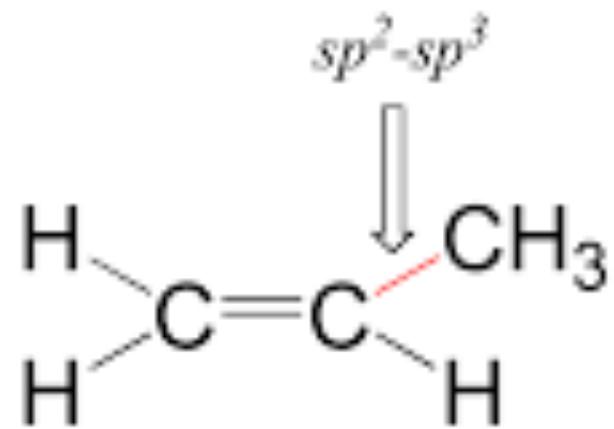


Ethene

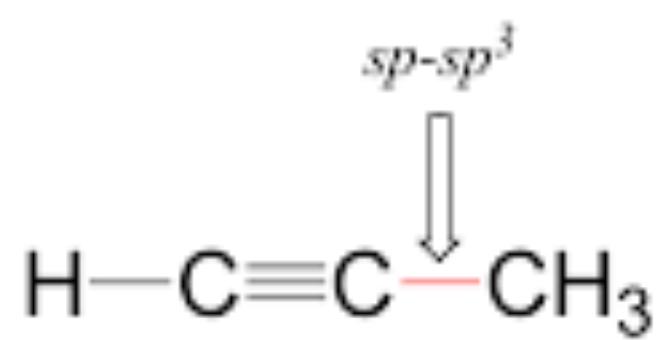




A



B

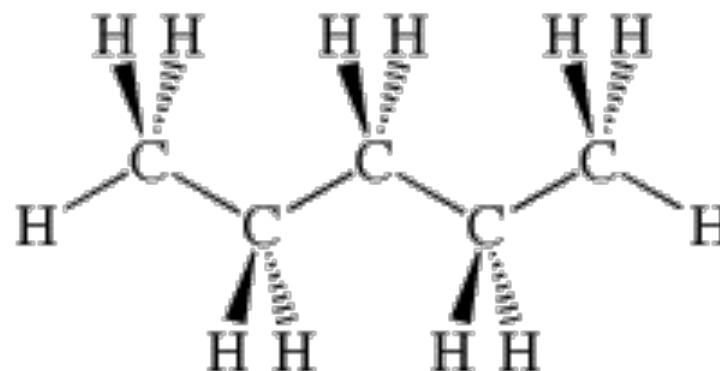


C

Why no quadruple bonds?



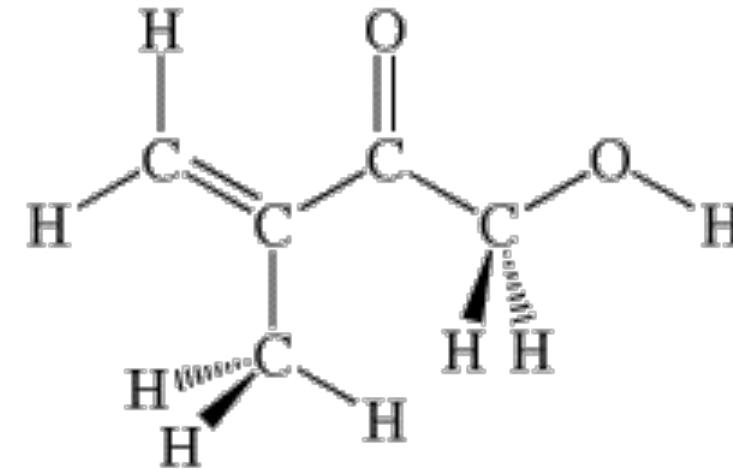
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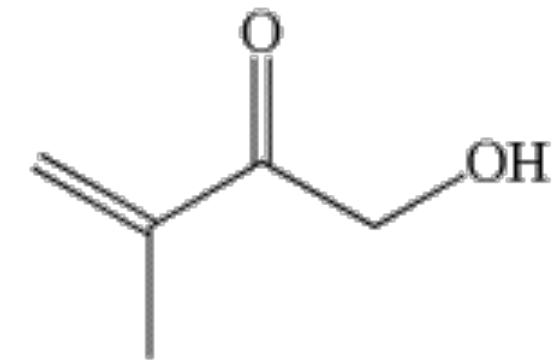
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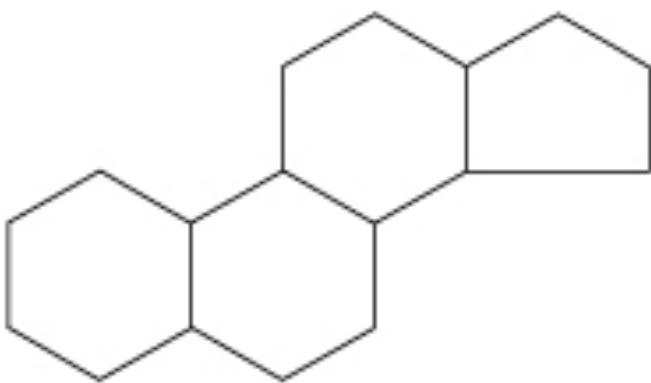


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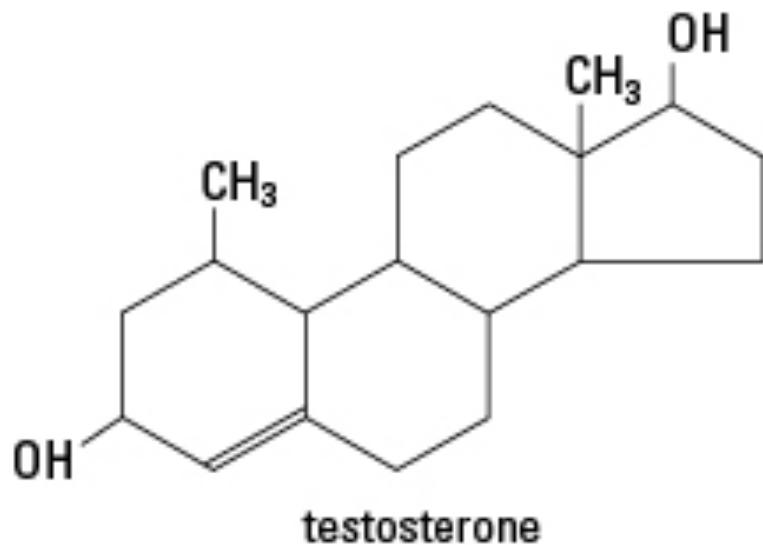


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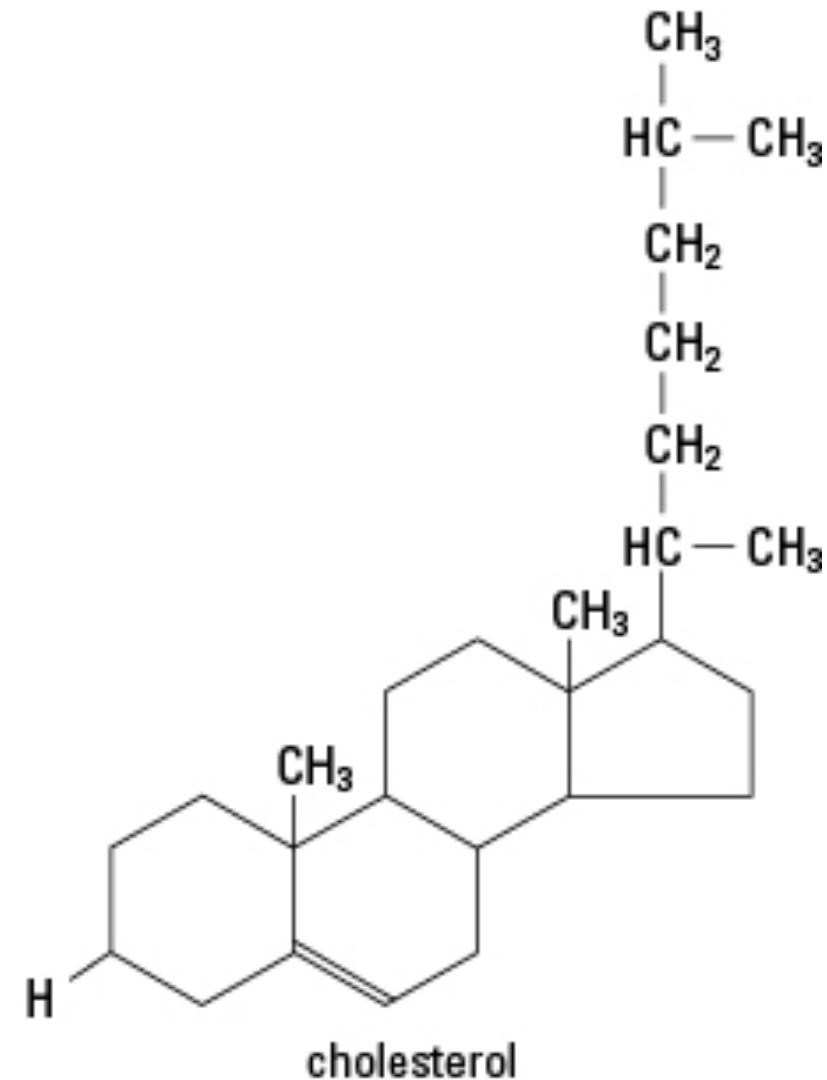




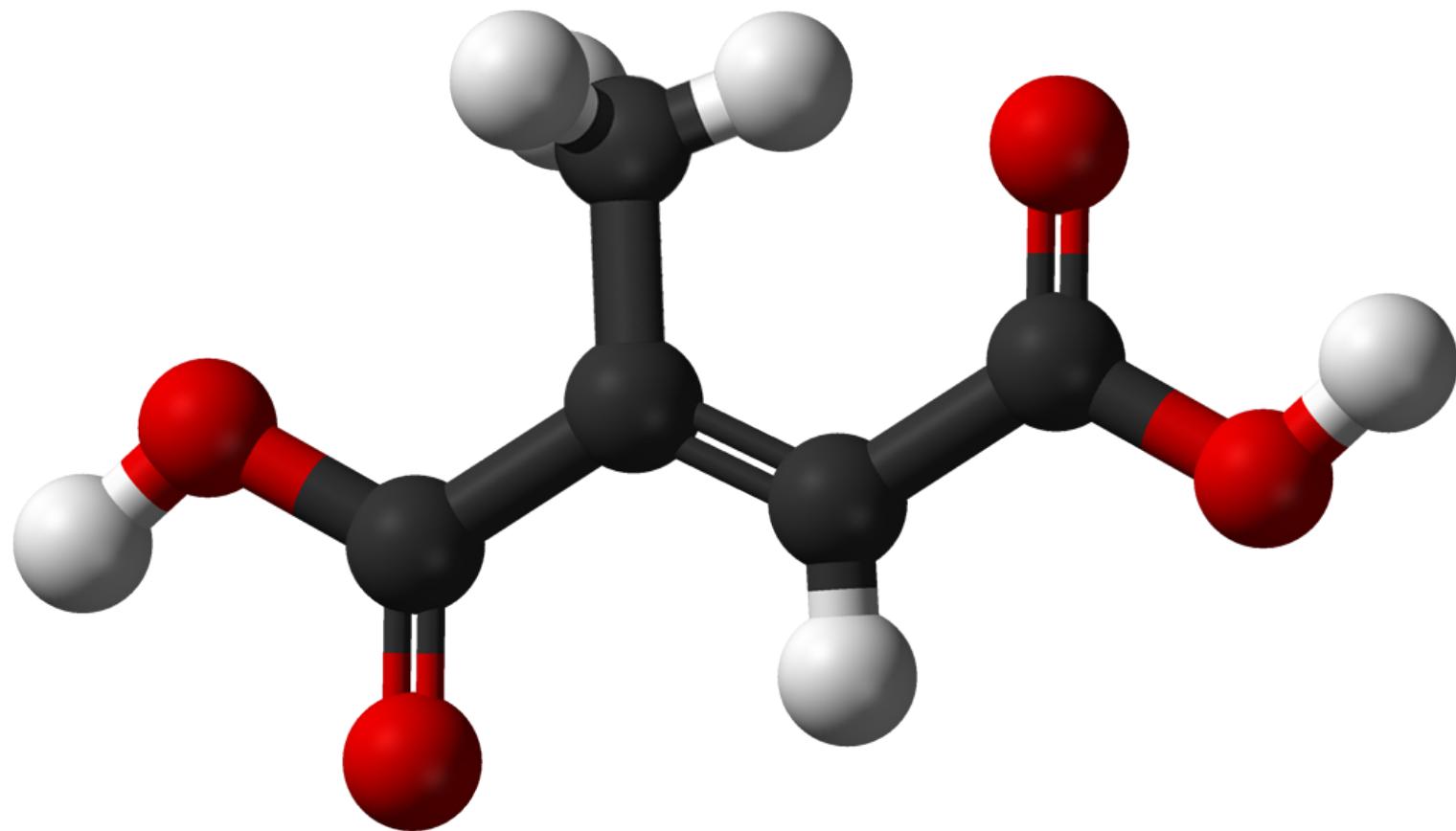
steroid backbone



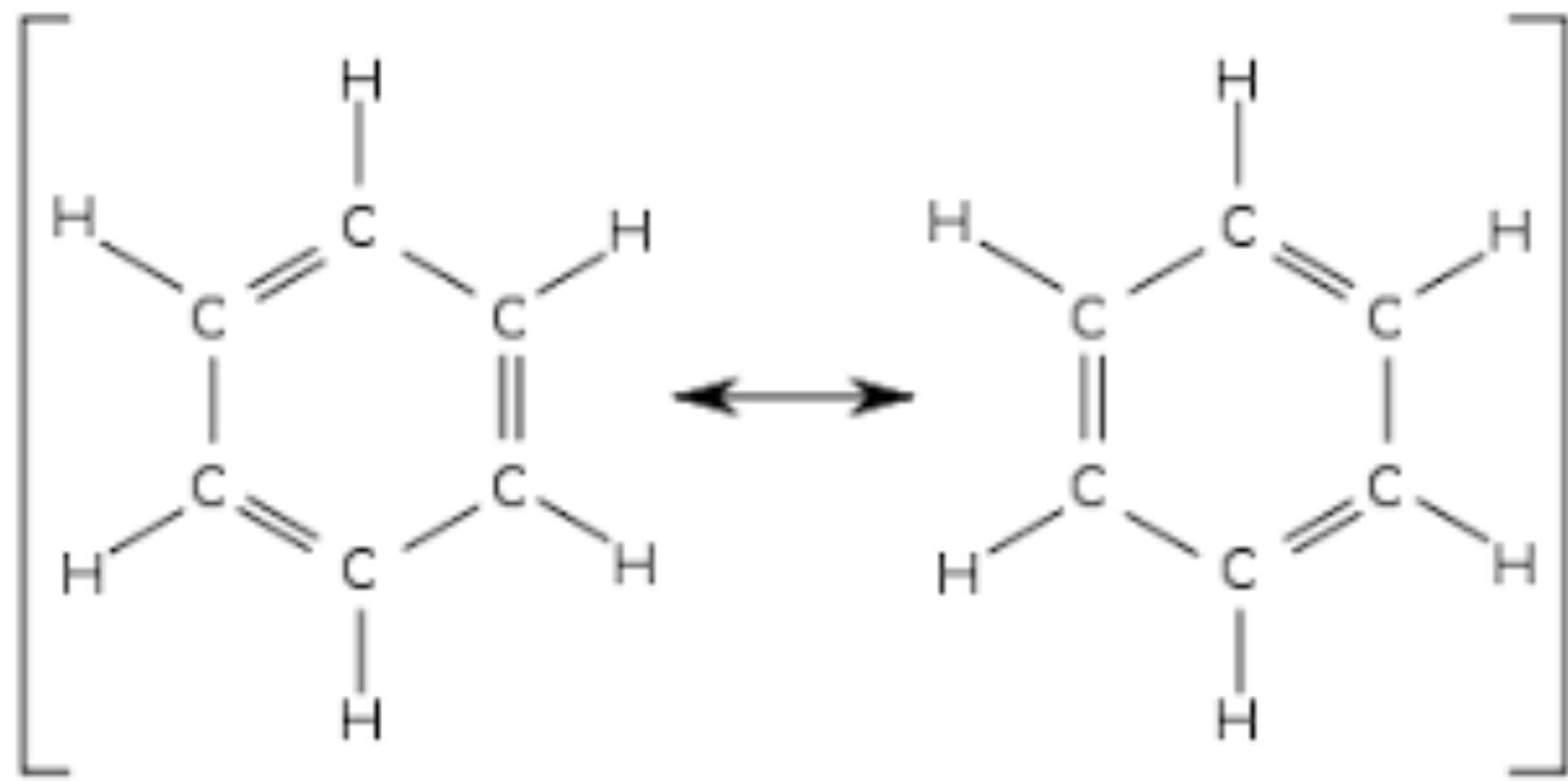
testosterone

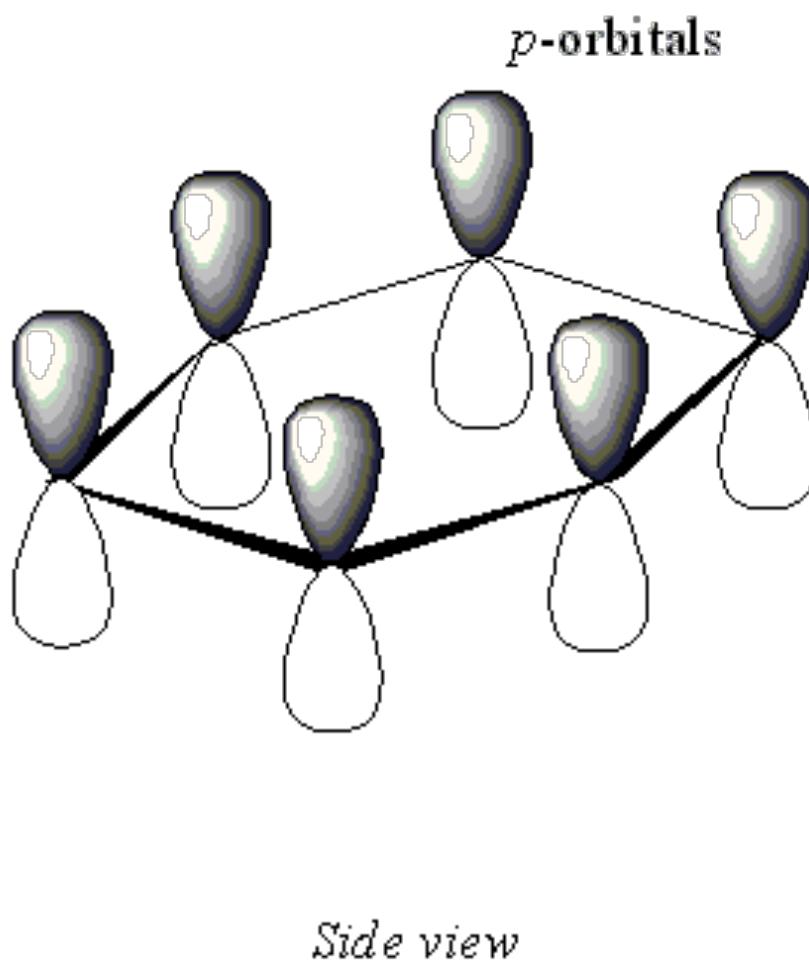
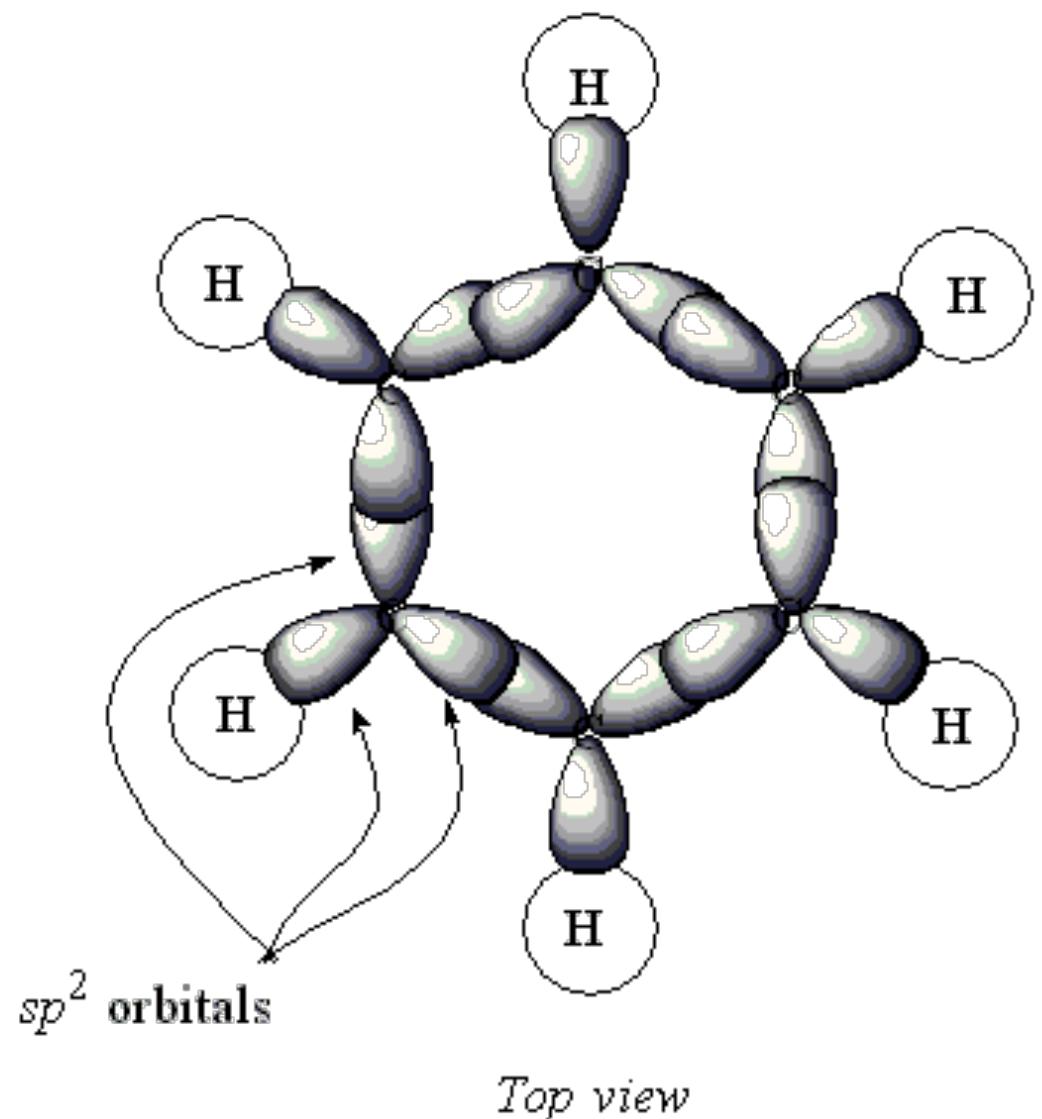


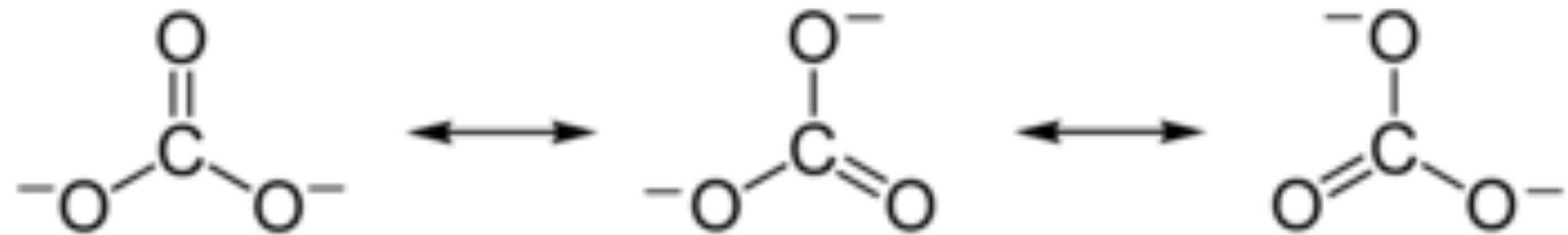
cholesterol

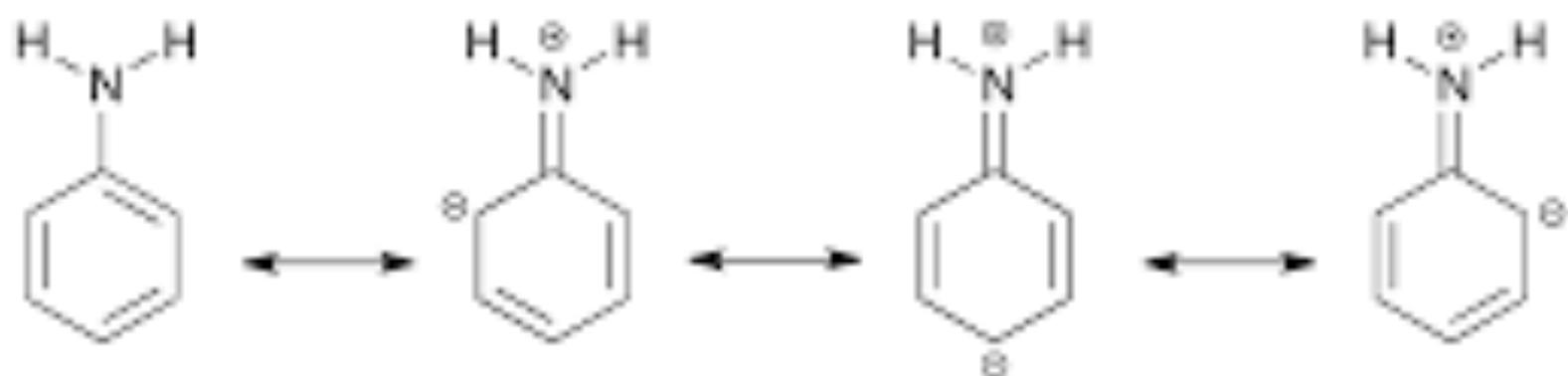


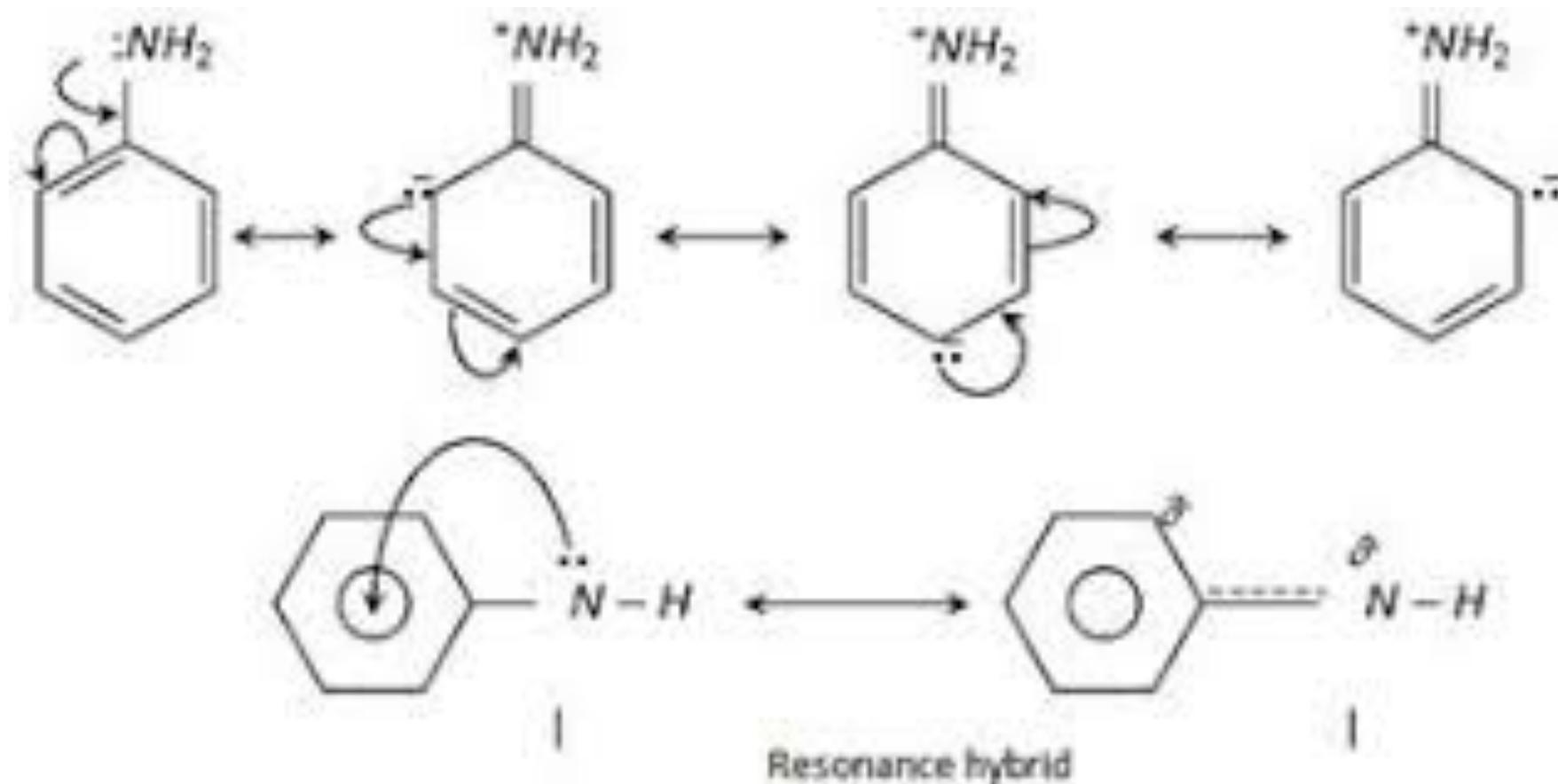
Resonance

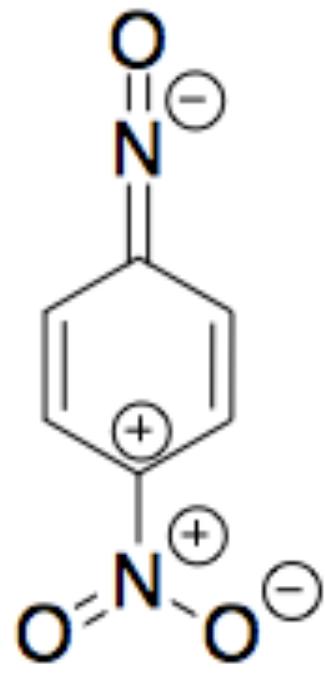




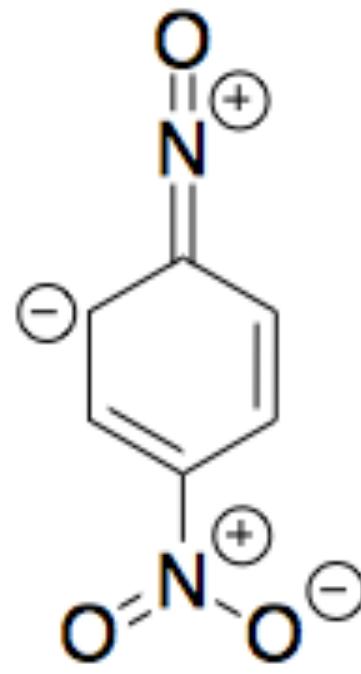




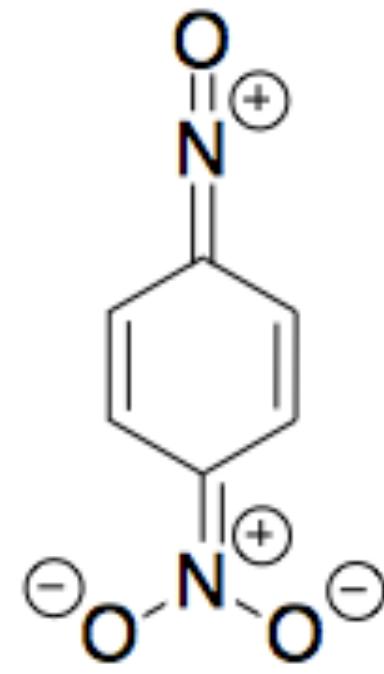




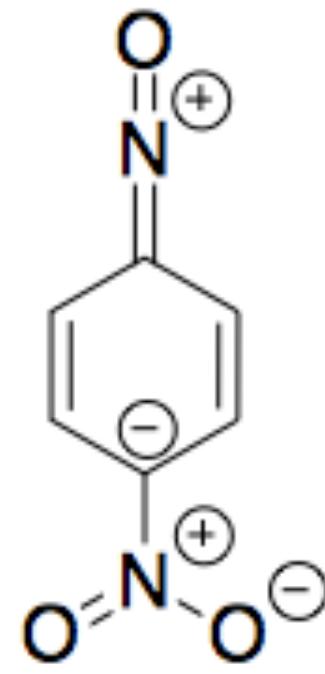
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2

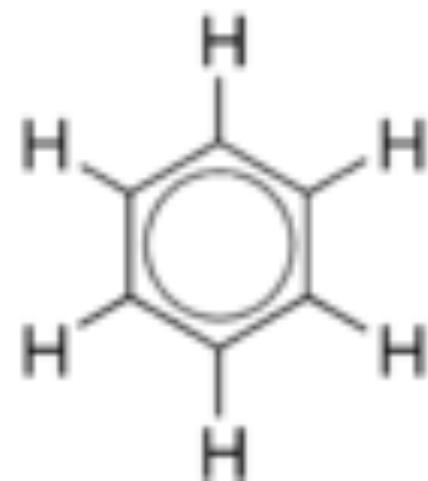
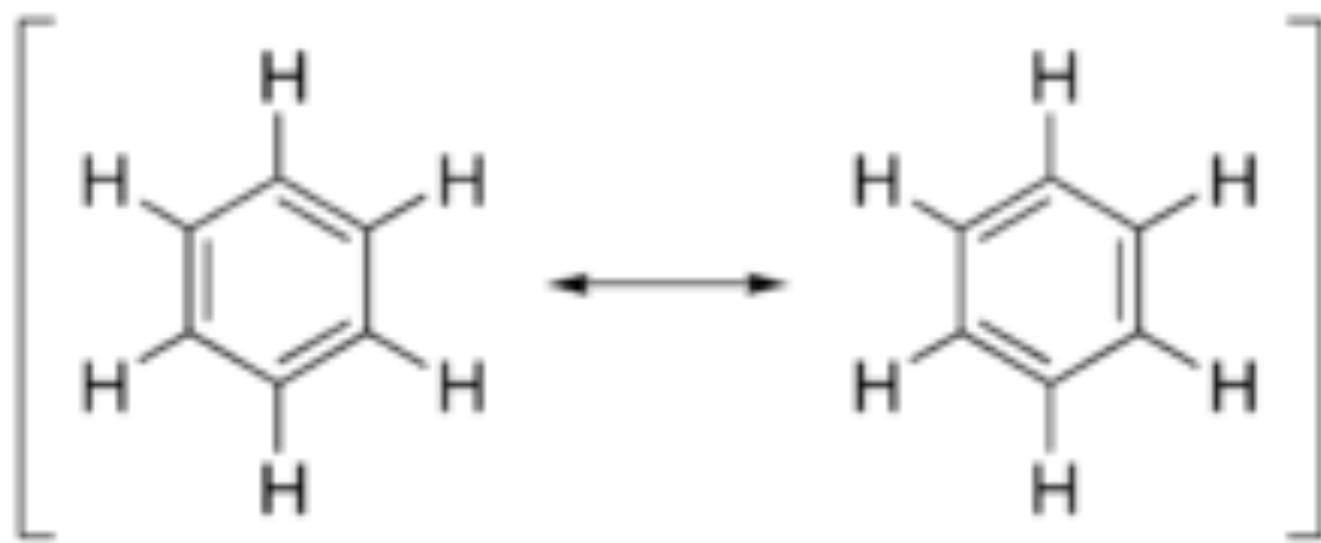


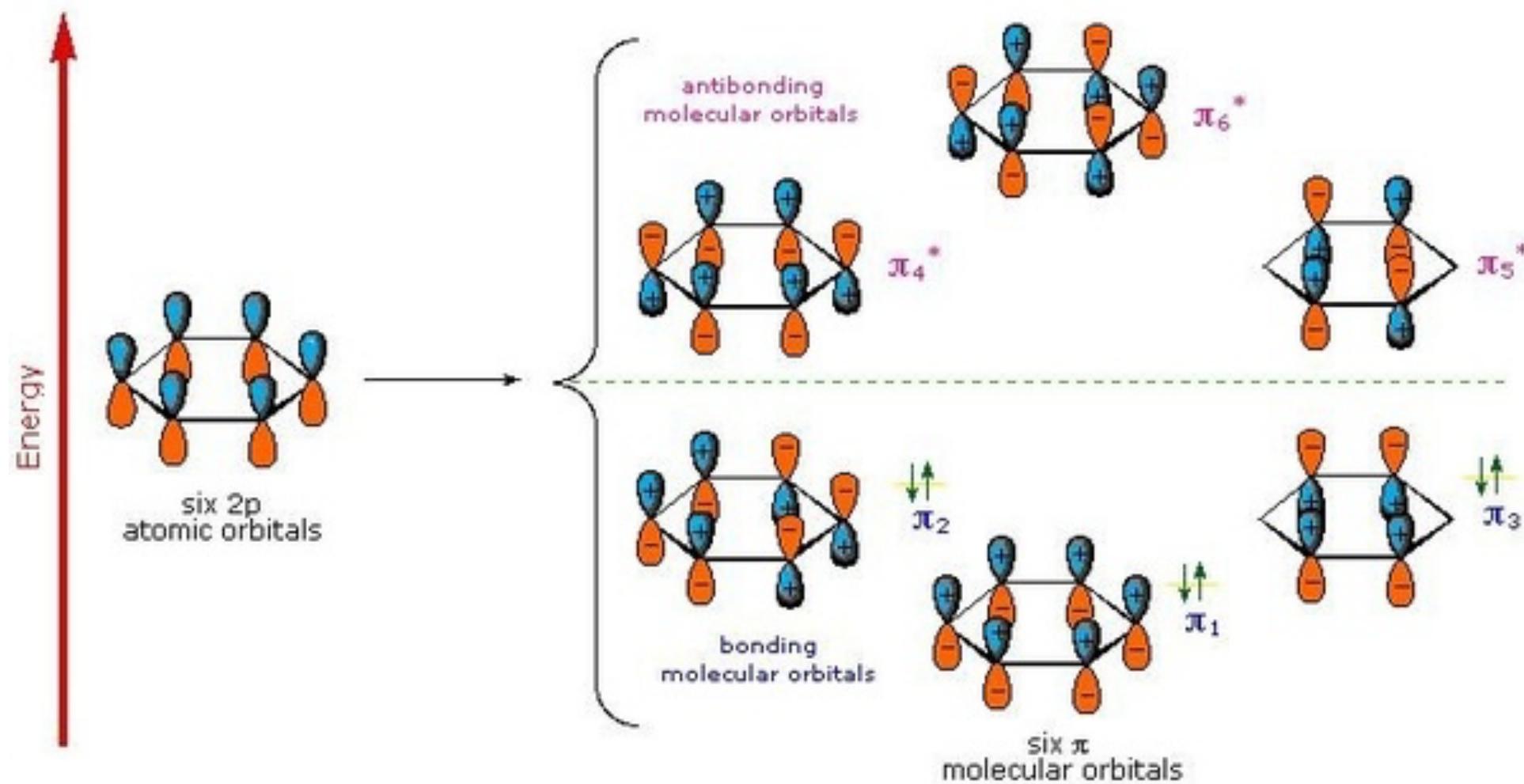
3

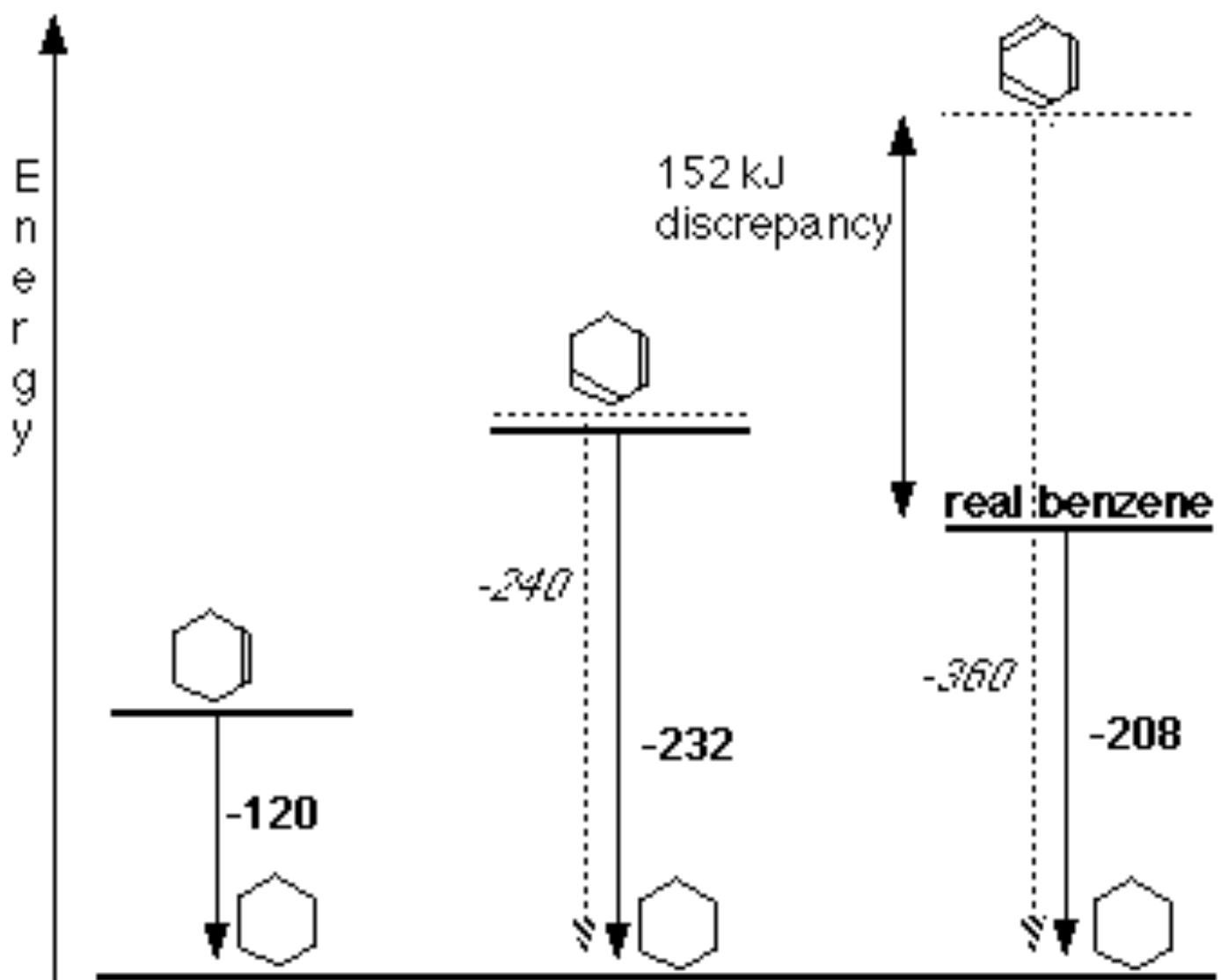


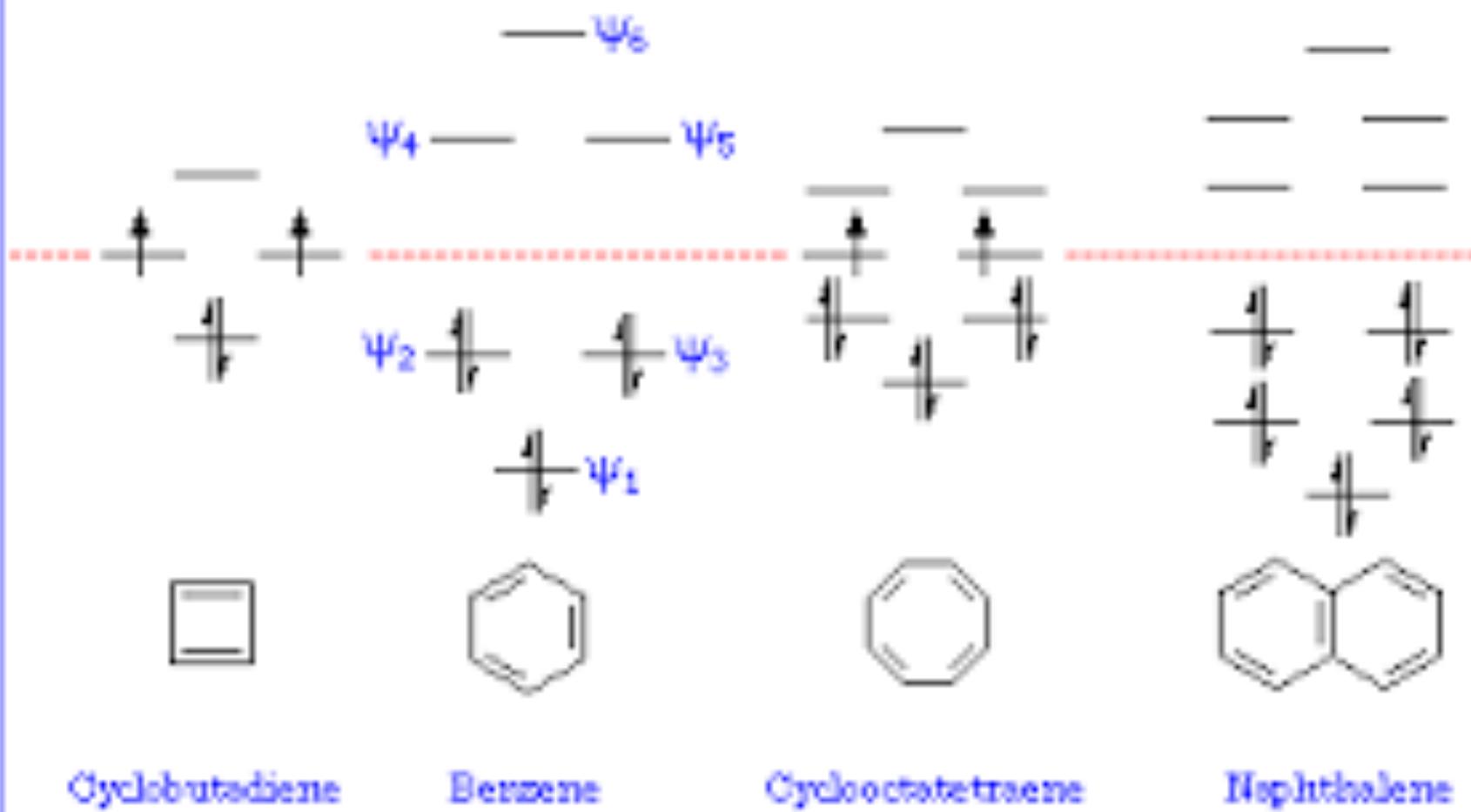
4

AROMATICITY









Aromatic

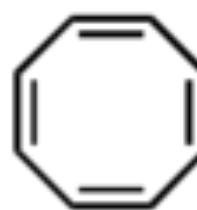
- Cyclic
- Conjugated
- $(4n+2)$ Pi electrons
- Flat

**benzene****Anti-Aromatic**

- Cyclic
- Conjugated
- $(4n)$ Pi electrons
- Flat

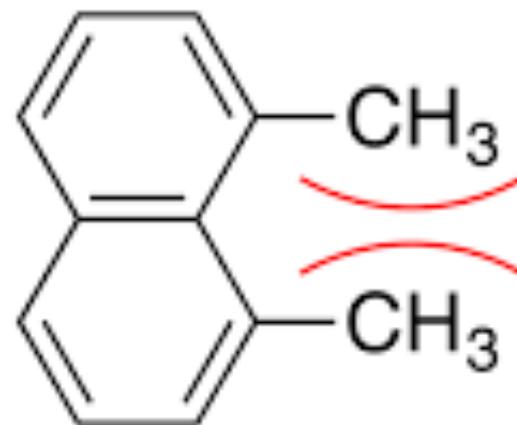
**cyclobutadiene****Non-Aromatic**

*Fails any one
of the criteria
on the left*

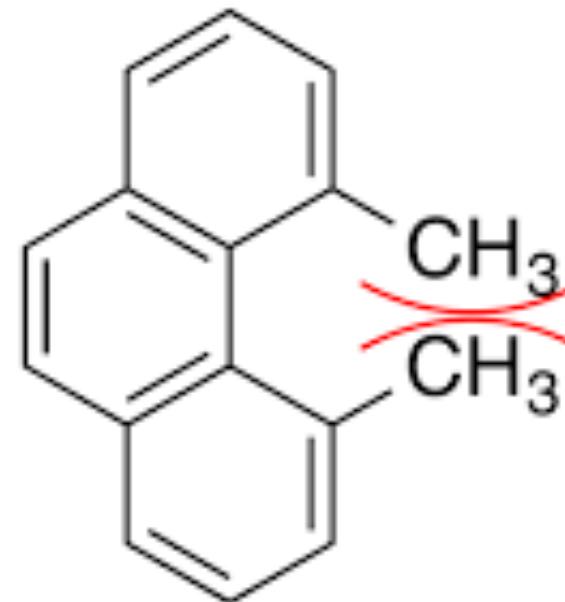
**cyclooctatetraene**
(?!!)

The Stability of Organic Molecules

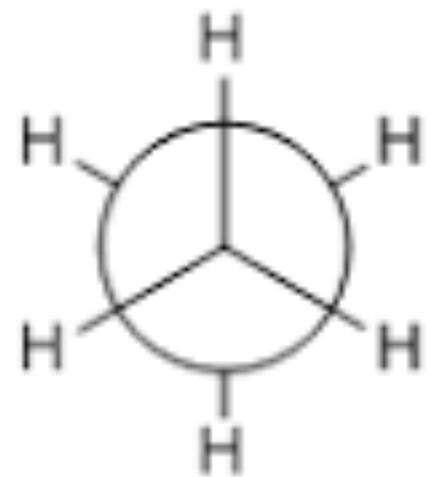
Torsional Strain



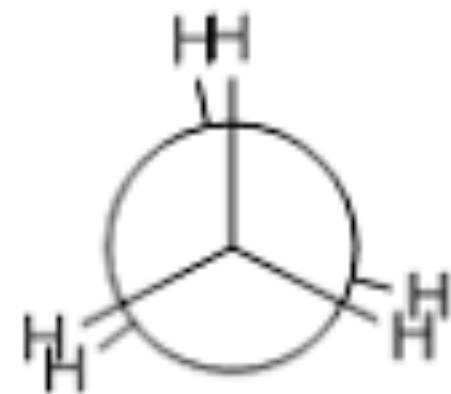
7.6 kcal/mol



12–15 kcal/mol

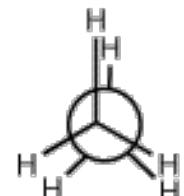


staggered



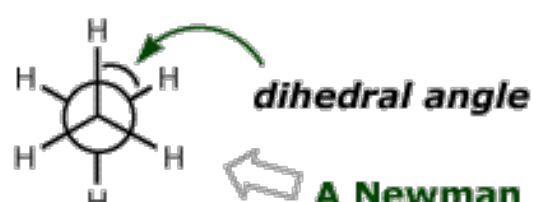
eclipsed

ECLIPSED CONFORMATION



least stable

STAGGERED CONFORMATION

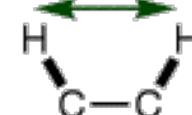
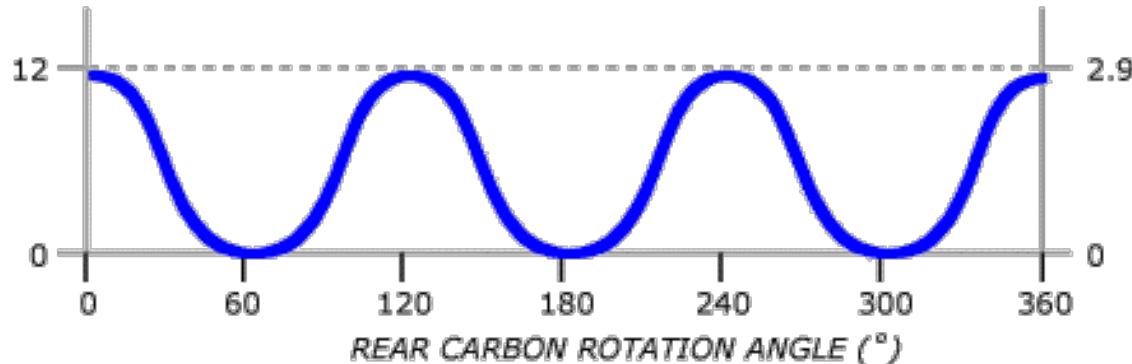


most stable

dihedral angle

A Newman projection

ENERGY (kJ/mol)

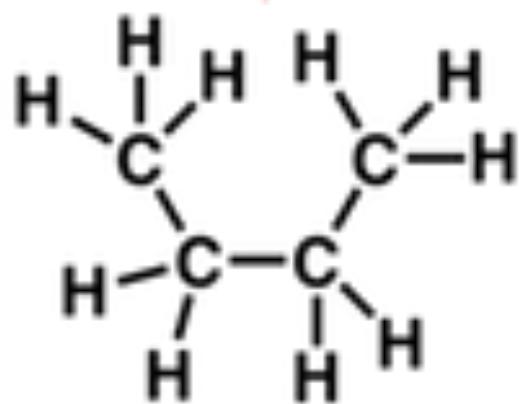


Eclipsed: 2.29 Å
Staggered: 2.55 Å

TORSIONAL STRAIN
(Mutual repulsion of
eclipsed bonds)
Each 'costs' 4 kJ/mol

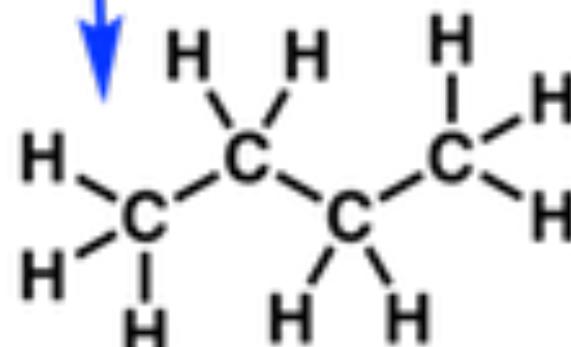
Steric Strain

Steric strain caused by two eclipsed CH₃ groups



Eclipsed Conformation

The two CH₃ groups
are 180° apart



Anti Conformation

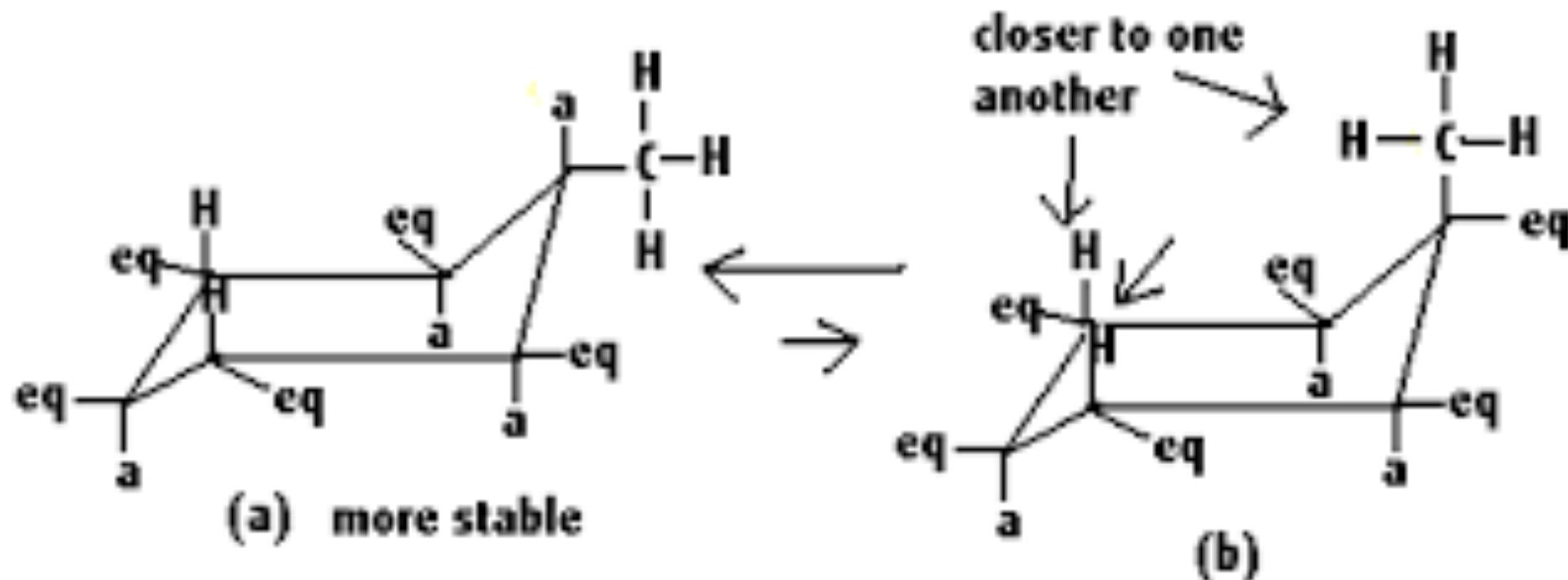
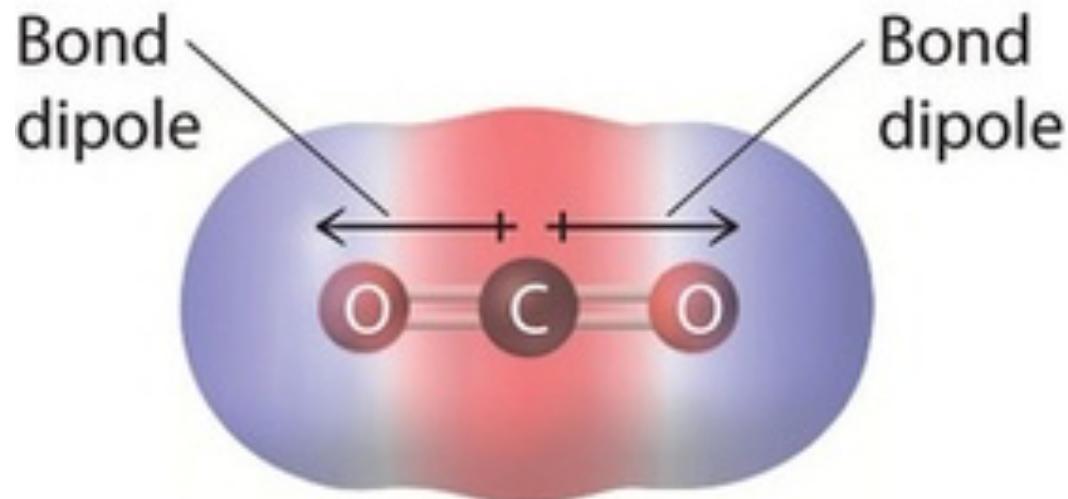
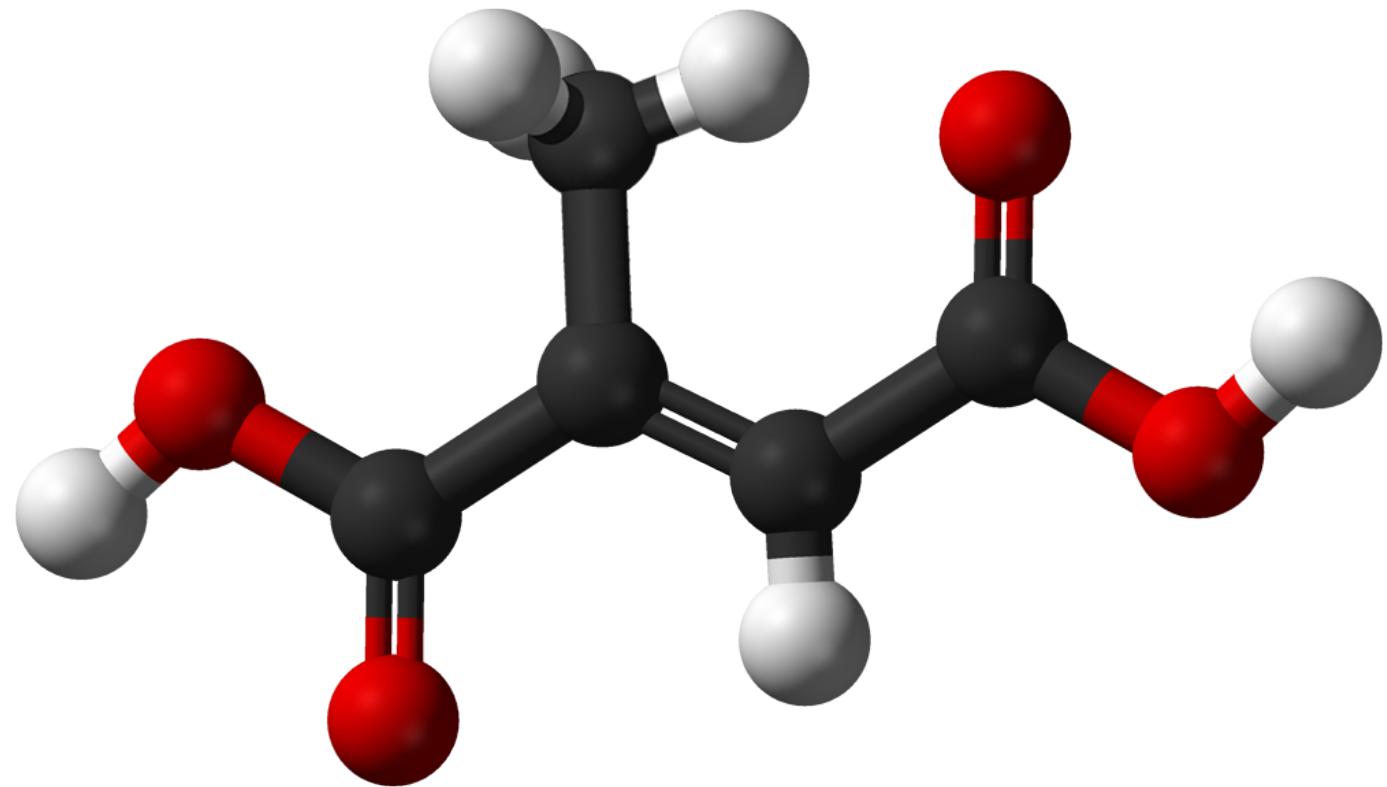


Fig 8- Methyl Cyclohexane Conformers

A Preview of What's Next:

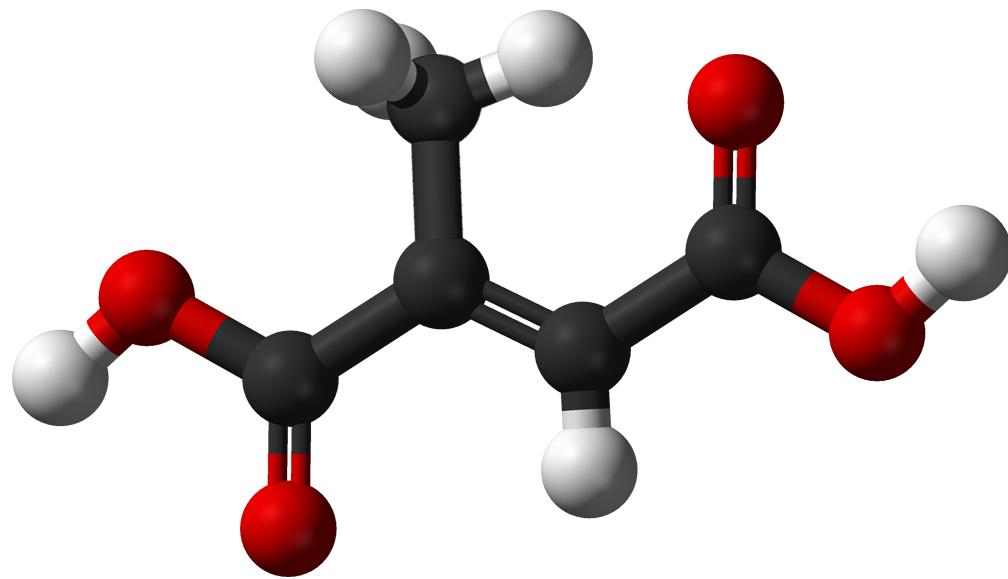


(a) No net dipole moment



ORGANIC CHEMISTRY II:

Reactions of Small Molecules

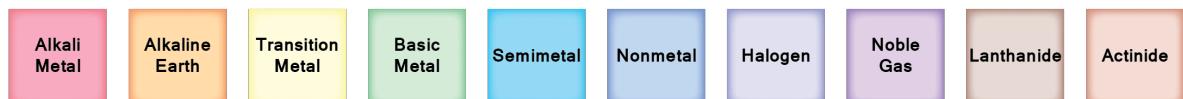


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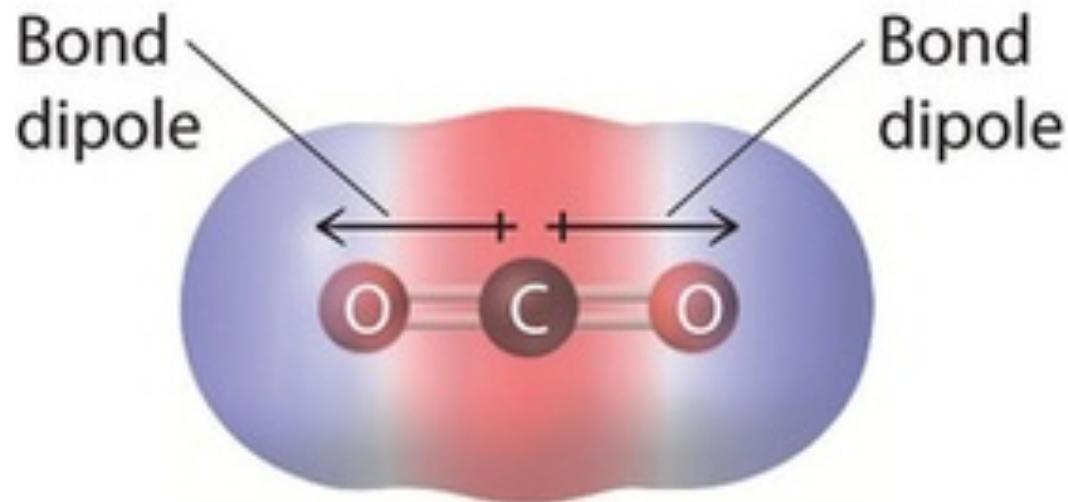
Periodic Table of the Elements

1 IA 1A		18 VIIA 8A																			
1 H Hydrogen 1.008	2 Be Beryllium 9.012																				
3 Li Lithium 6.941	4 Mg Magnesium 24.305	5 VB 5B	6 VIB 6B	7 VIIIB 7B	8	9	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIA 8A						
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIIB 7B	8	9	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIA 8A				
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 83.798				
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294				
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71 [57-71]	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018				
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 [89-103]	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]				

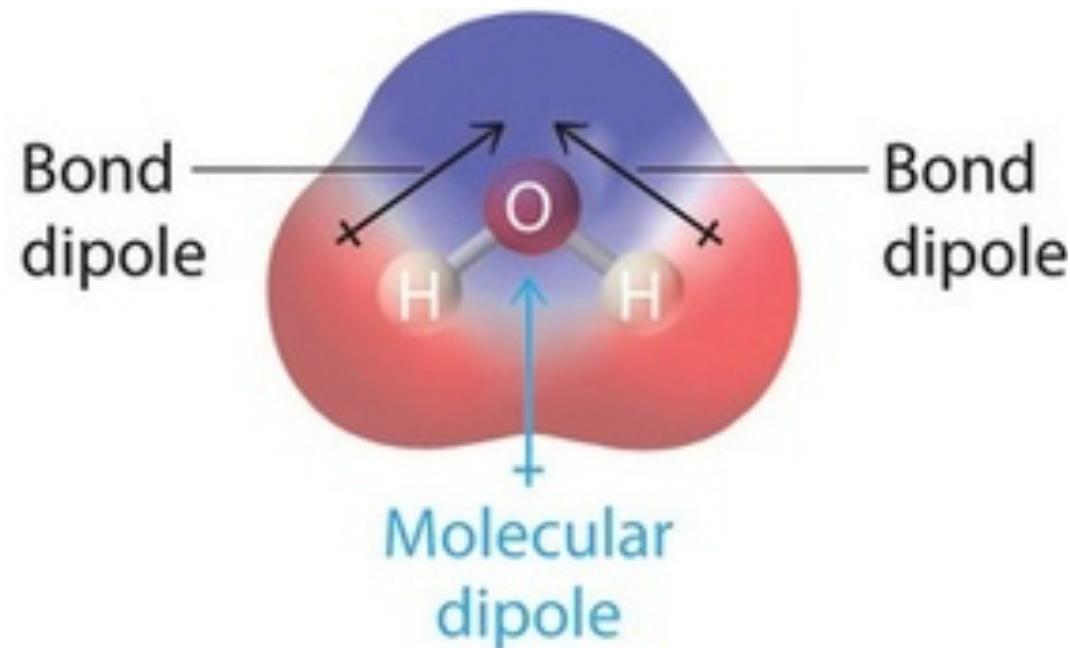
Lanthanide Series	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.242	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]



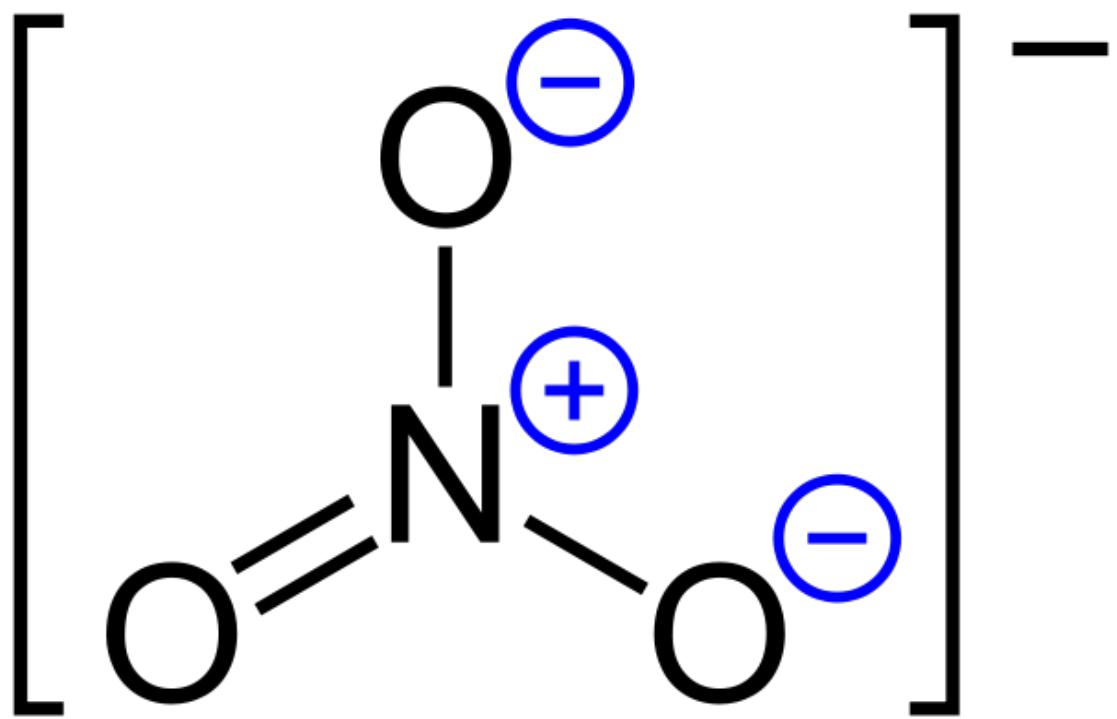
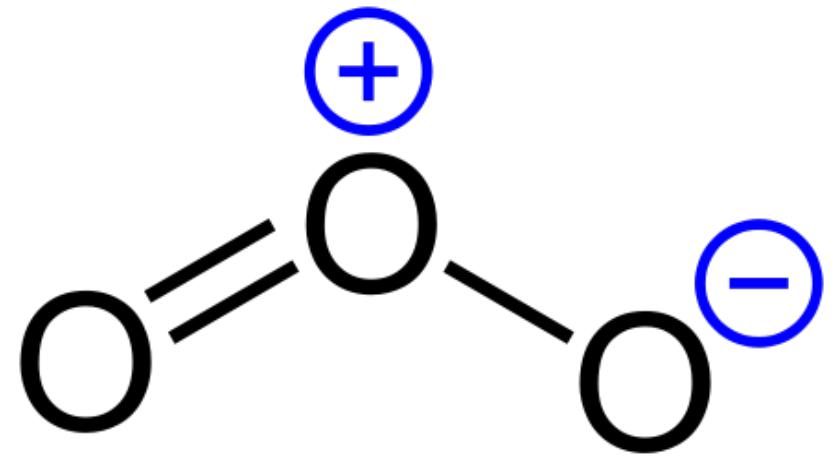
Molecular Charge Distribution

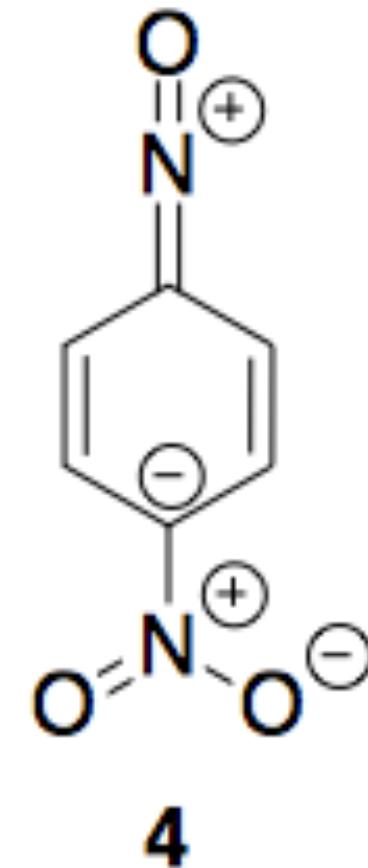
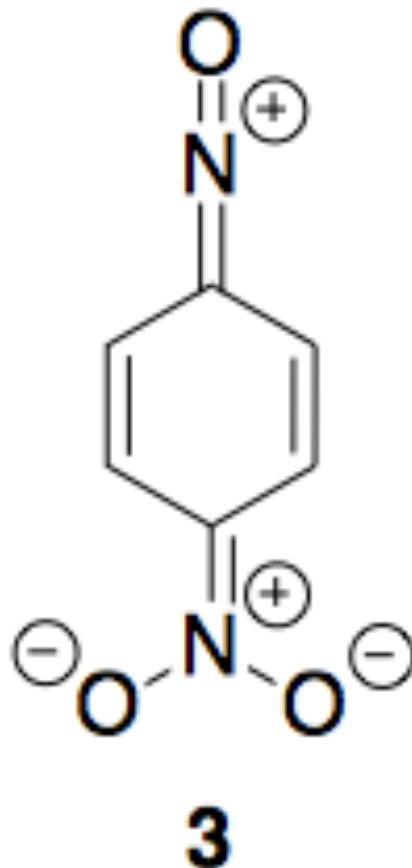
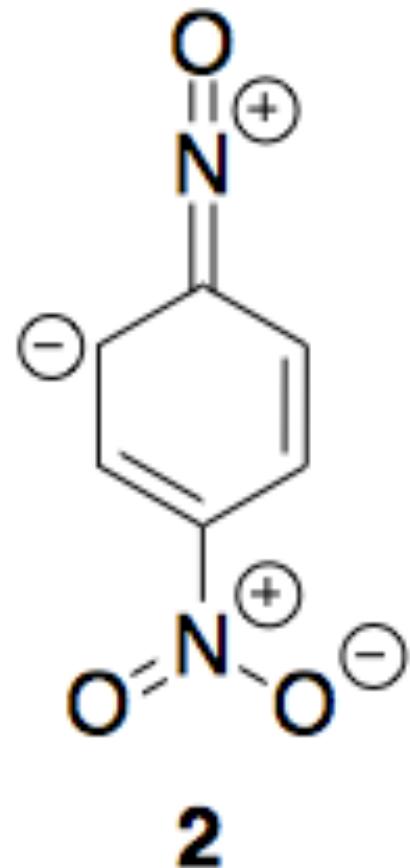
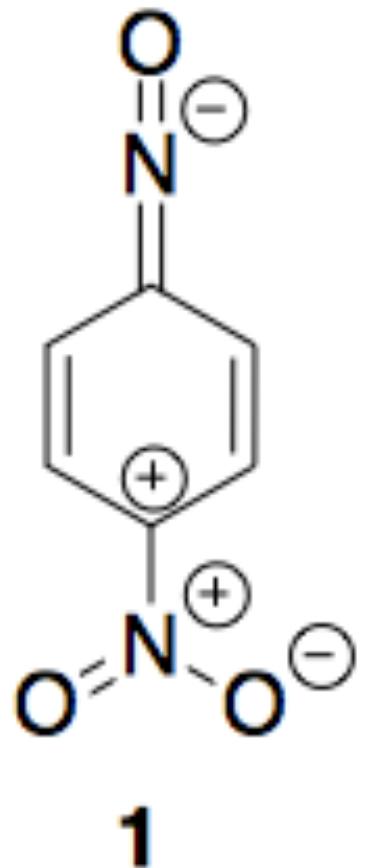


(a) No net dipole moment

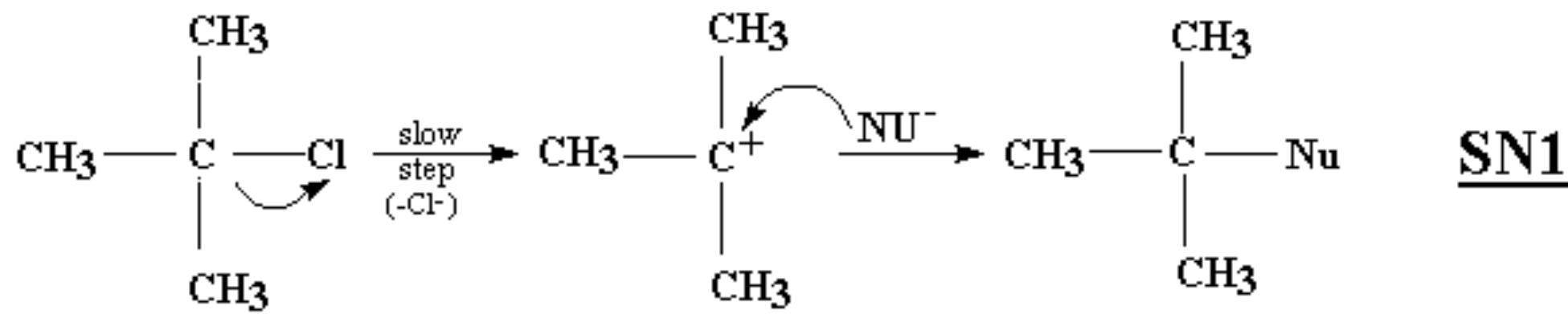


(b) Net dipole moment



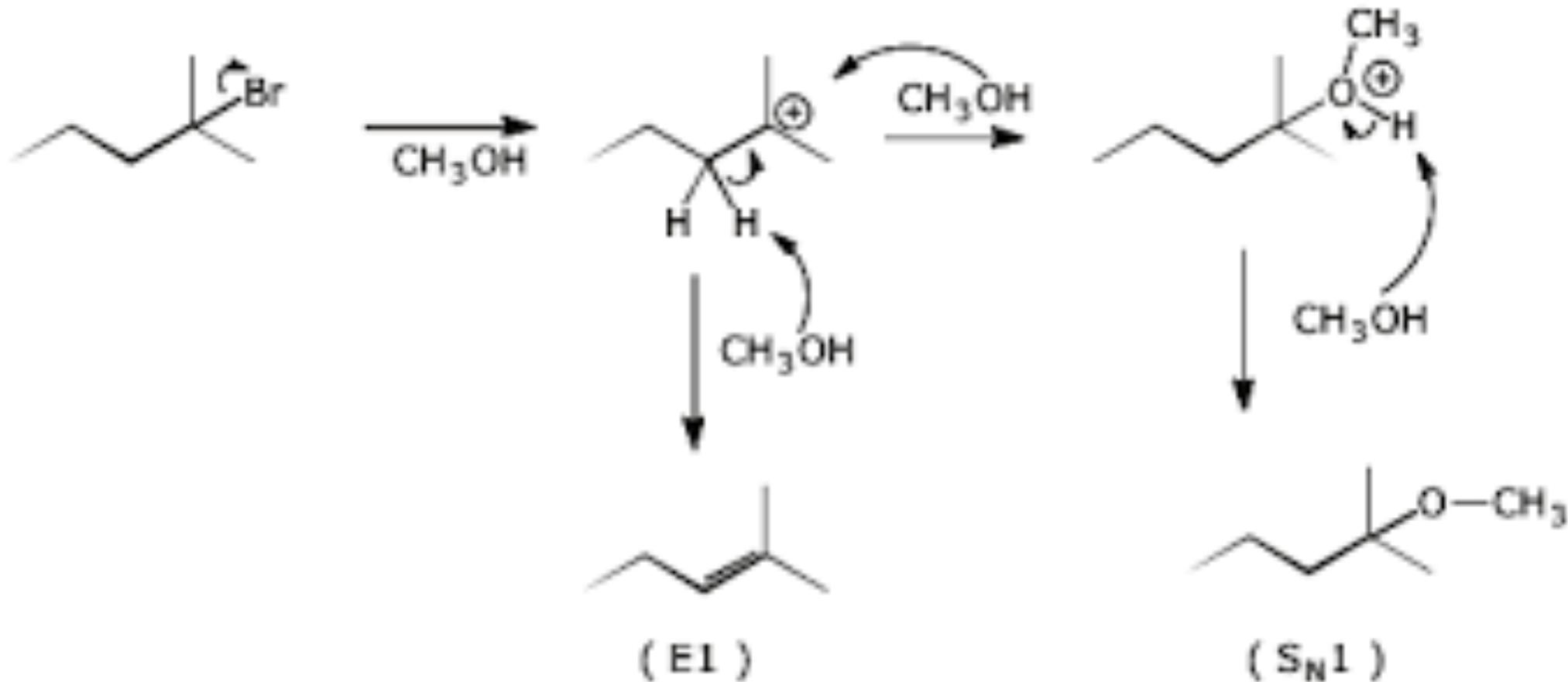


SN1 Reactions

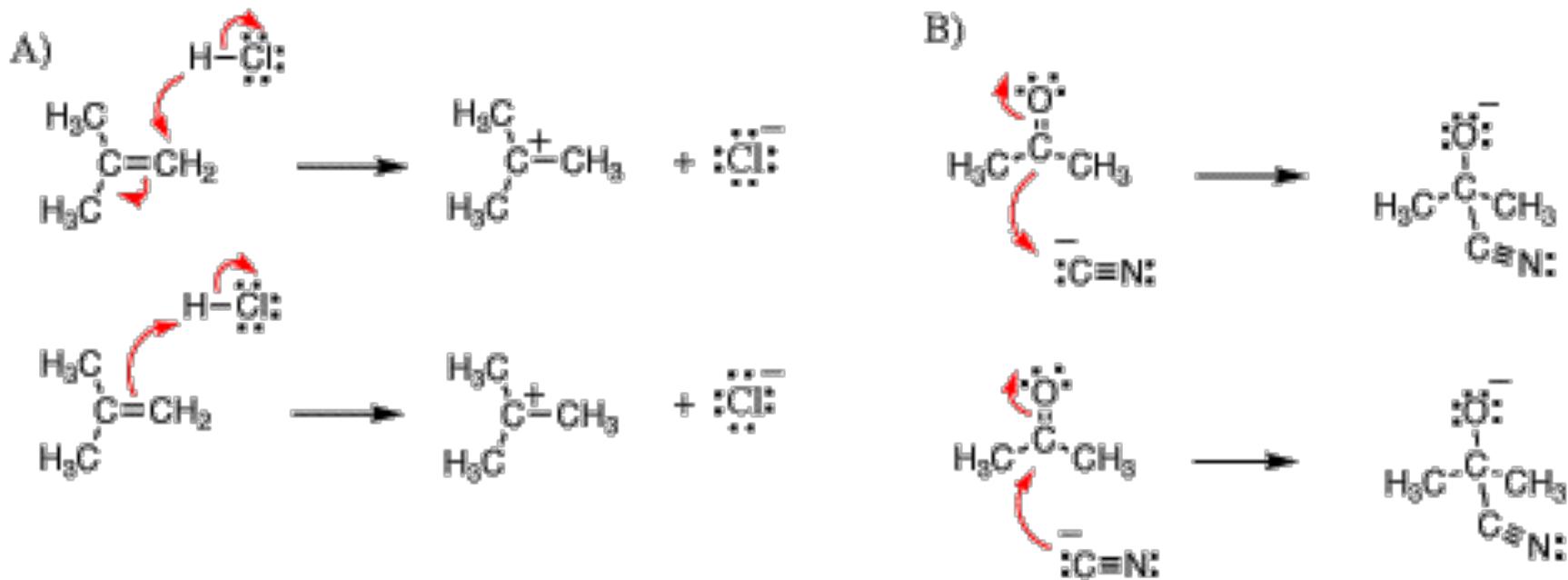


S_N1

Elimination reactions

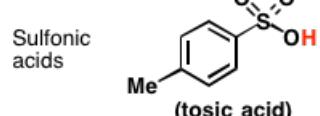
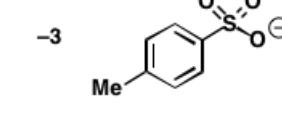
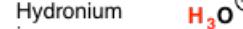
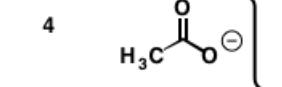


Alternate Formation of Intermediate



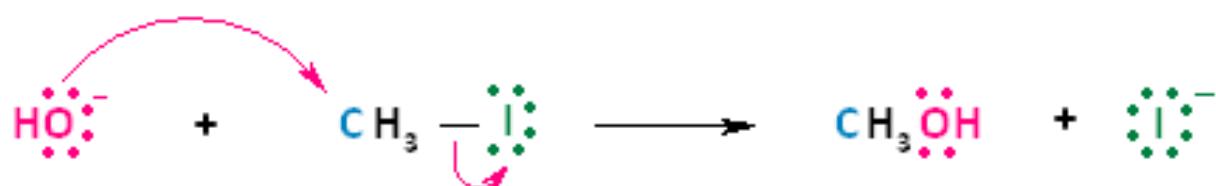
Leaving Group Stability

A pKa table is a handy guide to leaving groups

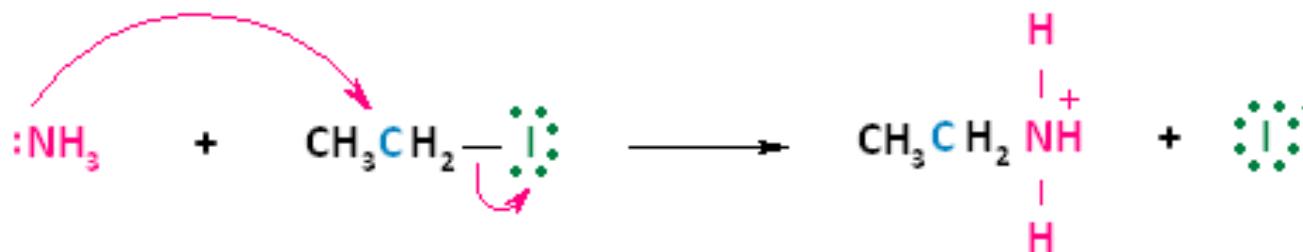
Functional group / Example	pKa	Conjugate base	
Hydroiodic acid 	-10	I^-	
Hydrobromic acid 	-9	Br^-	
Hydrochloric acid 	-6	Cl^-	
Sulfuric acid 	-3	HSO_4^-	
Sulfonic acids  (tosic acid)	-3		<i>Excellent leaving groups (extremely weak bases)</i>
Hydronium ion 	-1.7	H_2O	
Hydrofluoric acid 	3.2	F^-	<i>Exception:</i> F^- is typically an extremely poor leaving group (forms strong bonds)
Carboxylic acids 	4		<i>Moderate leaving groups (weak bases)</i>
Protonated amines 	9-11	NH_3	
Water 	16	HO^-	<i>Poor leaving groups (strong bases)</i>
Alcohols 	16-18	CH_3O^-	
Amine 	~35	NH_2^-	
Hydrogen 	42	H^-	<i>Extremely poor leaving groups (very strong bases)</i>
Alkane 	~50		

SN₂ Reactions

Example #1



Example #2



Nucleophilic Strength

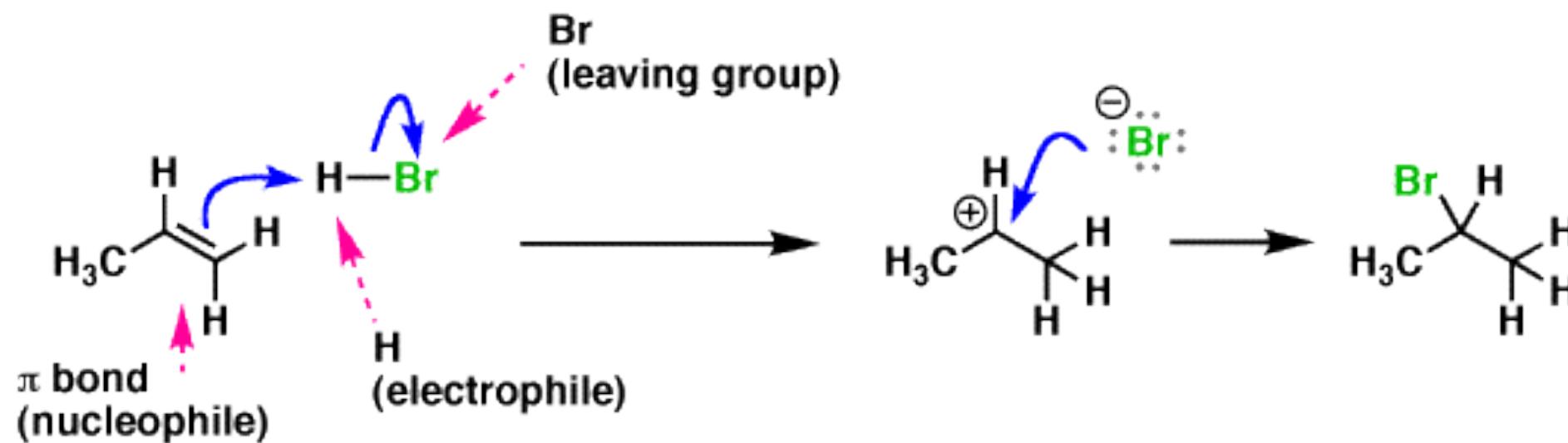
TABLE 6-3 Some Common Nucleophiles, Listed in Decreasing Order of Nucleophilicity in Hydroxylic Solvents Such as Water and the Alcohols

strong nucleophiles	$(\text{CH}_3\text{CH}_2)_3\text{P}^-$ $-\ddot{\text{S}}-\text{H}$ $:\ddot{\text{I}}:-$ $(\text{CH}_3\text{CH}_2)_2\ddot{\text{N}}\text{H}$ $-\text{C}\equiv\text{N}$ $(\text{CH}_3\text{CH}_2)_3\text{N}^-$ $\text{H}-\ddot{\text{O}}^-$ $\text{CH}_3-\ddot{\text{O}}^-$	moderate nucleophiles	$:\ddot{\text{Br}}^-$ $:\text{NH}_3$ $\text{CH}_3-\ddot{\text{S}}-\text{CH}_3$ $:\ddot{\text{Cl}}^-$ weak nucleophiles $\text{CH}_3\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\ddot{\text{O}}^-$ $:\ddot{\text{F}}^-$ $\text{H}-\ddot{\text{O}}-\text{H}$ $\text{CH}_3-\ddot{\text{O}}-\text{H}$
---------------------	--	-----------------------	--

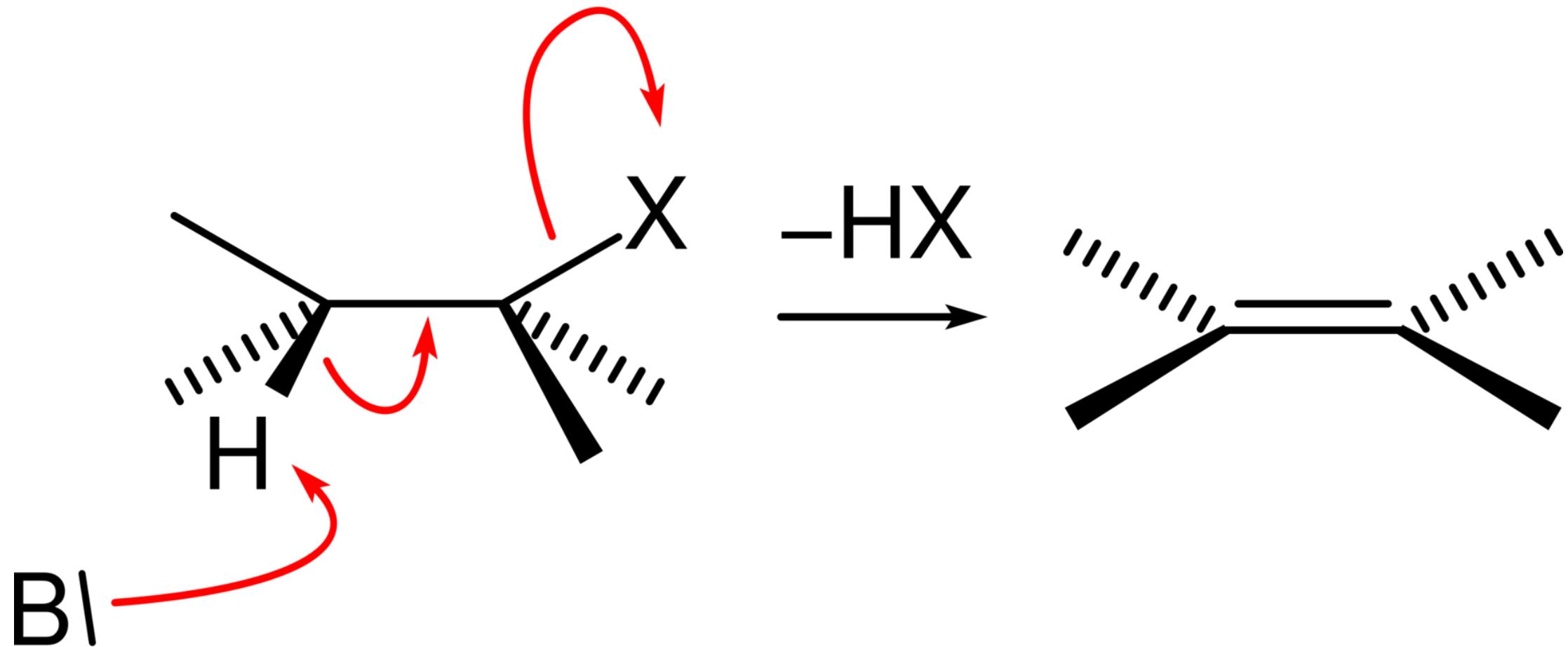
- Stronger nucleophiles **react faster** in $S_{\text{N}}2$.
- Strong bases are strong nucleophiles, but not all strong nucleophiles are basic.

Unconventional Nucleophile!

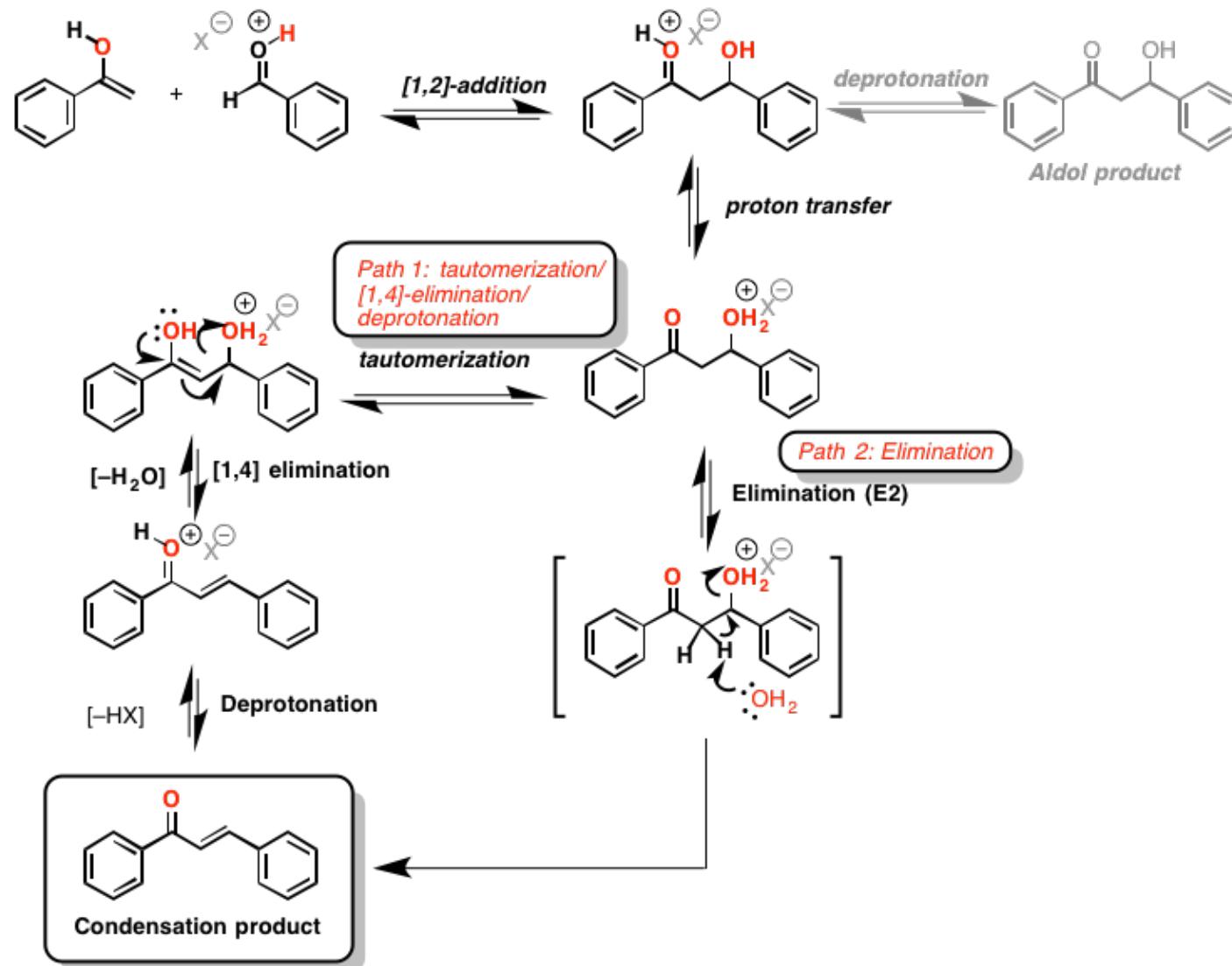
In "stepwise" alkene addition mechanisms, the arrows clearly show the role of each component in the reaction



E2 Elimination Pathway

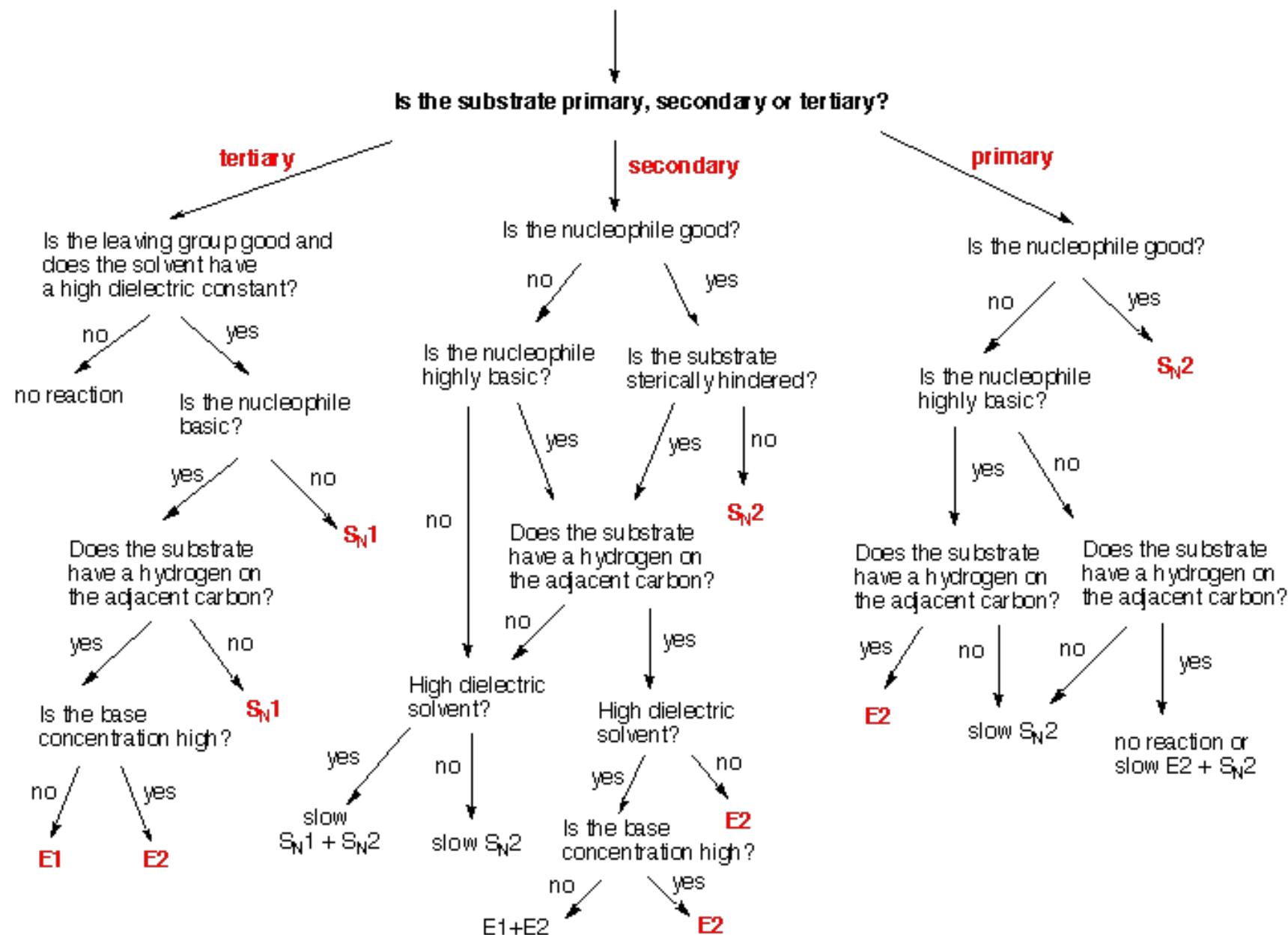


The Aldol Condensation : Two Paths to Elimination



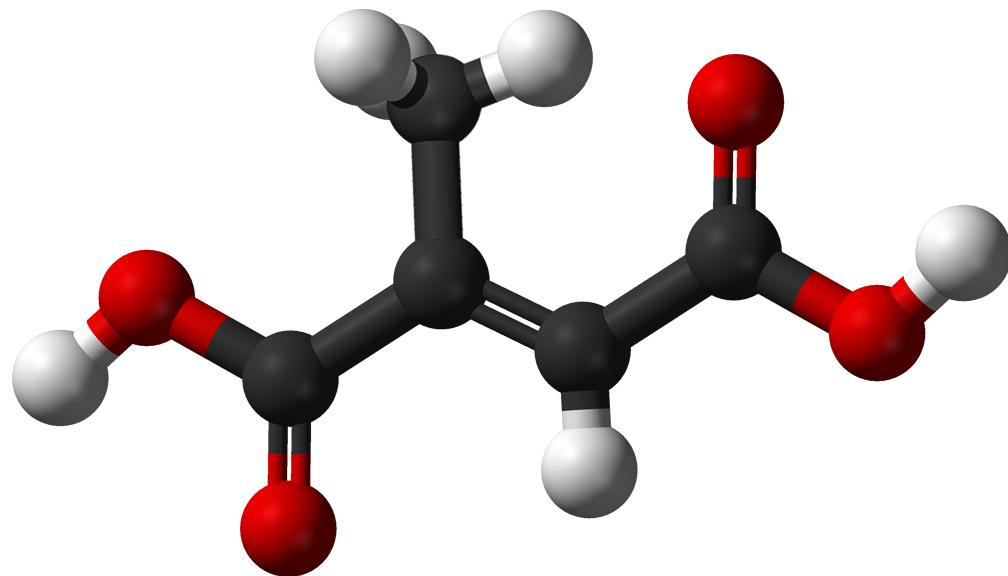
Putting it all together!

Will the predominant reaction mechanism be S_N2 , $E2$, S_{N1} or $E1$?



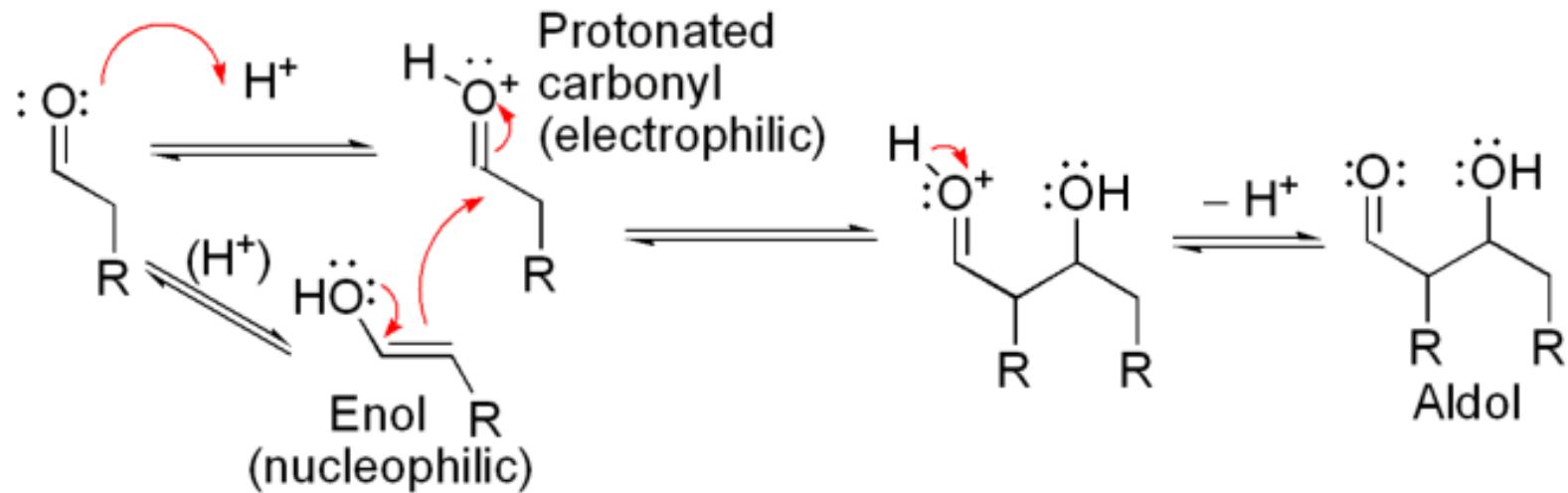
ORGANIC CHEMISTRY III:

Synthesis of Small Molecules



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Matthew Yarnall

Acid catalyzed aldol reaction



Acid catalyzed dehydration

