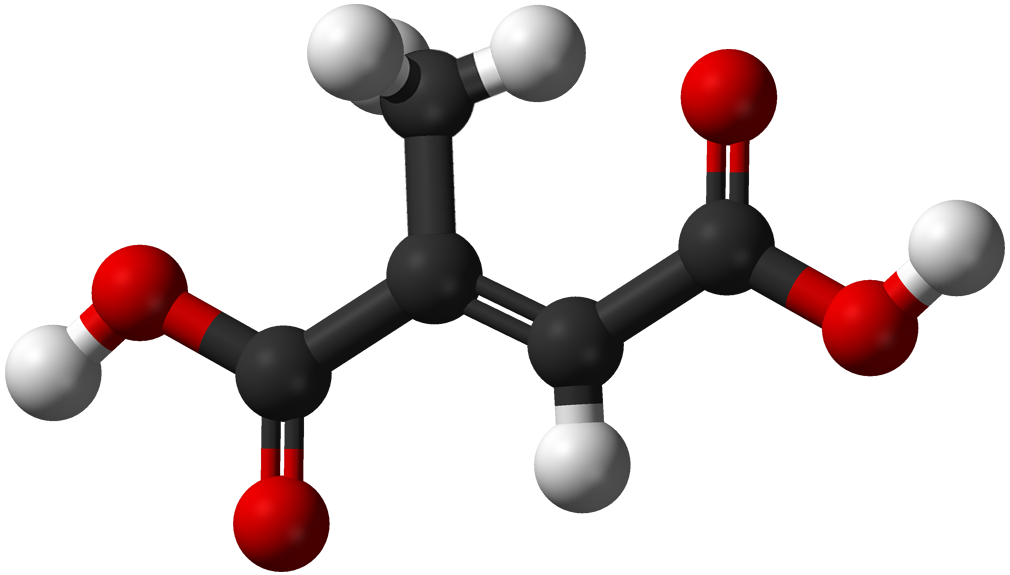
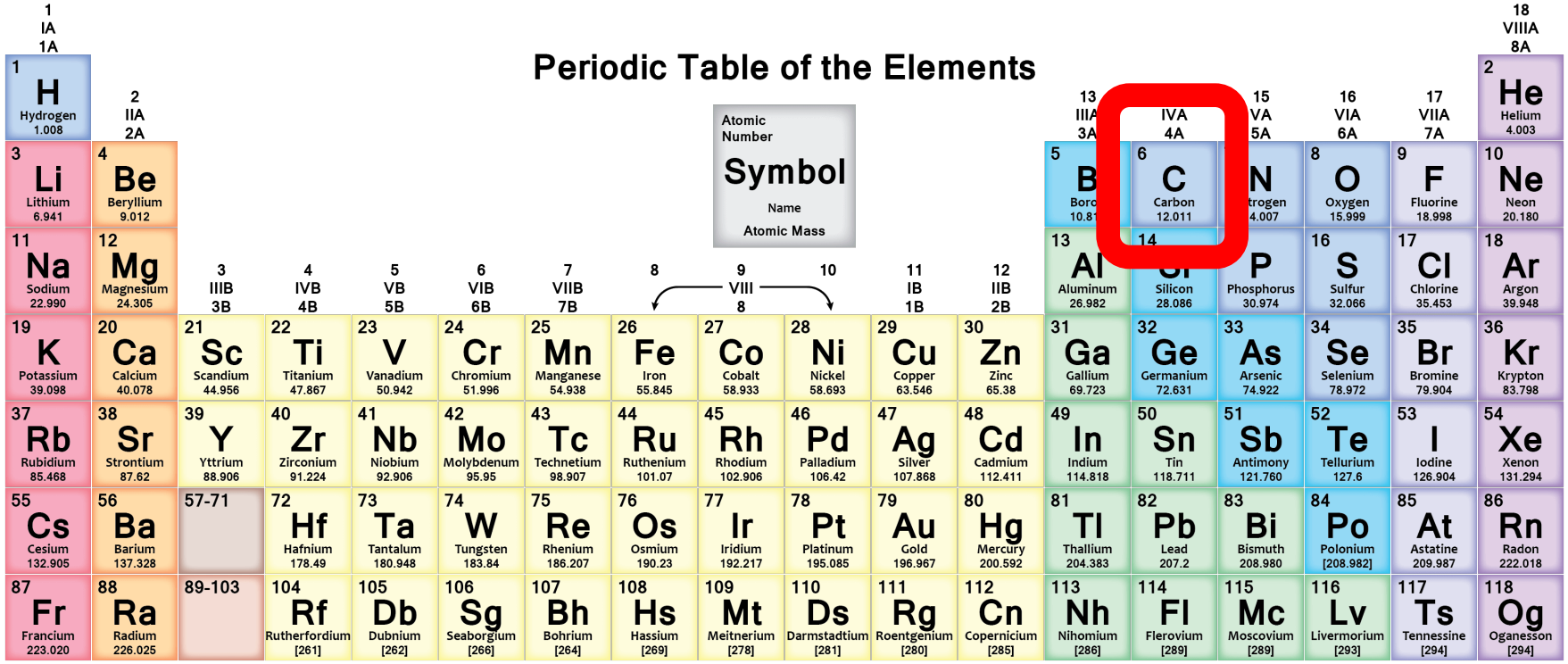
# FUNDEMENTALS OF ORGANIC CHEMISTRY



SPLASH 2018

Matthew Yarnall

# Periodic Table of the Elements

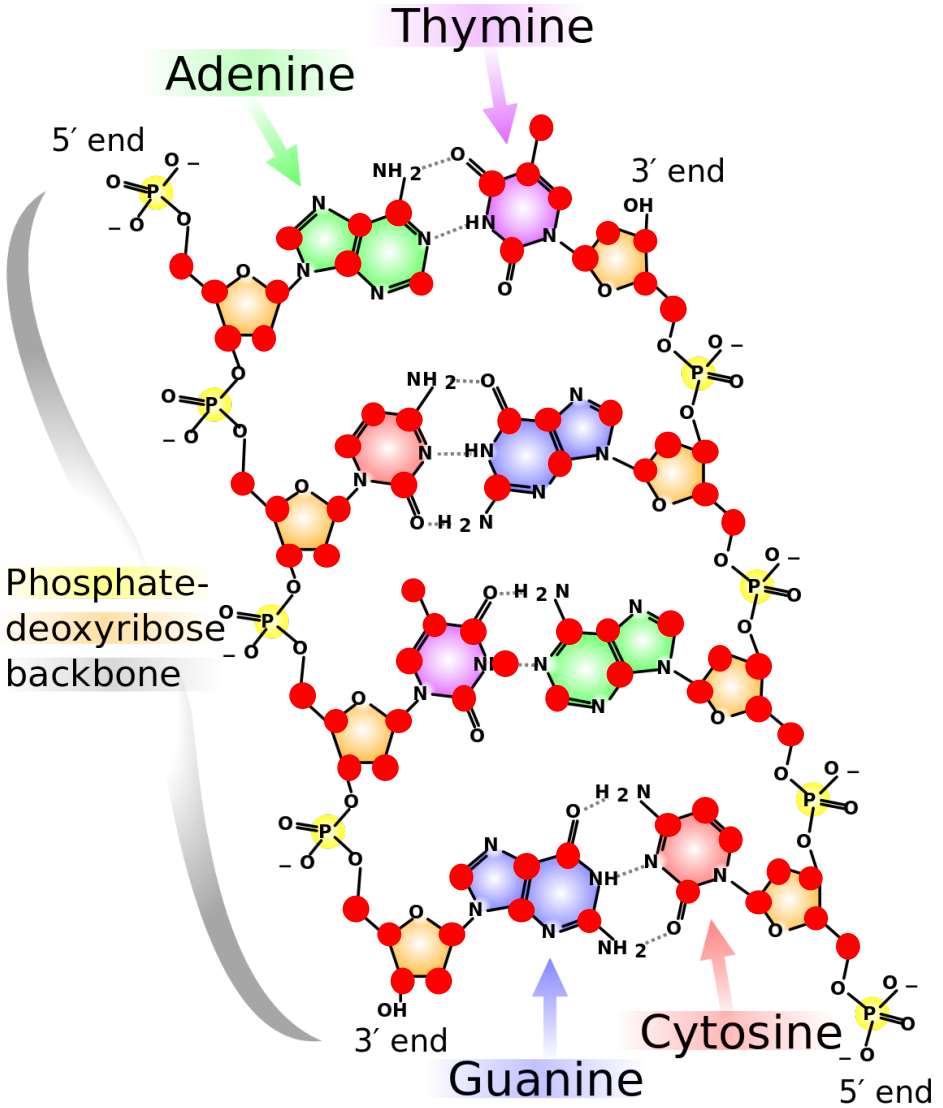



| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lanthanide Series | 57 La Lanthanum 138.905 | 58 Ce Cerium 140.116 | 59 Pr Praseodymium 140.908 | 60 Nd Neodymium 144.242 | 61 Pm Promethium 144.913 | 62 Sm Samarium 150.36 | 63 Eu Europium 151.964 | 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 |
| Actinide Series | 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 | Transition Metal | Basic Metal | Semimetal | Nonmetal | Halogen | Noble Gas | Lanthanide | Actinide

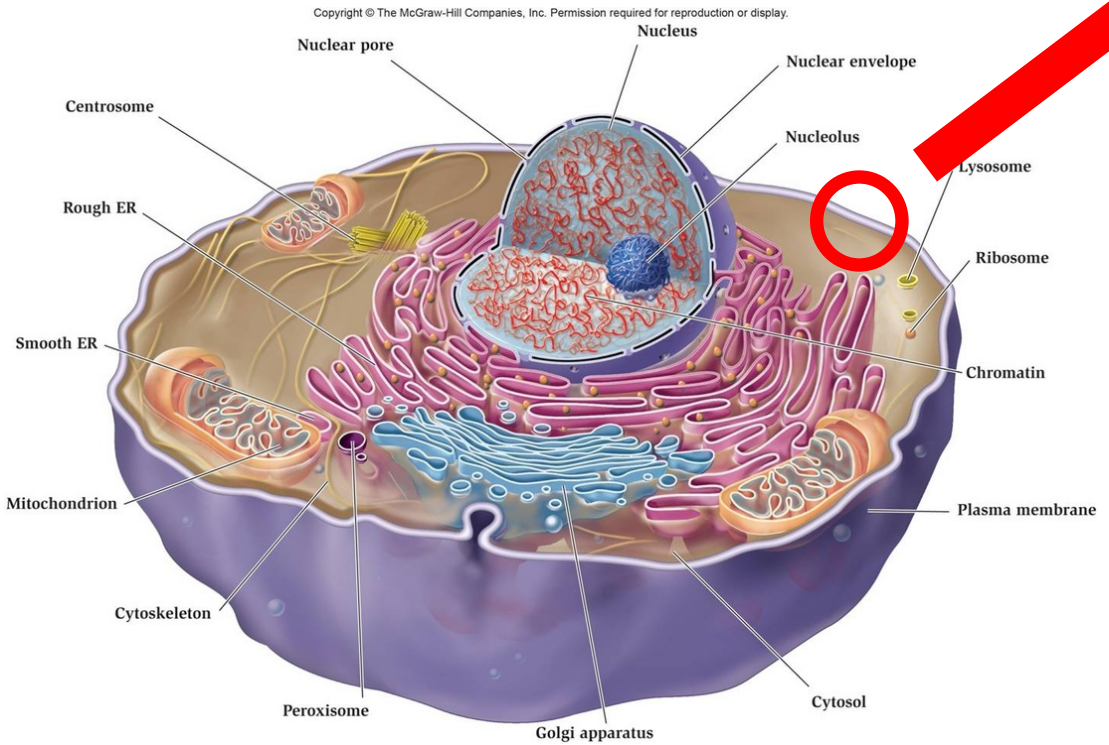
# Carbon is EVERYWHERE!

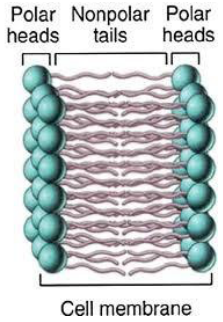
DNA

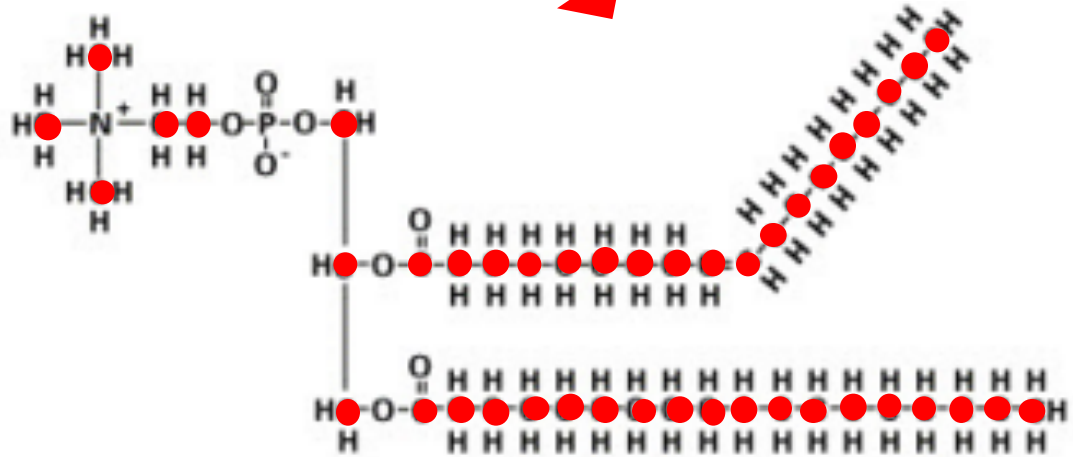


# Carbon is EVERYWHERE!

## Cell Membranes

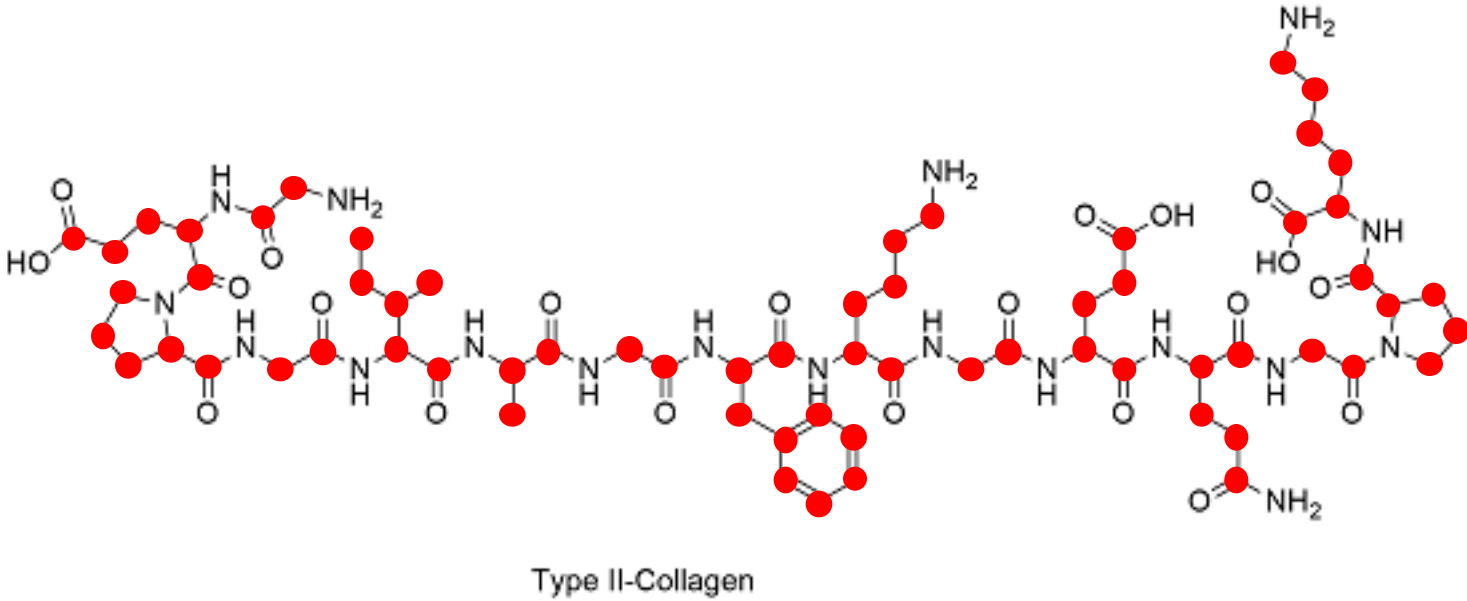


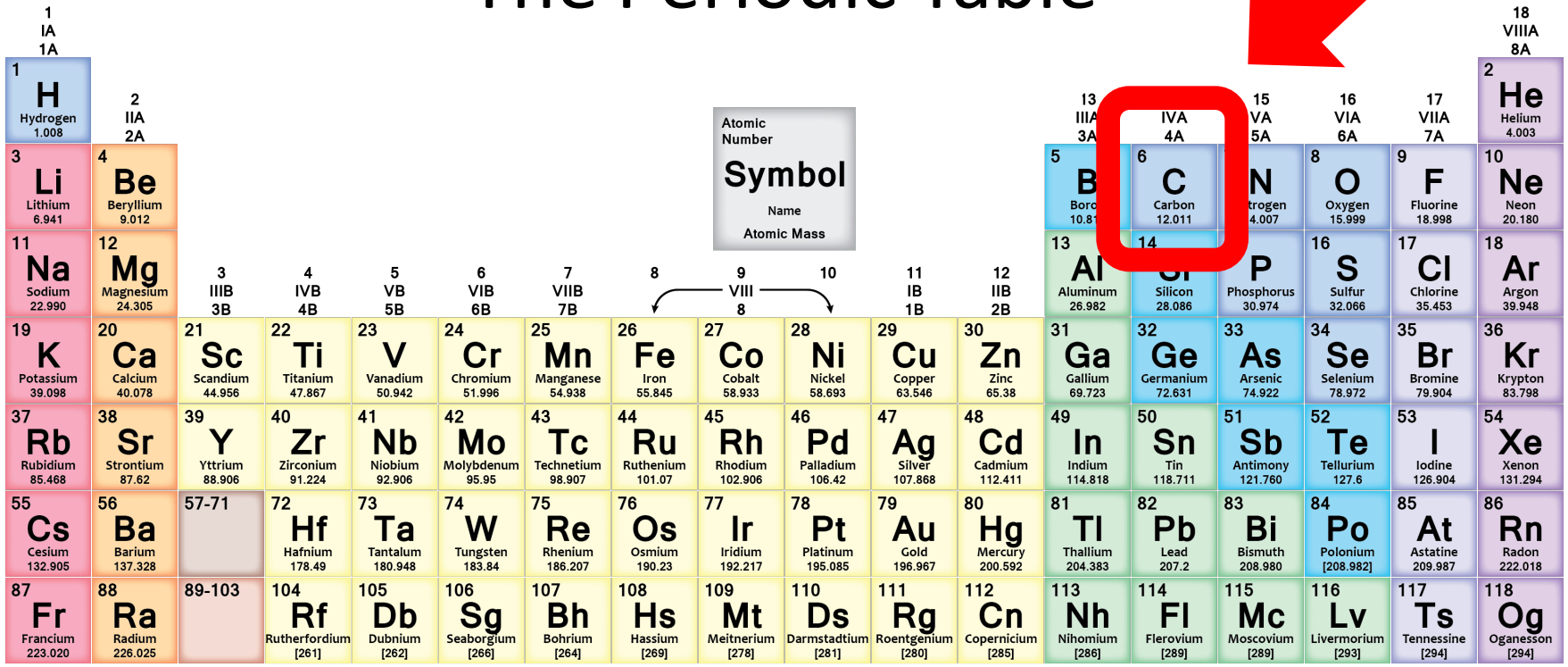
# Carbon is EVERYWHERE!

## Bones

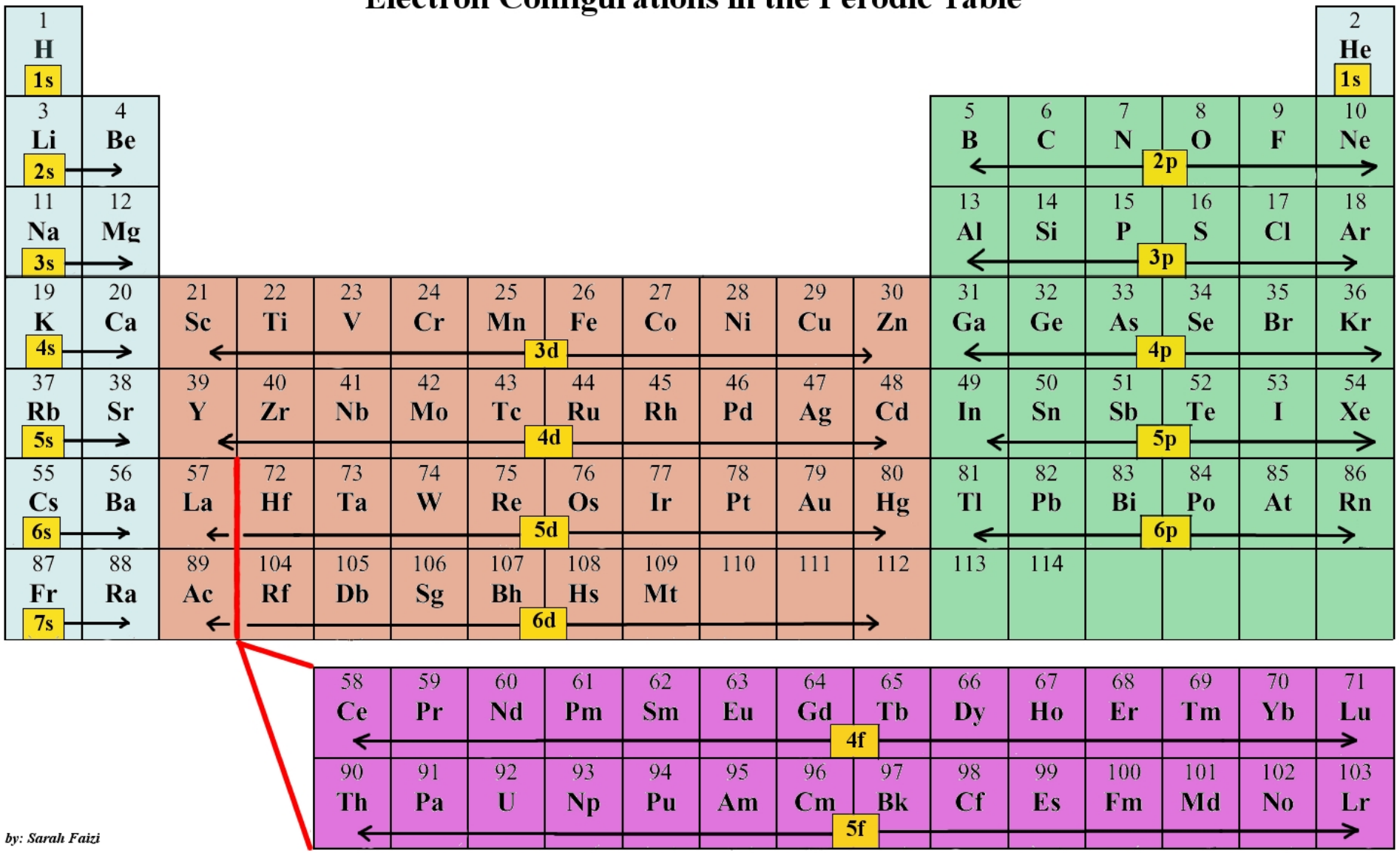


# The Periodic Table

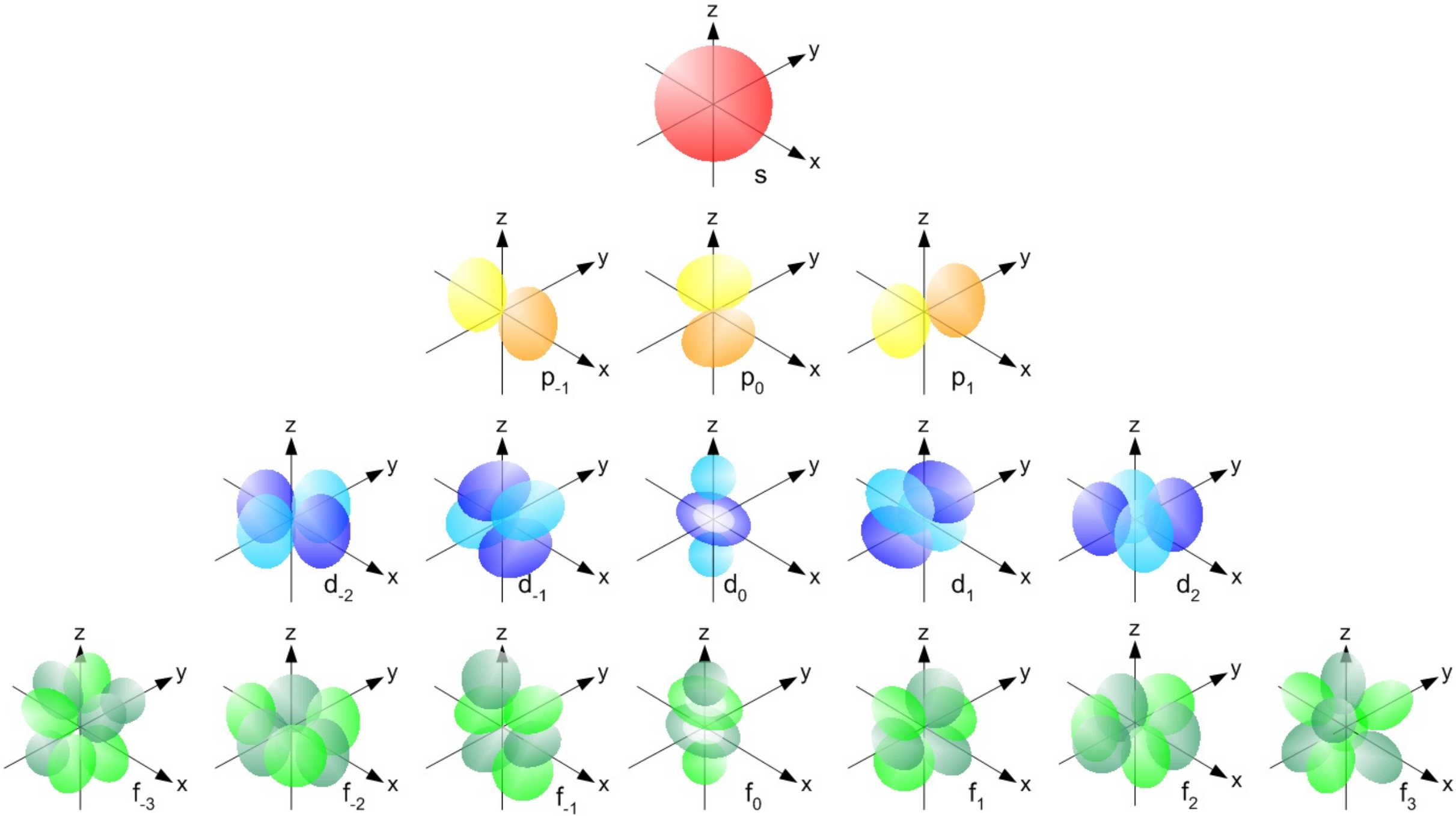
**Why Carbon?**



# Electron Configurations in the Perodic Table




*by: Sarah Faizi*


z
y
x
s
p-1
p0
p1
d-2
d-1
d0
d1
d2
f-3
f-2
f-1
f0
f1
f2
f3

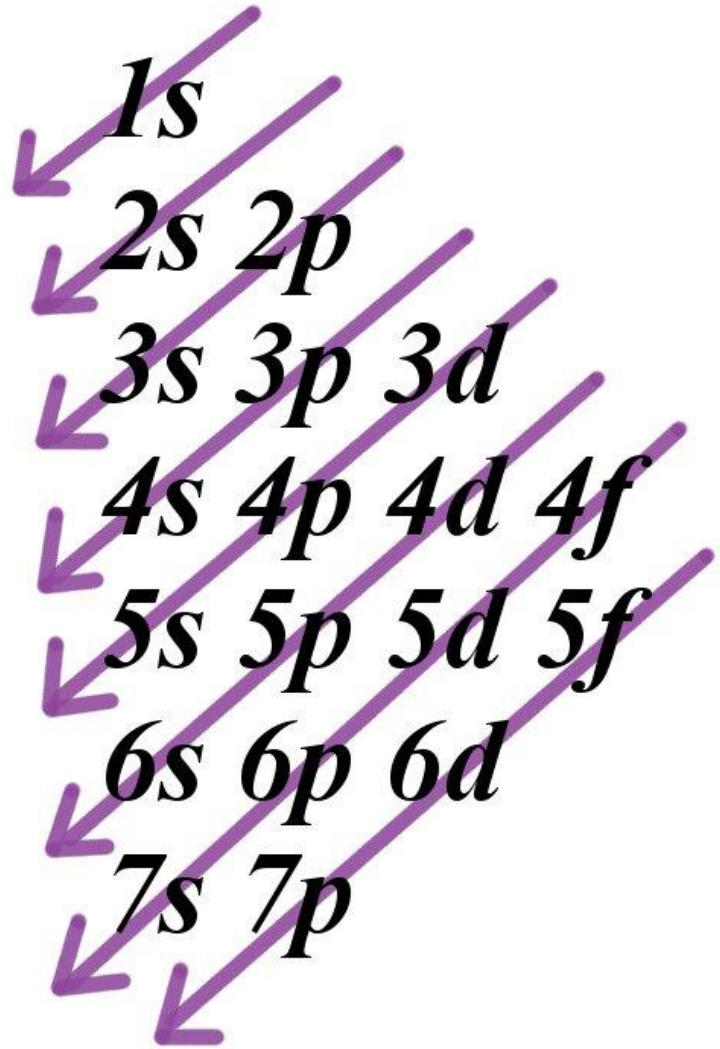
## Orbital diagram for $1s^2 2s^2 2p^5$

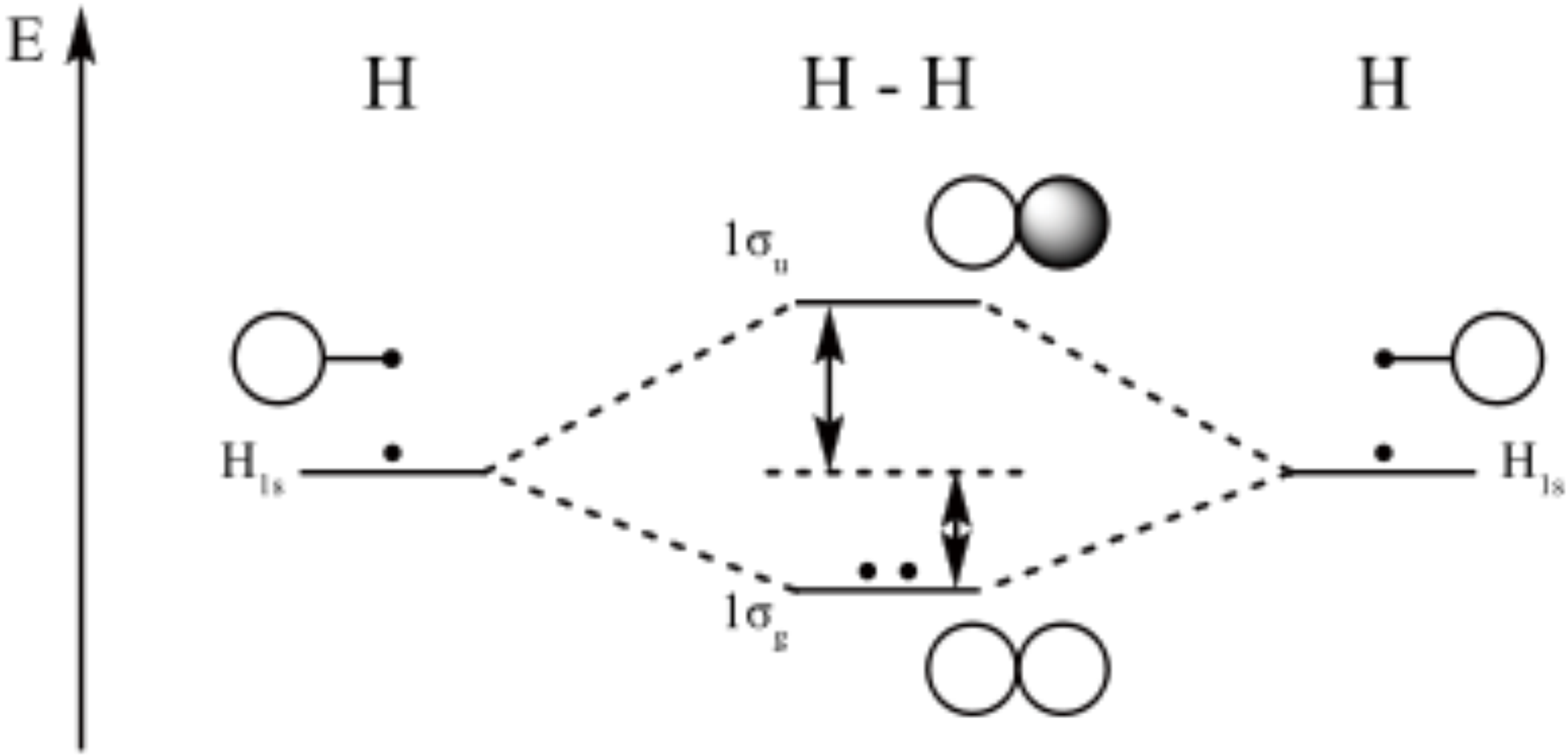

↑ : $e^-$ with spin = +1/2

↓ : $e^-$ with spin = -1/2

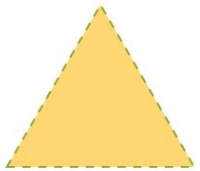
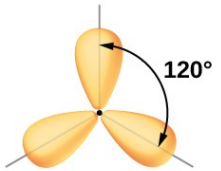
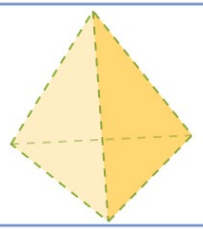
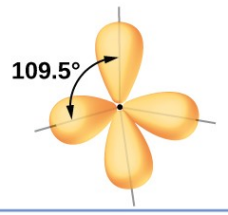
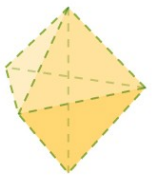
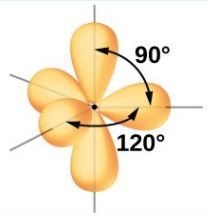
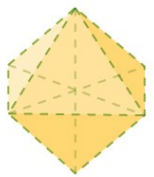
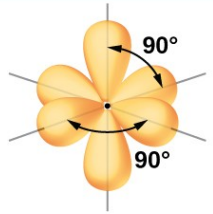
# : order $e^-$ is filled

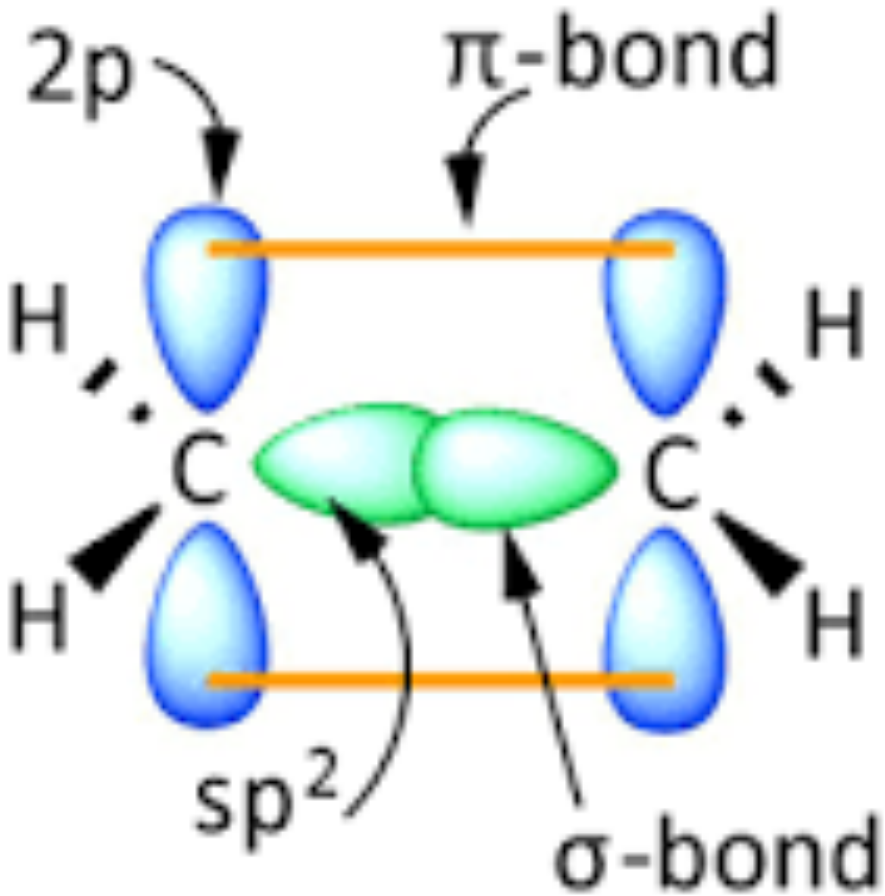
_____ : orbital


1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f
6s 6p 6d
7s 7p

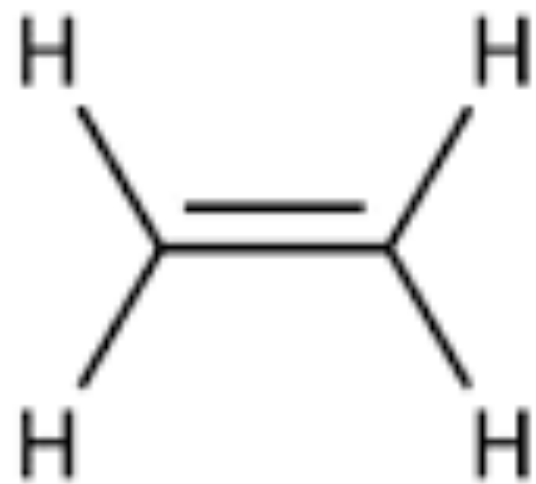

E
H
H - H
H
1σu
H1s
H1s
1σg

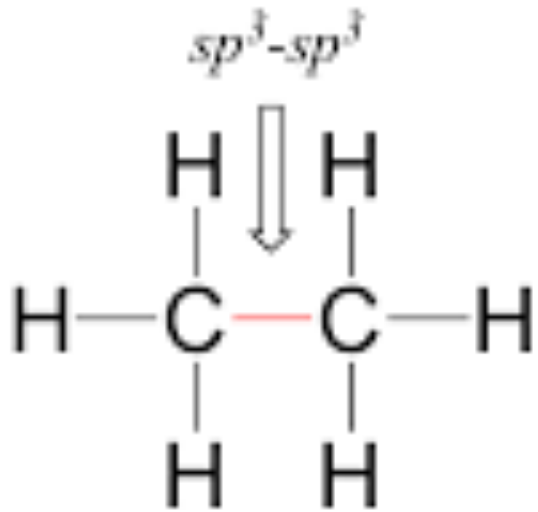
# Orbital Hybridization

| Regions of Electron Density | Arrangement | | Hybridization | |
|---|---|---|---|---|
| 2 |  | linear | *sp* |  |
| 3 |  | trigonal planar | $sp^2$ |  |
| 4 |  | tetrahedral | $sp^3$ |  |
| 5 |  | trigonal bipyramidal | $sp^3d$ |  |
| 6 |  | octahedral | $sp^3d^2$ |  |

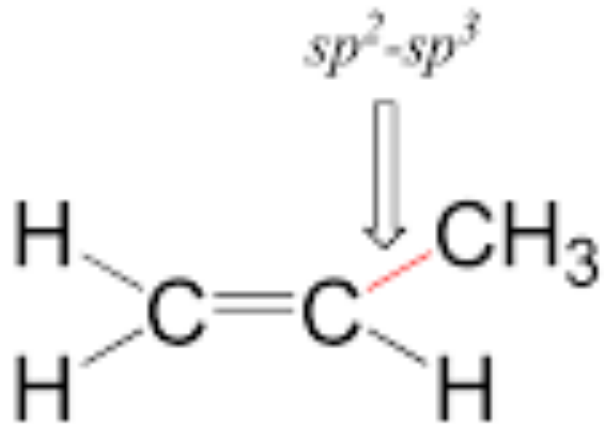



Ethene

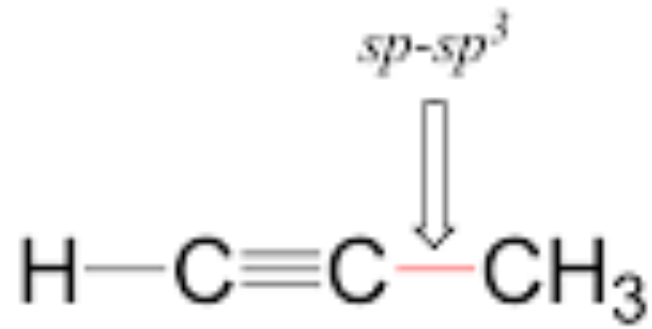





A

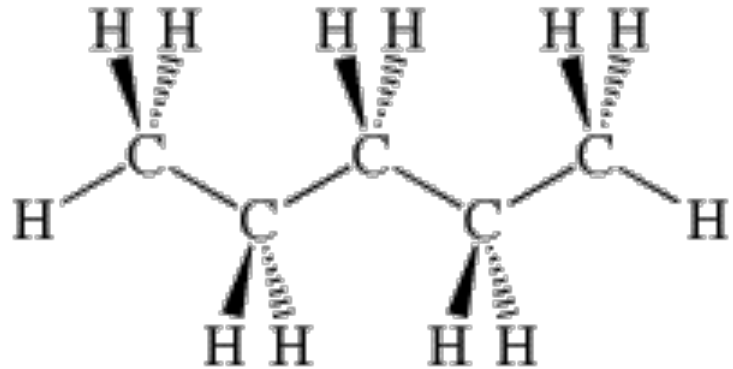


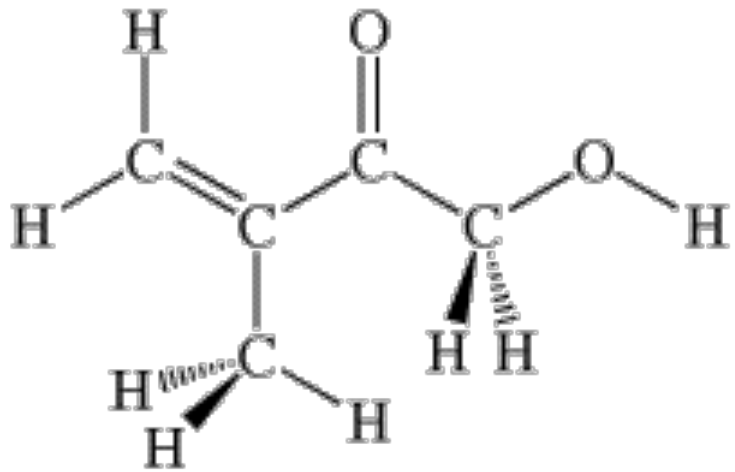
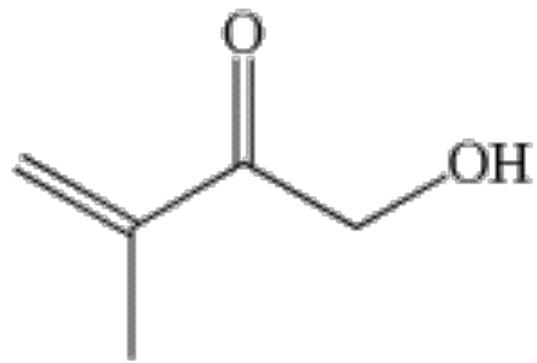

B

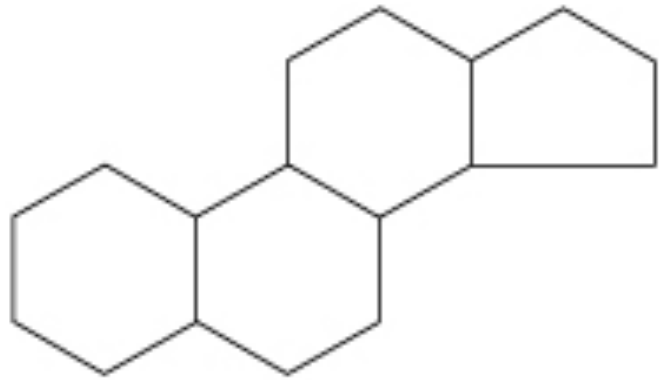



C

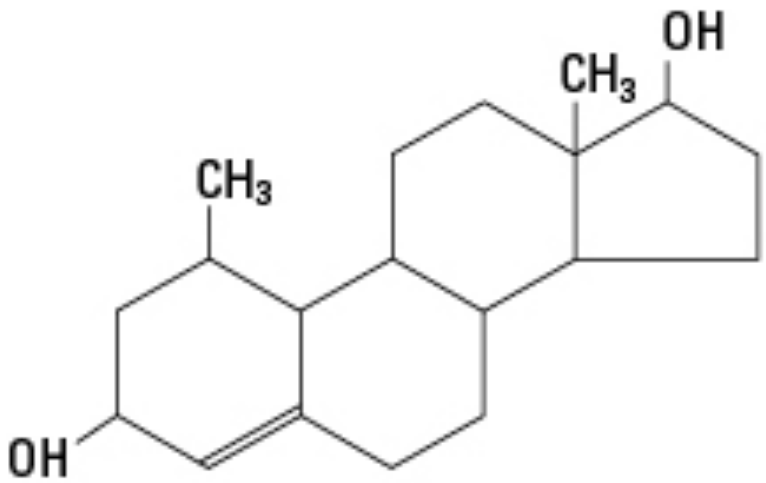
# Why no quadruple bonds?

$CH_3CH_2CH_2CH_2CH_3$ is  is 

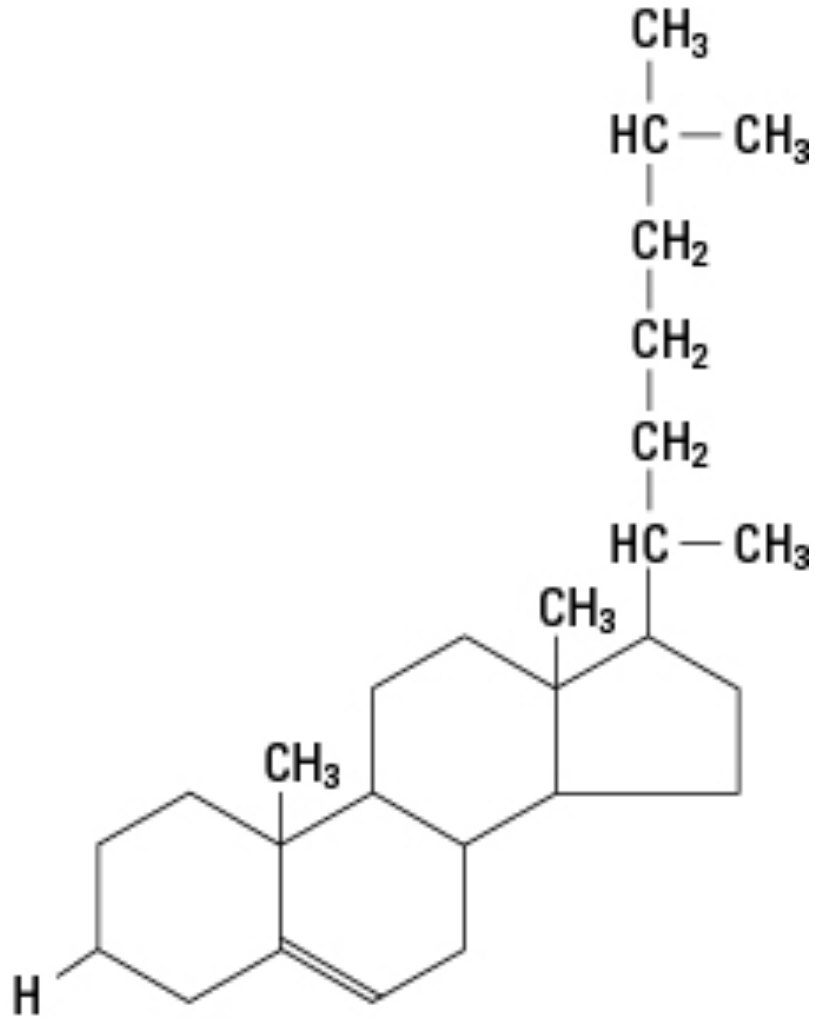
$CH_2=C(CH_3)C(O)CH_2OH$ is  is 



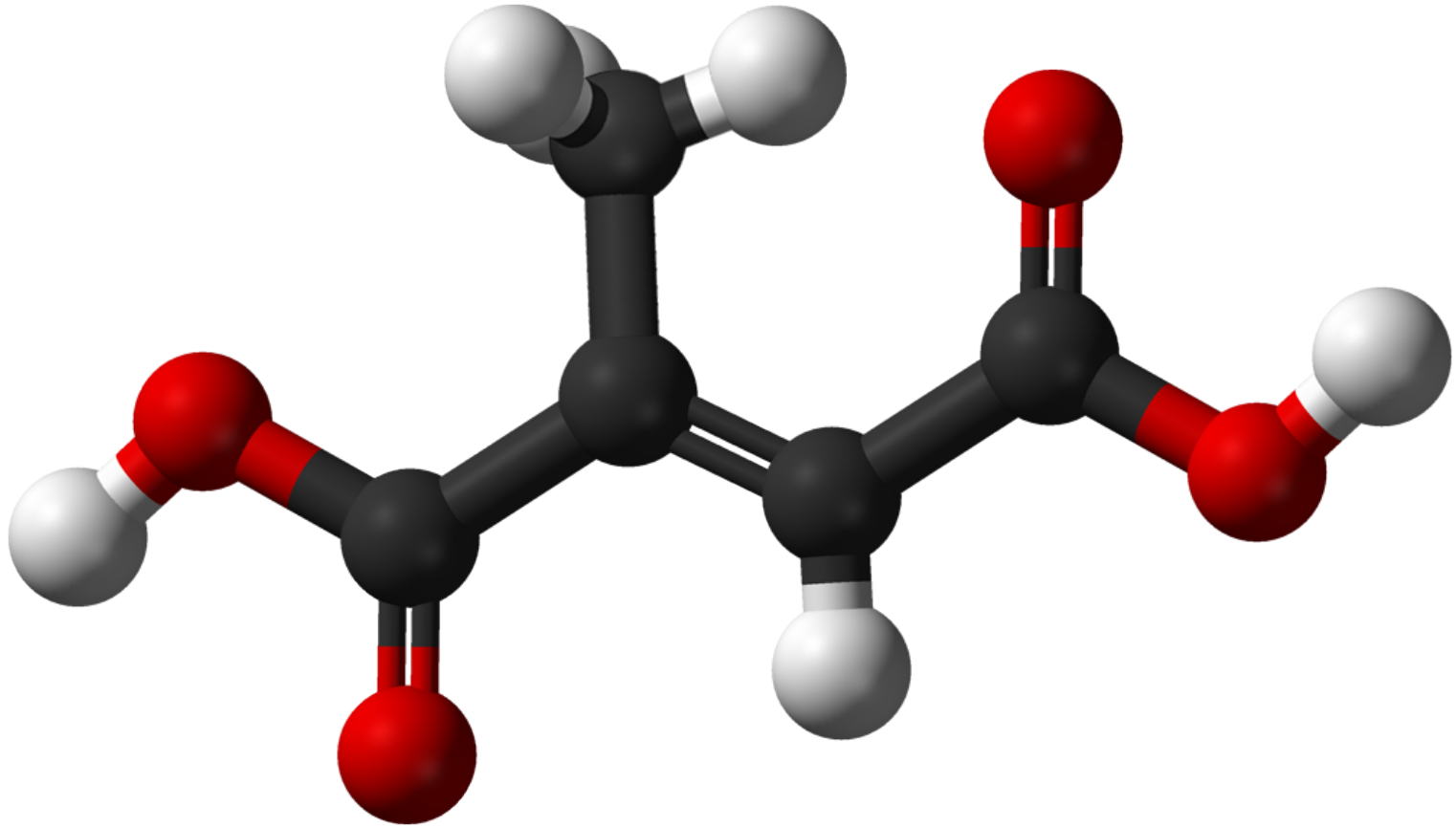
steroid backbone



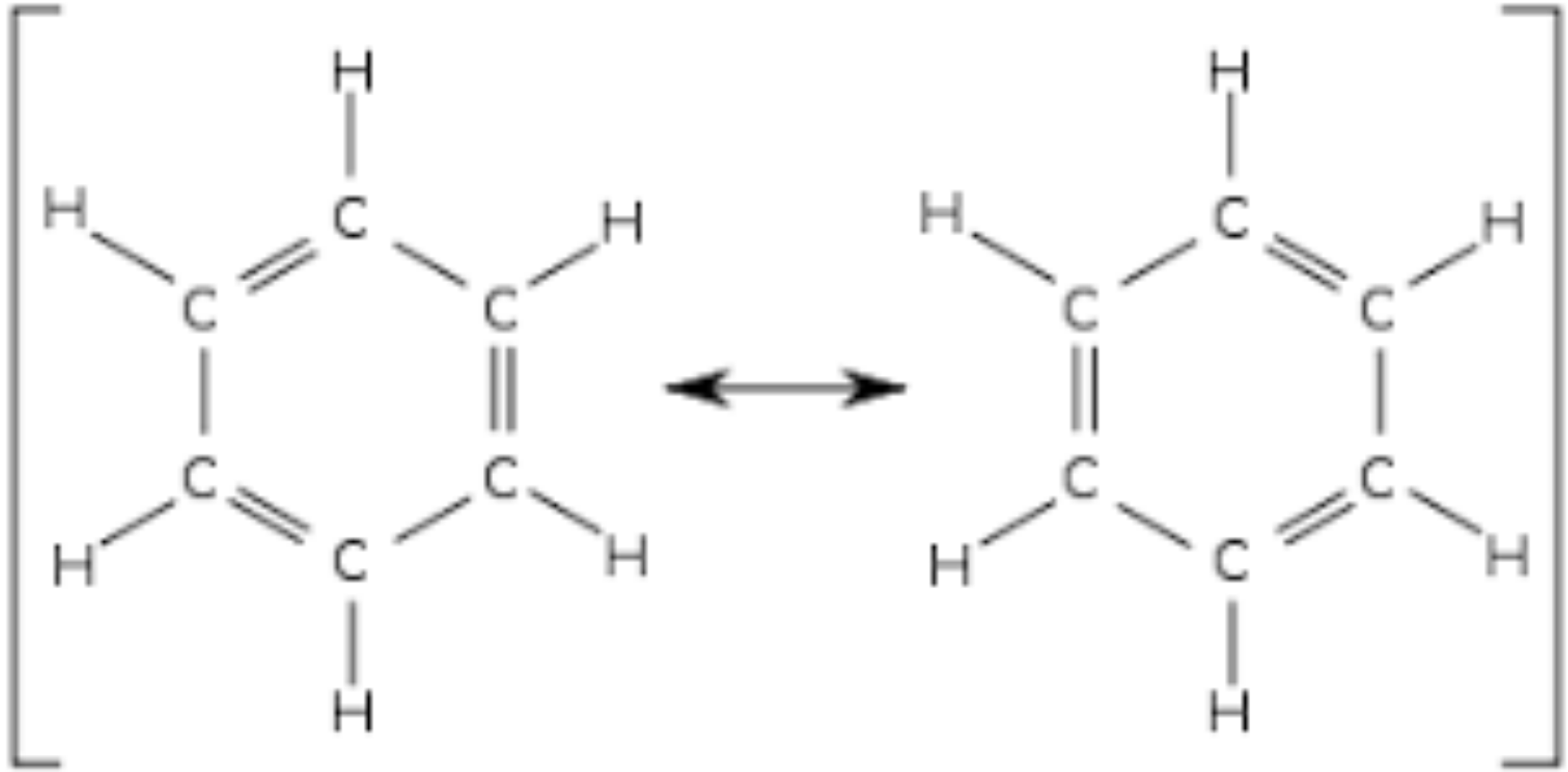

testosterone

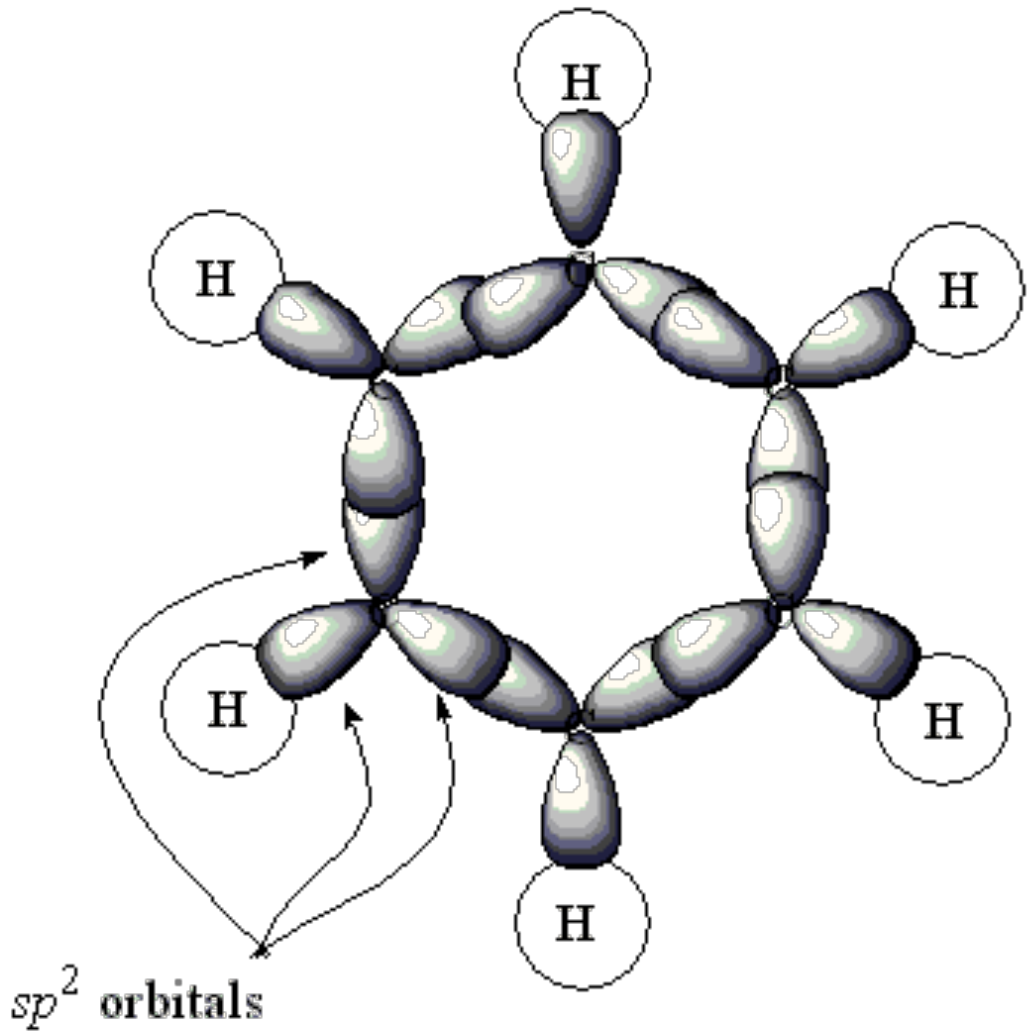



cholesterol

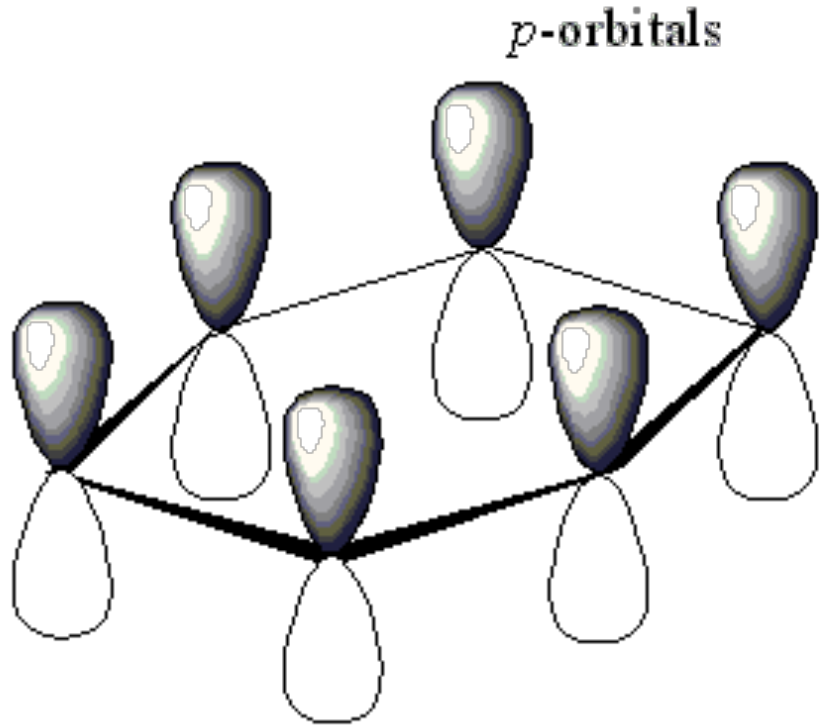


# Resonance

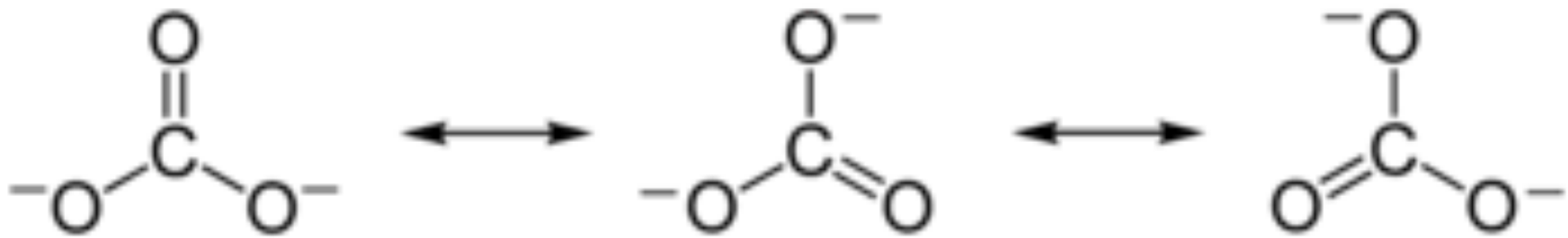

H
H
C
C
H
C
C
C
C
H
H
C
H
H
C
C
H
C
C
C
C
H
H
C
H

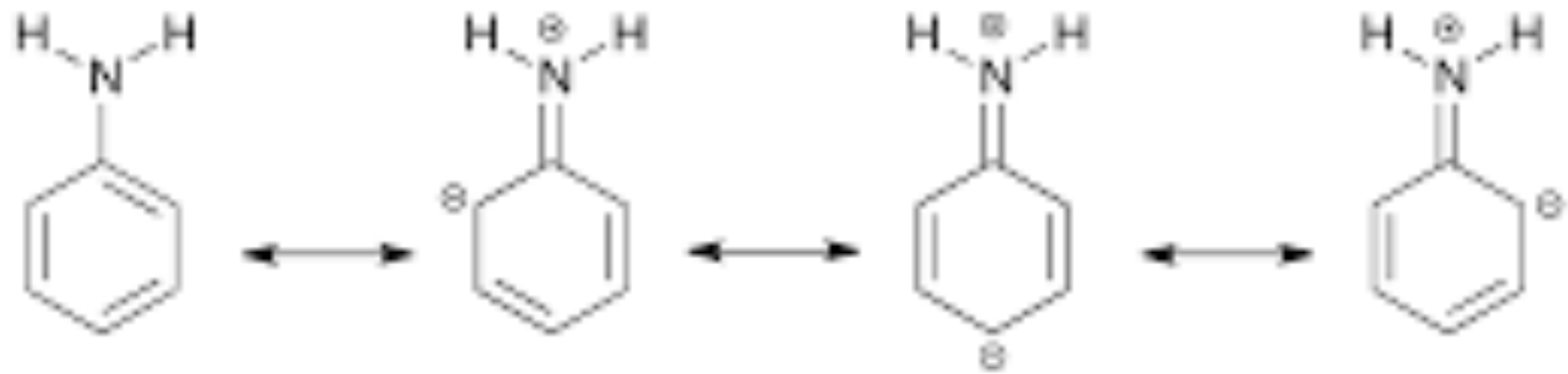


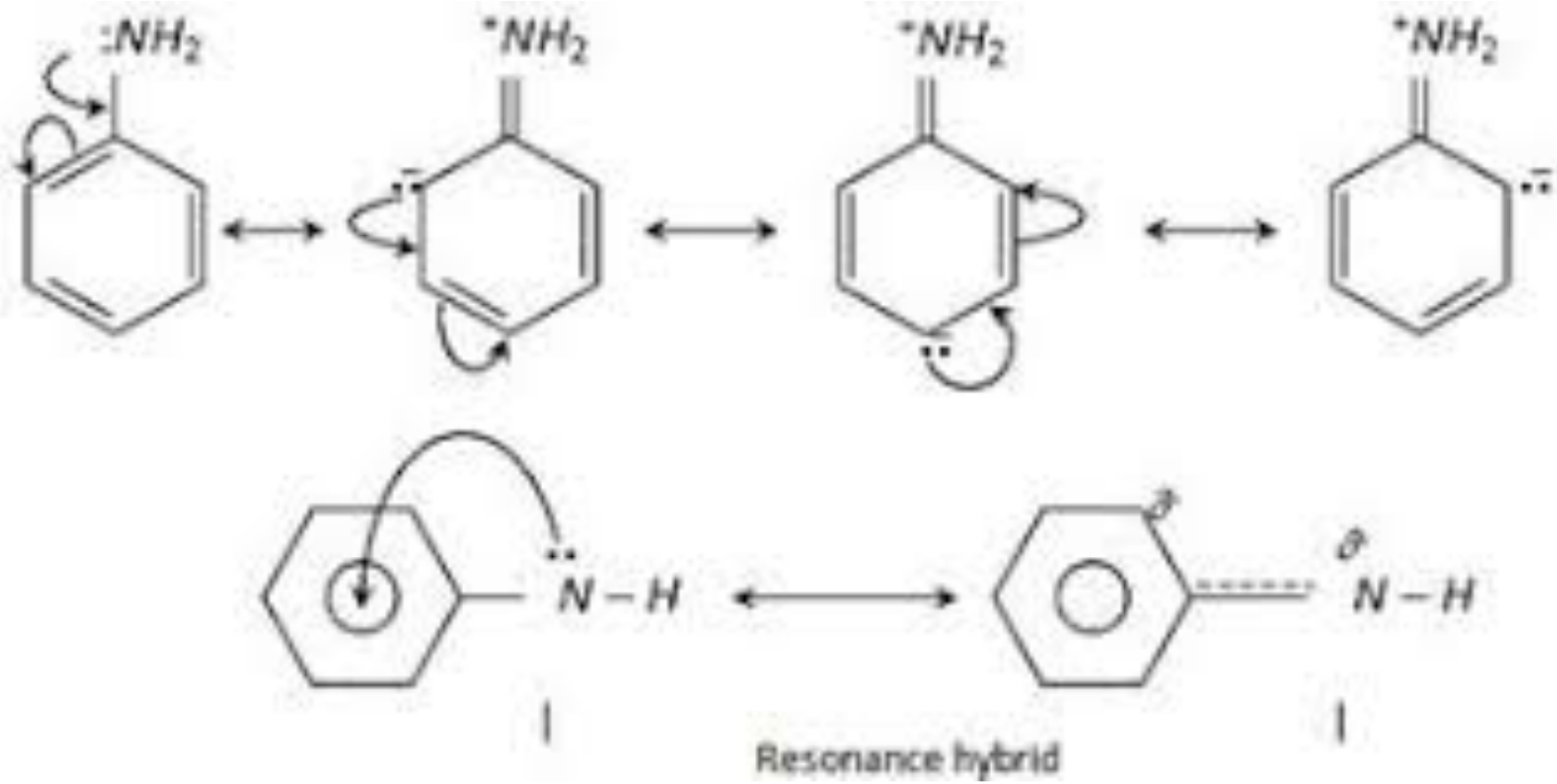

*Top view*

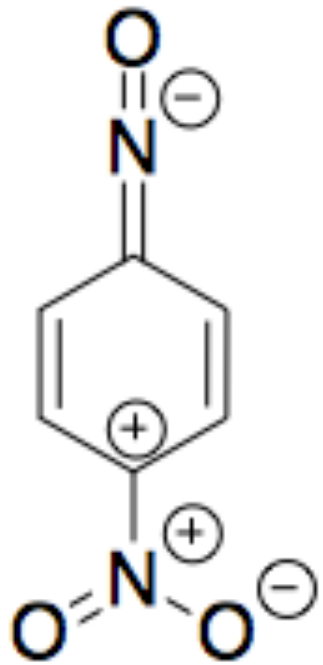



*Side view*

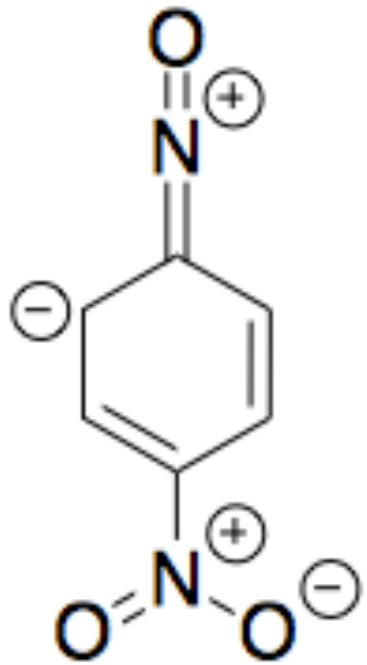




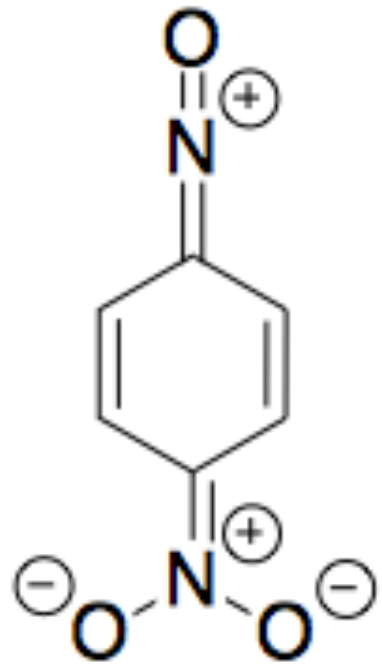

:NH2
+NH2
+NH2
+NH2
N – H
N – H
Resonance hybrid



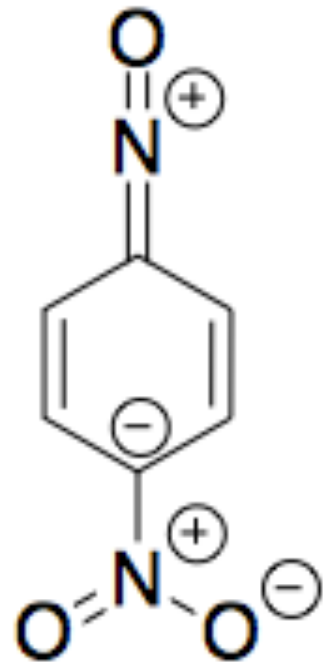
**1**



**2**

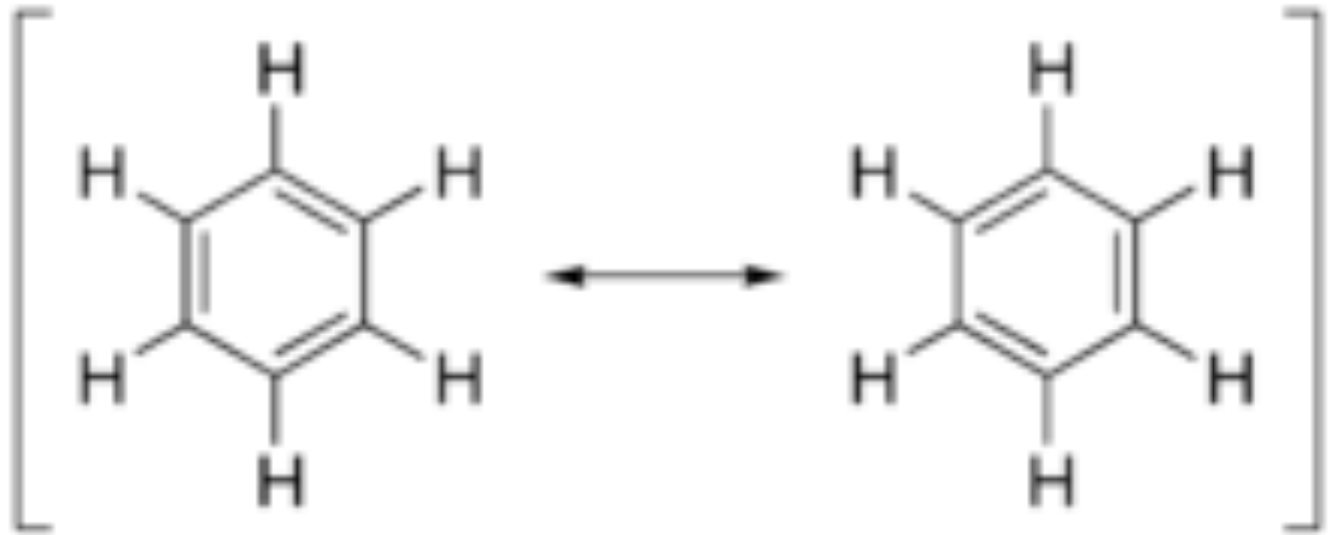


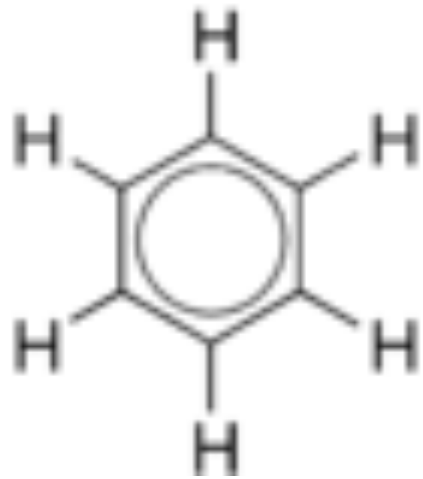
**3**

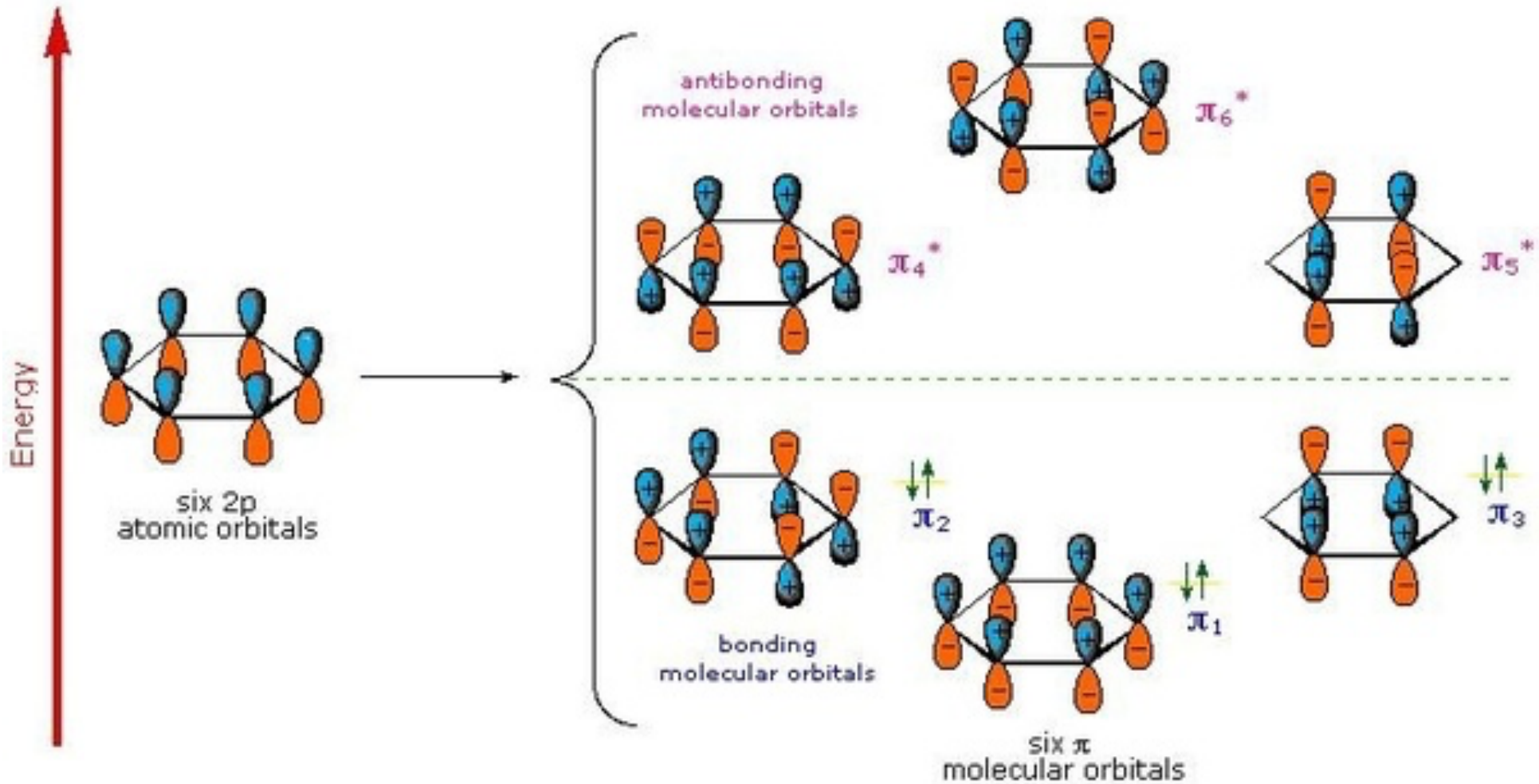


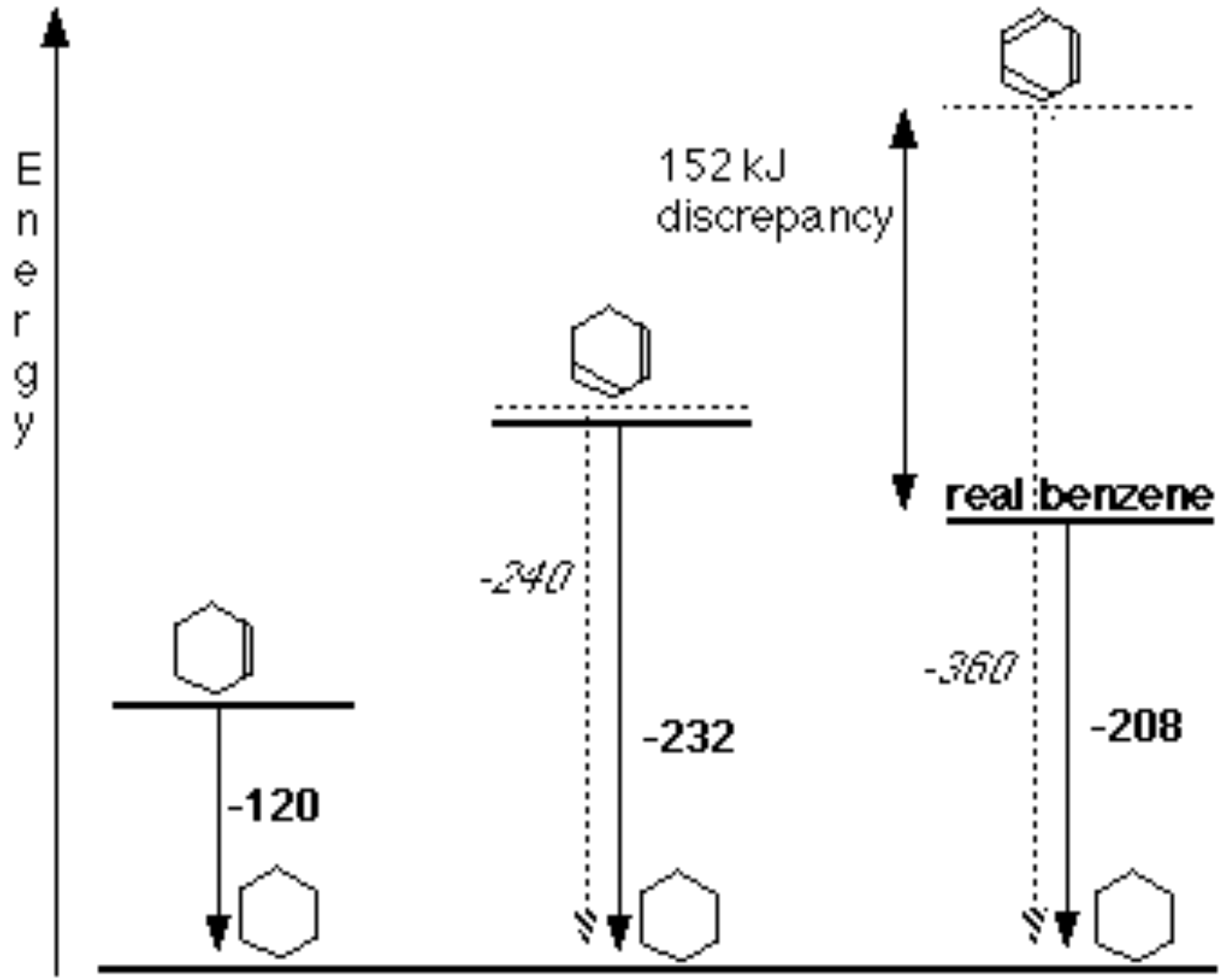
**4**

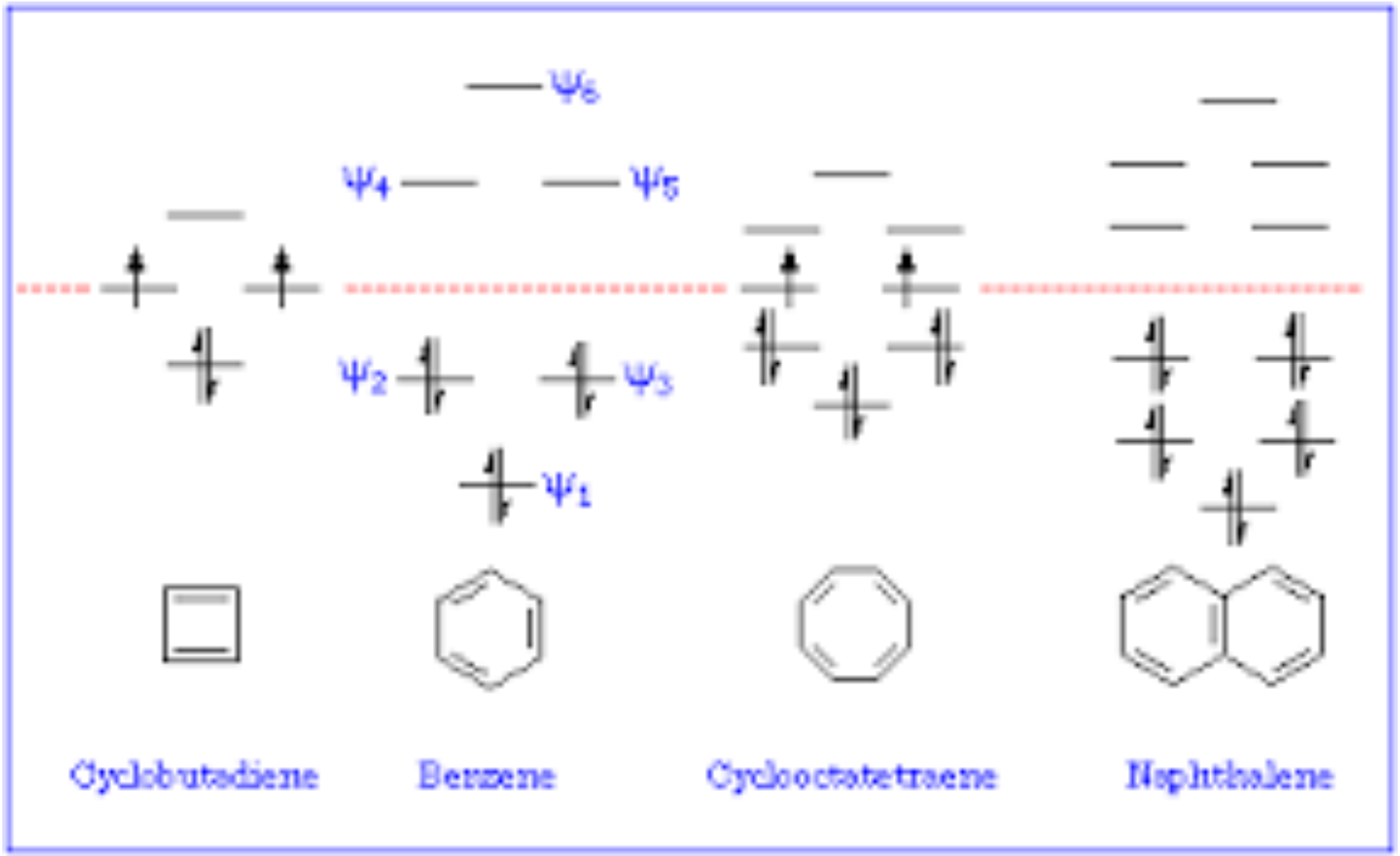
# AROMATICITY






Energy
six 2p
atomic orbitals
antibonding
molecular orbitals
$\pi_6^*$
$\pi_4^*$
$\pi_5^*$
$\pi_2$
$\pi_3$
$\pi_1$
bonding
molecular orbitals
six π
molecular orbitals

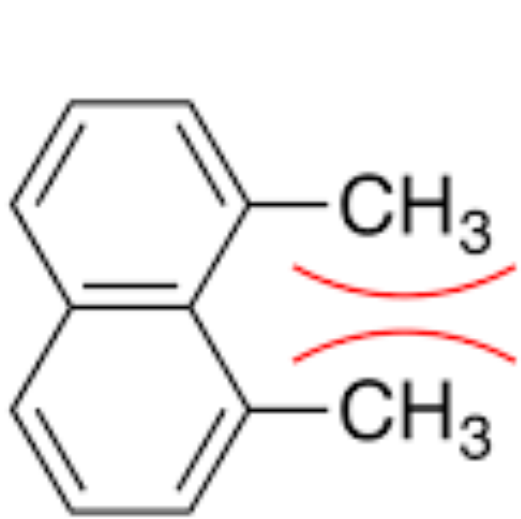

Energy
152 kJ
discrepancy
real benzene
-240
-360
-120
-232
-208


ψ6
ψ4
ψ5
ψ2
ψ3
ψ1
Cyclobutadiene
Benzene
Cyclooctatetraene
Naphthalene

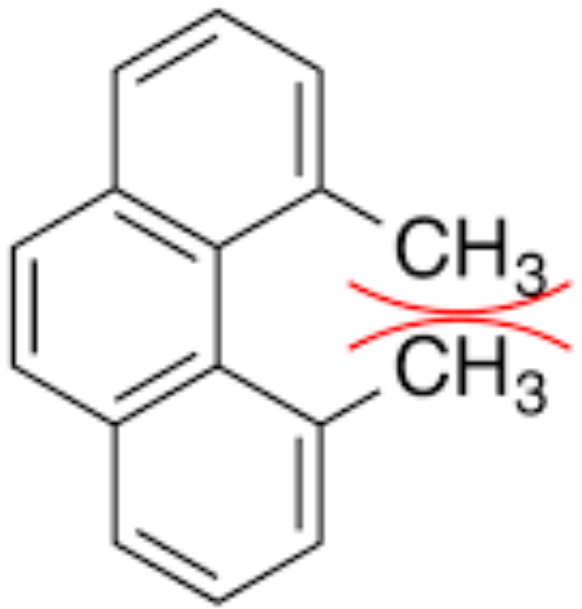
| Aromatic | Anti-Aromatic | Non-Aromatic |
| --- | --- | --- |
| •Cyclic<br>•Conjugated<br>•(4n+2) Pi electrons<br>•Flat | •Cyclic<br>•Conjugated<br>•(4n) Pi electrons<br>•Flat | *Fails any one of the criteria on the left* |
|  |  |  |
| **benzene** | **cyclobutadiene** | **cyclooctatetraene**<br>*(?!!)* |

# The Stability of Organic Molecules

# Torsional Strain

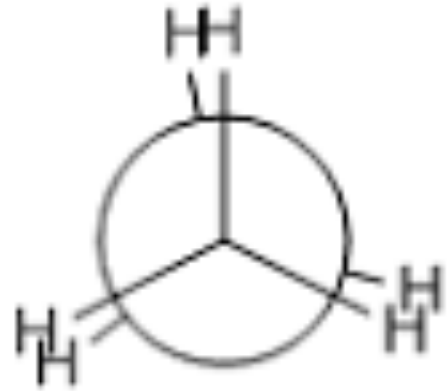



7.6 kcal/mol

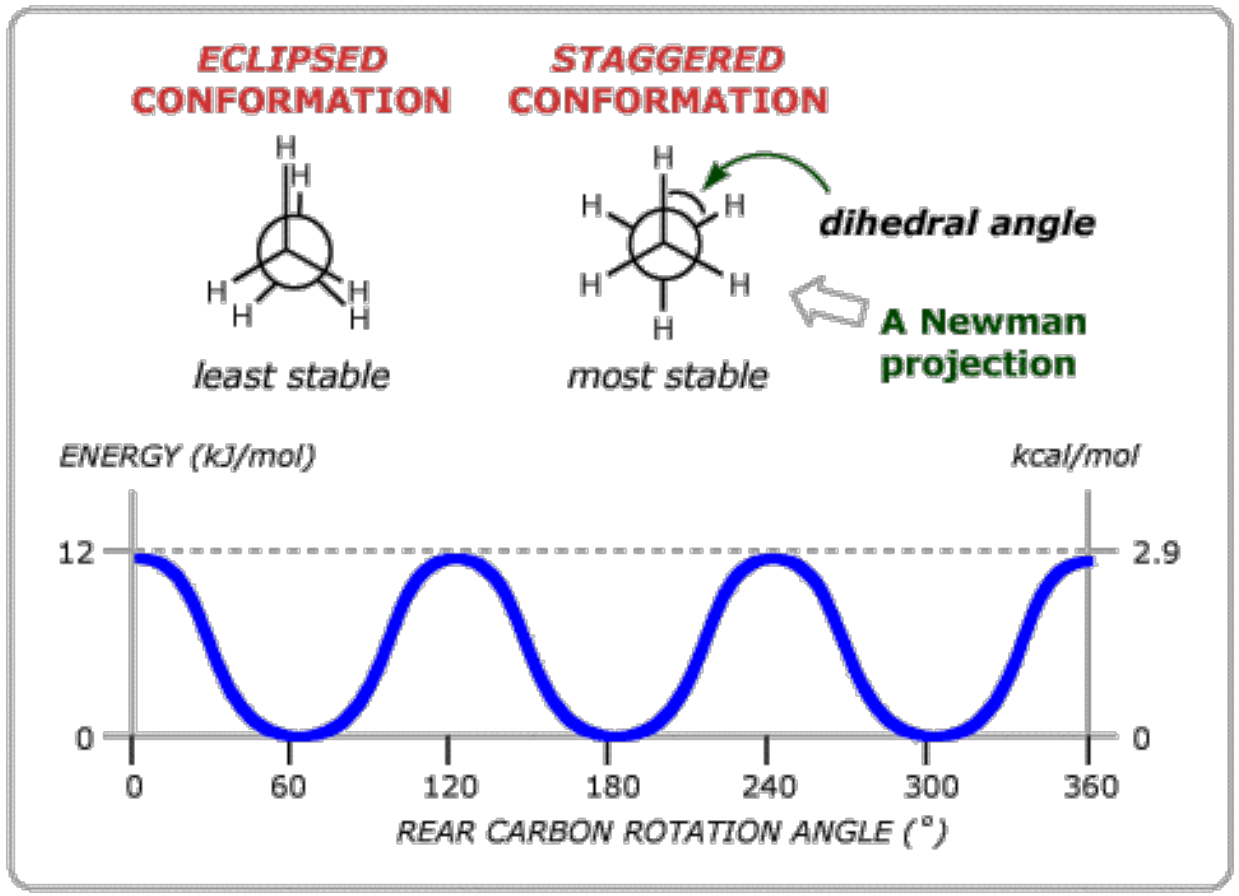


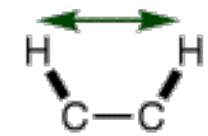

12–15 kcal/mol


staggered




eclipsed



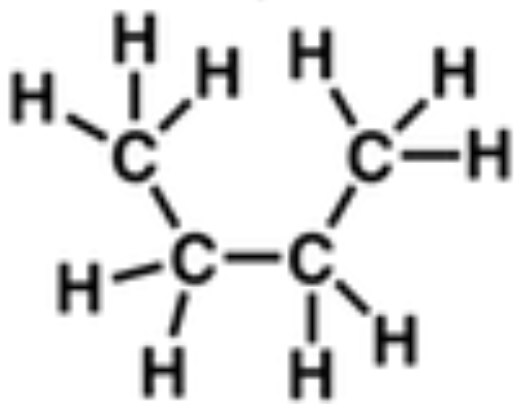




Eclipsed: 2.29Å
Staggered: 2.55Å

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

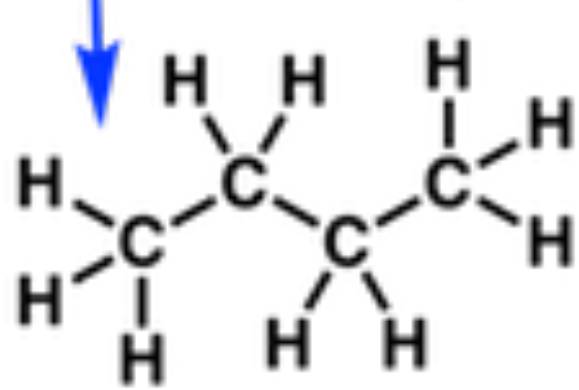
# Steric Strain

**Steric strain** caused by two eclipsed $CH_3$ groups



**Eclipsed Conformation**

The two $CH_3$ groups are 180° apart



**Anti Conformation**

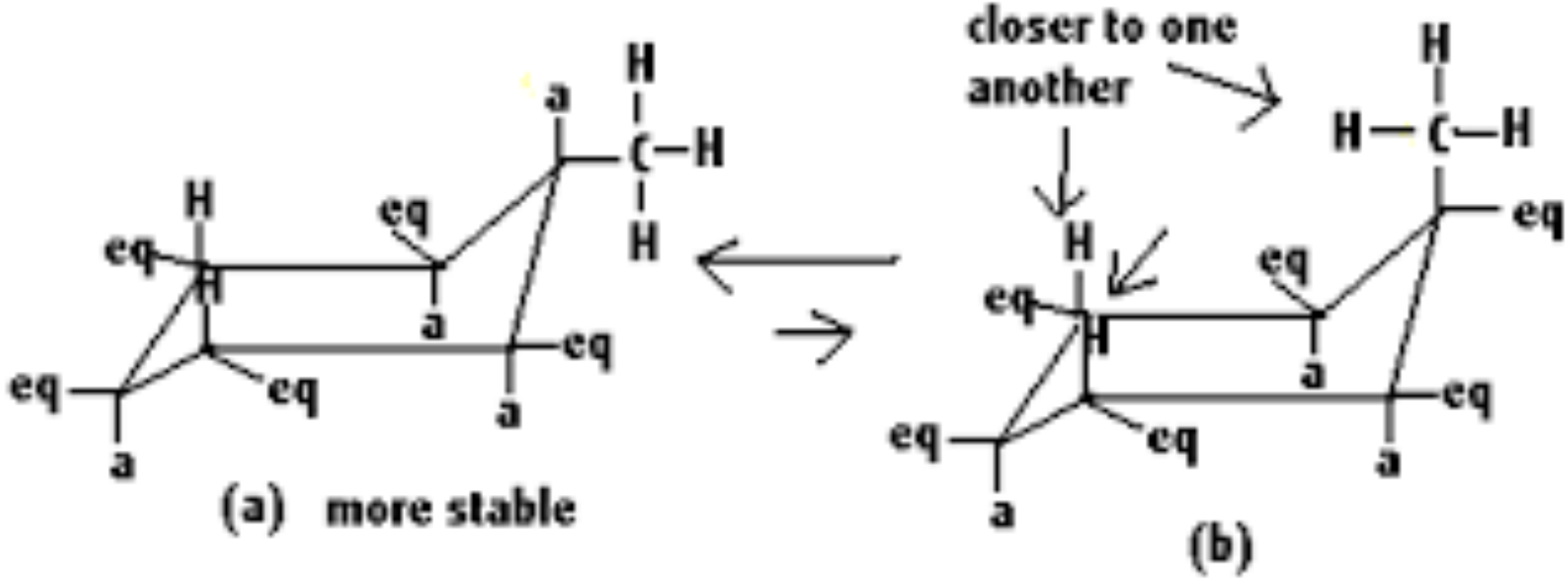
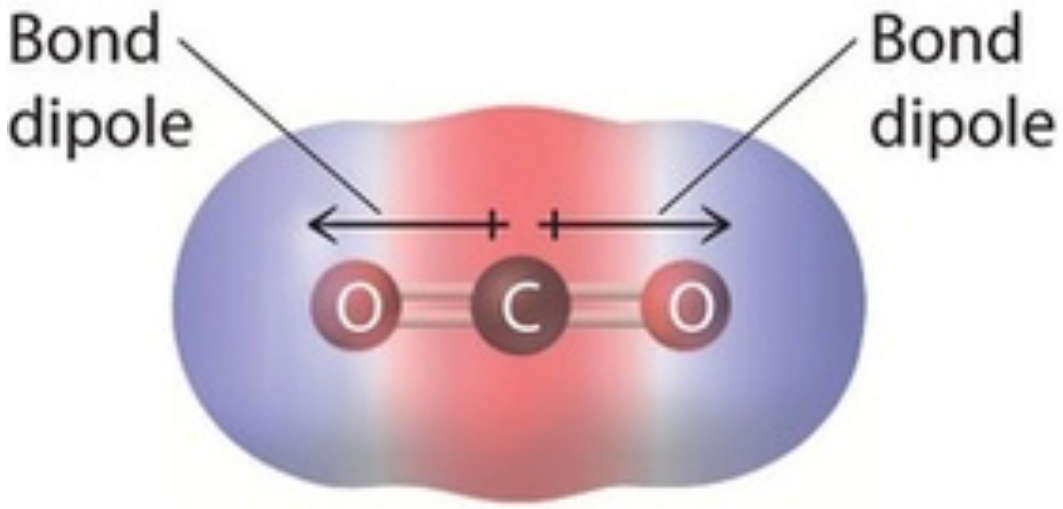
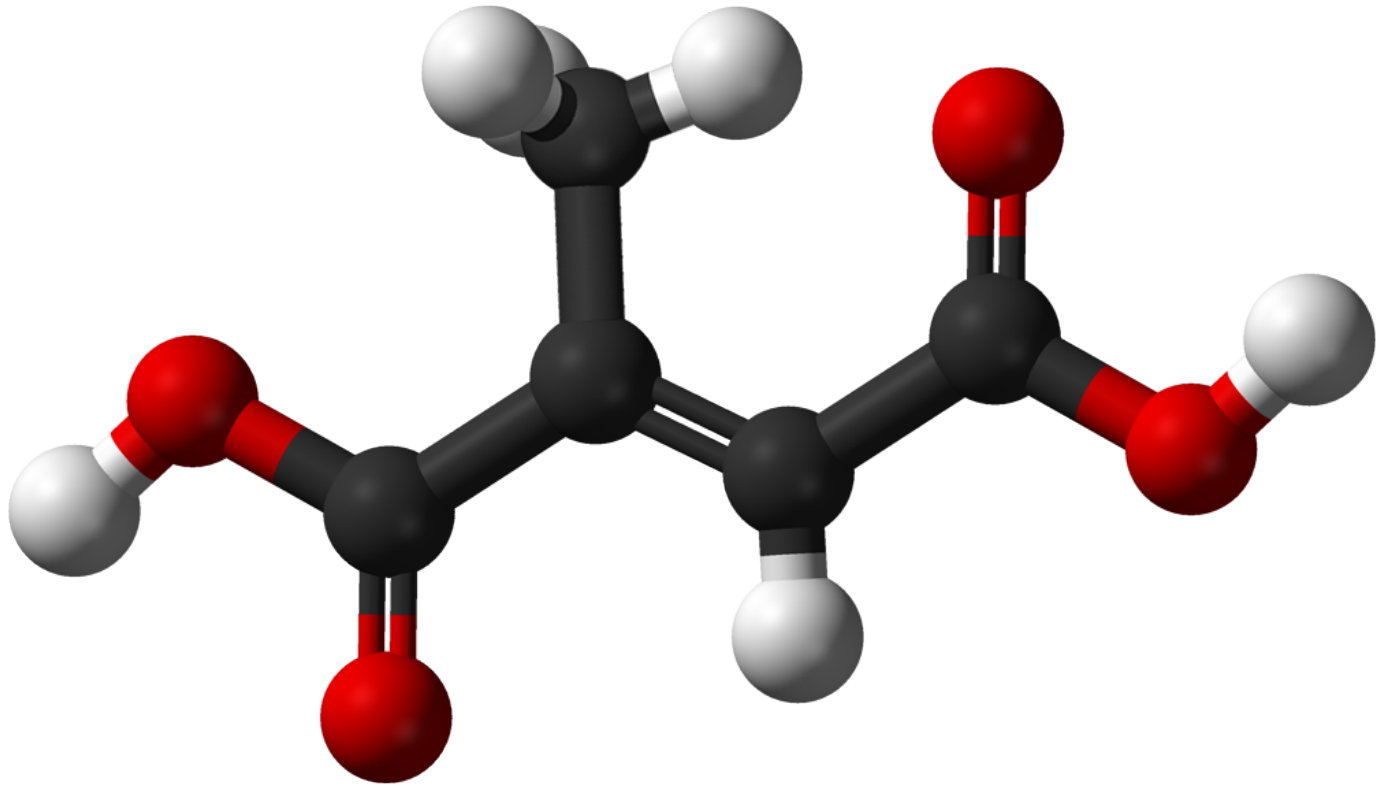



Fig 8- Methyl Cyclohexane Conformers

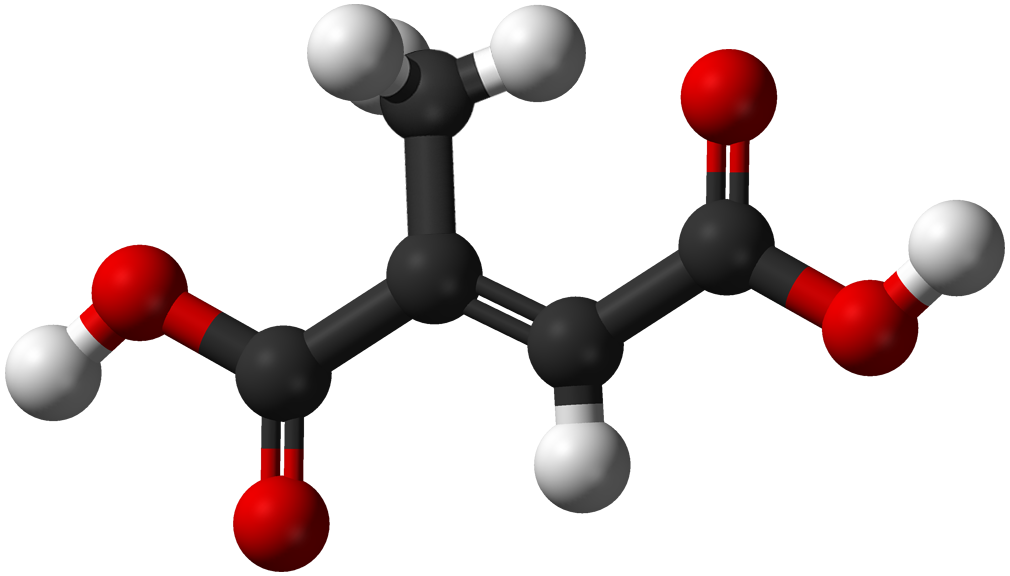
# A Preview of What's Next:




(a) No net dipole moment



# ORGANIC CHEMISTRY II:
# Reactions of Small Molecules



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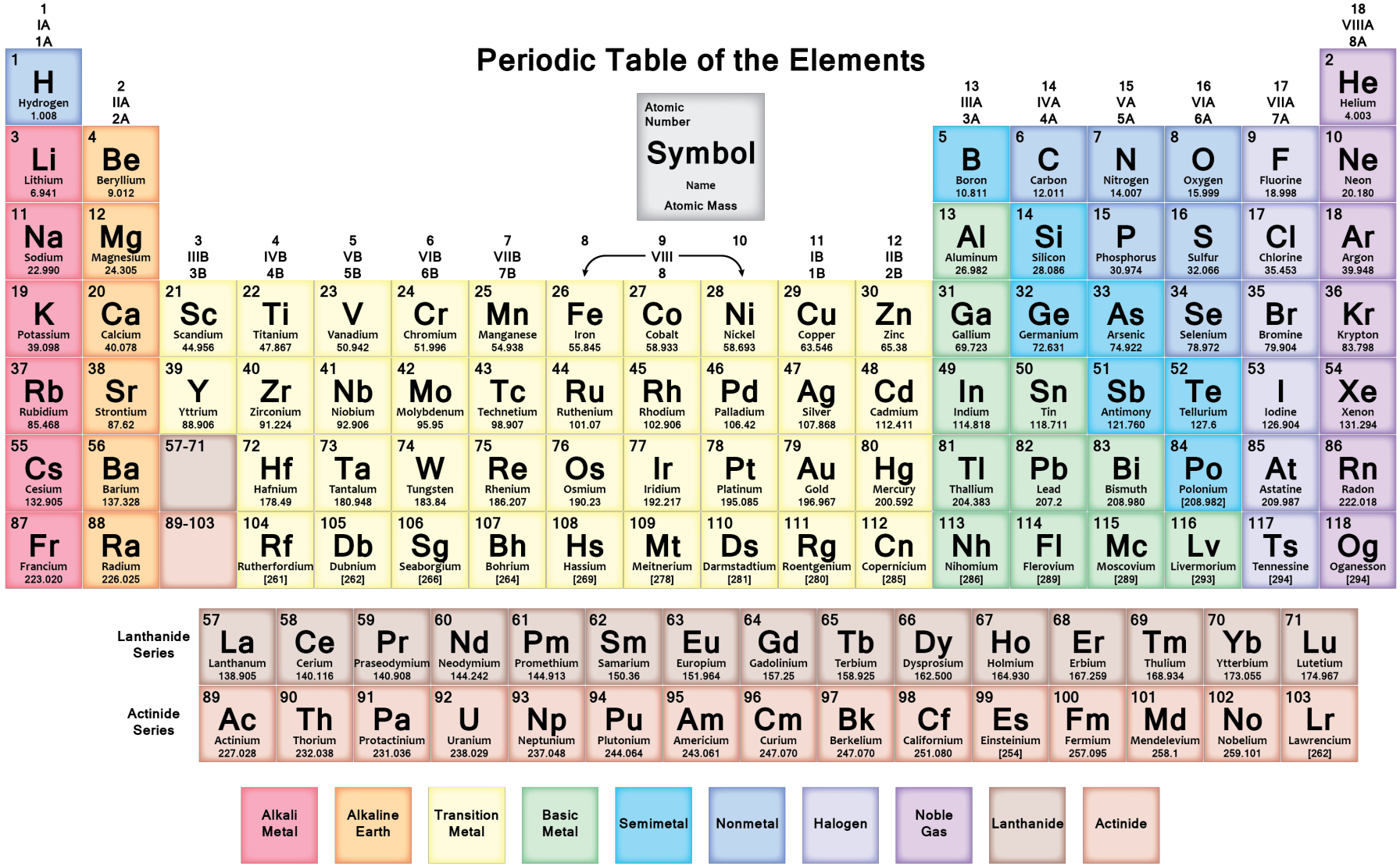
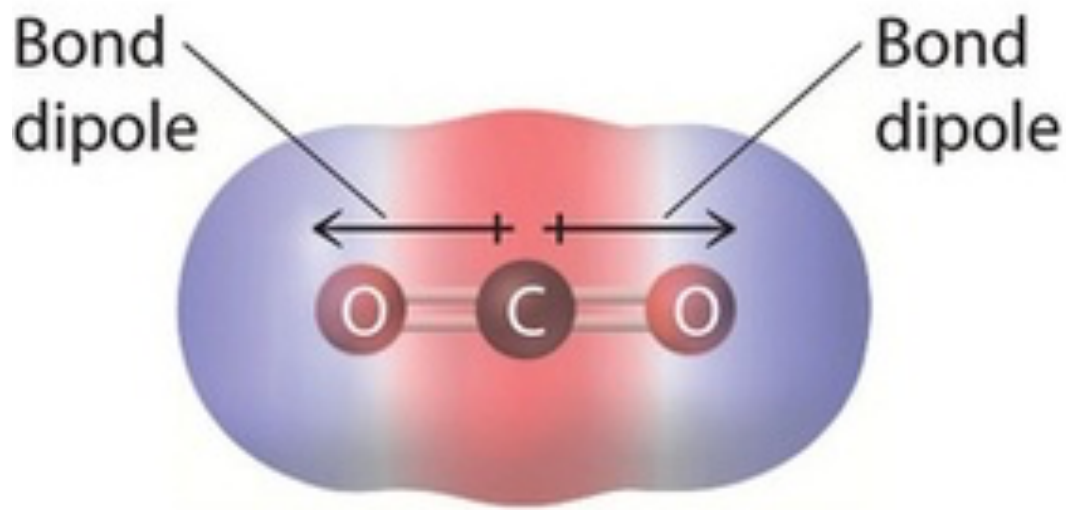
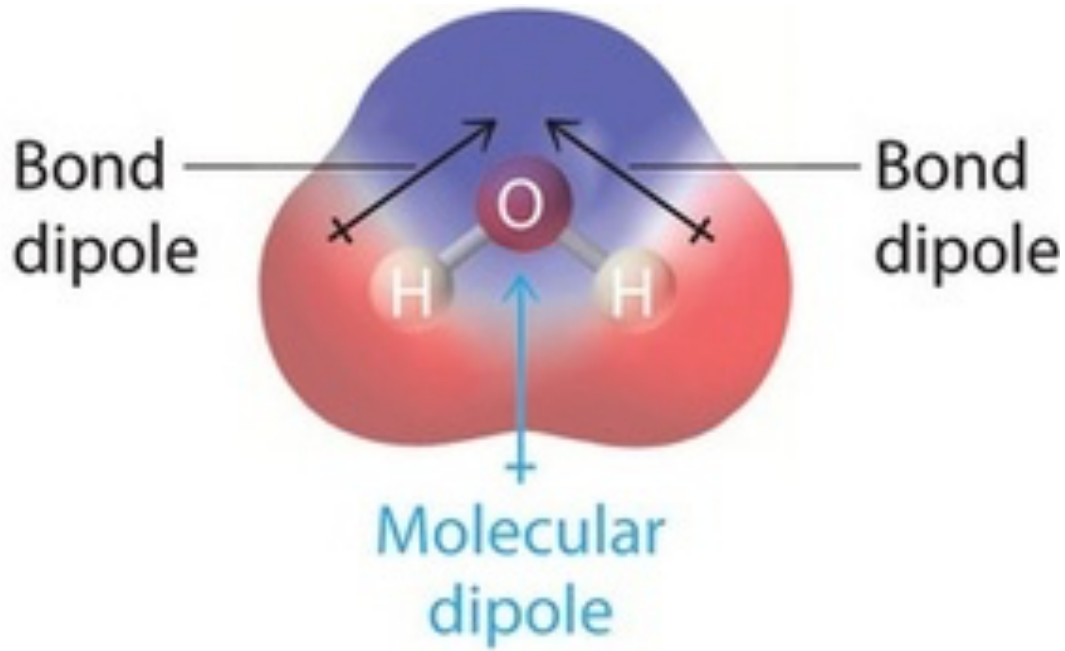
# Periodic Table of the Elements



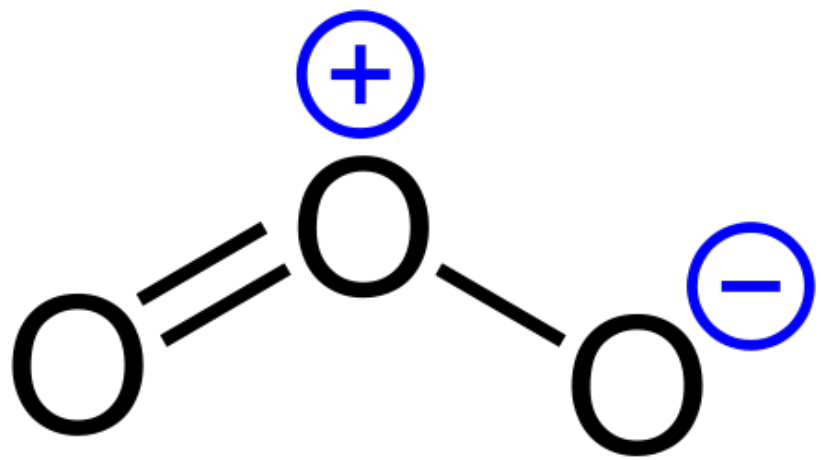
# Molecular Charge Distribution

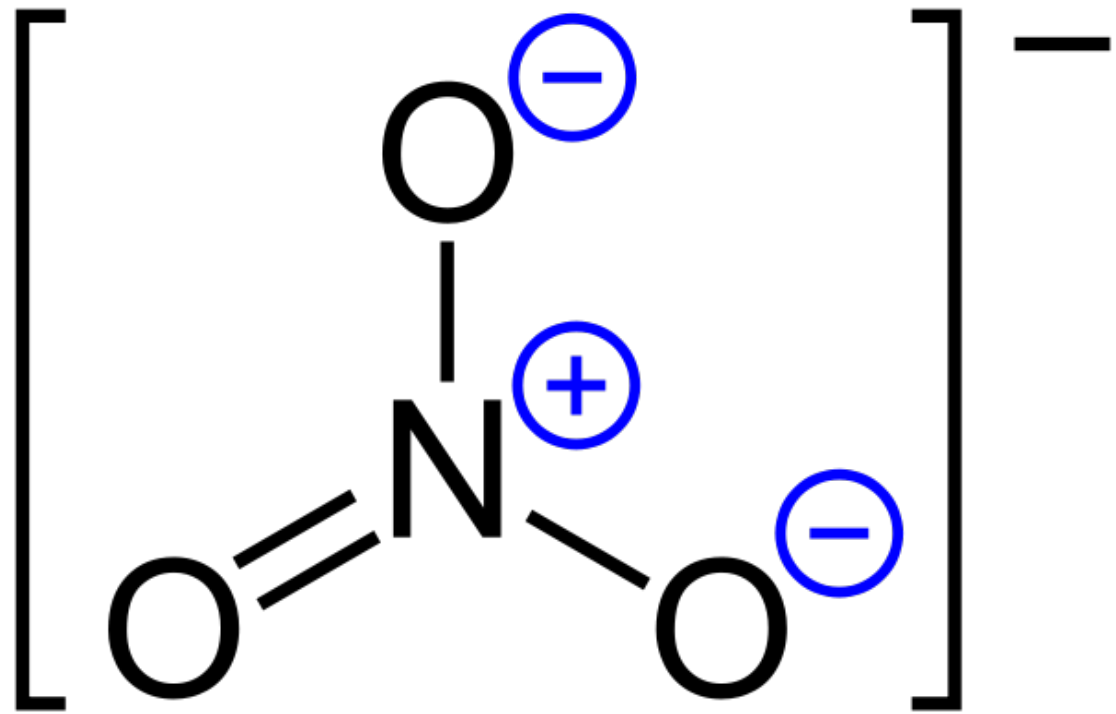


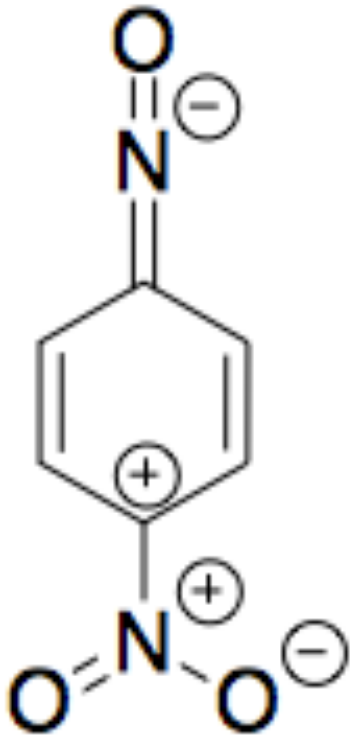

(a) No net dipole moment



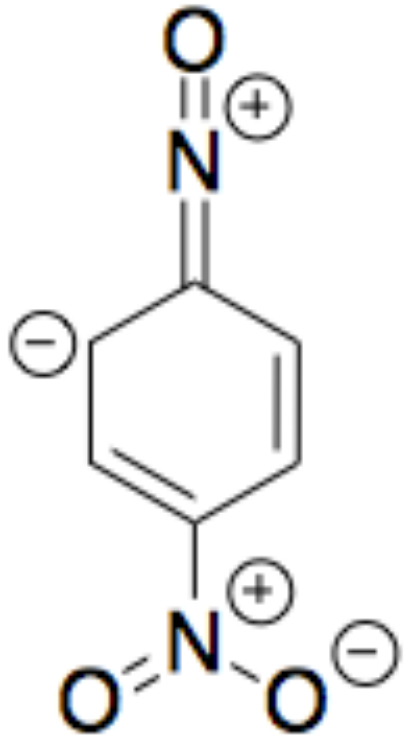

(b) Net dipole moment


O
O
O

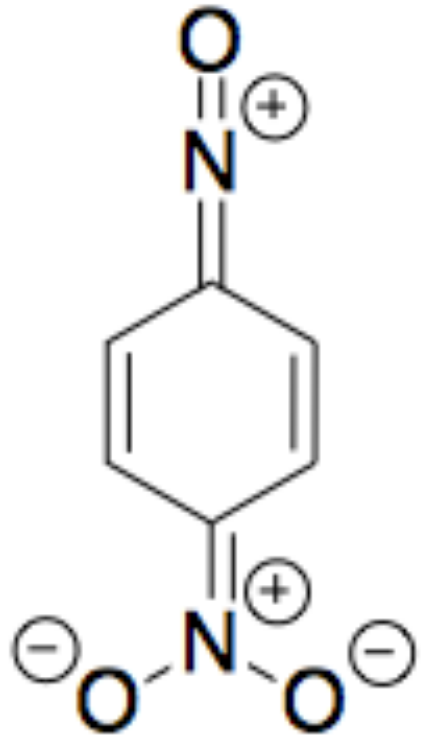

O
N
O
O



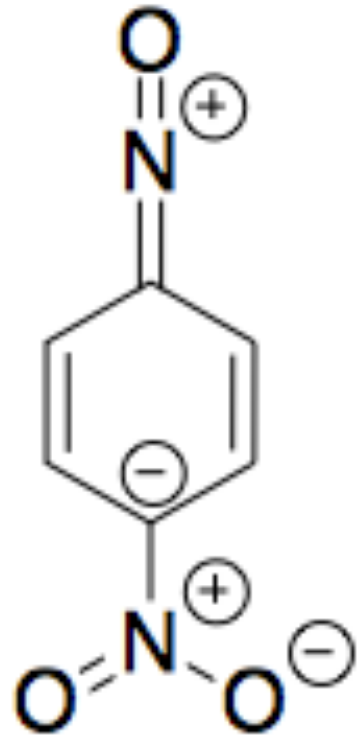
**1**



**2**

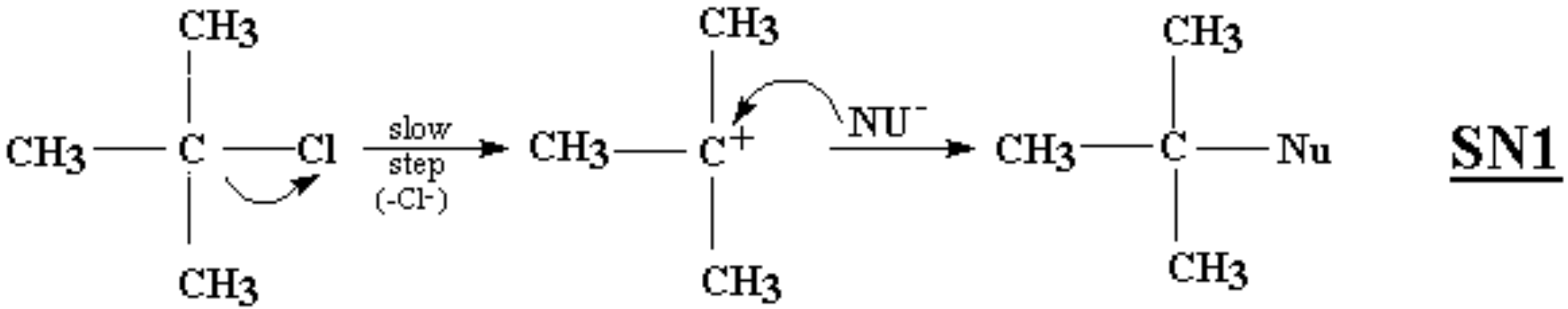


**3**



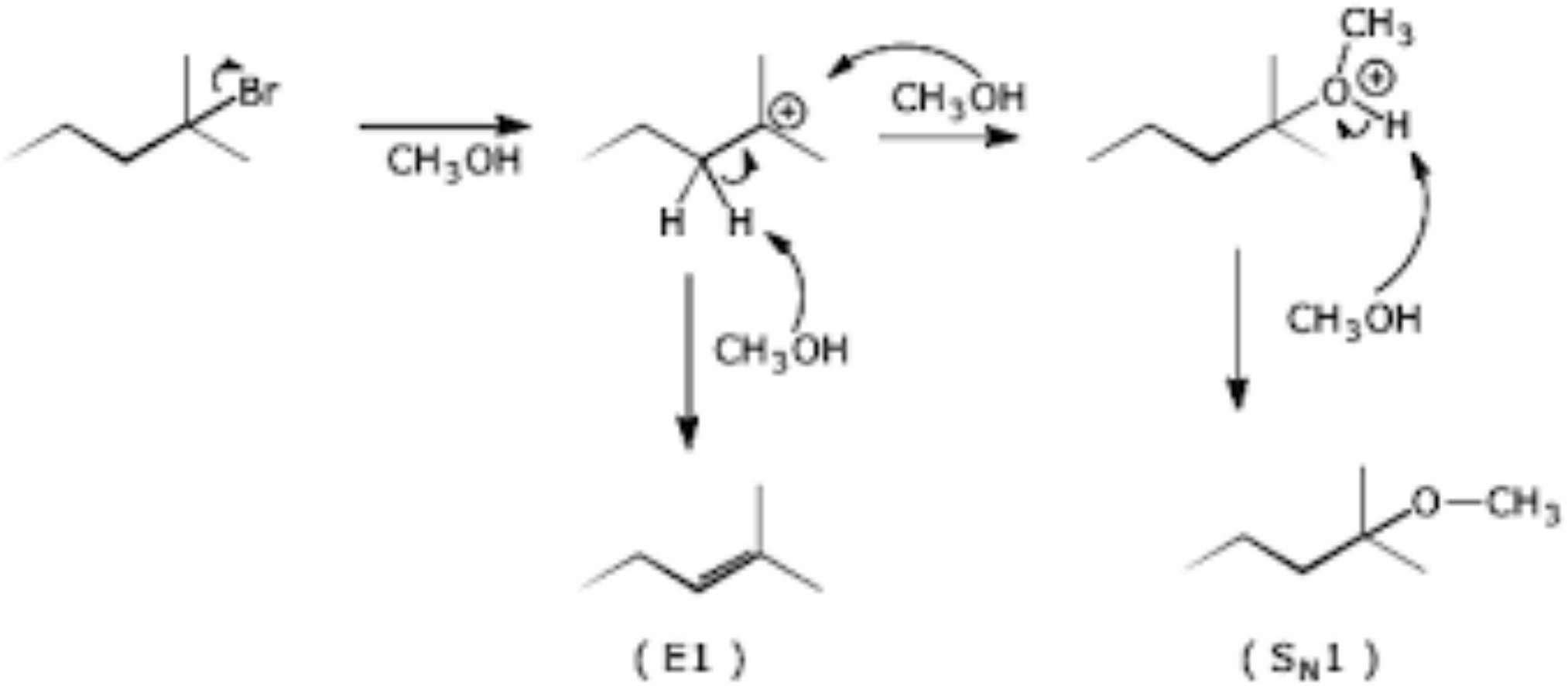
**4**

# SN1 Reactions

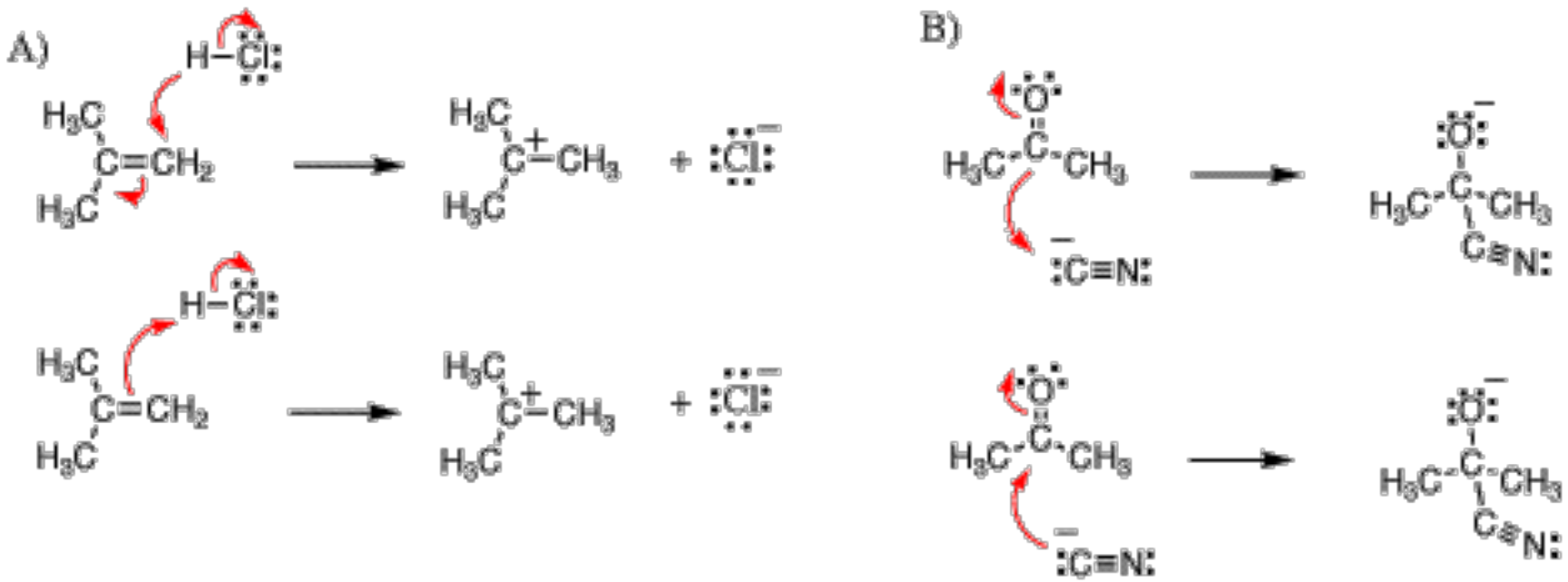



**SN1**

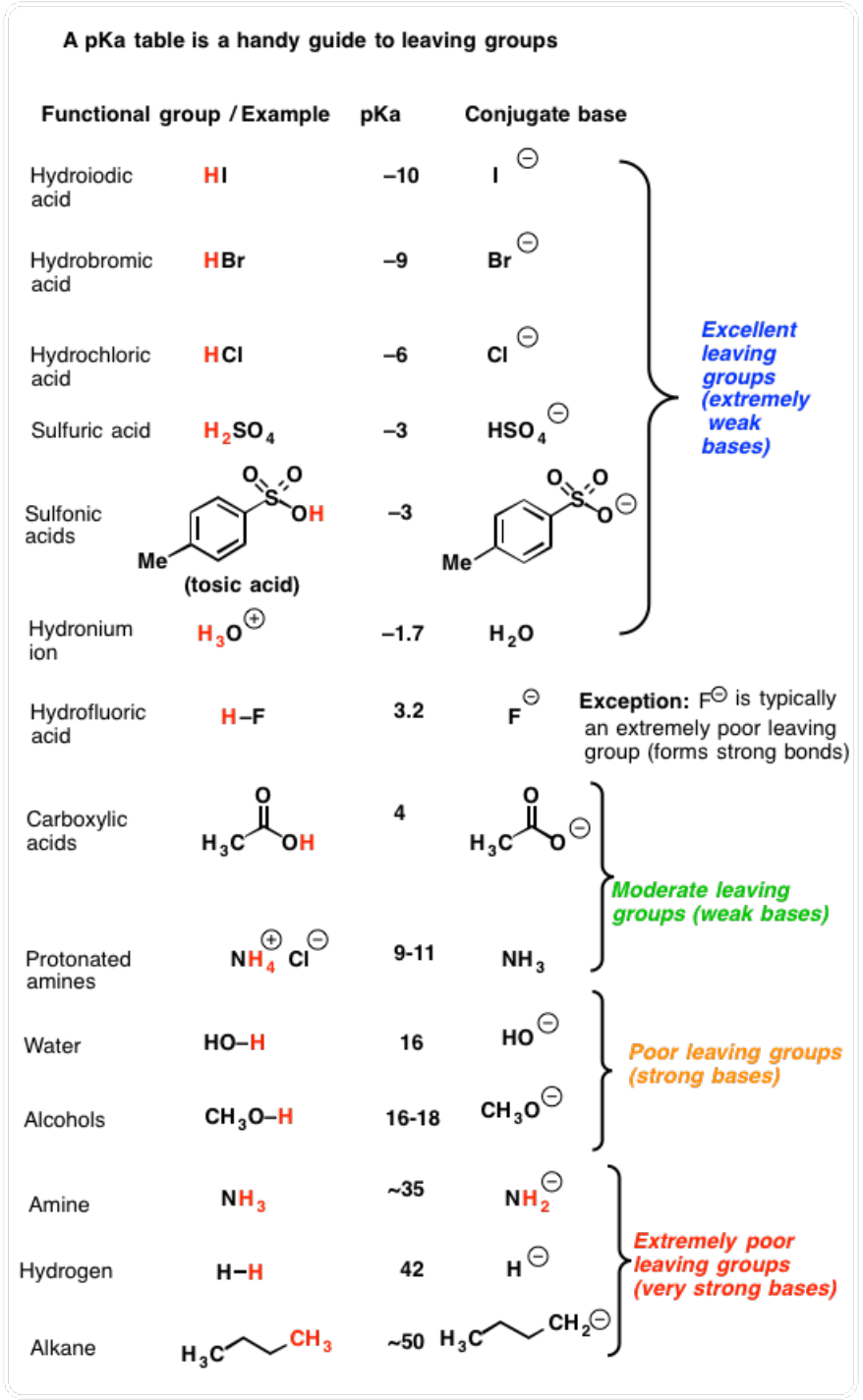
# Elimination reactions



# Alternate Formation of Intermediate

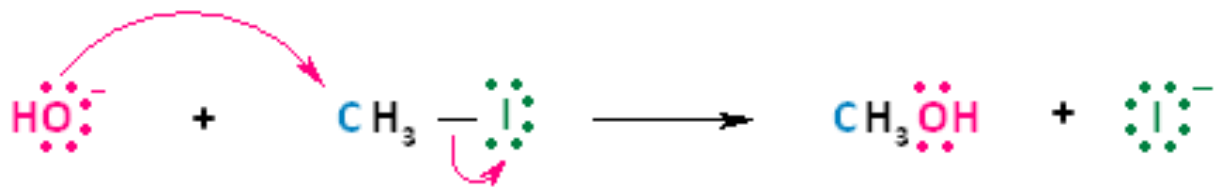


# Leaving Group Stability

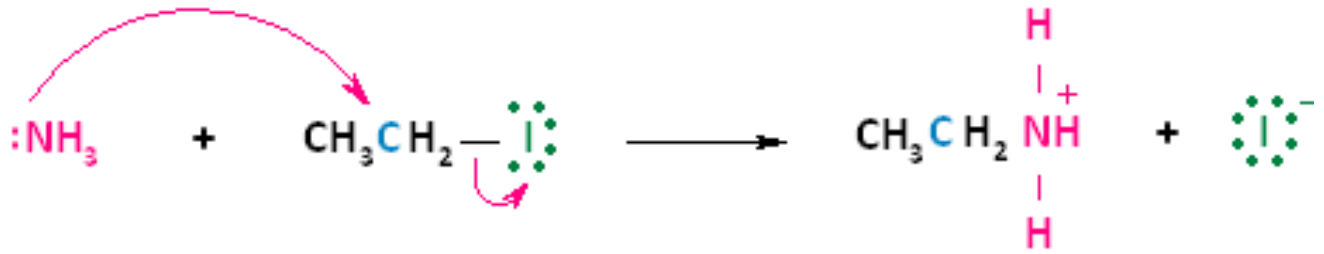


# SN2 Reactions

**Example #1**



**Example #2**



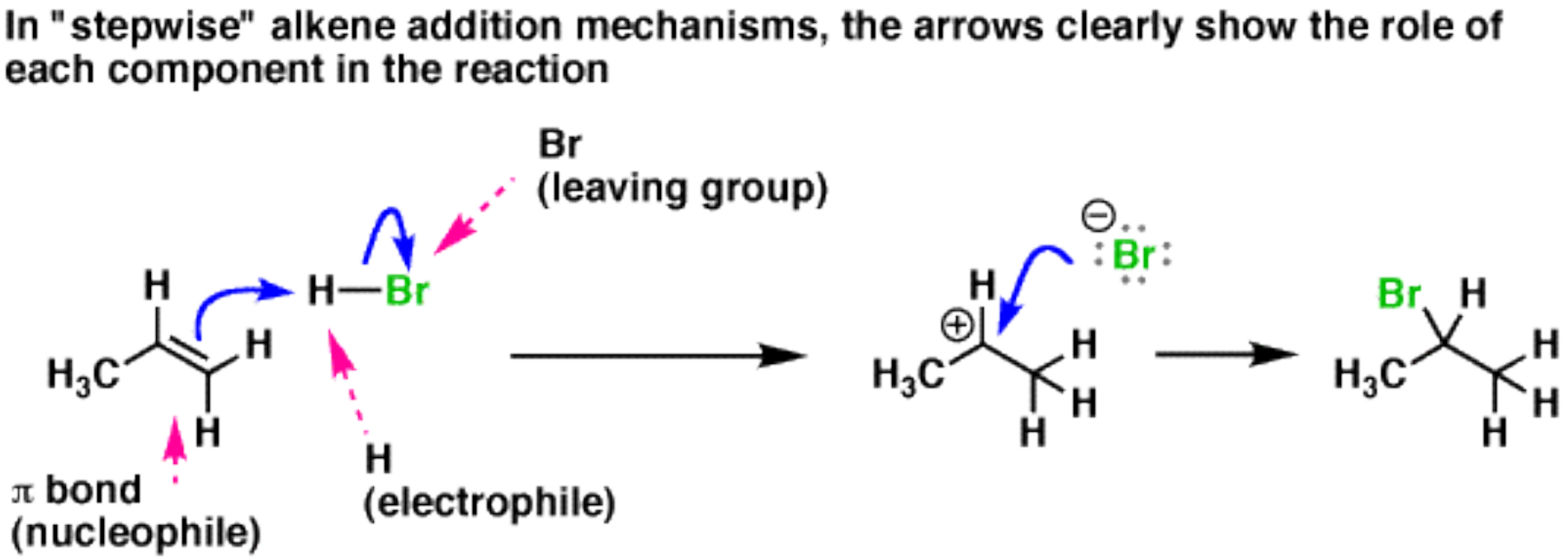
# Nucleophilic Strength

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

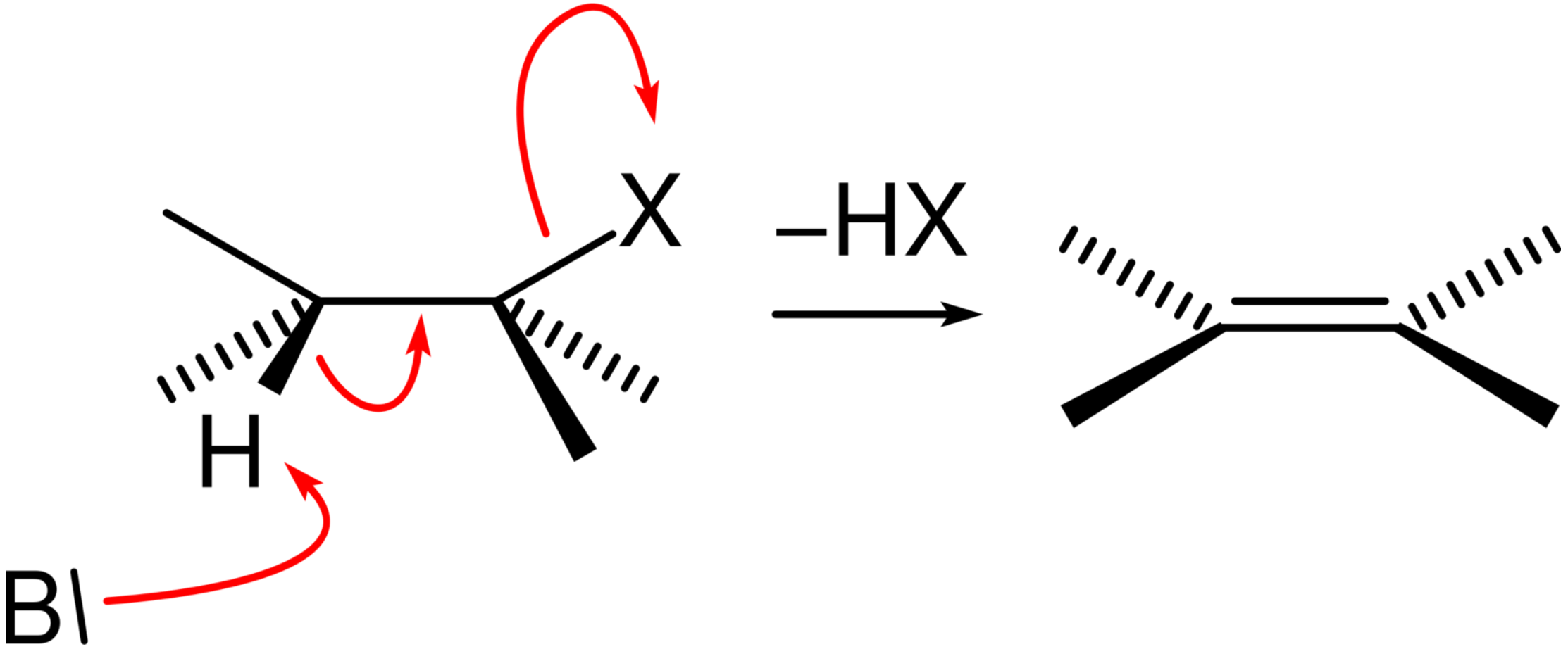
| | | | |
|---|---|---|---|
| strong nucleophiles | $(CH_3CH_2)_3P$: | moderate nucleophiles | $:\ddot{Br}:^-$ |
| | $^-:\ddot{S}-H$ | | $:NH_3$ |
| | $:\ddot{I}:^-$ | | $CH_3-\ddot{S}-CH_3$ |
| | $(CH_3CH_2)_2\ddot{N}H$ | | $:\ddot{Cl}:^-$ |
| | $^-:C\equiv N$ | | $CH_3C(=O)-\ddot{O}:^-$ |
| | $(CH_3CH_2)_3N$: | weak nucleophiles | $:\ddot{F}:^-$ |
| | $H-\ddot{O}:^-$ | | $H-\ddot{O}-H$ |
| | $CH_3-\ddot{O}:^-$ | | $CH_3-\ddot{O}-H$ |

- Stronger nucleophiles **react faster** in $S_N2$.
- Strong bases are strong nucleophiles, but not all strong nucleophiles are basic.

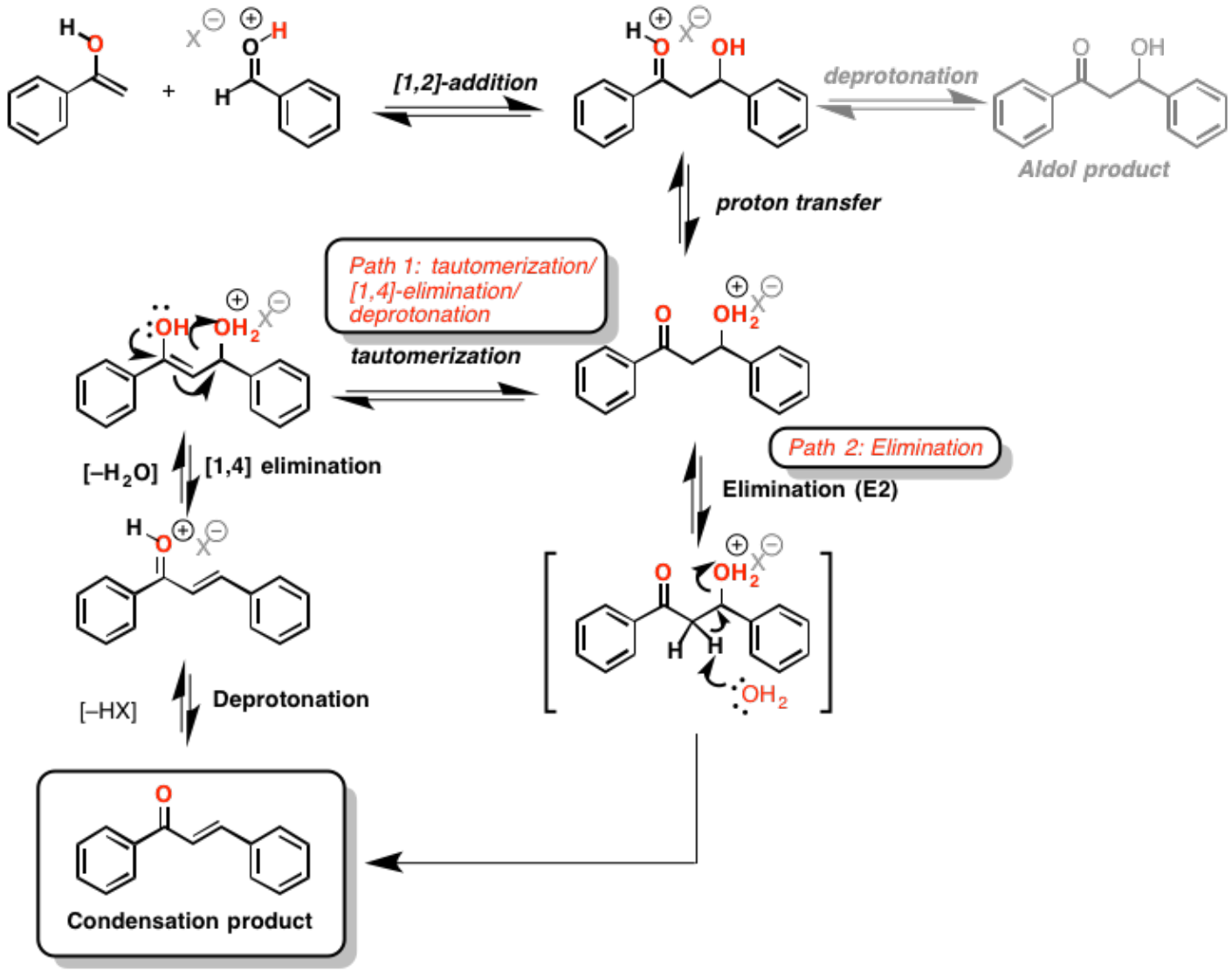
# Unconventional Nucleophile!



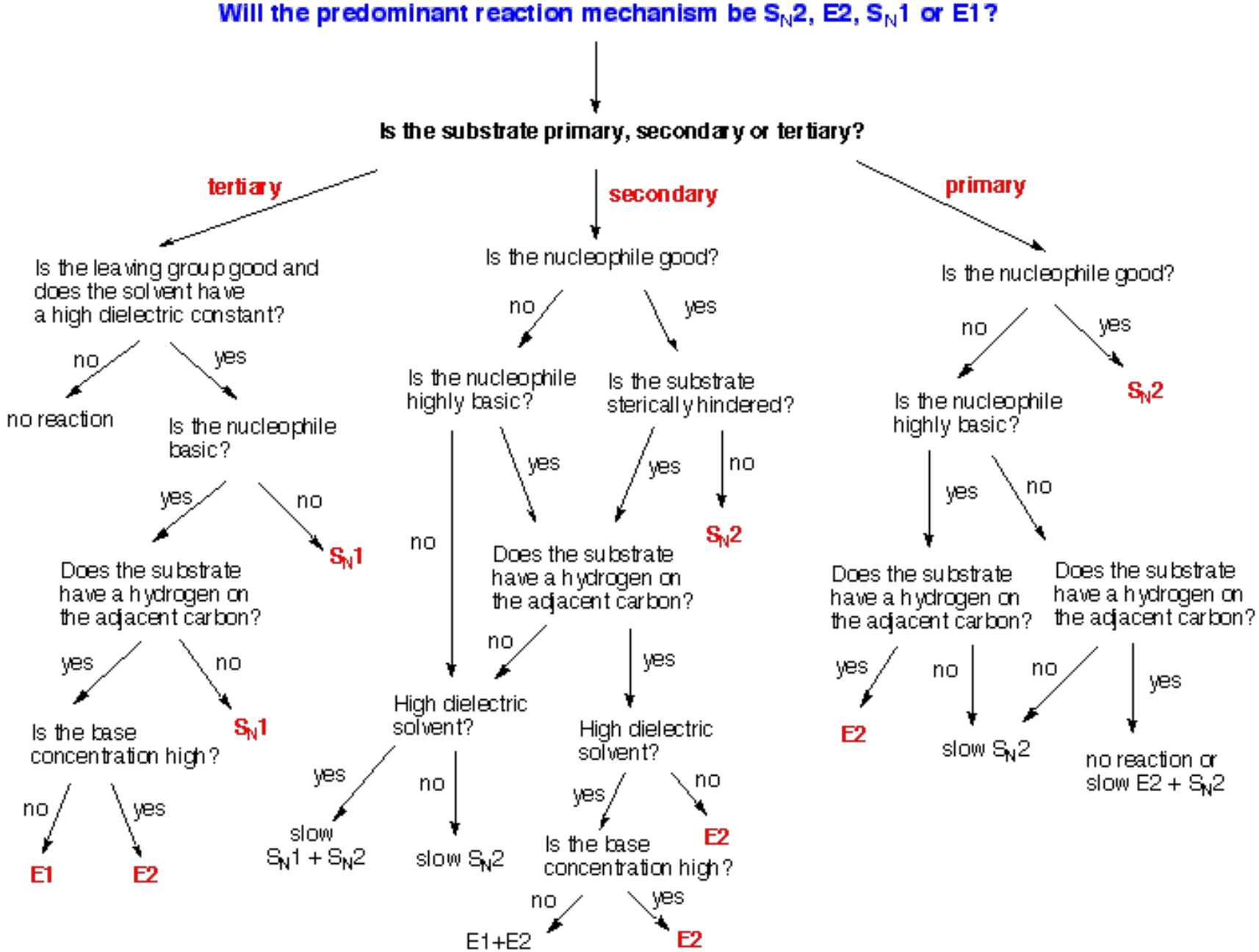
# E2 Elimination Pathway



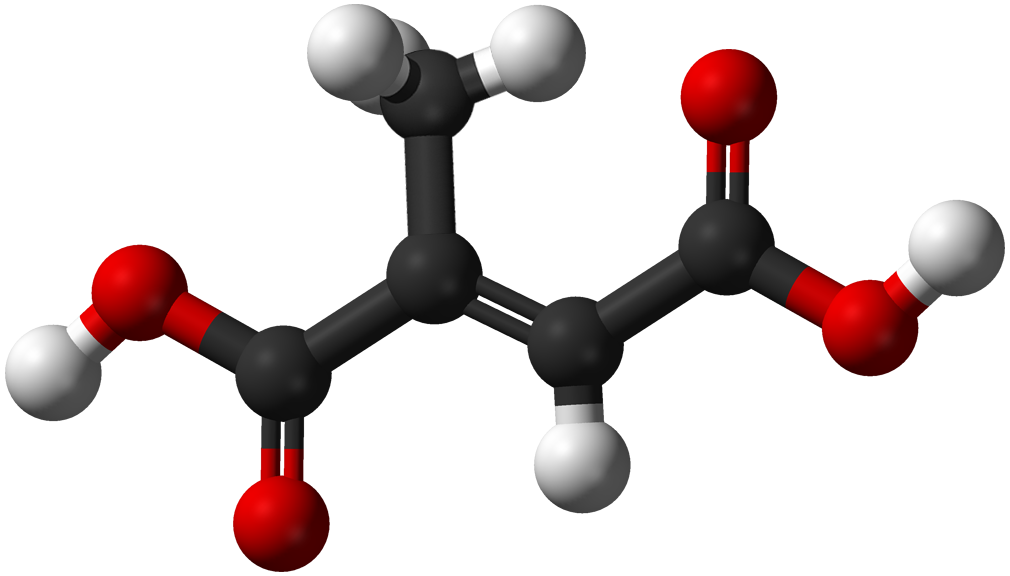
**The Aldol Condensation : Two Paths to Elimination**



# Putting it all together!


Will the predominant reaction mechanism be $S_N2$, E2, $S_N1$ or E1?
Is the substrate primary, secondary or tertiary?
tertiary
secondary
primary
Is the leaving group good and does the solvent have a high dielectric constant?
no
yes
no reaction
Is the nucleophile basic?
yes
no
$S_N1$
Does the substrate have a hydrogen on the adjacent carbon?
yes
no
$S_N1$
Is the base concentration high?
no
yes
E1
E2
Is the nucleophile good?
no
yes
Is the nucleophile highly basic?
Is the substrate sterically hindered?
yes
yes
no
$S_N2$
no
Does the substrate have a hydrogen on the adjacent carbon?
no
yes
High dielectric solvent?
High dielectric solvent?
yes
no
slow $S_N1 + S_N2$
slow $S_N2$
yes
no
E2
Is the base concentration high?
no
yes
E1+E2
E2
Is the nucleophile good?
no
yes
$S_N2$
Is the nucleophile highly basic?
yes
no
Does the substrate have a hydrogen on the adjacent carbon?
Does the substrate have a hydrogen on the adjacent carbon?
yes
no
E2
no
yes
slow $S_N2$
no reaction or slow E2 + $S_N2$

# ORGANIC CHEMISTRY III:
# Synthesis of Small Molecules



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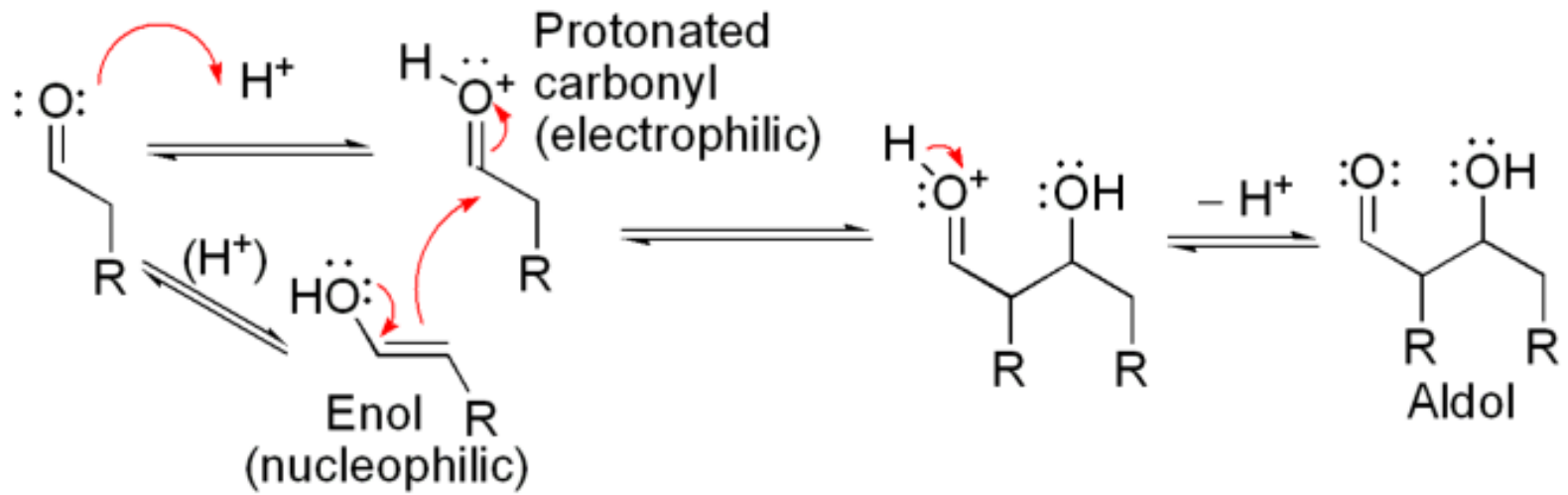
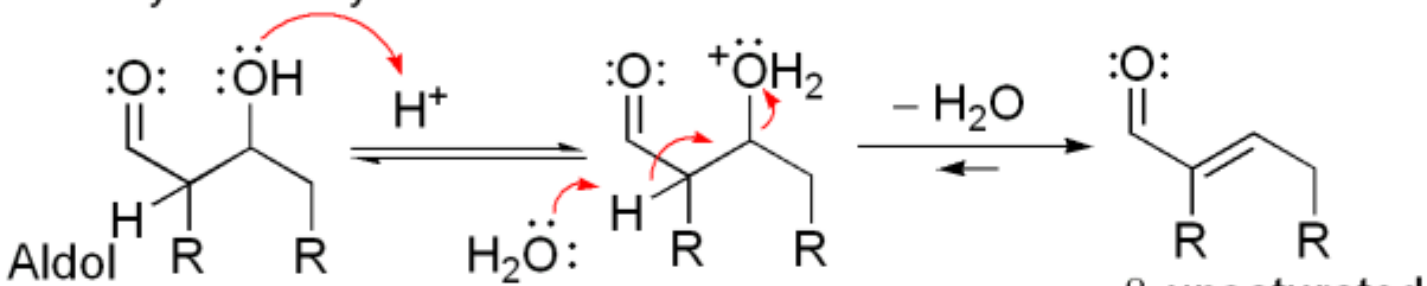
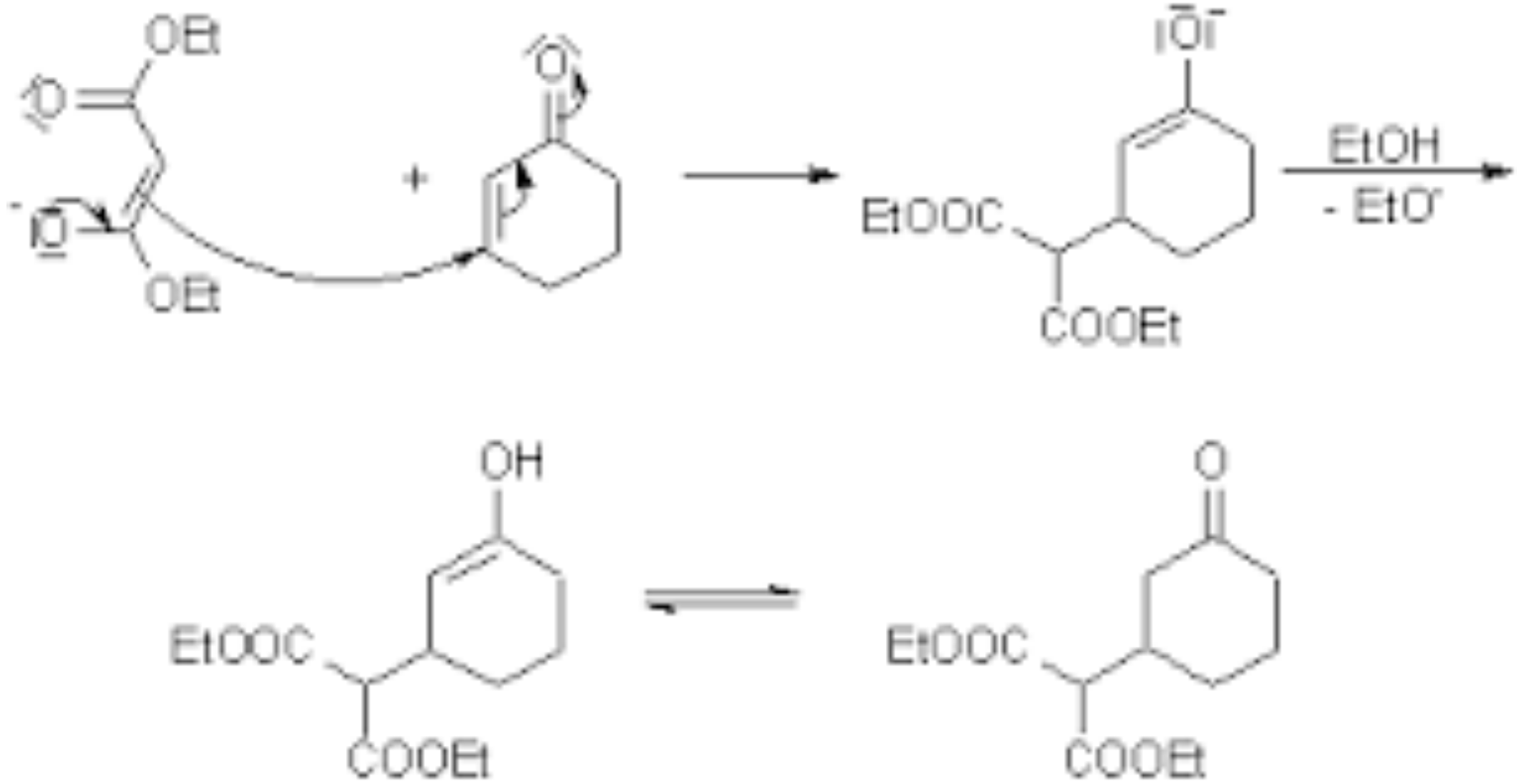
Acid catalyzed aldol reaction

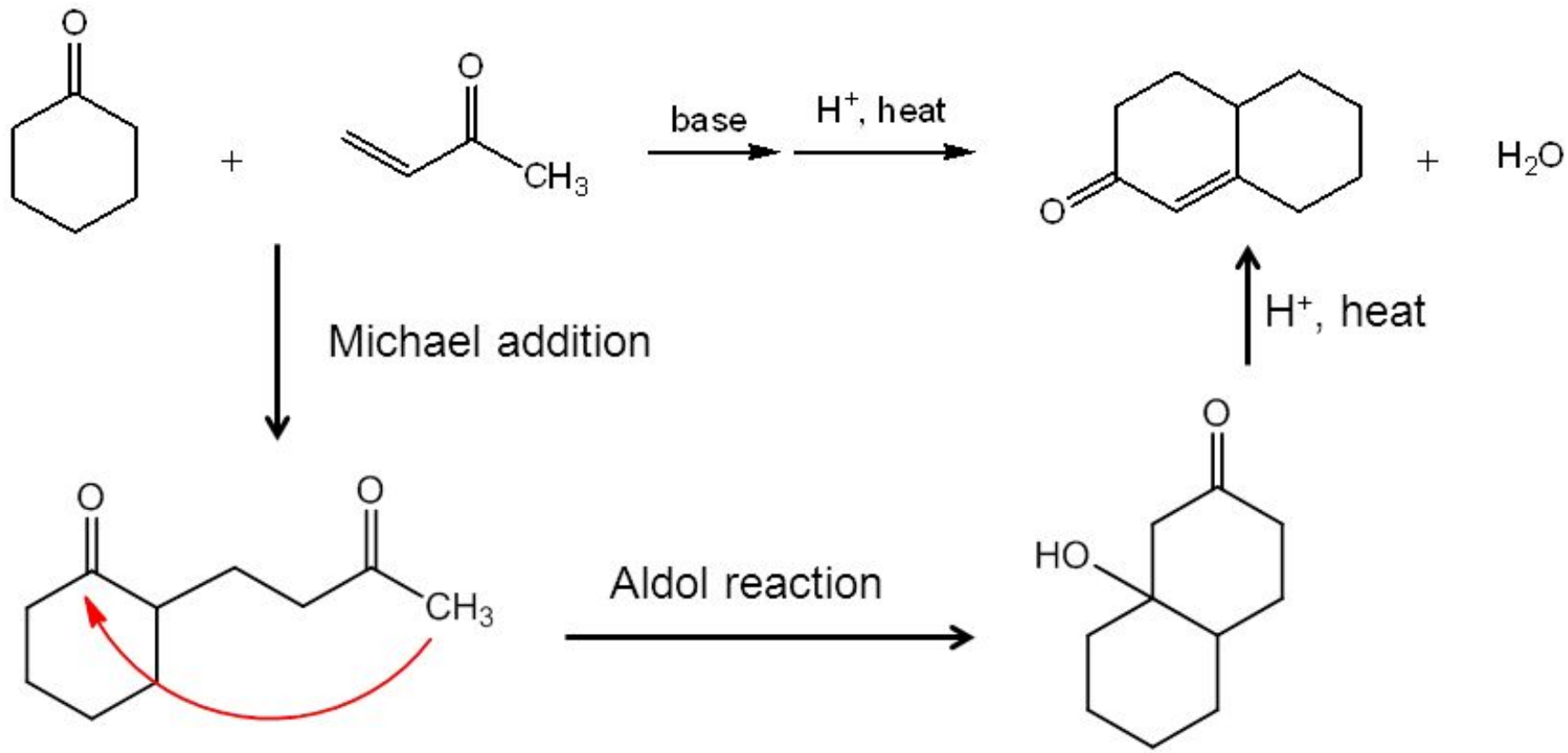


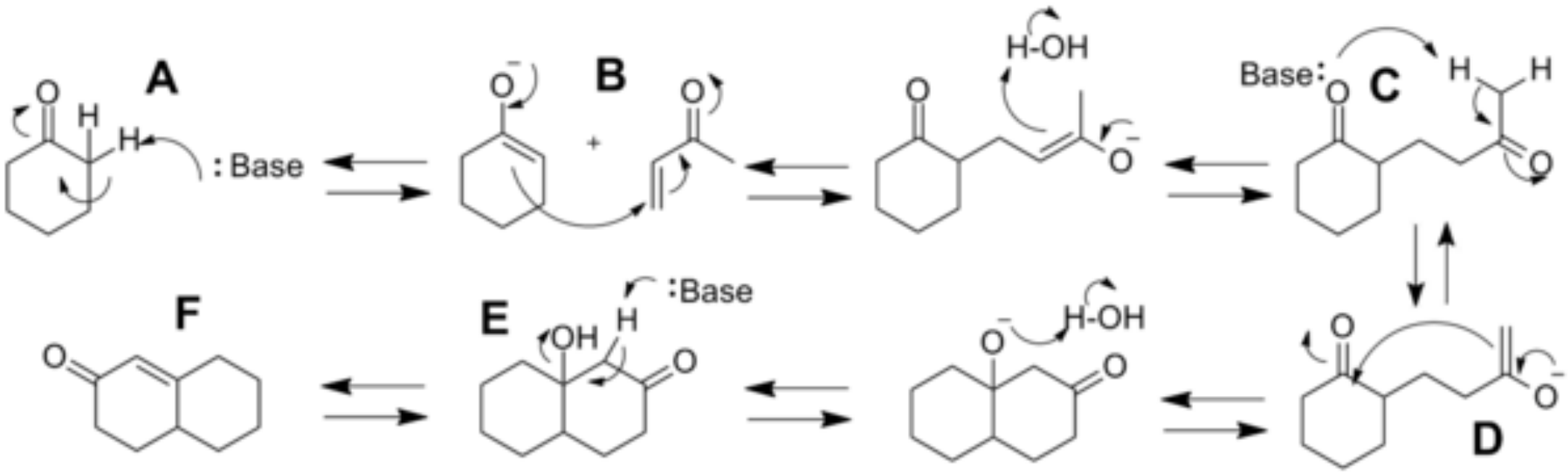

Acid catalyzed dehydration




(Lost H shown for clarity)


OEt
O
O
OEt
+
O
EtOOC
COOEt
EtOH
- EtO⁻
OH
EtOOC
COOEt
O
EtOOC
COOEt


O
O
CH3
base
H+, heat
O
+
H2O
Michael addition
H+, heat
O
O
CH3
Aldol reaction
O
HO


A
B
C
D
E
F
:Base
H-OH
Base:
:Base
H-OH