Solutions Mock Exam

BIO-110: Bio-Organic Chemistry (2024)

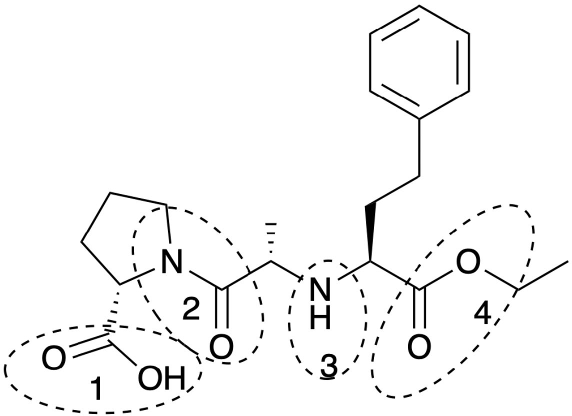
Important: This Exam will NOT be corrected individually. It serves simply as a guidance for students to get an overview of the exam concept. The topics covered in the mock exam do not necessarily reflect what will be asked in the final exam. Ultimately, it is a selection of exercises from the pool of topics we covered during the course, the exercise sessions and discussions.

Good Luck! :)

1. Structure & Bonding

1.1. Functional Groups

Name all functional groups of Enalapril. (Circled with dashed lines)

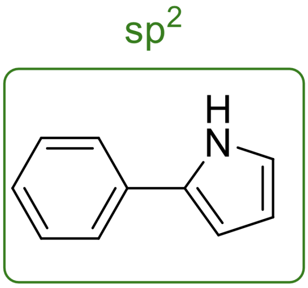


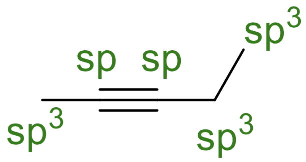
Enalapril

1: Carboxylic Acid
2: Amide
3: Amine
4: Ester

1.2. Hybridization

Indicate the hybridization of all atoms except hydrogen for the following molecules.

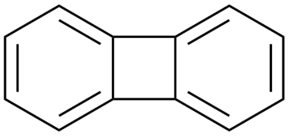




1.3. Aromaticity

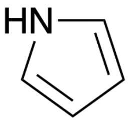
Classify the following as aromatic, non-aromatic or anti-aromatic.

1



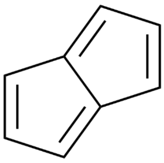
☐ aromatic
☐ non-aromatic
☐ anti-aromatic

2



☐ aromatic
☐ non-aromatic
☐ anti-aromatic

3



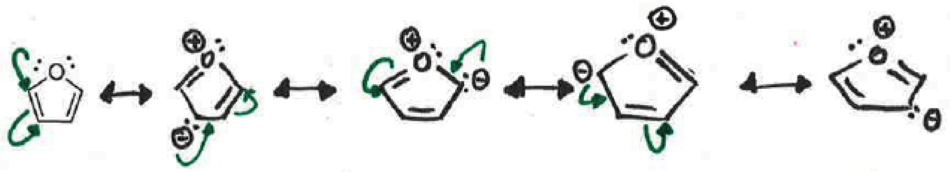
☐ aromatic
☐ non-aromatic
☐ anti-aromatic

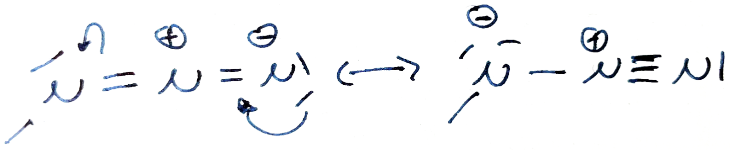
1: **Anti-aromatic**, there are 12p electrons
2: **Aromatic**, lone pair is delocalized in the cycle -> 6p electrons
3: **Anti-aromatic**, there are 8p electrons

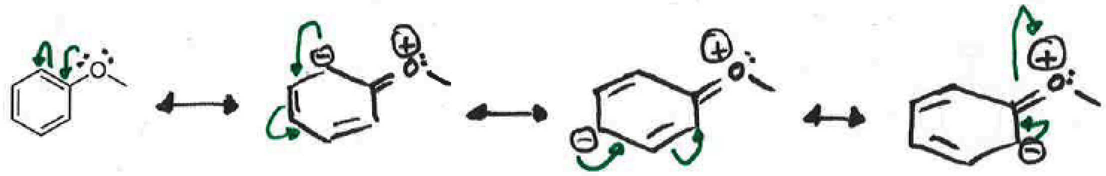
2. Conformation & Stereochemistry

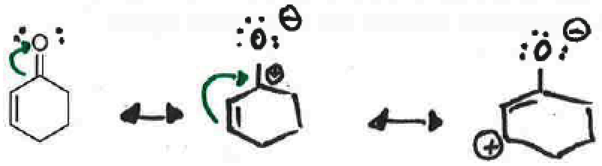
2.1. Resonance structures

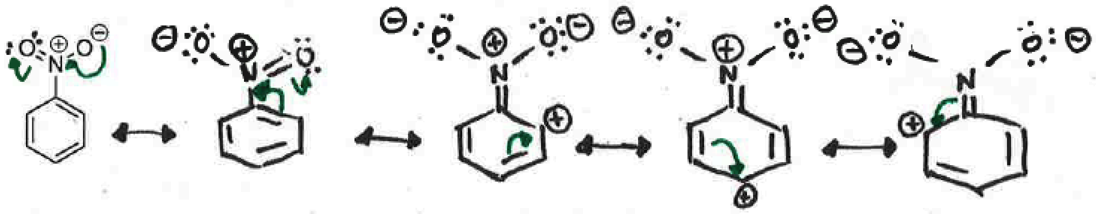
Draw the Lewis structure of each resonance contributor for the following molecules.







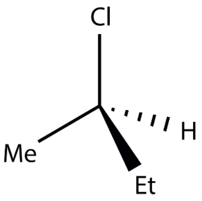




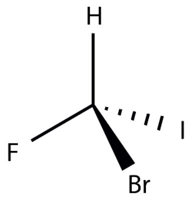
2.2. Chirality

Assign the chiral center as R or S.

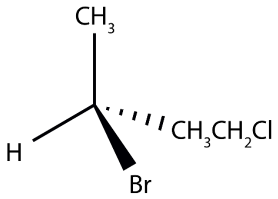
I)



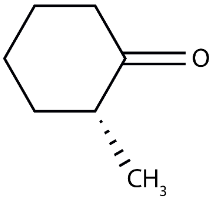
II)



III)



IV)



I) R

II) S

III) S

IV) R

3. IR & NMR & MS

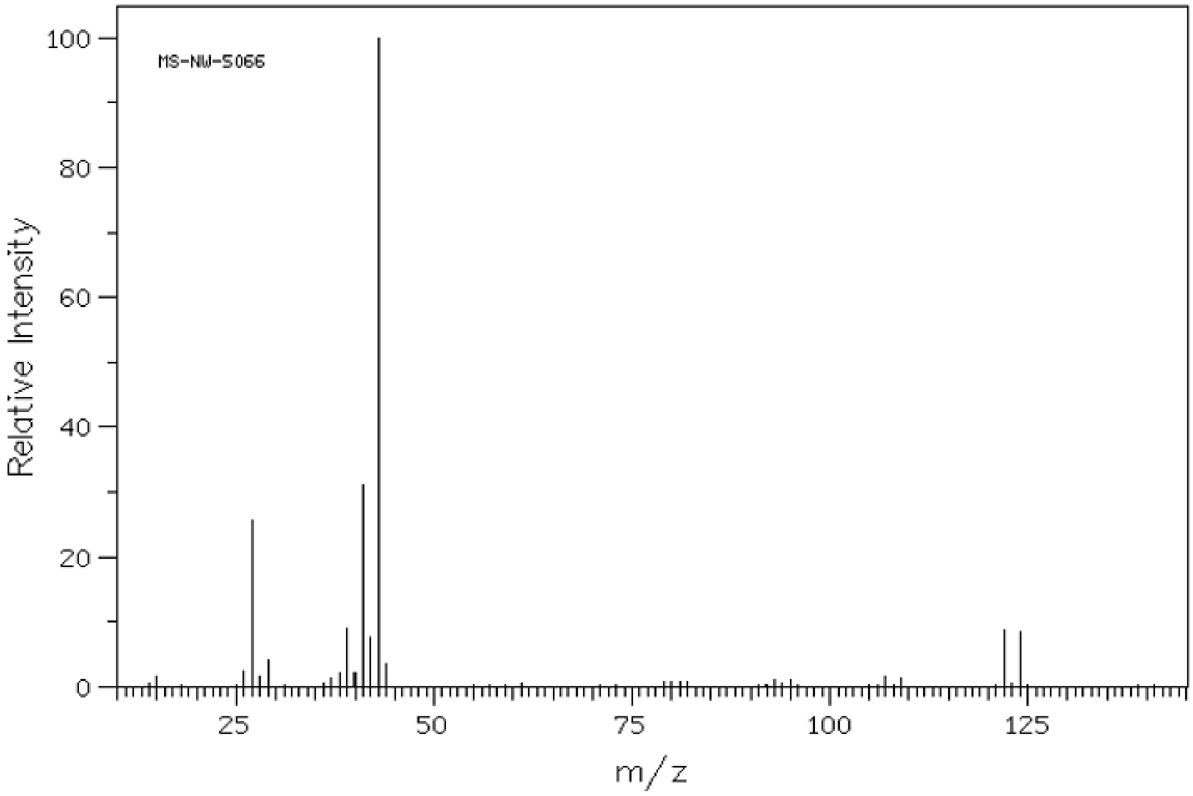
3.1 MS

a) From the spectra below indicate the m/z number corresponding to the base peak, the parent peak and the M+2 peak.

Base peak: 43 m/z

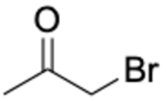
Parent peak: 122 m/z

M+2 peak: 124 m/z

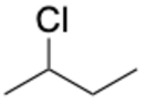


b) Which of the following compounds correspond to the spectra shown above:

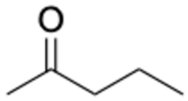
A)



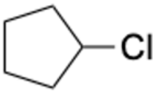
B)



C)



D)



E)

F)

The M and M+2 peak are almost identical in intensity, which tells us that the molecule must contain Br. If we then calculate the Mw of the two compounds that contain Br and compare it to the M peak in the spectra, it becomes evident that it must be E.

Mw A): (3x12Da)+(1x16Da)+(5x1Da)+(79Da) = 136Da

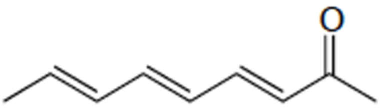
Mw E): (3x12Da)+(7x1Da)+(79Da) = 122Da

3.2 UV-VIS and IR

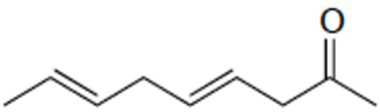
a) Which would be more useful in distinguishing the two compounds shown below: IR or UV spectroscopy?

One would use UV, as they have different extended conjugated systems and will therefore absorb at different wavelengths.
IR would not tell us much as they both have a carbonyl as a functional group.

b) Which molecule absorbs at a longer wavelength?



A



B

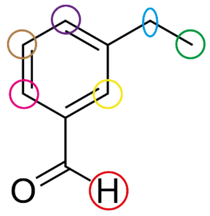
A>B: In general, the longer the system of conjugated pi-bonds the longer the wavelength it absorbs, as the energetic HOMO-LUMO gap shrinks. A has the longer conjugated system, while B does have two isolated, non-conjugated double bonds.

3.3 NMR

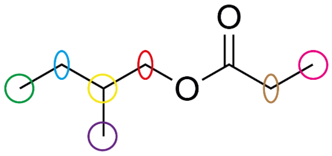
a) For each of the structures indicate the chemically equivalent protons and how many peaks would be found in the 1H NMR spectrum. Additionally, indicate for each structure which peak you expect to have the highest PPM.

I) 7 peaks, the one with highest PPM is the one closest to the oxygen (in red).
II) 7 peaks, the one with highest PPM is the one closest to the oxygen (in red).
III) 9 peaks, the one with highest PPM is the one closest to the oxygen (in red).
IV) 7 peaks, highest peak is from one of the hydrogens attached to the double bond (in red/green/blue).

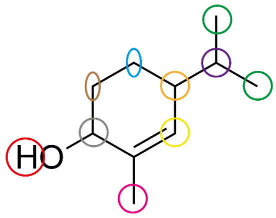
I)



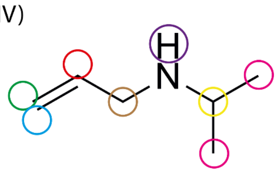
II)



III)

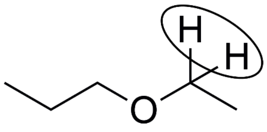


IV)

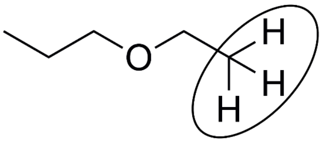


b) Sketch 1H-NMR peak shapes for the circled protons in the following partial structures.

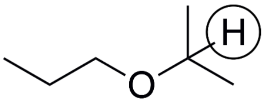
I)



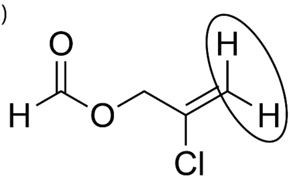
II)



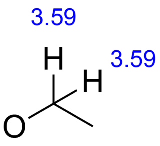
III)

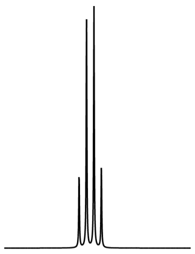


IV)

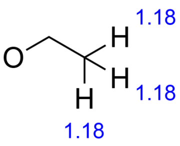


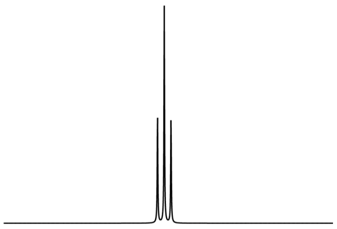
I) Two chemically equivalent protons with three neighbors show as a quartet peak.



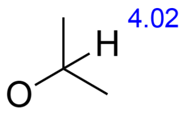


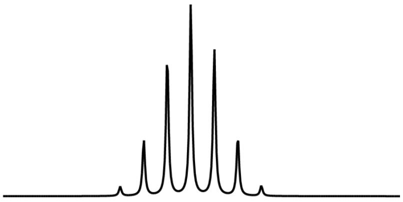
II) Three chemically equivalent protons with two neighbors give a triplet peak.



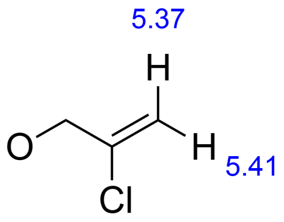


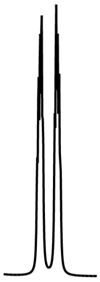
III) One proton with six neighbors gives a septet (or multiplet) peak.





IV) These two protons are not chemically equivalent! Both have no neighbors hence we will see two singlet peaks on the 1H NMR spectrum.

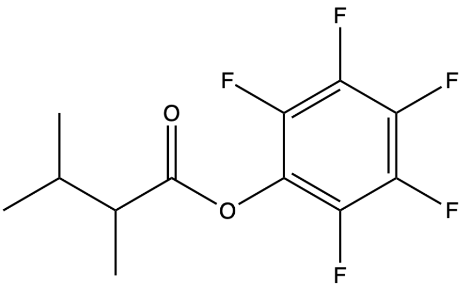




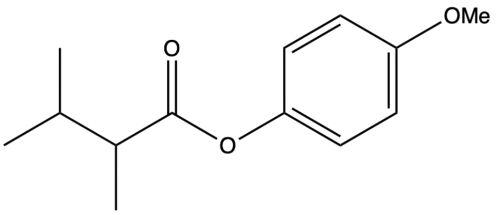
4. Organic Reactivity

4.1. Reactivity

a) Compare the reactivity of the following compounds towards benzylamine. Which one would you expect to react faster and why?



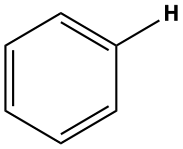
vs

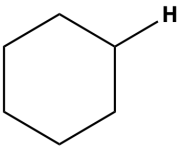


The compound on the left is expected to react faster. The carbonyl carbon is more electrophilic due to the many electronegative fluorines on the aromatic substituent. An alternative explanation would be that the negative charge on either leaving group would be stabilized by fluorine, while it is destabilized by the pi donating methoxy group.

b) Compare the highlighted protons and determine which one is more acidic. Give a brief explanation.

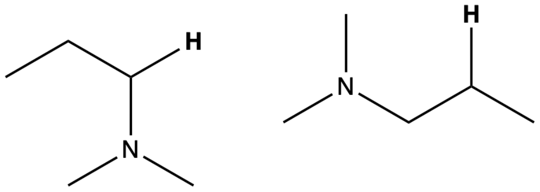
i)





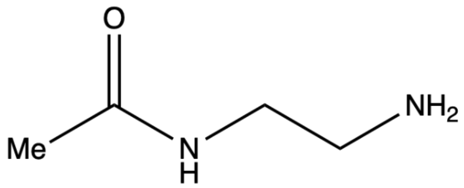
The proton on the left side is more acidic. Protons on sp3-hybridised carbons are less acidic than on sp2-hybridised carbons. Higher s-character stabilizes negative charges.

ii)



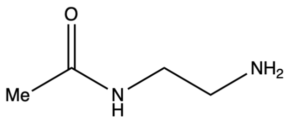
The proton on the left compound is more acidic due to the electron withdrawing effect of the nitrogen, which would be closer to the negative charge.

c) Order the heteroatoms in the compound below from least to most basic.

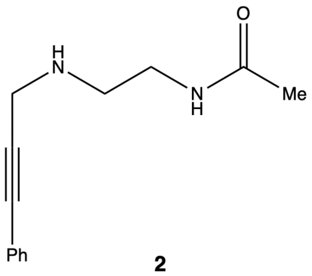


The amide nitrogen is the least basic. Its lone pair is delocalized to the oxygen and hence well stabilized. The oxygen is very electronegative and hence also not as basic as the primary amine. The primary amine's nitrogen is the most basic.

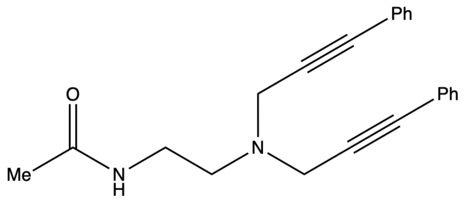
d) Order compounds 1, 2, 3 from least to most basic. Explain your answer.



1



2



3

Alkylgroups are donors that stabilize the positive charge resulting from protonation. Hence: (most basic) 3 > 2 > 1 (least basic)

5. Nucleophilic Substitutions & Eliminations

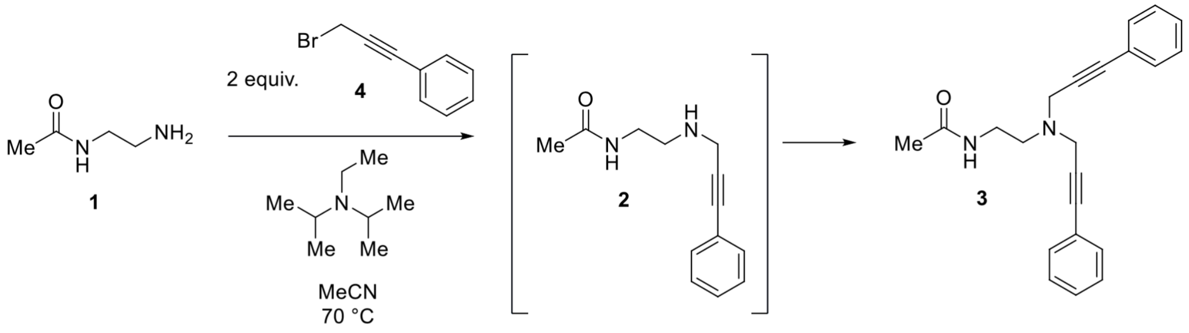
5.1. Reaction Control

Answer the following questions by ticking the corresponding correct answers. Wrong answers will result in a deduction of points, no less than 0 points can be achieved.

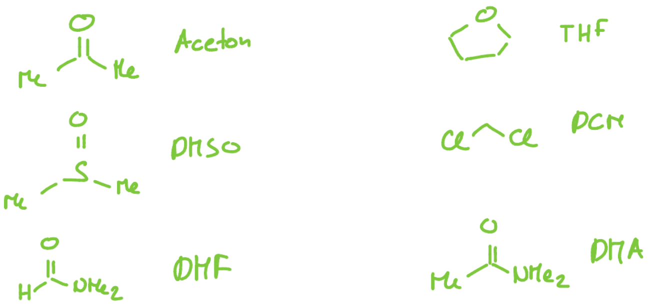
a) Tick the factors that clearly favor the S_N1 mechanism over the S_N2 mechanism:
   i) good nucleophile
   ii) presence of a strong base
   iii) large steric demands of the substrate
   iv) strong electron-donor substituents at the reactive center
   v) good leaving group
   vi) basic leaving group

b) Tick the factors that clearly favor the S_N2 mechanism over the E2 elimination mechanism:
   i) good nucleophile
   ii) strong π acceptors close to the reactive center
   iii) lower temperature
   iv) good leaving group
   v) absence of a strong base
   vi) possibility of anti-arrangement of leaving group and proton

5.2. Reaction Mechanisms



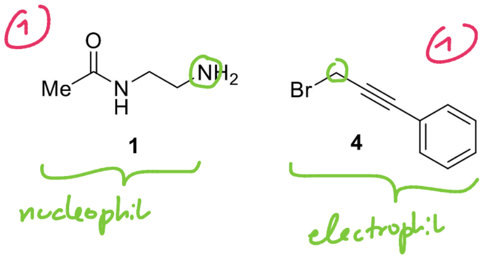
a) The reaction shown above takes place in MeCN (acetonitrile), a polar, aprotic solvent. Give one further example of a polar, aprotic solvent including its structures (you may use the common abbreviations for the names of the solvents).



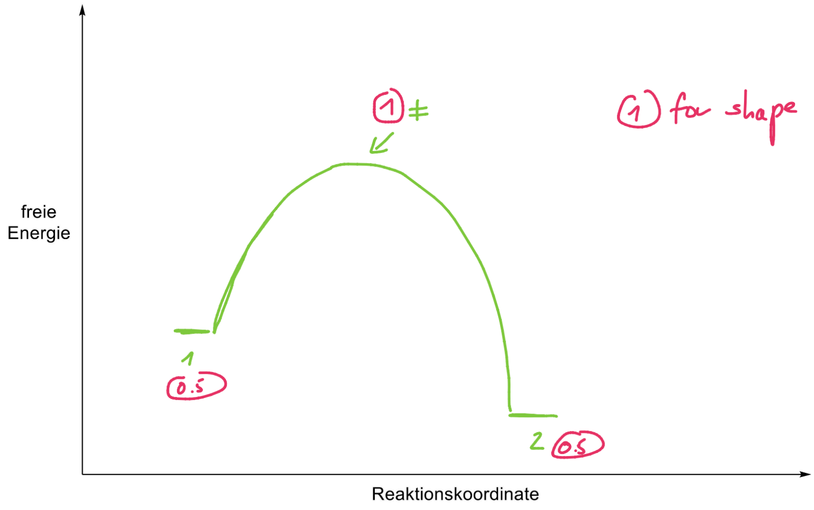
0.5 for structure
0.5 for names

b) What kind of reaction is this? Which of the molecules shown below reacts as a nucleophile and which as an electrophile? Circle the nucleophilic and electrophilic sites in the molecules (only those sites that take part in the reaction).

S_N2 ①

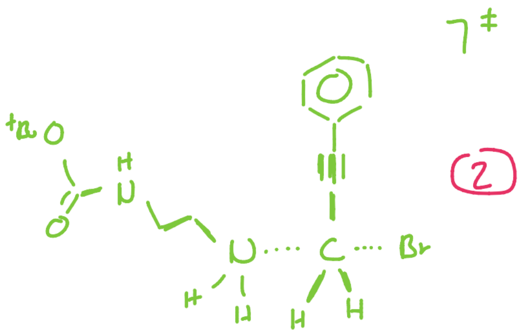


c) Sketch the reaction diagram (free energy versus reaction coordinate) for the reaction from 1 to 2. State the energy levels of the reactants, any intermediates and products. Draw in your diagram where the rate-determining transition state is.



① for shape

d) Draw the structure of the rate-determining transition state from 1 to 2.

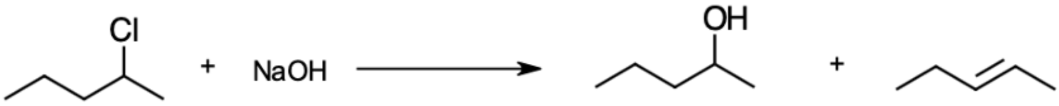


(2) - trigonal planar
- correct structures

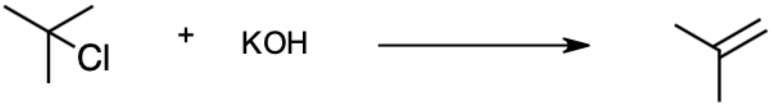
5.3 Substitution vs Elimination

Predict the mechanism (SN1, SN2, E1, or E2) and draw the organic product(s) for each reaction. Account for any regioselectivity and stereoselectivity where relevant.

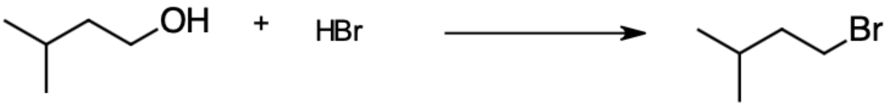
a) SN2 and E2 reactions: secondary (2°) substrate; Cl^- is a good leaving group; OH^- is a strong base and a strong nucleophile.



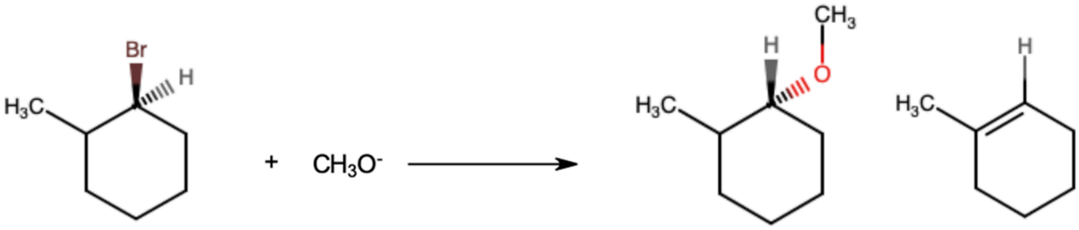
b) E2: tertiary (3°) substrate; Cl^- is a good leaving group; OH^- is a strong base and a strong nucleophile.



c) SN2: primary (1°) substrate; OH^- in acidic environment can get protonated and become H2O, which is a good leaving group; Br^- is a strong nucleophile.

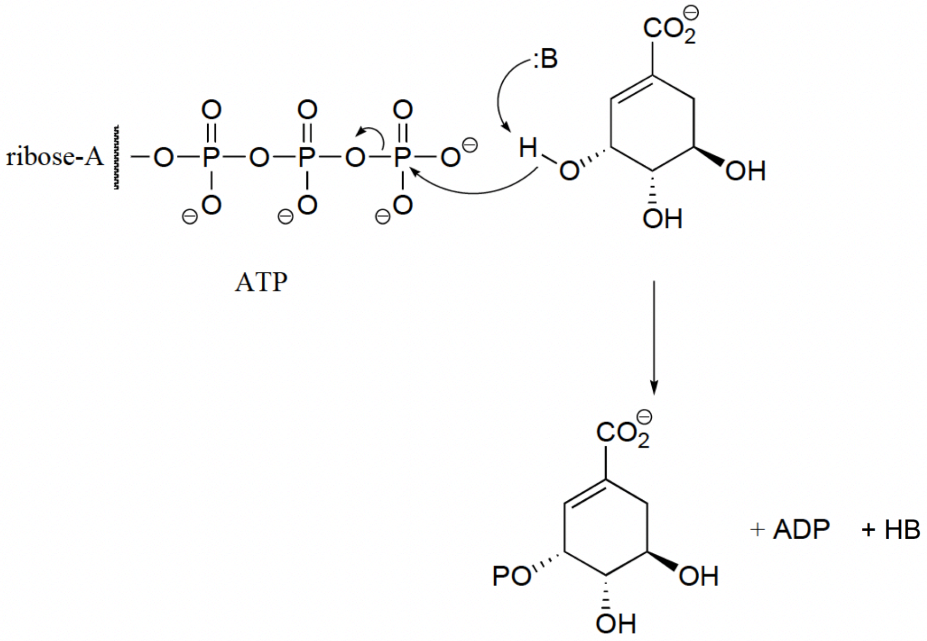


d) SN2 and E2: secondary (2°) substrate; Br^- is a good leaving group; CH3O$^-$ is a strong base and a strong nucleophile. SN2 mechanism leads to the inversion of stereochemistry.



6. Phosphate Transfer Reactions

Draw a likely mechanism for reaction catalyzed by shikimate kinase in the aromatic amino acid biosynthesis pathway. Stereochemistry of the product is not indicated in the figure below - in your mechanism, show the stereochemistry of the product, and explain how you are able to predict it from your knowledge of kinase reactions.

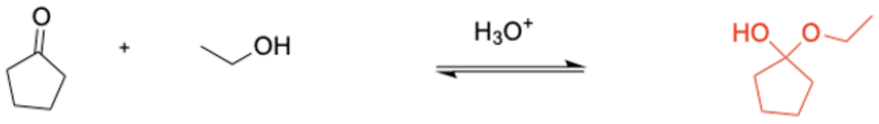


7. Carbonyl Chemistry I

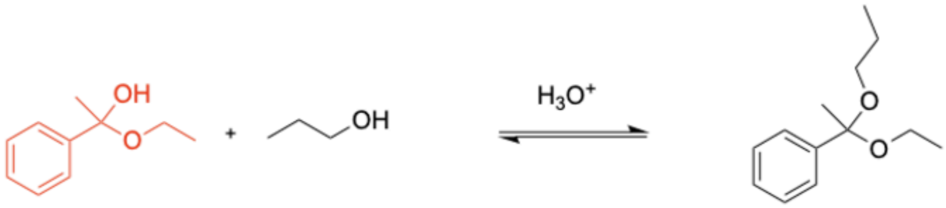
7.1. Reactions

a) For the following 3 reactions, categorize the functional group of compounds A), B), C), as a hemiacetal, hemiketal, acetal, ketal, aldehyde, ketone or imine.

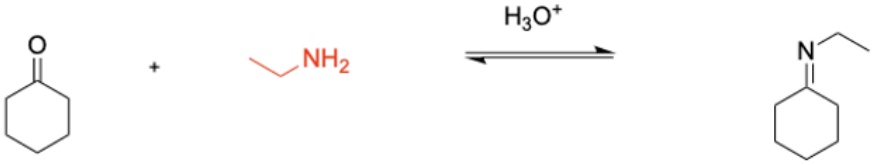
b) Draw the missing reactants/products of the reactions depicted below.



A) Ketone



B) Ketal



C) Imine

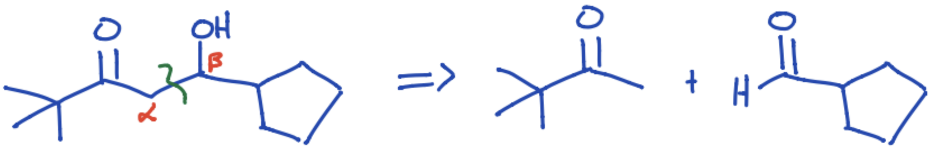
c) Indicate if the following statements are right or wrong (no negative points).

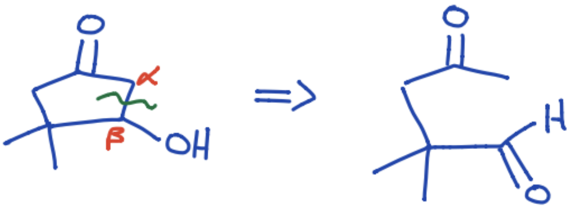
A. In a non-enzymatic addition reaction to a carbonyl the resulting product will be a 50/50 mixture of the two enantiomers (racemate).	[✓ *Right*]	*Wrong*
B. The carbon of a carbonyl group is a good nucleophile.	*Right*	[✓ *Wrong*]
C. Hydrolysis of a hemiacetal leads to an aldehyde.	[✓ *Right*]	*Wrong*
D. A ketone can never be transformed into an imine.	*Right*	[✓ *Wrong*]

8. Carbonyl Chemistry II

8.1. Retro Aldol Reaction

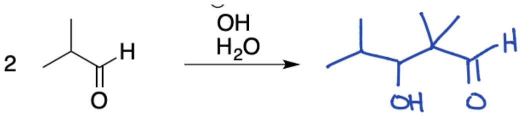
What starting material(s) is/are needed to prepare each compound below via an aldol reaction?





8.2. Aldol Reaction

Draw the product formed in the aldol reactions below. If multiple products are possible, explain why your choice is the preferred product.

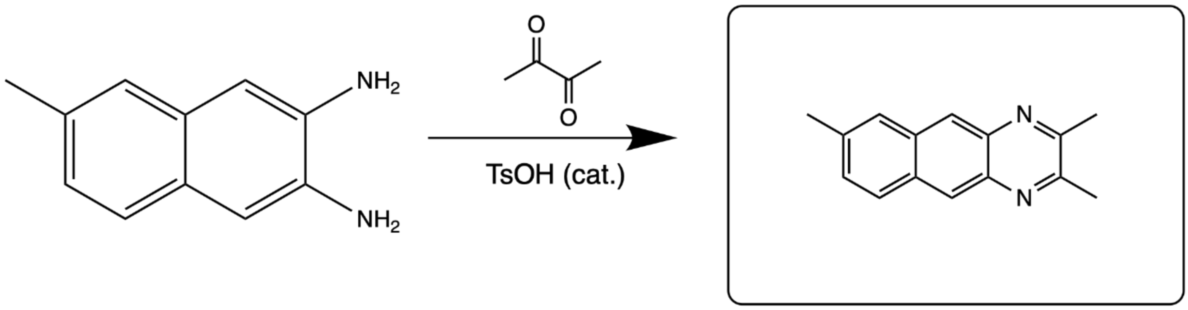


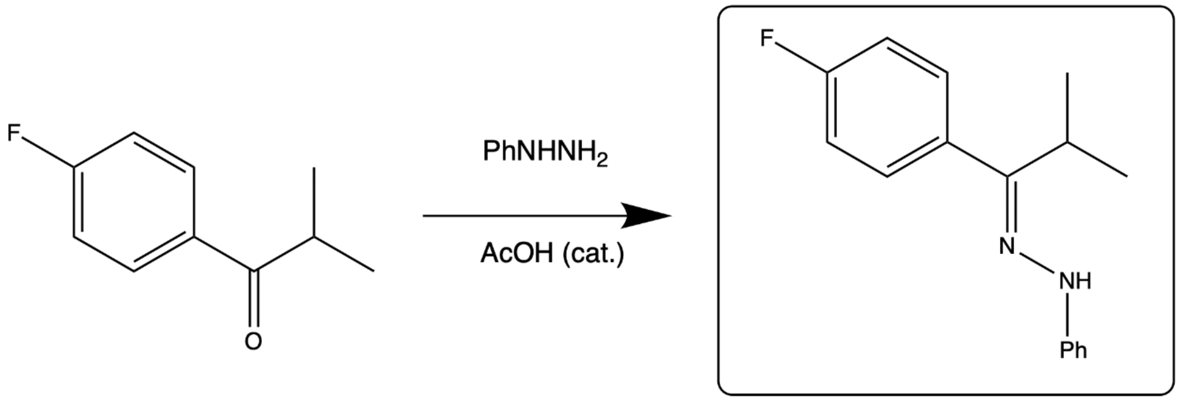
No β-H for elimination (dehydration) step.

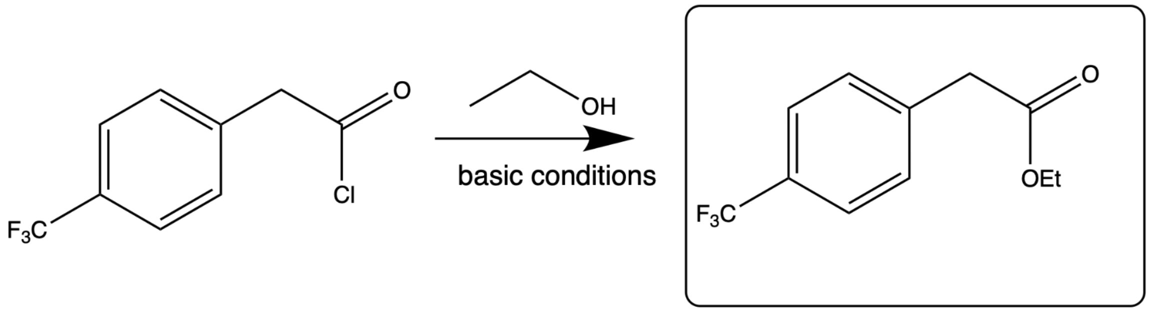
For the second reaction: Intramolecular Aldol only works well with reactions that form 5-6 rings. -> Stable ring pushes reaction

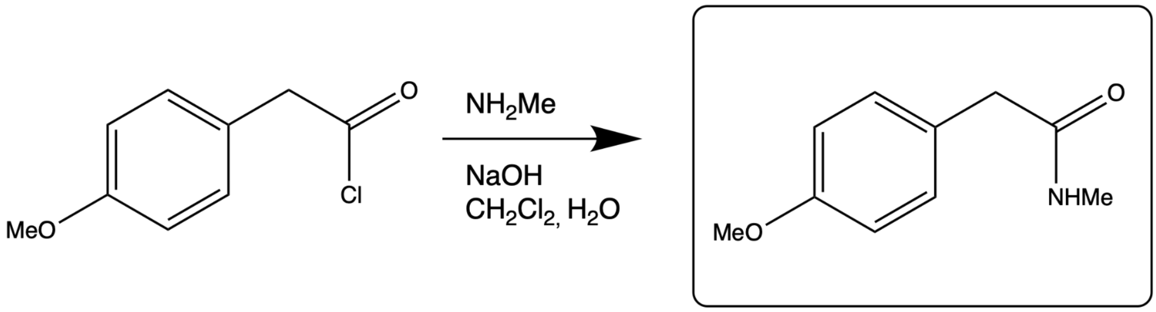
8.3 Reactions

Draw the main product for each of the following reactions in the corresponding empty box. (Hint: Ph = Phenyl, Me = Methyl, Ac = Acetyl, TsOH = Tosylic acid)





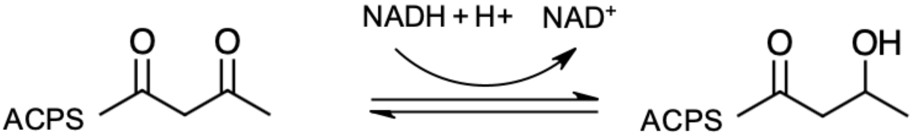




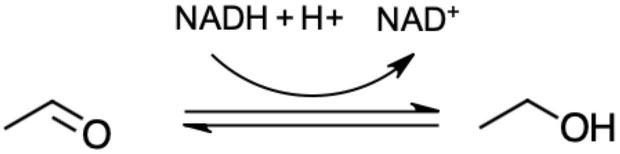
9. Oxidations & Reductions

Complete the redox reactions, indicating hydride ion movement and identifying which compound undergoes oxidation and which undergoes reduction.

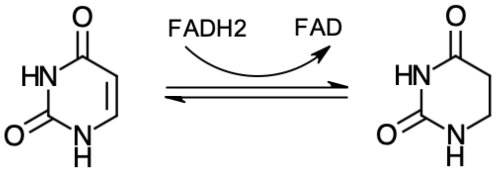
a) Hydride ion (H-) from NADH is transferred to the electrophilic carbonyl carbon (C=O) of the substrate's ketone group. NADH undergoes oxidation and substrate undergoes reduction.



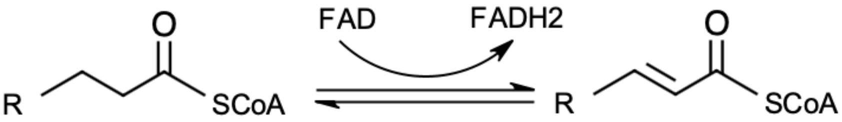
b) Hydride ion (H-) from NADH is transferred to the electrophilic carbonyl carbon (C=O) of the substrate's ketone group. NADH undergoes oxidation and substrate undergoes reduction.

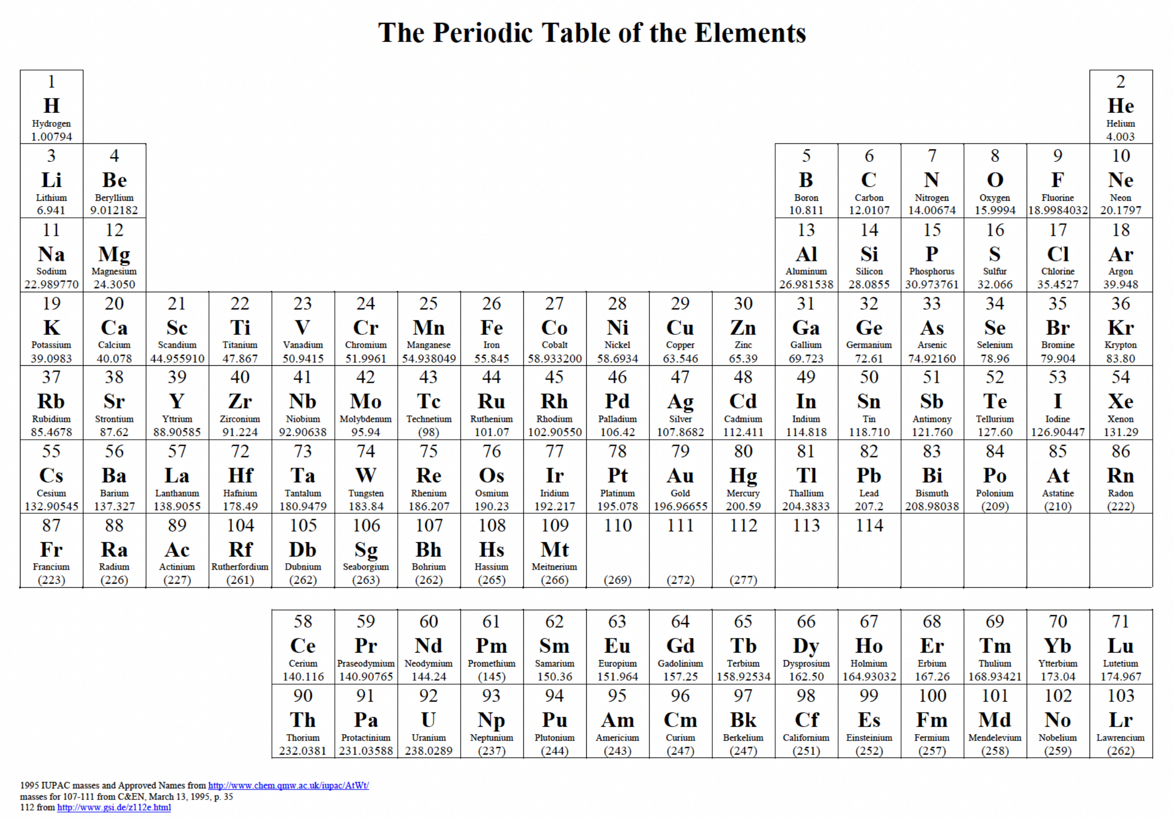


c) A hydride ion (H-) from FADH2 is transferred to the electrophilic β-carbon (Cβ) of the substrate's α,β-unsaturated carbonyl compound (or simply to the alkene). FADH2 undergoes oxidation, and the substrate undergoes reduction.



d) Hydride ion (H-) from substrate is transferred to the nitrogen atom of FAD. Substrate undergoes oxidation and FAD undergoes reduction.



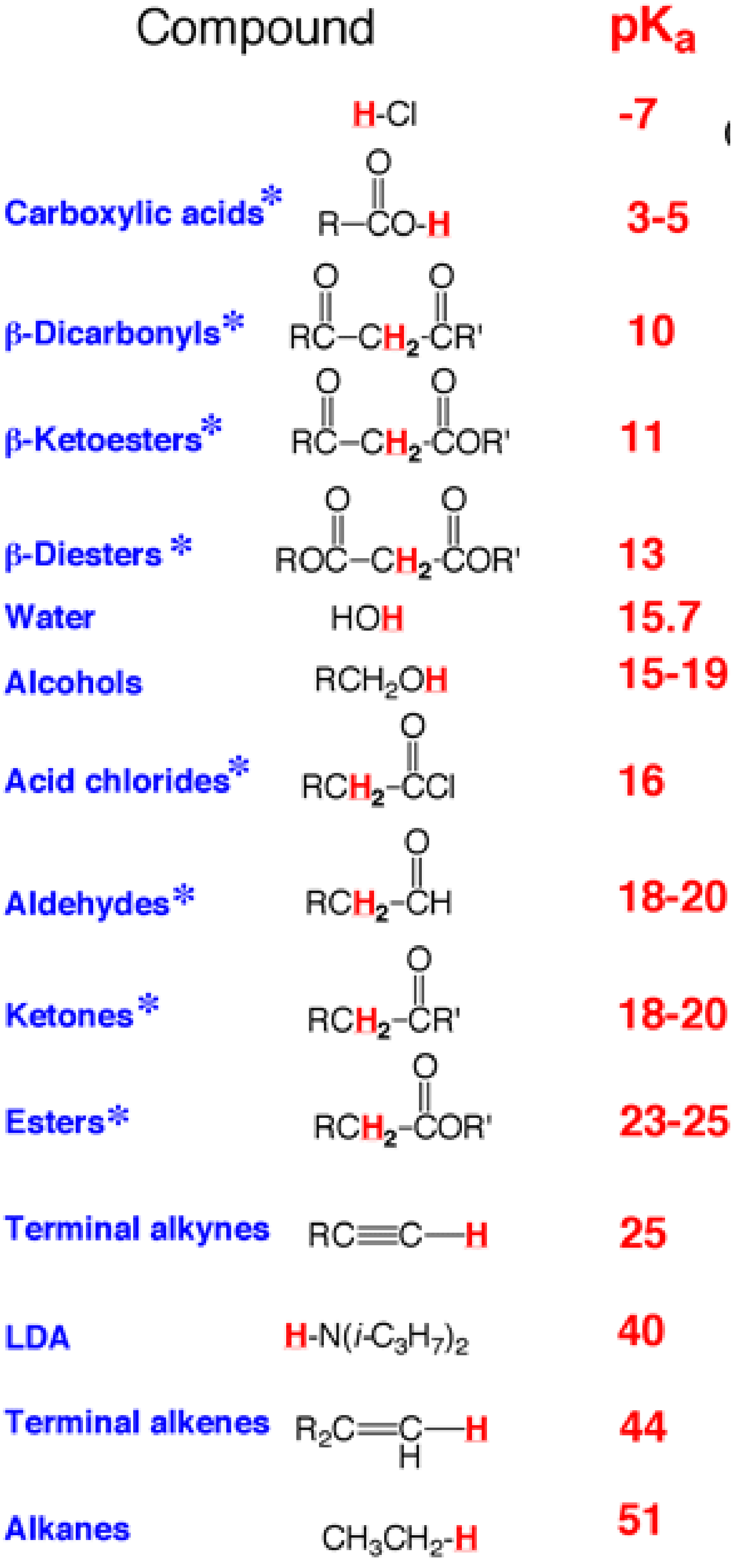


The Periodic Table of the Elements

1 **H** Hydrogen 1.00794																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
11 **Na** Sodium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973761	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.955910	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938049	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933200	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96655	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

1995 IUPAC masses and Approved Names from http://www.chem.qmw.ac.uk/iupac/AtWt/
masses for 107-111 from C&EN, March 13, 1995, p. 35
112 from http://www.gsi.de/z112e.html



	Compound	pK_a
	$H-Cl$	-7
Carboxylic acids*	$R-\overset{O}{\overset{\|}{C}}O-H$	3-5
β-Dicarbonyls*	$R\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}R'$	10
β-Ketoesters*	$R\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}OR'$	11
β-Diesters *	$RO\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}OR'$	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides*	$RCH_2-\overset{O}{\overset{\|}{C}}Cl$	16
Aldehydes*	$RCH_2-\overset{O}{\overset{\|}{C}}H$	18-20
Ketones*	$RCH_2-\overset{O}{\overset{\|}{C}}R'$	18-20
Esters*	$RCH_2-\overset{O}{\overset{\|}{C}}OR'$	23-25
Terminal alkynes	$RC\equiv C-H$	25
LDA	$H-N(i\text{-}C_3H_7)_2$	40
Terminal alkenes	$R_2C=\underset{H}{C}-H$	44
Alkanes	CH_3CH_2-H	51

Source: https://keski.condesan-ecoandes.org/organic-chemistry-pka-chart/