uc3m | Universidad Carlos III de Madrid

OpenCourseWare (2023)

CHEMISTRY II

Verónica San Miguel Arnanz

Teresa Pérez Prior

Berna Serrano Prieto

Department of Materials Science and Engineering and Chemical Engineering

SOLUTIONS OF EVALUATION TEST 4

1. *(3 points)* Fill the spaces with the correct word/-s in the next statements. (Correct statements mark as **+0.3 points**).

A	In the following cell: $Mg\ (s)\ \vert\ Mg^{2+}(0.1\ M)\ \Vert\ Mg^{2+}(0.5\ M)\ \vert\ Mg\ (s)$ the more _____solution is reduced in the cathode.
Concentrated	

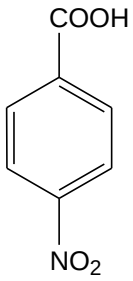
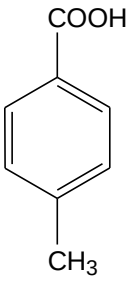
B	Given the following standard reduction potentials: Ag^+/Ag = +0.80 V and Cl_2/Cl^- = +1.36 V. _____is a stronger oxidizing agent than_____.
Cl_2/Ag^+	

C	_____ is a type of corrosion which occurs when a tensile stress is applied on the material under a corrosive environment.
Stress corrosion cracking	

D	A radical is stabilized by resonance and hyperconjugation (an electron interaction between a _____ bond and a _____ orbital).
sigma; p	

E	A S_N2 reaction predominates in _____ solvents, when a _____ carbocation is formed, and the better the nucleophile is.
aprotic; primary	

F	*Trans*-disubstituted alkenes present a _____ melting point than the corresponding *cis*-disubstituted.
higher	

G	Given the following benzoic acids:  **I**  **II** Compound I has _____acidity than compound II, because nitro group is an _____ group.
higher; electron withdrawing	

H	In an _____ inhibition, the inhibitor can bind ONLY to enzyme-substrate complex, not to free enzyme.
uncompetitive	

I	Fatty acids are composed of a long hydrocarbon chain (_____) ranging from 4 to 36 carbons long and a terminal _____ group (head).
tail; carboxyl	

J	A nucleotide has three characteristic components: (1) a nitrogenous base, (2) a _____, and (3) one or more phosphates. The molecule without a phosphate group is called a _____.
pentose; nucleoside	

2. *(1.5 points)* Consider the electrolysis of an aqueous solution of KBr:

a) *(1 p)* Write the half-reactions and indicate the products formed at the anode and cathode.

b) *(0.5 p)* If the initial concentration of the salt (KBr in aqueous solution) is 0.5 M. Determine the pH of the medium after electrolysis.

Data: $E^0(K^+/K) = -2.93$ V; $E^0(Br_2/Br^-) = +1.07$ V; $E^0(O_2/H_2O, H^+) = +1.23$ V; $E^0(H_2O/H_2, OH^-) = -0.83$ V.

SOLUTION

a)

Oxidation (Anode) $2\,Br^- \rightarrow Br_2 + 2\,e^-$ $\quad E^0 = -1.07$ V

$2\,H_2O \rightarrow O_2 + 4\,e^- + 4H^+$ $\quad E^0 = -1.23$ V

Reduction (Cathode) $K^+ + e^- \rightarrow K$ $\quad E^0 = -2.93$ V

$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$ $\quad E^0 = -0.83$ V

Overall Reaction $2\,Br^- + 2\,H_2O \rightarrow Br_2 + H_2 + 2\,OH^-$ $\quad E^0 = -0.73$ V

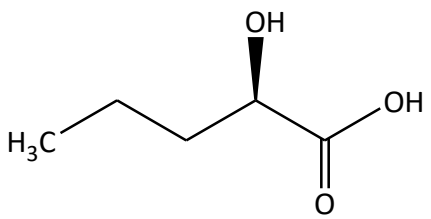
Br_2 is produced at the anode and H_2 at the cathode.

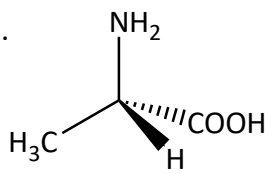
b)

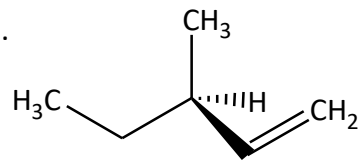
[Br-] = [OH-] = 0.5 M → pH = 13.7.

3. *(1.75 points)* Answer the following questions:

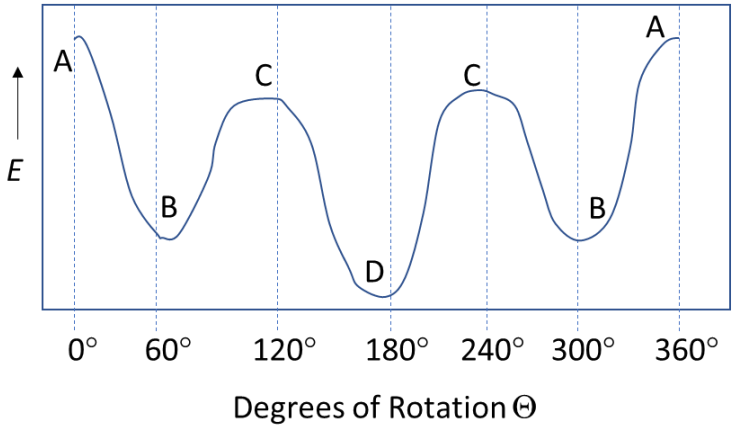
a) *(0.75 p)* Write the name including the absolute configuration of the following compounds. (**Hint**: when alcohol group is not the main functional group, that is denominated as "hydroxy-" before the name of the main chain)

1. 

2. 

3. 

b) *(1 p)* Starting from the eclipsed conformation (A) for butane, draw and indicate the type of conformation using the Newman projections for B, C, D, and E according to the rotation of the C2–C3 bond indicated in the following graph. Deduce which of the structures is more stable and why.

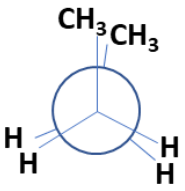


SOLUTION

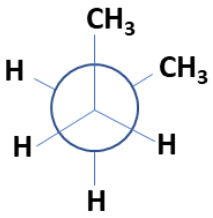
a) 1. (2*R*)-2-hydroxypentanoic acid
2. (2*S*)-2-aminopropanoic acid
3. (3*R*)-3-methylpent-1-ene

b) There are two different types of alternate arrangements in butane. One in which the two terminal methyl groups are separated by 180 degrees (anti), and two in which they are separated by 30 degrees (gauche). They are connected by two types of alternate conformations: one in which the two methyl groups pass between each other, and two in which the methyl groups pass through hydrogen atoms.

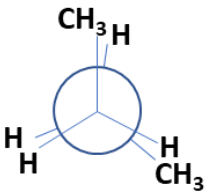
(A) Eclipsed



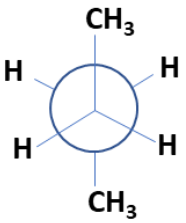
(B) Gauche



(C) Eclipsed



(D) Anti

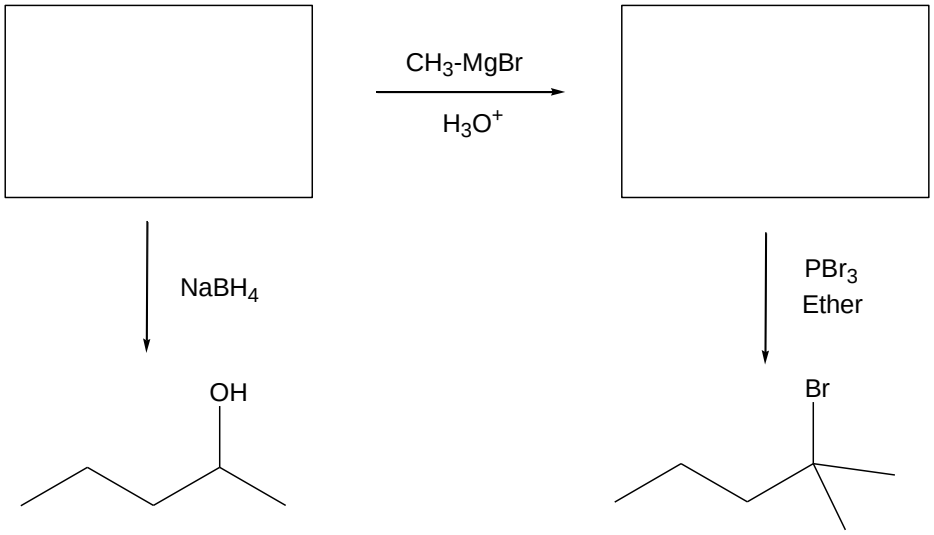


The most stable one is D, where the two methyl groups are in the ANTI position.

4. *(2.25 points)* Complete the following schemes:

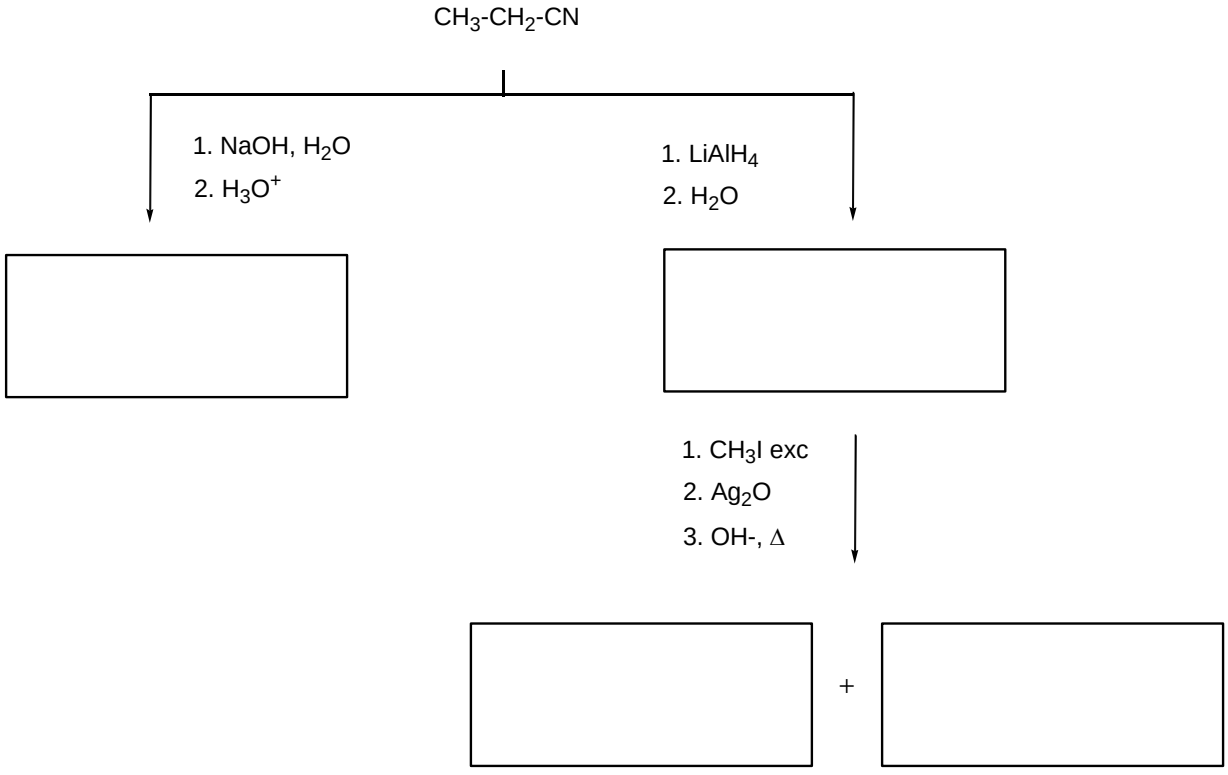
a) *(0.75 p)*

A



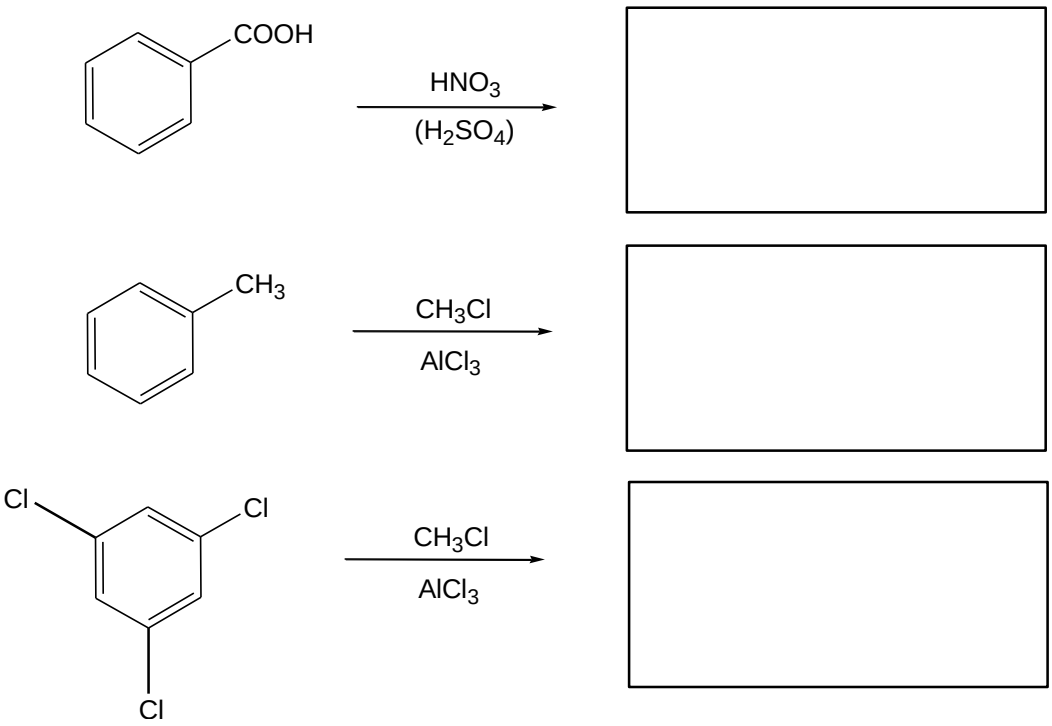
b) *(0.75 p)*

B



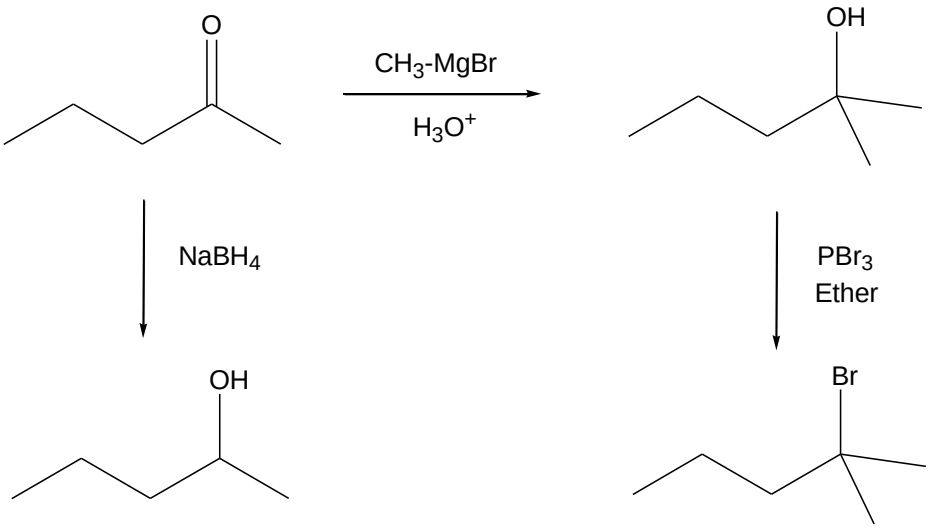
c) *(0.75 p)*

C

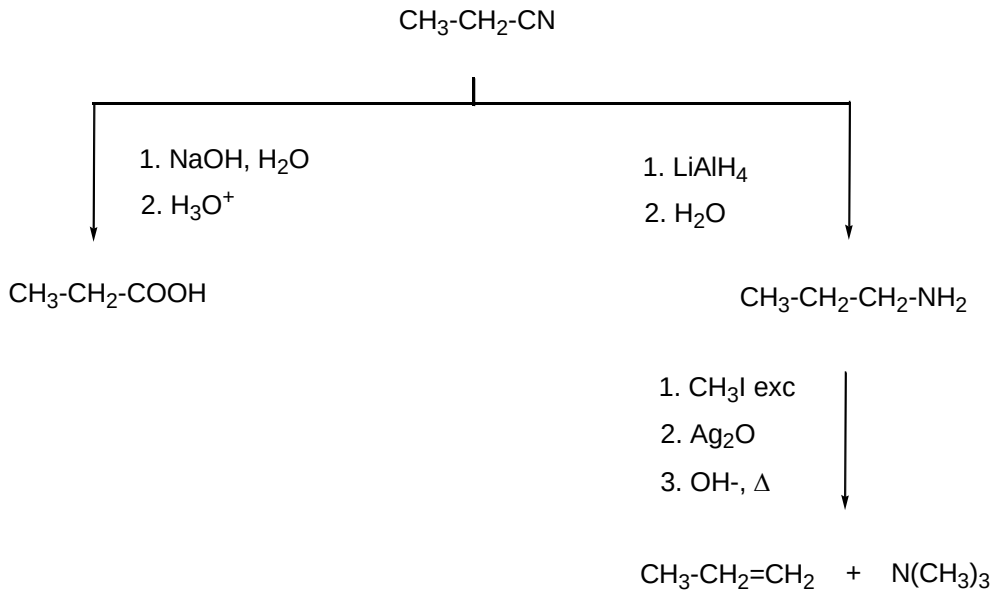


SOLUTION

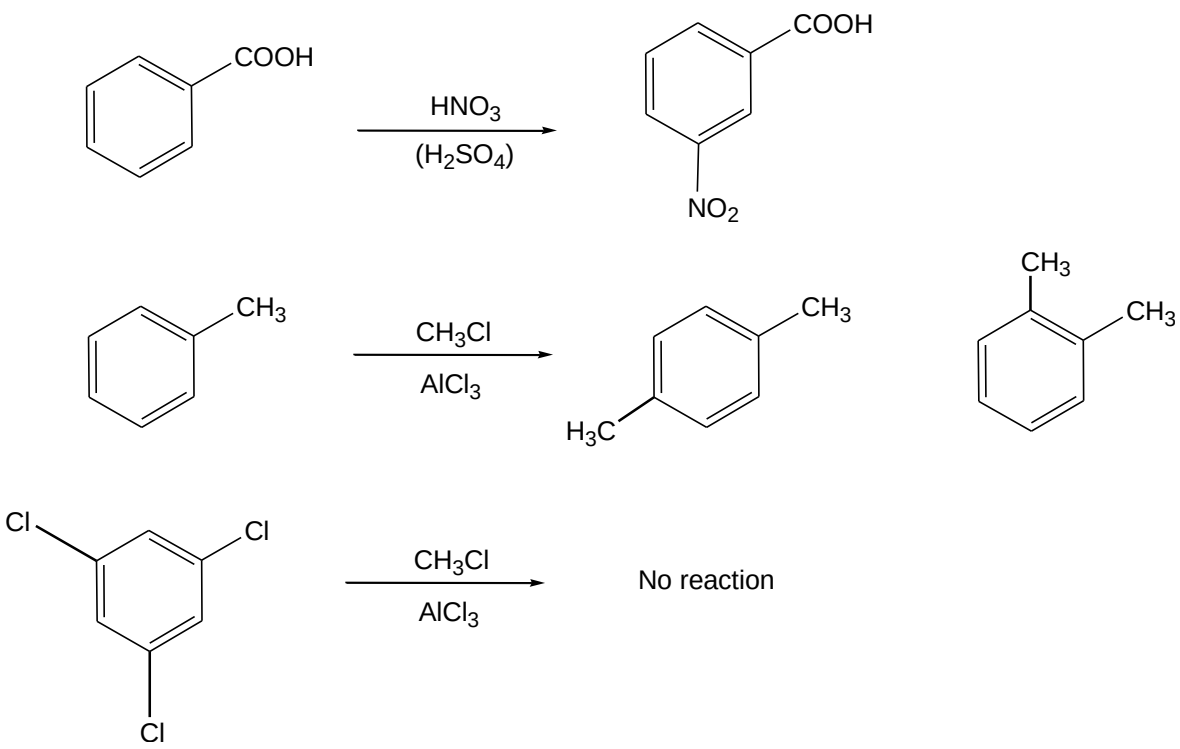
A



B


CH3-CH2-CN
1. NaOH, H2O
2. H3O+
1. LiAlH4
2. H2O
CH3-CH2-COOH
CH3-CH2-CH2-NH2
1. CH3I exc
2. Ag2O
3. OH-, Δ
CH3-CH2=CH2 + N(CH3)3

C


COOH
HNO3
(H2SO4)
COOH
NO2
CH3
CH3Cl
AlCl3
CH3
H3C
CH3
CH3
Cl
Cl
Cl
CH3Cl
AlCl3
No reaction

5. *(1.5 points)* A compound with the formula $C_3H_5BrO_2$ exhibits the following ^{1}H-NMR, ^{13}C-NMR, and IR spectra, respectively:

^{1}H-NMR: δ = 2.93 (t, 2 H), 3.57 (t, 2 H), >9.0 (low field,1 H very broad) ppm.

^{13}C-NMR: δ = 24.3, 38.6, 178.6 ppm.

IR: characteristic bands 3067, 1717 cm^{-1}.

a) *(0.25 p)* Determine the degree of unsaturation.

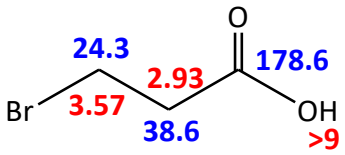
b) *(1.25 p)* Justify its structure.

SOLUTION

a) $\boldsymbol{Degree\ of\ unsaturation = (3+1) - \frac{(5+1)}{2} = 1}$ **(1 double bond or ring)**

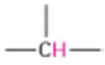
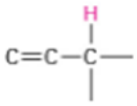
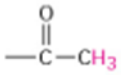
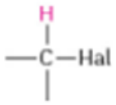
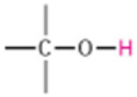
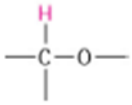
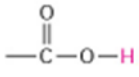
b) IR spectrum gives the information that there is a possible carboxylic acid in the structure. Carbon spectrum exhibits a peak corresponding to a quaternary carbon at 178.6 ppm.

Therefore, regarding the NMR spectra, the proposed structure would be the following:



ANNEX

Chemical Shifts in ^1H NMR

Type of hydrogen		Chemical shift (δ)
Reference	$Si(CH_3)_4$	0
Alkyl (primary)	$-CH_3$	0.7–1.3
Alkyl (secondary)	$-CH_2-$	1.2–1.6
Alkyl (tertiary)		1.4–1.8
Allylic		1.6–2.2
Methyl ketone		2.0–2.4
Aromatic methyl	Ar–CH_3	2.4–2.7
Alkynyl	$-C\equiv C-H$	2.5–3.0
Alkyl halide		2.5–4.0
Alcohol		2.5–5.0
Alcohol, ether		3.3–4.5
Vinylic		4.5–6.5
Aryl	Ar–H	6.5–8.0
Aldehyde		9.7–10.0
Carboxylic acid		11.0–12.0

Characteristic IR bands of some common functional groups:

Functional Group		Absorption (cm^{-1})	Intensity
Alkane	C–H	2850–2960	Medium
Alkene	=C–H	3020–3100	Medium
	C=C	1640–1680	Medium
Alkyne	≡C–H	3300	Strong
	C≡C	2100–2260	Medium
Alkyl halide	C–Cl	600–800	Strong
	C–Br	500–600	Strong
Alcohol	O–H	3400–3650	Strong, broad
	C–O	1050–1150	Strong
Arene	C–H	3030	Weak
Aromatic ring		1660–2000	Weak
		1450–1600	Medium
Amine	N–H	3300–3500	Medium
	C–N	1030–1230	Medium
Carbonyl compound	C=O	1670–1780	Strong
	Aldehyde	1730	Strong
	Ketone	1715	Strong
	Ester	1735	Strong
	Amide	1690	Strong
	Carboxylic acid	1710	Strong

Chemical Shifts in ^{13}C NMR

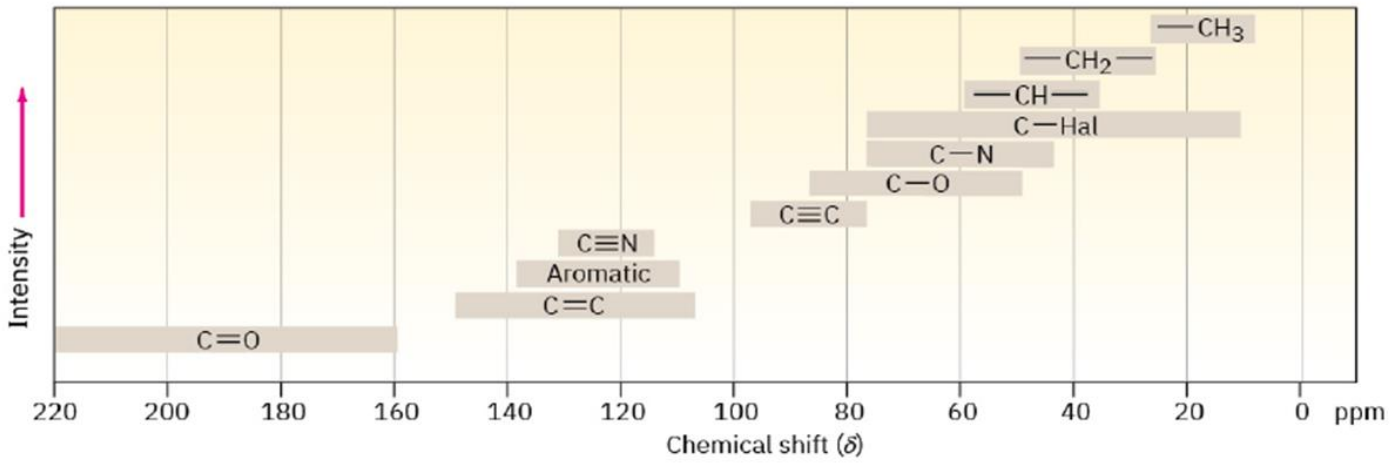


IMAGE CREDITS

- Images were made by authors.
- Tables and image of Annex: Organic Chemistry. A tenth Edition. John McMurry, Cornell University (Emeritus), CC BY-SA 4.0, https://openstax.org/details/books/organic-chemistry.