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OpenCourseWare (2023)

CHEMISTRY II

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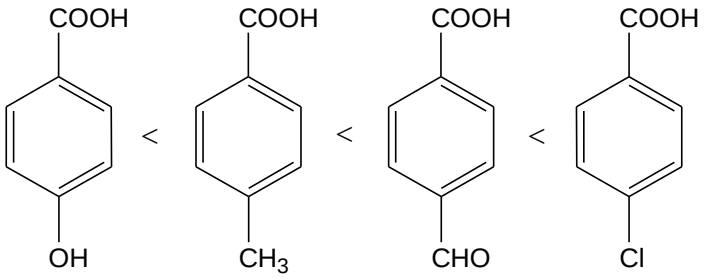
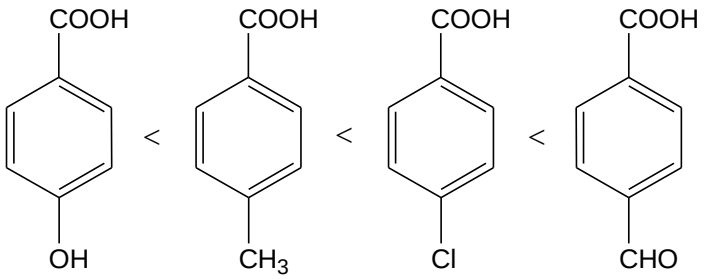
SOLUTIONS OF EVALUATION TEST 3

1. *(2 points)* Justify if the following statements are TRUE or FALSE. (Correct answers mark as **+ 0.4 points**).

A	The main products generated from the electrolysis of molten $CuBr_2$ are Cu and OH^-.
F	**The main products are Cu and Br_2.**

B	Crevice corrosion is favored in the metal region that has the lowest oxygen concentration.
T	**Metal is oxidized in this region while oxygen is reduced outside the crevice.**

C	S_N1 reaction presents an energy diagram with two transition states during which a carbocation intermediate is formed.
T	**S_N1 is a unimolecular reaction because only the haloalkane is involved in the rate-determining step. It takes place by losing the leaving group, forming a carbocation before the nucleophile approaches.**

D	The effect that substituents have on acidity of the following *p*-substituted benzoic acids can be indicated as follows: 
F	

E	The genetic code is the set of rules that link the RNA sequence to the encoded protein sequence.
F	**DNA is the genetic material containing all the information essential for life and the basis for heredity**

2. *(1.5 points)* Given the following cell in basic medium (pH = 10):

$$Mn_2O_3(s) + Au^{3+}(ac) \rightarrow MnO_2(s) + Au(s)$$

a) *(0.5 p)* Write the balanced oxidation and reduction half-reactions and the global reaction.

b) *(0.5 p)* Determine the standard potential at 25 °C if [Au^{3+}] = 0.1 M, and indicate if the reaction is spontaneous or not under these conditions.

c) *(0.5 p)* Determine the amount of metal deposited on the cathode if the charge which passes is 85000 C.

Data: $E^0(Au^{3+}/Au)$ = 1.470 V; $E^0(MnO_2/Mn_2O_3)$ = 0.118 V; F = 96500 C mol^{-1}; R = 8.314 J mol^{-1} K^{-1}; M(Au) = 197.0 g mol^{-1}.

SOLUTION

a)

3 Mn_2O_3 + 6 OH^- +2 Au^{3+} → 6 MnO_2 + 3 H_2O + 2 Au

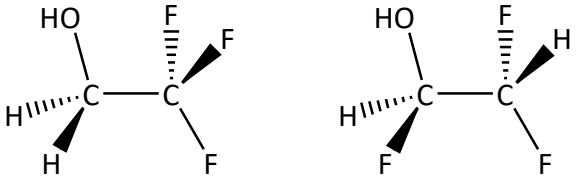
b)

Nernst Equation

E = 1.096 V

c) Faraday Law: m_{Au} = 57.84 g

3. *(1.75 points)* In the next figure, you may find the 3D structural formulas of compounds CF_3–CH_2(OH) and CF_2H–CH(OH)F. (Hint: group the O and H atoms in a single group)



CF_3-CH_2(OH) CF_2H-CH(OH)F

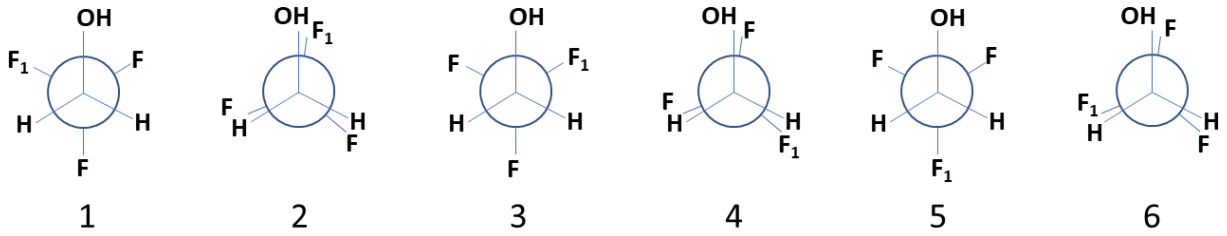
a) *(0.75 p)* Draw the Newman projections of both molecules along C-C axis and schematically draw the variation of the potential energy as a function of rotation angle in 60° steps. Assume that the main substituents (–OH and –F) have the same size.

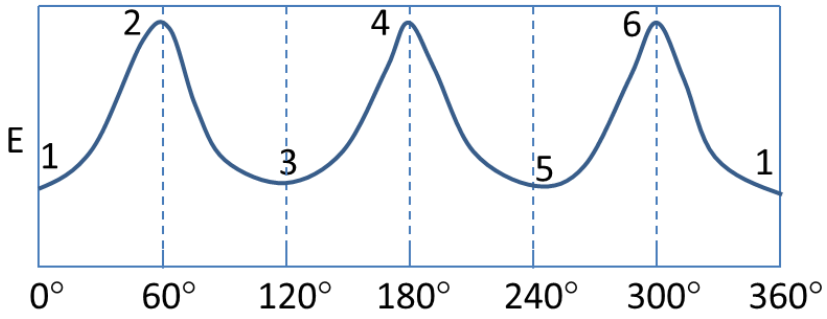
b) *(0.5 p)* Explain the main differences between both molecules regarding their energy diagrams.

c) *(0.5 p)* Assign *R* or *S* configuration to the chiral carbon.

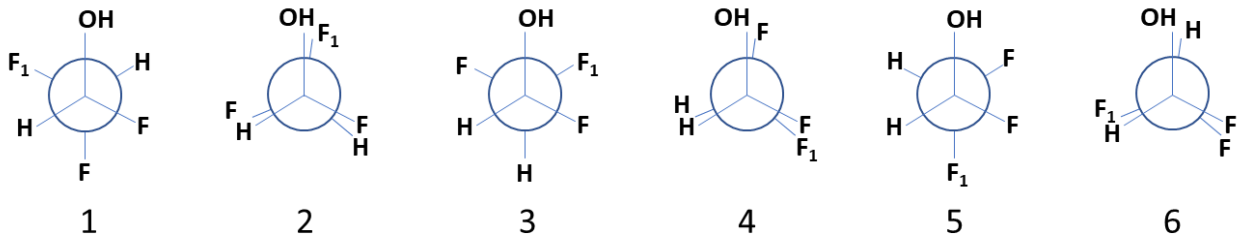
SOLUTION

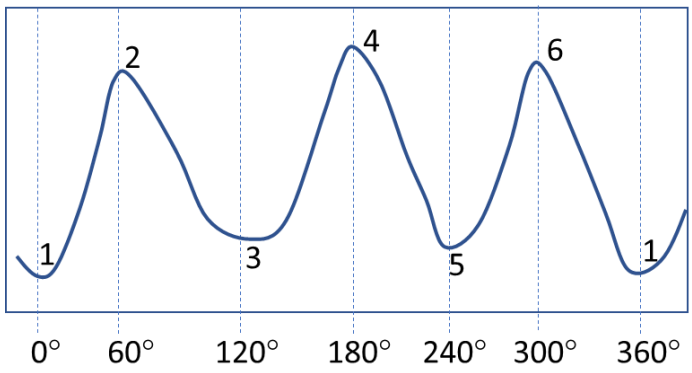
a) CF_3–CH_2(OH):





CF_2H–CH(OH)F:





Three maxima in both.

b)

The values of the potential energy at the maxima and the minima for CF_3–CH_2(OH) are:

Energy:
1 = 3 = 5 < 2 = 4 = 6

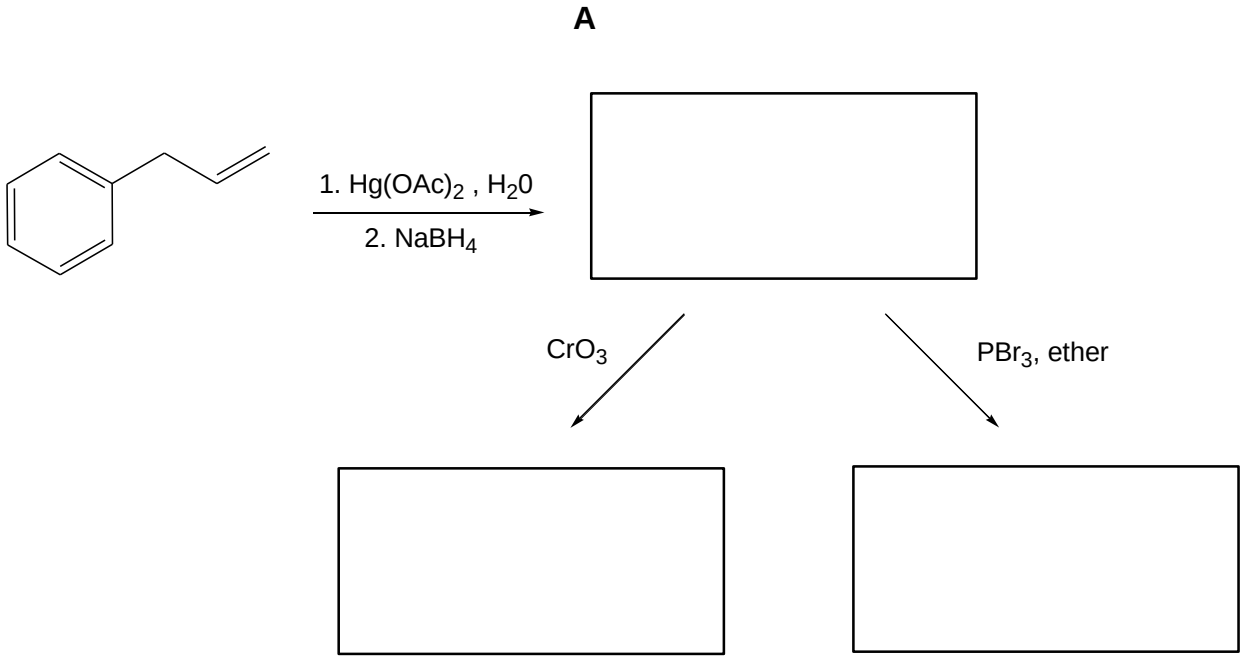
The values of the potential energy at the maxima and at the minima for CF_2H–CH(OH)F are:

Energy:
1 < 3 = 5 < 2 = 6 < 4

c) **There is only one chiral C in both molecules: CF_2H–CH(OH)F. It is a *R* configuration.**

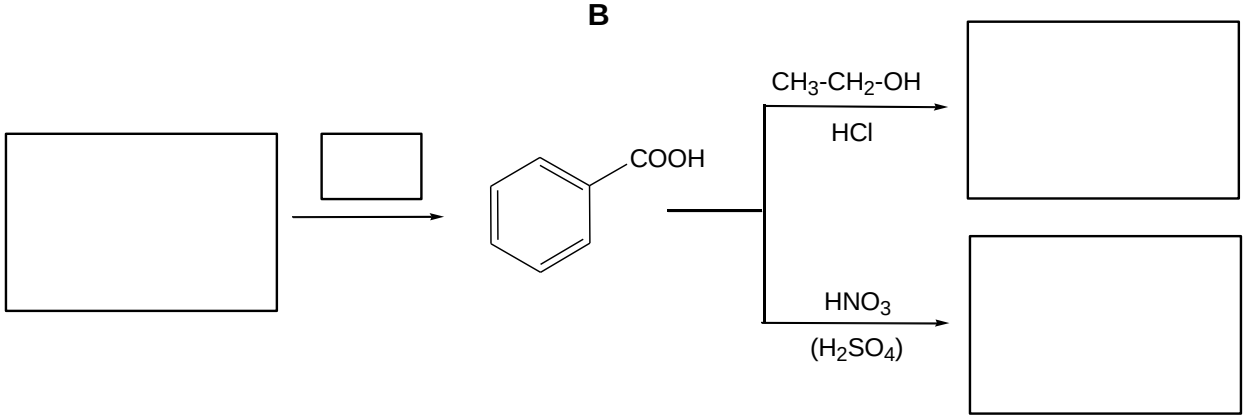
4. *(2.25 points)* Complete the following schemes. Each box corresponds to one compound.

a) *(0.75 p)*



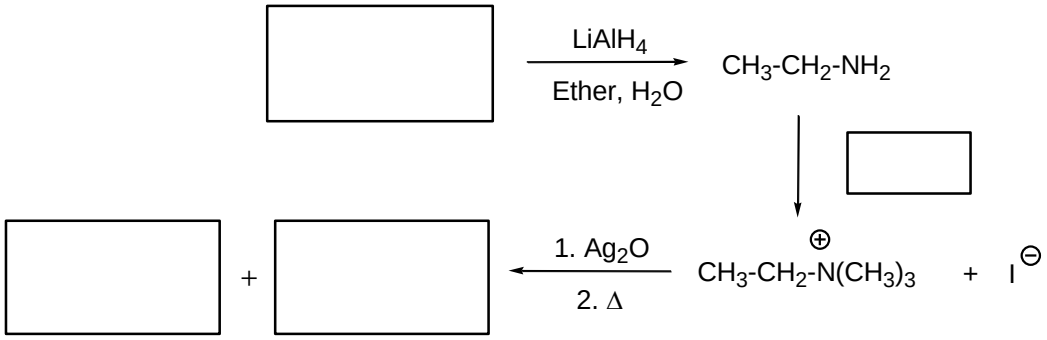
b) *(0.75 p)*

B



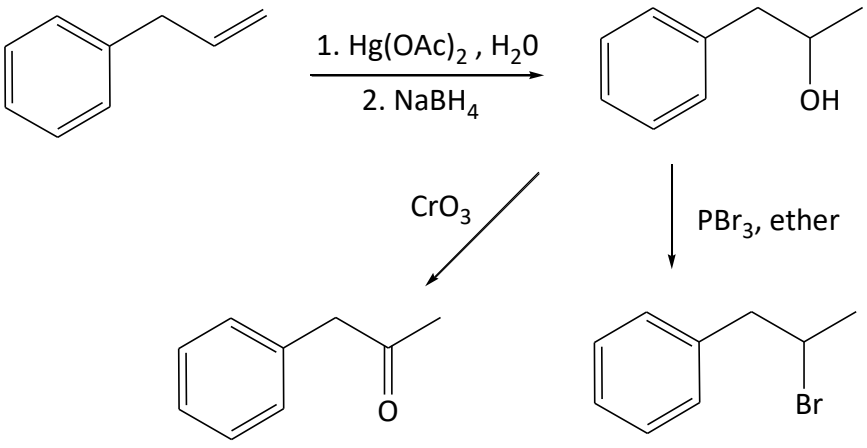
c) *(0.75 p)*

C

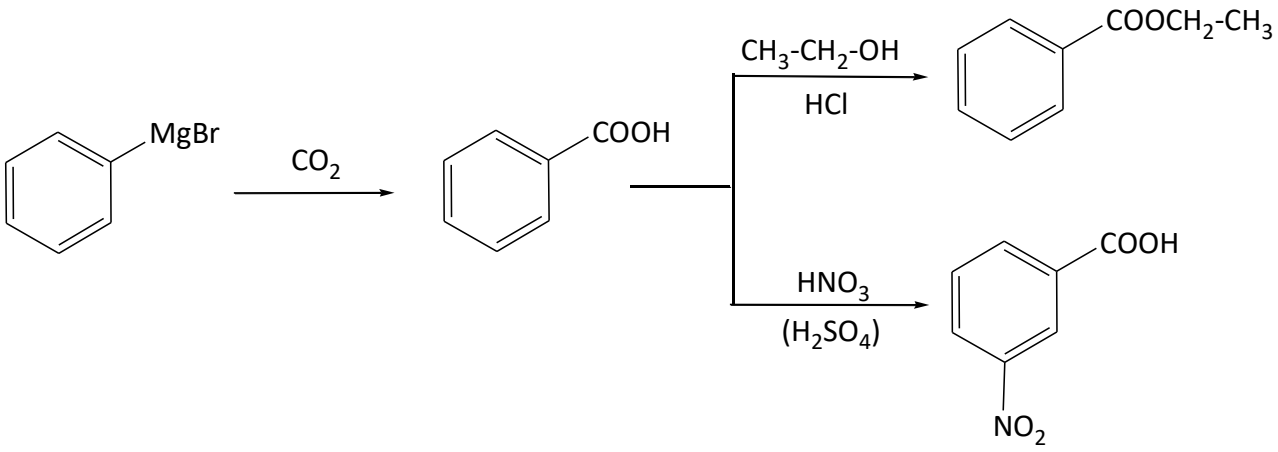


SOLUTION

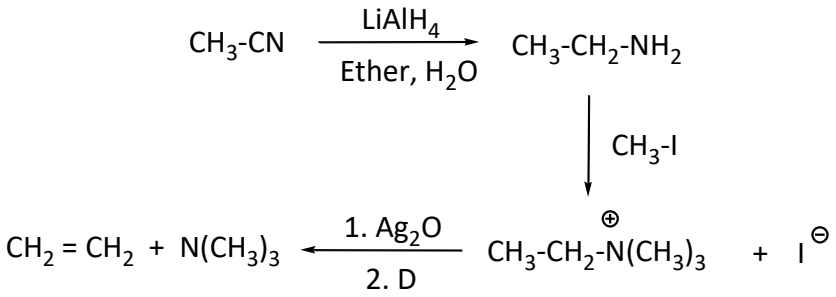
A



B



C



5. *(1.5 points)* A compound with the formula $C_{10}H_{12}O$ shows large intensity infrared absorption peak at around 1710 cm^{-1} and exhibits the following ^1H NMR spectrum:

CHEMICAL SHIFT (δ in ppm)	SPLITTING PATTERN	NUMBER OF HYDROGENS
2.09	Singlet	3 H
2.78	Triplet	2 H
2.83	Triplet	2 H
7.08	Triplet	1 H
7.12	Doublet	2 H
7.21	Triplet	2 H

a) *(1 p)* Deduce its structure.

b) *(0.5 p)* Name the compound and number in the structure the carbons which will have resonance line in its ^{13}C NMR spectrum.

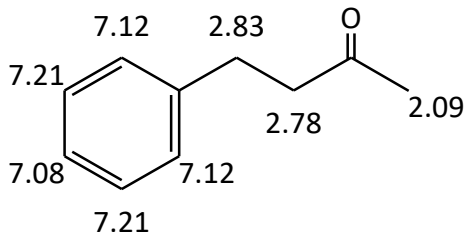
SOLUTION

a) $\boldsymbol{Degree\ of\ unsaturation = (10 + 1) - \frac{(12+1)}{2} = 5}$

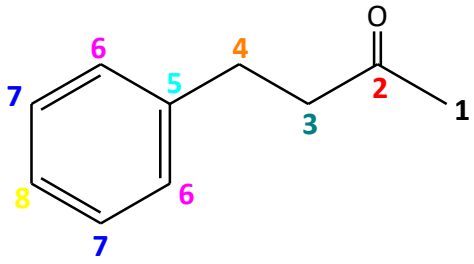
IR spectrum gives the information that there is a possible ketone in the structure.

From a first observation of the proton NMR spectrum data and considering the degree of unsaturation, we can deduce that it is a monosubstituted aromatic ring (several signals situated in the range 7.08-7.21). The signal present at a higher field is a singlet that integrates 3 H (a group - CH_3), so it will not be coupled. Between 2 and 3 ppm appear the two triplets which integrate 2 H (two groups CH_2) that they will consequently be at such low field because they will suffer the unprotection effect of the oxygen from the CO group and the benzene ring. Finally, the three signals of the aromatic ring correspond to a triplet integrating 1 H (coupling with 2 H), a doublet integrating 2 H (coupling with 1 H), and a triplet integrating 2 H (coupling with 2 H).

Therefore, the proposed structure would be the following:



b) Name: 4-Phenyl-butan-2-one.
There will be eight different peaks in the ^{13}C spectrum:



6. *(1 point)* Answer, briefly, the following questions:

a) What can reduce the effect of a competitive inhibitor of an enzyme?
b) According to the Michaelis-Menten model, at which reaction rate does K_m equal the substrate concentration?
c) In a cyclized monosaccharide, how is the most oxidized chiral carbon named?
d) Indicate two factors that will influence the melting point of lipids and how that influence will be.
e) How could denaturation of a protein take place?

SOLUTION

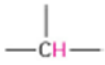
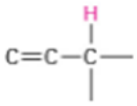
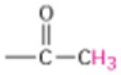
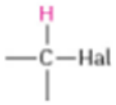
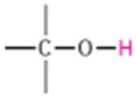
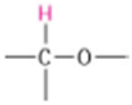
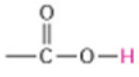
a) It can be reduced by increasing the substrate concentration.
b) K_m equals the substrate concentration at half of its maximal value.
c) It is named anomeric carbon.
d) Melting point of lipids will be influenced by the length of the hydrocarbon chain and its degree of unsaturation. When the length of the hydrocarbon chain increases, the van der Waals interactions are stronger and the melting point increases. The presence of double bonds

produces pronounced bends in the hydrocarbon chains since rotation around double bonds is hindered. These bends prevent close packing and extensive van der Waals interactions among the hydrocarbon chains. Consequently, cis unsaturated fatty acids have lower melting points than saturated fatty acids.

e) Environmental changes or chemical treatments may disrupt the native conformation of a protein, with concomitant loss of biological activity. Such disruption is called denaturation.

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

IMAGE CREDITS

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