Key.

CHM 2120C - MIDTERM #2

Date : June 18, 2019 **Duration : 90 minutes**

Professor : Claudia El Nachef

First name: _____ Last name: _____

Student #: _____

- **Nombre total de points est : 73**
- Molecular model is allowed.
- Faculty-approved calculator is permitted.
- Scratch papers to be submitted with the exam copy.
- A simplified pKa table, Infrared and ^1H NMR are provided on the last page.

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106 106												

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
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

Cellular phones, unauthorized electronic devices or course notes (unless an open-book exam) are not allowed during this exam. Phones and devices must be turned off and put away in your bag. Do not keep them in your possession, such as in your pockets. If caught with such a device or document, the following may occur: academic fraud allegations will be filed which may result in your obtaining a 0 (zero) for the exam.

By signing below, you acknowledge that you have read and ensured that you are complying with the above statement.

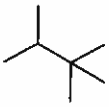
Signature: _____

GOOD LUCK!

1. What is the number of signals that should be observed in the ^{1}H NMR spectra of each of these molecules? **(6 points)**

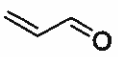
(2 pts each)

a.



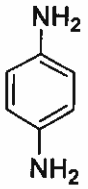
3

b.



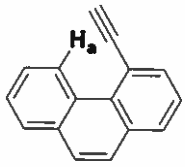
4

c.

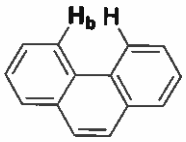


2

2. Which one of these protons is the most deshielded in the following structures : **H_a** of structure I or **H_b** of structure II? Explain briefly your reasoning. **(4 points)**



I

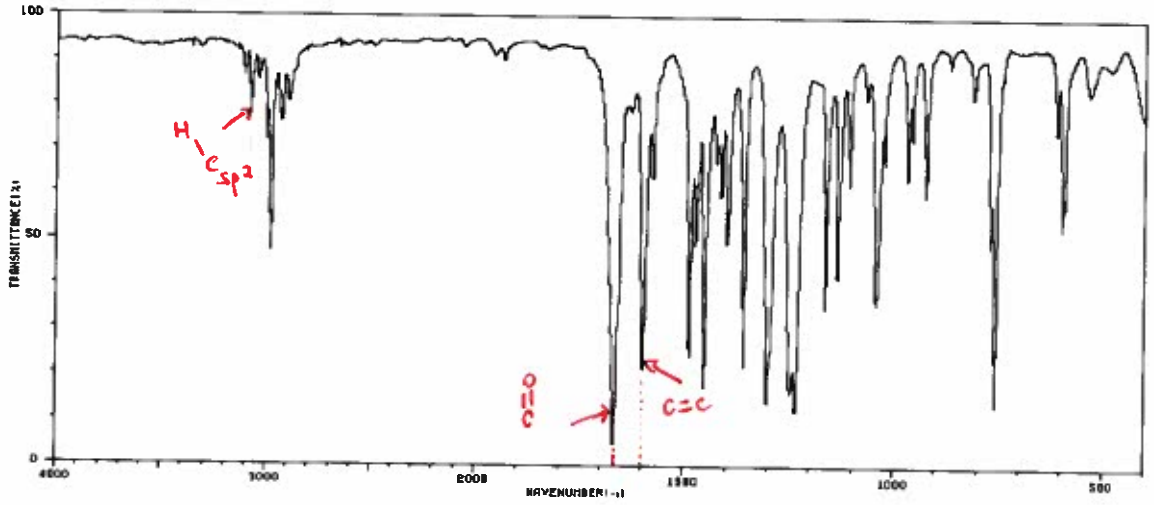


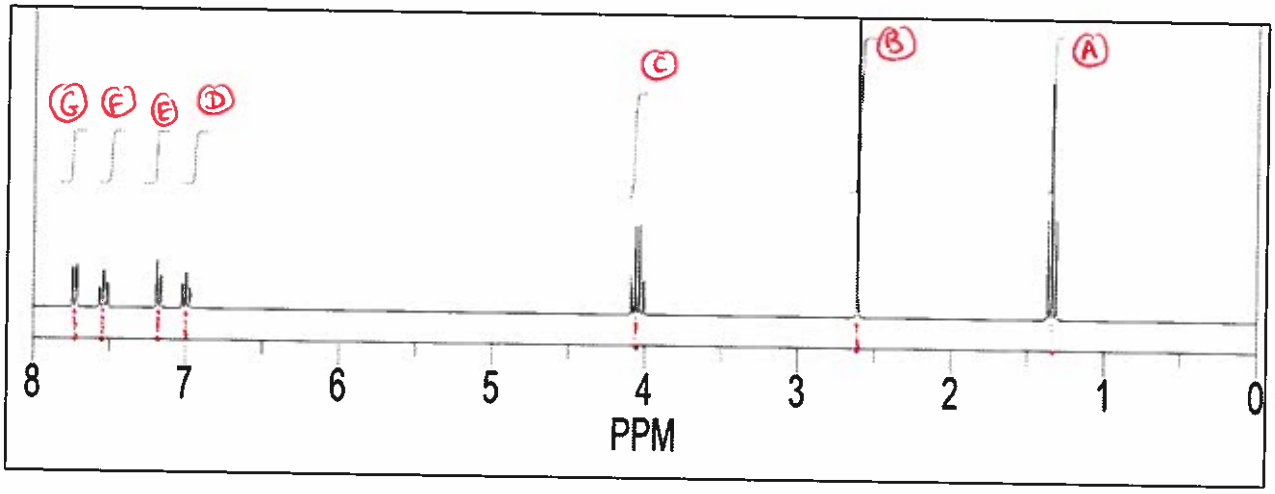
II

(1) H_a is the most deshielded because of magnetic anisotropy (1) of the alkyne.

(2) H_a is located in the deshielding zone of the alkyne where the induced magnetic field align with the applied external magnetic field B_o.

3. The IR and the ^{1}H NMR spectra of an unknown with a molecular formula of **$C_{10}H_{12}O_2$** are shown below. The questions that follow will guide you in the determination of its structure. **(15 points en total)**





a- Determine the degree of unsaturation. *Show your calculation.* **(2 points)**

$$DU = \frac{2C + 2 - H + N - X}{2} = \frac{2\times10 + 2 - 12 + 0 - 0}{2} = 5$$ (1) (1)

b- Analyze **three significant bands** in the IR spectra that conclude on the existing functions in the molecule. **(3 points)**

(1) $\overline{\nu}_{C=O} \simeq 1680\ cm^{-1}$ stretching band of carbonyl.

(1) $\overline{\nu}_{C=C} \simeq 1600\ cm^{-1}$ stretching band of double bond C-C.

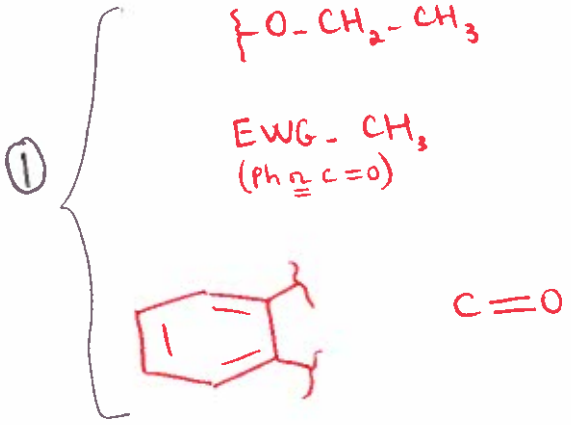
(1) $\overline{\nu}_{H-C(sp^2)} \simeq 3050\ cm^{-1}$ stretching band of H-C (sp^2)

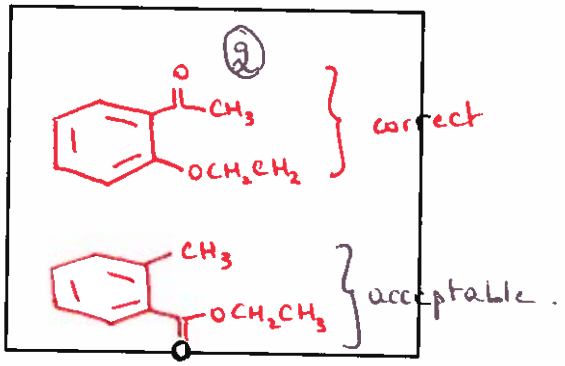
c- Fill in the table with all ^1H NMR characteristics for each signal and write down pertinent comments/ideas. **(7 points)** (1/4 per signal) (3/4) → (1/4) for neighbourings protons. (1/2) for chemical shift interpretation & conclusion (except for signal A)

Signal	δ (ppm)	Integration	Multiplicity	Comments/ideas
A	1.35	3	t	CH_3 next to 2 H => (3/4) CH_3-CH_2
B	2.60	3	s	CH_3 (1/4) next to 0 H (zero) / and CH_3 (1/4) – EWG { EWG: Ph (1/4) or C=O (1) => $C-CH_3$, $Ph-CH_3$
C	4.05	2	q	CH_2 (1/4) next to 3H / and CH_2 (1/4) – EWG { EWG: oxygen O (1/4) => $O-CH_2-CH_3$
D	7.00	1	t	CH (1/4) next to 2 H
E	7.20	1	d	CH (1/4) next to 1 H
F	7.55	1	t	CH (1/4) next to 2 H
G	7.70	1	d	CH (1/4) next to 1 H

(1) disubstituted benzene and ortho with no plane of symmetry.

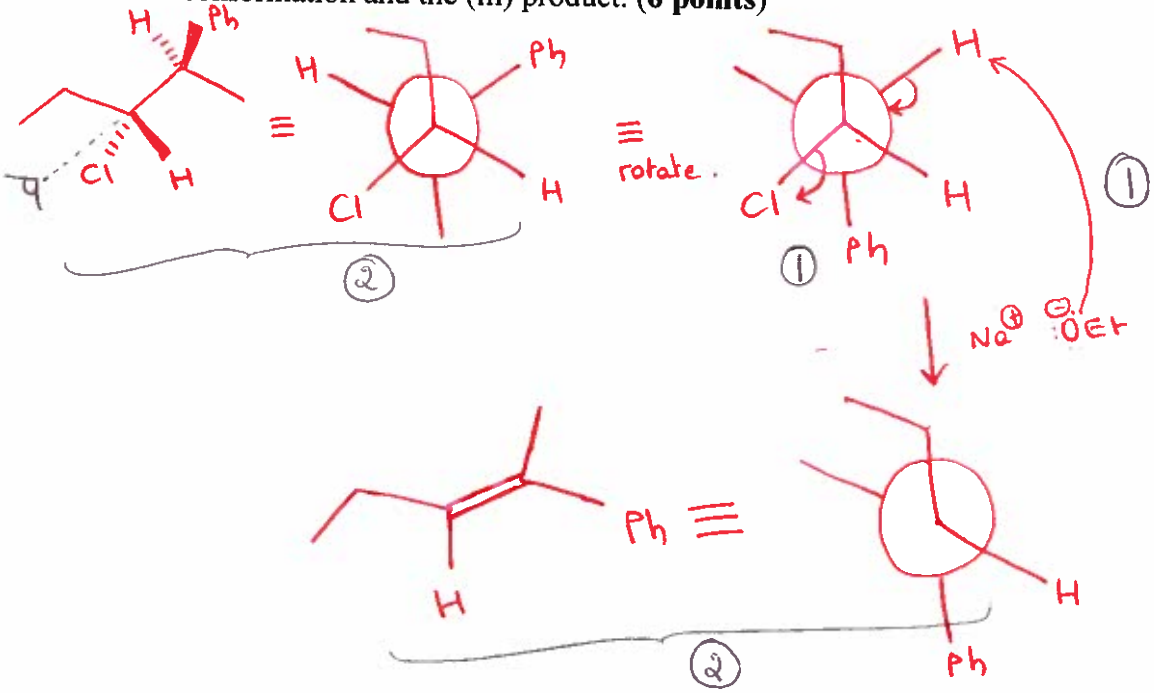
d- Identify the possible fragments then draw the final structure of the unknown in this box below. **(3 points)**
PS : all fragments should add up to give the same number of atoms in the molecular formula.





Final Structure

4. When (3*R*,4*R*)-3-chloro-4-phenylpentane is treated with sodium ethoxide, alkenes are generated as well as a nucleophilic substituted product.
   a- Draw the mechanism leading to the major product of this reaction. To support your answer, make sure to include the Newman projection of: (i) the starting material, (ii) the reactive conformation and the (iii) product. **(6 points)**

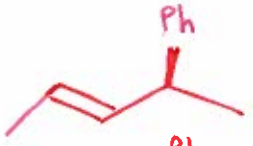


   b- What type of reaction led to the major product in (a)? **(1 point)**

① E2 elimination reaction.

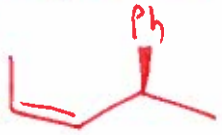
c- Determine (*without mechanism*) all the minor products from this reaction. **(4 points)**

E2 Hoffman products :



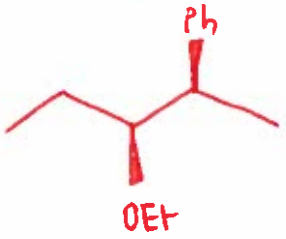
(1)

+



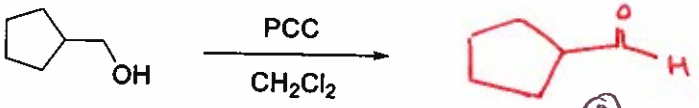
(1)

S_N2 Substitution product :



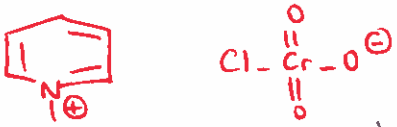
(2)

5. a- Determine the product of this following reaction. **(2 points)**



(2)

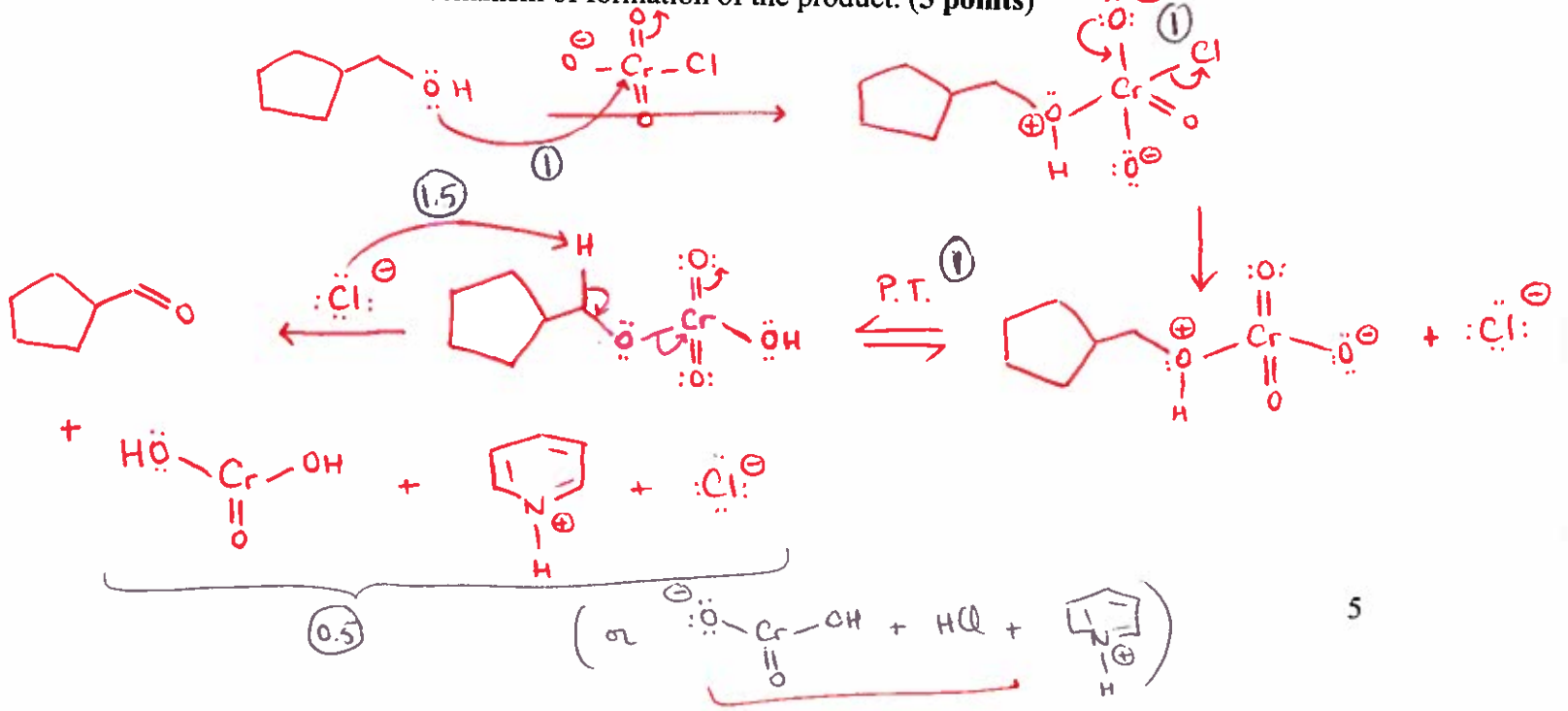
b- PCC is the acronym for what molecule? Draw its structure. **(2 points)**



(Pyridinium Chloro Chromate).

(2)

c- Draw the mechanism of formation of the product. **(5 points)**



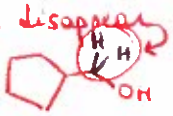
d- While using both spectroscopic methods (IR and ^{1}H NMR), how could you determine whether the reaction took place? Describe **two different points** observed and give precise values **for each method of analysis. (4 points)**

IR: (any two ① pt each)

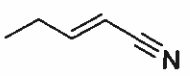
- Disappearance of a broad stretching band for O–H ≈ 3300 cm^{-1}
- Appearance of a sharp intense stretching band for C=O ≈ 1700 cm^{-1}
- Appearance of a medium stretching band for H–CO (aldehyde C–H) ≈ 2800 cm^{-1}

NMR: (any two ① pt each)

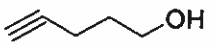
- Disappearance of a broad singlet for O–H
- Appearance of the aldehydic proton C(=O)–H ≈ 9–10 ppm (singlet)
- Number of signals decreased from 5 to 4
- A signal as a triplet (integrating for 2H) in the region between 3.5 and 4.5 ppm will disappear



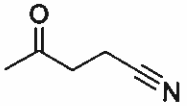
6. Circle the molecule that corresponds to the IR spectra provided below. **Show on the spectra** the significant bands that led to your conclusion. **(4 points)**



A ②

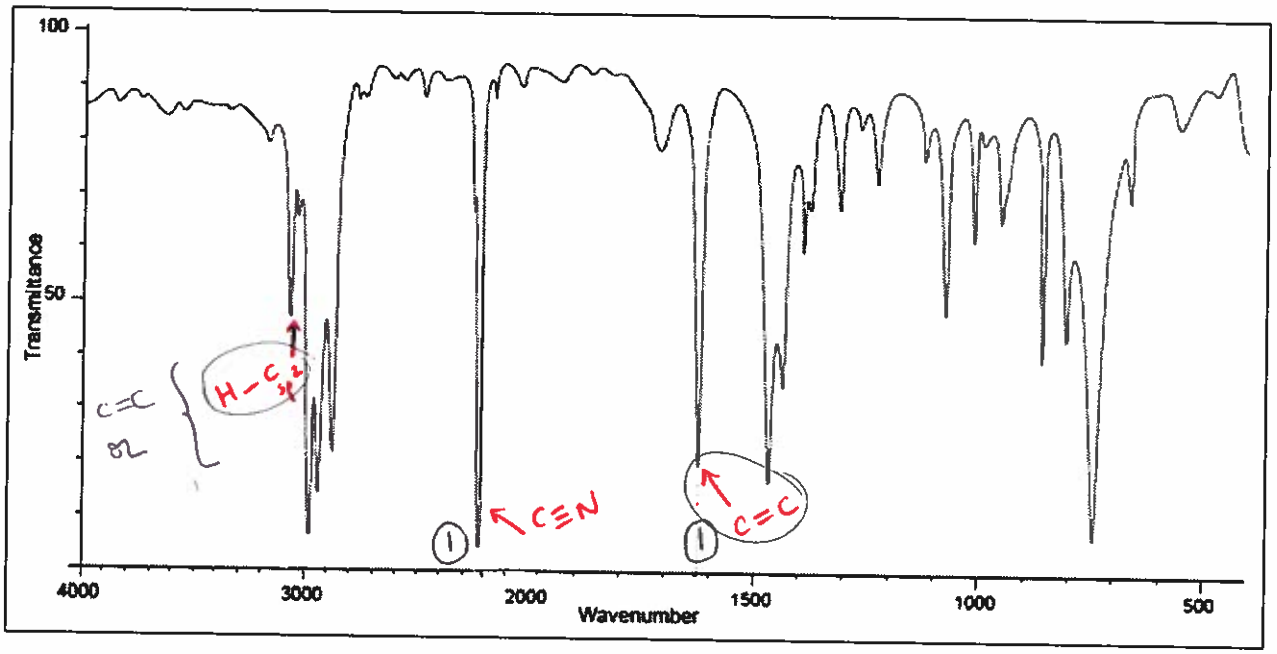


B



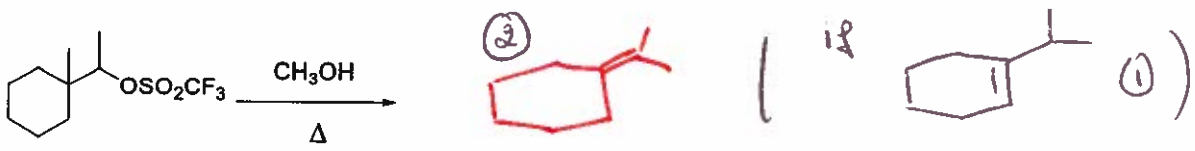
C

if © ①

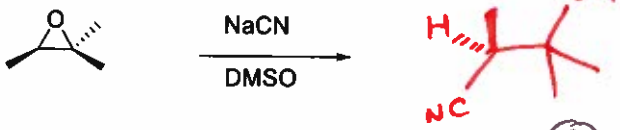


7. Draw **only** the major product(s) or determine the missing reagents for the following reactions (*no mechanism is needed*). **(20 points)**

a)

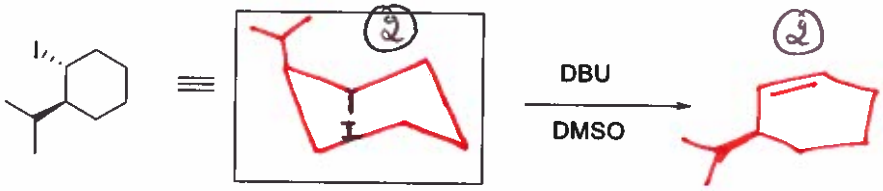


b)



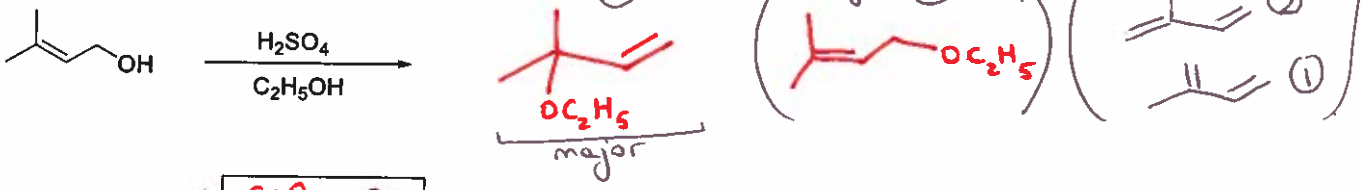
c)

d)

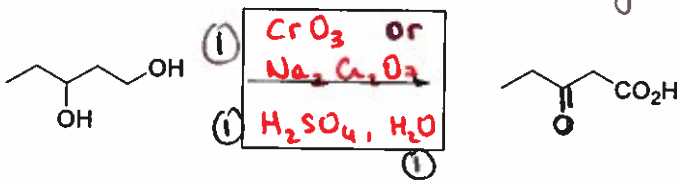


Reactive chair conformation

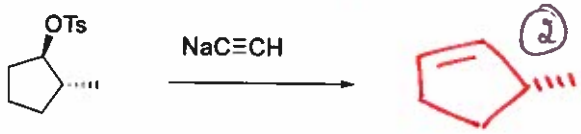
e)



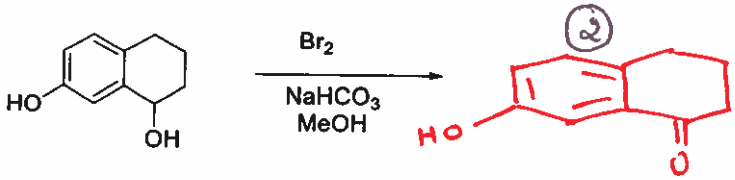
f)



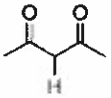
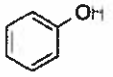
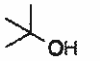
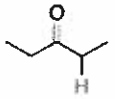
g)



h)



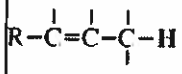
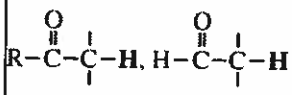
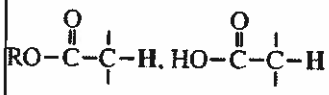
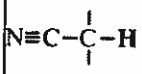
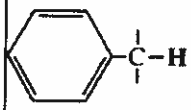
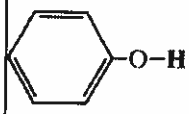
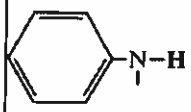
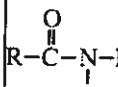
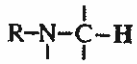
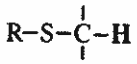
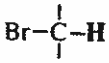
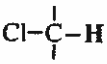
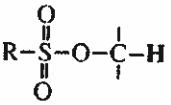
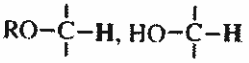
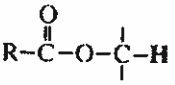
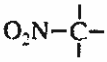
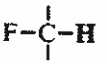
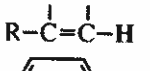
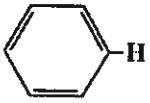
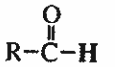
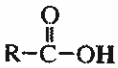
pK_a Table

Acid	pK_a value (H_2O solvent)	Acid	pK_a value (H_2O solvent)
HI	-10		9
HBr	-9		
HCl	-8		9.9
	-6.2		10.6
	-3.8	H_2O	15.7
H_2SO_4	-3		17
	-2.6		20
$CH_3OH_2^+$	-2.2		
H_3O^+	-1.7		24
HNO_3	-1.3	H_2	36
HF	3.17	NH_3	38
	4.76		50
			51

IR important absorption bands (cm^{-1}): stretching

C-H Alkyl	C-H	2850-2960	m, sharp
Alkene	C-H	≥3000	m, sharp
	C=C	1650	w, sharp
Alcohol	R**O-H**	3200-3650	s, broad (*hydrogen bonded)*
Carboxylic acid	RC(=O)**O-H**	2500-3300	s, broad
Amine	R2**N-H**	3300-3500	m, a little broad
*Carbonyl	R2**C=O**	1650-1780	s, sharp
Nitrile	R**C≡N**	2220-2260	s, sharp
Alkyne	C≡C-**H**	~3300	w, sharp
	C≡C	2100-2260	w, sharp
Ether	C-O-C	~1200	s, sharp
Phenyl	**C=C**	1450-1600	m
	C-H	3030	w to m
Nitro	NO_2	1350-1560	s
Aldehyde	**H-C**=O	2830-2695	m

Tableau de valeurs approximatives de déplacement chimiques des protons les plus communs.

$R-CH_3$		0.7 – 1.3
$R-CH_2-R$		1.2 – 1.4
R_3CH		1.4 – 1.7
		1.6 – 2.6
		2.1 – 2.4
		2.1 – 2.5
		2.1 – 3.0
		2.3 – 2.7
$R-C\equiv C-H$		1.7 – 2.7
$R-S-H$	var	1.0 – 4.0[b]
	var	0.5 – 4.0[b]
$R-O-H$	var	0.5 – 5.0[b]
	var	4.0 – 7.0[b]
	var	3.0 – 5.0[b]
	var	5.0 – 9.0[b]
		2.2 – 2.9
		2.0 – 3.0
		2.0 – 4.0
		2.7 – 4.1
		3.1 – 4.1
		ca. 3.0
		3.2 – 3.8
		3.5 – 4.8
		4.1 – 4.3
		4.2 – 4.8
		4.5 – 6.5
		6.5 – 8.0
		9.0 – 10.0
		11.0 – 12.0