Key.

CHM 2120C - MIDTERM #1

Date: May 23, 2019 **Duration: 90 minutes**

Professeur : Claudia El Nachef

First name: _____ Last name: _____

Student #: _____

- **Total number of points : 77**
- Molecular model is allowed.
- Faculty-approved calculator is permitted.
- Scratch papers to be submitted with the exam copy.
- A simplified pKa table is 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.

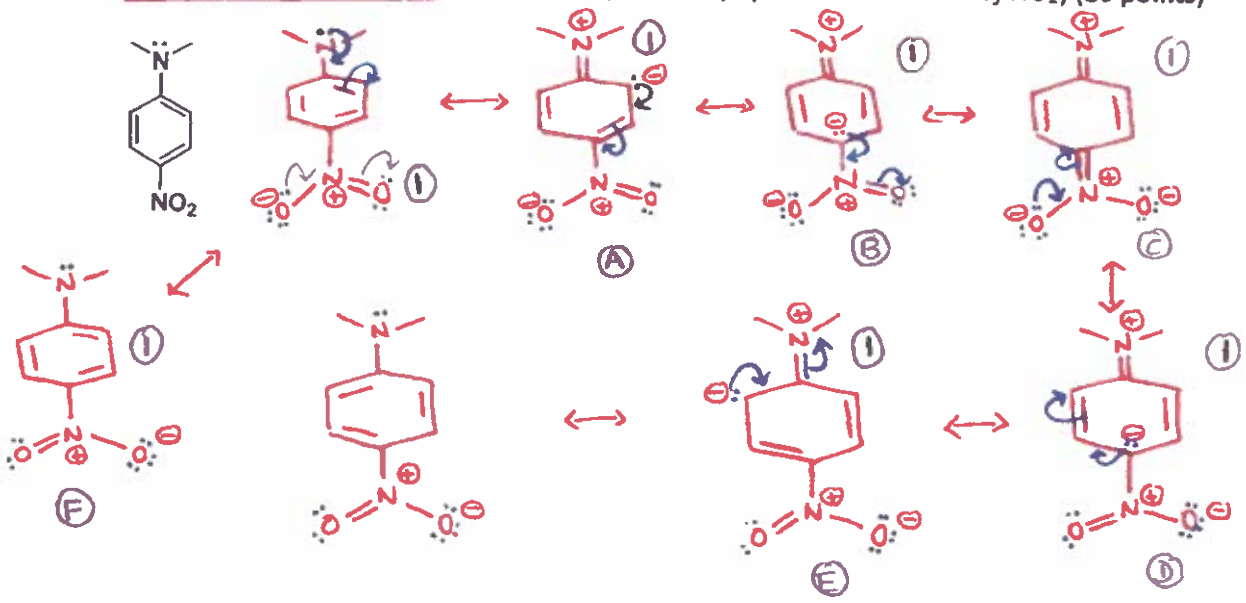
By signing below, you acknowledge that you have read and ensured that you are complying with the above statement.

_____

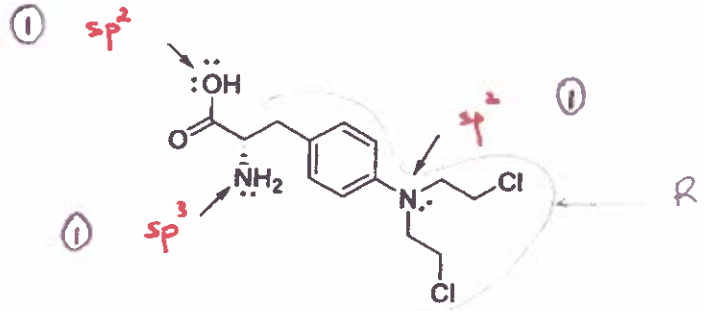
GOOD LUCK!

1. Draw the resonance structures of the following molecule, using curved arrows to show electron movement and appropriate arrows to show the relationship between the structures. All lone pairs and charges must be clearly shown. (*Expand the structure of NO_2*) **(10 points)**

0.5 pt per each form for correct charge/lone pair (A-F)



2. a) Determine the hybridization state of the oxygen and both nitrogen atoms indicated with an arrow in the following structure. **(3 points)**

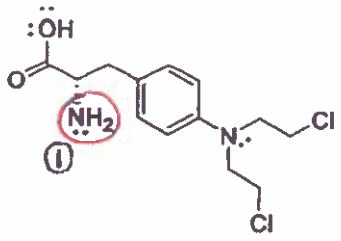


b) Indicate in what orbital do each of the lone pairs of that oxygen (indicated with an arrow) reside. Explain your answer using appropriate structure. **(4 points)**

(3) * One of these lone pairs should reside in a p orbital because it is conjugated to the pπ system of the carbonyl C=O

(1) * The other lone pair would reside in a hybridized type of orbital sp^2 / sp type

c) Circle the **most basic nitrogen** on the structure and explain briefly your choice. **(3 points)**



* It is the most basic because its lone pair is available and not conjugated to any π system as in the case of the other aniline nitrogen. (2) on either

* + (sp^3 vs sp^2)
↓
less s character, less retained

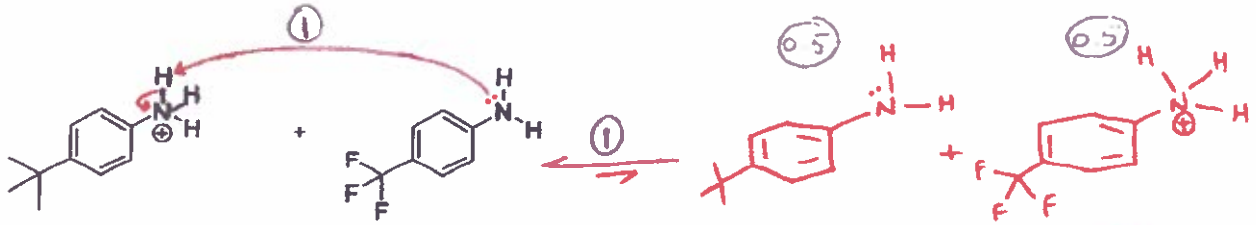
3. Complete each of the following reversible reactions. Use curved arrows to show the mechanism. Once products are established, show by using uneven equilibrium arrows, in each of the following cases, what side does the equilibrium favor, the starting materials or the products? justify your answer. **(10 points)**

a)

* pKa ≈ 24 most acidic — stronger base → weaker base. pKa ≈ 45 weaker acid (acceptable if 50)

either (2) * sp anion are more stable than sp^2 anion because the negative charge is better retained with higher s-character.
⇒ sp anion is therefore the weaker base.

b)



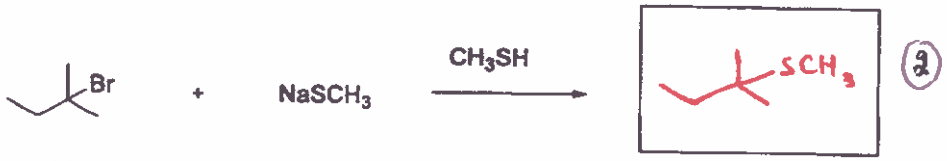
weaker acid — weaker base — stronger Base — stronger acid

For either comparison (acids or bases), inductive effect is the argument.

For acids: the reagent with CH_3 is the weaker acid due to the inductive effet of the electronegative atom F which decrease the electron density around the proton.

For bases: the reagent with CF_3 is a more stable base therefore a weaker base because the electron are distributed between multiple atoms due to the inductive effect of CF_3.

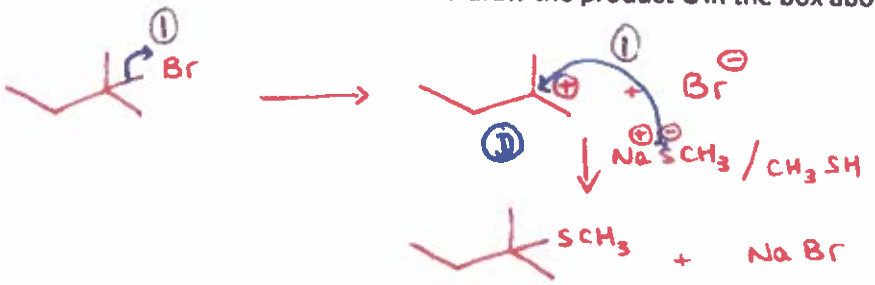
4. The substitution reaction below of 1.0 mM of compound **A** with 1.0 M of sodium methanethiolate **B** gave product **C**. This reaction has a rate constant k of $5.0 \times 10^2\ s^{-1}$.



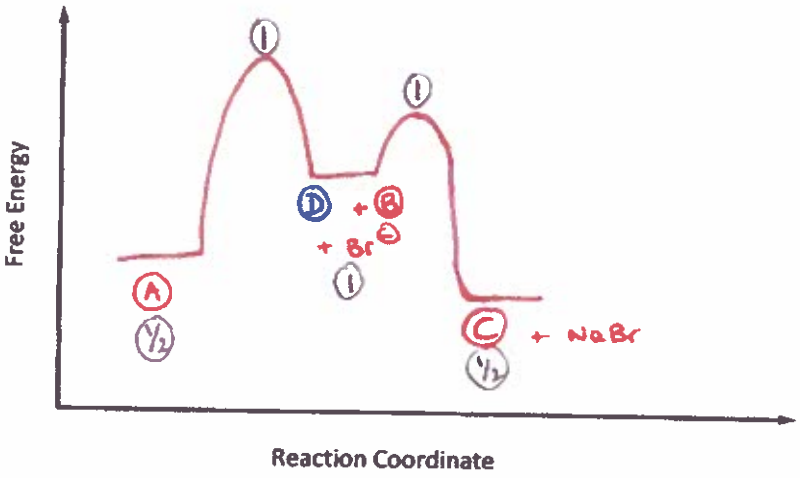
2

A **B** **C**

a) Show the reaction mechanism and draw the product **C** in the box above. **(4 points)**



b) Draw the energy diagram of the reaction: **(4 points)**



It's okay if $Br^{\ominus}$ and NaBr were not added.

c) Now that you have identified how the substitution reaction is proceeding, determine from the list below the rate of this reaction: (*Circle the correct answer*) **(2 points)**

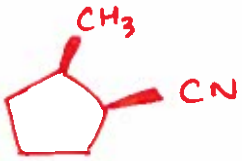
2

i) $2{,}5 \times 10^{-2}\ s^{-1}$
ii) $1{,}0 \times 10^{1}\ M \cdot s^{-1}$
iii) $5{,}0 \times 10^{1}\ M \cdot s^{-1}$
iv) $2{,}5 \times 10^{2}\ M \cdot s^{-1}$

5. Draw the product (s) of the following reactions. Indicate what **type of substitution** reaction takes place. **(20 points)**

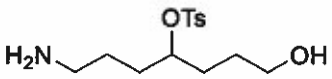
Type of S_N

a) 



(2)

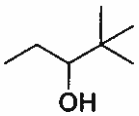
S_N2 (1)

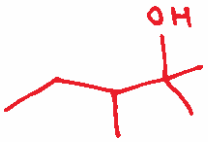
b) 

NaH, THF


(2)

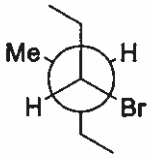
S_N2 (1)

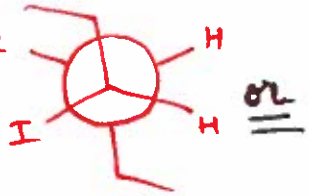
c) 

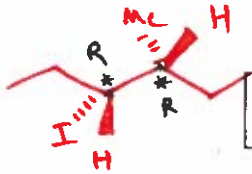
H_2SO_4


(2)

S_N1 (1)

d) 

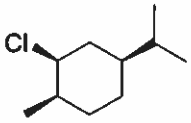
NaI
Acetone


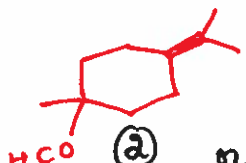
or


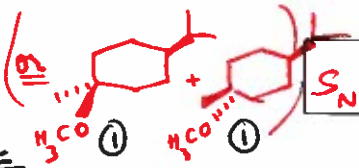
S_N2 (1)

(3R, 4R) - 3-Iodo-4-methylhexane
(1) (1) (1)

Name the product following IUPAC

e) 

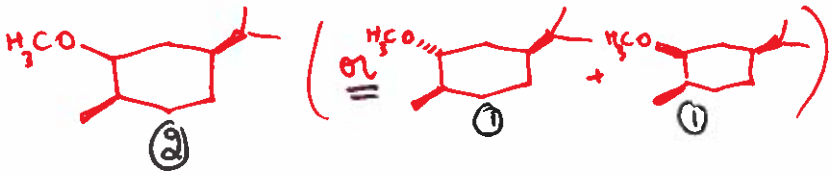
CH_3OH


(2)
or


(1) (1)

S_N1 (1)

Other acceptable products :

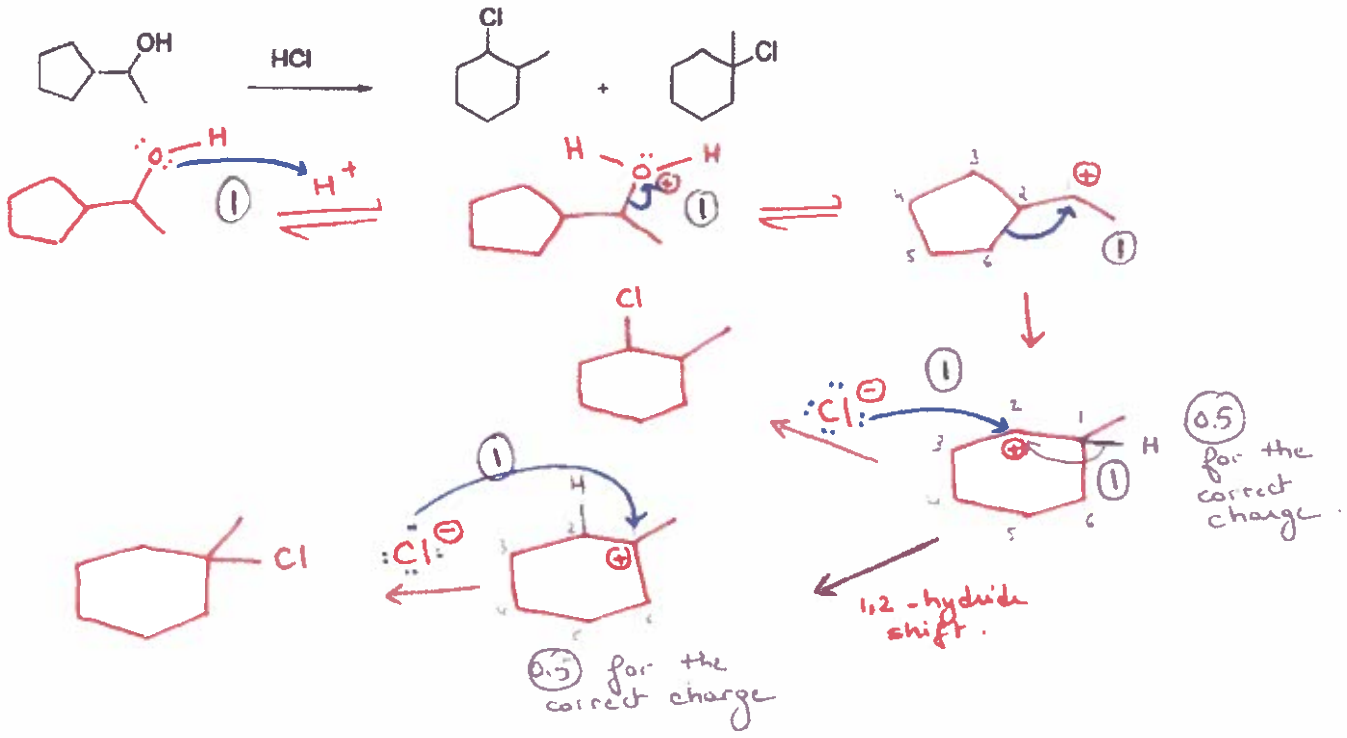


(2) (1) (1)

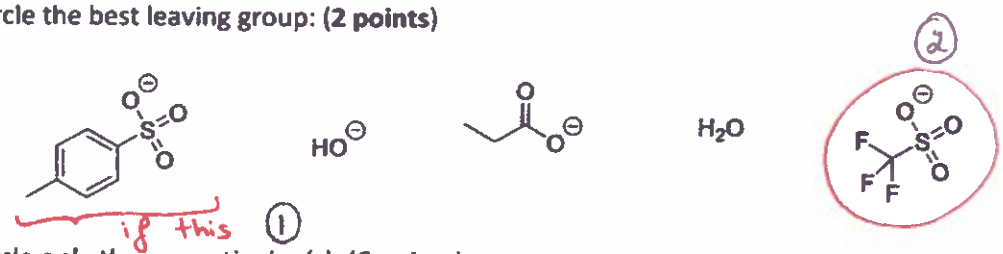
Draw in this box the most stable chair conformation

total mark is (5)

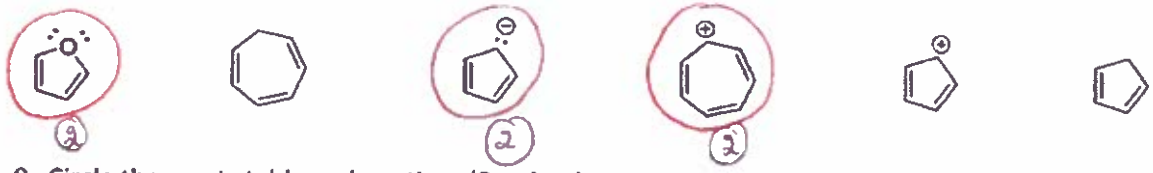
6. Provide a detailed mechanism for this following reaction: **(7 points)**



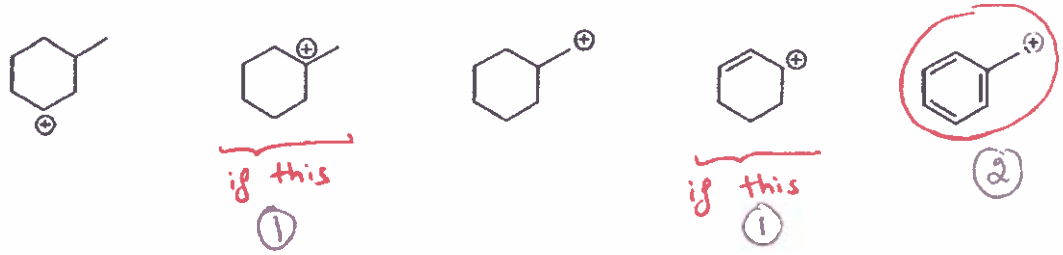
7. Circle the best leaving group: **(2 points)**

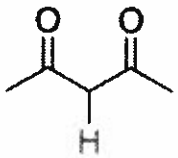
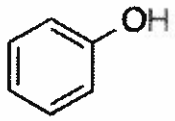
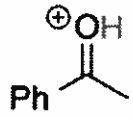
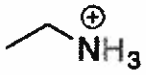
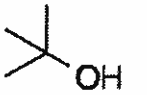
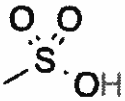
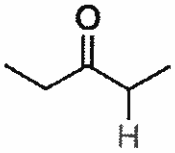
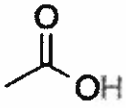


8. Circle **only** the aromatic ring(s). **(6 points)**



9. Circle the most stable carbocation. **(2 points)**



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
H_2S	7.00	BuSH PhSH	10-11 ≈7