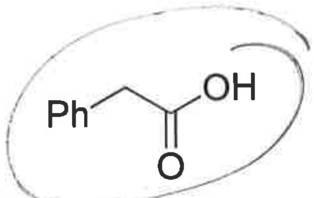
CHEM 344 Fall 2013 Midterm Quiz A **100 pts**

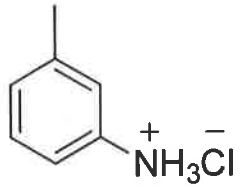
Name: ANSWER KEY

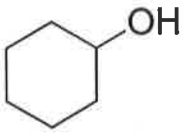
TA Name:

NO HALF POINTS

1) Circle each molecule that reacts with aq. NaOH solution to form water-soluble organic products (6 pts).

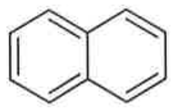






2 pts 2 pts no circle 2 pts no circle

2) Draw a bullet point list to describe the most efficient way to separate a 1:1 mixture of solid potassium carbonate (K_2CO_3) and solid naphthalene ($C_{10}H_8$, shown below) into its individual solid components (6 pts).



Naphthalene

K_2CO_3 Insoluble in organic solvent
Naphthalene soluble in organic solvent

- Add solid mixture to an organic solvent (2 pts)
- Filter the resultant suspension to isolate K_2CO_3 (2 pts
- Remove organic solvent from solution to isolate Naphthalene (2 pts)

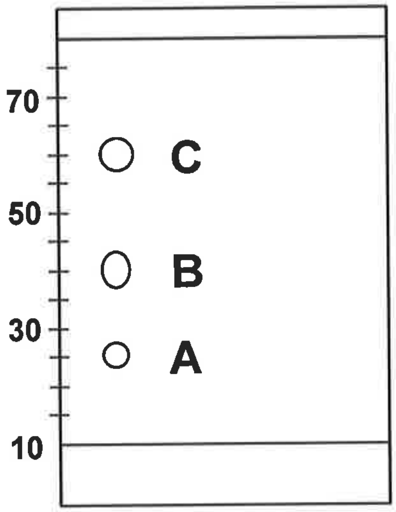
— — — — — — — — — —

- could swap organic solvent for water then would filter off Naphthalene and remove water to isolate K_2CO_3. This would be less efficient but still worth full credit

- any use of acid in the process = 0 pts

3) A reaction mixture was analyzed by TLC. The resultant TLC plate is shown below.

a) Showing all work, calculate the R_f values (as decimals) for compounds A, B and C (6 pts).



A: 15/70 = 0.214

B: 30/70 = 0.428

C: 50/70 = 0.714

2pts each

NO PARTIAL CREDIT

b) The reaction mixture analyzed by TLC contained an ester, a carboxylic acid, and an aromatic hydrocarbon. Assign each of the spots as one of these three compounds and explain your reasoning (5 pts).

A=acid

B= ester

C= aromatic hydrocarbon

} 1pt each.

Acid is most polar thus will not travel up the plate as much as the ester or the aromatic ~~co~~ hydrocarbon.

Anything similar to above = 2pts

4) 1,4-Dimethylbenzene (C_8H_{10}, *p*-xylene) was to be used as a solvent for a reaction. The ^{1}H-NMR spectrum of 1,4-dimethylbenzene (next page), taken in $CDCl_3$, shows that it is contaminated with another organic molecule. The formula of the contaminant is C_4H_8O, IHD = 1.

On the ^{1}H-NMR spectrum:

a) Draw a circle around the signals due to 1,4-dimethylbenzene; 2pts

b) Draw a square around the signals due to the contaminant; 5pts

c) Draw the structure of the contaminant, assigning the signals using the H_a, H_b etc notation used in problem sets, quizzes, and lab reports; 5pts

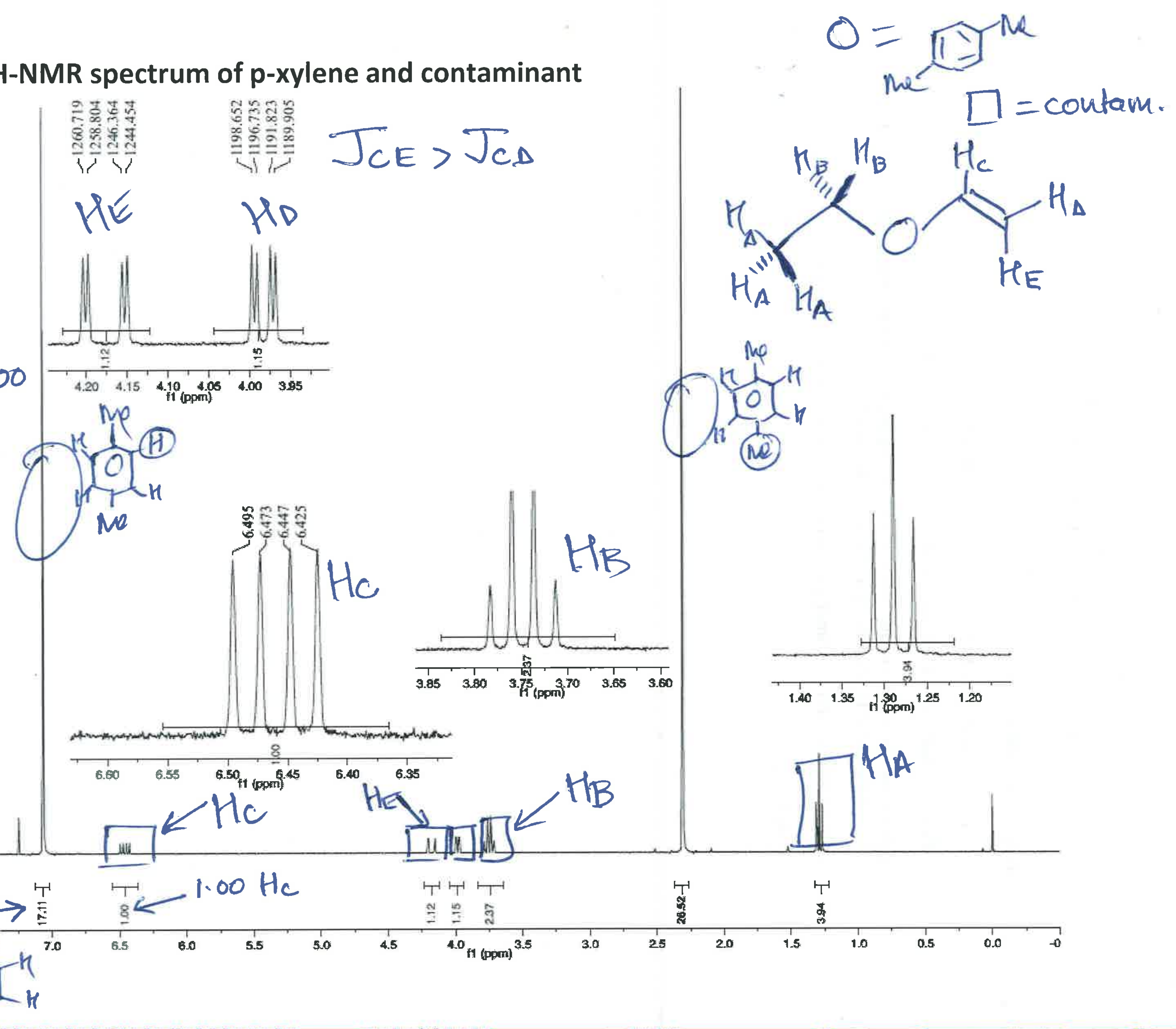
d) Calculate the ratio 1,4-dimethylbenzene : contaminant in terms of *x*:1. 2pts

(14 pts total)

Ethyl vinyl ether

Q4) ^{1}H-NMR spectrum of p-xylene and contaminant

$$\frac{17.11}{4} \doteq 1.00 = 4.27:1$$



5) A potential energy (PE) surface for the reaction A → X+Y is shown over the page.

a) On the PE surface, draw a circle around the kinetic product and draw a square around the thermodynamic product (4 pts)

SEE PE surface

b) The ratio of products X:Y was calculated to be 3:2 by ^{1}H-NMR and GC data. Has the reaction ~~has~~ achieved equilibrium under the experimental conditions? Explain your answer (4 pts).

No, the reaction has not reached equilibrium (1pt)

The 3:2 X:Y ratio shows that the Kinetic product is still formed (rxn is under kinetic control), and thus the reaction is irreversible (3 pts)

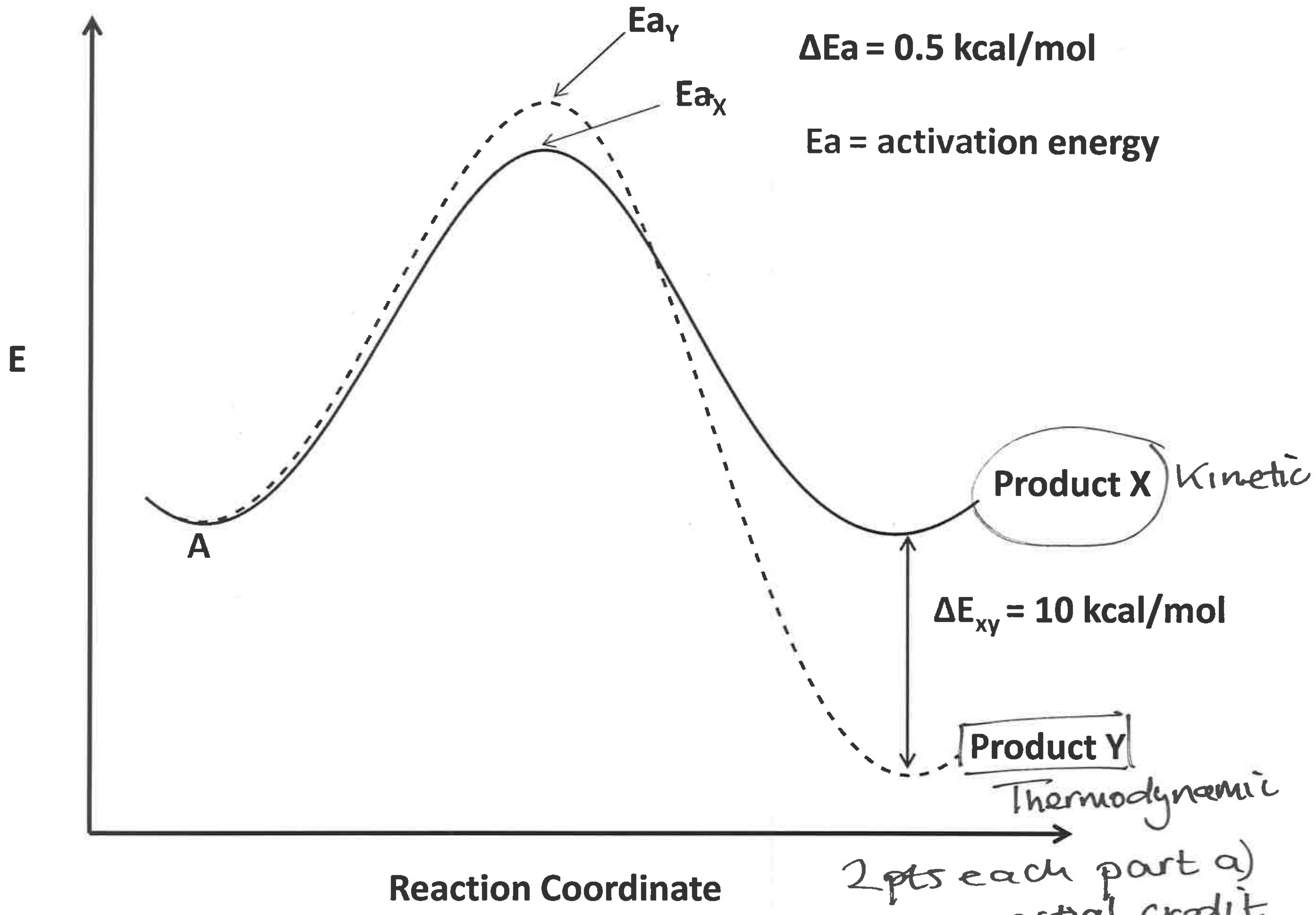
c) Assume that, **under different experimental conditions**, that the reaction A → X+Y is fully reversible. How would such reversibility affect the ratio X:Y? Explain your answer (4 pts).

Under reversible conditions (thermodynamic control) the product ratio X:Y would (massively) favor Y, the thermodynamic product, because the system can achieve equilibrium.

Product Y would be strongly favored because of the large ΔE_{XY} (10 kcal/mol).

(Product X may not even be obtained under such conditions).

Q5 Potential energy surface A→ X + Y



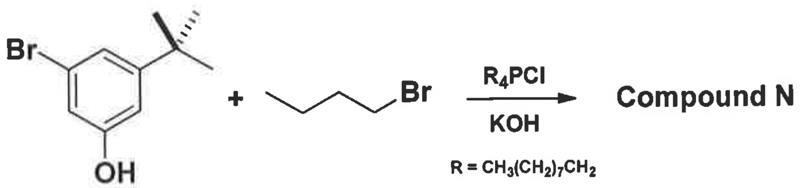
ΔEa = 0.5 kcal/mol

Ea = activation energy

ΔE_{xy} = 10 kcal/mol

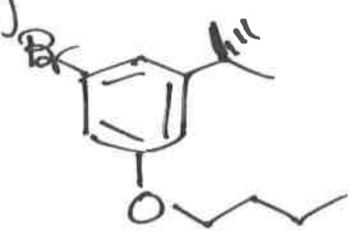
2 pts each part a)
no partial credit

6) In the lab you performed a reaction similar to the one shown below.



a) State the mechanism of the above reaction and draw compound N (3 pts).

S_N2 (1pt)



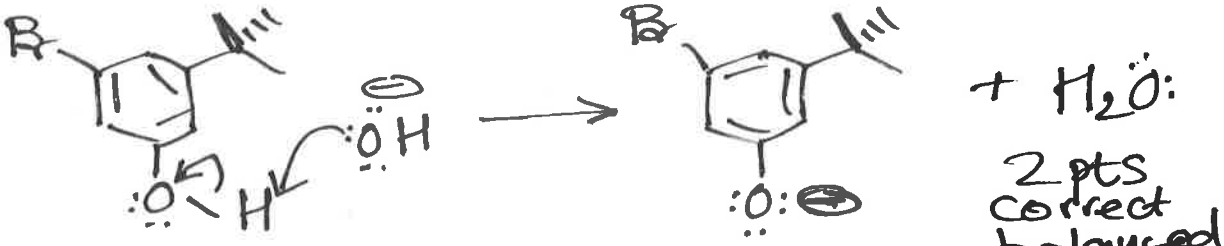
Cpd. N (2pts)

b) State the role of R_4PCl in this reaction (2 pts).

Phase transfer catalyst / agent 2pts

c) State the role of KOH in this reaction. Include a balanced electron-pushing mechanism in your answer (3 pts).

KOH is a base used to deprotonate the phenol and form the Nu:⊖ (1pt)



2 pts correct balanced eqn.

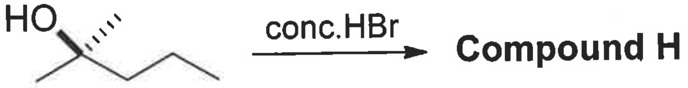
d) Compound N is soluble in hexane at room temperature. Would hexane be a good solvent for recrystalization of the Compound N? Briefly explain your answer (2 pts)

No, not a good solvent (1pt)

Cpd. N is soluble at room temp. and so will not precipitate from the solution (1pt)

Note: for a solvent to be useful for recrystallization, it needs to have a narrow window in which the solid is soluble. Typically, the solid should be soluble at high temp and insol at room temp.

7) In the lab you performed a reaction similar to the one shown below.



Compound G

a) State the mechanism of the reaction being performed and draw the structure of compound H (3 pts).

S_N1
(1pt)

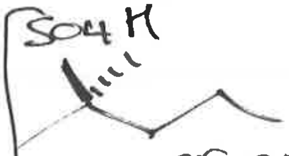
Cpd. H (2pts)
anything else = 0

b) In error, a student used conc. H_2SO_4 rather than conc. HBr in this reaction. Draw the organic product(s) of the reaction between compound G and conc. H_2SO_4 (3 pts).

+

1 pt

2 pts



or anything similar = 0 pts

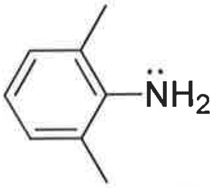
c) During the work-up of the reaction performed in *b)* the organic layer was washed with 2 x 5 mL saturated aq. K_2CO_3 solution. Briefly explain why this step was performed. Include a balanced chemical equation in your answer (4 pts).

K_2CO_3 solution used to neutralize any excess H_2SO_4 (~~1pt~~). (2pts)

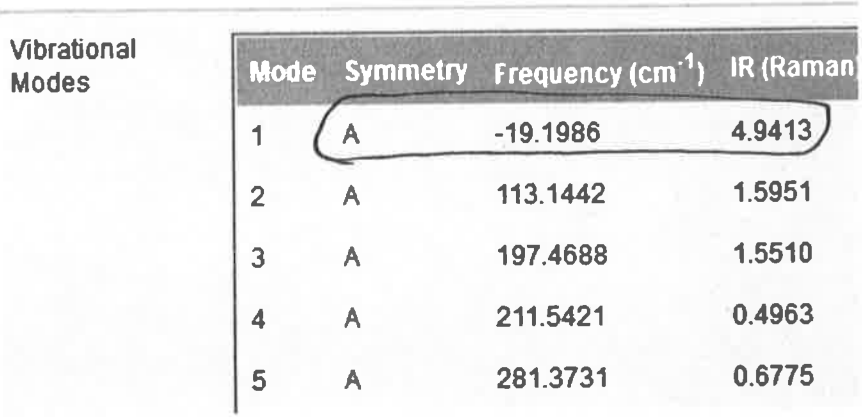
$K_2CO_3 + H_2SO_4 \longrightarrow K_2SO_4 + H_2O + CO_2$ } 2pts

($K_2SO_4 + H_2CO_3$ = 1 pt)

8) 2,6-Dimethylaniline was submitted for a B3LYP/6-31G(d) Opt+Vib Freq calculation in WebMO. The resultant vibrational mode table is shown below.



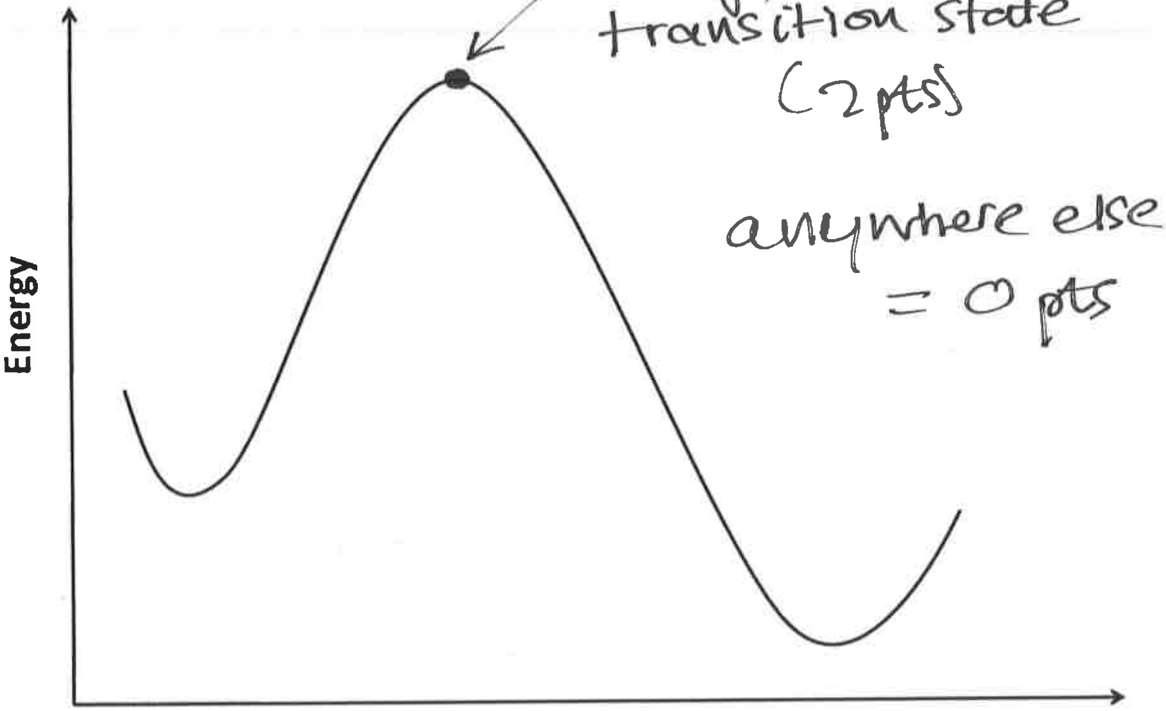
2,6-Dimethylaniline



Vibrational Modes

Mode	Symmetry	Frequency (cm^{-1})	IR (Raman
1	A	-19.1986	4.9413
2	A	113.1442	1.5951
3	A	197.4688	1.5510
4	A	211.5421	0.4963
5	A	281.3731	0.6775

Identify a possible location on the potential energy surface for this optimized molecule and briefly explain your reasoning (4 pts).



energy maximum or transition state

(2pts)

anywhere else = 0 pts

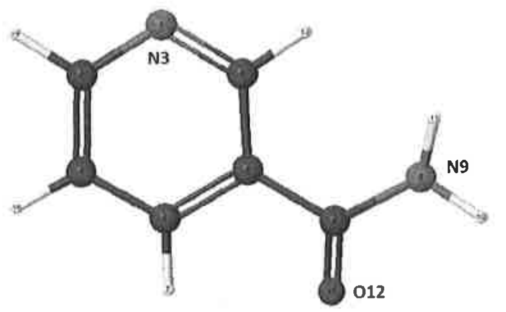
the vib. freq. table shows a $\ominus$ve vibrational mode

= transition state

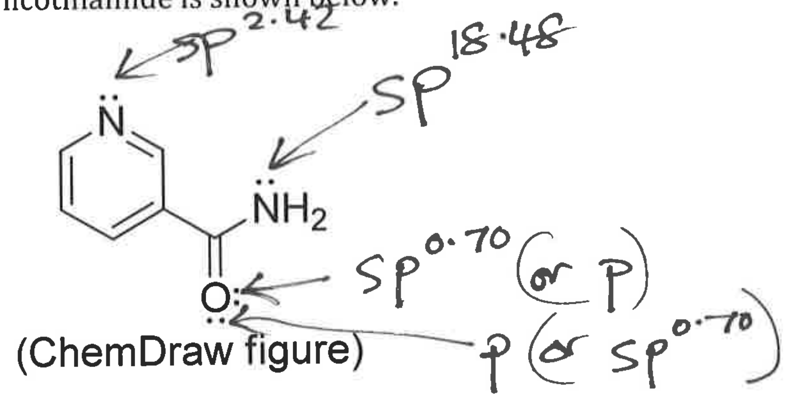
= energy maximum

(2pts)

9) A table of Natural Hybrid Orbitals for nicotinamide is shown below.

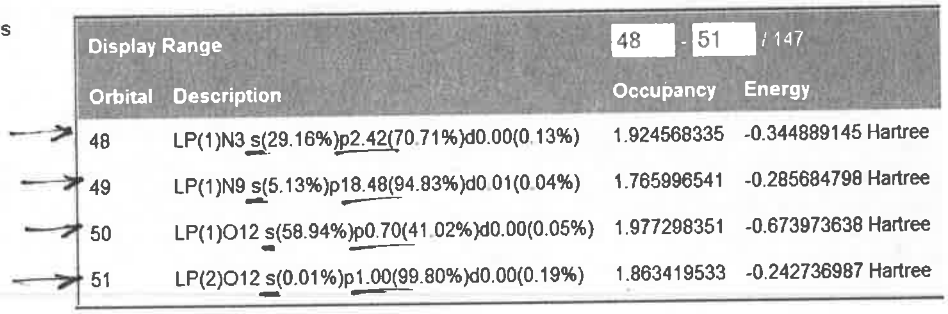


Nicotinamide



(ChemDraw figure)

Natural Hybrid Orbitals



Display Range 48 - 51 / 147

Orbital	Description	Occupancy	Energy
48	LP(1)N3 s(29.16%)p2.42(70.71%)d0.00(0.13%)	1.924568335	-0.344889145 Hartree
49	LP(1)N9 s(5.13%)p18.48(94.83%)d0.01(0.04%)	1.765996541	-0.285684798 Hartree
50	LP(1)O12 s(58.94%)p0.70(41.02%)d0.00(0.05%)	1.977298351	-0.673973638 Hartree
51	LP(2)O12 s(0.01%)p1.00(99.80%)d0.00(0.19%)	1.863419533	-0.242736987 Hartree

a) How many atoms are involved in the π-system of nicotinamide (2 pts)?

9 (no partial credit)

b) Are the N-atom lone pairs of nicotinamide degenerate? How do you know? (2 pts)

No, not degenerate. (1 pt)

They have different hybridizations / energies

either acceptable for (1 pt)

c) Express the hybridization of each lone pair in nicotinamide in terms of sp^x and label each lone pair on the ChemDraw figure above with the appropriate hybridization (4 pts).

LP N3: $sp^{2.42}$

LP N9: $sp^{18.48}$

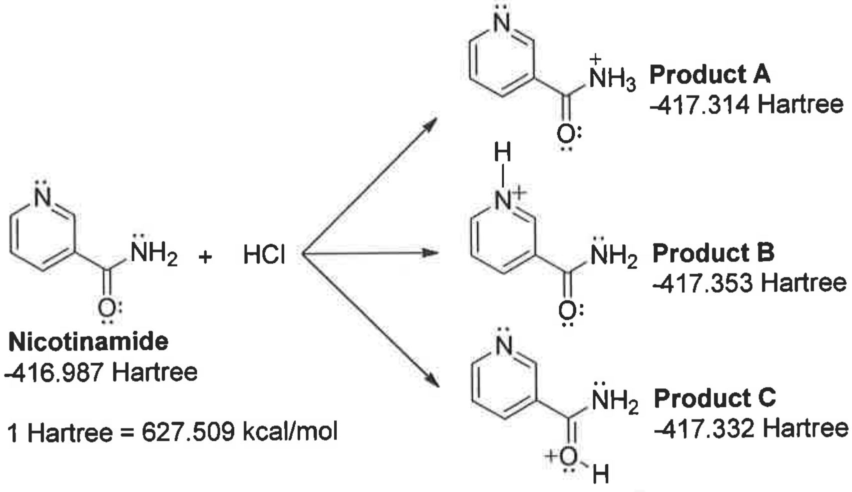
LP(1) O12: $sp^{0.70}$

LP(2) O12: s^0p^1

(100% p also ok).

1 pt each (4 pts total)

10) Three isomeric products can be formed upon treatment of nicotinamide with HCl.



1 Hartree = 627.509 kcal/mol

Showing all work, use the B3LYP/6-31G(d) data shown above to calculate:

a) the absolute energies (kcal/mol) of products A, B, and C; 3pts (1pt each)

b) the relative energy difference (kcal/mol) between A, B, and C. Use the lowest absolute energy (obtained from part *a*) as your reference value (9 pts total).

a) A: -417.314×627.509 Kcal/mol

$= -261868.290$ Kcal/mol

B: -417.353×627.509 Kcal/mol^{-1}

lowest Abs. E → $= -261892.763$ Kcal/mol

C: -417.332×627.509 Kcal/mol

$= -261879.585$ Kcal/mol

b) B = 0.0 Kcal/mol (most stable)

C = + 13.17 Kcal/mol

A = + 24.47 Kcal/mol (least stable)

↑ 6 pts (2pt each)

~~don't need ratios~~

(don't need values to be identical to mine.)

c) Which atom in nicotinamide is the most basic? Explain your answer (5 pts).

The N(3) atom (pyridine N-atom) is most basic (2pts) and thus is the atom which is protonated. N(3) is not part of the conjugated π-system b/c it is ~~pointed~~ /oriented out of the aromatic ring (it is ~$sp^{2.5}$ hybridized). The NH_2 and O-atom lone pairs are part of a conjugated system (think urea from the WebMO lecture) and thus ~~protonating~~ are less available.

Anything like above is worth 3 pts

8+
(2+3=5 total)

11) In the lab you oxidized 4-*t*Bu-cyclohexanol to the corresponding ketone. The oxidizing agent was generated *in situ* by reaction of sodium hypochlorite (NaOCl) with acetic acid. The oxidizing agent was quenched with an aqueous solution of $NaHSO_3$.

a) Draw the balanced reaction of sodium hypochlorite with acetic acid and circle the oxidizing agent so formed (3 pts).

$$\mathrm{NaOCl + MeCO_2H \longrightarrow \boxed{HOCl +} MeCO_2Na}$$

2 pts correct balanced eqn.
1 pt correct circle

b) State the solvent you would use to prepare an aqueous $NaHSO_3$ solution (2 pts).

Water. (2pts)

Anything else = 0 pts.