

Chemistry 2600 Final Exam (Version A)
April 10th, 2019

INSTRUCTIONS

- 1) Read the exam carefully before beginning. There are 9 questions on pages 2 to 13 followed by a periodic table and a blank page for rough work. You are also provided with a Spectroscopy Data Package (as posted on the class website). **Please ensure that you have a complete exam. If not, let an invigilator know immediately.** All pages must be submitted.
- 2) You are allowed to bring one index card (maximum size 3"x5") into the exam with you as a "cheat sheet". This card must be submitted with your exam.
- 3) You are allowed to bring a ruler and a molecular model kit.
- 4) You may use a calculator. It may not have wireless capability. You may not have any other electronic devices (phone, iPod, etc.) with you when you write the exam.
- 5) If your work is not legible, it will be given a mark of zero.
- 6) Marks will be deducted for incorrect information added to an otherwise correct answer.
- 7) When drawing molecules, clearly show any relevant stereochemistry. If a mixture of diastereomers is produced, draw both/all of them.
- 8) **DO NOT OPEN THE EXAM UNTIL YOU ARE TOLD TO BEGIN.**
Beginning prematurely will result in removal of your exam paper and a mark of 0.
- 9) You have **3 hours** to complete this exam. Nobody may leave the exam room during the first hour or the last 15 minutes of the exam.

Comments in green are supplementary
(not required for full marks).

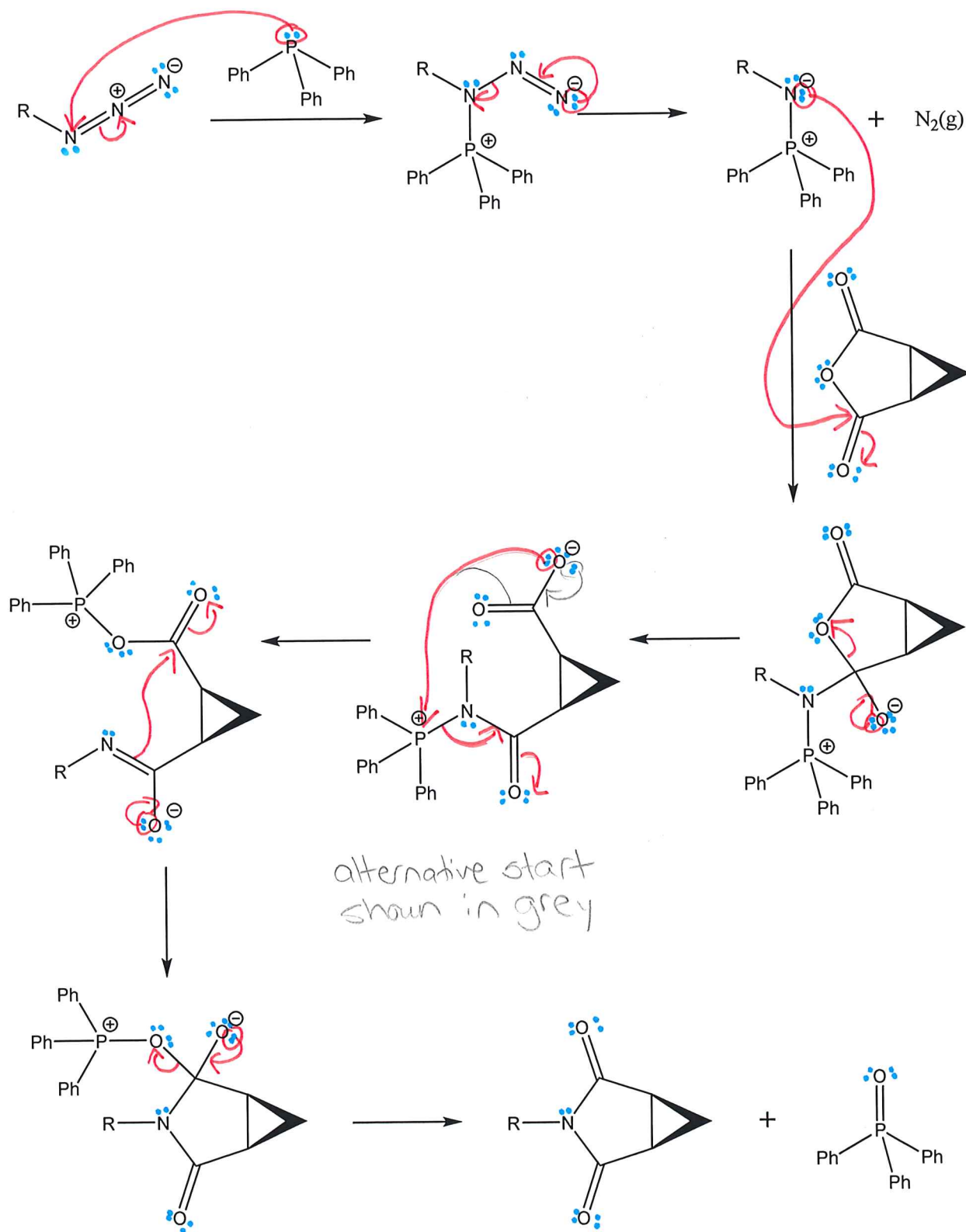
| Q | Mark |
|---|------|
| 1 | / 8 |
| 2 | / 12 |
| 3 | / 9 |
| 4 | / 8 |
| 5 | / 10 |

| Q | Mark |
|--------------|-------------|
| 6 | / 24 |
| 7 | / 18 |
| 8 | / 6 |
| 9 | / 1 |
| 10 | |
| Total | / 96 |

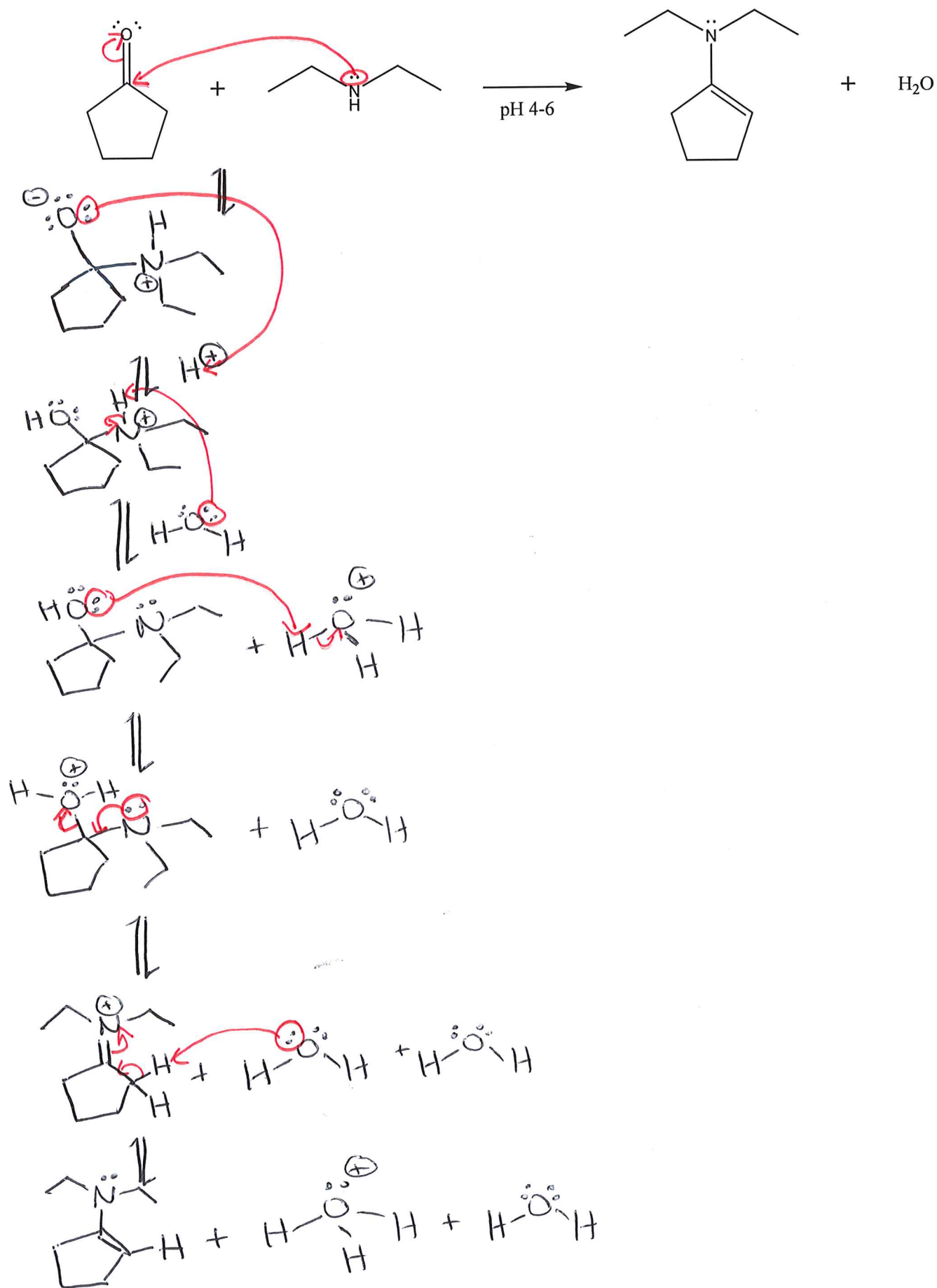
Name: _____

Student Number: _____

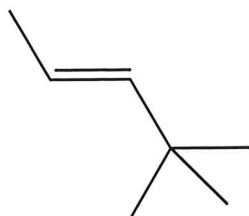
1. Complete the following mechanism by adding all lone pair electrons and curly arrows to show electron movement. [8 marks]



2. Propose a reasonable mechanism for the following reaction. You may assume the presence of water and catalytic amounts of H^+ . [12 marks]

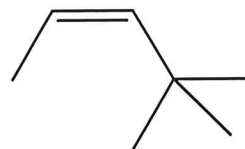


3. An alkyl bromide is reacted with sodium hydroxide. E2 reaction gives a mixture of the following two products (one major; one minor): [9 marks]



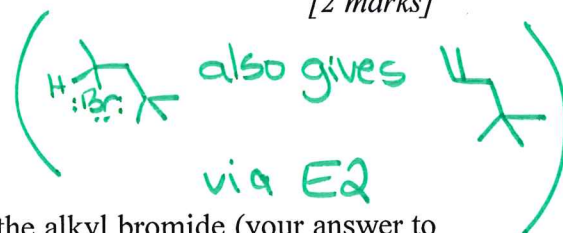
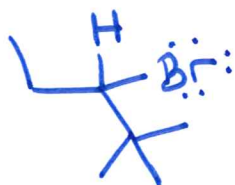
A

and



B

- (a) Draw the alkyl bromide that will only give these two products when reacted with hydroxide. [2 marks]



- (b) Briefly explain why no S_N2 reaction is observed when the alkyl bromide (your answer to part (a)) is reacted with hydroxide. [2 marks]

S_N2 reactions require an accessible electrophilic site. The quaternary carbon attached to the carbon-with-leaving group means that there is too much steric hindrance for hydroxide to act

- (c) Which is the major product, A or B? [1 mark]

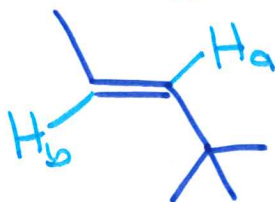
A

as a nucleophile (A carbon atom next to a quaternary carbon can be described as neopentyl)

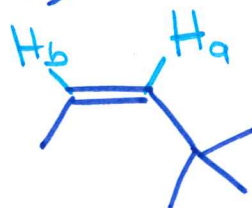
- (d) How could you use ¹H NMR spectroscopy to distinguish between A and B? [4 marks]
For full credit, your answer must be specific, including any relevant numerical values/ranges.

Look at the coupling constants of the two vinyl peaks (found between 5 and 6 ppm).

H_a will give a doublet (or doublet of quartets if long range coupling is observed). H_b will give a doublet of quartets.



trans ∴ ³J ≈ 15 Hz
between H_a and H_b



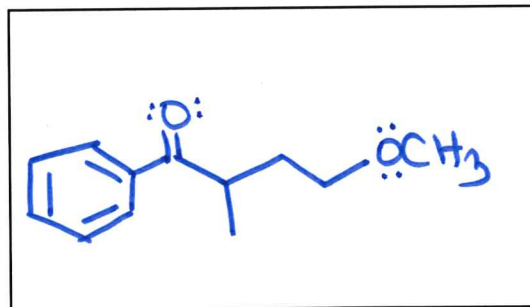
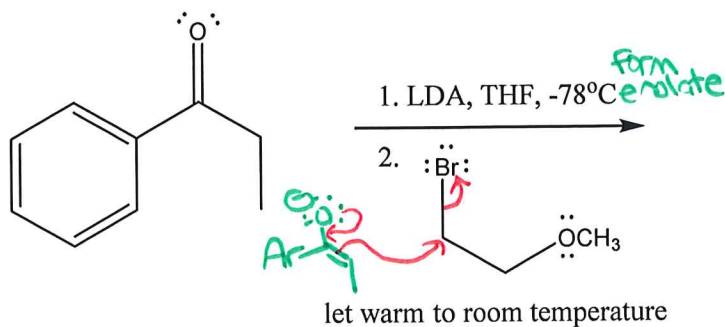
cis ∴ ³J ≈ 10 Hz
between H_a and H_b

Name: _____

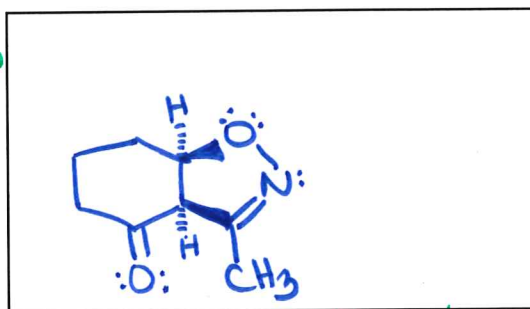
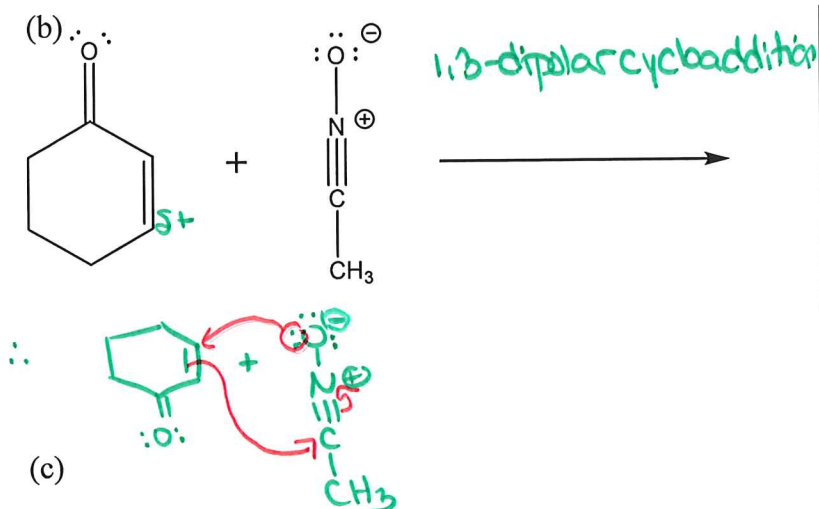
Student Number: _____

4. For each of the following reactions, draw the major organic product. Your answer should clearly show any relevant regiochemistry and/or stereochemistry. [8 marks]

(a)

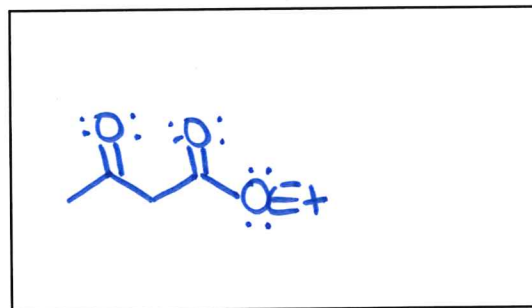
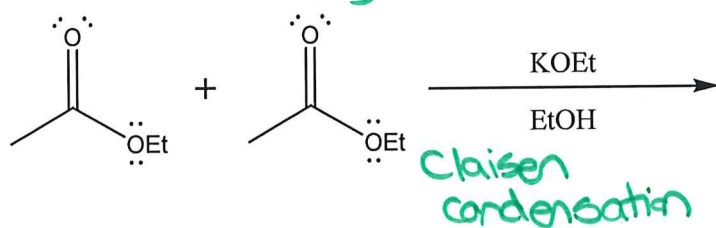


(b)

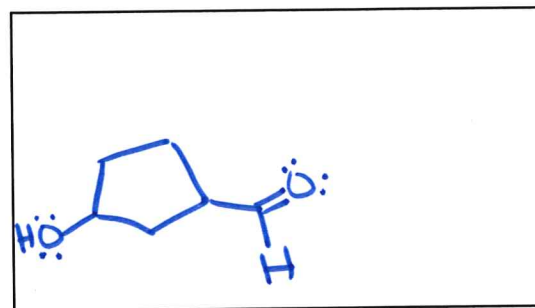
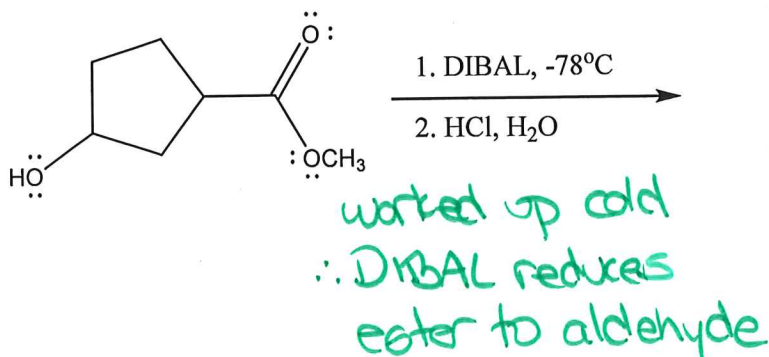


rings are cis-fused

(c)

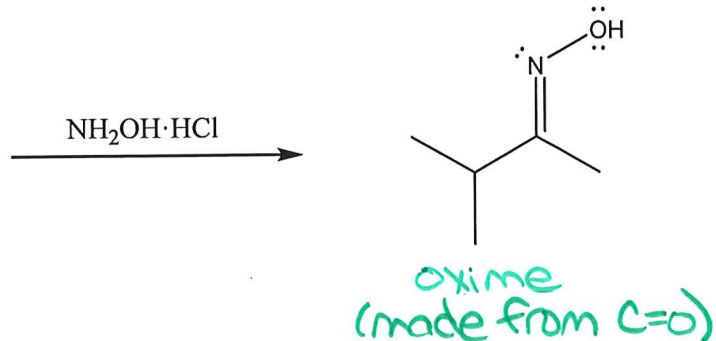
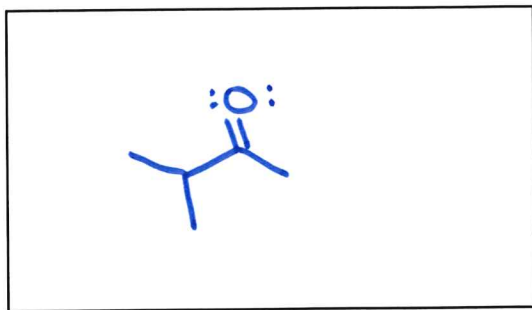


(d)

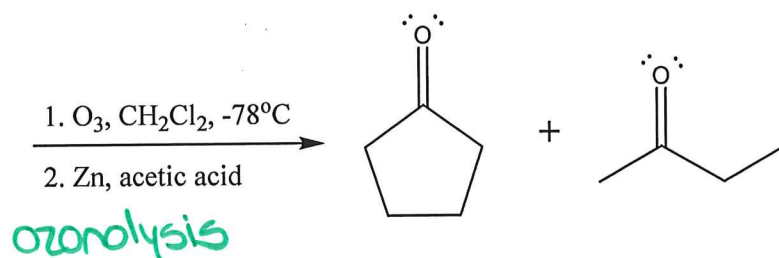
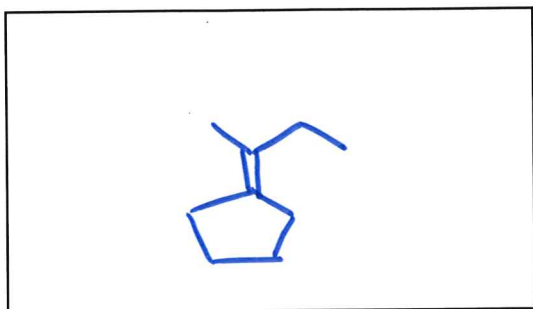


5. For each of the following reactions, draw the missing reactant(s). Your answer should clearly show any relevant regiochemistry and/or stereochemistry. [10 marks]

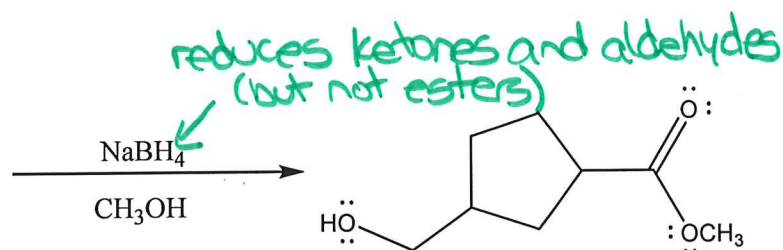
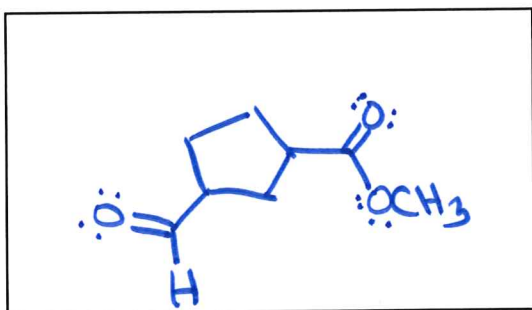
(a)



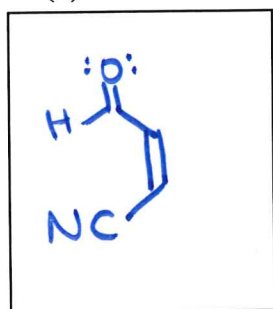
(b)



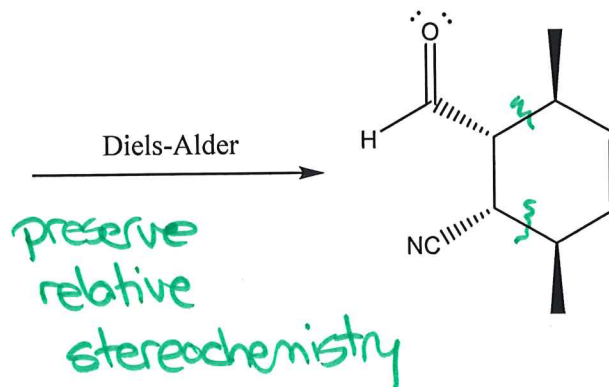
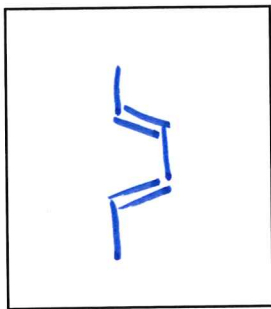
(c)



(d)



+



6. The following page contains spectra for Unknown X. [24 marks]
- (a) Identify Unknown X based on these spectra. Draw your answer in the box provided below.
- (b) Use this page to explain your logic (including how you determined the molecular formula).
- (c) On both NMR spectra, assign as many peaks as you can by numbering the peaks from left to right, redrawing Unknown X in the box provided, and labeling each carbon or hydrogen atom with the appropriate peak number. *For atoms that cannot be assigned with certainty, list the signals to which they might reasonably correspond.*
- (d) Label the numbered peaks on the MS with the formulas of the corresponding fragments.
- (e) Label any important peaks on the IR with the corresponding stretch.

Find molecular formula

$$M^+ : [M+2]^+ = 1:1 \quad \therefore \text{contains one Br}$$

$$M^+ \text{ is odd} \quad \therefore \text{contains odd \# of N}$$

$$M^+ = 147$$

$$\begin{array}{r} -79 \\ \hline 68 \end{array} \quad \text{Br}$$

$$\begin{array}{r} -14 \\ \hline 54 \end{array} \quad \text{N}$$

$$\begin{array}{r} -48 \\ \hline 6 \end{array} \quad \text{4C}$$

(4 peaks on ^{13}C NMR \therefore at least 4 C)
 \therefore must have 6H (works w/ ^1H NMR which has three peaks of equal integration)

$$\therefore \text{C}_4\text{H}_6\text{BrN}$$

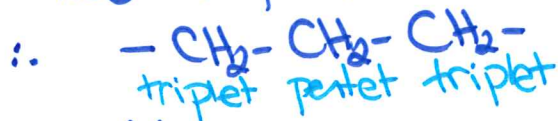
Calculation Degrees of Unsaturation

$$\text{DU} = \frac{2C + 2 + N - X - H}{2} = \frac{2(4) + 2 + 1 - 1 - 6}{2} = \frac{4}{2} = 2$$

Gather Useful Info.

\rightarrow peak @ 2249cm^{-1} on IR should be $\text{C}\equiv\text{N}$ or terminal $\text{C}\equiv\text{C}$
 but ^{13}C NMR only has one peak in alkyne region (70-100ppm)
 \therefore This should be $\text{C}\equiv\text{N}$

\rightarrow ^1H NMR has three peaks of equal integration \therefore three CH_2 .
 They are two triplets and a pentet



\therefore Assemble $-\text{Br}:$, $-\text{C}\equiv\text{N}:$ and $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$
 to give



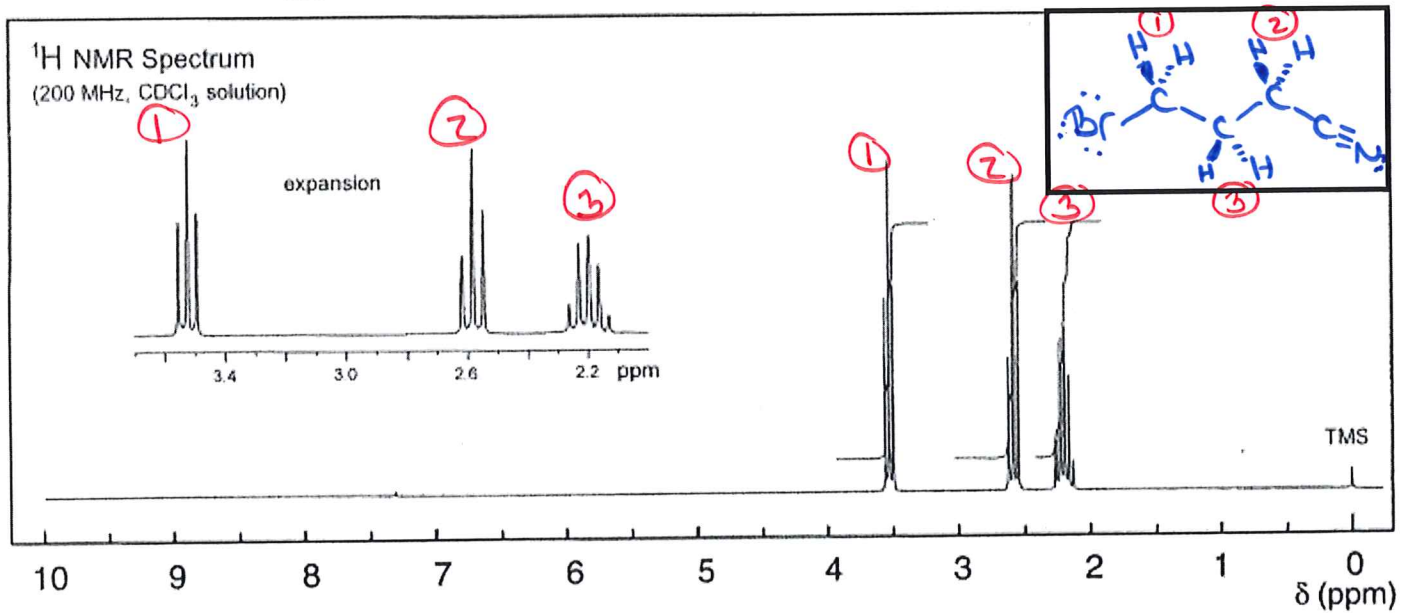
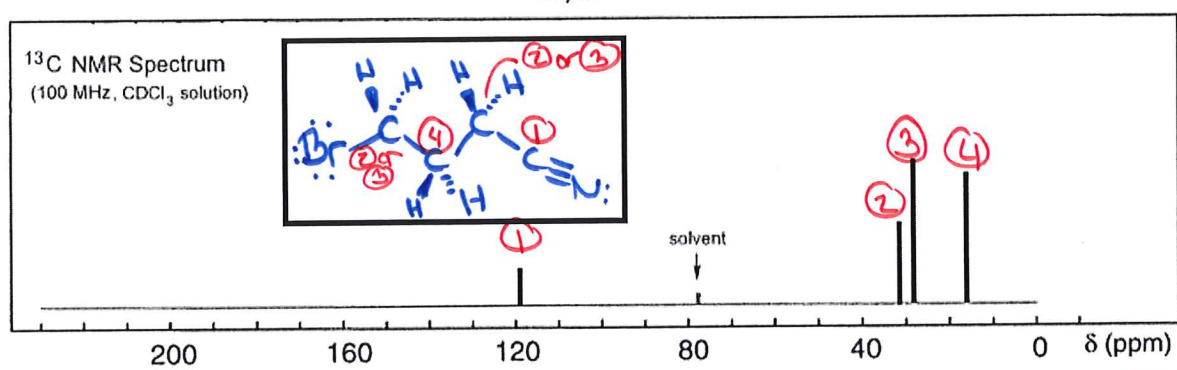
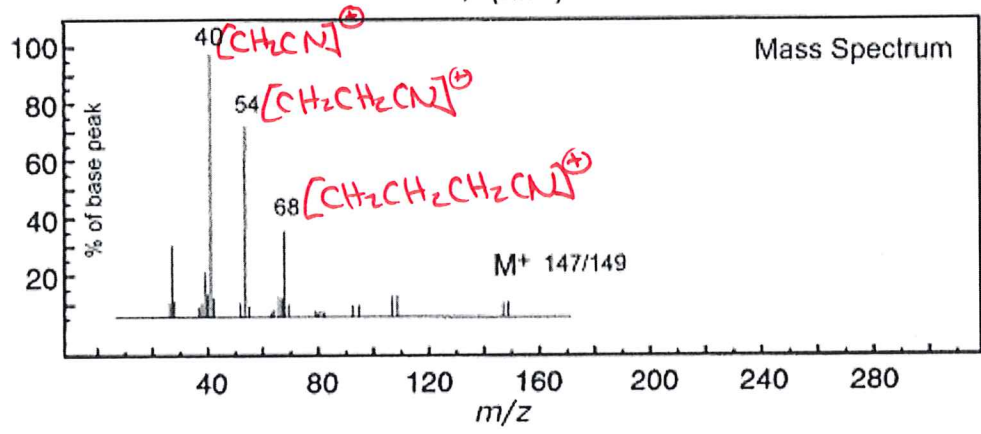
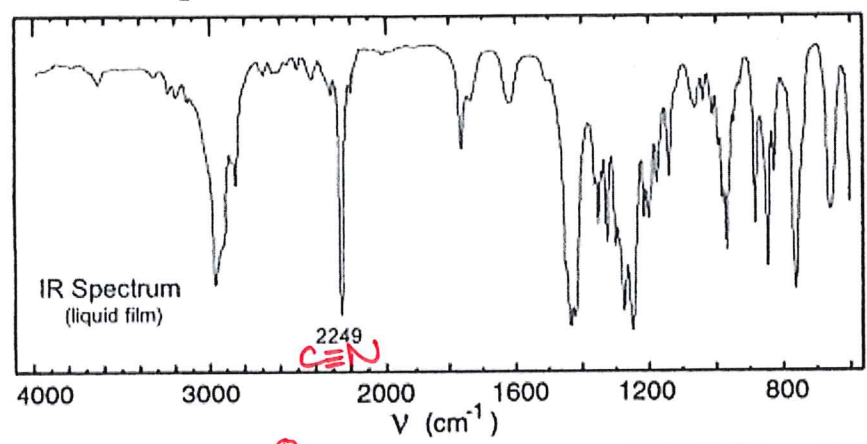
Unknown X:



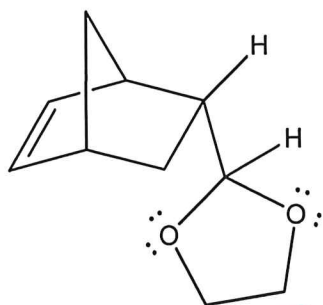
Name: _____

Student Number: _____

6. continued... (peaks on ¹³C NMR were darkened for clarity; each is a single line)

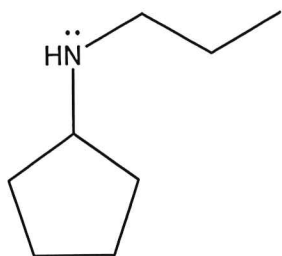
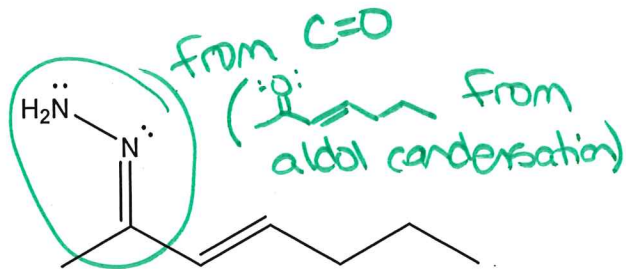


7. Choose any **three** of the molecules below and propose a synthesis for each one. [18 marks]
- If your synthesis involves more than one step, write an equation for each step. Show all required reactants. Number steps within a reaction if order of addition is important.
 - All organic reactants must be stable compounds containing **no more than five carbon atoms**. They may be **hydrocarbons, alkyl halides or alcohols** and may contain C=C or C≡C bonds. The only exception to this rule is that you are **also allowed** to use **benzene, bromobenzene or phenol**. ← no extra bits attached!
 - If you wish to use an organic reactant (including Grignard reagent) that does not meet these requirements, you must show how to make it from starting materials that do.
 - You may use any inorganic reagents, acids, bases, catalysts, etc.
 - Acids, bases, catalysts, etc. do not need to meet the "organic reactant" requirements if the organic part will not be present in the final product.
 - Clearly indicate stereochemistry of reaction products where appropriate. Assume that all stereochemistry shown is relative and that you are to make racemic product.
 - You are **not** required to show mechanisms for this question.
 - There are three pages after this page. Use one of those pages for each synthesis and clearly identify the synthetic target at the top of the page. This page is scrap paper.
 - If you give more than three syntheses, I will only mark the first three (ignoring any that are crossed out).

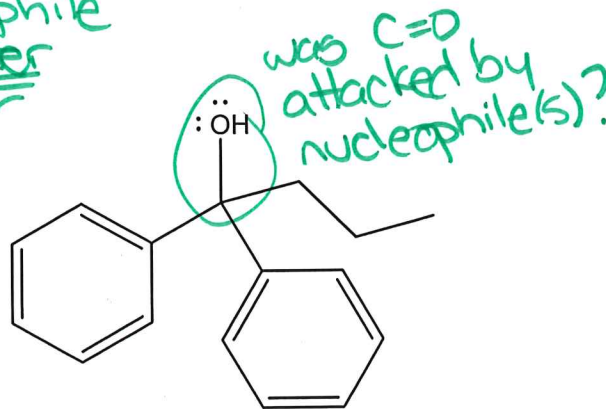


Diels-Alder?

- endo product ∴ low temp.
- want EWG on dienophile
- ∴ form acetal after Diels-Alder

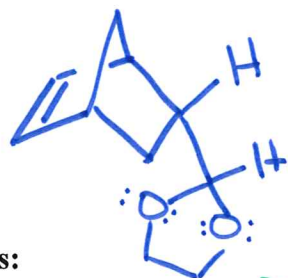
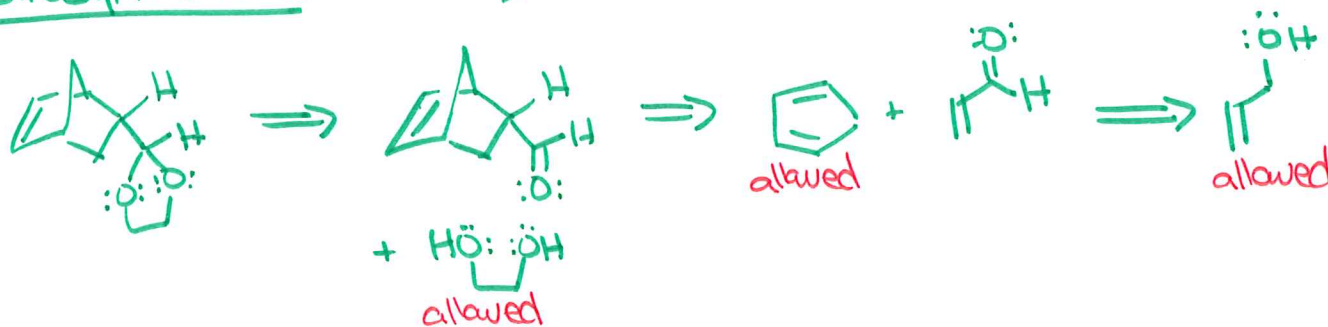


reductive amination?

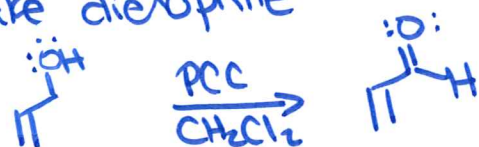


7. continued...

[6 marks]

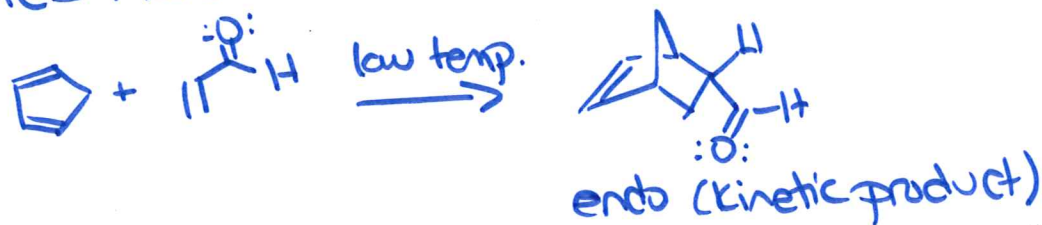
Synthetic Target #1:**Synthesis:**Retroanalysis ("The Plan")

① Make dienophile

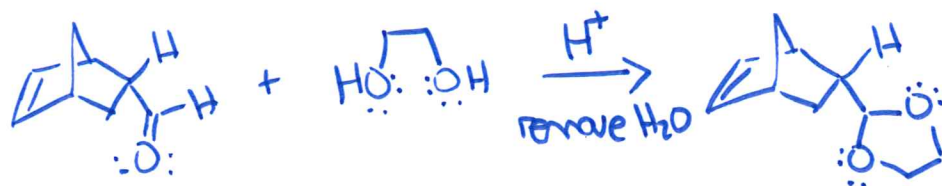


or other oxidation that stops at aldehyde

② Diels Alder



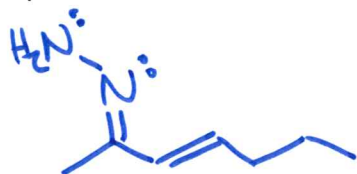
③ Form acetal



7. continued...

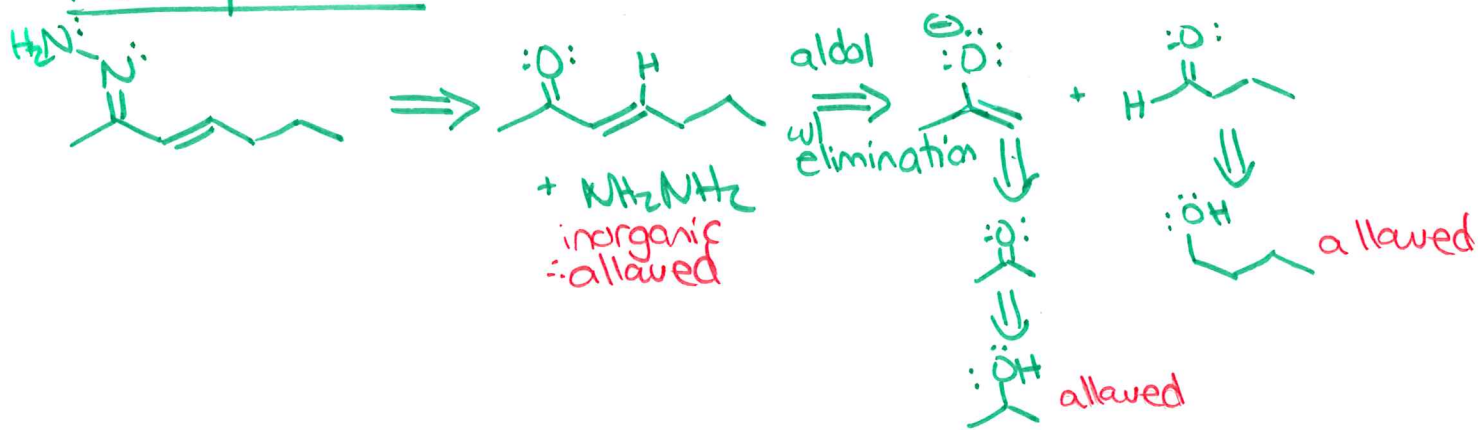
[6 marks]

Synthetic Target #2:

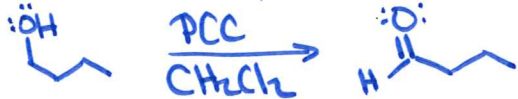


Synthesis:

Retrosynthesis ("The Plan")

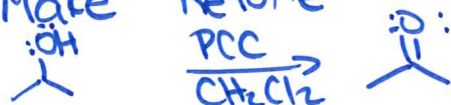


① Make aldehyde (electrophile)

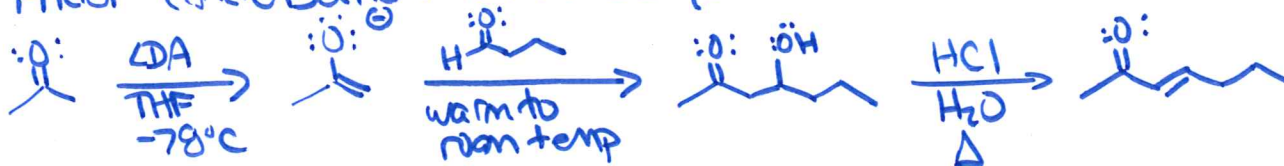


or other oxidation that stops at aldehyde
(or ozonolysis of 1-pentene with reductive workup)

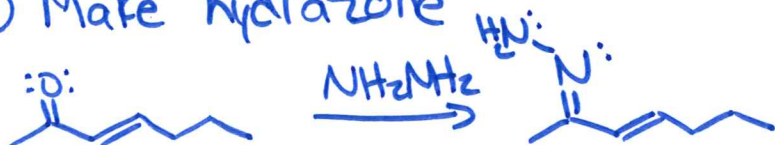
② Make ketone



③ Aldol condensation with dehydration



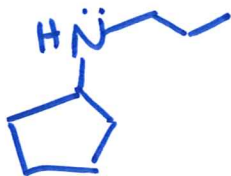
④ Make hydrazone



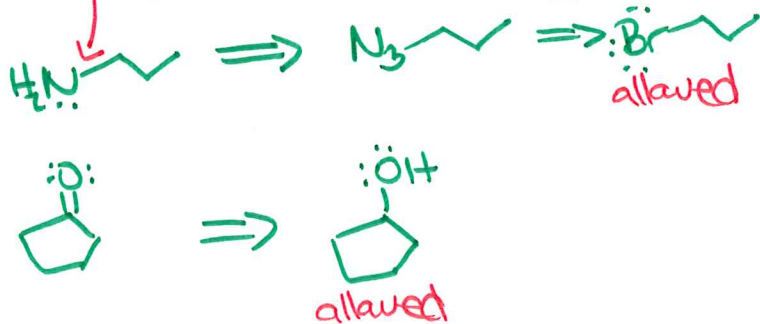
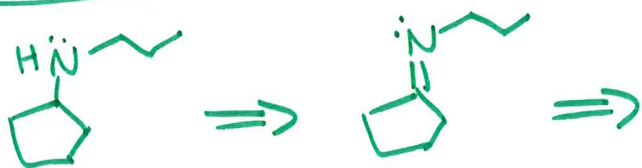
7. continued...

[6 marks]

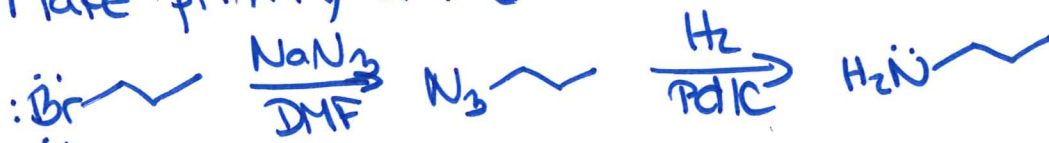
Synthetic Target #3:



Synthesis:

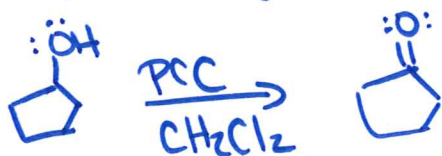
Retrosynthesis ("The Plan")

① Make primary amine

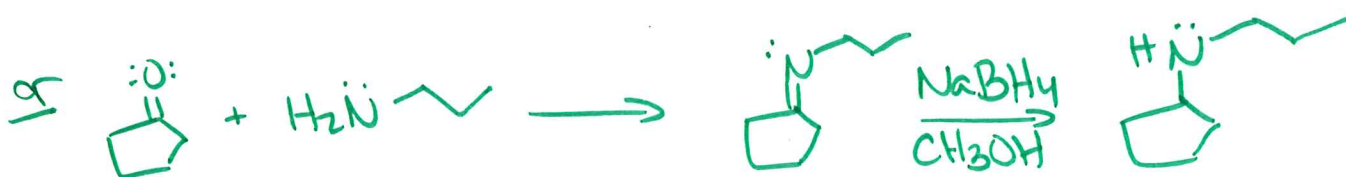
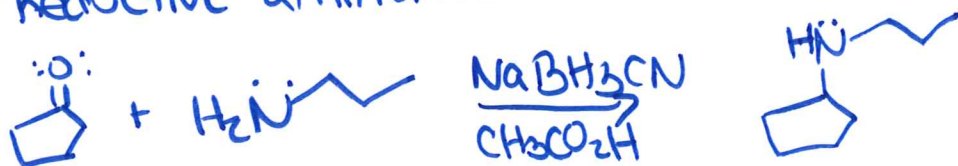


or other valid
approach.
cannot use NH3
+ 1-bromopropane
(will not stop at
primary amine)

② Make ketone

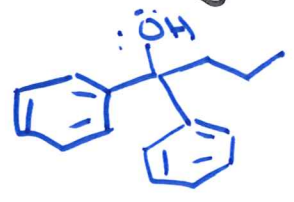


③ Reductive amination



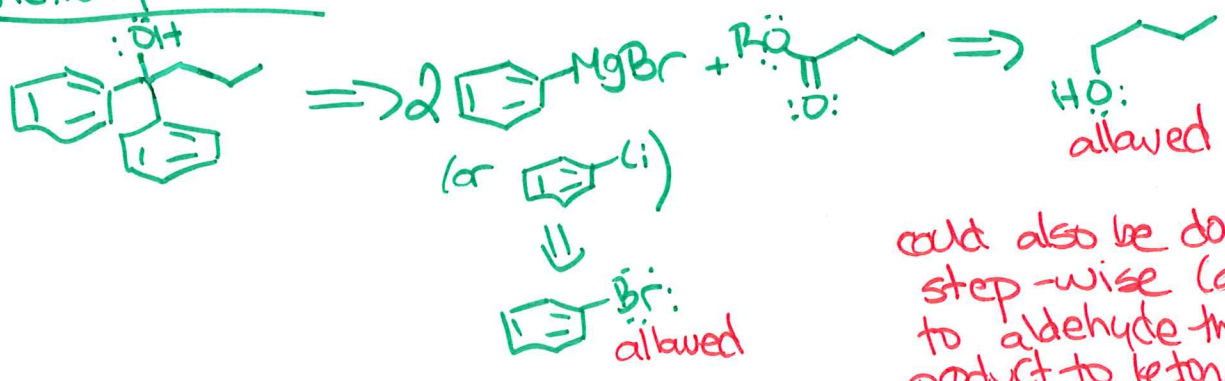
7. continued...

Synthetic Target #4



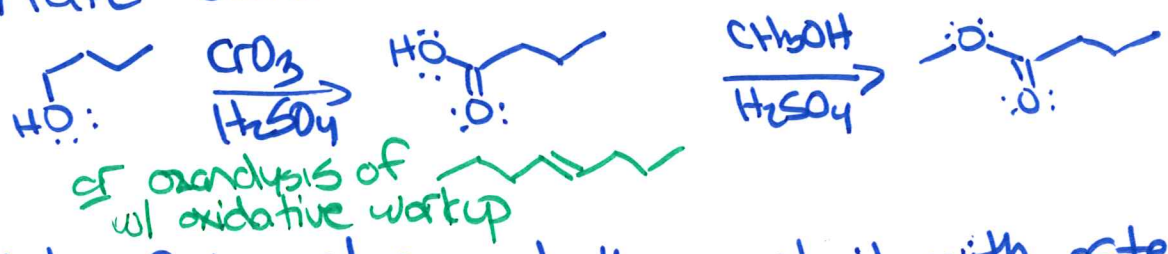
Synthesis:

Retrosynthesis ("The Plan")

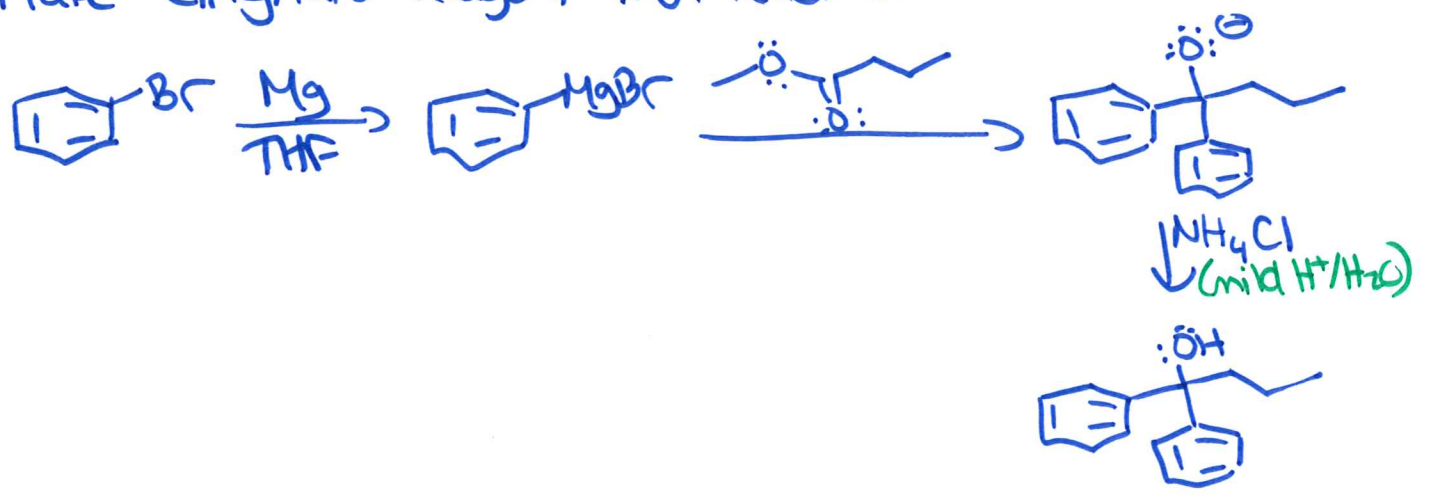


could also be done step-wise (add c1ccccc1MgBr to aldehyde then oxidize product to ketone then add another c1ccccc1MgBr)

① Make ester



② Make Grignard reagent then react it with ester

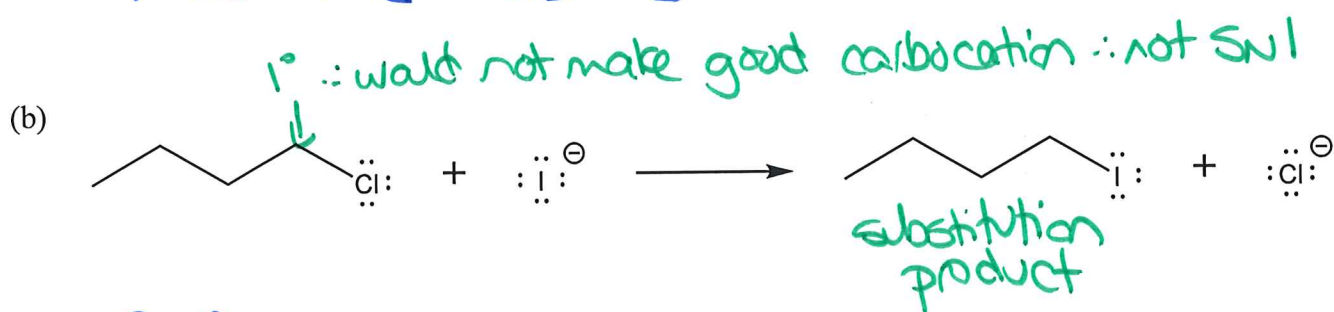
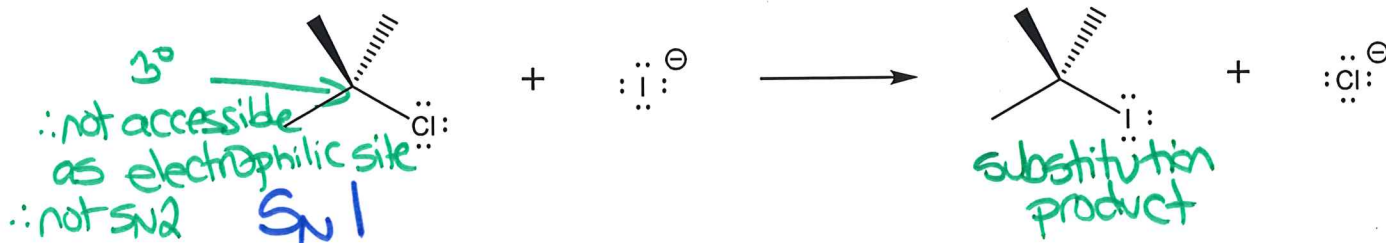


Name: _____

Student Number: _____

8. For each of the following reactions, [6 marks]
- classify it as E1, E2, S_N1 or S_N2, and
 - write the rate law.

(a)

S_N2

9. What was the most interesting and/or useful thing you learned in CHEM 2600? [1 mark]

...AND THAT'S ALL FOR CHEM 2600.
HAVE A GREAT SUMMER!

DATA SHEET/SCRAP PAPER

CHEM 1000 Standard Periodic Table

| | | | | | | | | | | | | | | | | | |
|----------------------------|----------------------------|----------------------------|---------------------------|----------------------------|----------------------------|----------------------------|---------------------------|----------------------------|---------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|---------------------------|----------------------------|----------------------------|
| 1 | | | | | | | | | | | | | | | | | 18 |
| 1.0079 H 1 | | | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 4.0026 He 2 |
| 6.941 Li 3 | 9.0122 Be 4 | | | | | | | | | | | 10.811 B 5 | 12.011 C 6 | 14.0067 N 7 | 15.9994 O 8 | 18.9984 F 9 | 20.1797 Ne 10 |
| 22.9898 Na 11 | 24.3050 Mg 12 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 26.9815 Al 13 | 28.0855 Si 14 | 30.9738 P 15 | 32.066 S 16 | 35.4527 Cl 17 | 39.948 Ar 18 |
| 39.0983 K 19 | 40.078 Ca 20 | 44.9559 Sc 21 | 47.88 Ti 22 | 50.9415 V 23 | 51.9961 Cr 24 | 54.9380 Mn 25 | 55.847 Fe 26 | 58.9332 Co 27 | 58.693 Ni 28 | 63.546 Cu 29 | 65.39 Zn 30 | 69.723 Ga 31 | 72.61 Ge 32 | 74.9216 As 33 | 78.96 Se 34 | 79.904 Br 35 | 83.80 Kr 36 |
| 85.4678 Rb 37 | 87.62 Sr 38 | 88.9059 Y 39 | 91.224 Zr 40 | 92.9064 Nb 41 | 95.94 Mo 42 | (98) Tc 43 | 101.07 Ru 44 | 102.906 Rh 45 | 106.42 Pd 46 | 107.868 Ag 47 | 112.411 Cd 48 | 114.82 In 49 | 118.710 Sn 50 | 121.757 Sb 51 | 127.60 Te 52 | 126.905 I 53 | 131.29 Xe 54 |
| 132.905 Cs 55 | 137.327 Ba 56 | La-Lu | 178.49 Hf 72 | 180.948 Ta 73 | 183.85 W 74 | 186.207 Re 75 | 190.2 Os 76 | 192.22 Ir 77 | 195.08 Pt 78 | 196.967 Au 79 | 200.59 Hg 80 | 204.383 Tl 81 | 207.19 Pb 82 | 208.980 Bi 83 | (210) Po 84 | (210) At 85 | (222) Rn 86 |
| (223) Fr 87 | 226.025 Ra 88 | Ac-Lr | (265) Rf 104 | (268) Db 105 | (271) Sg 106 | (270) Bh 107 | (277) Hs 108 | (276) Mt 109 | (281) Ds 110 | (280) Rg 111 | (285) Cn 112 | (284) Nh 113 | (289) Fl 114 | (288) Mc 115 | (293) Lv 116 | (294) Ts 117 | (294) Og 118 |
| 138.906 La 57 | 140.115 Ce 58 | 140.908 Pr 59 | 144.24 Nd 60 | (145) Pm 61 | 150.36 Sm 62 | 151.965 Eu 63 | 157.25 Gd 64 | 158.925 Tb 65 | 162.50 Dy 66 | 164.930 Ho 67 | 167.26 Er 68 | 168.934 Tm 69 | 173.04 Yb 70 | 174.967 Lu 71 | | | |
| 227.028 Ac 89 | 232.038 Th 90 | 231.036 Pa 91 | 238.029 U 92 | 237.048 Np 93 | (240) Pu 94 | (243) Am 95 | (247) Cm 96 | (247) Bk 97 | (251) Cf 98 | (252) Es 99 | (257) Fm 100 | (258) Md 101 | (259) No 102 | (262) Lr 103 | | | |

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