Name: _____ Student Number: _____

Chemistry 2600 Final Exam (Version A)
April 22nd, 2017

INSTRUCTIONS

1) Read the exam carefully before beginning. There are 8 questions on pages 2 to 16 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.

Q	Mark
1	/ 17
2	/ 10
3	/ 5
4	/ 6
5	/ 16

Q	Mark
6	/ 15
7	/ 5
8	/ 1

Total	/ 75

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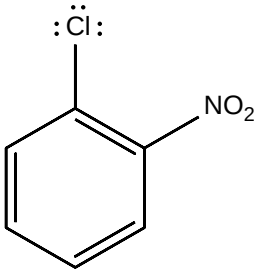
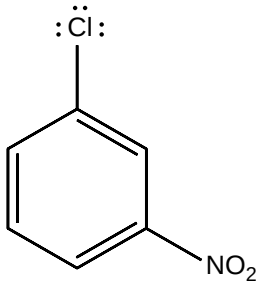
1. You wish to prepare various isomers of chloronitrobenzene from benzene. **[17 marks]**

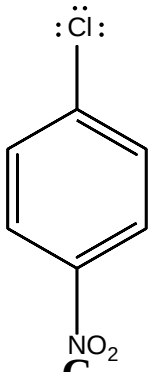
For simplicity, they have been labeled **A**, **B** and **C**:



A



B



C

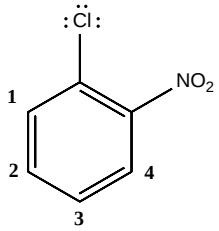
(a) Consider how ^{1}H NMR can be used to identify which product(s) are made from each reaction.

For each isomer, complete the table provided to clearly indicate:

- The relative integration of each peak
- The multiplicity of each peak <u>if</u> no long range coupling is observed
- If each peak could reasonably be expected to experience long range coupling.
- If long range coupling is expected, write the number for the proton(s) coupled to. If long range coupling is <u>not</u> expected, write "N/A" or leave the last box blank.

Isomer A has been numbered for you. Please number **Isomers B** and **C** on the pictures next to each table. Use one number for each peak expected on the ^{1}H NMR.

Isomer A *[3 marks]*



A

Peak	Integration	Multiplicity	Might have long range coupling? (yes/no)	Long range coupling is with which proton(s)?
1				
2				
3				
4				

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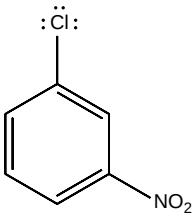
1. *continued…*

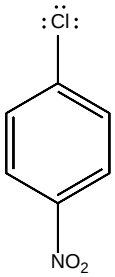
Isomer B *[3 marks]*



B

Peak	Integration	Multiplicity	Might have long range coupling? (yes/no)	Long range coupling is with which proton(s)?

Isomer C *[3 marks]*



C

Peak	Integration	Multiplicity	Might have long range coupling? (yes/no)	Long range coupling is with which proton(s)?

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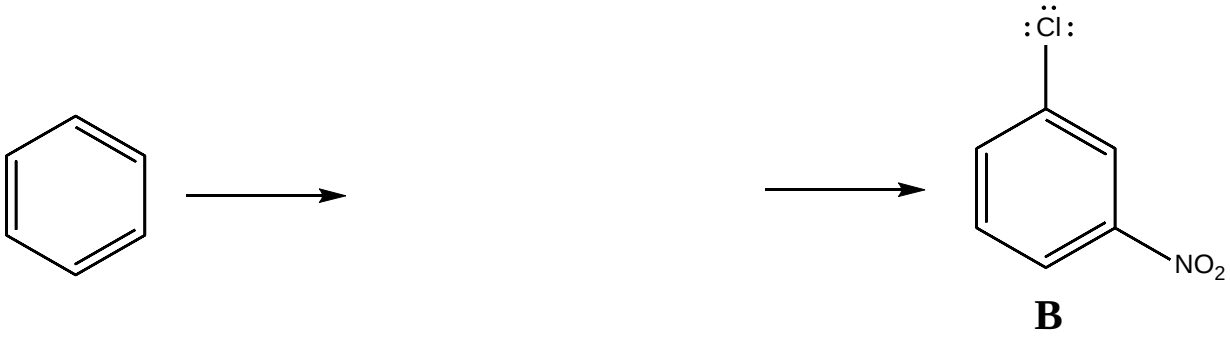
1. *continued…*

(b) If you wish to prepare **Isomer B** (as the major product), what sequence of reactions should you use?

Fill in the blanks in the reaction sequence below – including reagents for each arrow as well as the product of the first reaction. *[3 marks]*



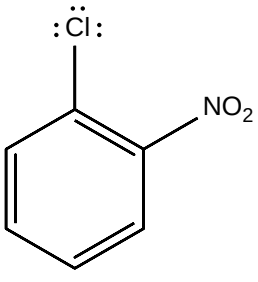
B

(c) If you wish to prepare **Isomer C** (as the major product), what sequence of reactions should you use?

Fill in the blanks in the reaction sequence below – including reagents for each arrow as well as the product of the first reaction. *[3 marks]*

C

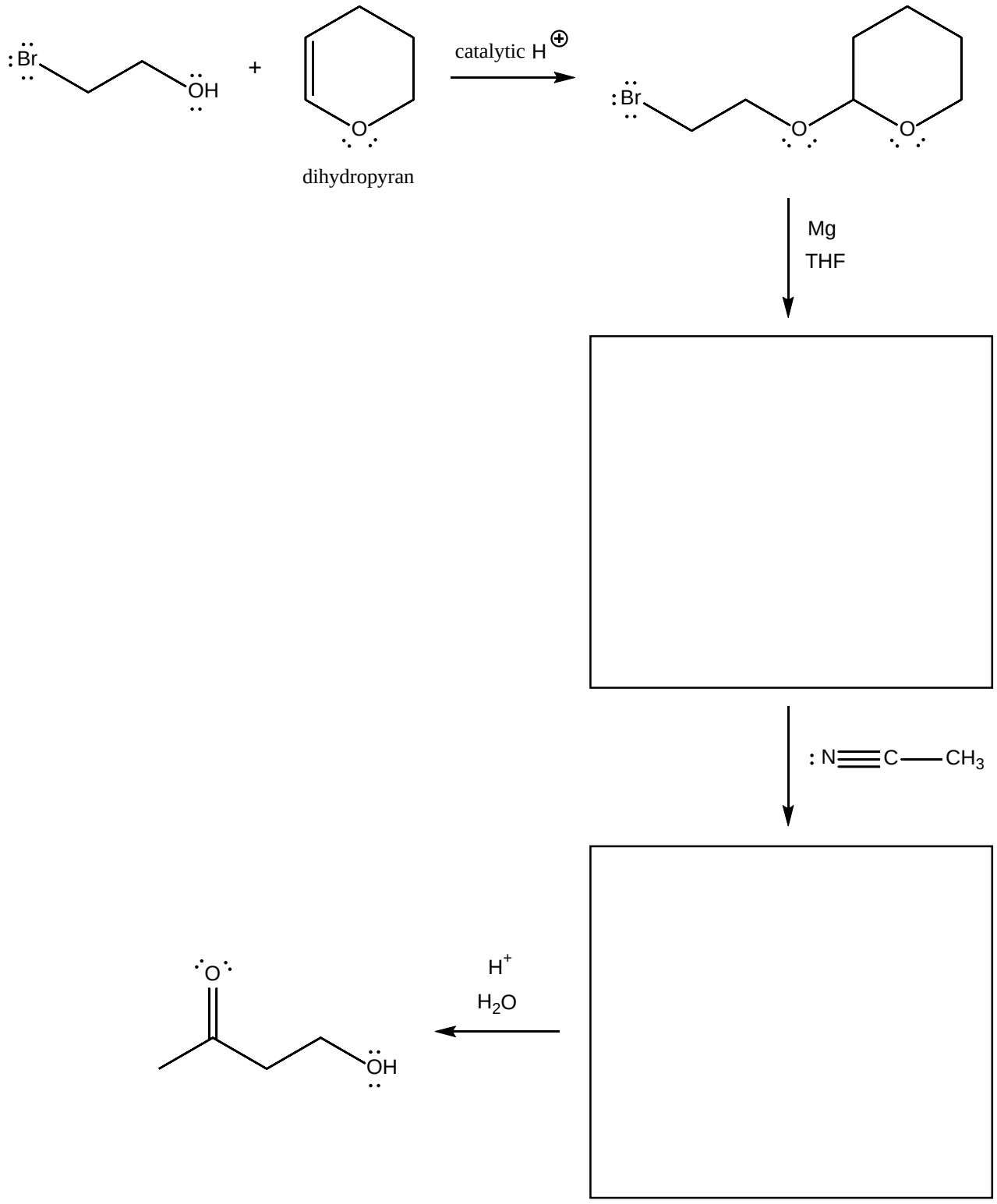
(d) Preparing **Isomer A** as the major product is a more difficult task. Even in the industrial process used to make it commercially, it's only a minor product (~35% Isomer A; ~65% something else). Why? *[2 marks]*



A

Name: _____ Student Number: _____

2. Dihydropyran can be used as a protecting group for alcohols: **[10 marks]**



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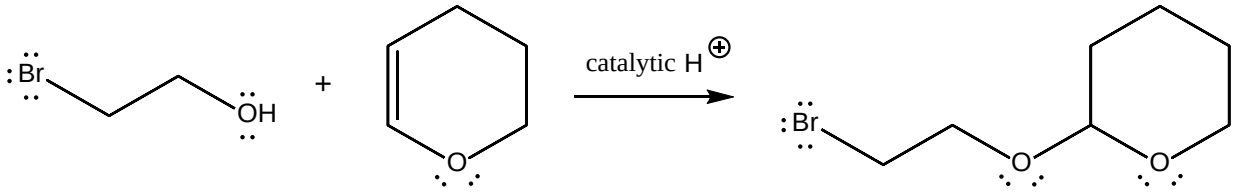
2. *continued…*

(a) **On the previous page**, draw the missing intermediate products in the boxes provided. *[2 marks]*

(b) Why is a protecting group necessary for this reaction sequence to work? *[2 marks]*

(c) Propose a reasonable mechanism for the reaction between 1-bromoethanol and dihydropyran. You may use *HA* as shorthand for the catalytic acid and A^- as shorthand for its conjugate base. *[3 marks]*



dihydropyran

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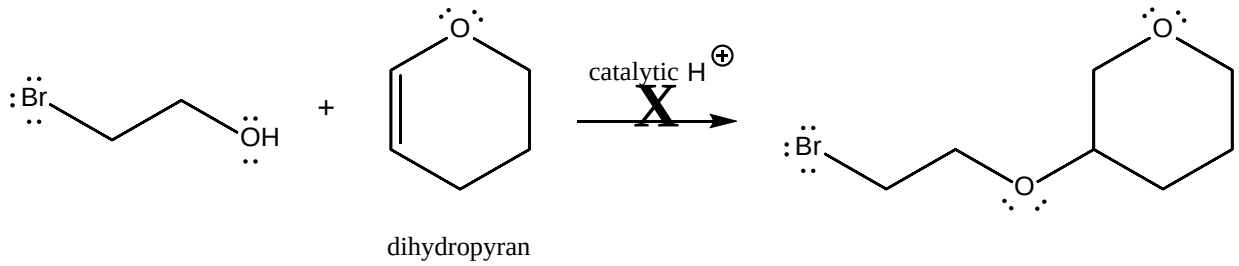
2. *continued…*

(d) With reference to your mechanism in part (c), explain the regiochemistry observed in the reaction between an alcohol and dihydropyran.

In other words, why does the reaction below **NOT** occur? *[3 marks]*



dihydropyran

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3. Explain why you cannot prepare a ketone by reacting an ester with a Grignard reagent. Your answer should include a mechanism. You may choose any ester and any Grignard reagent to illustrate your point. **[5 marks]**

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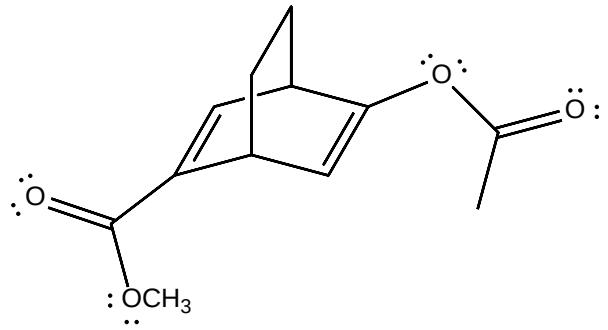
4. Consider the molecule below: **[6 marks]**



(a) What compounds would you react to prepare this compound using a normal Diels-Alder reaction? *[2 marks]*

(b) What compounds would you react to prepare this compound using an "inverse electron demand" Diels-Alder reaction? *[2 marks]*

(c) Is the compound above the *exo* product, the *endo* product, both or neither? Explain. Your answer should make it clear that you know what the terms *exo* and *endo* mean. *[2 marks]*

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5. The following page contains spectra for Unknown X. **[16 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).

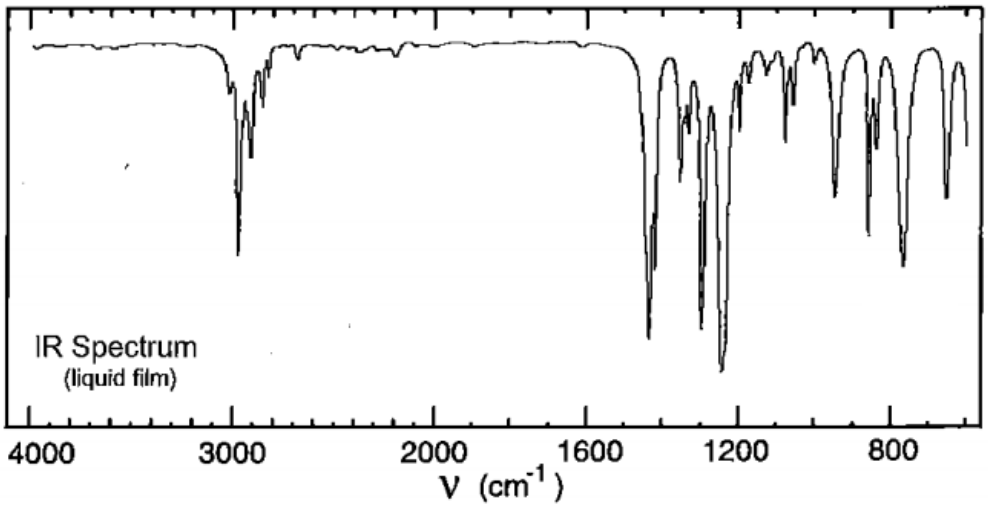
(c) On both NMR spectra, assign as many peaks as you can by numbering the peaks from left to right, redrawing Unknown X in the box provided, and labeling each carbon or hydrogen atom with the appropriate peak number. *For atoms that cannot be assigned with certainty, list the signals to which they might reasonably correspond.*

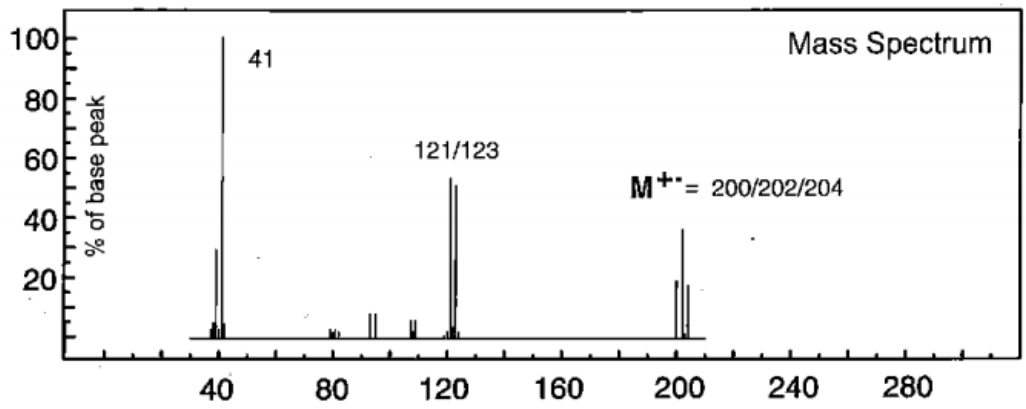
(d) Label any important peaks on the Mass Spectrum (with formulas of the fragments).

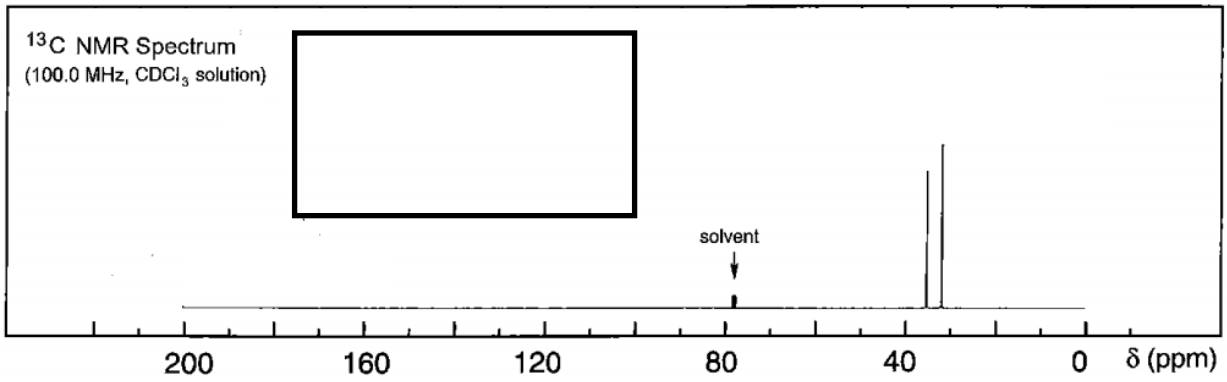
Unknown X:

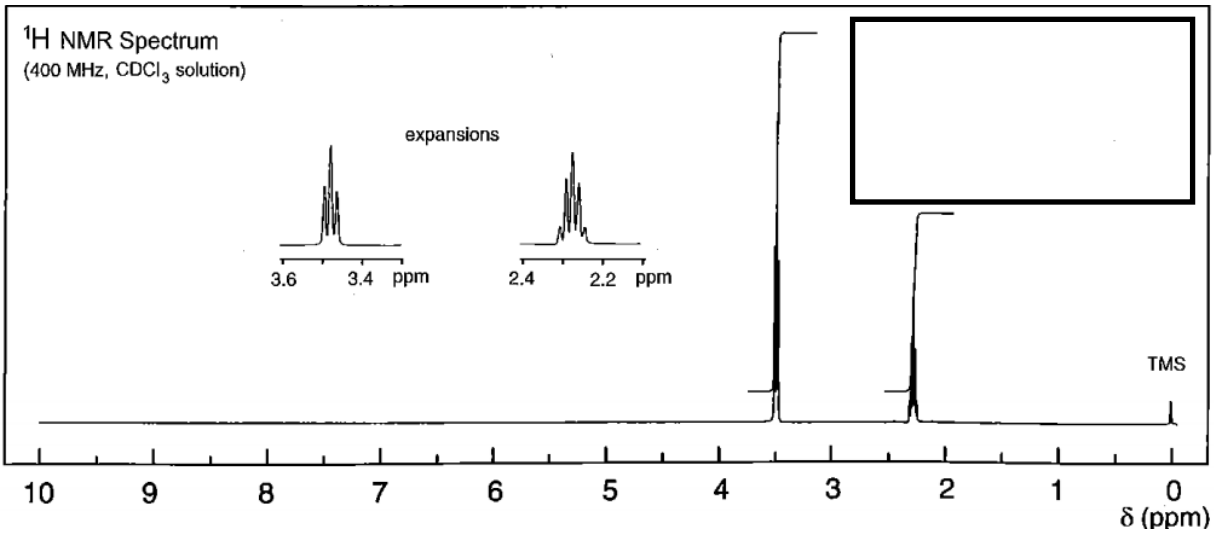
Name: _____ Student Number: _____

5. *continued…*









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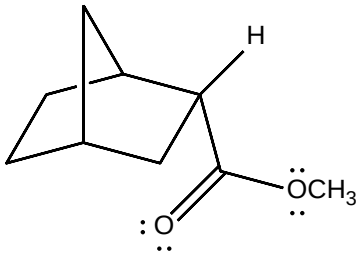
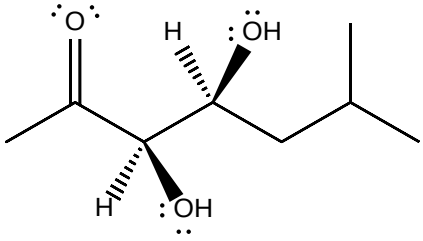
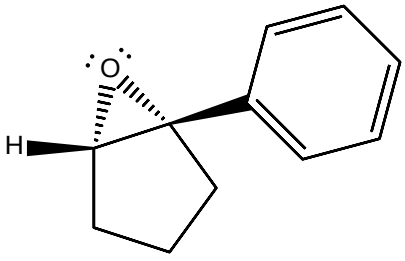
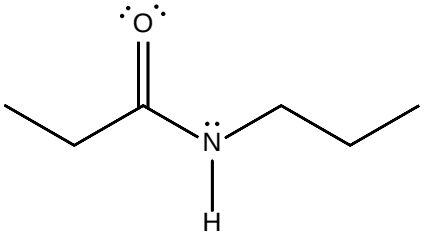
6. Choose any **three** of the molecules below and propose a synthesis for each one. **[15 marks]**

- 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**.
- 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).









Name: _____ Student Number: _____

6. *continued…* *[5 marks]*

Synthetic Target #1:

Synthesis:

Name: _____ Student Number: _____

6. *continued…* *[5 marks]*

Synthetic Target #2:

Synthesis:

Name: _____ Student Number: _____

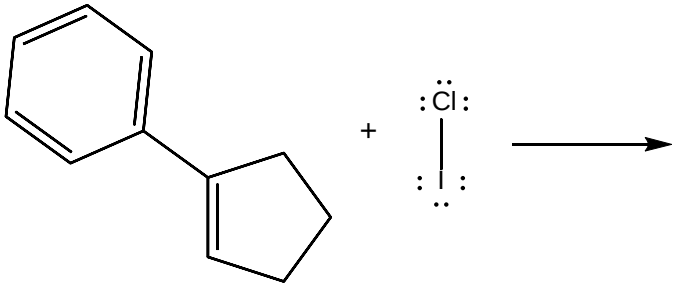
6. *continued…* *[5 marks]*

Synthetic Target #3:

Synthesis:

Name: _____ Student Number: _____

7. Show the mechanism for the reaction below and draw the major organic product. **[5 marks]** Clearly show any relevant regiochemistry and/or stereochemistry in the product.



8. 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												13	14	15	16	17	18
1.0079 **H** 1	2																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

Developed by Prof. R. T. Boeré (updated 2016)