CHEMISTRY 2500A: Organic Chemistry I
FINAL EXAM
Saturday, December 8th, 2018

Instructions:

- This exam consists of 16 questions.
- The exam is worth a total of 92 marks. Most of these marks are for explanation/showing your work rather than for reaching the correct answer. Explain all of your answers fully using diagrams where appropriate (a picture really is worth a thousand words!).
- Marks will be deducted for poorly drawn structures.
- No calculators allowed. No other electronic devices can be present with you during the exam unless authorized by the instructor.
- You may use a molecular model kit.
- There is a 3-hour time limit.
- If your work is not legible, it will be given a mark of zero.
- **Read the questions carefully**. Good luck.

Confidentiality Agreement:

I agree not to discuss (or in any other way divulge) the contents of this exam until they have all been marked. I understand that, if I were to break this agreement, I would be choosing to commit academic misconduct, a serious offense which will be punished. The minimum punishment would be a mark of 0 on this exam and removal of the "overwrite midterm mark with final exam mark" option for my grade in this course; the maximum punishment would include expulsion from this university.

Signature: _____
Course: CHEM 2500 (Organic Chemistry I)
Semester: Fall 2018
The University of Lethbridge

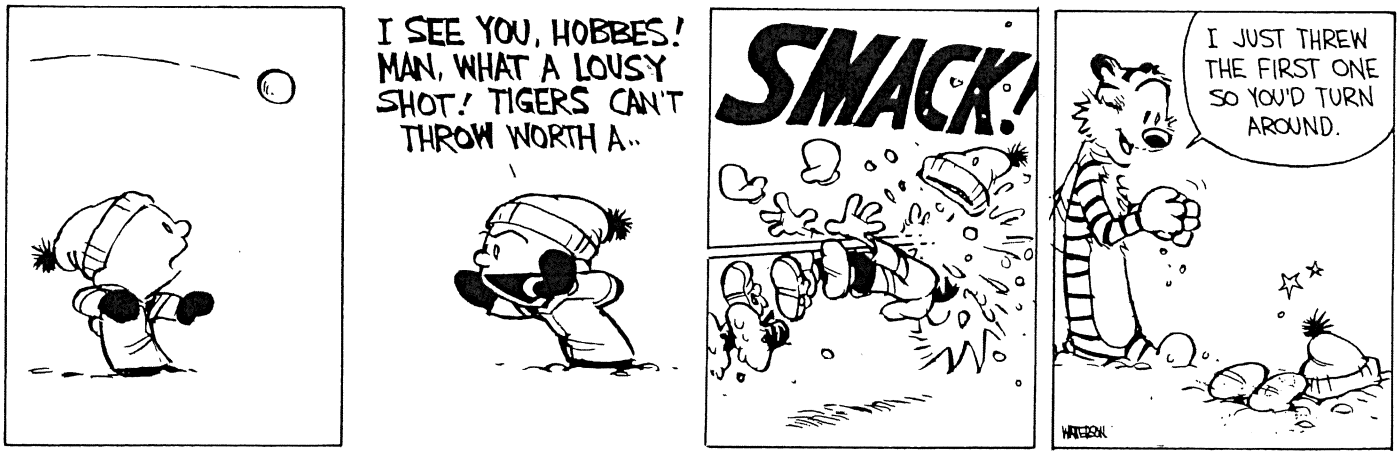
KEY

Question Breakdown

Q1	**/ 4**
Q2	**/ 4**
Q3	**/ 6**
Q4	**/ 4**
Q5	**/ 6**
Q6	**/ 10**
Q7	**/ 6**
Q8	**/ 5**

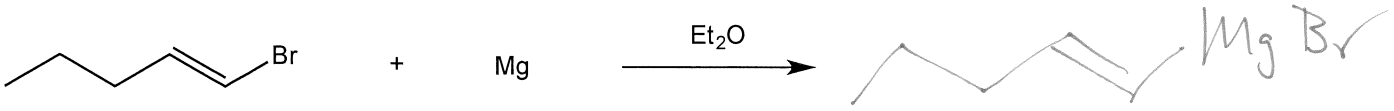
Q9	**/ 6**
Q10	**/ 5**
Q11	**/ 4**
Q12	**/ 8**
Q13	**/ 10**
Q14	**/ 8**
Q15	**/ 5**
Q16	**/ 1**

Total	**/ 92**

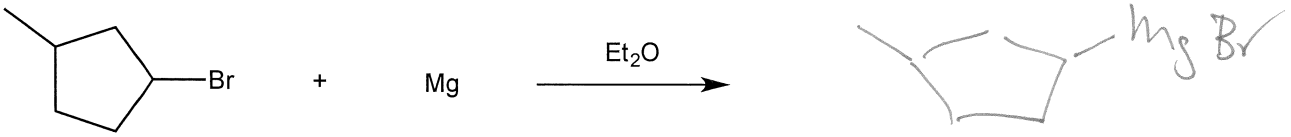


1. While working in the lab, Al Kane attempts to make four different Grignard reagents. For each reaction, determine if Al was successful in making the Grignard reagents. If the reaction worked, draw the structure of the Grignard reagent. If the reaction did not work, explain why. **[4 marks]**

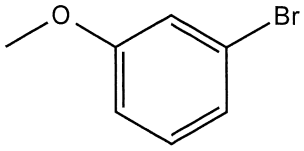
(a)



(b)

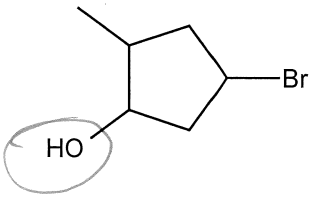


(c)



won't work, acidic proton.

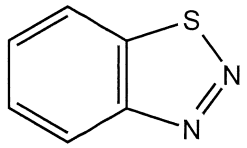
(d)



won't work, acidic proton.

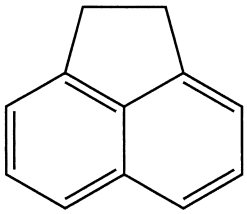
2. Predict whether the following molecules, as drawn, are aromatic, anti-aromatic, or non-aromatic.
Hint: start by adding all missing lone pairs. **[4 marks]**

(a)



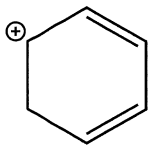
Aromatic.

(b)



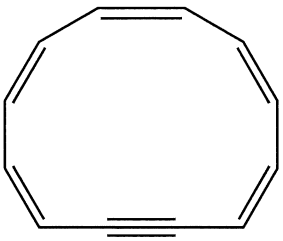
Aromatic.

(c)



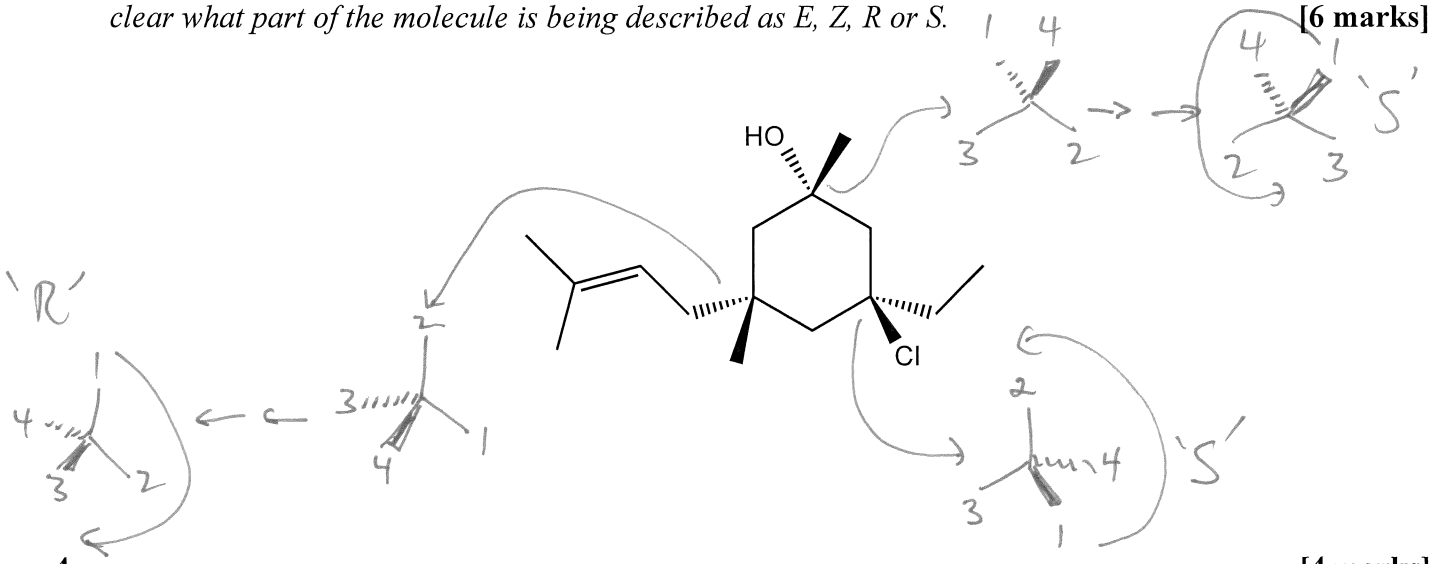
non-aromatic.

(d)



Anti-aromatic.

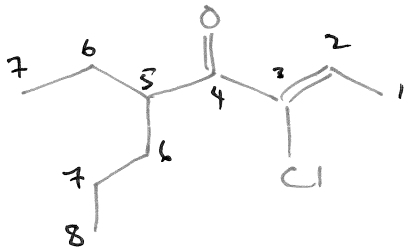
3. For the following molecule, where appropriate, assign the stereochemical configuration(s) as *E*, *Z*, *R* or *S*. *For full marks, you must show the priority numbers you used to assign each configuration and it must be clear what part of the molecule is being described as E, Z, R or S.* **[6 marks]**



4. **[4 marks]**

(a) The following molecule has been named incorrectly, however, the structure of the molecule can still be deduced. Draw the structure of the molecule using proper line-bond format.

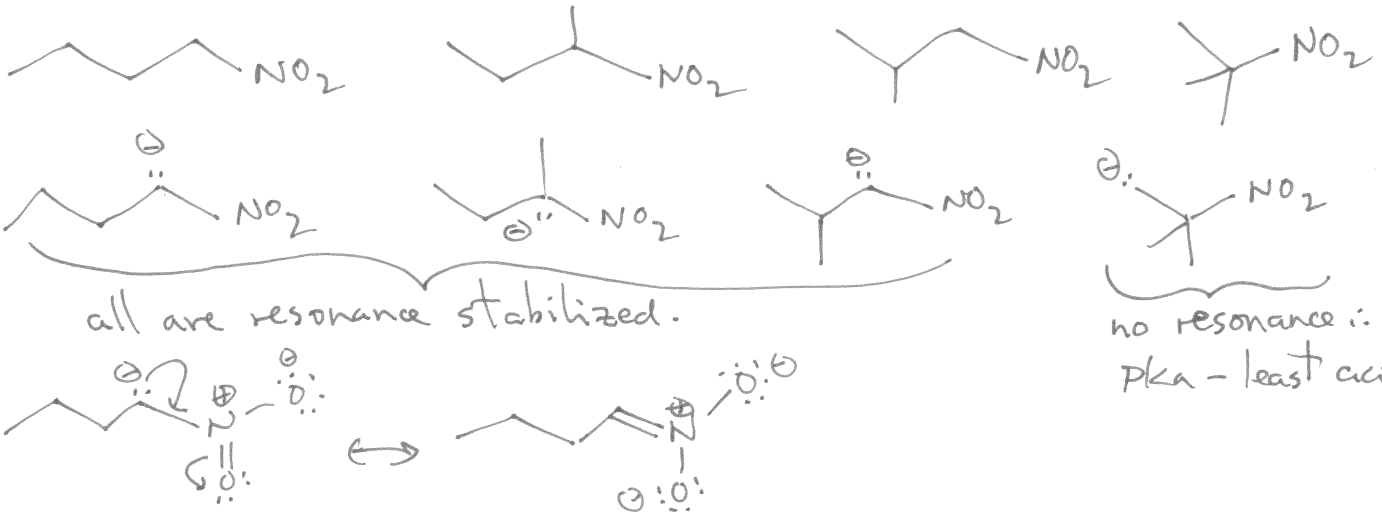
4-oxo-5-chloro-3-propylhept-5-ene



(b) Based on the structure above, give the correct name of this molecule according to IUPAC rules.

3-chloro-5-ethyloct-2-en-4-one.

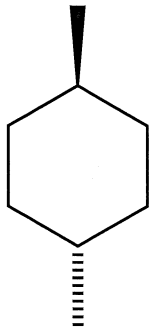
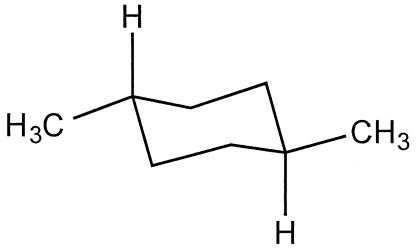
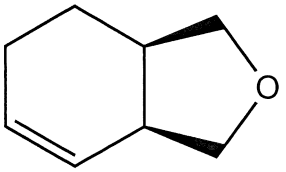
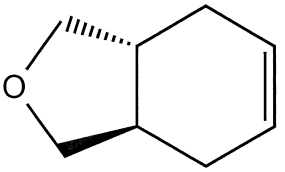
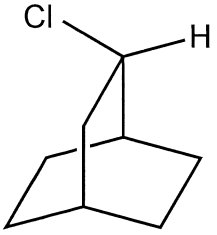
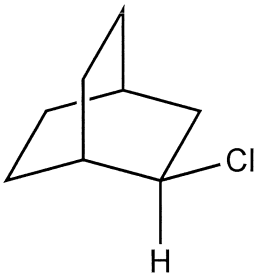
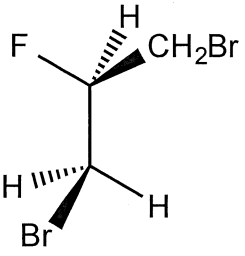
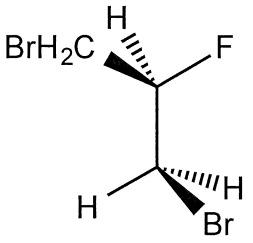
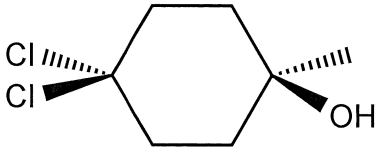
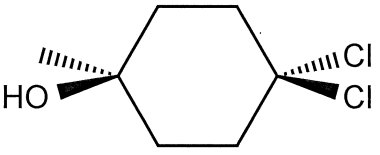
5. There are only 4 constitutional isomers with molecular formula $C_4H_9NO_2$ that contain a nitro group ($-NO_2$). Three of these isomers have similar pK_a values, while the fourth isomer has a much higher pK_a value. Draw all four isomers and identify which one has the higher pK_a. Explain your choice. **[6 marks]**



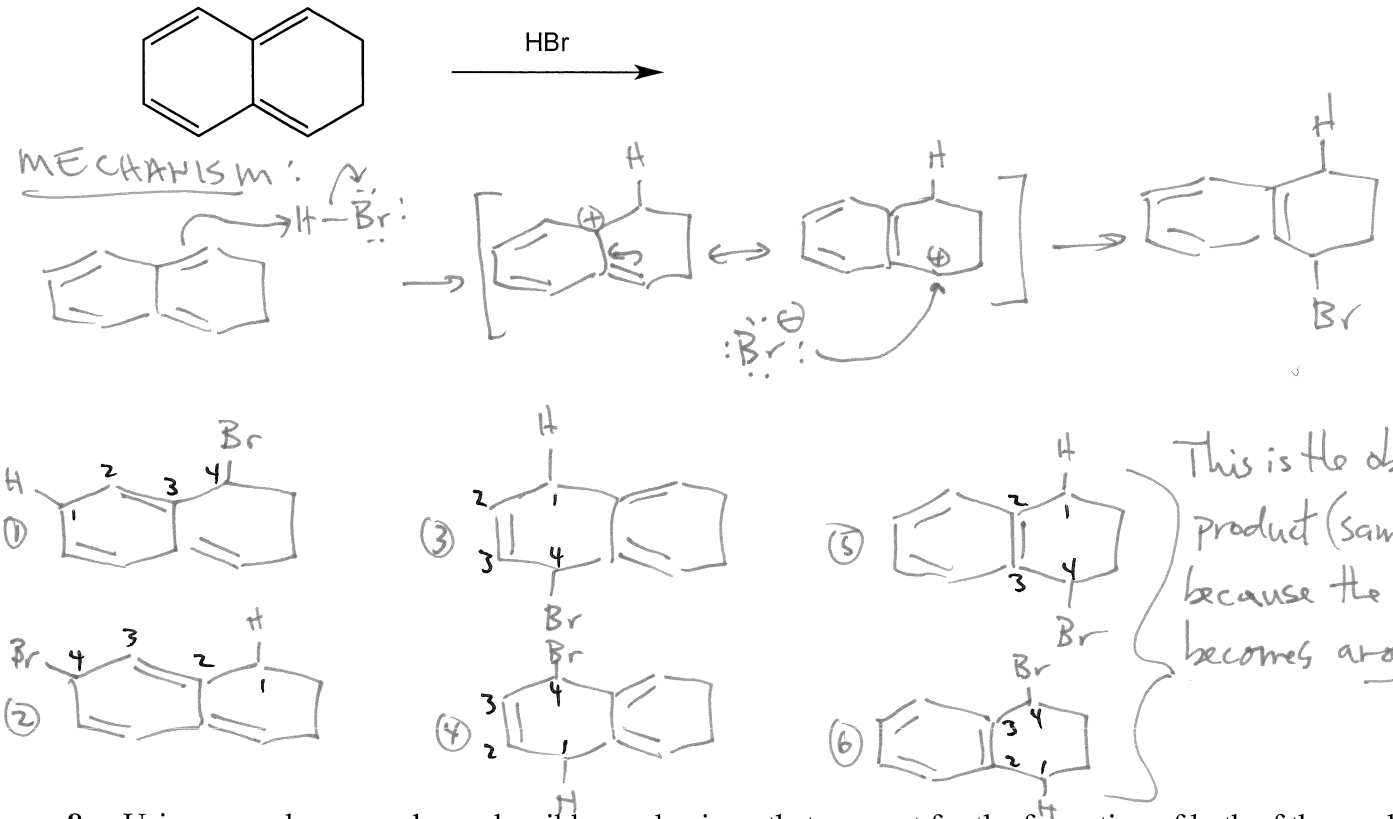
6. Using the appropriate letter or letters, indicate the relationship(s) between the following pairs of molecules. If there is more than one relationship, provide all the letters that apply. *No explanation is necessary.*

[10 marks]

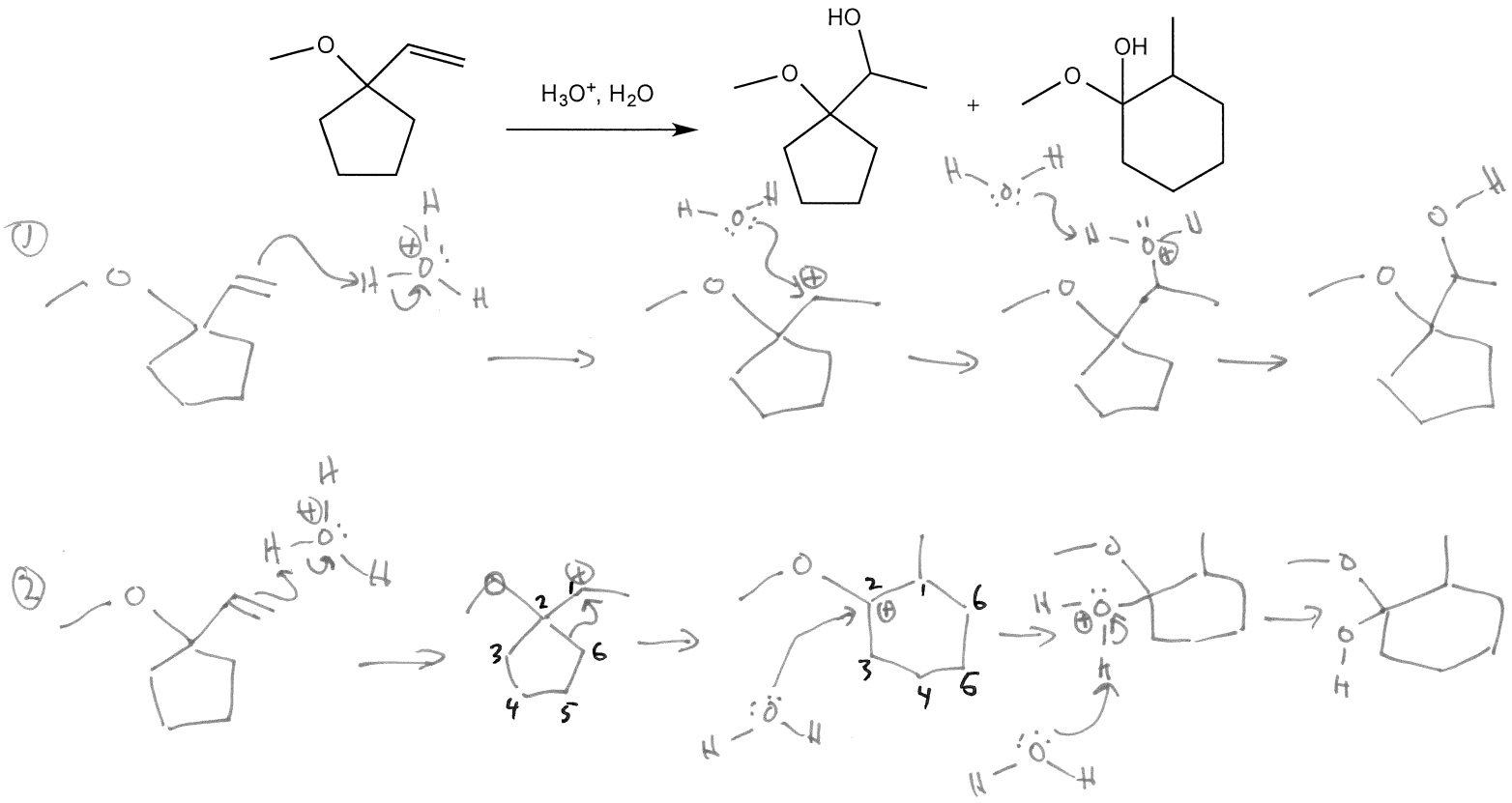
A = stereoisomers
B = constitutional isomers
C = conformers
D = diastereomers
E = enantiomers
F = identical molecules
G = none of the above

	relationship(s)
 and 	F
 and 	B
 and 	A, E
 and 	F
 and 	F

7. In the addition reaction of HBr to the following molecule there are, in principle, several different possible 1,2- and 1,4- addition products. Only one 1,4-addition product is actually observed. Draw the structures of the 6 different possible 1,4-addition products and identify the one that is observed. Briefly explain why this is the only observed 1,4-addition product. Note that part of your answer must contain a mechanism of the formation of the observed 1,4-addition product. **[6 marks]**

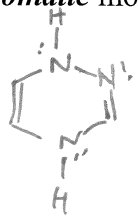


8. Using curved arrows, draw plausible mechanisms that account for the formation of both of the products for the following reaction. **[5 marks]**



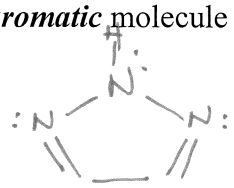
9. For the following question, your structures must be drawn in line-bond format, be valid Lewis structures, and contain NO charges. **[6 marks]**

(a) Draw an ***anti-aromatic*** molecule containing a 6-membered ring containing 3 nitrogen atoms.



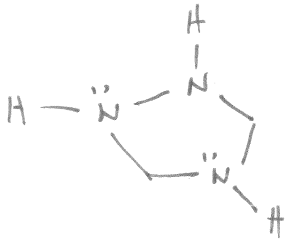
+ others.

(b) Draw an ***aromatic*** molecule containing a 5-membered ring containing 3 nitrogen atoms.



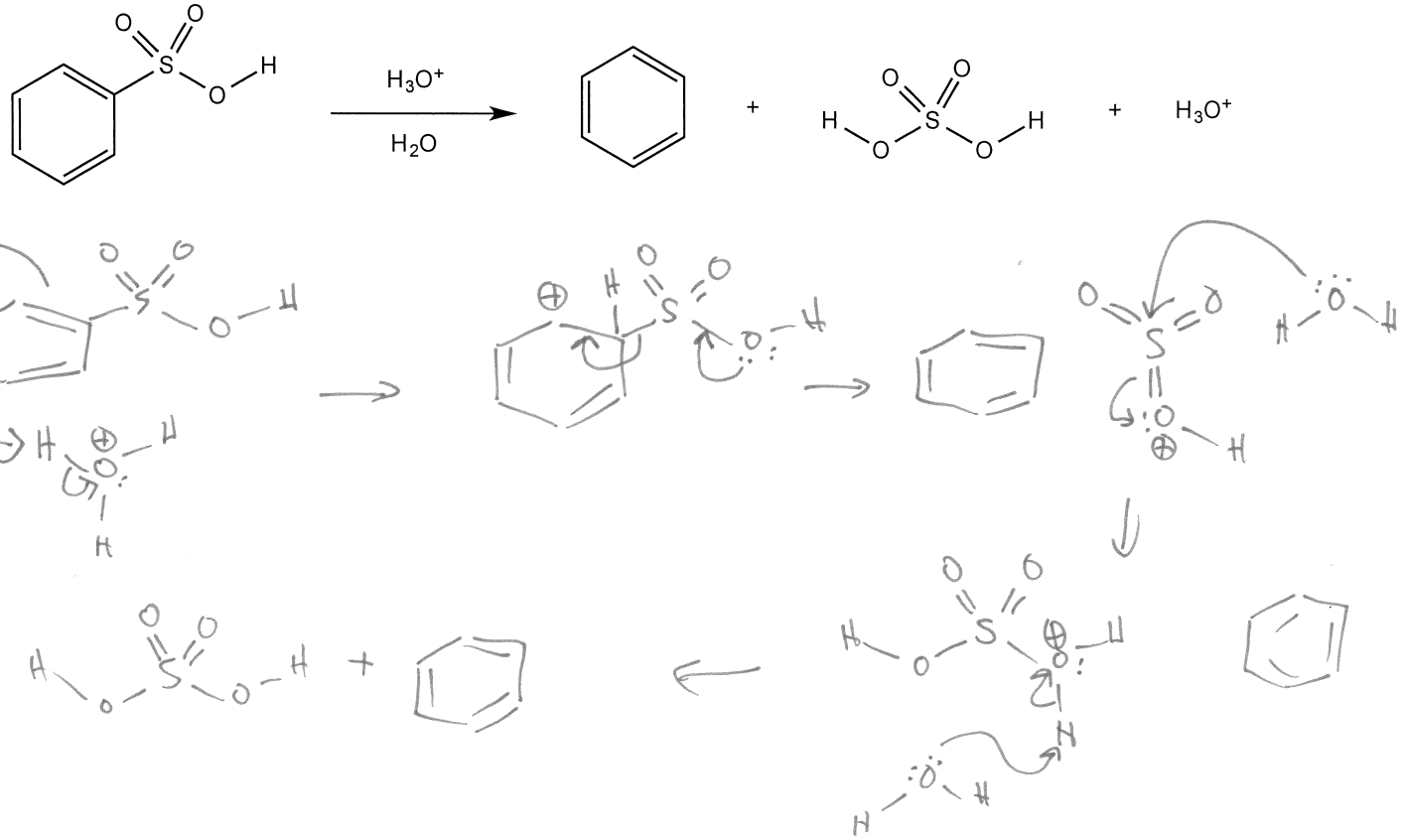
+ others.

(c) Draw a ***non-aromatic*** molecule containing a 5-membered ring containing 3 nitrogen atoms.



+ others.

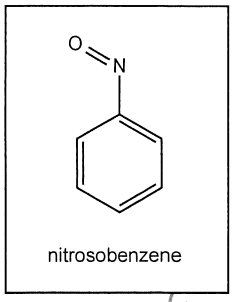
10. We saw that benzene can be sulfonated to benzenesulfonic acid with ***concentrated*** sulfuric acid (H_2SO_4). We also saw that this reaction is reversible in ***aqueous*** sulfuric acid. Draw the mechanism for the reverse reaction. Be sure your mechanism accounts for the formation of all 3 products; benzene, sulfuric acid, and the hydronium ion. **[5 marks]**



11. It can be argued that the nitroso group in nitrosobenzene can act as ***both*** an activating ortho/para director and a deactivating meta director in electrophilic aromatic substitution reactions. **[4 marks]**

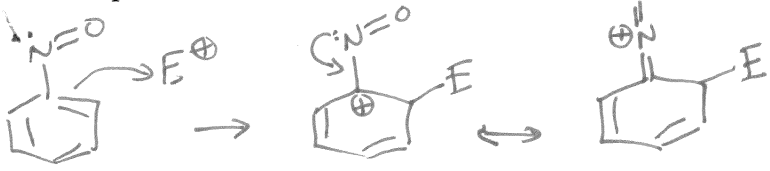
(a) Explain how the nitroso group can act as an activating ortho/para director in electrophilic substitution reactions.

(b) Explain how the nitroso group can act as a deactivating meta director in electrophilic aromatic substitution reactions.



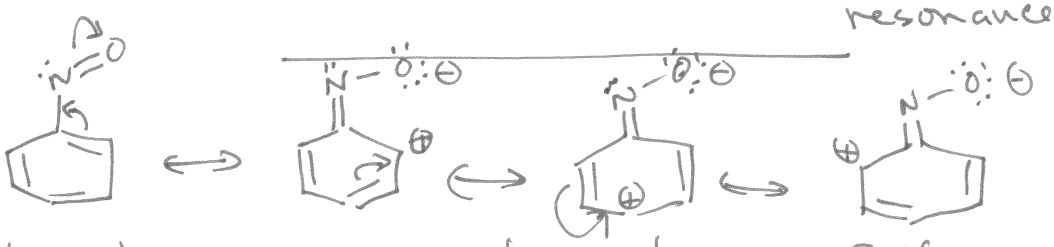
nitrosobenzene

a)



It can act as an o/p director because it can stabilize the resulting arenium ion via resonance.

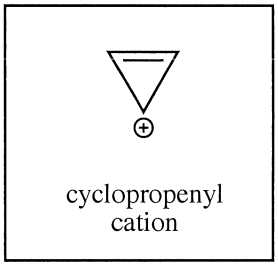
b)

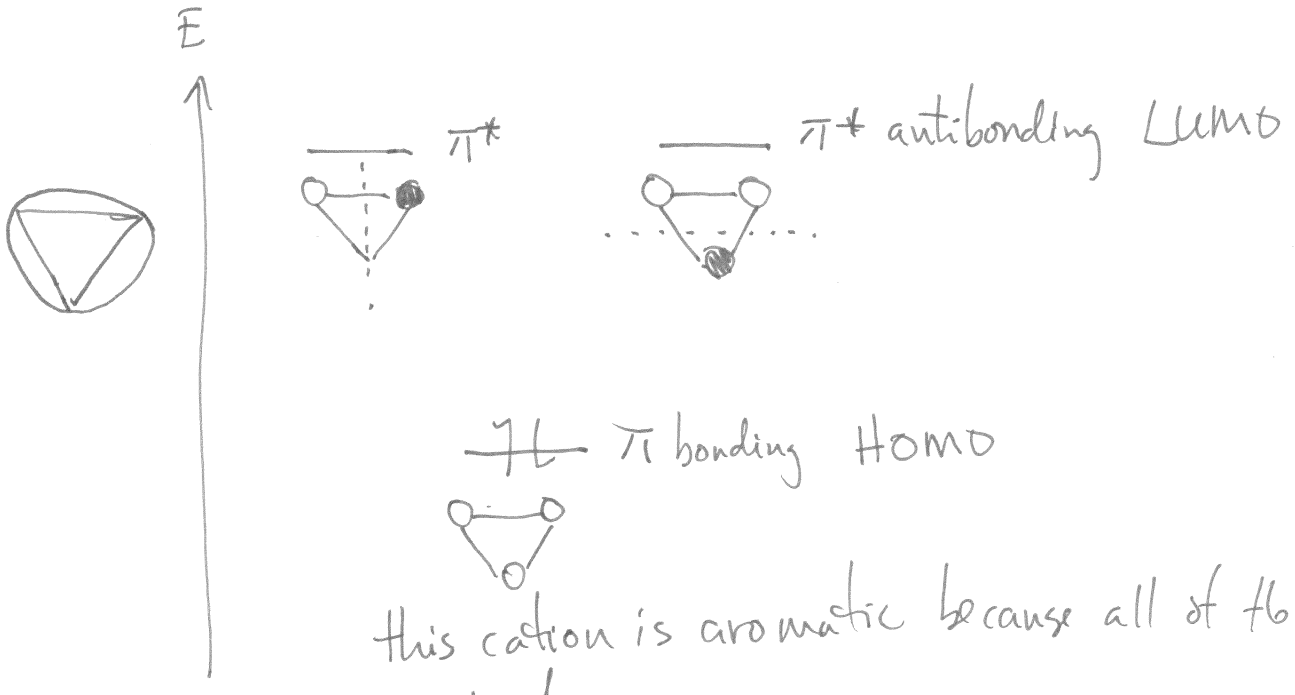


The nitroso group can also act as an EWG as shown by the following resonance structures. EWG destabilize the arenium ion intermediate if substituted o/p ∴ it directs the $E^{\oplus}$ to the meta position.

12. Sketch the π–MO energy level diagram for the cyclopropenyl cation. On your diagram: **[8 marks]**

- Determine the relative energy levels of the orbitals
- include the appropriate number of π–electrons
- label each energy level as bonding, non-bonding, or antibonding.
- label the HOMO and LUMO
- Sketch all π–MOs for this molecule
- According to your π–MO diagram, is the cyclopropenyl cation aromatic or anti-aromatic? Explain.

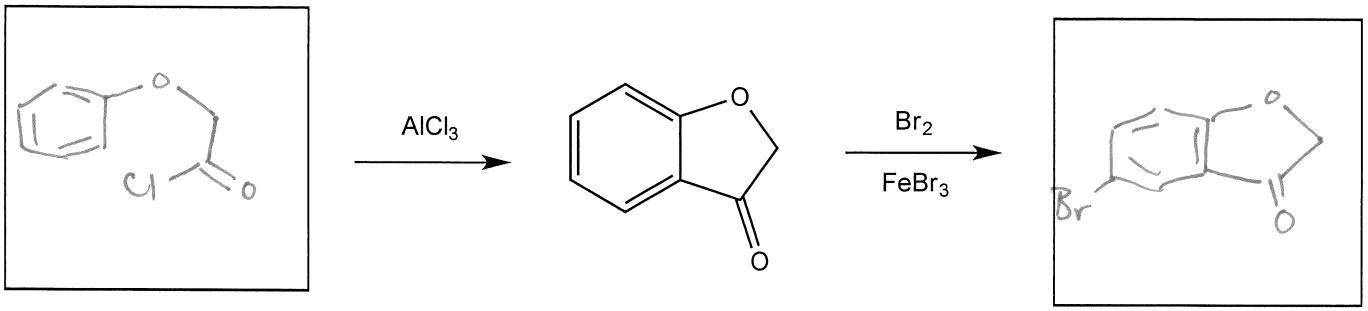

cyclopropenyl cation



this cation is aromatic because all of the πe^- are paired.

13. For the following reactions, fill in the missing starting materials, products, or reagents. Marks are given for correct connectivity and, where appropriate, correct stereochemistry and regiochemistry. If more than one organic product is possible, draw only the major product. **[10 marks]**

(a)



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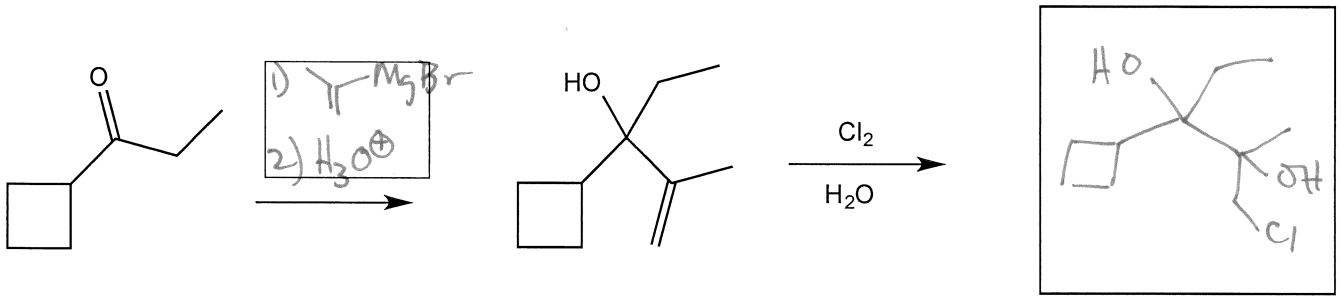

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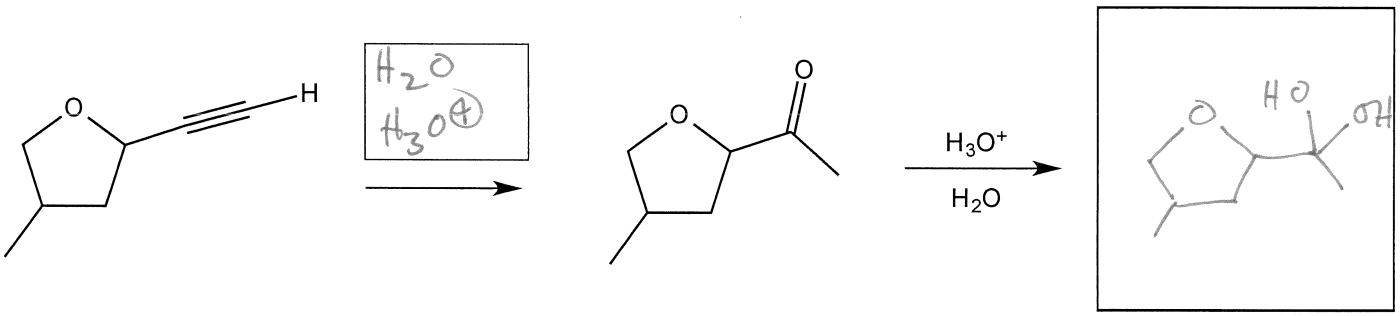

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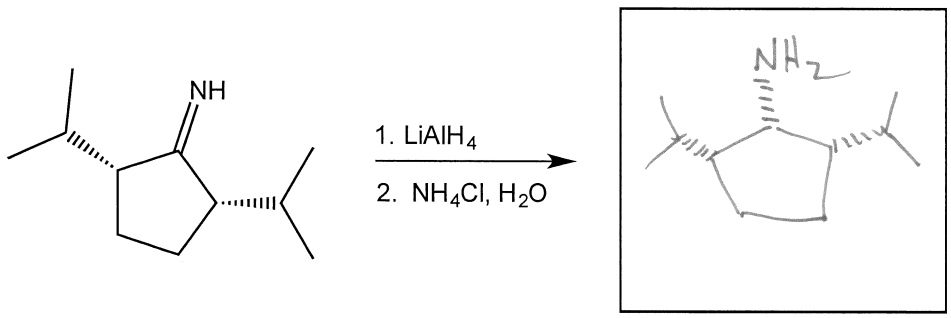
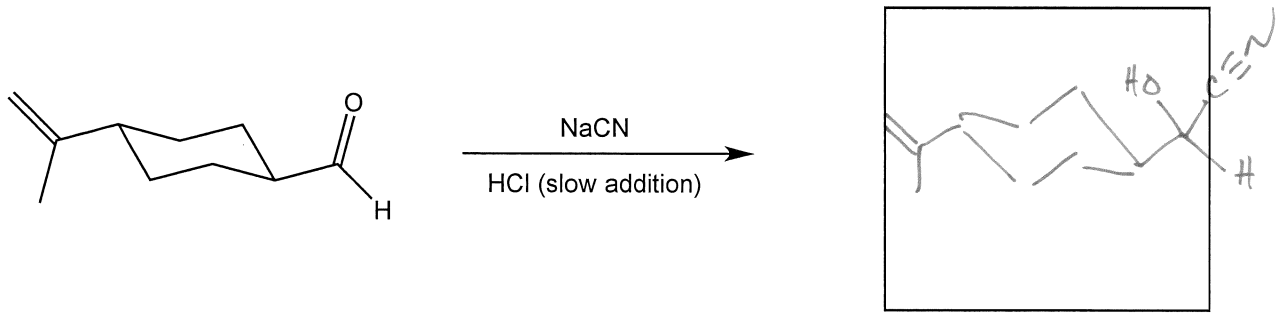
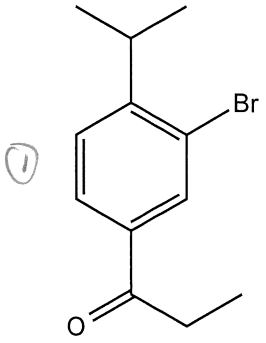
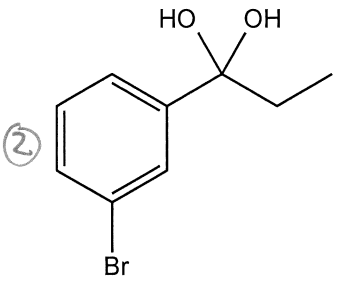


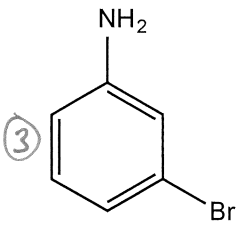
e)

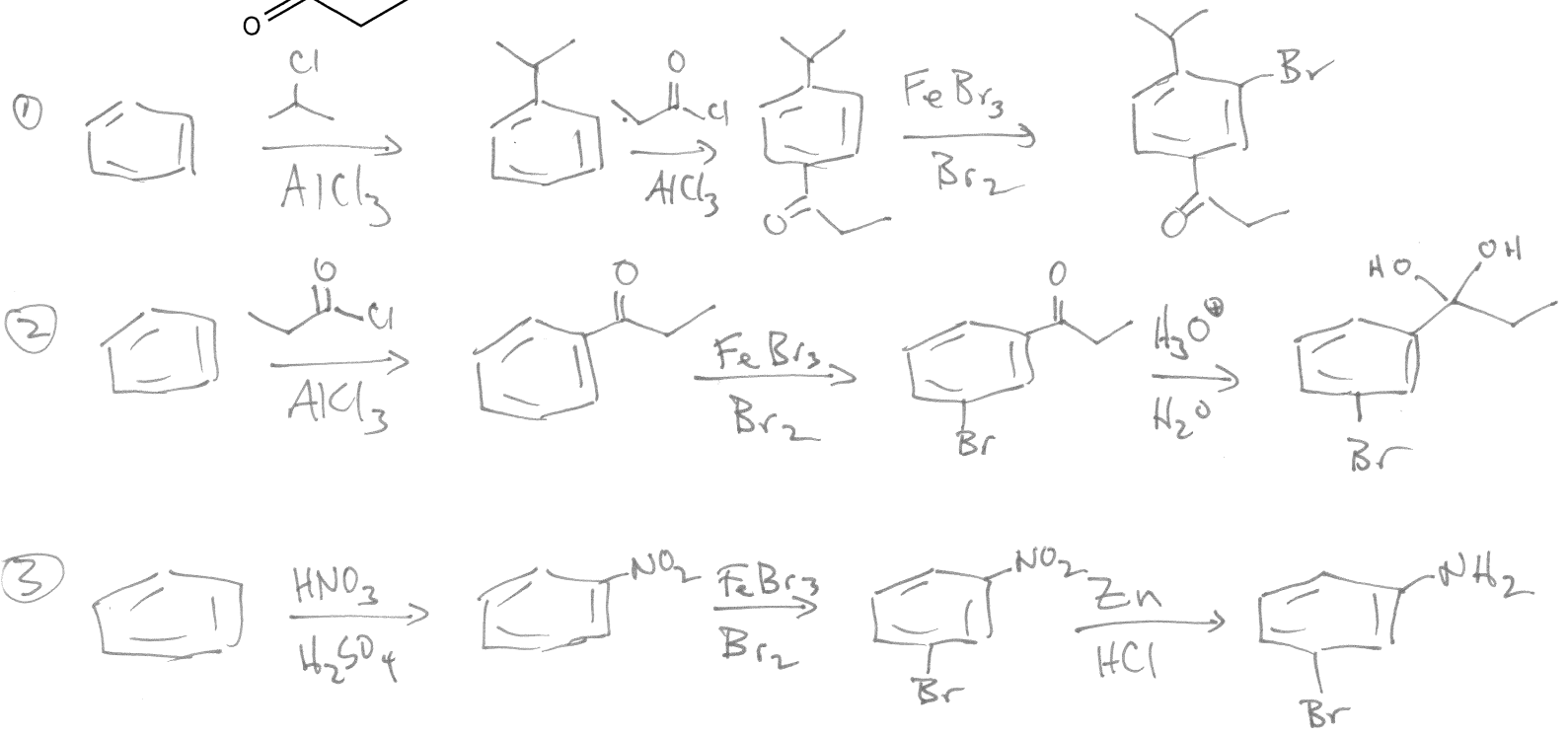


14. Starting from benzene, propose a workable synthesize for 2 of following molecules. You may use any other organic or inorganic reagents or solvents as needed. **[8 marks]**

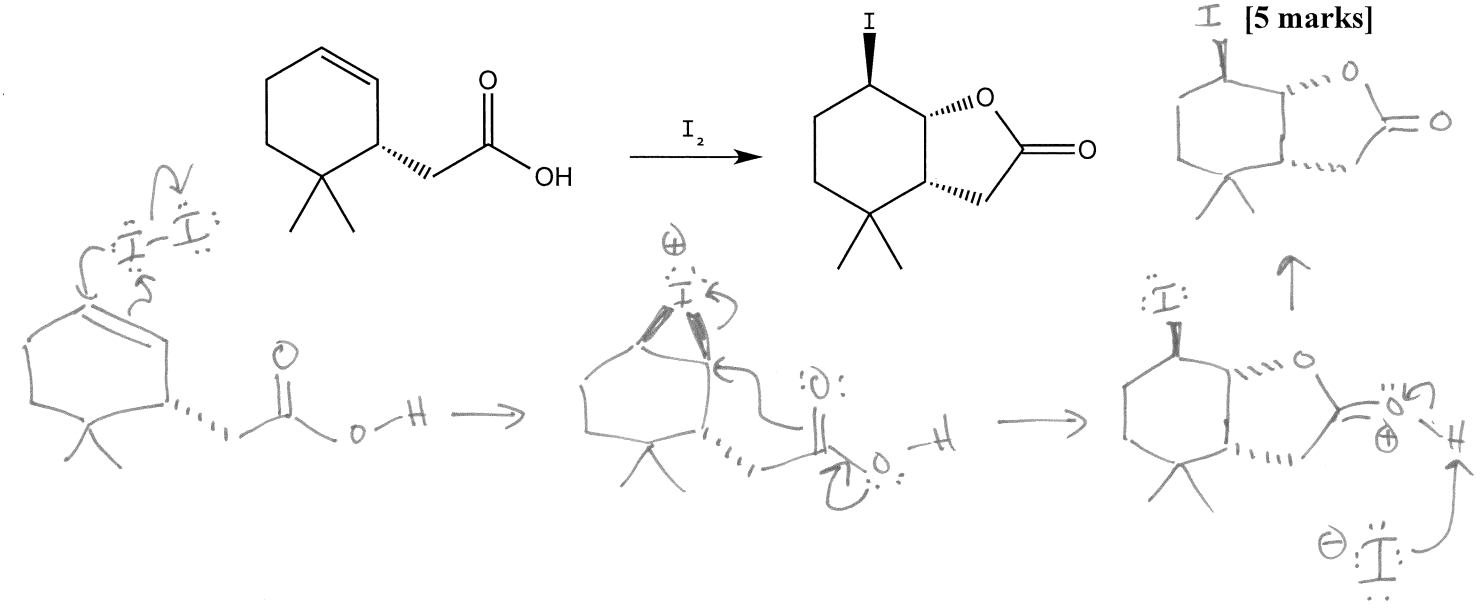






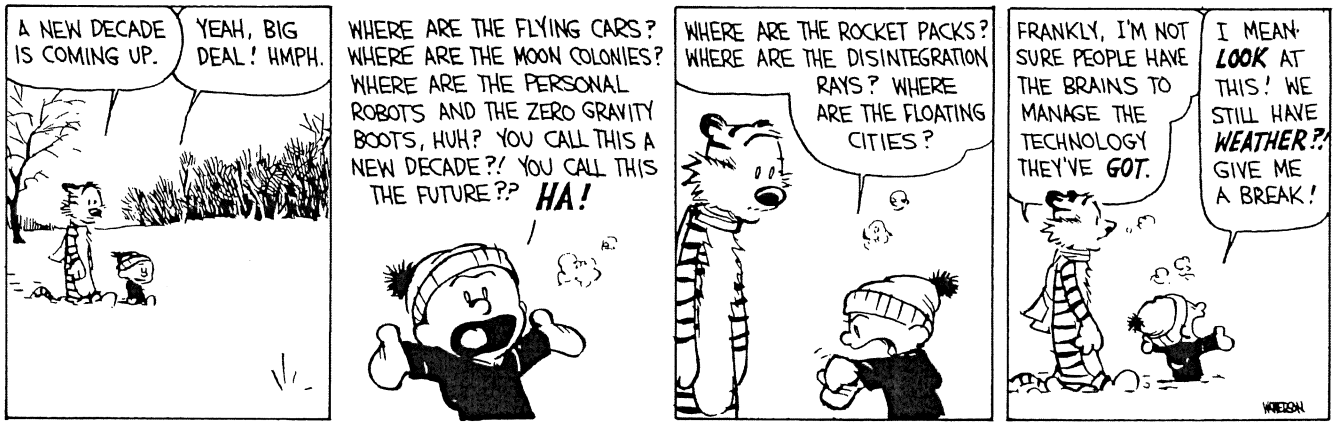


15. Use curved arrows to draw a plausible mechanism for the following process, called iodolactonization. **[5 marks]**



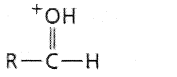
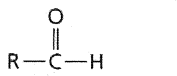
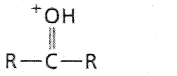
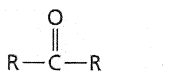
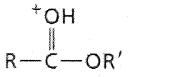
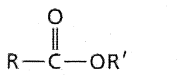
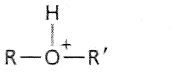
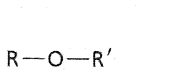
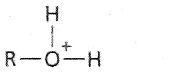
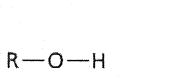
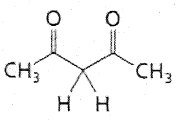
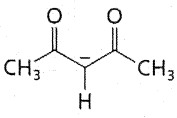
16. What was the most useful and/or interesting thing you learned in CHEM 2500? **[1 mark]**

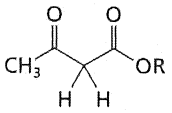
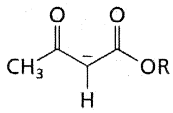
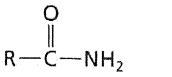
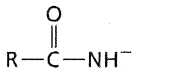
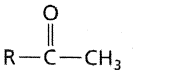
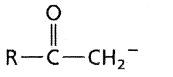
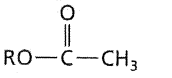
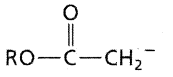
....HAVE A GREAT WINTER BREAK!!!



Extra space for: rough work, grocery list, poems, jokes, meaning of life, non-Euclidean proofs, cartoons, etc.

pKa values of molecules and ions commonly encountered in organic chemistry.

Acid	*Conjugate base*	pK_a
$HClO_4$	ClO_4^-	−10
HI	I^-	−9
		−9
HBr	Br	−9
H_2SO_4	HSO_4^-	−7
HCl	Cl^-	−7
		−7
$ArSO_3H$	$ArSO_3^-$	−6.5
		−6
		−3.5
		−2
H_3O^+	H_2O	−1.7
HNO_3	NO_3^-	−1.4
HSO_4^-	SO_4^{2-}	2
H_3PO_4	$H_2PO_4^-$	2.1
HF	F^-	3.1
HONO	NO_2^-	3.3
$ArNH_3^+$	$ArNH_2$	4
HN_3	N_3^-	4.6
RCOOH	$RCOO^-$	5
H_2CO_3	HCO_3^-	6.4
H_2S	HS^-	7
ArSH	ArS^-	7
		9

Acid	*Conjugate base*	pK_a
HCN	CN^-	9.2
NH_4^+	NH_3	9.2
ArOH	ArO^-	10
$R-CH_2NO_2$	$R-\bar{C}H-NO_2$	10
RNH_3^+	RNH_2	11
RSH	RS^-	11
		11
H_2O_2	HOO^-	11.6
PhNHCOR	$Ph\bar{N}-COR$	13
CH_3OH	CH_3O^-	15.2
H_2O	HO^-	15.7
RCH_2OH	RCH_2O^-	16
R_2CH-OH	R_2CH-O^-	17
R_3C-OH	R_3C-O^-	17
		17
$PhCH_2COR$	$Ph\bar{C}H-COR$	17
		20
		24
$R-CH_2CN$	$R-\bar{C}H-CN$	25
$H-C\equiv C-H$	$H-C\equiv C^-$	25
$PhNH_2$	$PhNH^-$	28
H_2	H^-	35
NH_3	NH_2^-	38
$Ph-CH_3$	$Ph-CH_2^-$	40
		43
$CH_2=CH_2$	$CH_2=CH^-$	44
CH_4	CH_3^-	48

Abbreviations: Ar = aryl; Ph = phenyl; R = alkyl.

Some Useful Data

Principal Functional Group Priority List

Carboxylic acid
Sulfonic acid
Ester
Acid chloride
Amide
Nitrile
Aldehyde
Ketone
Alcohol
Thiol
Amine

CHEM 1000 Standard Periodic Table

1																	18
1.0079 H 1	2											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	(261) Rf 104	(262) Db 105	(263) Sg 106	(262) Bh 107	(265) Hs 108	(266) Mt 109	(281) Dt 110	(283) Rg 111							

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	(260) Lr 103

Developed by Prof. R. T. Boeré