# 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:

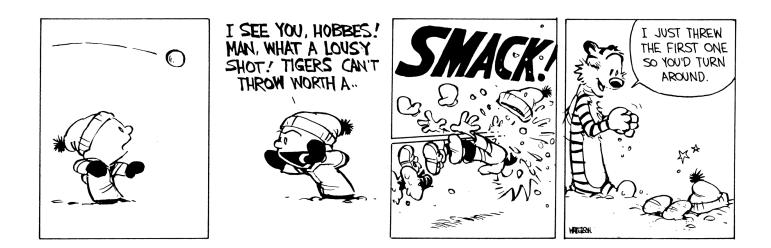
Course: CHEM 2500 (Organic Chemistry I) Semester: Fall 2018 The University of Lethbridge

#### **Question Breakdown**

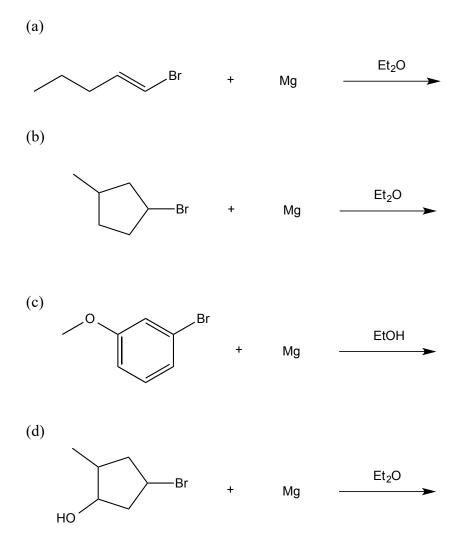
Q1	/ 4
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Q3	/ 6
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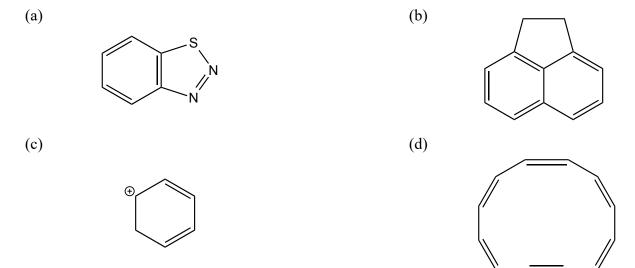
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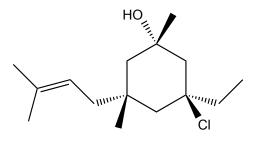
While working in the lab, Al Kane attempts to make four different Grignard reagents. For each reaction, determine if Al was successful in making the Grignard reagents. If the reaction worked, draw the structure of the Grignard reagent. If the reaction did not work, explain why. [4 marks]



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



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

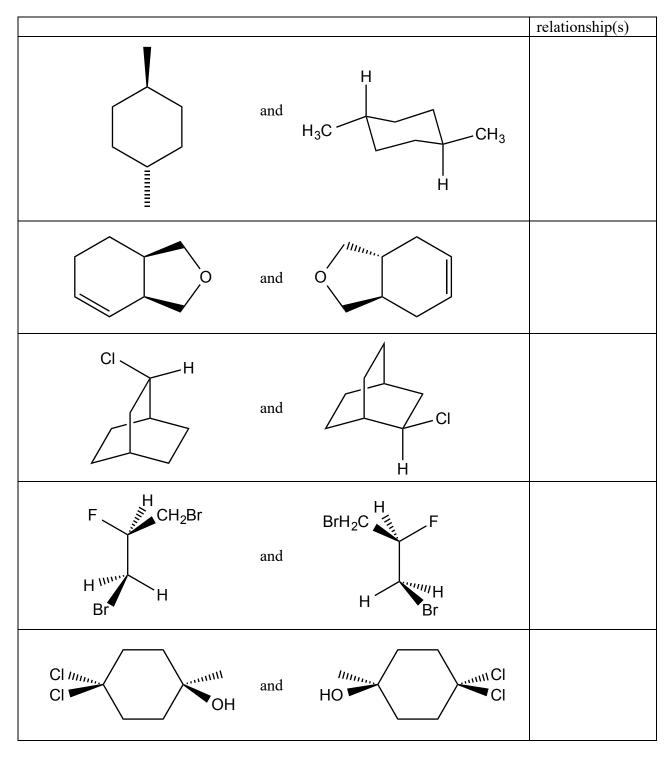
(b) Based on the structure above, give the correct name of this molecule according to IUPAC rules.

5. There are only 4 constitutional isomers with molecular formula  $C_4H_9NO_2$  that contain a nitro group (-NO<sub>2</sub>). 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.* 

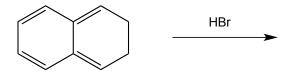
### [10 marks]

- A = stereoisomers
- B = constitutional isomers
- C = conformers
- D = diastereomers

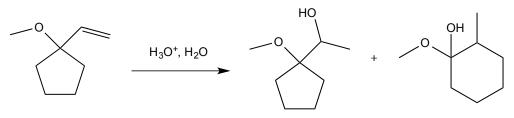
- E = enantiomers F = identical molecules
- G = none of the above



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]

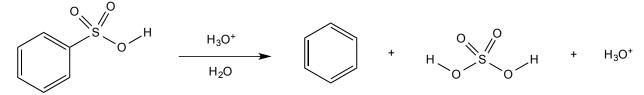


- 9. For the following question, your structures must be drawn in line-bond format, be valid Lewis structures, and contain NO charges. [6 marks]
- (a) Draw an *anti-aromatic* molecule containing a 6-membered ring containing 3 nitrogen atoms.

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

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

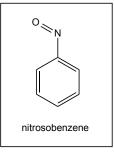
10. We saw that benzene can be sulfonated to benzenesulfonic acid with *concentrated* sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). We also saw that this reaction is reversible in *aqueous* sulfuric acid. Draw the mechanism for the reverse reaction. Be sure your mechanism accounts for the formation of all 3 products; benzene, sulfuric acid, and the hydronium ion. [5 marks]



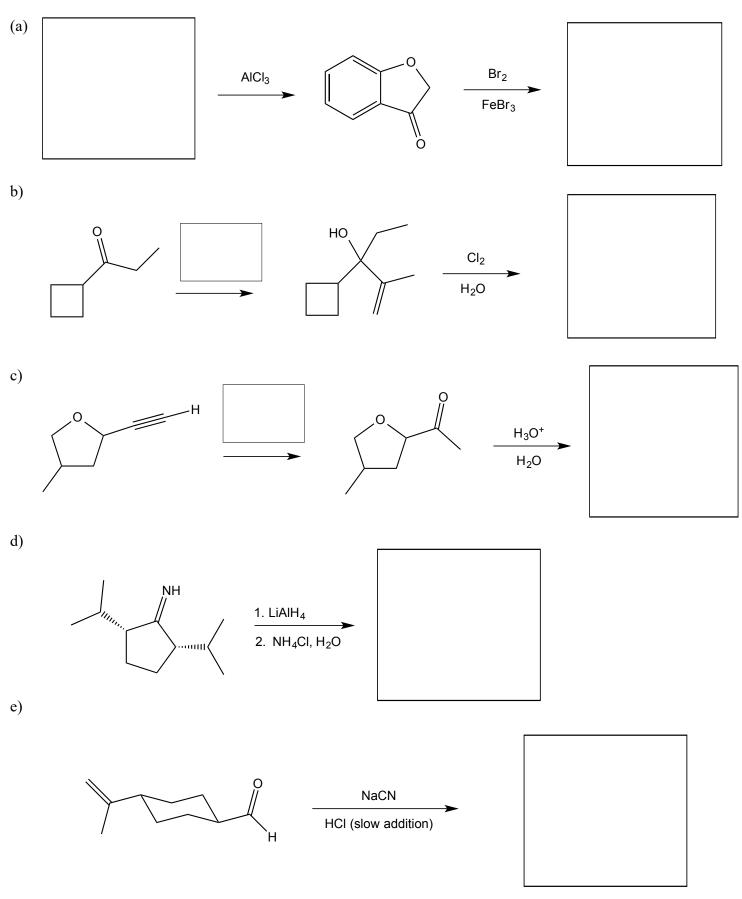
- It can be argued that the nitroso group in nitrosobenzene can act as *both* an activating ortho/para director and a deactivating meta director in electrophilic aromatic substitution reactions. [4 marks]
- (a) Explain how the nitroso group can act as an activating ortho/para director in electrophilic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



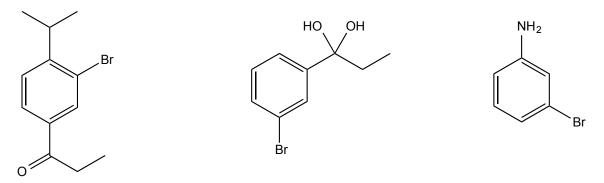
- 12. Sketch the π–MO energy level diagram for the cyclopropenyl cation. On your diagram: [8 marks]
  - diagram:Determine the relative energy levels of the orbitals
    - include the appropriate number of  $\pi$ -electrons
    - label each energy level as bonding, non-bonding, or antibonding.
    - label the HOMO and LUMO
    - Sketch all  $\pi$ –MOs for this molecule
    - According to your  $\pi$ -MO diagram, is the cyclopropenyl cation aromatic or anti-aromatic? Explain.



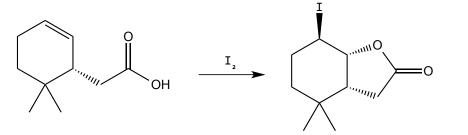
13. For the following reactions, fill in the missing starting materials, products, or reagents. Marks are given for correct connectivity and, where appropriate, correct stereochemistry and regiochemistry. If more than one organic product is possible, draw only the major product. [10 marks]



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

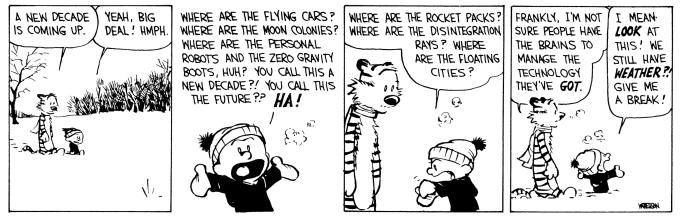


Use curved arrows to draw a plausible mechanism for the following process, called iodolactonization.
I [5 marks]



[1 mark]

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



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

Acid	Conjugate base	pK <sub>a</sub>	Acid	Conjugate base	pKa
HCIO <sub>4</sub>	CIO <sub>4</sub> <sup>-</sup>	- 10	HCN	CN <sup>-</sup>	9.2
ні	I_	- 9	NH4 <sup>+</sup>	NH <sub>3</sub>	9.2
+OH	O U		ArOH	ArO <sup>-</sup>	10
R−C−H	R—C−H	- 9	R-CH <sub>2</sub> NO <sub>2</sub>	R-CH-NO <sub>2</sub>	10
HBr	Br	- 9	RNH <sub>3</sub> <sup>+</sup>	RNH <sub>2</sub>	11
H <sub>2</sub> SO <sub>4</sub>	HSO4 <sup>-</sup>	-7	RSH	RS <sup>-</sup>	11
ICI	CI-	- 7	0 0	0 0	
<sup>+</sup> OH	0		CH <sub>3</sub> OR	CH <sub>3</sub> OR	11
	R—C—R	- 7	нн	н	
ArSO <sub>3</sub> H	ArSO <sub>3</sub> <sup>-</sup>	- 6.5	H <sub>2</sub> O <sub>2</sub>	HOO <sup>-</sup>	11.6
+OH	0		PhNHCOR	PhN-COR	13
	R—C—OR'	- 6	CH <sub>3</sub> OH	CH <sub>3</sub> O <sup>-</sup>	15.2
	K-C-OK		H <sub>2</sub> O	HO <sup>-</sup>	15.7
H I.			RCH <sub>2</sub> OH	RCH <sub>2</sub> O <sup>-</sup>	16
R = O = R'	R - O - R'	- 3.5	R <sub>2</sub> CH—OH	R <sub>2</sub> CH—O <sup>-</sup>	17
H			R <sub>3</sub> C—OH	R <sub>3</sub> C—O <sup>-</sup>	17
R—0 <sup>+</sup> −H	R—O—H	- 2	0	0	17
H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	- 1.7	R-C-NH <sub>2</sub>	R—Ċ—NH <sup>−</sup>	
INO <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	- 1.4	PhCH <sub>2</sub> COR	PhCH—COR	17
ISO4	SO4 <sup>2-</sup>	2	O II	0	. 20
I <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	2.1	R—C—CH₃	$R - C - CH_2^-$	20
łF	F <sup>-</sup>	3.1	0	0	
IONO	NO <sub>2</sub>	3.3		Î RO−C−CH₂⁻	24
ArNH <sub>3</sub> <sup>+</sup>	ArNH <sub>2</sub>	4			
IN <sub>3</sub>	N <sub>3</sub> <sup>-</sup>	4.6	R—CH <sub>2</sub> CN	R—ĒH—CN	25
соон	RCOO <sup>-</sup>	5	Н—С≡С—Н	H—C≡C <sup>−</sup>	25
I <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> <sup>-</sup>	6.4	PhNH <sub>2</sub>	PhNH <sup>-</sup>	28
1 <sub>2</sub> 5	HS <sup>-</sup>	7	H <sub>2</sub>	H <sup>-</sup>	35
ArSH	ArS <sup>-</sup>	7	NH <sub>3</sub>	NH <sub>2</sub> <sup>-</sup>	38
0 0	0 0		Ph—CH <sub>3</sub>	Ph-CH <sub>2</sub> -	40
CH <sub>3</sub> CH <sub>3</sub>	CH <sub>3</sub> CH <sub>3</sub>	9	H	-	43
нн	H				-TJ
			$CH_2 = CH_2$	CH <sub>2</sub> =CH <sup>-</sup>	44
			CH <sub>4</sub>	CH <sub>3</sub> <sup>-</sup>	48

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

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

## Some Useful Data

### **Principal Functional Group Priority List** Carboxylic acid Sulfonic acid

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

1			СН	EM 1(	)00 Sta	ndard	l Perio	odic Ta	able								18
1.0079 H																	4.0026 He
п 1	2											13	14	15	16	17	2
6.941	9.0122											10.811	12.011	14.0067	15.9994	18.9984	20.1797
Li	Be											В	С	Ν	0	F	Ne
3	4											5	6	7	8	9	10
22.9898	24.3050											26.9815	28.0855	30.9738	32.066	35.4527	39.948
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	Р	S	Cl	Ar
11	12	-	4		6		-					13	14	15	16	17	18
39.0983	40.078	44.9559	47.88	50.9415	51.9961	54.9380	55.847	58.9332	58.693	63.546	65.39	69.723	72.61	74.9216	78.96	79.904	83.80
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
85.4678	87.62	88.9059	91.224	92.9064	95.94	(98)	101.07	102.906	106.42	107.868	112.411	114.82	118.710	121.757	127.60	126.905	131.29
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
37	38	39	40	41	42 183.85	43 186.207	44	45	46	47 196.967	48 200.59	49 204.383	50	51	52	53	54
132.905	137.327	La-Lu	178.49	180.948			190.2	192.22	195.08				207.19	208.980	(210) D	(210)	(222)
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
55	56 226.025		72 (261)	73	74 (263)	75 (262)	76	77	78 (281)	79 (283)	80	81	82	83	84	85	86
(223) E		Ac-Lr		(262)	. ,	( )	(265) Hs	(266) Mt									
<b>Fr</b> 87	<b>Ra</b> 88	AC-LI	<b>Rf</b> 104	<b>Db</b> 105	Sg 106	<b>Bh</b> 107	108	109	<b>Dt</b> 110	<b>Rg</b>							
0/	00		104	105	100	107	108	109	110	111	J						
	1	138.906	140.115	140.908	144.24	(145)	150.36	151.965	157.25	158.925	162.50	164.930	167.26	168.934	173.04	174.967	1
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dv	Но	Er	Tm	Yb	Lu	
		57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	
		227.028	232.038	231.036	238.029	237.048	(240)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)	1
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	
		89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	

Developed by Prof. R. T. Boeré