

CHM 1321B
SAMPLE Final Exam

IMPORTANT: this is a *sample final only, to be used as a practice as part of your studying*

TIPS ARE IN BLUE
TIP: this is the actual first page

April 2012

Professor: Alison Flynn

Time: 3 hours

Last Name: _____ First Name: _____

Student Number: _____ Seat number: _____

Notes:

- The marks are given as a guide and are subject to minor changes
- A faculty-approved calculator and molecular models are permitted
- Show stereochemistry where applicable
- The final page of the exam has a pK_a table and a periodic table
- Total number of pages: 15
- Approximate number of points: 148

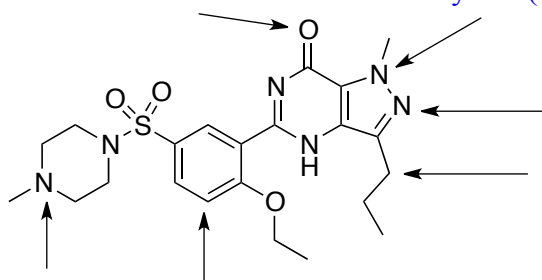
1. Draw 2-methyl-4-(1-methylethyl)octane

Remember to include R/S and E/Z, if applicable.

2. Draw para-nitrotoluene

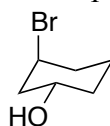
3. Identify the hybridization of each of the indicated atoms in viagra, an erectile dysfunction drug, shown below.

Remember to consider the resonance hybrid (it's the real structure)



4. Model time!

- Draw the following compound in two dimensions.
- Name the compound

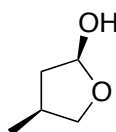


Remember that even in 2D, you have to include stereochemistry (wedges and hashes) for chiral centres.

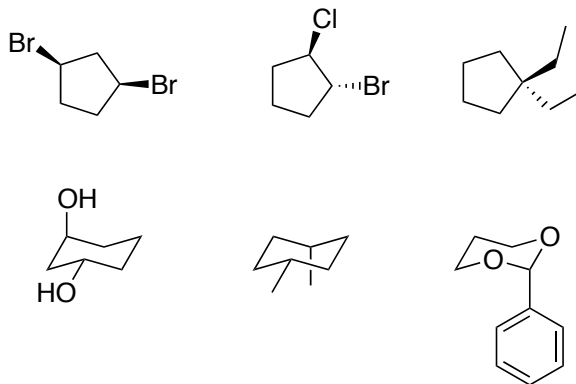
5. Draw (2S,2S)-2-bromo-3-chloropentane in a Newman projection (staggered conformation) looking down the C2-C3 bond.

Model time!

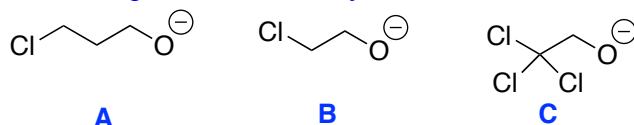
6. Draw a diastereomer of the structure shown.



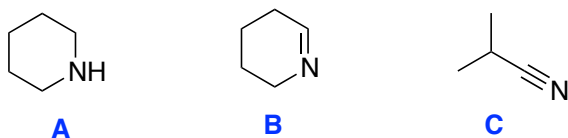
7. Circle the chiral molecule(s) and underline the meso compound(s):
 Model time!



8. Rank the bases in each group in increasing order of basicity (base strength):
 a. Read the questions carefully—be sure to answer all parts of the question

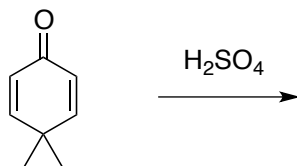


b.



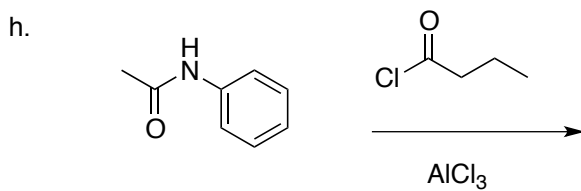
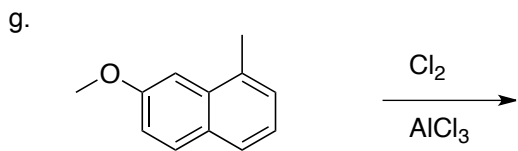
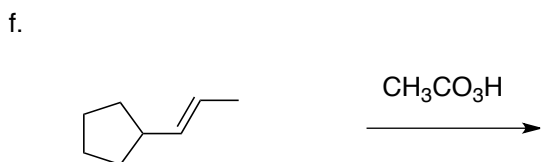
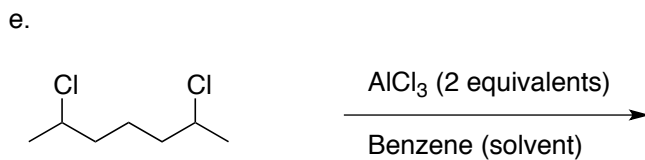
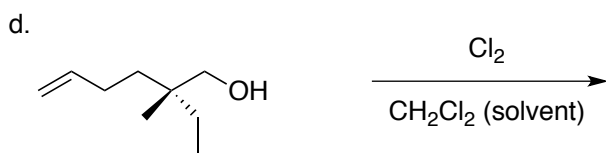
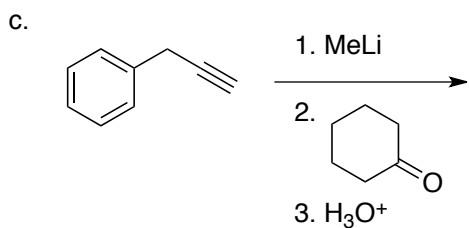
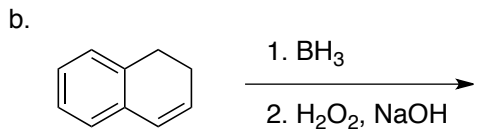
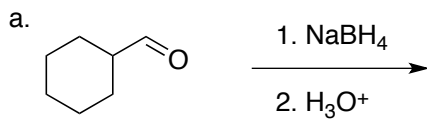
To answer these questions, refer back to the section on the notes about the factors that contribute to base stability.

9. Propose a mechanism for the following transformation, which gives a more stable constitutional isomer of the starting material.

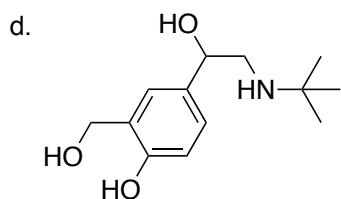
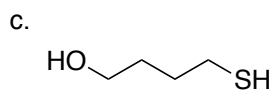
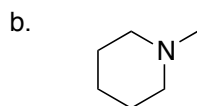
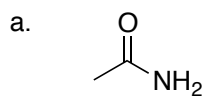


This is an example of a “challenge” question. To answer it, you have to draw from multiple parts of the course. In this case, you would have to pull in concepts from acid/base, resonance, rearrangements (covered in the Friedel-Crafts alkylation section), and aromaticity). I recommend that you do these harder questions at the end, once you are confident that you have answered the other questions as well as possible

10. Give the major organic product of each of the following transformations:



11. Draw the conjugate acid of each of the following compounds: **part d requires that you first determine the most basic atom, then protonate it.**



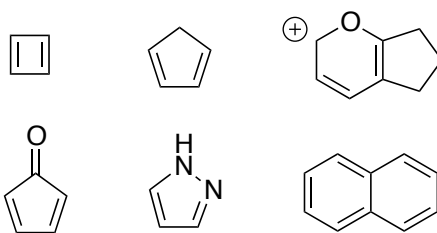
Ventolin (Salbutamol) - asthma drug

12. Circle the form of ventolin (above) that would be found in the body at physiological pH (7.4).

13. Draw the orbitals that show the location of lone pair(s) and π electrons for the following compound.

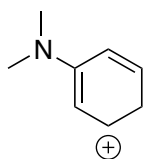


14. Circle the aromatic ring(s), underline the anti-aromatic ring(s), and do nothing with the non-aromatic ring(s).



15.

a. Draw the important resonance structures of the following ion.



Important resonance structures don't usually have more than two charges. Multiple charges usually means a less important (minor) structure.

- b. Label the major resonance structure.
c. Explain your choice in part b.

Remember that full orbitals (i.e., a complete octet) is more important than whether the molecule is neutral or charged.

16. For the following reaction:

a. Draw the mechanism and products.



Tip! Draw out the protons on the nitrogen so that you can show the N-H bond breaking (worth 1 point). Remember that mechanisms must start from electrons and point to an atom.

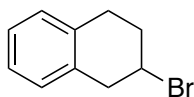
b. Predict the direction of the equilibrium.

c. Explain your choice in part b.

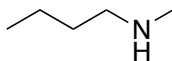
With any comparison, be sure to mention aspects of BOTH compounds/atoms/etc (don't just talk about one and not the other, or it's not a comparison).

17. Draw the starting materials that should be used to form each of the compounds below. One of the starting materials in each set should contain a π bond.

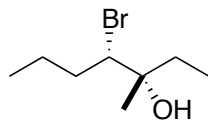
a.



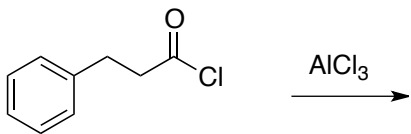
b.



c.



18. Give the full mechanism of the following reaction, including resonance structures.



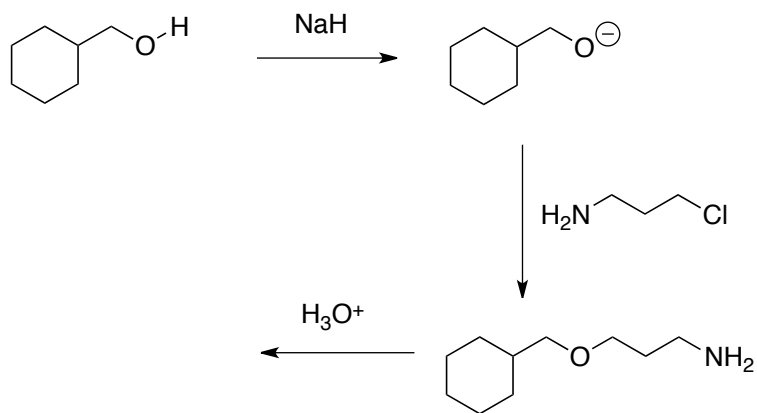
Remember that mechanisms must start from electrons and point to an atom.

Be sure to include formal charges ($\text{FC} = \# \text{ electrons in the neutral atom's valence} - \# \text{ bonds} - \# \text{ non-bonding electrons}$).

Eg, for O: $\text{FC} = 6 - 2 - 4 = 0$

19. Complete the mechanism for each step of the following reaction and predict the structure of the final product.

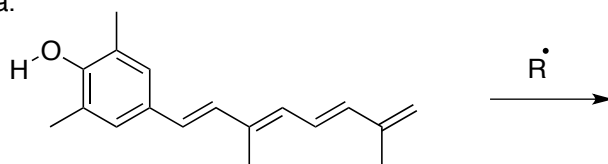
A great first step is to add in any lone pairs and identify which bonds have been broken/formed.



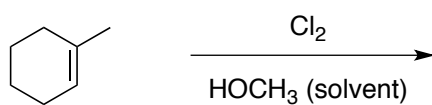
20. Give the full mechanism for each of the following reactions (show the major organic product only).

See mechanism tips on the previous page

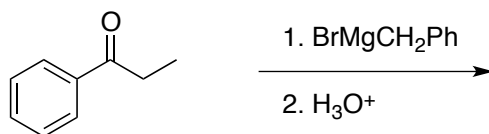
a.



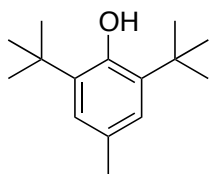
b.



c.

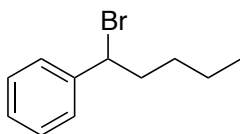


21. Propose a synthesis of the antioxidant BHT, shown below, from phenol (hydroxybenzene) and using any other reagents that you require. You must include a retrosynthesis.

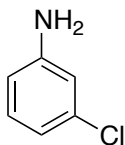


The answers show exactly what I would be looking for when marking synthesis questions. Follow the instructions given (i.e., if no mechanism is asked, no mechanism is required).

22. Propose a synthesis of the following compound from benzene and using any other reagents that you require.



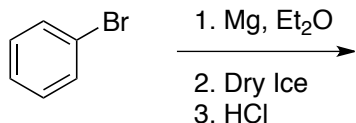
23. Propose a synthesis of the following compound from benzene and using any other reagents that you require. An analysis and brainstorming are also required. **Note that because an analysis and brainstorming are required that there will be marks allocated for these parts.**



24. BH_3 is stabilized for storage through a reaction with a solvent such as diethyl ether (Et_2O). Propose a mechanism for that reaction.

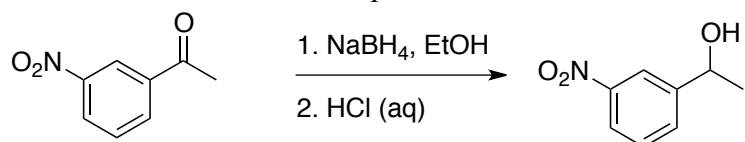
This is another “challenge” question. A good starting point is to draw out the Lewis structures and draw on your knowledge from the course. In this case, hybridization and acid/base reactions, plus formal charge, are key.

25. Consider the Grignard reaction of bromobenzene.



- Draw the Lewis structure of dry ice.
- The literature mp of benzoic acid is $122\text{ }^\circ\text{C}$. If you obtain a melting point of $115\text{ }^\circ\text{C}$, what does that tell you about your product?
- When the solution boils during this reaction, what is present in the bubbles? Name the molecule(s), as appropriate.
- Draw and label the apparatus used in that reaction.

26. Consider the reduction of nitroacetophenone:



Procedure: After adding a solution of 3M HCl to the reaction mixture, pour the mixture into a separatory funnel and rinse the flask with approximately 5 mL of dichloromethane (density = 1.32 g/mL). Extract the aqueous layer with 2 additional portions of 5 mL portions of dichloromethane and collect all the organic extracts in the same flask.

- a. Draw and label a diagram of the separatory funnel when the mixture (and dichloromethane) are first poured in.

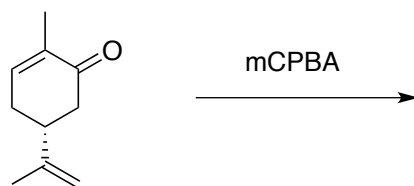
- b. Draw two mechanisms to explain the two key roles of the HCl.

- c. A solution of HCl(aq) contains almost no HCl. What are the species that are actually present?

Another “challenge” question. Best starting point again is to draw the Lewis structures of everything there (in this case, the HCl and the water) and try to figure out what could happen. Also consider the amounts of each species for this type of question.

27.

- a. Draw the mechanism for the reaction of carvone with mCPBA.



You should be able to draw the Lewis structure for all reagents and solvents used in the lab, especially ones that are part of the main reaction, such as mCPBA.

- b. Explain the regioselectivity of the reaction (i.e. why does one π bond react preferentially over the other)?
- c. When you did a TLC of the reaction mixture, you dipped the TLC plate in a solution of potassium permanganate (the purple solution). Why did the spots on the TLC change colour?
- d. This (R) enantiomer of carvone smells like spearmint, while the (S) enantiomer smells like caraway (a spice). Explain why there is a difference in smells when the structures are so similar.

1																		18																	
1A																		8A																	
1	H																	2	He																
Hydrogen	1.01																	Helium	4.00																
2	3	4															5	6	7	8	9	10													
Li	Be															B	C	N	O	F	Ne														
Lithium	6.94	Beryllium	9.01															Boron	10.81	Carbon	12.01	Nitrogen	14.01	Oxygen	16.00	Fluorine	19.00	Neon	20.18						
3	11	12															13	14	15	16	17	18													
Na	Mg															Al	Si	P	S	Cl	Ar														
Sodium	22.99	Magnesium	24.31	3	4	5	6	7	8	9	10	11	12	Aluminum	26.98	Silicon	28.09	Phosphorus	30.97	Sulfur	32.07	Chlorine	35.45	Argon	39.95										
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36																	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																		
Potassium	39.10	Calcium	40.08	Scandium	44.96	Titanium	47.87	Vanadium	50.94	Chromium	52.00	Manganese	54.94	Iron	55.85	Cobalt	58.93	Nickel	58.69	Copper	63.55	Zinc	65.39	Gallium	69.72	Germanium	72.61	Arsenic	74.92	Selenium	78.96	Bromine	79.90	Krypton	83.80
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																		
Rubidium	85.47	Strontium	87.62	Yttrium	88.91	Zirconium	91.22	Niobium	92.91	Molybdenum	95.94	Technetium	(98)	Ruthenium	101.07	Rhodium	102.91	Palladium	106.42	Silver	107.87	Cadmium	112.41	Indium	114.82	Tin	118.71	Antimony	121.76	Tellurium	127.60	Iodine	126.90	Xenon	131.29

Key

11	—	Atomic number
Na	—	Element symbol
Sodium	—	Element name
22.99	—	Average atomic mass*

Acid	Approximate pK _a
HSbF ₆	< -12
HI	-10
H ₂ SO ₄	-9
HBr	-9
HCl	-7
C ₆ H ₅ SO ₃ H	-6.5
(CH ₃) ₂ OH ⁺	-3.8
(CH ₃) ₂ C=OH ⁺	-2.9
CH ₃ OH ₂ ⁺	-2.5
H ₃ O ⁺	-1.74
HNO ₃	-1.4
CF ₃ CO ₂ H	0.18
HF	3.2
C ₆ H ₅ CO ₂ H	4.21
C ₆ H ₅ NH ₃ ⁺	4.63
CH ₃ CO ₂ H	4.75
H ₂ CO ₃	6.35
CH ₃ COCH ₂ COCH ₃	9.0
NH ₄ ⁺	9.2
C ₆ H ₅ OH	9.9
HCO ₃ ⁻	10.2
CH ₃ NH ₃ ⁺	10.6
H ₂ O	15.7
CH ₃ CH ₂ OH	16
(CH ₃) ₃ COH	18
CH ₃ COCH ₃	19.2
HC≡CH	25
H ₂	35
NH ₃	38
CH ₂ =CH ₂	44
CH ₃ CH ₃	50