

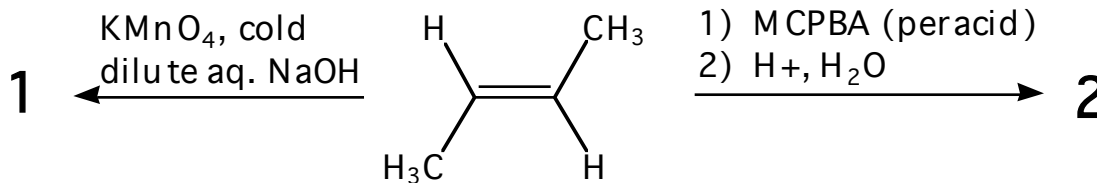
Chem 2600 Final Exam 2004, April 21st, 9:00 am to 12:00 am

You are permitted the use of a model kit, cards prepared by hand and by yourself and a periodic table. Print and sign your name below. Your signature indicates that you agree not to divulge or discuss the contents of this exam in any way until the final marks have been released. 92 marks available.

Name: _____ Signature: _____

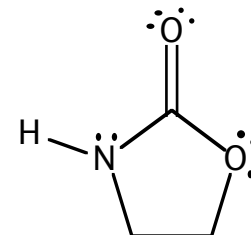
Question One (5 marks)

Give the structures of products 1 and 2 below and indicate clearly how and why they are different.



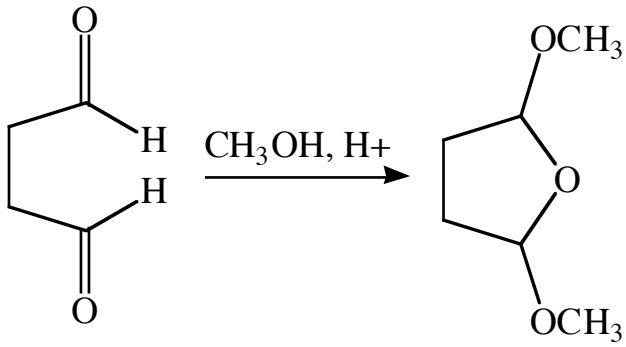
Question Two (4 marks)

- i) The carboxylic acid derivative shown to the right is a carbamate. Speculate as to its reactivity in nucleophilic acyl substitution reactions relative to the ester and amide functional groups. Be sure to show any relevant resonance structures.

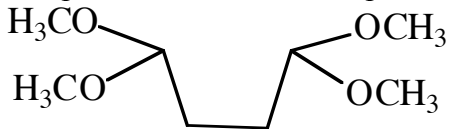


Question Three (6 marks)

Give a mechanism for the following transformation.

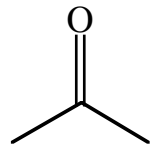


The product below is also a possible product of this reaction, but it is not observed. Why not?



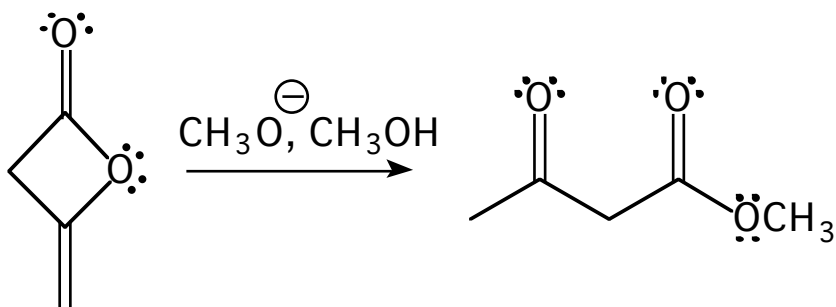
Question Four (1 mark)

In the S_N2 reaction, the nucleophile attacks the backside of the carbon-leaving group bond. Keeping this in mind, sketch an arrow on one (and only one) of the diagrams given showing the optimal path of attack for a nucleophile in the nucleophilic addition to a carbonyl.



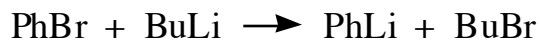
Question Five (4 marks)

Propose a mechanism for the following reaction of methanol and diketene.

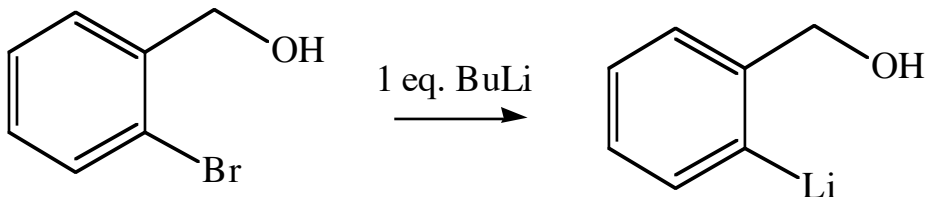


Question Six (4 marks)

We learned in class that organolithium compounds can be prepared from alkyl and aryl halides and lithium metal. There is an additional way to prepare aryllithiums using a process known as metal-halogen exchange. The following reaction shows how phenyllithium can be prepared from bromobenzene and 1 equivalent of butyllithium:



This technique fails when applied to the bromobenzyl alcohol shown below.

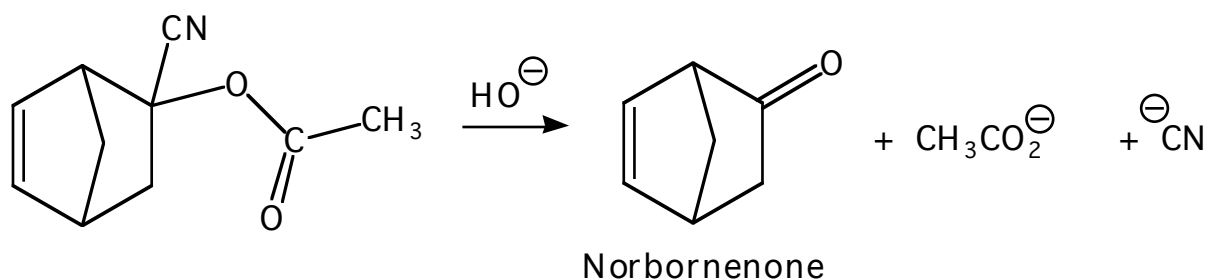


i) Why does this fail?

ii) Offer a solution to this problem.

Question Seven (7 marks)

i) Give a mechanism for the following reaction.

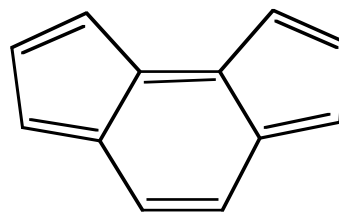
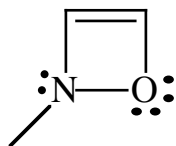
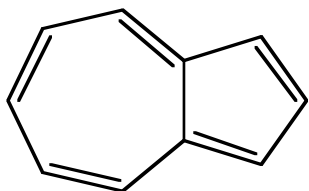


ii) The reactant above is the product of a Diels-Alder reaction. Give the structures of the diene, dienophile and the endo diastereomer (endo with respect to the CN functional group) of the product.

iii) In principle, norbornenone can be made directly by Diels-Alder reaction of what dienophile? (In fact, this dienophile is unreactive in Diels-Alder reactions.)

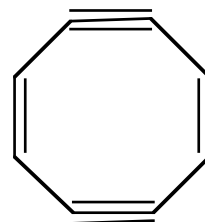
Question Eight (6 marks)

i) For each of the following molecules, indicate whether they would be expected to be aromatic or antiaromatic. Assume all are planar. Briefly give your reasoning.



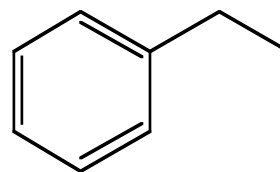
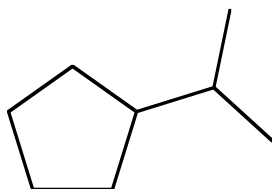
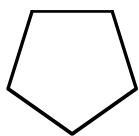
ii) A guest speaker came to Lethbridge this term and told me about a remarkable compound he had prepared. It contains the substructure shown to the right – a cyclooctadienediyne. This ring is planar and *antiaromatic*.

Is this what you'd expect at first glance? Explain. Think carefully about the pi orbitals involved and explain why this molecule is antiaromatic.



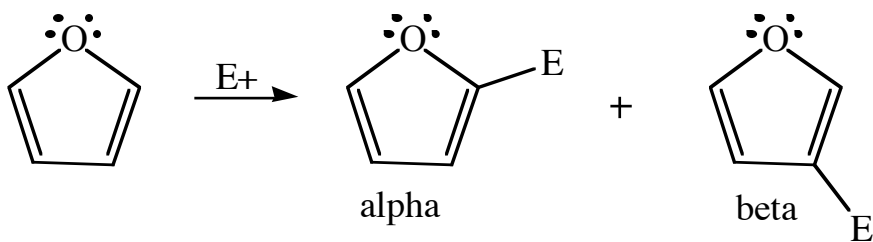
Question Nine (6 marks)

Which of the following reactants will give mixtures of monobrominated products under conditions of radical bromination? Explain all cases.



Question Ten (6 marks)

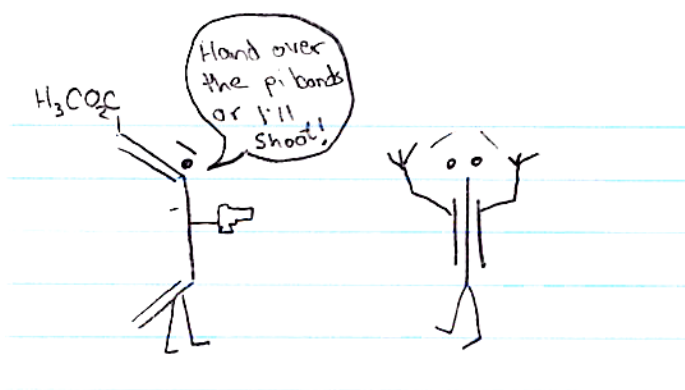
Furan, the reactant below, undergoes electrophilic aromatic substitution reactions analogous to benzene. Give a mechanism for the formation of both products that shows all resonance structures of the intermediates and determine which of the two products will be favoured.



Question Eleven (5 marks)

I found the cartoon to the right on my lectern after class one morning. It alludes to the terms “good” and “bad” as applied to substituents and the reactivity of dienes and dienophiles in the Diels-Alder reaction. As opposed to their moral character, which has little relevance in organic chemistry. But I digress...

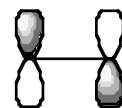
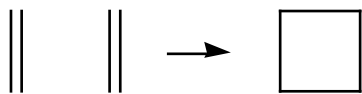
What kind of substituents make a diene good and a dienophile good? Explain briefly in orbital terms the effect of substituents.



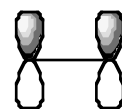
What happens when good dienes go bad

Question Twelve (4 marks)

i) Is the dimerization of ethylene to form cyclobutane a thermally allowed process? Explain.



ii) This reaction can be done photochemically (i.e. by shining UV light on it). How does this work?

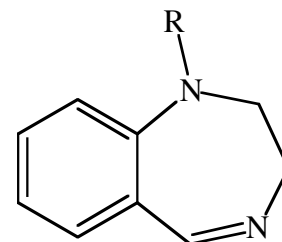
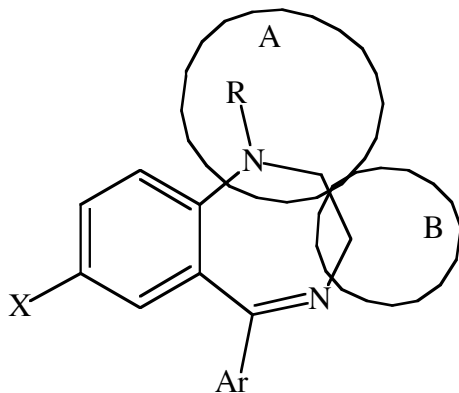


Question Thirteen (7 marks)

Shown below is the skeleton of a benzodiazepine. Several analogues (Valium, for example) have anxiolytic (anti-anxiety) activity. Structure activity relationships indicate the following structural features enhance activity.

- Ar should be a substituted aromatic that is electron-withdrawing but as small as possible.
- X should be an o,p directing group but electron-withdrawing
- Regions A and B should both be polar but lack H-bond donor groups.

- i) Design an analogue of this compound that you think will exhibit enhanced activity. Draw it on the skeleton provide above. I'd use pencil.



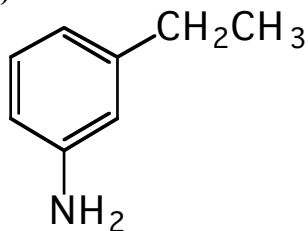
- ii) What is the basis for the biological activity of certain organic compounds?

Question Fourteen: Syntheses

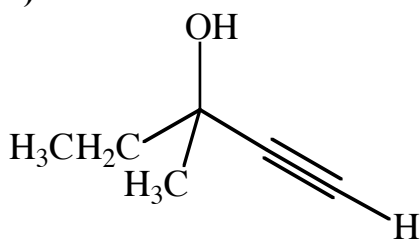
Fine print: you may use benzene, toluene (PhCH₃), phenol (PhOH), and any organic reactant of four carbons or less. If you use a Grignard or alkyllithium you must show how it is prepared. Be as complete with reaction conditions as possible. You may use common acronyms for reagents rather than formulae. If your catalyst or solvent has more than four carbons, that's OK. Just the molecules that you use to make up your target are limited to four carbons. Pay attention to issues of relative stereochemistry.

Part 1 (12 marks): Answer on this page. These are short syntheses of one to four steps. I will mark them all and take the best 4.

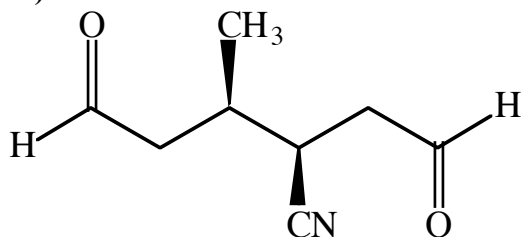
i)



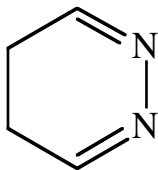
ii)



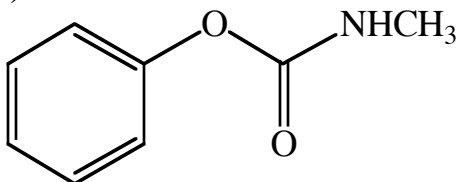
iii)



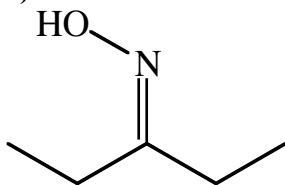
iv)



v)



vi)



Part 2 (15 marks): Answer in the booklet provided. Do any three.

