Second Midterm – CHM1321-B

Professor Sandro Gambarotta

Date:_29 March 2018 Length:__80 min_____ Last Name: ________________________

First Name:_________________________

Student #________________

- **Instructions:**
  - **Molecular Model Kit recommended**
  - **Closed book exam**

Read carefully:

By signing below, you acknowledge that you have read and ensured that you are complying with the above statement.

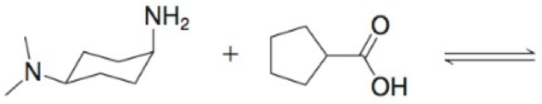
Cellular phones, unauthorized electronic devices or course notes (unless an open-book exam) are not allowed during this exam. Phones and devices must be turned off and put away in your bag. Do not keep them in your possession, such as in your pockets. If caught with such a device or document, the following may occur: you will be asked to leave immediately the exam, academic fraud allegations will be filed which may result in you obtaining a 0 (zero) for the exam.

Signature:__________________________________

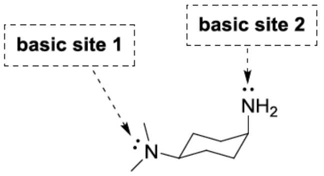
Question	scores
1	…. / 2
2	…. / 2
3	…. / 5
4	…. / 3
5	…. / 2
6	…. / 4
7	…. / 4
8	…. / 3
9	…. / 5

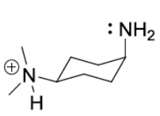
Total ….. / 30 …./15

1. (2 points)
Predict the product of the following acid-base reaction and draw a curved-arrow mechanism showing its formation. Note that there are multiple basic sites.

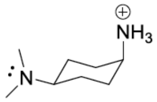


Answ.



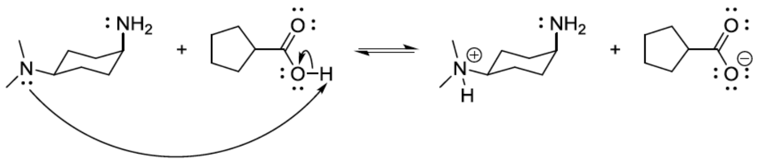


CA1



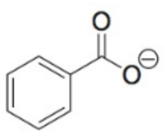
CA2

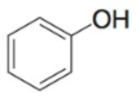
The only significant difference between the two conjugate acids is the number of alkyl groups attached to the N bearing the positive charge. Since the weakly electron-donating abilities of the methyl groups will better stabilize the positive charge, **CA1** is more stable than **CA2**, making the N at **site 1** more basic than **site 2**. The reaction mechanism and products can now be drawn as follows:

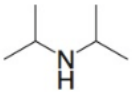


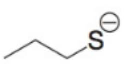
2. (2 points) *pKa data are at the end of this booklet*

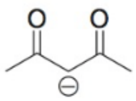
Use pK_a data to determine which of the following bases would react with acetic acid (CH_3CO_2H) to yield a reaction that would favour the products.



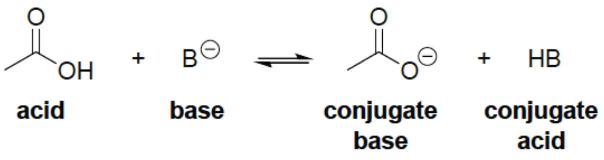




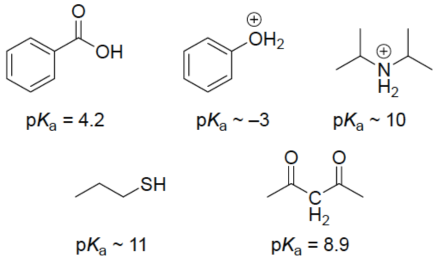




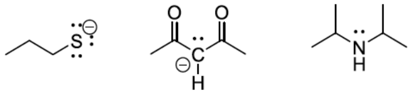
answ



For the above equilibrium to favour the products, the conjugate acids formed as products must be weaker than the reactant acid, acetic acid (i.e., the pK_a of HB, the conjugate acid of the base, must be lower than 4.8, the pK_a of acetic acid). The conjugate acids of the five bases and their pK_a are



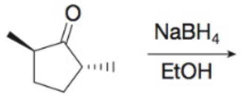
Therefore, the three bases that would react with acetic acid and favour the products at equilibrium are



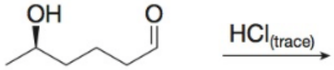
3. (5 points)

Predict the products of the following reactions, including all possible stereoisomers. Indicate which stereoisomer, if any, the reaction will favour.

a)

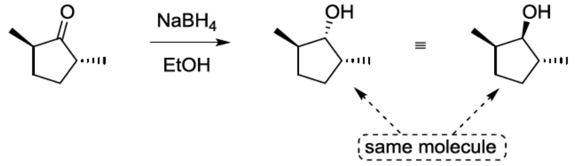


b)

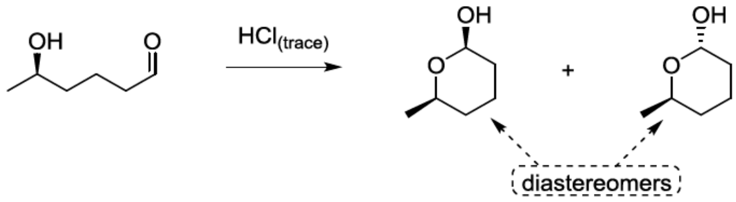


answ.

Due to the symmetry of the molecule, addition on either face is equally likely and leads to the same stereoisomer.



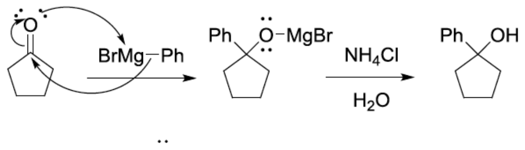
There is no preferred side for the nucleophilic attack.



4. (3 points)
Predict the product formed when cyclopentanone is treated according to the sequence below.
Write the mechanism

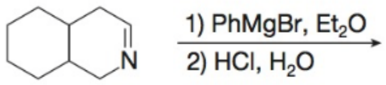
$PhMgBr$ in THF, then NH_4Cl in H_2O

answ.

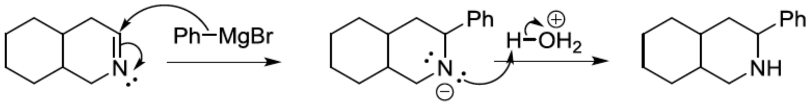


5. (2 points)

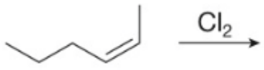
Draw a mechanism and predict the product of the following reaction:

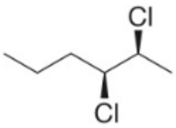


answ.

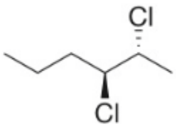


6. (4 points)
Identify the major product of the following reaction (Use the models!)

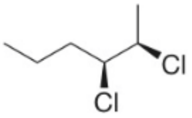




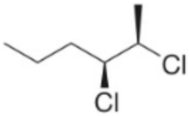
A



B



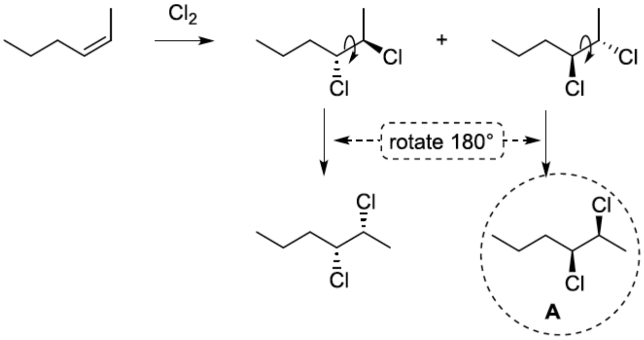
C



D

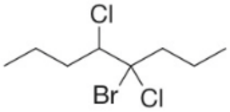
Answ.

Add the chlorine atoms *trans* to each other, then rotate into the conformation shown.



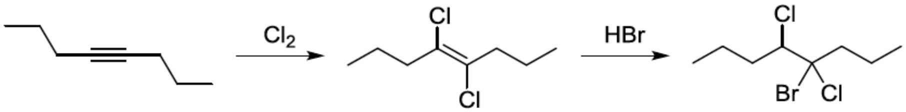
7. (4 points)

Show how you could synthesize the following molecule from an alkyne of your choice.

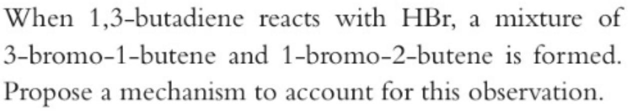


answ.

To add three halogens to a triple bond, a hydrohalogenation step and a halogenation step are required. There is no stereochemistry to consider, so Cl_2 addition followed by a HBr addition would give the desired product.

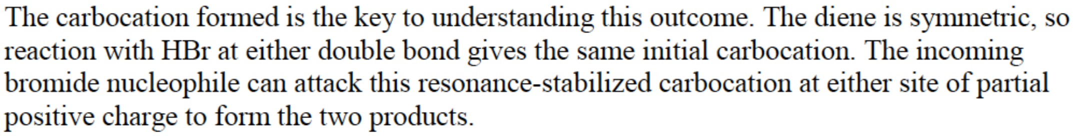


8. (3 points)

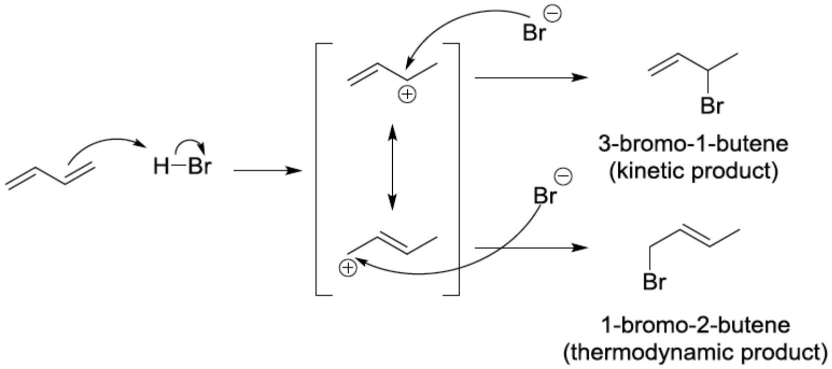


When 1,3-butadiene reacts with HBr, a mixture of 3-bromo-1-butene and 1-bromo-2-butene is formed. Propose a mechanism to account for this observation.

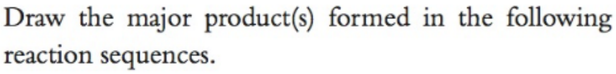
answ.



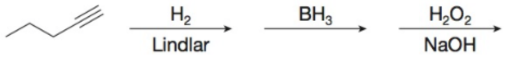
The carbocation formed is the key to understanding this outcome. The diene is symmetric, so reaction with HBr at either double bond gives the same initial carbocation. The incoming bromide nucleophile can attack this resonance-stabilized carbocation at either site of partial positive charge to form the two products.



9. (5 points)

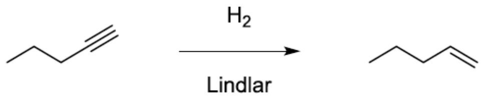


Draw the major product(s) formed in the following reaction sequences.

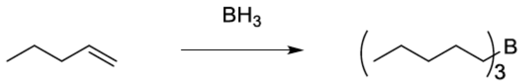


answ.

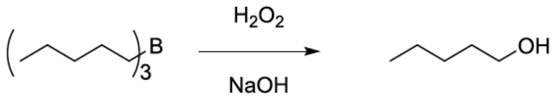
The first step is hydrogenation, with a poisoned catalyst giving only a single reduction.

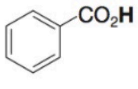
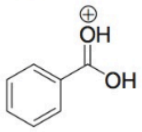
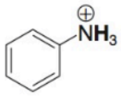
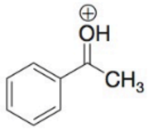
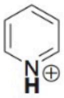
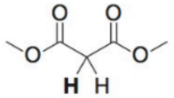
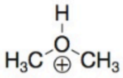
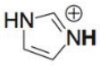
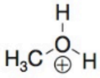
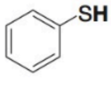
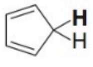
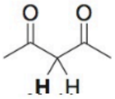
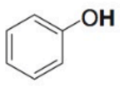
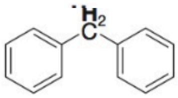
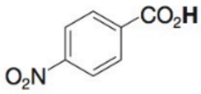
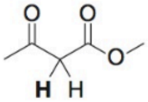
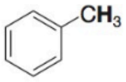
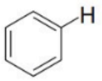


Then, the resulting alkene undergoes hydroboration.



Oxidative removal of the borane gives the final alcohol product.



Compound	pK_a	Compound	pK_a	Compound	pK_a
HBr	–9		4.2	$CH_2(C{\equiv}N)_2$	11
	–8		4.6	H_2O_2	11.6
	–6	CH_3CO_2H	4.8	CCl_3CH_2OH	12.2
HCl	–7		5.2		13
	–3.8	H_2CO_3	6.4	$CHCl_2CH_2OH$	12.9
H_2SO_4	–3		6.9	CH_3CHO	13.6
	–2.2	H_2S	7.0	CH_2ClCH_2OH	14.3
CH_3SO_3H	–2.6		7.8		15
H_3O^+	–1.7	$CH_3C(O)OOH$	8.2	CH_3OH	15.5
HNO_3	–1.3		9	H_2O	15.7
CF_3CO_2H	–0.2	$NH_4{}^+$	9.2	CH_3CONH_2	15.1
CCl_3CO_2H	0.6	$H{-}C{\equiv}N$	9.4	$(CH_3)_3COH$	17
$CHCl_2CO_2H$	1.3	$^-CO_2CH_2NH_3{}^+$	9.7	CH_3COCH_3	20
$CH_2(NO_2)CO_2H$	1.6	$(CH_3)_3NH^+$	9.8	$HC{\equiv}CH$	24
H_3PO_4	2.1		10.0	$N{\equiv}C{-}CH_3$	25
CH_2ClCO_2H	2.9	CH_3CH_2SH	10.5		34
HF	3.2	CH_3NO_2	10.3	H_2	36
	3.4		11	NH_3	38
$CH_3OCH_2CO_2H$	3.6				41
HCO_2H	3.8				43
				$CH_2{=}CH{-}CH_3$	43
				$CH_2{=}CH_2$	44
				CH_3CH_3	48