Name ____________________________

Chem 204 Midterm 2

March 27, 2020

Show all of your work for full marks.

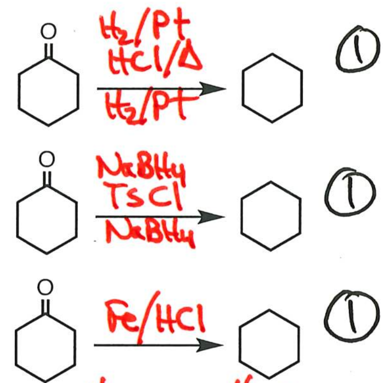
(3) 1) Mark each statement as **T** (True) or **F** (False). No explanation required.

a) Certain Diels-Alder reactions could benefit from shining light on them. __F__ - See MO reasons (1)

b) Margarine is dyed with coloured molecules extracted from butter. __F__ (1)

c) A diazonium salt like R-N_2Cl has overall acidic properties. __T__ (1)

(3) 2) From the grab-bag of reagents, write three (3) ways of reducing the C=O group. <u>You may only use a reagent a maximum of two times (that's 2) in this entire question.</u> It may take any number of reagents to do the job per reaction.

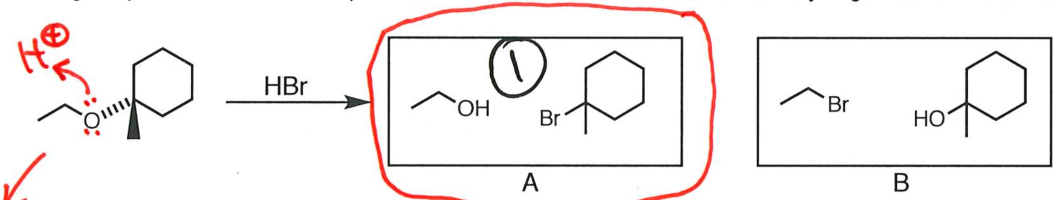


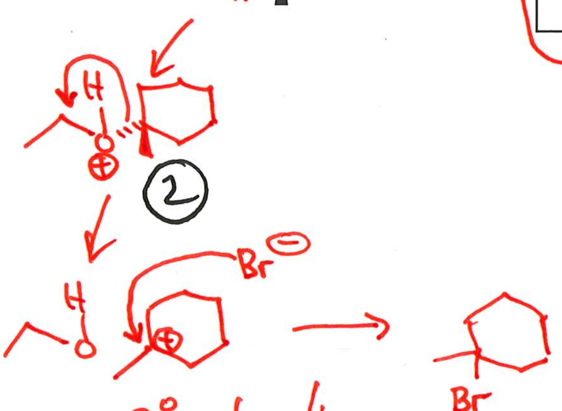
there are others...

Grab-Bag of Reagents

Pt
HCl
$NaBH_4$
Fe
TsCl
HONO
NaOH
O_3/Zn
$SOCl_2$
$KMnO_4$
H_2

(5) 3) Below is an example of an ether cleavage reaction. Write the mechanism for this reaction. Circle either the A <u>or</u> B box containing the products that form. Explain if this is an S_N2 or S_N1 reaction. Bonus if you give me two reasons.





3° carbocation
= flat
∴ Br⊖ attacks both faces of carbocation

1) S_N1 reaction = stable 3° carbocation (1) (1)

2) " " = no stereochem in products due to

bonus (+1)

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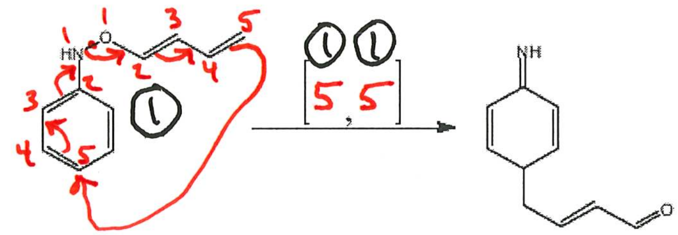
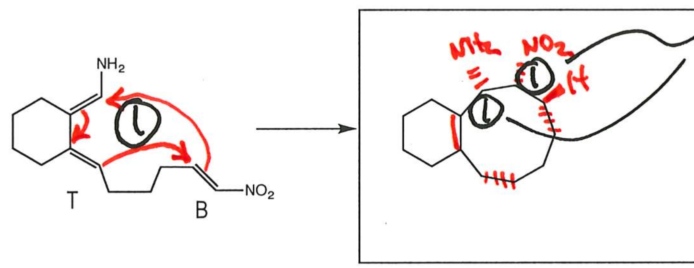
(3) 4) Fill in the square brackets and briefly explain how you got your answer. Bonus: What is this type of reaction called?

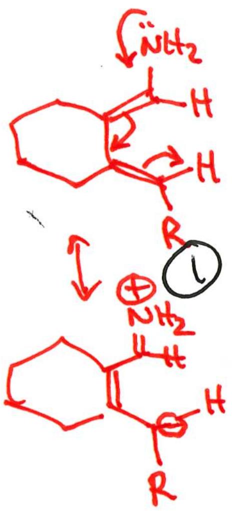
sigmatropic rearrangement (+1)

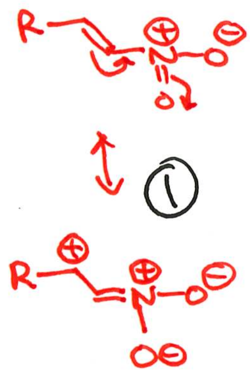


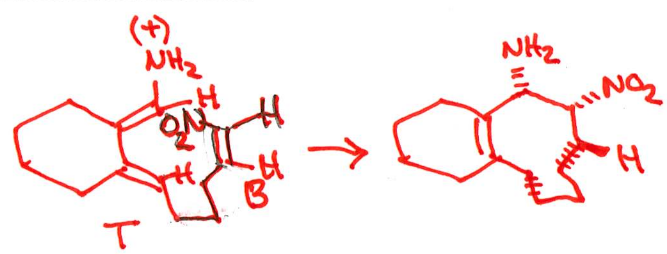
(5) 5) This is an intramolecular Diels-Alder reaction. The diene part is off the ring. Show the mechanism and all the reasoning "layers" (not HOMO/LUMO) and draw the product showing stereochemistry in the box. The diene is on top (T), dienophile is on bottom (B). It's not easy drawing large membered rings so let me give you a bit of a headstart on the product.

stereochem & position



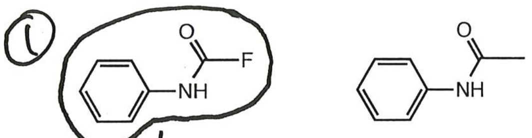


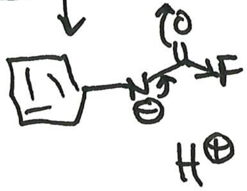




most acidic (1)

(3) 6) Circle the molecule having the H atom (shown) with the lowest pK_a. Very briefly explain why.





stabilized additionally by inductive FX (1)

DBE = 5 (1) $\overset{O}{\parallel}$–CH_3 (1) conj C=O str (1) oop bend = para subst (1) aromatic CH (1)

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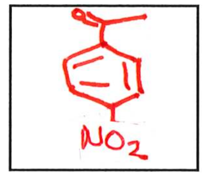
(7) 7) Compound **A** was stirred with NaOI/base to give a brilliant yellow ppt. **A** was stirred with $SnCl_2$ followed by HONO/H^+ and finally NaBr to yield compound **B** (C_8H_7OBr). The ^{13}C 135° DEPT NMR spectrum of **B** showed peaks at 132(+), 130(+) and 27(+) ppm and its partial IR spectrum showed a large band at 1685 cm^{-1} and 800 cm^{-1}. Compound **B** was reacted with LDA then CH_3OTs to give compound **C**. The ^1H NMR spectrum of **C** showed two coupled doublets between 7-8 ppm, a quartet at 2.1 ppm and triplet at 1.0 ppm. Explain **ALL** the data and draw the structures for **A**, **B** and **C** below.

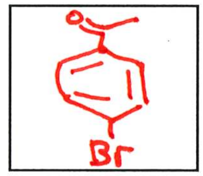
CH_3 (1) para

Ketonic CH CH_2CH_3 (1)

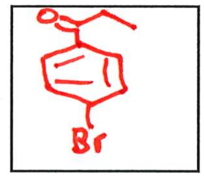
As you can see, getting 4 marks for the clues isn't a problem.



A (1)

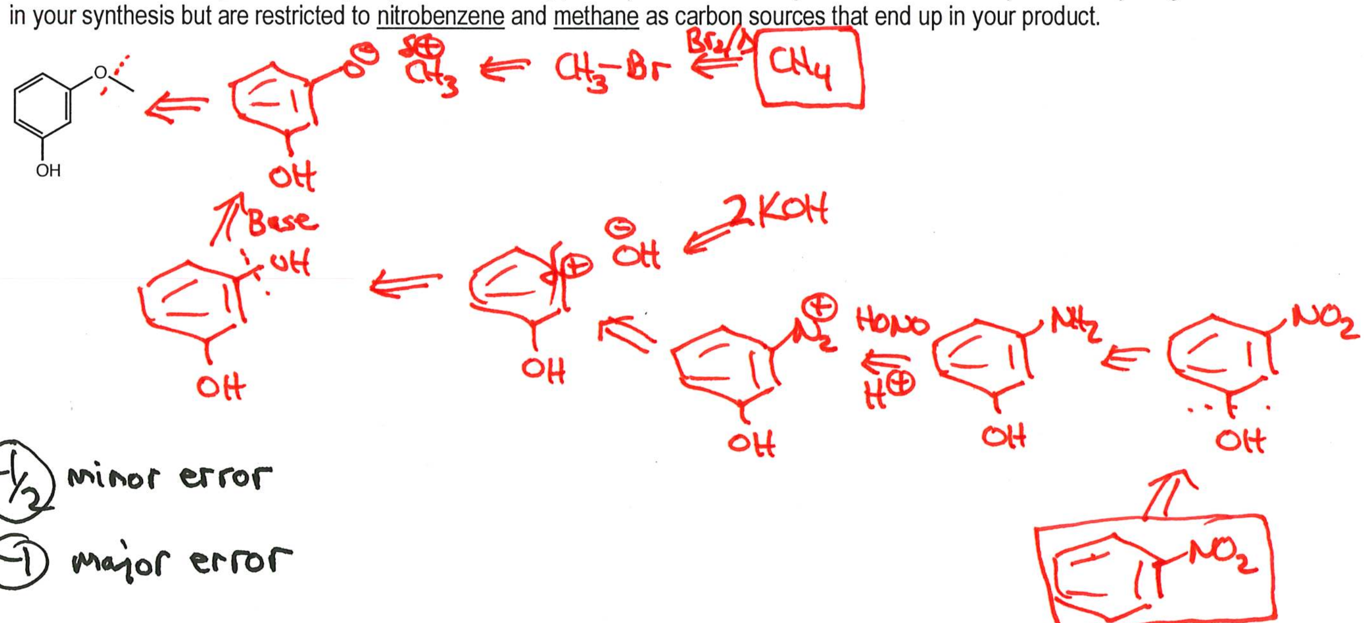


B (1)



C (1)

(4) 8) Demonstrate a retrosynthetic analysis (disconnection approach) to make the target molecule. You may invoke any reagent in your synthesis but are restricted to nitrobenzene and methane as carbon sources that end up in your product.



(-½) minor error

(-1) major error

$H_2O_2 + H^{\oplus} \Longrightarrow OH^{\oplus}$

(1) **Bonus**: How many online lectures did I post to you so far? ____4____ (1)