Columbia University **92CORG13.DOC CHEM S3443D**
Summer 1992
Professor Grace B. Borowitz Exam No. **3** June 25, 1992
Name: _____ ***Grade:*** ___

Please use a **non-red** pen. Answer questions in the provided space. If you write any answers on the back of the page, indicate this on the **front** of that page. Points appear in parentheses **( ).** ***Good Luck!***

Question		**Max. Pts.**	**Points**
1. 3 + 9 + 3 + 5	**=**	**20**	
2. 4 (3) + 3 + (2 + 3)	**=**	**20**	
3. 4 + 3 + 3 + 6 + 4	**=**	**20**	
4. 5 + 5 + 6 + 6 + 3	**=**	**25**	
5. 5 (3)	**=**	**15**	
Total	**=**	**100**	

1. **(20)** a. Which of the following correctly lists the compounds in order of decreasing acidity?

(1) $H\text{-}C{\equiv}C\text{-}H$ > H_2O > NH_3 > $CH_3{-}CH_3$

(2) H_2O > NH_3 > $H\text{-}C{\equiv}C\text{-}H$ > $CH_3{-}CH_3$

(3) H_2O > $H\text{-}C{\equiv}C\text{-}H$ > NH_3 > $CH_3{-}CH_3$

(4) $CH_3{-}CH_3$ > $H\text{-}C{\equiv}C\text{-}H$ > NH_3 > H_2O

(5) $CH_3{-}CH_3$ > $H\text{-}C{\equiv}C\text{-}H$ > H_2O > NH_3

b. (1) Draw the **6** non-cyclic isomers for a compound with the molecular formula $\mathbf{C_5H_{10}}$. Name them by IUPAC nomenclature, including ***(E)*** or ***(Z)***designation when appropriate,

(2) Rank them in decreasing order of stability, from most stable to least stable.

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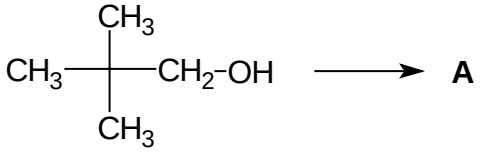
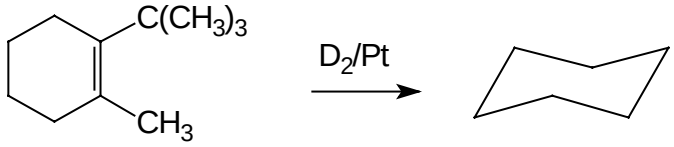
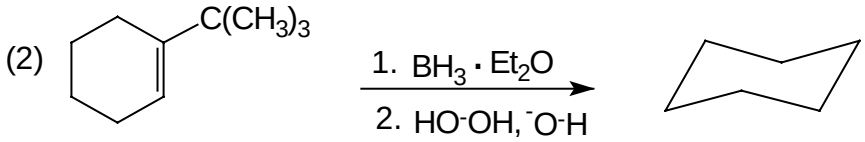
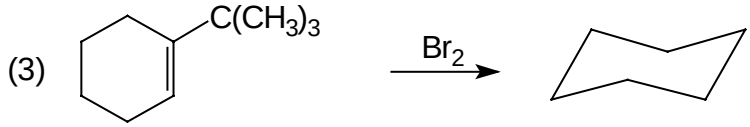
(3) Show the step-by-step mechanism, using arrows to show the direction of electron flow, and the reagents needed to convert the following alcohol into the most stable isomer of $C_5\mathbf{H_{10}}$, compound **A**.

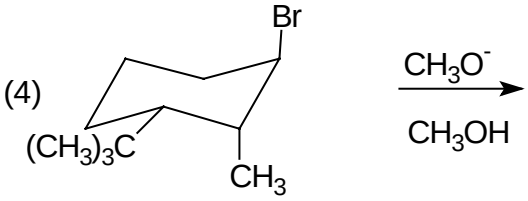


2. **(20)** Show the products of the following reactions and state the mechanistic interpretation with regard to type of addition or elimination, ***syn or anti***. Show the particular constitutional or stereoisomer of the cyclohexane or cyclohexene products in their proper conformation in parts (1)-(3).

(1)


(2)


(3)


(4)


b. Your task is to convert 2-bromobutane to 1-butene in highest yield. Which reagents would you use?

(1) KOH/H_2O (2) KOH/CH_3OH (3) CH_3ONa/CH_3OH
(4) CH_3CH_2ONa/CH_3CH_2OH (5) $(CH_3)_3COK/(CH_3)_3COH$

c. Compute **ê**, the index of hydrogen deficiency, for the molecule $\mathbf{C_{10}H_8}$. Draw **1** molecule with just such a molecular formula. Show your calculation.

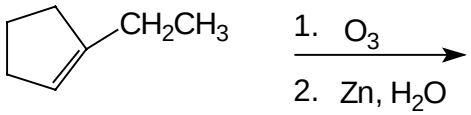
3. **(20)** a. Which alkene would be most reactive towards acid-catalyzed hydration? **Draw the structures** for each of the alkene molecules listed below to guide you in answering the question. Then, state **why** you chose your answer for the most reactive alkene in this reaction.

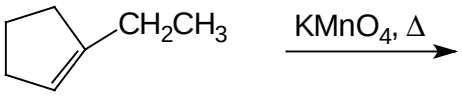
(1) 1-pentene (2) *(Z)*-2-pentene (3) *(E)*-2-pentene (4) 2-methyl-2-pentene

(5) *(Z)*-4-methyl-2-pentene (6) *(E)*-4-methyl-2-pentene (7) 3-methyl-1-pentene

Why?

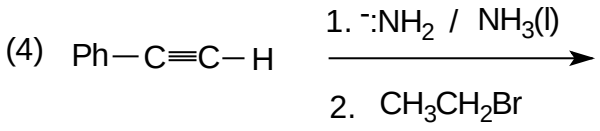
b. Fill in the missing reactants, reagents/conditions, intermediates, and products in the following reaction sequences.

(1) 

(2) 

(3) 

name this polymer:_____

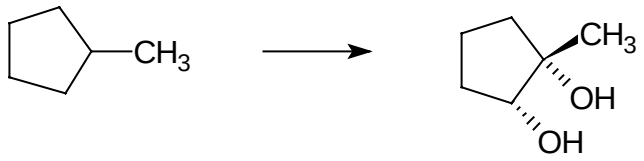
(4) 

4. **(25)** a. Complete the following conversions using any inorganic or organic reagents and conditions as needed. Note that more than one step may be needed and that working backwards is a good idea.

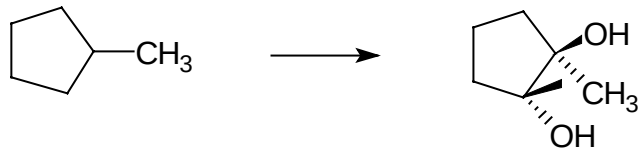
(1) $(CH_3)_3C\text{-}CH_2\text{-}CH_2\text{-}Br \longrightarrow (CH_3)_3C\text{-}CH(OH)\text{-}CH_3$

(2) $(CH_3)_3C\text{-}CH_2\text{-}CH_2\text{-}Br \longrightarrow (CH_3)_3C\text{-}CH_2\text{-}CH_2\text{-}OH$

(3)



(4)



b. Which reaction of an alkene proceeds with anti addition?

(1) Hydroboration/Oxidation (2) Bromination (3)Permanganate Oxidation

(4) Hydrogenation

(5) Epoxidation

5. **(15)** a. A method for converting ***trans*-2-butene** into ***cis*-2-butene** would be:

(1) *trans*-2-butene $\xrightarrow[(P\text{-}2)]{Ni_2B + H_2}$

(2) *trans*-2-butene $\xrightarrow[CCl_4]{Br_2}$ $\xrightarrow[NH_3(l)]{2\ NaNH_2}$ $\xrightarrow[NH_3(l)]{Na}$

(3) *trans*-2-butene $\xrightarrow[\Delta]{+ H^+}$

(4) *trans*-2-butene $\xrightarrow[CCl_4]{Br_2}$ $\xrightarrow[NH_3(l)]{2\ NaNH_2}$ $\xrightarrow[(P\text{-}2)]{H_2/Ni_2B}$

(5) none of these

b. An unknown compound, **B**, has the molecular formula $\mathbf{C_7H_{12}}$. On catalytic hydrogenation 1 mole of **B** absorbs 2 moles of H_2 and yields 2-methylhexane. When **B** is treated with a solution of $Ag(NH_3)_2OH$, a precipitate forms; an analysis of the precipitate shows that it contains silver, and treatment of the precipitate with dilute HNO_3 regenerates B. Which compound represents **B**?

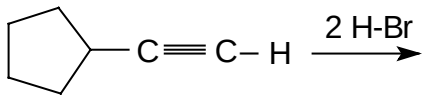
(1) $CH_3CH_2CH_2CH_2CH_2-C\equiv C-H$ (2) $CH_3-C\equiv C-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(3) $CH_2=CH-CH=CH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ (4) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-C\equiv C-H$

(5) $CH_2=C(CH_3)-CH_2-CH_2-CH=CH_2$

c. Complete the following reactions.

(1) $CH_3CH_2^-C\equiv C-H \xrightarrow[H_2SO_4\ ,\ H_2O]{HgSO_4}$

(2)  $\xrightarrow{2\ H\text{-}Br}$

d. Contrast **atactic and stereoregular (isotactic and syndiotactic) polystyrene** with regard to physical characteristics and nature of the chiral centers. Show reagents and equation for the Ziegler-Natta type of polymerization, by which the stereoregular polymer is made.

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