Columbia University C99ORG14.DOC S3443D Summer 99
Professor Grace B. Borowitz Exam No. 4 - Final July 1, 1999

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	Points	Max. Points	Points Earned
1.	**3 + 3 + 4**	**= 10**	
2.	**3 + (6 + 2 + 2) + 2.5 + 2.5**	**= 18**	
3.	**3 + (5 + 5)+5**	**= 18**	
4.	**4 + 2 + 4 + 6**	**= 16**	
5	**(2 + 2) + 3 + 3**	**= 10**	
6.	**2 + 2 + 2 + 2 + 2 + 2**	**= 12**	
7.	**2 + 2 + 2 + 2**	**= 08**	
8.	**2 + 2 + 2 + 2**	**= 08**	
Total		**= 100**	

1. **(10) a.** The conversion of **$(CH_3)_3C$-CH=CH_2** to **$(CH_3)_3C$-CH(OH)-CH_3** is best accomplished in the laboratory with which set of reagents?

(1) First B_2H_6, then H_2O_2 in aqueous NaOH (2) Dilute cold aqueous $KMnO_4$ containing NaOH
(3) Hot aqueous NaOH (4) Aqueous $Hg(OAc)_2$, then aqueous $NaBH_4$

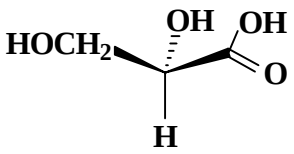
3

b. Which of the following substances does **NOT** function as a Lewis Acid (electrophile)?

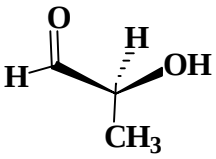
(1) $(CH_3)_3C^+$ (2) BF_3 (3) $:N(CH_2CH_3)_3$ (4) $AlBr_3$

3

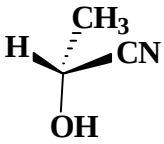
c. Which molecule has the ***(S)*** configuration? Show how you arrived at your answer for assigning the ***(S)*** configuration.



(1)



(2)



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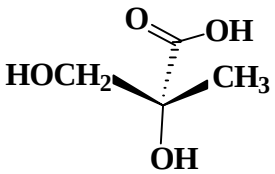
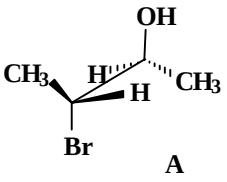


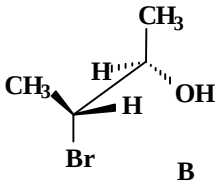
(4)

4

2. **(18)** a. What is the stereochemical relationship between the following molecules?



A



B

(1) conformers (2) identical (3) diastereomers (4) enantiomers

3

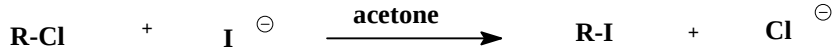
b. Name the molecules **A** and **B** according to ***IUPAC*** nomenclature. Label the chiral carbons in the compounds above ***(R)*** or ***(S)*** according to Cahn-Ingold-Prelog Sequence Rules and include those designations in their names. Also, designate **A** and **B** according to the appropriate descriptive terms from the following selections: ***meso, dl, erythro (dl),*** or ***threo (dl)***.

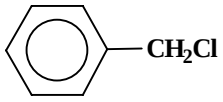
6

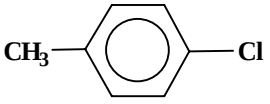
2 **A** _____

2 **B** _____

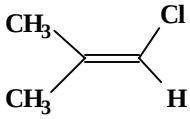
c. Which of the compounds below would react most rapidly with iodide ion in the S_N2 reaction illustrated below?



(1) 

(2) 

(3) $(CH_3)_2CH\text{-}CH_2\text{—}Cl$

(4) 

2.5

d. Of the following, which is the best method to prepare *t*-butyl methyl ether?

(1) $(CH_3)_3C\text{-}OH \xrightarrow{CH_3OH}$

(2) $CH_3OH \xrightarrow{K}$ $\xrightarrow{(CH_3)_3C\text{-}Cl}$

(3) $(CH_3)_3C\text{-}OH \xrightarrow{K}$ $\xrightarrow{CH_3\text{-}I}$

(4) $CH_3\text{-}I \xrightarrow{Mg}$ $\xrightarrow{(CH_3)_3C\text{-}OH}$

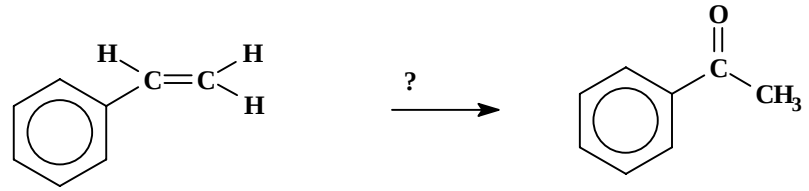
2.5

3. **(18)** a.. The **more stable chair** conformation of ***trans*--3-methyl-1-*tert*-butylcyclohexane** has:

(1) both alkyl groups in axial positions.
(2) both alkyl groups in equatorial positions.
(3) an axial methyl group and an equatorial ***tert***-butyl group.
(4) an axial ***tert***-butyl group an equatorial methyl group.

3

b. Carry out the following conversion **2** different ways using any needed organic and inorganic reagents.



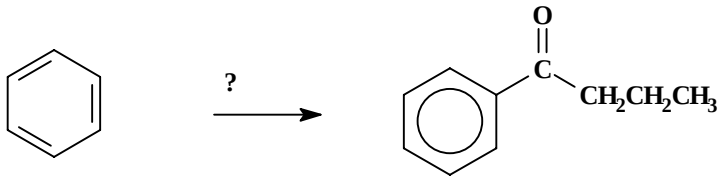
(1)

5

(2)

5

c. Carry out the following conversion using the Grignard or organocopper reaction as one of the steps. You may use any other needed organic and inorganic reagents. Show all the intermediate steps.



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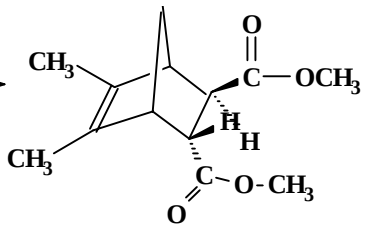
4. **(16)** a. Fill in the missing reactants, reagents, conditions, intermediates, or products in the following reaction sequences.

a. **?** + **?** → 

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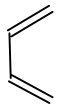
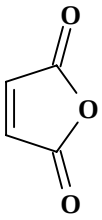
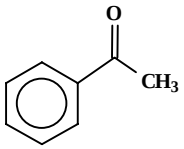
b.  +  → **?**

2

c.  **1. $NaBH_4$/MeOH** **2. H_2SO_4, Δ** → **?**

W• → **?**

(Free Radical Catalyst)

(Polymer, name and write sample structure).

4

d. Fill in all the reagents and steps necessary to carry out the following conversions.

Ph–Br ⟶ **Ph–CH_2–OH** ⟶ **Ph–$CH_2CH_2CH_2$–OH** ⟶ **Ph–CH_2CH_2-C(=O)–H**

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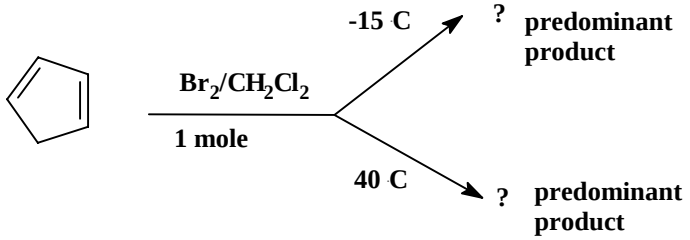
5. **(10)** a. Fill in the missing predominant organic products in the following reaction. Briefly explain why each product predominates at the given temperature in terms of type of control.



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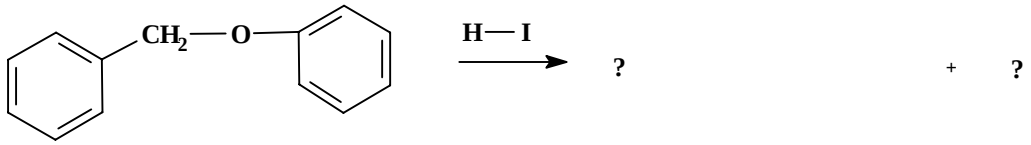
Explanation:

2

b. Briefly show the mechanism that gives rise to each product.

3

c. Fill in the missing organic products in the following reaction.



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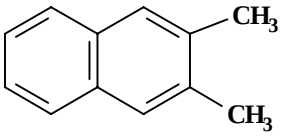
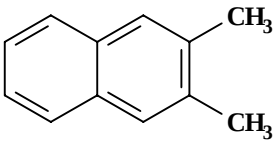
6. **(12)** a. Label each set of molecules as one of the following: **conformers, enantiomers, diastereomers, tautomers, resonance forms, or constitutional isomers.**

(1)  **and** 

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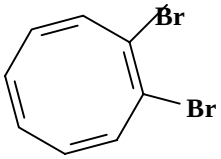
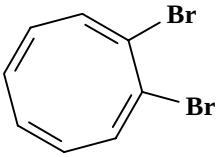
(2)  **and** 

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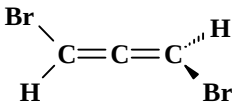
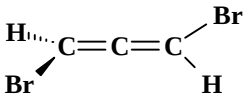
(3)  **and** 

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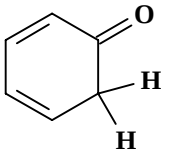
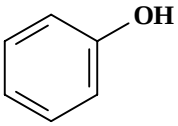
(4)  **and** 

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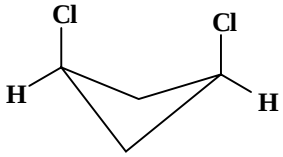
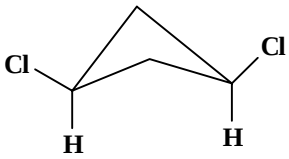
(5)  **and** 

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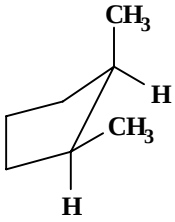
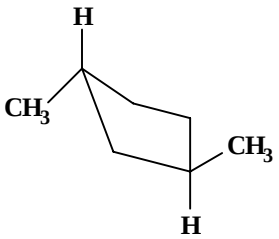
(6)  **and** 

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7. **(08)** a. Show the distribution and relative energy levels in the molecular orbital model of benzene. Fill the orbitals with electrons as occurs in the ground state

2

b. Show the pictures of the lowest energy and the highest energy molecular orbitals of benzene.

lowest energy mo **highest energy mo**

2

c. Briefly, define **Resonance Energy** or **Delocalization Energy**. How is it shown in the energy profile for hydrogenation of benzene and the hypothetical cyclohexatriene?

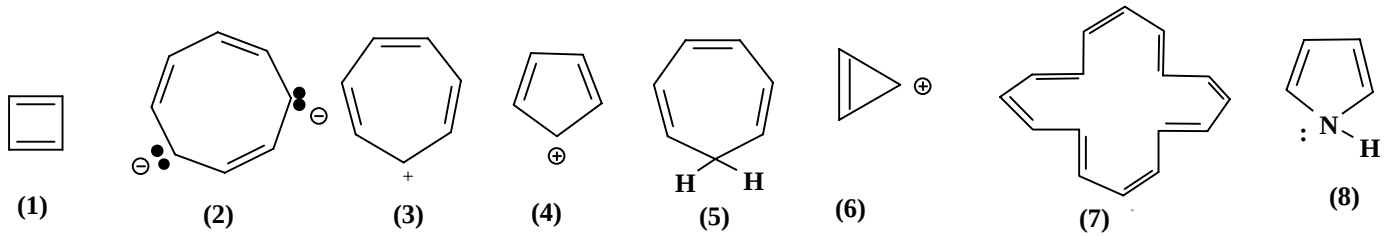
Definition: Resonance Energy or Delocalization Energy

2

d. Mention **4** characteristics that together define an aromatic system.

2

8. **(8)** a. Which of the following would you expect to be aromatic? More than one answer may be possible.



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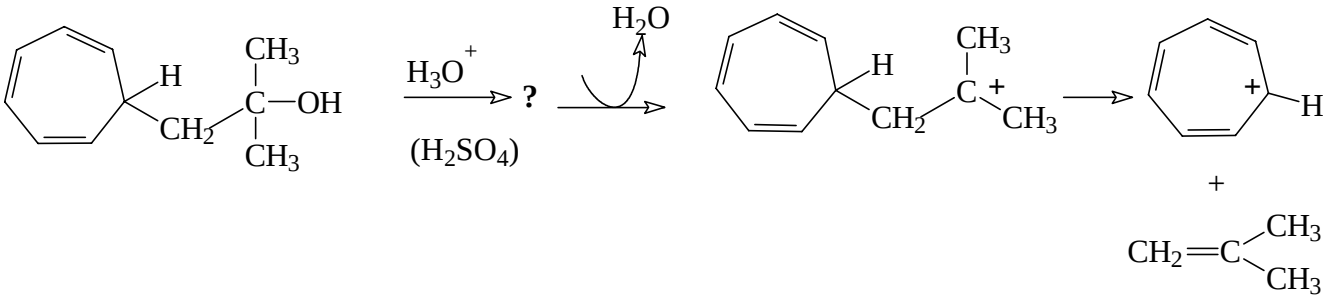
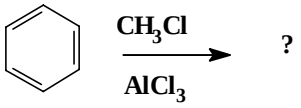
b. Explain why is the following reaction so favorable? Fill in the missing intermediate (?) and mechanistic arrows.



c. Name the type of substitution and give the detailed mechanism and products for the following reaction.



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d. Cite a problem that occurs with this particular reaction. Show the equation.

Scrap Paper

Happy 4th of July. We hope to see you soon. Good luck in attaining your career choice. Happy Summer.

Sincerely, Drs. Grace and Irv Borowitz

Scrap Paper