EXAM 3

CHEMISTRY 220a

Friday, November 13, 2009

NAME (print): _____

TA:_____ Sect. Day:_____ Sect. Time:_____

Take a few moments to look over the exam. Answer each question on the exam paper.

No calculators. You may use molecular models. Important clues and structures are in **bold**.

Do all **preliminary** drawing or computations on the work sheets at the end of the exam. The work sheets will not be graded.

The exam is 55 minutes.

STOP writing and hand in your exam when you are asked to do so.

REMEMBER: Neatness is to your advantage.

1. (20 pts) Reactions (Do 3 of 4) _____

2. (20 pts) Structure Determination _____

3. (20 pts) Synthesis _____

4. (20 pts) Potpourri _____

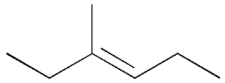
5. (20 pts) Mechanisms (Do 1 of 3) _____

_____

Total (100 pts)

1) **Reactions:** (20 pts.) **Do 3 of 4** of the following questions. Identify the unknown compounds and rationalize their formation. Pay attention to stereochemical and mechanistic issues**.** No mechanisms required. **If you do more than three questions, cross out the one you do not want graded.**

a)



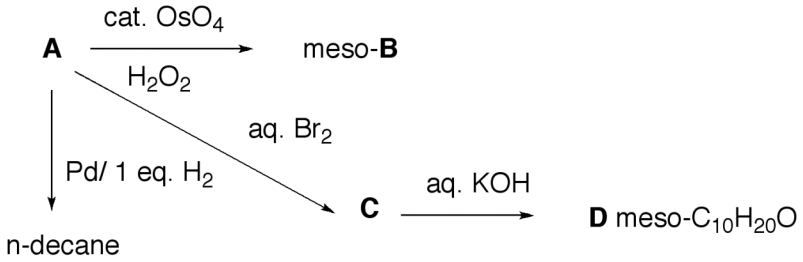
1

1) BH_3

2) aq. NaOH, H_2O_2

A → (TsCl, pyr.) → **B** → (aq. KOH) → (*Z*) - **1**

b)



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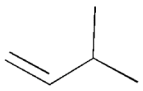
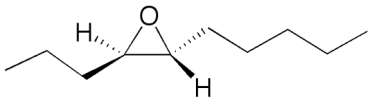
c)  $\xrightarrow[H_2O_2]{HCl}$ **A** $\xrightarrow[CH_3OH]{CH_3ONa}$ **B** $\xrightarrow[2)\ (CH_3)_2S]{1)\ O_3}$ **C** (C_2) + **D** (C_3)

d) **A** $\xrightarrow{Na\ /\ NH_3}$ **B** $\xrightarrow[CCl_4]{Br_2}$ **C** meso-4,5-dibromooctane

2) **Structure:** (20 pts) Compound **A** ($C_{10}H_{20}$) undergoes ozonolysis to produce a **single, optically active** compound (*S*)-**B**. [At this point you should know everything but one fact.] The reaction of compound **A** with Br_2 in CCl_4 provides a **single, optically active** compound **C**. What are the structures of **A-C**? Show their stereochemistry. Show your reasoning. [A similar problem appeared on PS7.]

3) **Synthesis:** (20 pts) Design a synthesis of the racemic epoxide shown on the right using 1-pentyne as your **only** source of carbon. Think backwards (retrosynthesis). All reagents and reactions are available to you. **Show work.** (Mechanisms are not required,; just reaction conditions and steereochemistry.)	

4) **Potpourri:** (20 pts.; equal weight) Answer each of the following questions.

a) Given that 1-hexyne has ΔH_f^o = +29.2 kcal/mol, what normal chain, terminal alkyne has a heat of formation of ~ 0 kcal/mol. **Show work and structure/name** of the alkyne.

b) **Circle** the terms that apply to the conversion of an alkene to an alcohol via hydroboration.

retention of configuration anti-Markovnikov addition of water

regioselective stereospecific Markovnikov addition of borane

c) **Circle** the reagents that add to a double bond in a syn fashion.

BH_3 $KMnO_4$ RCO_3H $Zn(Cu)$; CH_2I_2 OsO_4

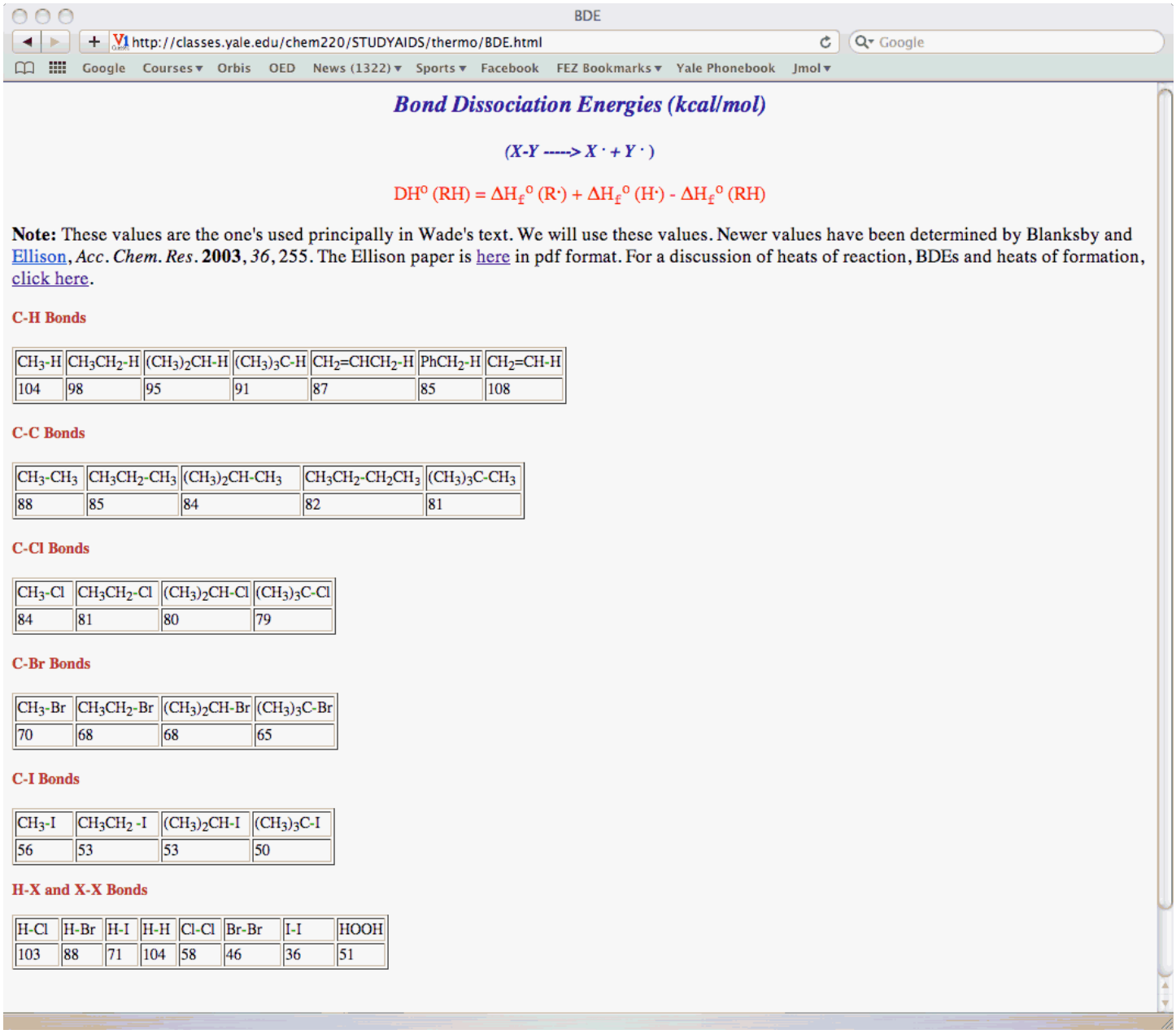
d) The BDE of the double bond in (*E*)-3-hexene is 144 kcal/mol (σ- and π-bonds together). Using the BDE Table (page 8), show that the bromination of (*E*)-3-hexene has ΔH_{rxn}^o = -28 kcal/mol. **Show work.**

5) **Mechanisms:** (20 pts.) Provide a mechanism for one and only one of the following reactions using the curved arrow formalism. Pay attention to stereochemistry where it applies. **If you do more than one question, cross out the one(s) you do not want graded.**

a) Hydroboration of (*Z*)-3-methyl-3-hexene followed by oxidation to form an alcohol.

b) Ozonolysis and reduction of (*Z*)-3-methyl-3-hexene.

c) Mercuric ion-catalyzed hydration of 3-hexyne to form 3-hexanone.



Bond Dissociation Energies (kcal/mol)

(X-Y -----> X · + Y ·)

DH^{o} (RH) = ΔH_f^{o} (R·) + ΔH_f^{o} (H·) - ΔH_f^{o} (RH)

Note: These values are the one's used principally in Wade's text. We will use these values. Newer values have been determined by Blanksby and Ellison, *Acc. Chem. Res.* **2003**, *36*, 255. The Ellison paper is here in pdf format. For a discussion of heats of reaction, BDEs and heats of formation, click here.

C-H Bonds

CH_3-H	CH_3CH_2-H	$(CH_3)_2$CH-H	$(CH_3)_3$C-H	CH_2=$CHCH_2$-H	$PhCH_2$-H	CH_2=CH-H
104	98	95	91	87	85	108

C-C Bonds

CH_3-CH_3	CH_3CH_2-CH_3	$(CH_3)_2$CH-CH_3	CH_3CH_2-CH_2CH_3	$(CH_3)_3$C-CH_3
88	85	84	82	81

C-Cl Bonds

CH_3-Cl	CH_3CH_2-Cl	$(CH_3)_2$CH-Cl	$(CH_3)_3$C-Cl
84	81	80	79

C-Br Bonds

CH_3-Br	CH_3CH_2-Br	$(CH_3)_2$CH-Br	$(CH_3)_3$C-Br
70	68	68	65

C-I Bonds

CH_3-I	CH_3CH_2 -I	$(CH_3)_2$CH-I	$(CH_3)_3$C-I
56	53	53	50

H-X and X-X Bonds

H-Cl	H-Br	H-I	H-H	Cl-Cl	Br-Br	I-I	HOOH
103	88	71	104	58	46	36	51

Work Sheets

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