EXAM 2

CHEMISTRY 220

Friday, October 15, 2010

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 or electronic devices. You may use molecular models. Important clues and structures are in **bold**. There is a **Periodic Table** on page 10.

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

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. (30 pts) Reactions I (Do 5 of 6) _____

2. (24 pts) Reactions II (Do 4 of 5) _____

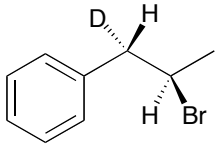
3. (22 pts) Thermochemistry _____

4. (24 pts) Potpourri (Do 4 of 5) _____

_____

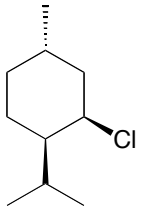
Total (100 pts)

1) **Reactions I:** (30 pts.; equal weight) Provide the structures of the product(s) in **5 of 6** of the following reactions. Answer any queries that are posed, (e. g.; opt. act.?). **Very brief** commentary is welcome. **If you do more than five questions, cross out the one that you do not want graded. Pay attention to stereochemistry, mechanisms and optical activity!**

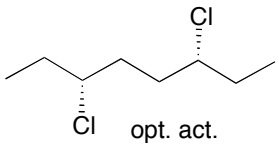
a) 

opt. act.

C_2H_5ONa / C_2H_5OH → **A** (opt. inact.)

b) 

KOH / CH_3OH → **A** ($C_{10}H_{18}$)

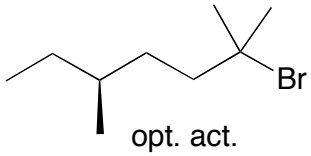
c) 

opt. act.

Na_2S / C_2H_5OH → **A** ($C_8H_{16}S$) opt. act.?

(R,S - configuration if applicable)

…continued

d) 

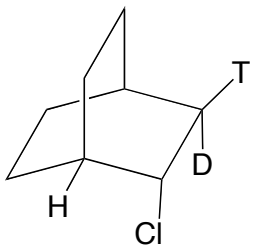
excess
CH_3OH

A (major) + **B** (minor)

opt. act.? opt. act.?

(R,S - configuration if applicable)

e) (R) - $CH_3(CH_2)_3CDHBr$ $\xrightarrow[CH_3OH]{KOH,\ CH_3SH}$ **A** (R,S - configuration?)

f) 

$\xrightarrow[C_2H_5OH]{C_2H_5ONa}$ **A**

(T = tritium)

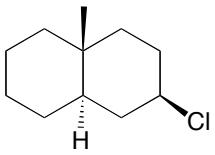
2) **Reactions II:** (24 pts., equal weight) Answer **4 of 5** of the following questions. **Be succinct! If you do more than four questions, cross out the one that you do not want graded.**

a) (*R*)-1-Bromo-2-methylbutane (**1**) has been reported to give a 2/3 ratio (S_N2/E2) of products upon treatment with sodium ethoxide in ethanol. What **percentage** of S_N2 product might you expect when the reaction is conducted with (±)-**1**? **Explain briefly**. Draw the structures of the reaction products derived from (*R*)-**1**.

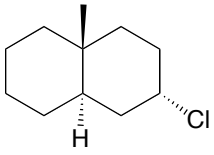
b) Will potassium tertiary butoxide [$(CH_3)_3COK$] or sodium methoxide give a higher S_N2/E2 ratio upon reaction with 1-bromopentane? **Explain and illustrate briefly**.

…continued

c) **Circle** the compound that will remain in excess when a limited amount (less than stoichiometric) of KOH in ethanol reacts with equal amounts of **1** and **2**. **Draw** the structures of the two possible chlorine-free, non-oxygen containing products. **Give brief explanations.**

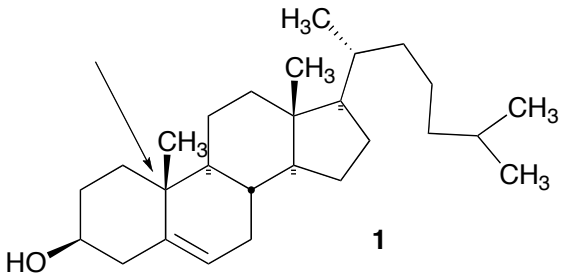


1



2

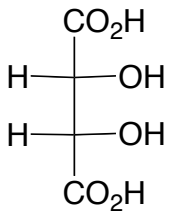
d) Cholesterol **1** is the enantiomer shown below. Excluding the geometry of the double bond, how many stereoisomers of cholesterol are possible? **Show work.** Provide the CIP designation for the quaternary carbon designated by the arrow.



1

…continued

e) Structure **1** has a plane of symmetry and must be optically inactive. But yet structure **1** must be an eclipsed comformation which is high in energy and therefore not well-populated. Name structure **1**. Assign R,S centers where needed. Why is structure **1** optically inactive in spite of the eclipsed conformation?

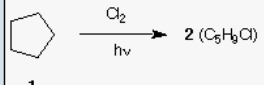


1

3) **Thermochemistry:** (22 pts.) Problem Set 3 directed you to the alkane module of Organic Reactions Go Online (ORGO). Here is the solution to #2. Answer the three underlined questions under a), b) and c). For part b you will also be asked to compute the heats of the two propagation steps and the heat of the overall reaction.

Alkane 2:

Problem



1

Solution

2 Cyclopentane **1** (C_5H_{10}) has 10 equivalent hydrogens. The conditions presented are those of a free radical chain chlorination. The formula of **2** tells us that one hydrogen atom has been substituted for a chlorine atom. The product is chlorocyclopentane. What is the initiation step in this reaction?

Write equations for the two propagation steps. You may wish to review Alkane 1 first.

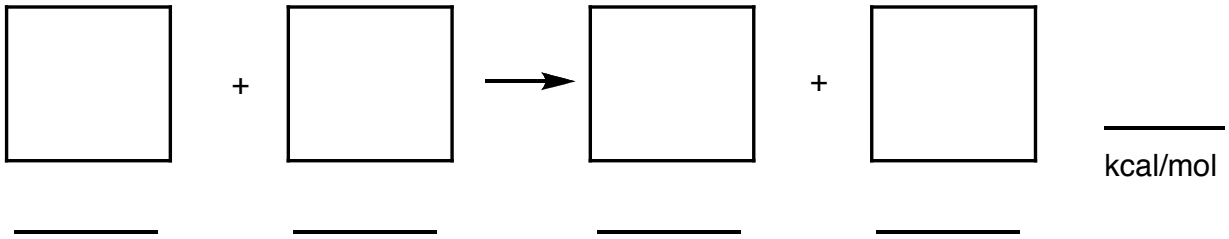
Although chlorocyclopentane is the major product of the reaction when cyclopentane **1** reacts with one molar equivalent of chlorine, some dichloro products can also be formed. During the latter stages of the conversion of **1** to **2**, the amount of **2** increases over the unreacted **1**. Because there is more **2** than **1**, dichlorination can occur. How many dichlorocyclopentanes are possible?

a) (5 pts.) The initiation step?

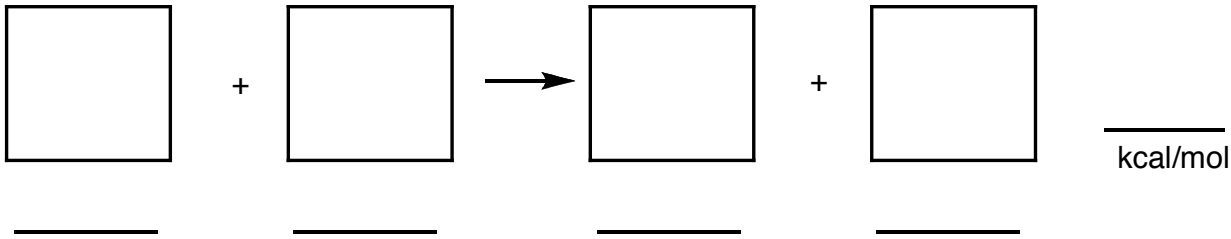
…continued

b) (12 pts.) Provide the two propagation steps and the overall reaction for this process**. Place the reactants and products in the appropriate boxes.** Compute the heats of each reaction using the data in the BDE Table (pg. 10)

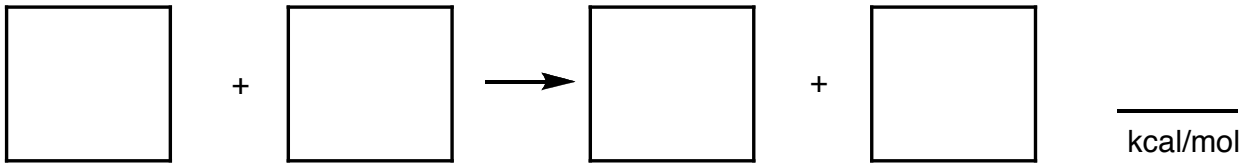
Propagation step 1



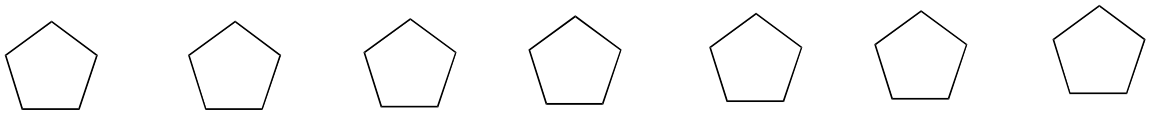
Propagation step 2



Overall reaction

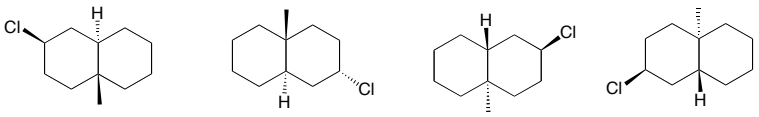


c) (5 pts.) How many dichlorocyclopentanes are possible?. **Draw** them with the aid of the templates below. No need to worry about enantiomers.



4) **Potpourri:** (20 pts.) Do **4 of 5** questions. **You may do either b) or d). If you do more than four questions, cross out the one that you do not want graded, either b) or d).**

a) One of these enantiomers is not like the others. **Circle** it and provide its R,S – configuration at the relevant centers. Is it dextro- or levorotatory?



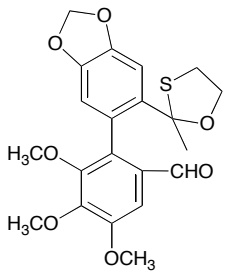
b) Natural tartaric acid has a specific rotation of $[\alpha] = +12^{o}$. What is the observed specific rotation of a solution containing a 2/1 ratio of natural and meso-tartaric acid, respectively? **Show reasoning**.

c) **Circle** the terms that apply to E2 reactions.

Isotope effect 1st order reaction stepwise rehybridization intermediate

d) A 3:1 mixture of (*S*)- and (*R*)-carvone, respectively, has an optical rotation of $+36^{o}$. What is the rotation of the pure (*S*)-enantiomer? The (*R*)-enantiomer? **Show work**.

e) In 1978 racemic **1** was synthesized and was found to be a mixture of two racemic diastereomers. The method used was similar to the methodology of the 2010 Nobel Prize Medalists, only copper was used instead of palladium. i) What C-C bond was formed? ii) Why is structure **1** a mixture of two racemates?



1

BDE

http://classes.yale.edu/chem220/STUDYAIDS/thermo/BDE.html

Google Courses Orbis OED News (1322) Sports Facebook FEZ Bookmarks Yale Phonebook Jmol

Bond Dissociation Energies (kcal/mol)

(X-Y -----> X · + Y ·)

$DH^{o}(RH) = \Delta H_f^{o}(R\cdot) + \Delta H_f^{o}(H\cdot) - \Delta H_f^{o}(RH)$

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	$(CH_3)_2CH$-H	$(CH_3)_3C$-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	$(CH_3)_2CH$-CH_3	CH_3CH_2-CH_2CH_3	$(CH_3)_3C$-CH_3
88	85	84	82	81

C-Cl Bonds

CH_3-Cl	CH_3CH_2-Cl	$(CH_3)_2CH$-Cl	$(CH_3)_3C$-Cl
84	81	80	79

C-Br Bonds

CH_3-Br	CH_3CH_2-Br	$(CH_3)_2CH$-Br	$(CH_3)_3C$-Br
70	68	68	65

C-I Bonds

CH_3-I	CH_3CH_2 -I	$(CH_3)_2CH$-I	$(CH_3)_3C$-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

hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 ✶	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 ✶ ✶	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]			

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
**Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Work Sheets

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