

Exam Booklet No.

CHEM 2410 – Organic Chemistry 1 – Fall 2017

Instructors: Erin Witteck & Paul Bracher

Hour Examination #3Wednesday, November 15th, 2017

6:10–8:10 p.m. in the Lecture Halls at Saint Louis University

Student Name (Printed)	
Student Signature	

Instructions & Scoring

- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- You may use a plastic model kit. No electronic resources or note sheets are permitted, and you may not communicate with others.
- Your exam answer sheet may be copied or scanned.
- The examination room may be monitored by audio, photo, and/or video recording.

Problem	Points Earned	Points Available
I		60
II		6
III		12
IV		12
V		10
TOTAL		100

This exam focuses on Chapters 9, 10, 11, and 12 in Janice Smith's *Organic Chemistry*, 4th ed.

Examination Instructions

DO NOT TURN THE PAGE ON THIS BOOKLET UNTIL DIRECTED BY A PROCTOR TO BEGIN

Please Make Sure to Do the Following Before Starting Your Exam

1. Both print your name and sign the front of the answer sheet and this exam booklet in the appropriate boxes.
2. Also print your name at the top of the back of the answer sheet.
3. Enter your SLU Banner ID number on the front of the answer sheet and bubble the corresponding numbers. Failure to do this correctly will result in the loss of 2 points.
4. Write the serial number of this exam booklet on your answer sheet in the appropriate box.
5. Check the “Hold for Pick-Up” box on the back of the answer sheet if you want your graded sheet withheld from the distribution pile on Monday and handed back to you privately. Checking this box will delay your receipt of your graded exam.

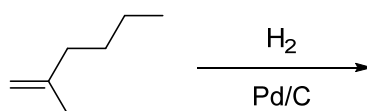
Please Make Sure to Do the Following After Completing Your Exam

1. Ensure that all of your selected circles are darkened completely.
2. Submit your answer sheet, exam booklet, data tables, and scratch paper to the proctors. You may not remove these items from the exam room.

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Problem I. Multiple Choice (60 points total). Correct answers score +3 points, answers of 'E' score +1 point, and incorrect answers score 0 points. Questions filled with zero or multiple responses will score 0 points. For each question, select the best and most complete answer of the choices given. Bubble the answer, darkly, in the space provided on the answer sheet. For all questions that ask you to name or count compounds or products, include all distinct compounds that not interconvertible under ambient conditions (i.e., include or count different constitutional isomers and stereoisomers separately, but not different conformations that can interconvert).

- (1) _____ How many products will be generated in significant yield in the following reaction?
Count different stereoisomers as different products.

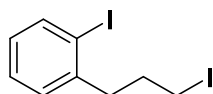
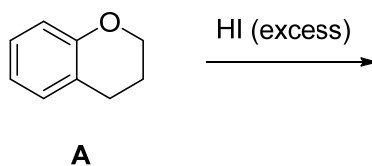


- (A) one product
- (B) two products
- (C) three products
- (D) four products

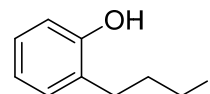
- (2) _____ Which of the following statements is true about the reaction in question #1?

- (A) both carbon atoms of the C=C bond are oxidized
- (B) both carbon atoms of the C=C bond are reduced
- (C) one carbon atom is oxidized, one carbon atom is reduced
- (D) this is not an oxidation/reduction reaction

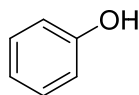
- (3) _____ What product is formed in highest yield from the reaction of compound **A** with excess hydroiodic acid?



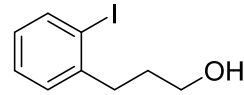
(A)



(B)



(C)

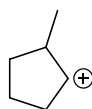


(D)

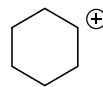
- (4) _____ Which of the following carbocations is most prone to rearrangement?



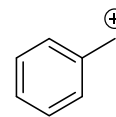
(A)



(B)

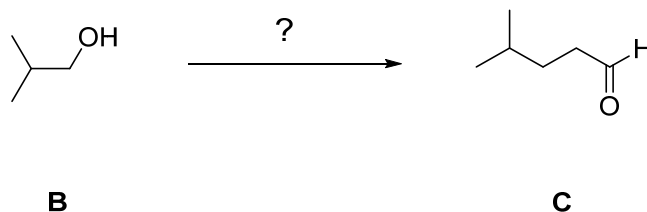


(C)



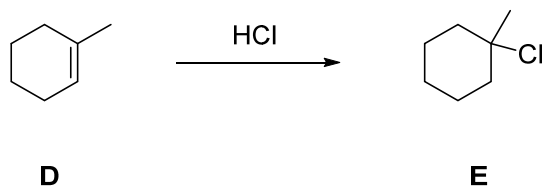
(D)

- (5) _____ Which of the following sequences of reactions is the best choice to convert compound **B** to compound **C**?



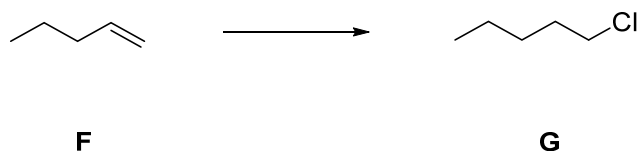
- (A) $\xrightarrow[\text{H}_2\text{SO}_4, \text{H}_2\text{O}]{\text{K}_2\text{Cr}_2\text{O}_7}$ $\xrightarrow[2. \text{H}_2\text{O}_2, \text{NaOH}]{1. \text{9-BBN}}$
- (B) $\xrightarrow[\text{pyridine}]{\text{TsCl}}$ $\xrightarrow{\text{NaC}\equiv\text{CH}}$ $\xrightarrow[2. \text{CH}_3\text{SCH}_3]{1. \text{O}_3}$
- (C) $\xrightarrow[\text{pyridine}]{\text{SOCl}_2}$ $\xrightarrow{\text{NaC}\equiv\text{CH}}$ $\xrightarrow[2. \text{H}_2\text{O}_2, \text{NaOH}]{1. \text{9-BBN}}$
- (D) $\xrightarrow{\text{NaC}\equiv\text{CH}}$ $\xrightarrow[\text{Lindlar catalyst}]{\text{H}_2}$ $\xrightarrow[2. \text{CH}_3\text{SCH}_3]{1. \text{O}_3}$

- (6) _____ Which of the following statements is correct regarding the conversion of **D** to **E** depicted in the scheme below?



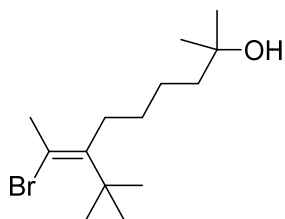
- (A) HCl is a catalyst for this reaction
- (B) the reaction proceeds via a chloronium intermediate where the Cl atom is temporarily in a bridged, three-membered ring
- (C) as shown, this addition follows Markovnikov's Rule
- (D) the conversion of **E** back to **D** is accomplished in high yield by treatment with potassium *tert*-butoxide (KO*t*Bu)

- (7) _____ Which of the following sequences will accomplish the synthesis of **G** from **F**?



- (A) HCl
- (B) 1. H₂O/H₂SO₄; 2. HCl
- (C) 1. 9-BBN; 2. H₂O₂, NaOH, H₂O; 3. TsCl, pyridine
- (D) 1. BH₃·THF; 2. H₂O₂, NaOH, H₂O; 3. SOCl₂, pyridine

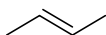
(8) _____ What is the IUPAC name for compound **H**?



H

- (A) (7Z)-8-bromo-7-*tert*-butyl-2-methylnon-7-en-2-ol
 (B) (7E)-8-bromo-7-*tert*-butyl-2-methylnon-7-en-2-ol
 (C) (2Z)-2-bromo-3-*tert*-butyl-8-methylnon-2-en-8-ol
 (D) (2E)-2-bromo-3-*tert*-butyl-8-methylnon-2-en-8-ol

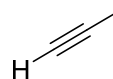
(9) _____ Rank the following compounds in order of their heats of complete/exhaustive hydrogenation to an alkane with excess H_2 and Pd/C as a catalyst. List the least exothermic first and the most exothermic last.



J



K



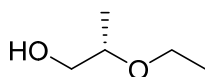
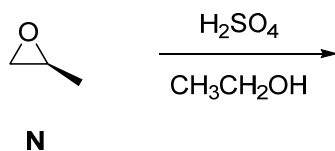
L



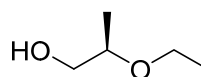
M

- (A) $J < K < L < M$
 (B) $J < K < M < L$
 (C) $M < L < J < K$
 (D) $L < M < K < J$

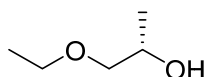
- (10) _____ What is the product of the reaction of compound **N** with ethanol and a tiny drop of sulfuric acid?



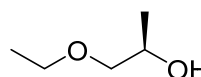
(A)



(B)

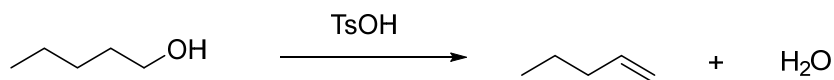


(C)



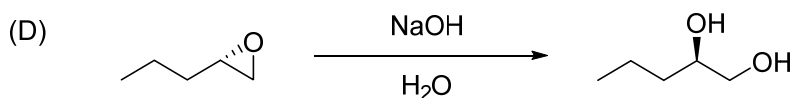
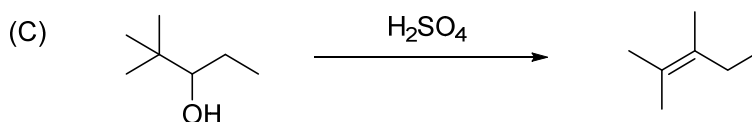
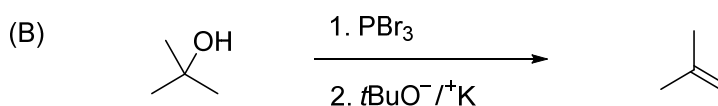
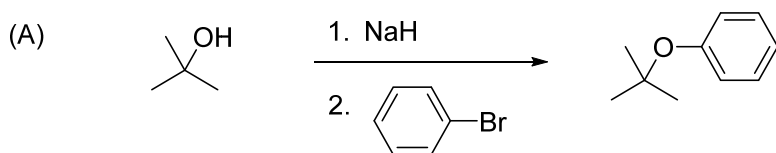
(D)

- (11) _____ Which of the following statements about the reaction shown below is true?

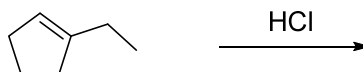


- (A) the mechanism of this reaction is E1
- (B) TsOH converts $-\text{OH}$ to $-\text{OTs}$, which is a better leaving group
- (C) ΔH° is positive for this reaction
- (D) addition of TsOH shifts the equilibrium further to the right

- (12) _____ Which of the following reactions is not significantly flawed and will proceed as drawn?

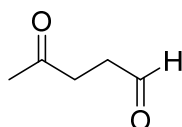
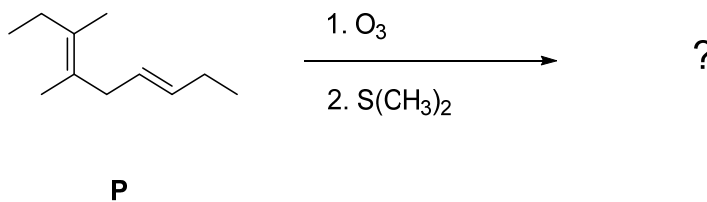


- (13) _____ Which of the following terms accurately describes the stereochemistry of the product(s) of this reaction?

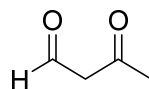


- (A) one meso compound
(B) one achiral compound that is not meso
(C) a racemic mixture of enantiomers
(D) two diastereomers

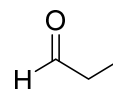
- (14) _____ Which of the following compounds is not a product of ozonolysis of compound **P**?



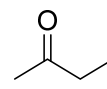
(A)



(B)

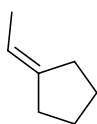
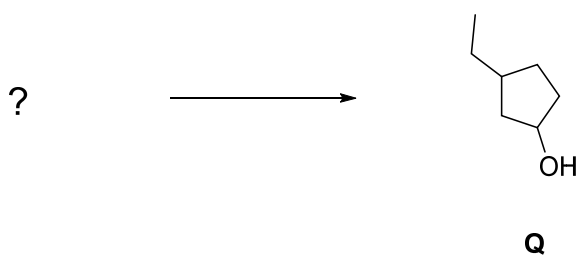


(C)

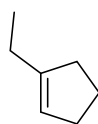


(D)

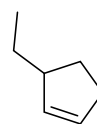
- (15) _____ Which of the following alkenes is the best starting material to synthesize **Q**, 3-ethylcyclopentanol, without regard for stereochemistry?



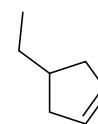
(A)



(B)

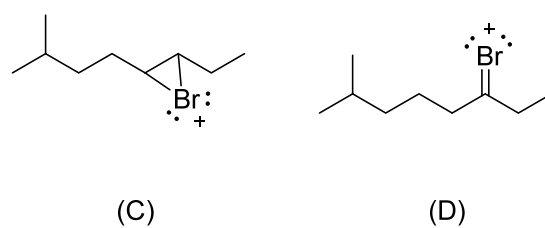
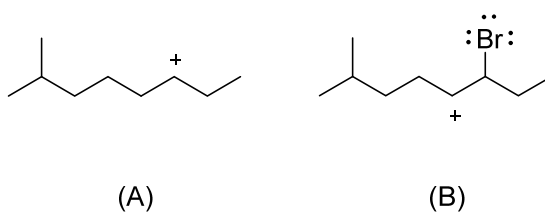
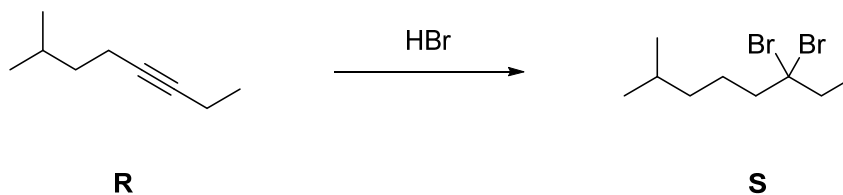


(C)

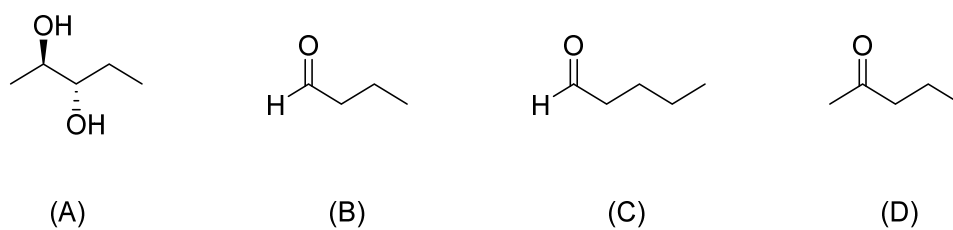
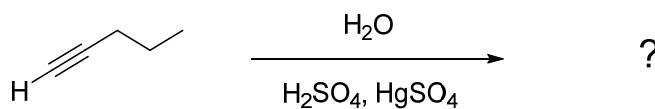


(D)

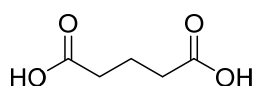
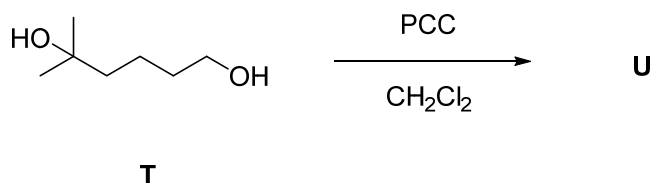
- (16) _____ Which of the following is an intermediate in the mechanism for the conversion of compound **R** to compound **S** upon treatment with HBr?



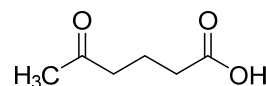
- (17) _____ What is the product of the following reaction?



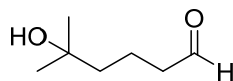
- (18) _____ What is the major product **U** generated when compound **T** is treated with pyridinium chlorochromate (PCC) with dichloromethane as the solvent?



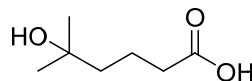
(A)



(B)

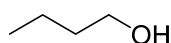


(C)

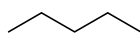


(D)

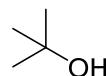
- (19) _____ Rank the following compounds from highest to lowest boiling point. List the compound with the highest boiling point first.



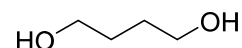
I



II



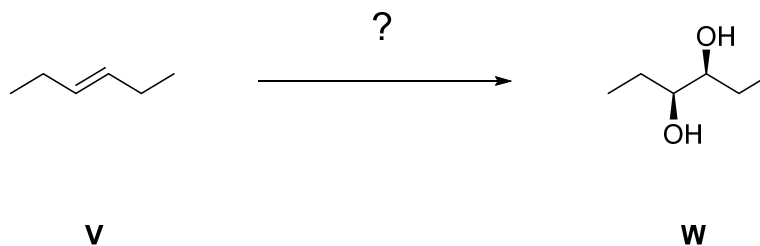
III



IV

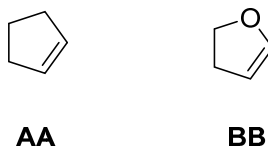
- (A) IV > I > III > II
(B) II > I > III > IV
(C) IV > III > I > II
(D) III > I > II > IV

(20) _____ Which of the following sequences will carry out the conversion of **V** to **W**?



- (A) cold dilute KMnO_4 , NaOH , H_2O
- (B) 1. *m*CPBA; 2. catalytic H_2SO_4 , H_2O
- (C) 1. *m*CPBA; 2. catalytic NaOH , H_2O
- (D) both (B) and (C) will carry out this conversion

Problem II. Explanation (6 points). HBr adds faster to the $\text{C}=\text{C}$ bond of compound **BB** than compound **AA**. On your answer sheet, explain why compound **BB** reacts faster than **AA** in this reaction using drawings and a maximum of one sentence.

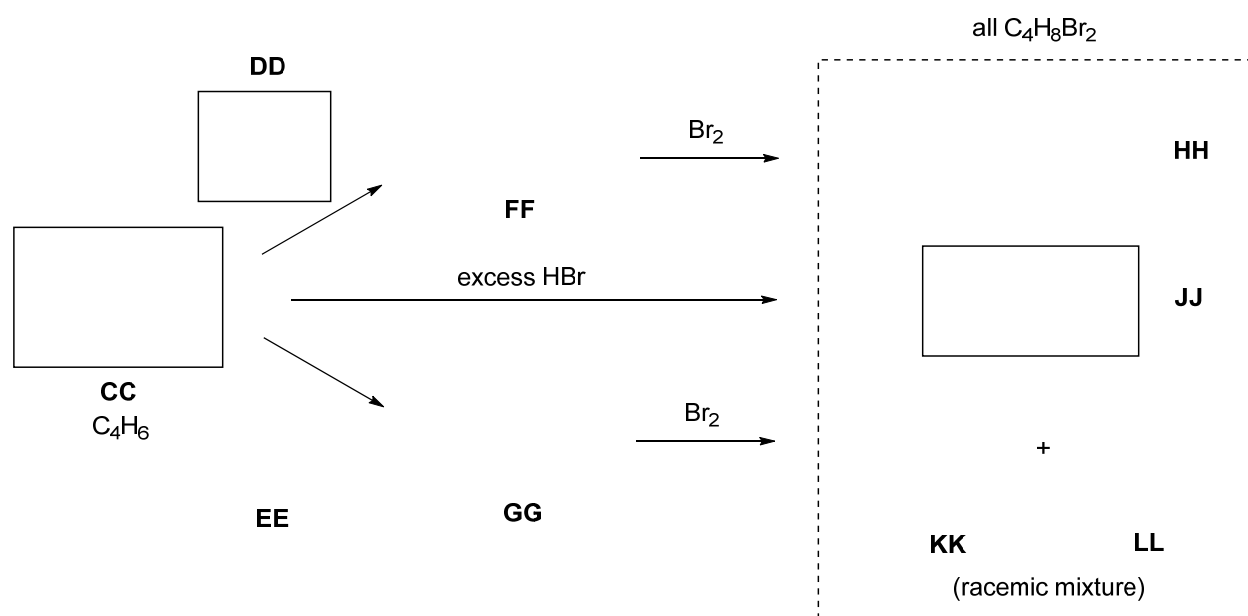


One-sentence explanation:

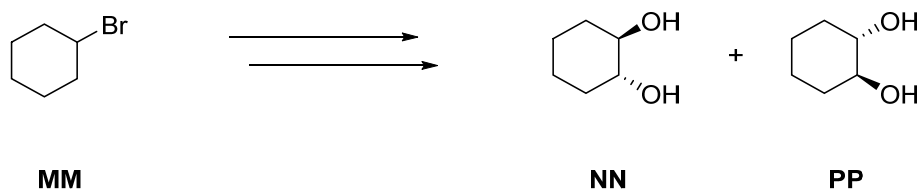
Problem III. Roadmap Problem. (12 points) Identify compounds/reagents **CC**, **DD**, and **JJ** in the reaction scheme below. Do not write the structures of the other compounds on your answer sheet.

Unknown compound **CC**, with molecular formula C_4H_6 , reacts with reagent(s) **DD** to produce **FF**. **FF** reacts with Br_2 to form a single organic product, **HH**, of molecular formula $C_4H_8Br_2$. Compound **CC** reacts with reagent(s) **EE** to produce **GG**. **GG** reacts with Br_2 to form a racemic mixture of two products, **KK** and **LL**, both of molecular formula $C_4H_8Br_2$. Compound **CC** reacts with excess HBr to produce **JJ**, also of molecular formula $C_4H_8Br_2$. Compounds **FF** and **GG** are stereoisomers of each other.

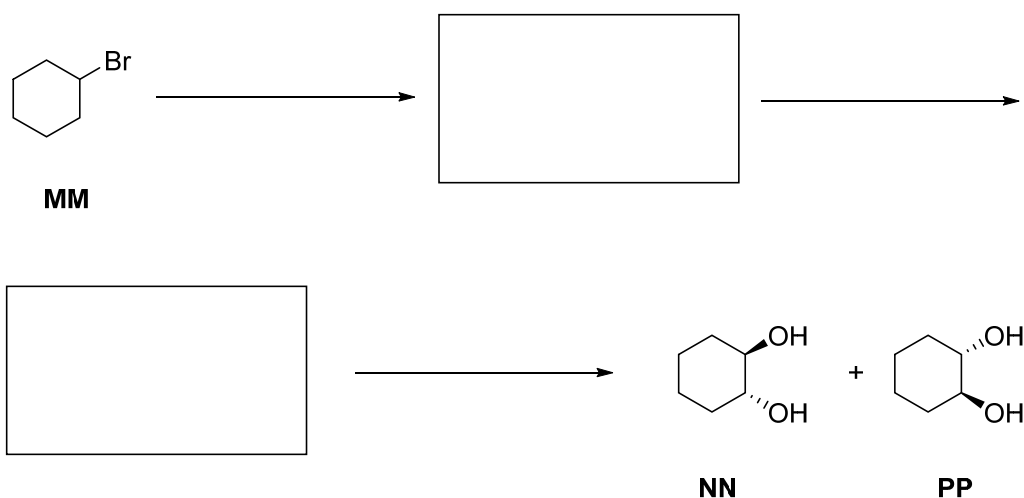
On your answer sheet, identify **CC**, **DD**, and **JJ**. Your proposals should be consistent with all of the data provided above. Do not provide the structures of other compounds/reagents.



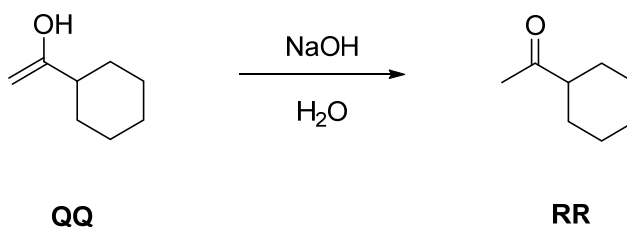
Problem IV. Synthesis (12 points). Provide a synthetic route—i.e, a sequence of reactions—to produce a racemic mixture of *trans*-1,2-cyclohexanediol (**NN + PP**) from bromocyclohexane (**MM**) and any reagents you wish. Draw each synthetic intermediate in the boxes in the template on your answer sheet and provide the necessary reagents above/below the reaction arrows. (Note: There are multiple correct answers. If you choose to complete this synthesis in fewer than three steps, just cross out any unused arrows and boxes.) Please do not draw curved arrows; we are not asking for mechanisms.



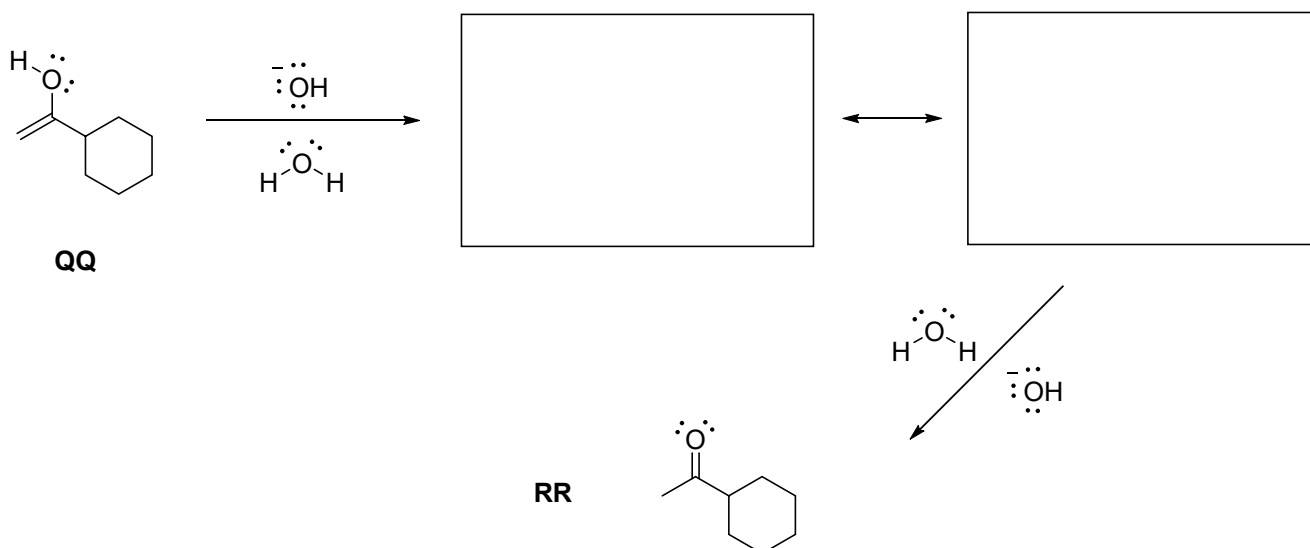
Template:



Problem V. Mechanism (10 points). Draw a sensible mechanism for the isomerization of **QQ** to **RR** in aqueous base. Remember to use proper “curved arrow notation” to account for the redistribution of electrons in the making and breaking of bonds. Show all intermediates in the reaction and any significant resonance forms that account for the stability of these intermediates. Use the template provided on your answer sheet and draw one structure in each empty box.



Template:



1																		2
H																		He
hydrogen																		helium
1.008																		4.003
3	4																	10
Li	Be																	Ne
lithium	beryllium																	neon
6.94	9.01																	20.180
11	12																	18
Na	Mg																	Ar
sodium	magnesium																	argon
22.990	24.305																	39.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
potassium	calcium	scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc	gallium	germanium	arsenic	selenium	bromine	krypton	
39.098	40.078	44.956	47.867	50.942	51.996	54.938	55.845	58.933	58.693	63.546	65.38	69.723	72.631	74.922	78.972	79.904	83.798	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
rubidium	strontium	yttrium	zirconium	niobium	molybdenum	technetium	ruthenium	rhodium	palladium	silver	cadmium	indium	tin	antimony	tellurium	iodine	xenon	
85.468	87.62	88.906	91.224	92.906	95.95	(98)	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.76	127.60	126.90	131.29	
55	56		72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
Cs	Ba	* lanthanides	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
cesium	barium		hafnium	tantalum	tungsten	rhenium	osmium	iridium	platinum	gold	mercury	thallium	lead	bismuth	polonium	astatine	radon	
132.91	137.33		178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)	
87	88		104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	
Fr	Ra	** actinides	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og	
francium	radium		rutherfordium	dubnium	seaborgium	bohrium	hassium	meitnerium	darmstadtium	roentgenium	copernicium	nihonium	flerovium	moscovium	livermorium	tennessine	oganeson	
(223)	(226)		(267)	(268)	(269)	(270)	(277)	(278)	(281)	(282)	(285)	(286)	(289)	(290)	(293)	(294)	(294)	

*	57	La lanthanum 138.91	58	Ce cerium 140.12	59	Pr praseodymium 140.91	60	Nd neodymium 144.24	61	Pm promethium (145)	62	Sm samarium 150.36	63	Eu europium 151.96	64	Gd gadolinium 157.25	65	Tb terbium 158.93	66	Dy dysprosium 162.50	67	Ho holmium 164.93	68	Er erbium 167.26	69	Tm thulium 168.93	70	Yb ytterbium 173.05	71	Lu lutetium 174.97
	89	Ac actinium (227)	90	Th thorium 232.04	91	Pa protactinium 231.04	92	U uranium 238.03	93	Np neptunium (237)	94	Pu plutonium (244)	95	Am americium (243)	96	Cm curium (247)	97	Bk berkelium (247)	98	Cf californium (251)	99	Es einsteinium (252)	100	Fm fermium (257)	101	Md mendelevium (258)	102	No nobelium (259)	103	Lr lawrencium (266)

pK_a Table

<chem>Cl-H</chem>	-8.0	<chem>CCS</chem>	10-11	<chem>C#C</chem>	25
<chem>[OH2+]</chem>	-1.7	<chem>CC[NH3+]</chem>	10.6	<chem>H-H</chem>	36
<chem>F-H</chem>	3.2	<chem>HO-H</chem>	15.7	<chem>HN-H</chem>	38
<chem>CC(=O)O</chem>	4.8	<chem>CCO</chem>	15.9	<chem>c1ccccc1</chem>	43
<chem>c1ccccc1O</chem>	10.0	<chem>CC(=O)C</chem>	19-20	<chem>C=C</chem>	44
				<chem>CCCC</chem>	~50

Bond Dissociation Energies (BDEs)

Average Bond Dissociation Energies, <i>D</i> (kJ/mol) ^a											
H—H	436 ^a	C—H	410	N—H	390	O—H	460	F—F	159 ^a		
H—C	410	C—C	350	N—C	300	O—C	350	Cl—Cl	243 ^a		
H—F	570 ^a	C—F	450	N—F	270	O—F	180	Br—Br	193 ^a		
H—Cl	432 ^a	C—Cl	330	N—Cl	200	O—Cl	200	I—I	151 ^a		
H—Br	366 ^a	C—Br	270	N—Br	240	O—Br	210	S—F	310		
H—I	298 ^a	C—I	240	N—I	—	O—I	220	S—Cl	250		
H—N	390	C—N	300	N—N	240	O—N	200	S—Br	210		
H—O	460	C—O	350	N—O	200	O—O	180	S—S	225		
H—S	340	C—S	260	N—S	—	O—S	—				
Multiple covalent bonds											
C=C	611	C≡C	835	C=O	732	O=O	498 ^a	N≡N	945 ^a		

^a Exact value

Scratch Paper

You may rip this sheet out of the exam booklet, but you are responsible for turning it in at the end of the exam.

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