Chemistry 3351 Organic Chemistry
Tuesday: Oct. 23 / @ **7:00pm → 9:00** / 2nd Exam

Name: Ryo Tamura (please print, 1pt)

Page	Possible Points	Score
1	1	
2	9	
3	9	
4	9	
5	6	
6	12	
7	10	
8	8	
9	8	
10	8	
11	10	
12	10	
TOTAL	100	

1. (3 pts each) *Clickers* in action:

i) Addition of HCl to 3-methyl-1-pentene gives TWO products. One of these is 2-chloro-3-methylpentane. Identify the other product.

A) 1-Chloro-3-methylpentane

B) 3-Chloro-3-methylpentane

C) 3-Chloro-2-methyl pentane

D) 2-Chloro-2-methylpentane

ii) Predict the major product in the reaction of 3-methyl-2-pentene with Cl_2 in H_2O as the solvent.

A) 2-Chloro-3-methyl-pentan-3-ol

B) 3-Chloro-3-methyl-pentan-2-ol

C) 4-Chloro-3-methyl-pentan-3-ol

D) 3-Chloro-3-methyl-pentan-4-ol

iii) Predict the product in the reaction between 3-methyl-2-pentene and Cl_2 in CCl_4 as the solvent.

A) 2, 3-Dichloro-2-methylpentane

B) 2, 3-Dichloro-3-methylpentane

C) 2, 2-Dichloro-3-methylpentane

D) 3, 3-Dichloro-2-methylpentane

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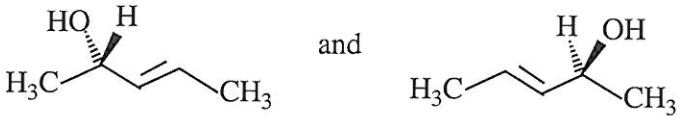
iv) How are these molecules related?



A) Constitutional Isomers

B) Diastereomers

C) Enantiomers

D) Identical

v) Which compound would have the highest heat of combustion (ΔH_{comb}), the energy released as heat when a compound undergoes complete combustion with oxygen under standard conditions?

A) Methylcyclobutane

B) Cyclopentane

C) *cis*-1,2-dimethylcyclopropane

D) *trans*-1,2-dimethylcyclopropane

vi) Which reaction conditions would you select to synthesize 3-methylpentan-2-ol from 3-methylpent-2-ene?

A) H_2O, concentrated H_2SO_4

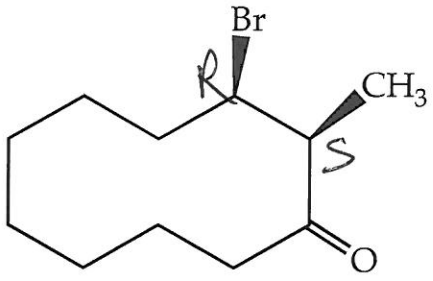
B) Br_2, H_2O

C) BH_3, THF; followed by H_2O_2/ $^{\ominus}OH$

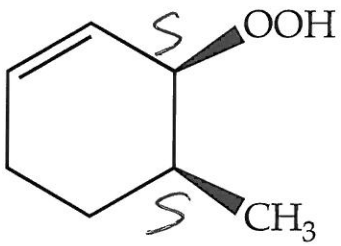
D) $Hg(OAc)_2$, THF-H_2O; followed by $NaBH_4$, $^{\ominus}OH$

2. (9 pts) For each of the following compounds, assign **R** or **S** at each asymmetric carbon.

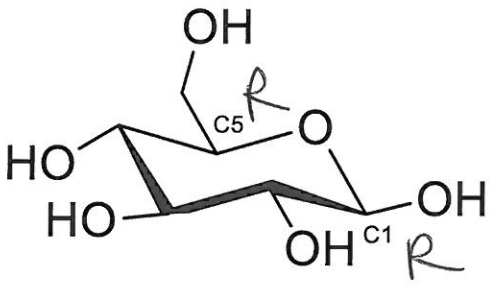
a)



b)



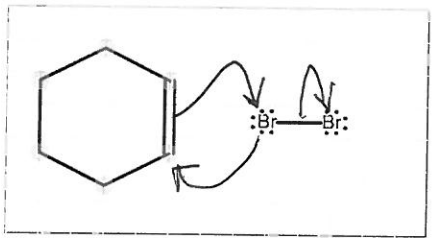
c) Assign C1 and C5 carbons only:



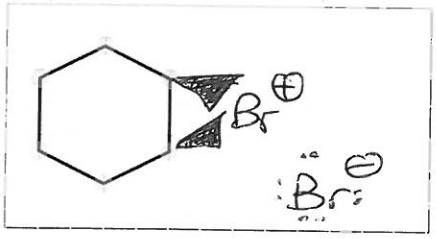
3. (6 pts)

Show the mechanism for the following reaction conducted at –5 °C in CCl_4:
cyclohexene + bromine yields a dibromocyclohexane
Draw structures – including charges and electrons – and add curved arrows. Details count.

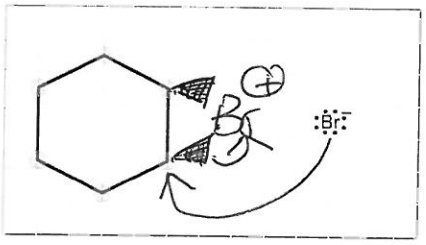
Step 1
Add three curved arrows to the first step.



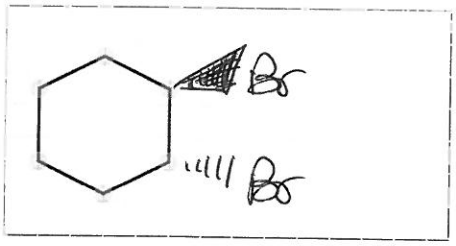
Draw the step 1 products:
1 organic species;
1 inorganic species.



Step 2
• Reproduce the step 1 products.
• Add two curved arrows to show the bromide ion reacting with the organic species.



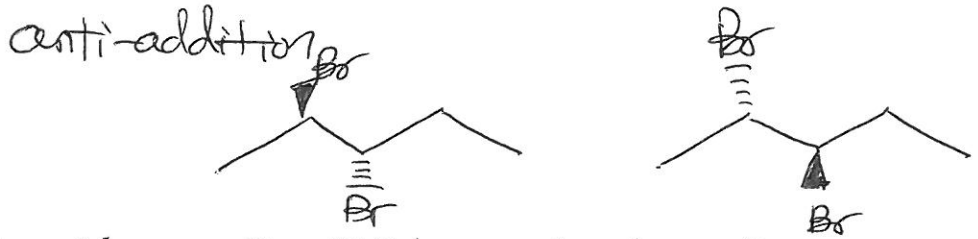
Draw the final product.



racemic

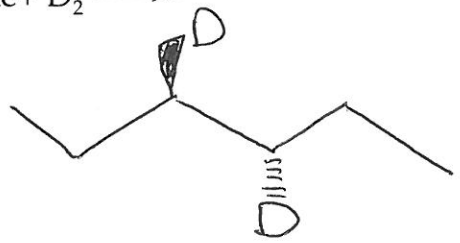
4. (12 pts) Give the structure and stereochemistry of all products formed in each of the following reasons.

a) *trans*-2-pentene + Br_2 ⟶



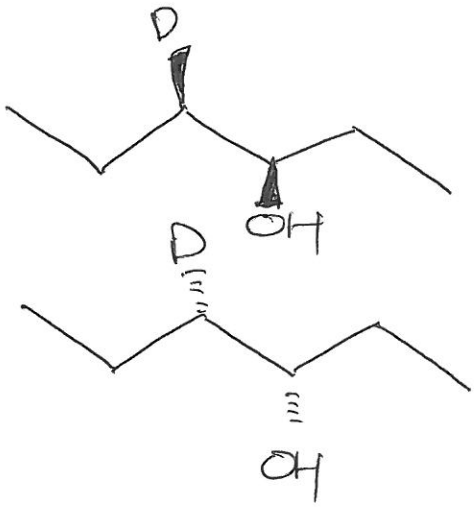
b) *trans*-3-hexene + Br_2 + H_2O (excess solvent) ⟶

c) *cis*-3-hexene+ D_2 $\xrightarrow{Pt/C}$



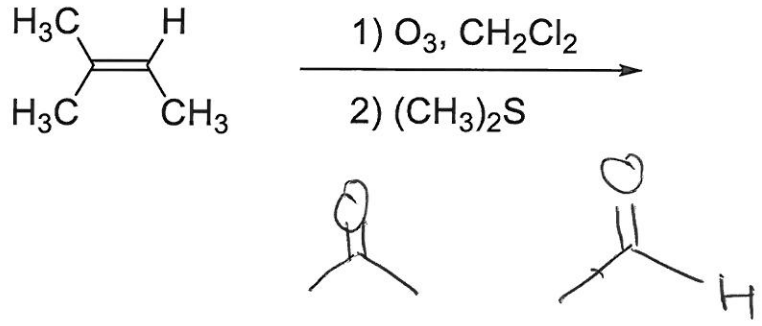
meso-hexane-3,4-d_2

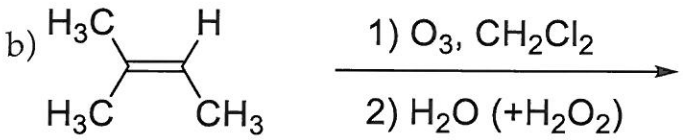
d) *cis*-3-hexene +BD_3 $\xrightarrow{THF}$ $\xrightarrow{H_2O_2/OH^-}$



racemic

5. (10 pts) Provide the ozonolysis products.

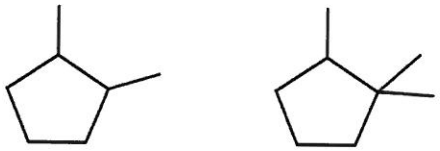
a) 

b) 

6. (8 pts) Identify each pair of compounds as constitutional isomers, stereoisomers, identical molecules, or other.

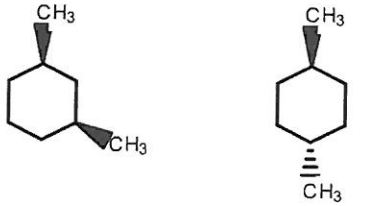
(a)

- ☒ other
- ○ stereoisomers
- ○ constitutional isomers
- ○ identical molecules



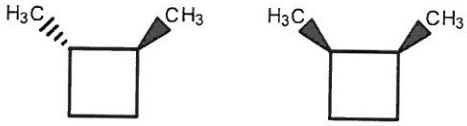
(b)

- ○ other
- ○ identical molecules
- ○ stereoisomers
- ☒ constitutional isomers



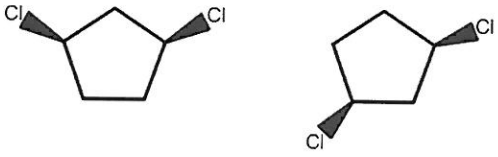
(c)

- ☒ stereoisomers
- ○ other
- ○ constitutional isomers
- ○ identical molecules



(d)

- ○ constitutional isomers
- ☒ identical molecules
- ○ other
- ○ stereoisomers

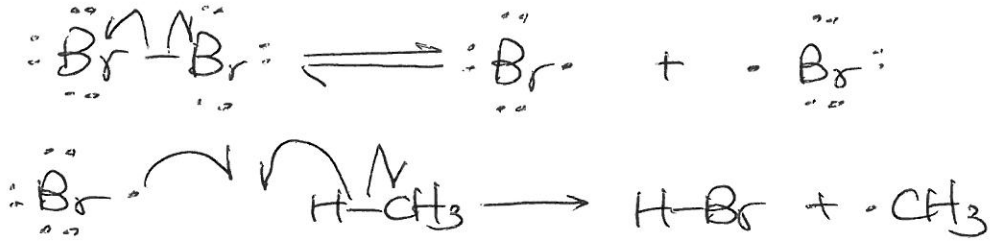


7. (8 pts) Draw a mechanism for the two propagation steps in the bromination of methane. The overall reaction is shown here:

$$CH_4 + Br_2 \xrightarrow{h\nu} CH_3Br + HBr$$

For full credit, include all curved arrows, unpaired electrons, lone pairs of electrons, and any non-zero formal charges.

First propagation step:



Second propagation step:

Calculate the overall enthalpy change for this bromination. The bond dissociation energies you will need are given below. Draw a box around your answer.

C-H in methane: 104 kcal/mol; Br-Br: 46 kcal/mol; H-Br: 88 kcal/mol

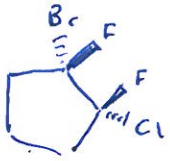
C-Br in CH_3Br: 70 kcal/mol

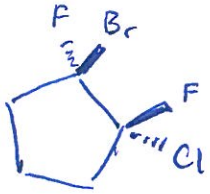
$\oplus 104 - 88 = 16$

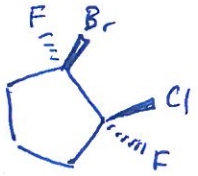
$\oplus 46 - 70 = -24$

$\Delta H_{rxn} = -8$ kcal/mol

8. (8 pts) Draw every stereoisomer for 1-bromo-2-chloro-1,2-difluorocyclopentane. Use wedge-and-dash bonds for the substitutent groups, and be sure that they are drawn on the outside of the ring, adjacent to each other.

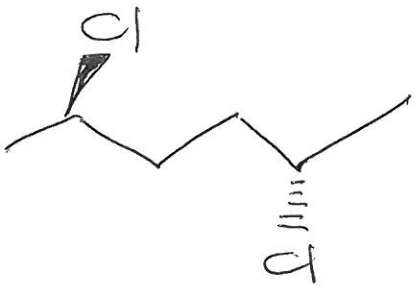






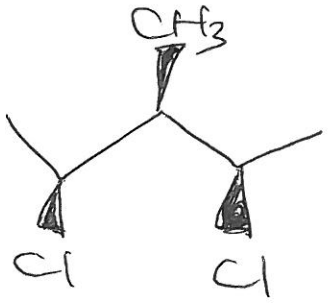
9. (10 pts) How many distinct *meso* compounds are possible for $C_6H_{12}Cl_2$? Draw the structures of each *meso* compound and indicate plane of symmetry.

(1)

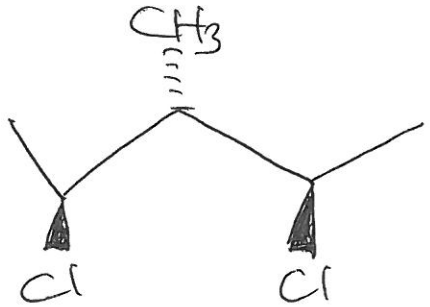


(2)

(3)

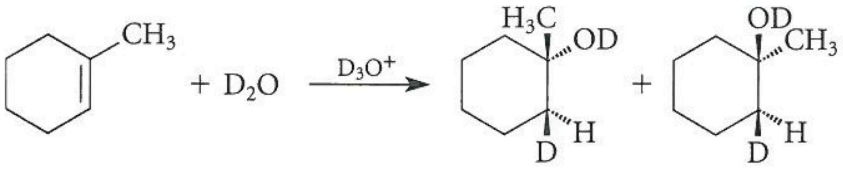


(4)



(5)

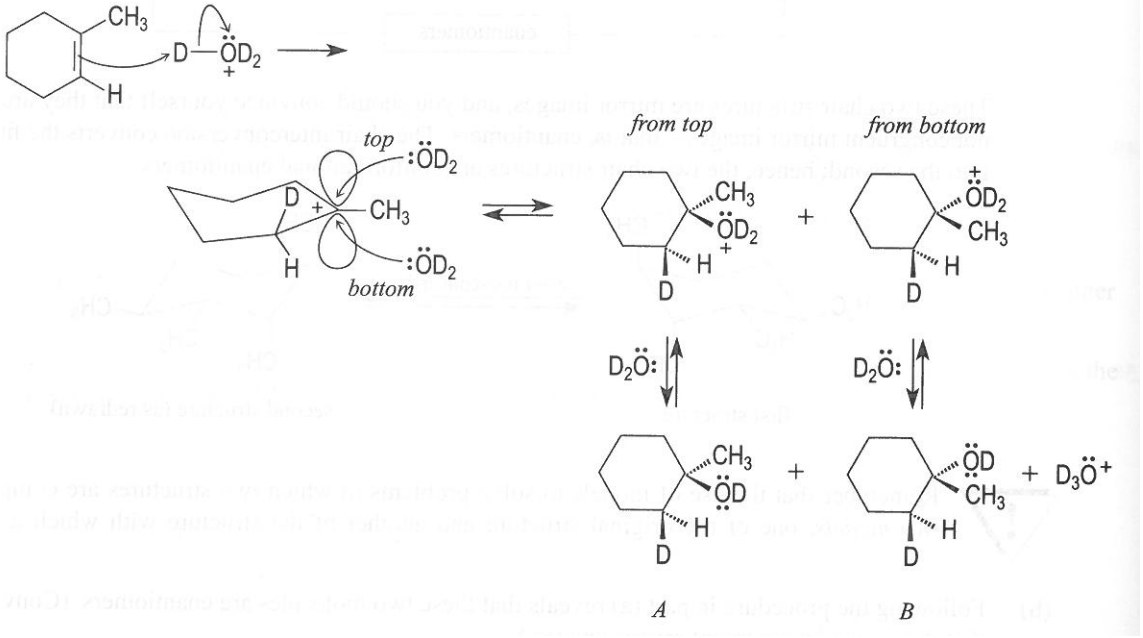
10. (10 pts) When 1-methylcyclohexene undergoes hydration in D_2O, the product is a mixture of diastereomers; the hydration is thus not a stereoselective reactions:



both compounds are racemates

(a) Show why the accepted mechanism of this reaction is consistent with these stereochemical results.

Hydration involves a carbocation intermediate. Because a carbocation can react with a nucleophile at either face of its vacant 2*p* orbital, a mixture of stereoisomeric hydration products *A* and *B* is expected.



(b) Why must D_2O rather than H_2O be used to investigate the stereoselectivity of this addition reaction?

The use of D_2O allows us to differentiate the protons of the solvent from those of the starting materials.

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