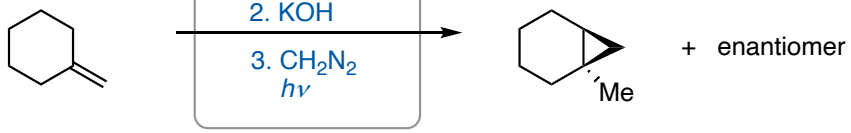
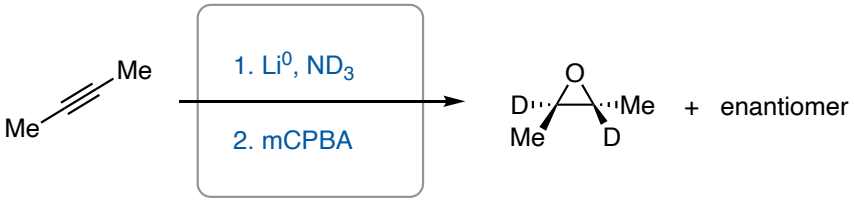
21 pts. **1.** Fill in the reagents or draw the structure of the missing reactant in the boxes below. Feel free to use any reagent and any source of carbon to obtain the products shown in as many steps necessary. The only products for each reaction are listed.

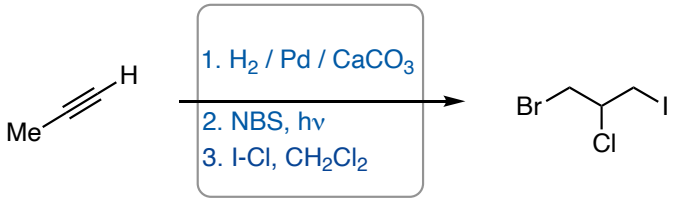
A



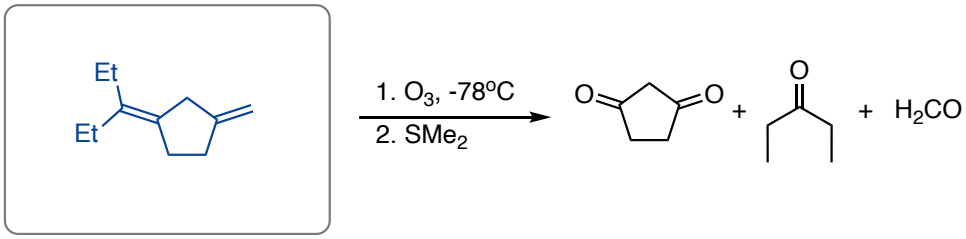
B



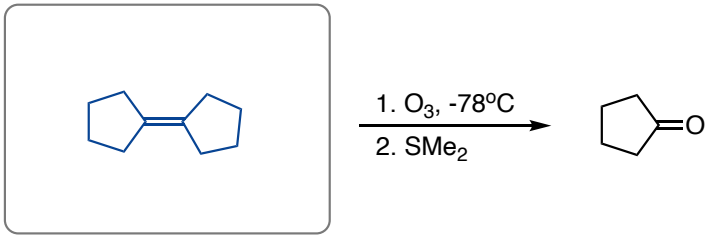
C



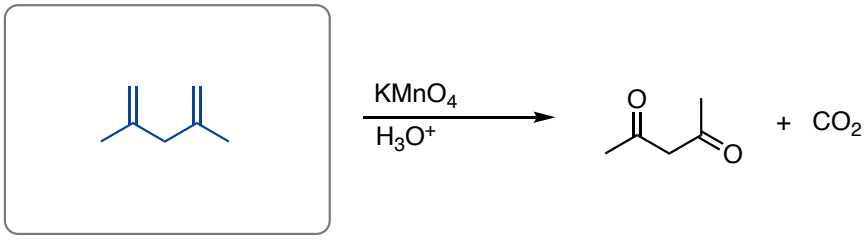
D



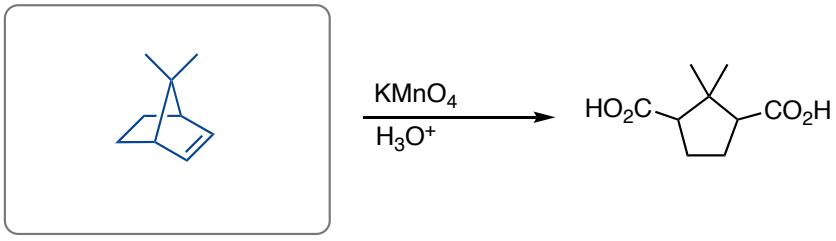
E



F

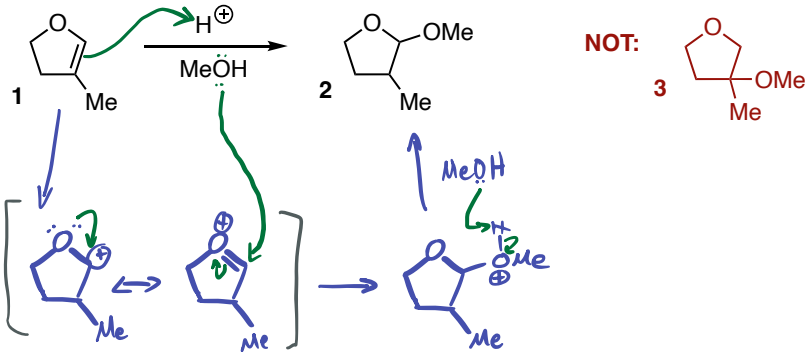


G



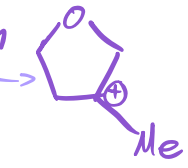
pts. this pg.

4 pts. **2a.** The reaction below yields **only product 2**, NOT product **3**. Draw the best mechanism that accounts for the formation of **2**.



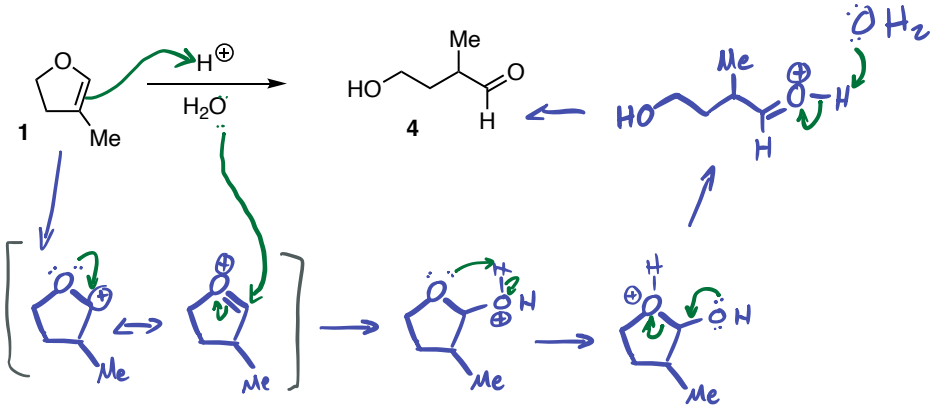
3 pts. **2b.** Why is the Anti-Markovnikov product **3** not formed? Draw any chemical structure(s) as part of your answer.

Compound 3 is not formed because the carbocation intermediate is derived from a 3° cation that is only stabilized by hyperconjugation.



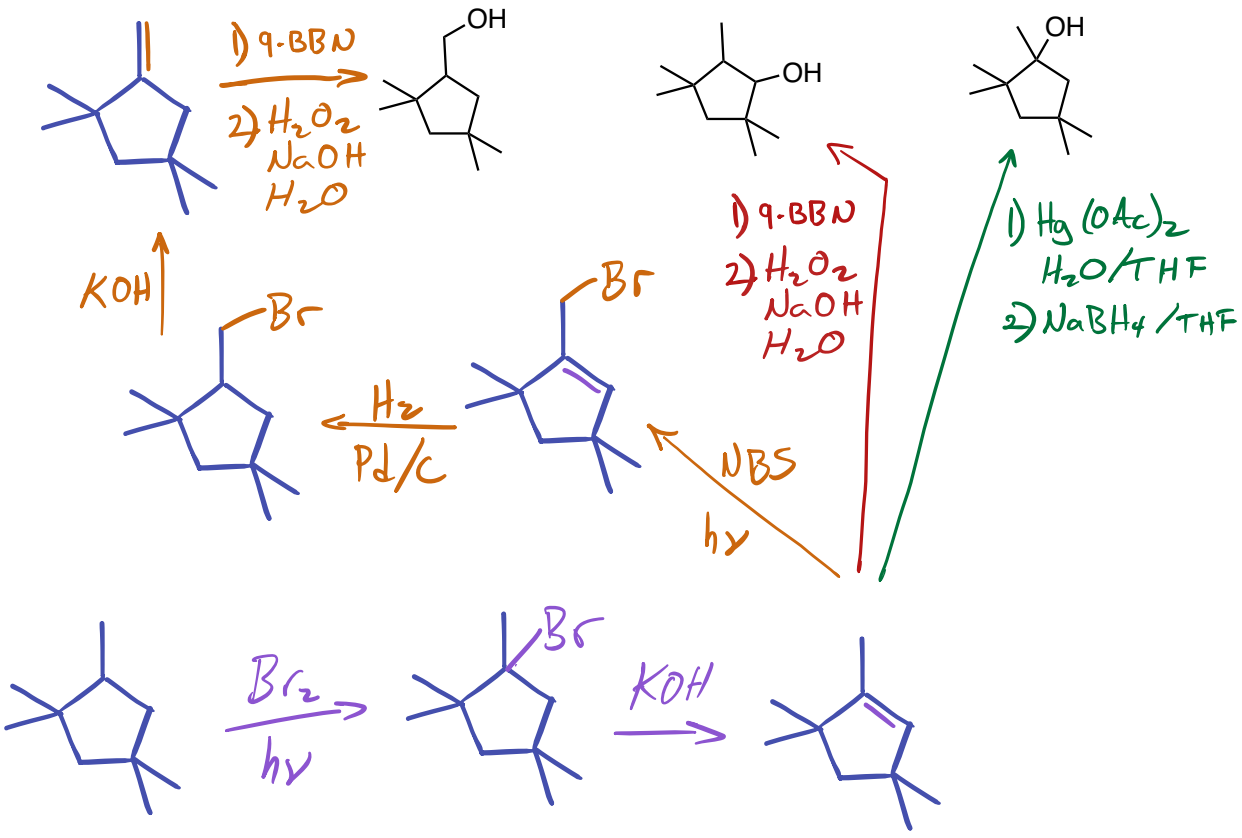
Since the cation formed above is more stable due to resonance (see mech), despite only being a 2° cation, compound 2 is preferred.

5 pts. **2c.** When water is used instead of using methanol, the reaction below yields product **4.** Draw the best mechanism that accounts for the formation of **4**.



pts. this pg.

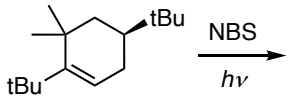
10 pts. **3**. Starting from 1,1,2,4,4-pentamethylcyclopentane, propose **the synthesis** of each of the three alcohols below. Avoid reactions that lead to rearrangements. You may use any reagents of your choice, as many number of steps, and you can reuse any compound you synthesize as part of this problem.



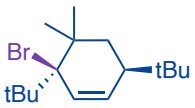
pts. this pg.

6 pts. **4a.** The bromination of each enantiomer of 1,4-di-*tert*-butyl-6,6-dimethylcyclohex-1-ene yields only one stereoisomer product with two chiral centers with high diastereoselectivity. In the respective boxes below, draw the structure of the observed products in each reaction (**A** and **B**). *Hint: do problem **4b** first.*

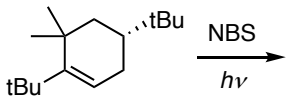
Rxn 1



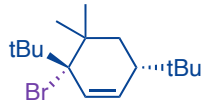
A



Rxn 2

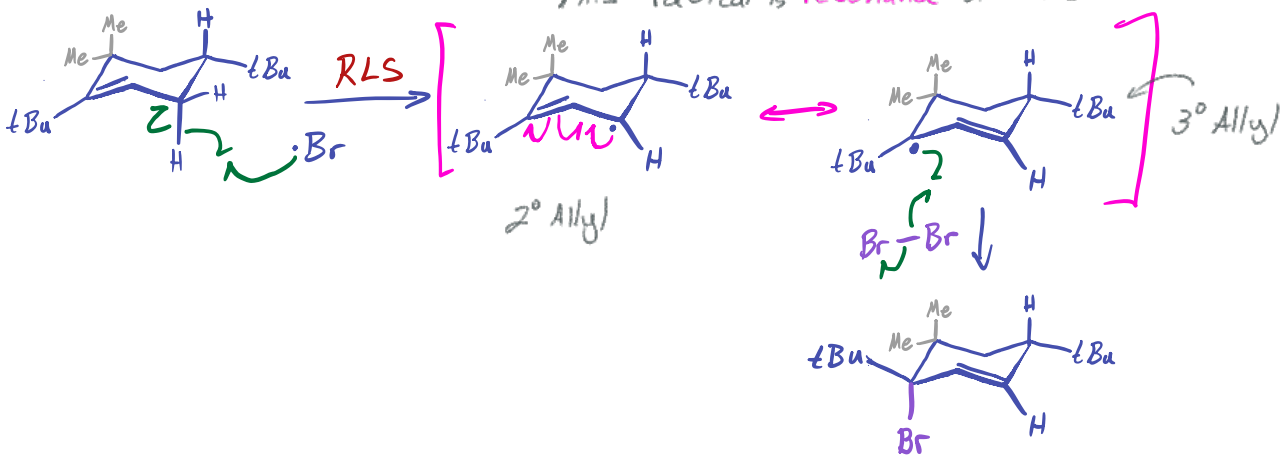


B



5 pts. **4b.** Draw **only the Propagation Steps** of **Rxn 1** and label the **RLS.** *Note: you do not need to show initiation (i.e. formation of* •Br*).*

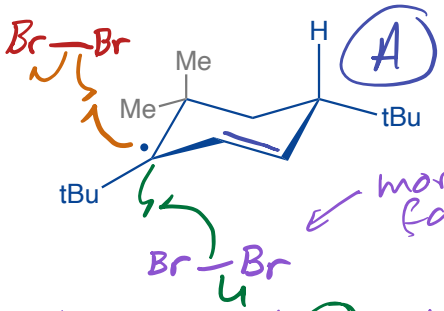
this radical is resonance-stabilized.



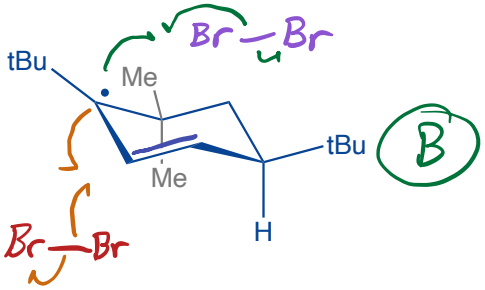
5 pts. **4c.** In the space below, explain why only one diastereomer is formed in each reaction above. Draw the best representation of the intermediate or transition state structure that *sets the stereochemistry* in each **A** and **B**.

These are the two intermediates that set the stereoche @ the RLS.

less favored approach



more favored



In both (A) & (B), the Br_2 approaches from the face that will lead to the Br in the axial position since the tBu group has the highest 1,3-diaxial strain.

If Br_2 approaches as shown above in red, the resulting product will be more strained because the tBu group will end up in the axial position.

pts. this pg.

The hydrogenation of 5 cycloalkene isomers (**A** – **E**) of molecular formula C_6H_{10} yields methylcyclopentane:

Compounds **A** through **E** + H_2 + Pd/C $\rightarrow$ methylcyclopentane

Please provide the correct structure in the corresponding boxes that **fit the appropriate description**. Draw dashes and wedges, where necessary, to show stereogenic centers.

4 pts. **5a**. Compounds **A** and **B** are enantiomers of one another.

A has *(R)* configuration and **B** has *(S)* configuration.

A, *(R)*-configuration

B, *(S)*-configuration

12 pts. **5b.** The remaining three isomers are achiral (**C**, **D**, and **E**), and when used in reactions as described below can yield products selectively or as racemic mixtures. Show the single product arising from the chemoselective reaction. For the reactions that yield racemic mixtures, draw each structure of the possible products (use **dashes** and **wedges** where necessary).

C and **D** $\xrightarrow{HCl}$

only one achiral chloroalkane

E

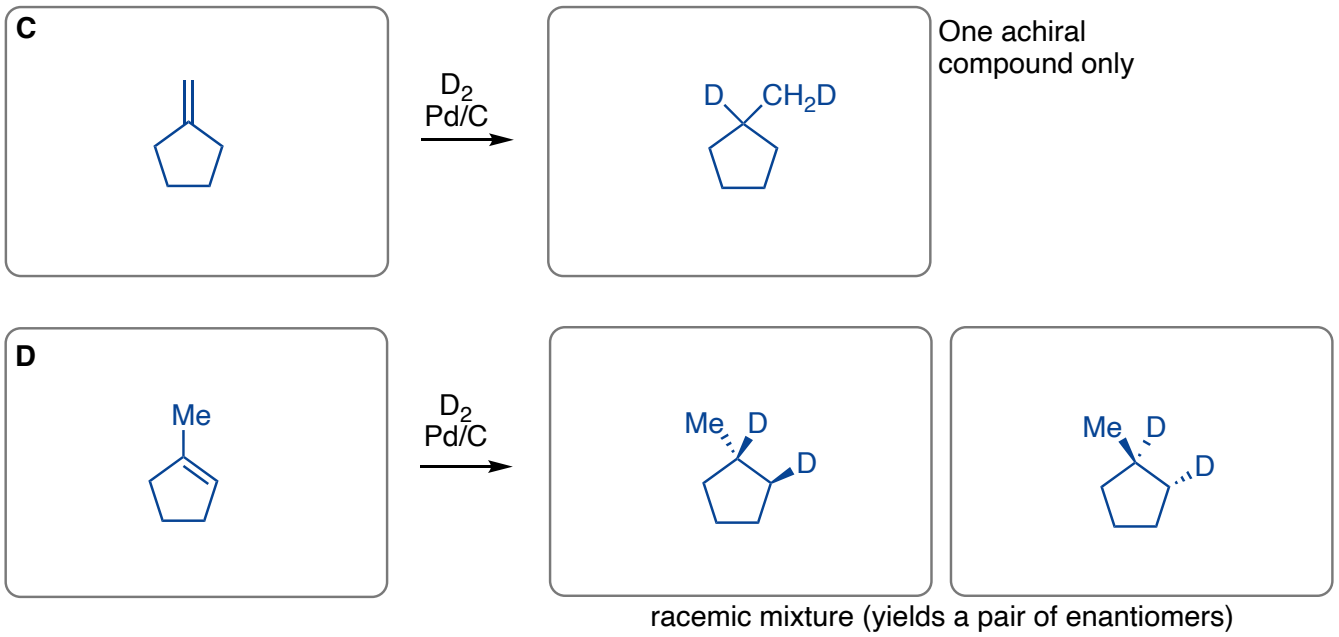
$\xrightarrow{HCl}$

Four stereoisomers of $C_6H_{11}Cl$

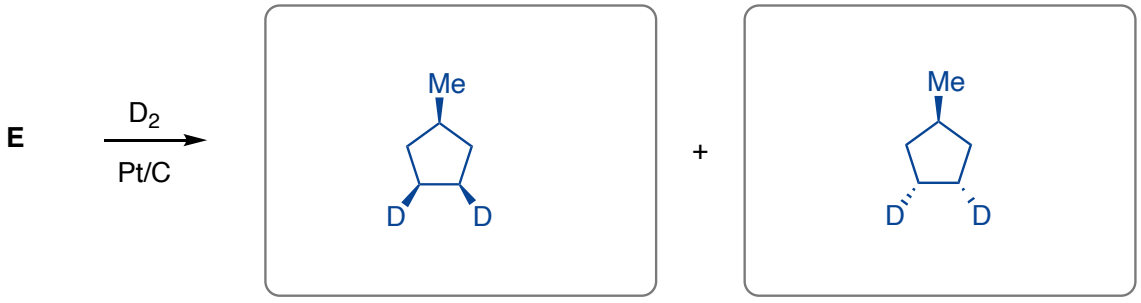
continued (next page)

pts. this pg.

10 pts. **5c.** When compounds **C** and **D** are reacted with D_2 in the presence of a catalyst, we observe the formation of different products that meet the criteria below. In the boxes, fill in the correct structures (use dashes and wedges where necessary).



4 pts. **5d.** When compound **E** reacts with D_2 in the presence of a catalyst, we observe the formation of two achiral products.



Two different achiral compounds

2 pts. **5e.** What is the relationship between the compounds above in **5d**? Circle one.

Constitutional Isomers **Same** **Diastereomers**

Enantiomers **Conformational Isomers**

pts. this pg.