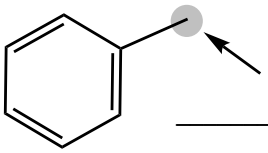
CONCEPT: REACTIONS AT BENZYLIC POSITIONS



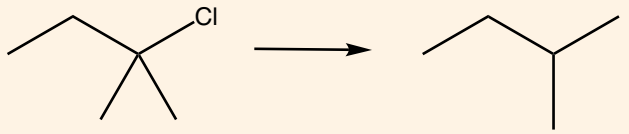
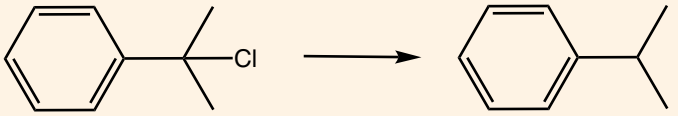
_____ Position

- Benzylic positions are _____ due to stable reaction intermediates.
  - 1) S_N1/E1: _____ formation.
  - 2) S_N2/E2: benzylic _____.
  - 3) Oxidation of benzylic _____.

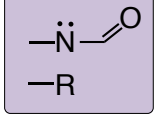
1) S_N1/E1 Reactions of Benzylic Compounds

- Carbocation intermediate formation is the _____-determining step.
  - □ Benzylic carbocations form _____ than their non-benzylic counterparts.
    - **Alkyl C^+:** stabilized by _____conjugation.
    - **Benzylic C^+:** stabilized by _____.

Carbocation Formation

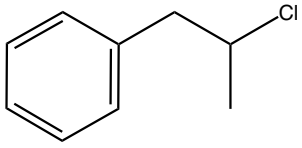
Reaction	Relative Rate
	_____
	_____

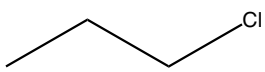
EDGs:

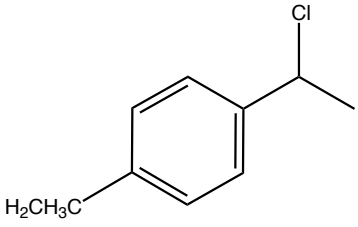


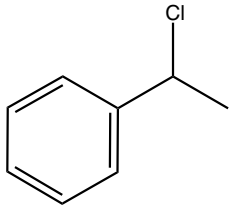
  - □ Ortho & para substituents that act as electron _____ groups _____ S_N1 rates at benzylic positions.

EXAMPLE: Which of the following alkyl halides will form a carbocation the fastest?

a) 

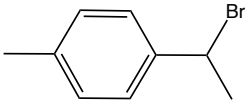
c) 

b) 

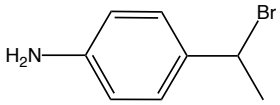
d) 

CONCEPT: REACTIONS AT BENZYLIC POSITIONS

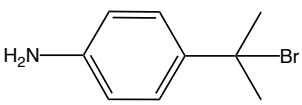
PRACTICE: Rank the following alkyl halides in increasing order of reactivity in S_N1 reaction.



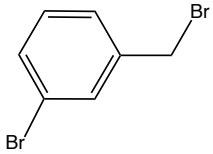
I



II



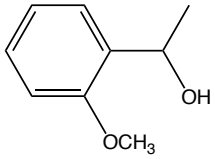
III



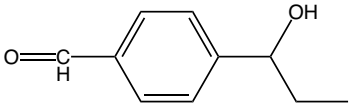
IV

PRACTICE: Which of the following alcohols will undergo acid-catalyzed dehydration the fastest and which one the slowest?

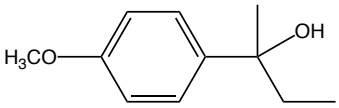
1)



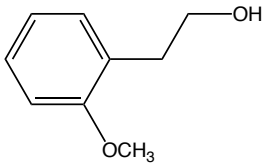
2)



3)



4)



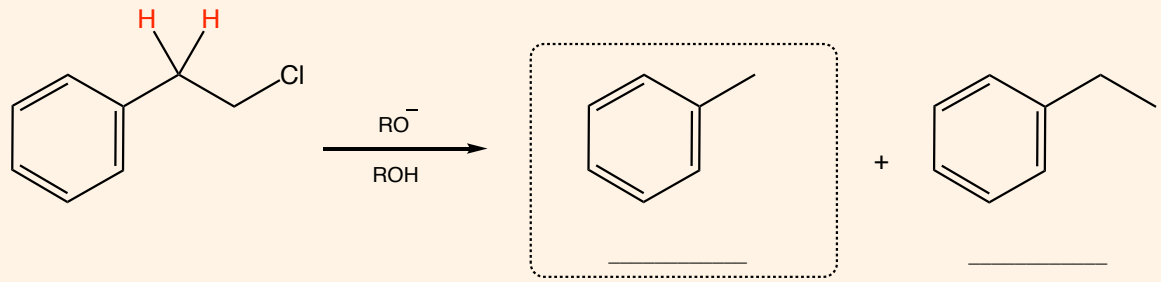
a) 1 and 2 b) 3 and 2 c) 2 and 3 d) 3 and 4

CONCEPT: REACTIONS AT BENZYLIC POSITIONS

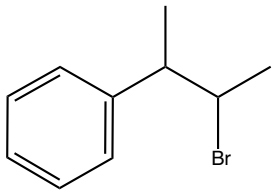
2) E2 Reactions of Benzylic Hydrogens

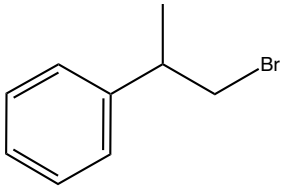
- Due to higher _____ of benzylic β-hydrogens, _____ products predominate.
  - □ Alkene products of such eliminations are conjugated and are stabilized by _____.

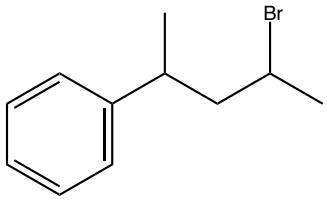
E2 Reaction of Benzylic Halides



EXAMPLE: Select a compound that will have the fastest rate of E2 reaction with a small strong base.

a) 

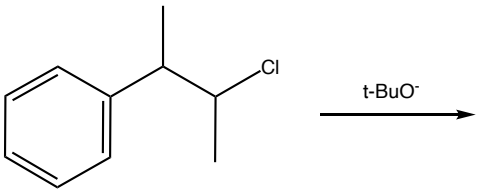
b) 

c) 

d) both a and b

e) both a and c

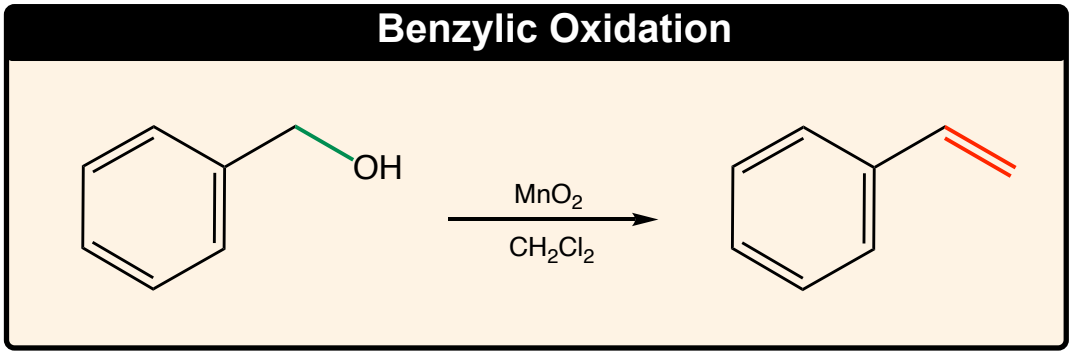
PRACTICE: Provide mechanism and structure of major elimination product of the following reaction.



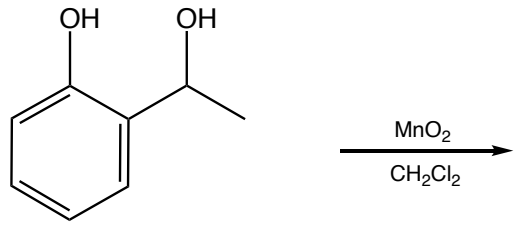
CONCEPT: REACTIONS AT BENZYLIC POSITIONS

3) Benzylic Alcohol Oxidation

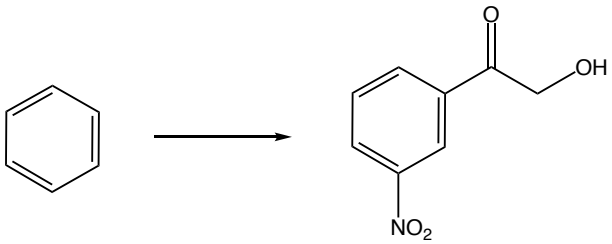
- A weak oxidation where _____/CH_2Cl_2 _____ oxidizes the benzylic –OH group.
  - □ Benzylic alcohols are much more _____ than non-benzylic alcohols.



EXAMPLE: Give structure of product of following oxidation reaction.



PRACTICE: Supply the reagents necessary to accomplish the following transformation.



a) 1. $CH_3CH_2Br/AlBr_3$
2. NBS/hv
3. NaOEt/EtOH
4. $OsO_4/NaHSO_3$, H_2O
5. MnO_2/CH_2Cl_2
6. HNO_3/H_2SO_4

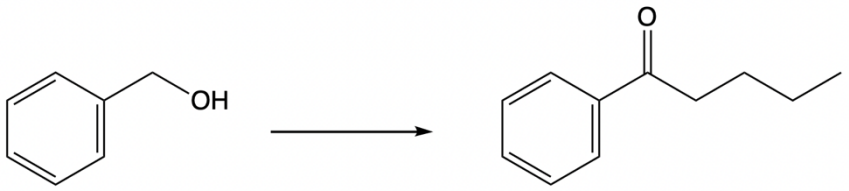
b) 1. HNO_3/H_2SO_4
2. $CH_3CH_2Br/AlBr_3$
3. NBS/hv
4. NaOEt/EtOH
5. $OsO_4/NaHSO_3$, H_2O
6. MnO_2/CH_2Cl_2

c) 1. $CH_3CH_2Br/AlBr_3$
2. NBS/hv
3. NaOEt/EtOH
4. $BH_3 \cdot THF/H_2O_2$, NaOH
5. MnO_2/CH_2Cl_2
6. $Br_2/FeBr_3$

d) 1. HNO_3/H_2SO_4
2. NaOEt/EtOH
3. $CH_3CH_2Br/AlBr_3$
4. NaOEt/EtOH
5. H_3O^+
6. PCC/CH_2Cl_2

CONCEPT: REACTIONS AT BENZYLIC POSITIONS

PRACTICE: Provide the chemical steps necessary for the following synthesis.



PRACTICE: Beginning with benzene, provide a method to prepare the following compound.