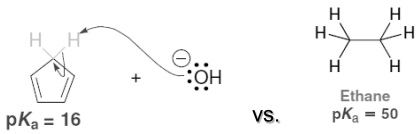
Chemical Behavior of Aromatic Compounds

Acidity

Aromatic Ions / Acidity

- The pK_a value for cyclopentadiene is much lower than typical C-H bonds.

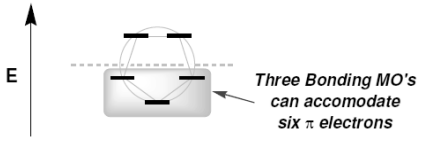


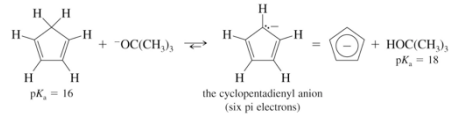
pK_a = 16 vs.

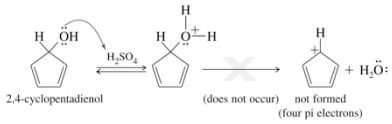
Why?

Aromatic Ions / Acidity

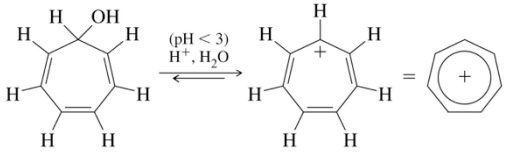
- If six pi electrons are present, the ion is aromatic. What is the ion's formal charge?
- Why does acid-base equilibrium favor the ion?





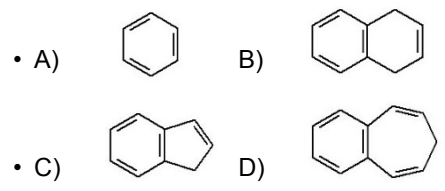


Can carbocations be aromatic?



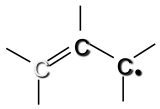
Question

- Which compound has the lowest pK_a?

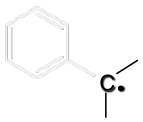


Free-Radical Halogenation
of Alkylbenzenes

The Benzene Ring as a Substituent



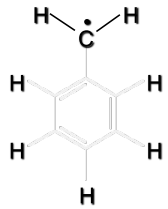
allylic radical



benzylic radical

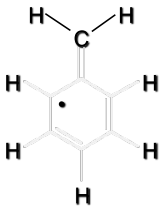
Benzylic carbon is analogous to allylic carbon.

Resonance in Benzyl Radical



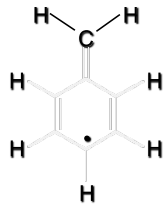
Unpaired electron is delocalized between benzylic carbon and the ring carbons that are ortho and para to it.

Resonance in Benzyl Radical



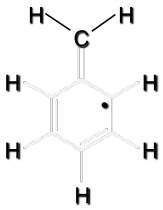
Unpaired electron is delocalized between benzylic carbon and the ring carbons that are ortho and para to it.

Resonance in Benzyl Radical



Unpaired electron is delocalized between benzylic carbon and the ring carbons that are ortho and para to it.

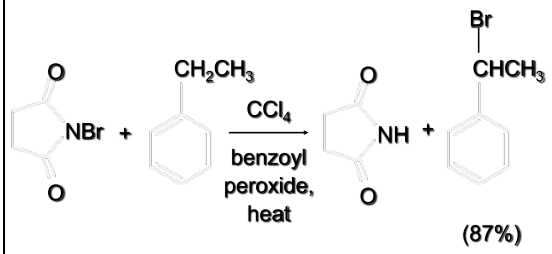
Resonance in Benzyl Radical



Unpaired electron is delocalized between benzylic carbon and the ring carbons that are ortho and para to it.

N-Bromosuccinimide (NBS)

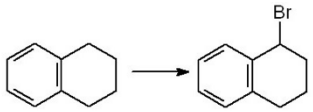
is a convenient reagent for benzylic bromination



(87%)

Question

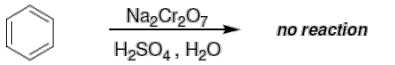
- Which reagent would you use for the reaction below?



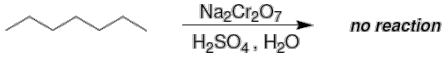
- A) Br_2, CCl_4
- B) $HBr_{aqueous}$
- C) HBr, peroxides
- D) NBS, peroxides, heat

Oxidation of Alkylbenzenes

Reactions at the Benzylic Carbon Position

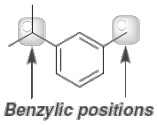


no reaction



no reaction

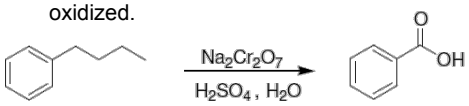
Benzylic Oxidation Occurs:



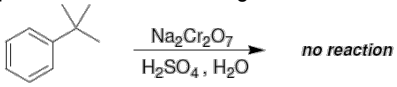
Benzylic positions

Reactions at the Benzylic Carbon Position

- In general, benzylic positions can readily be fully oxidized.

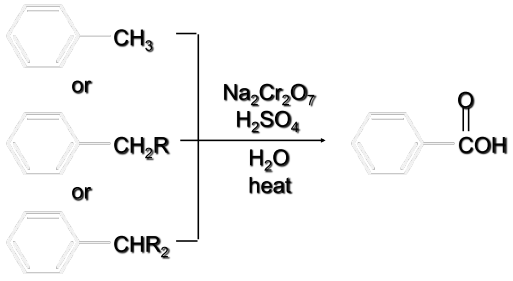


- The benzylic position needs to have at least one proton attached to undergo oxidation.

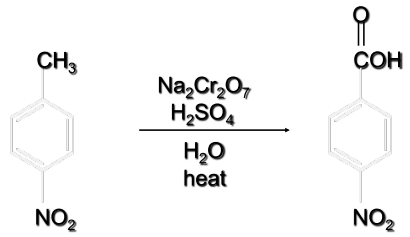


no reaction

Oxidation of a Benzylic Carbon



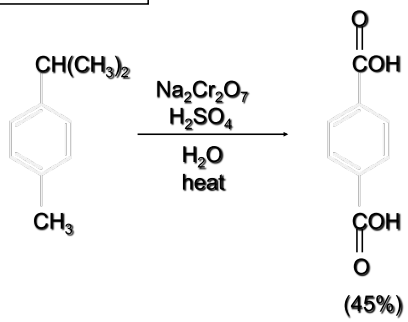
Example



p-Nitrotoluene

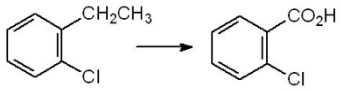
p-Nitrobenzoic acid (82-86%)

Example



(45%)

Question

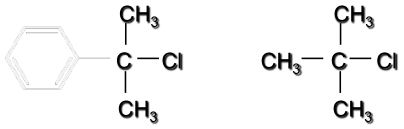
- Select the best reagent(s) to accomplish the transformation shown.
- 

- A) PCC, CH_2Cl_2
- B) $K_2Cr_2O_7$, H_2SO_4, heat
- C) $LiAlH_4$ then H_2O
- D) NBS then CH_3ONa

S_N1 Reactions of Benzylic Halides

Benzylic S_N1 Reactions

Relative solvolysis rates in aqueous acetone:

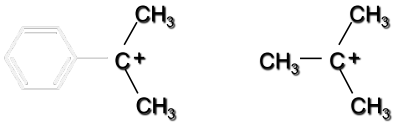


620 1

Tertiary benzylic carbocation is formed more rapidly than tertiary carbocation; therefore, more stable.

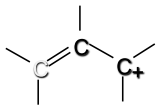
Benzylic S_N1 Reactions

Relative rates of formation:

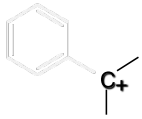


more stable less stable

Compare



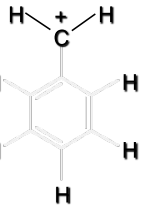
allylic carbocation



benzylic carbocation

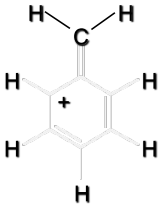
Benzylic carbon is analogous to allylic carbon.

Resonance in Benzyl Cation



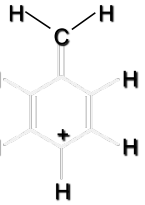
Positive charge is delocalized between benzylic carbon and the ring carbons that are ortho and para to it.

Resonance in Benzyl Cation



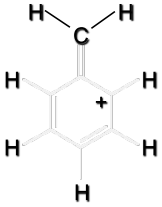
Positive charge is delocalized between benzylic carbon and the ring carbons that are ortho and para to it.

Resonance in Benzyl Cation



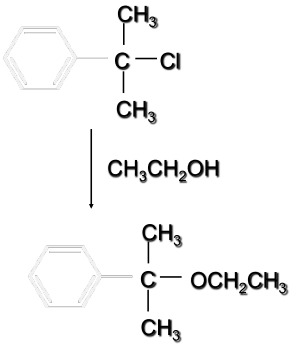
Positive charge is delocalized between benzylic carbon and the ring carbons that are ortho and para to it.

Resonance in Benzyl Cation



Positive charge is delocalized between benzylic carbon and the ring carbons that are ortho and para to it.

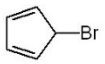
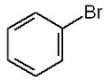
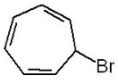
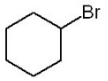
Solvolysis



(87%)

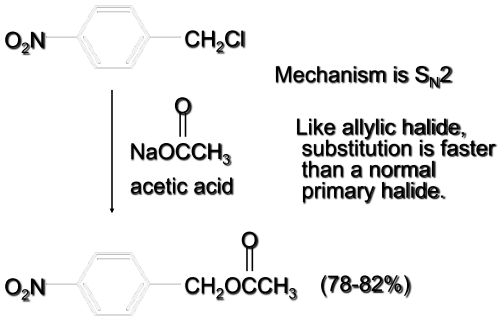
Question

- Which compound would undergo solvolysis at a faster rate?

- A) 
- B) 
- C) 
- D) 

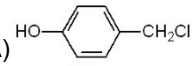
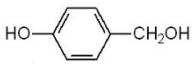
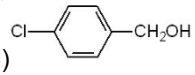
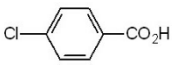
S_N2 Reactions of Benzylic Halides

Primary Benzylic Halides

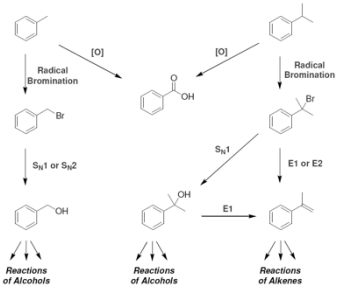


Question

- Which product will be siolated when 4 -chlorobenzyl chloride is treated with K_2CO_3 in H_2O?

- A) 
- 
- 
- C)
- D) 

Reactions Summary



- SEE: SKILLBUILDER 18.4.

Preparation of Alkenylbenzenes

•dehydrogenation

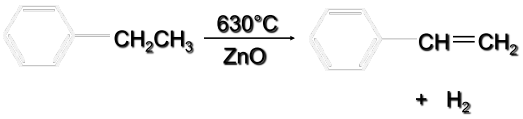
•dehydration

•dehydrohalogenation

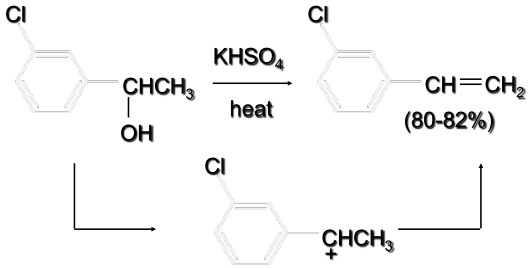
Dehydrogenation

•Industrial preparation of styrene

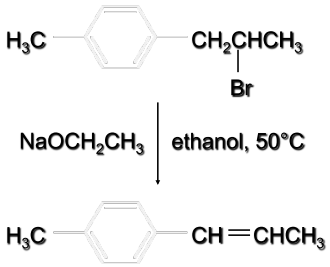
•Almost 12 billion lbs. produced annually in U.S.



Acid-Catalyzed Dehydration of Benzylic Alcohols



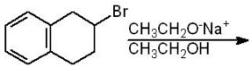
Dehydrohalogenation



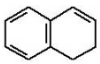
(99%)

Question

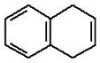
- Which product(s) will be isolated from the reaction shown



- A)



- B)



- C) Equal amounts of A and B.
- D) Neither A nor B.

Addition Reactions of Alkenylbenzenes

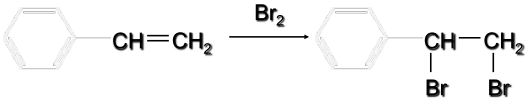
•halogenation

•addition of hydrogen halides

•Hydrogenation

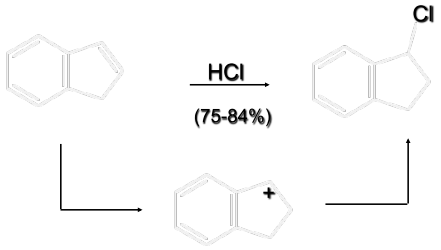
•Birch reduction of aromatics

Halogenation



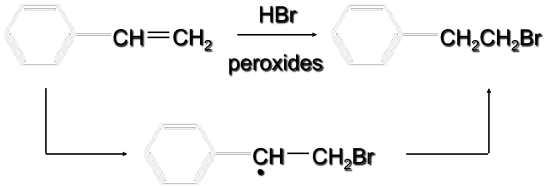
(82%)

Addition of Hydrogen Halides



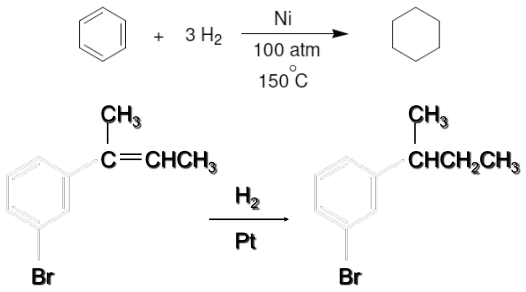
via benzylic carbocation

Free-Radical Addition of HBr



via benzylic radical

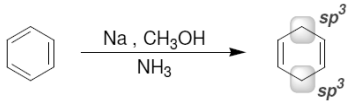
Hydrogenation



(92%)

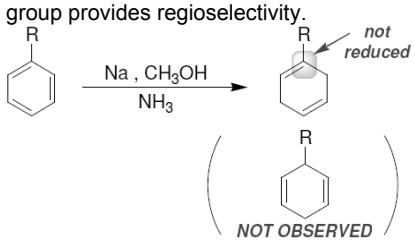
Reduction of Aromatics

- Like the BIRCH reduction with alkenes and alkynes, which adds hydrogen atoms. Aromatics are reduced by the same mechanism, where hydrogen atoms add to the ends of the ring.



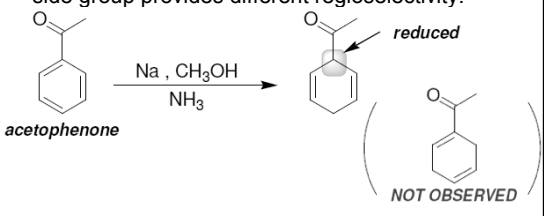
Reduction of Aromatics

- The presence of an electron donating alkyl side group provides regioselectivity.



Reduction of Aromatics

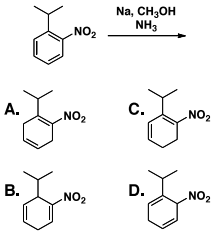
- The presence of an electron withdrawing carbonyl side group provides different regioselectivity.



- SEE: SKILLBUILDER 18.5.

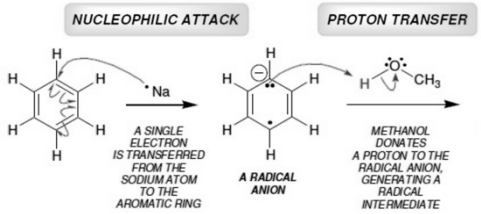
Question

What is the product of the following reaction?



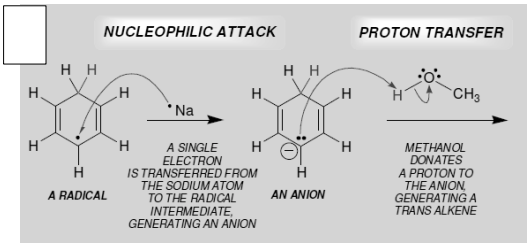
Birch Reduction Mechanism

- Step 1:



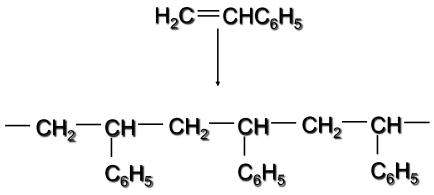
Birch Reduction Mechanism

- Step 2:



Polymerization of Styrene

Polymerization of Styrene



polystyrene