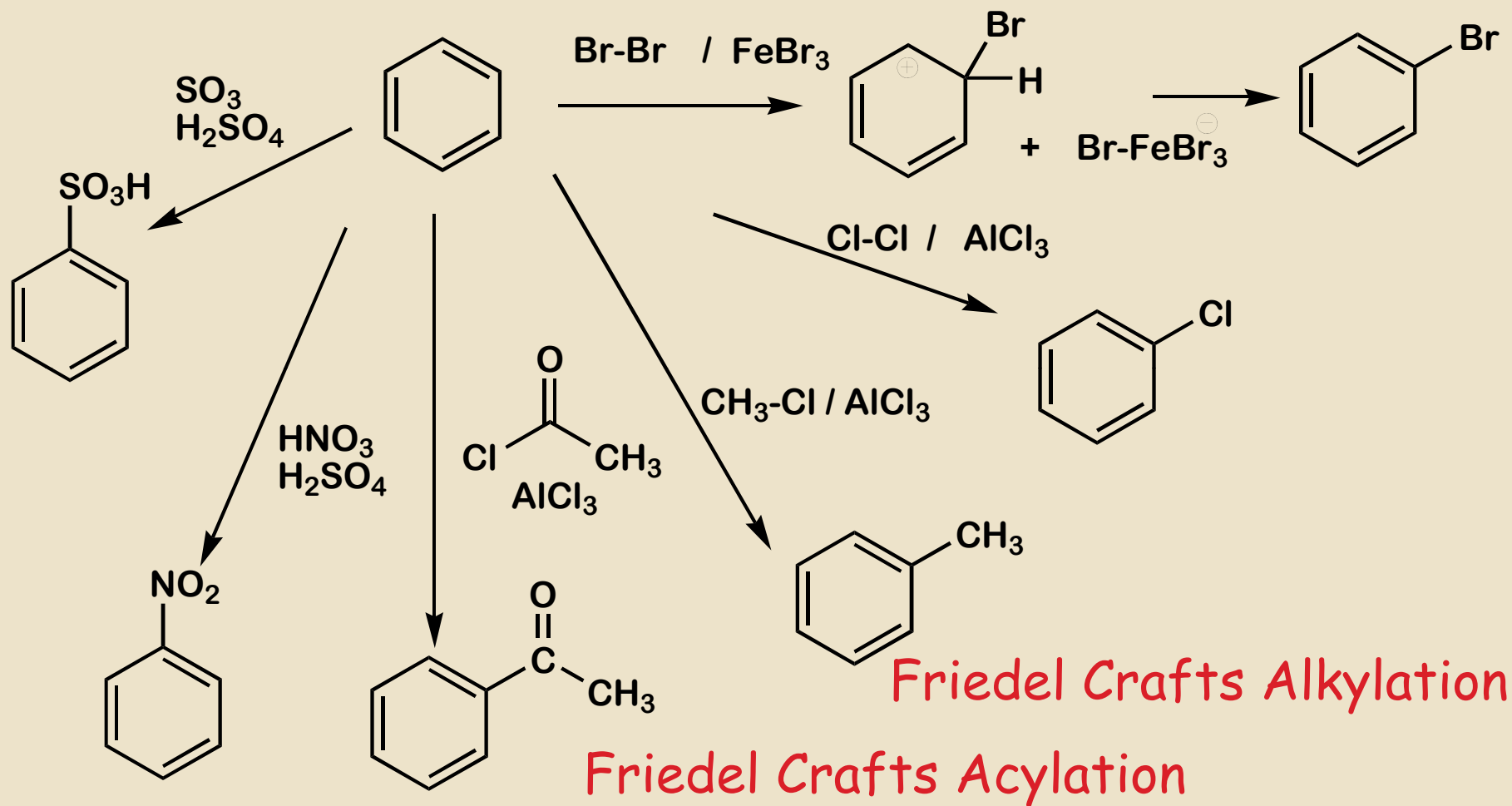


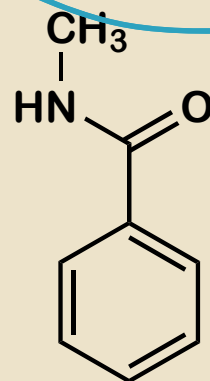
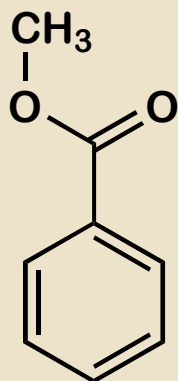
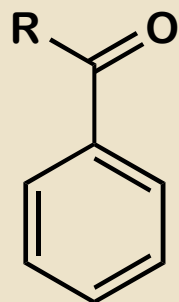
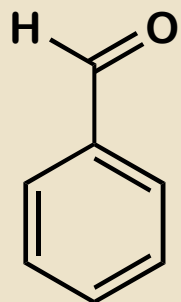
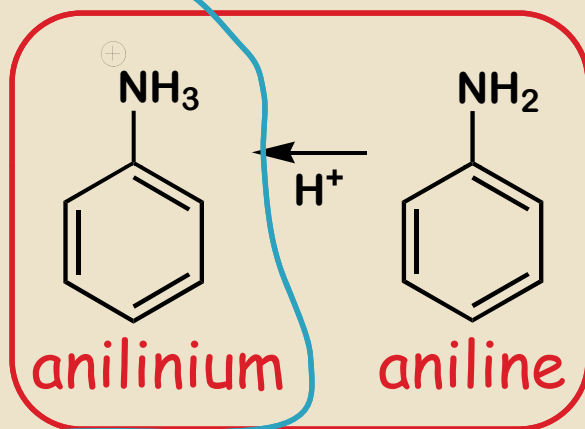
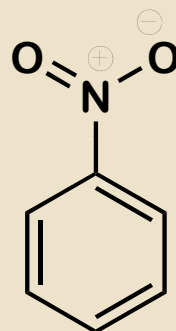
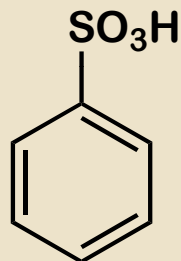
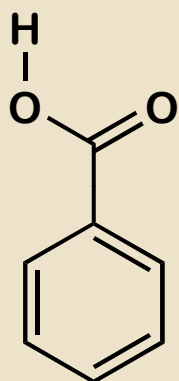
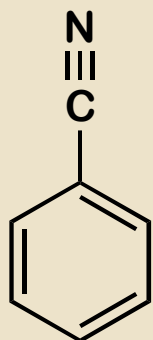
# Electrophilic Aromatic Substitution Reactions



Now that we have all our reactions, lets summarize activation and deactivation

Electron Withdrawing Groups deactivate the ring

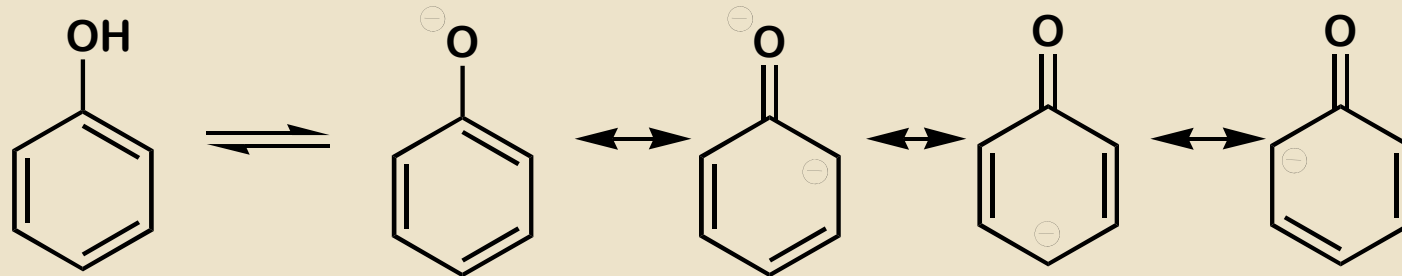
Best



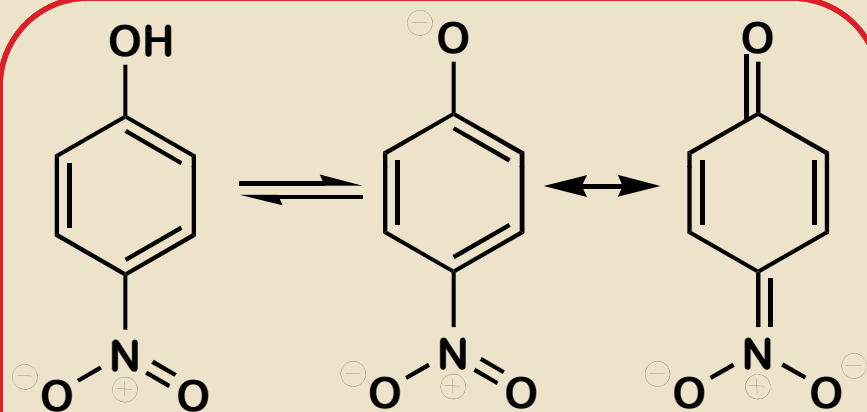
?

A. EDG  
or  
B. EWG

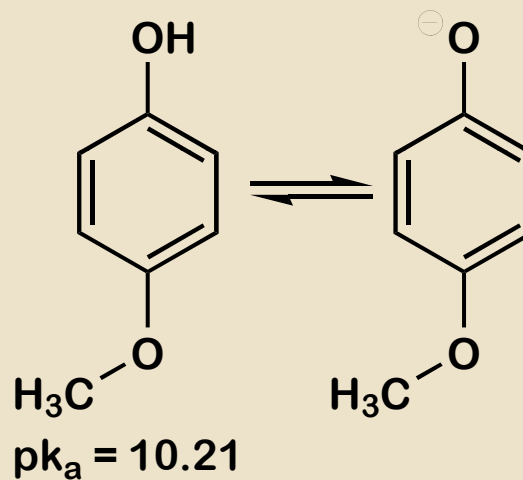
Direct substitution meta



$pK_a = 9.99$



$pK_a = 7.15$

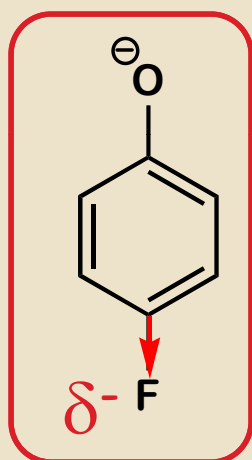
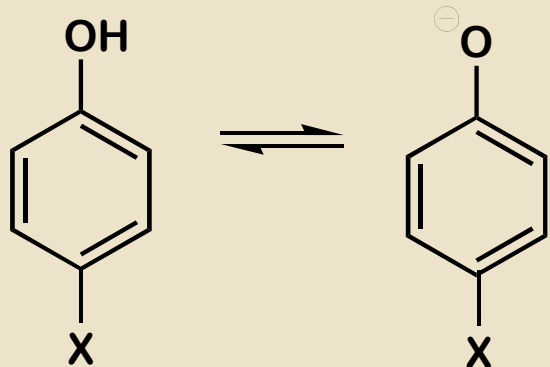


$pK_a = 10.21$

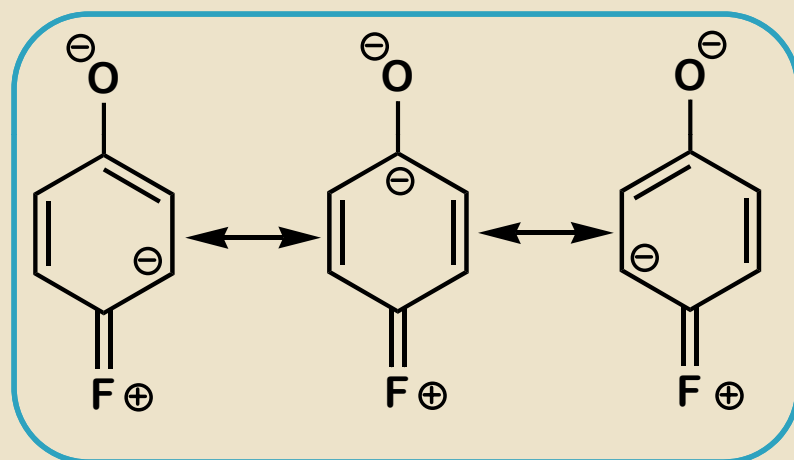
Predict  $pK_a$

A. less than 10

B. greater than 10

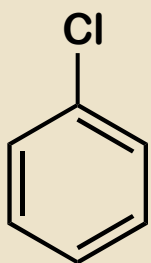


inductive effect

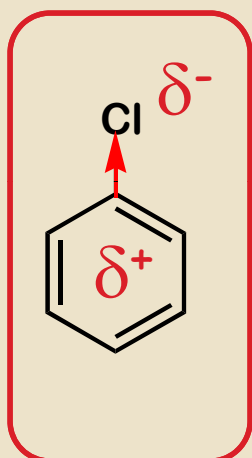


resonance effect

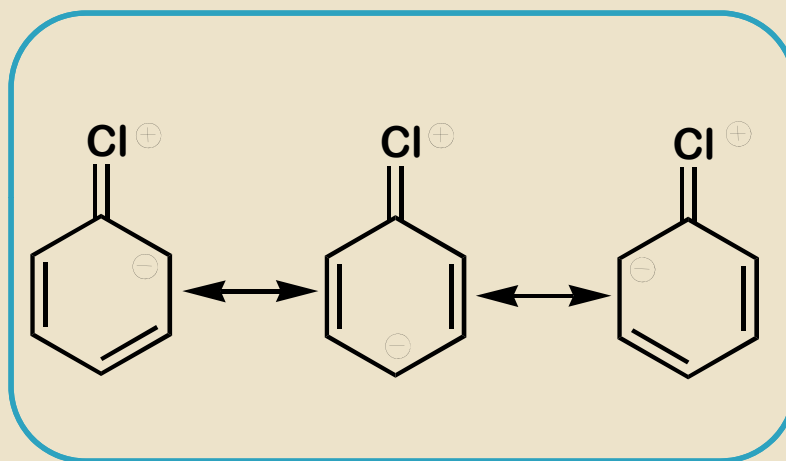
-X	pK <sub>a</sub>
-H	9.99
-NO <sub>2</sub>	7.15
-OCH <sub>3</sub>	10.21
-CH <sub>3</sub>	10.26
-CN	8.61
-COCH <sub>3</sub>	8.05
-CF <sub>3</sub>	8.68
-F	9.89
-Cl	9.41



What about a halide? Does a Cl activate or deactivate the ring?



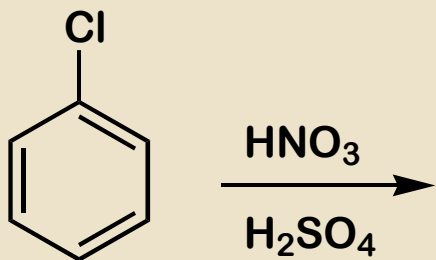
inductive  
effect



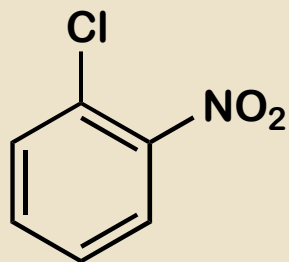
resonance  
effect

Cl poor at  
 $\pi$  bonding

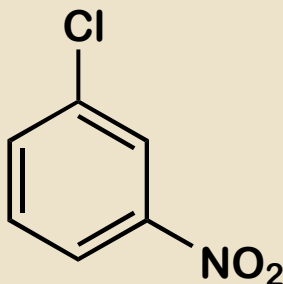
Deactivates, but directs ortho-para



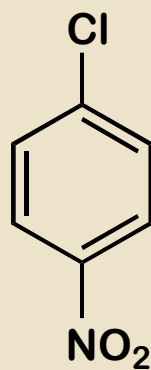
Predict the product



A



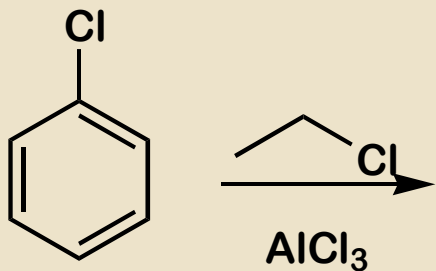
B



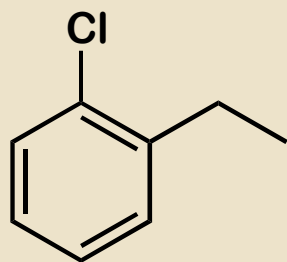
C

No Reaction

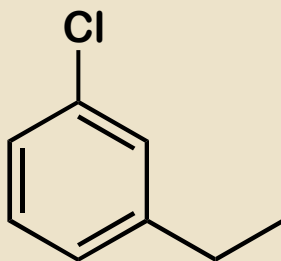
D



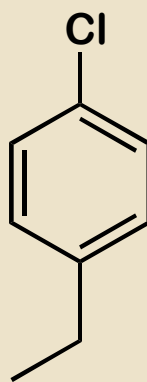
Predict the product



A



B



C

No Reaction

D

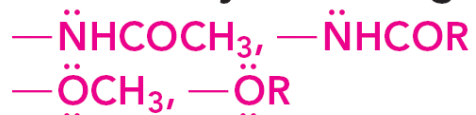
**TABLE 15.2** Effect of Substituents on Electrophilic Aromatic Substitution

Ortho-Para Directors

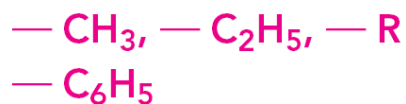
Strongly Activating



Moderately Activating



Weakly Activating

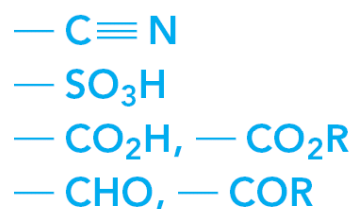


Weakly Deactivating

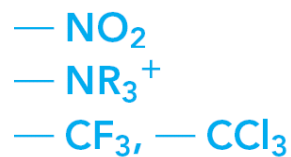


Meta Directors

Moderately Deactivating

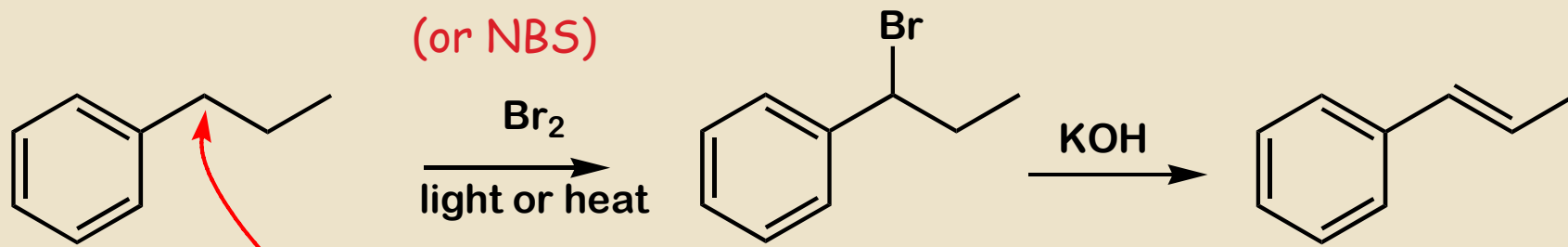


Strongly Deactivating

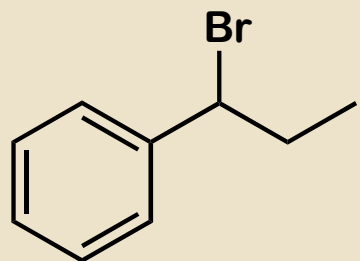


Friedel  
Crafts  
Difficult  
or  
impossible

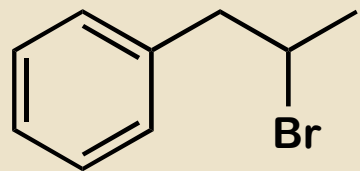




benzylic position  
similar to allylic position

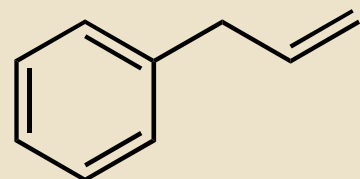


A



B

KO*t*-Bu



KOH

X

HBr

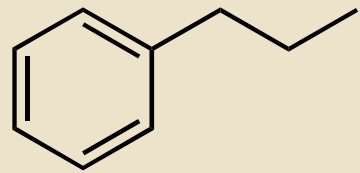
HBr

ROOR

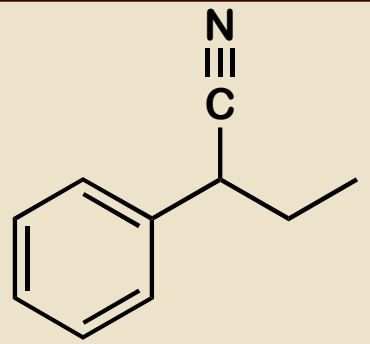
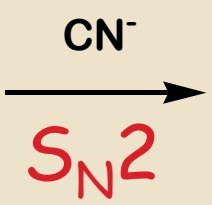
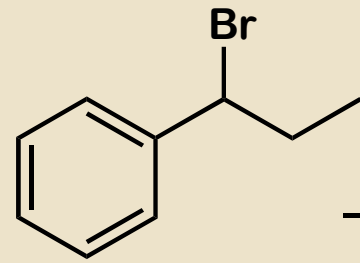
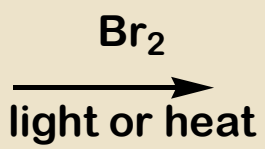
Y

What is X?

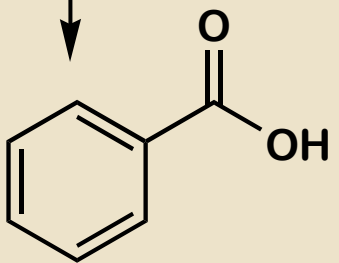
What is Y?



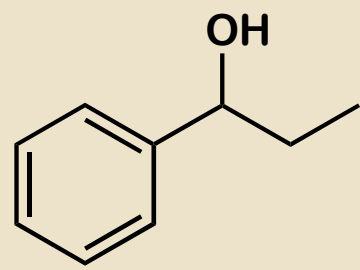
(or NBS)



1.  $\text{KMnO}_4 / \text{OH}^-$   
2.  $\text{H}^+$

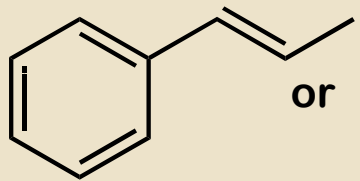


$\text{H}_2\text{O} / \text{H}^+$   
 $\text{S}_{\text{N}}1$

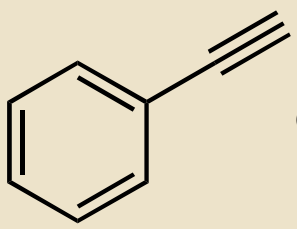


1.  $\text{KMnO}_4 / \text{OH}^-$   
2.  $\text{H}^+$

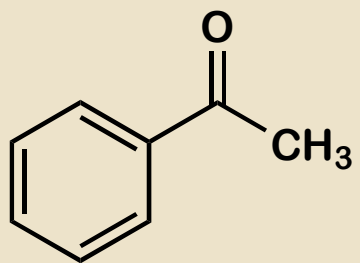
1.  $\text{KMnO}_4 / \text{OH}^-$   
2.  $\text{H}^+$



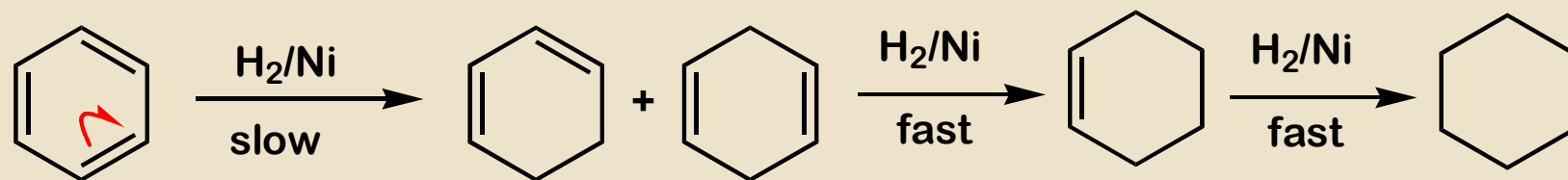
or



or

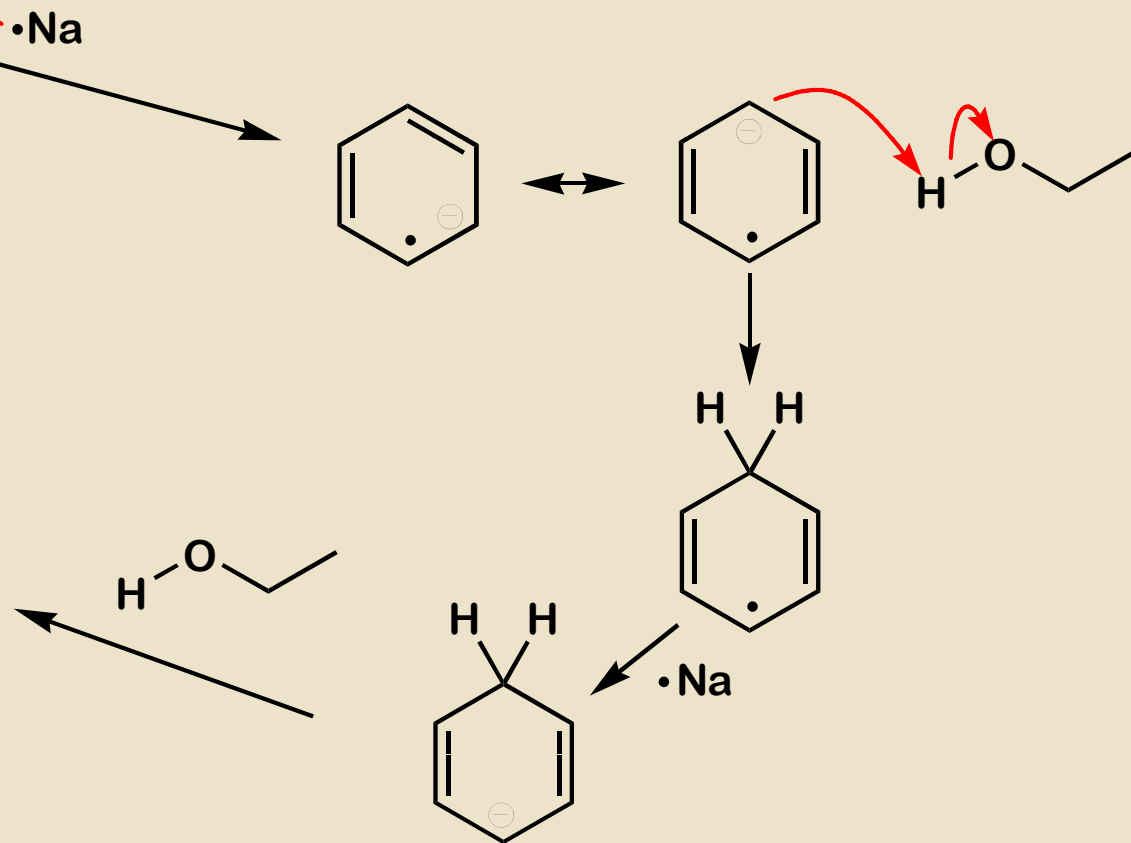
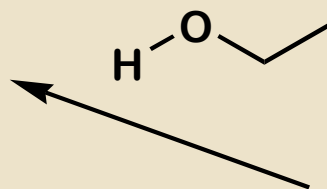
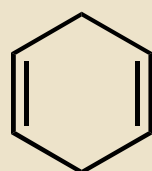


# What about reduction?

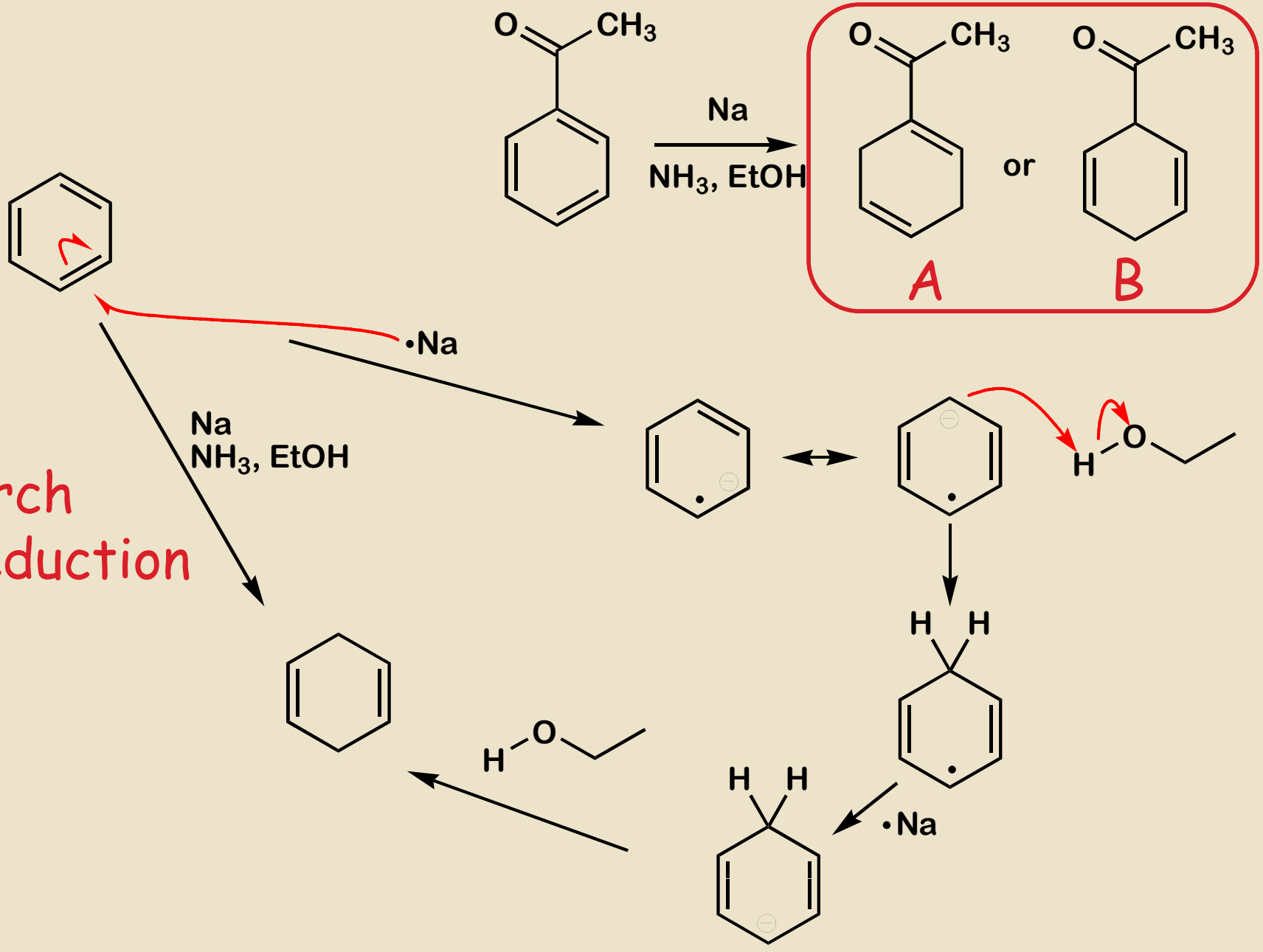


## Birch Reduction

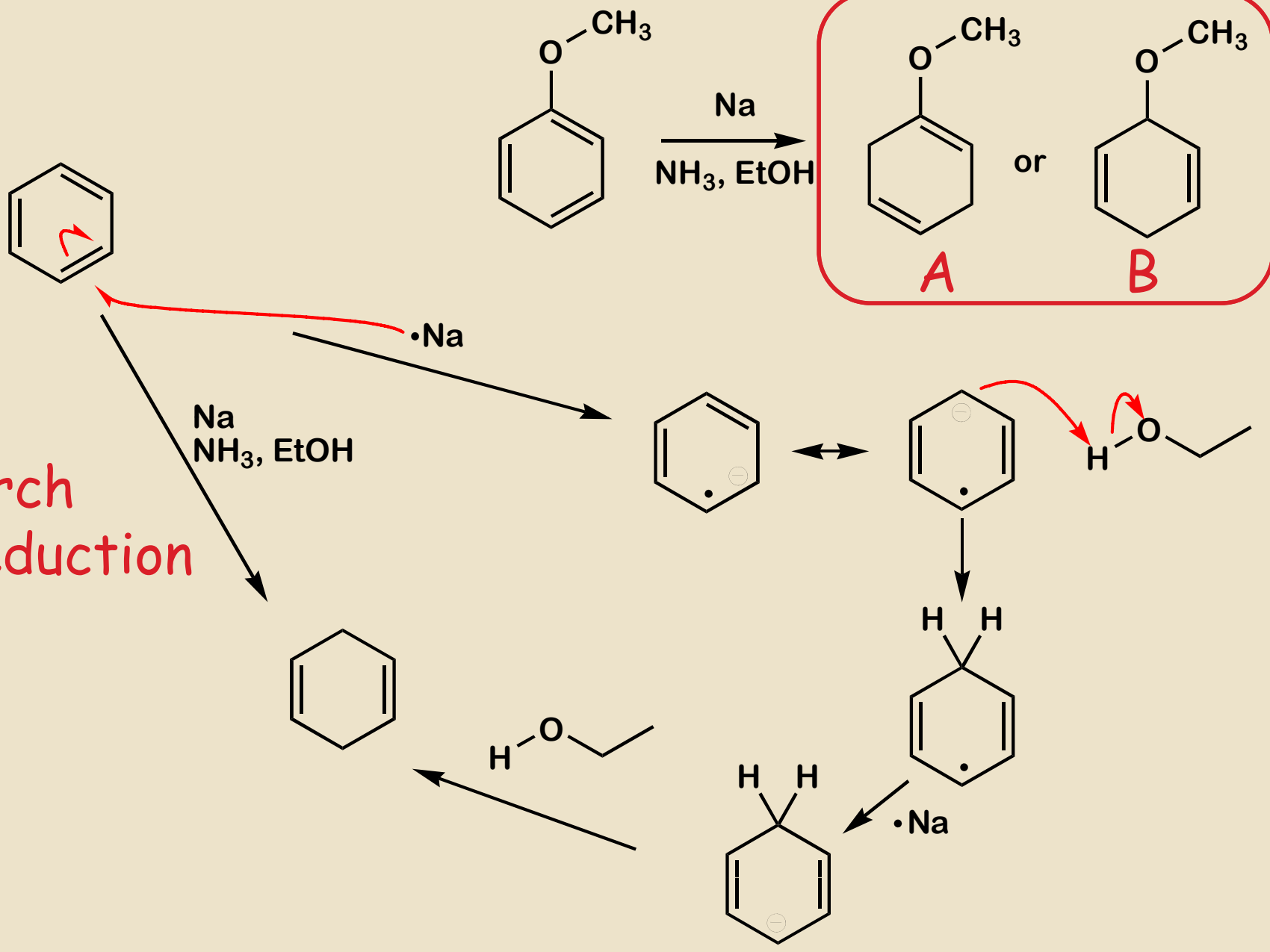
Na  
NH<sub>3</sub>, EtOH

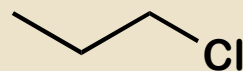
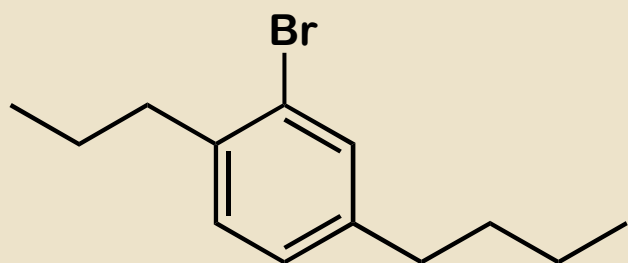


# Birch Reduction

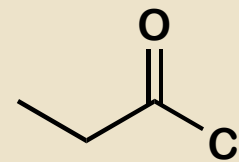


# Birch Reduction

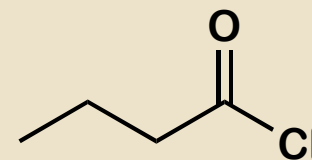




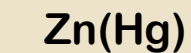
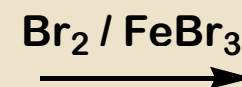
i.



ii.



iii.



iv.

A. i  $\rightarrow$  ii  $\rightarrow$  iii  $\rightarrow$  iv

B. i  $\rightarrow$  iii  $\rightarrow$  ii  $\rightarrow$  iv

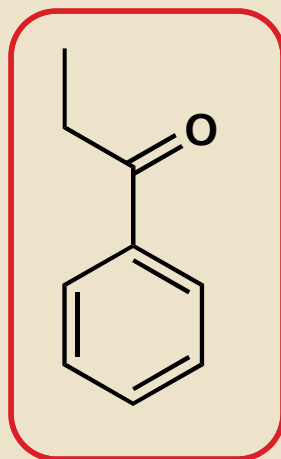
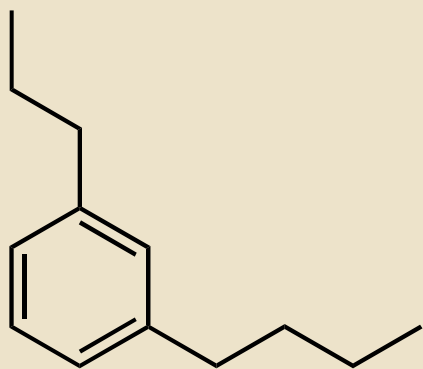
C. ii  $\rightarrow$  i  $\rightarrow$  iv  $\rightarrow$  iii

D. i  $\rightarrow$  iv  $\rightarrow$  ii  $\rightarrow$  iii  $\rightarrow$  iv

E. i  $\rightarrow$  iv  $\rightarrow$  ii  $\rightarrow$  iv  $\rightarrow$  iii

F. ii  $\rightarrow$  iv  $\rightarrow$  i  $\rightarrow$  iii  $\rightarrow$  iv

G. none will work very well



A.  $i \rightarrow ii \rightarrow iv$

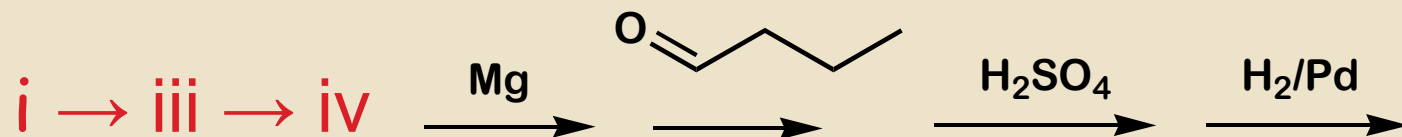
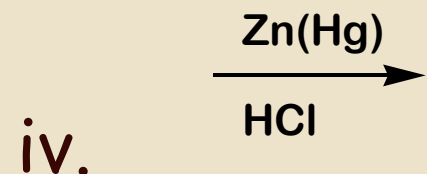
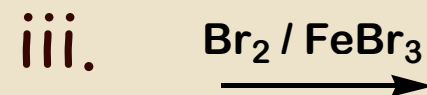
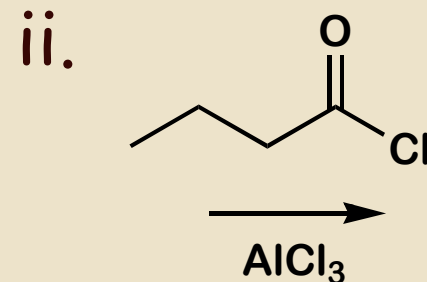
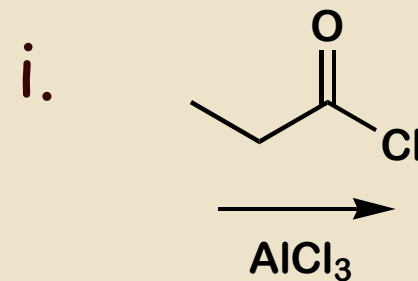
B.  $i \rightarrow iv \rightarrow ii \rightarrow iv$

C.  $ii \rightarrow i \rightarrow iv$

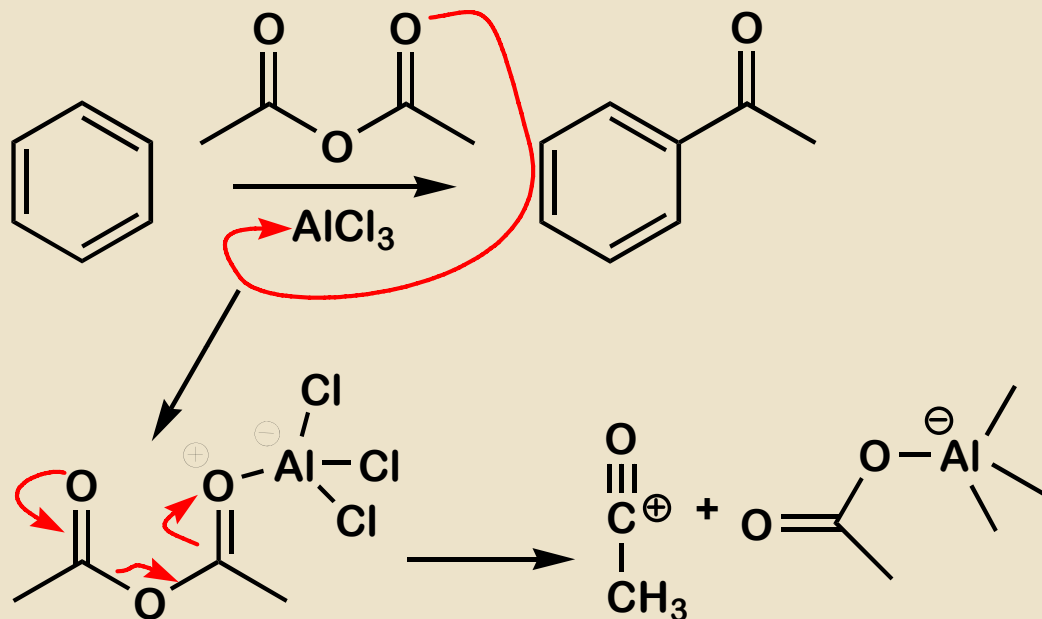
D.  $ii \rightarrow iv \rightarrow i \rightarrow iv$

E. none will work very well

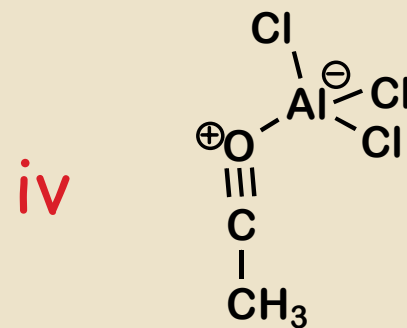
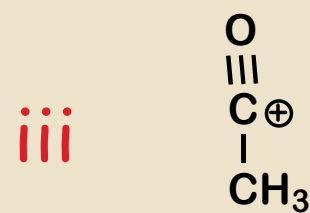
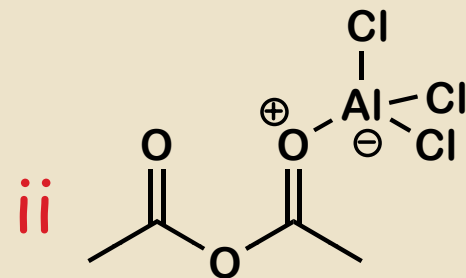
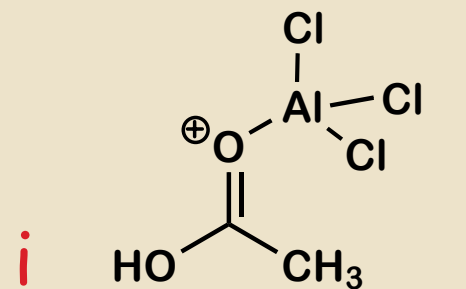
Deactivated  
no more  
Friedel  
Crafts



Draw a mechanism

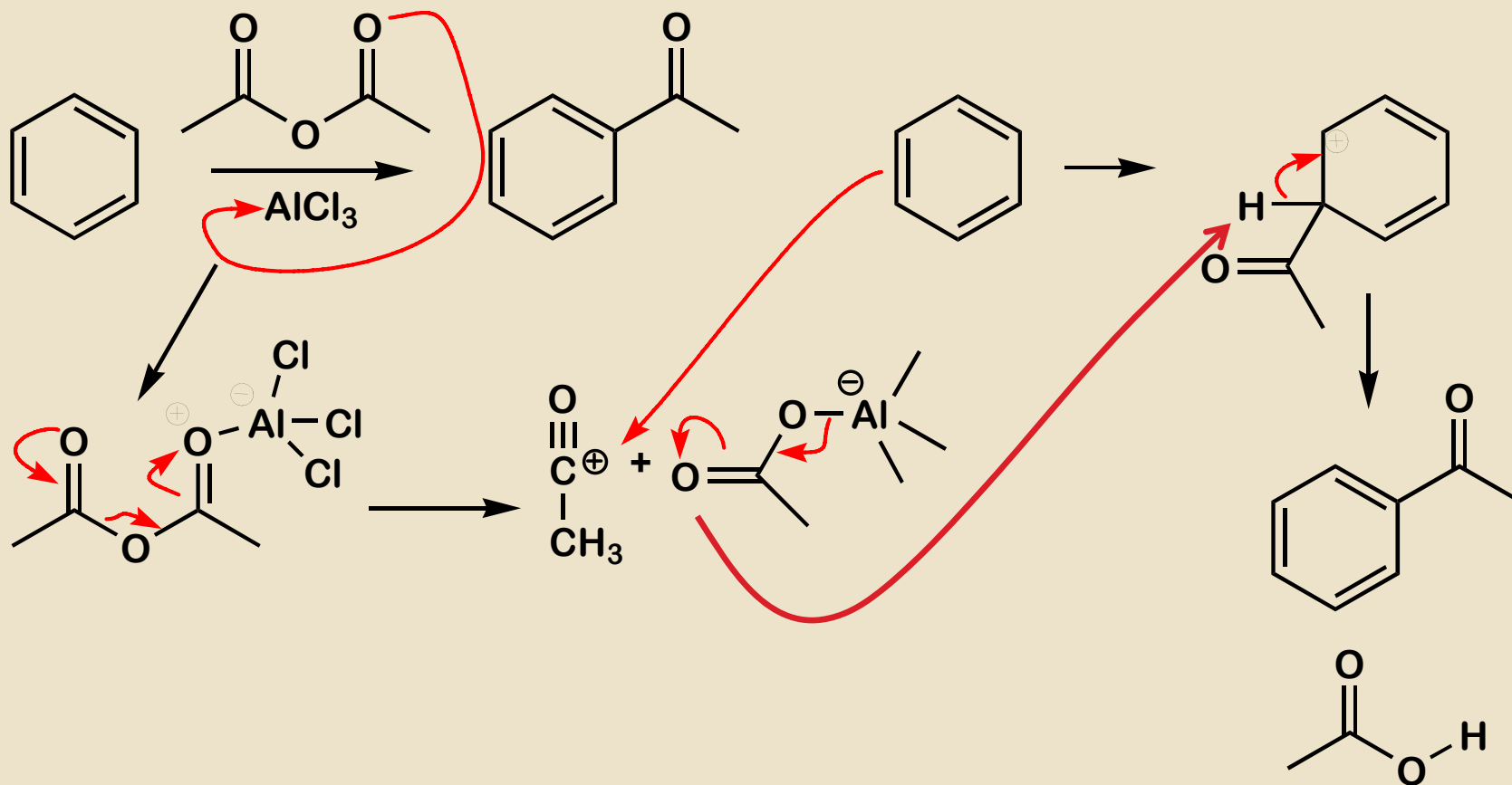


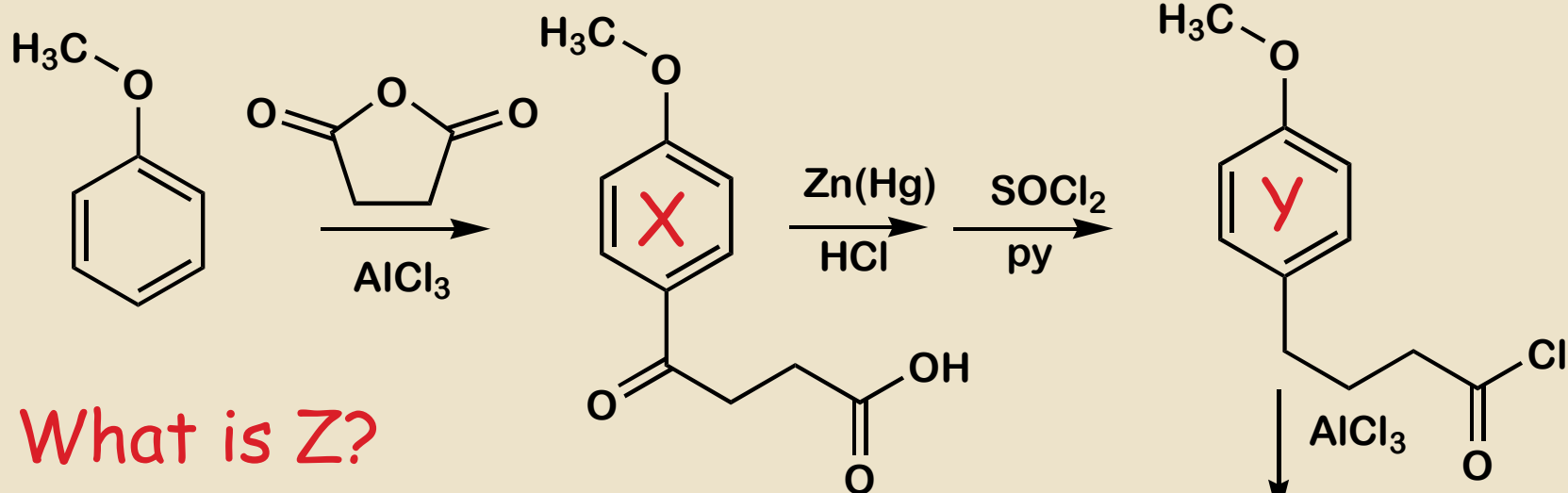
A i    B ii    C iii    D iv  
 E i + ii    F ii + iii    G ii + iv



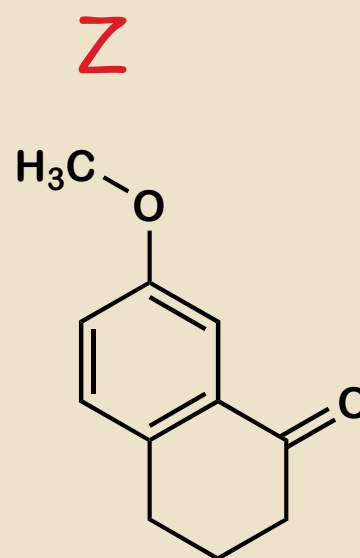
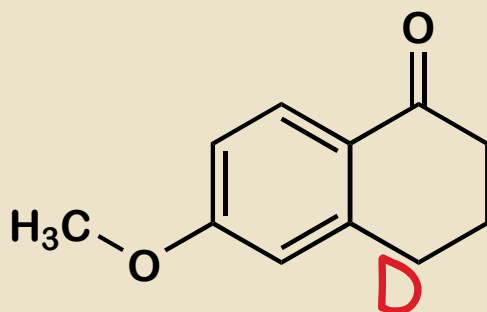
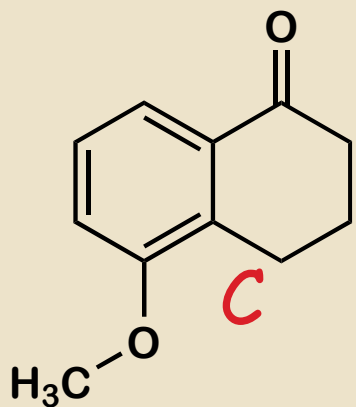
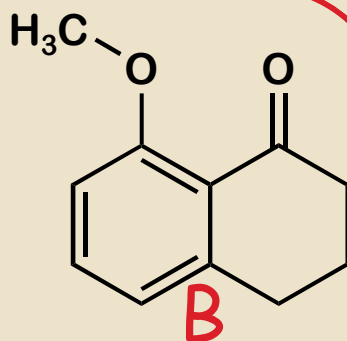
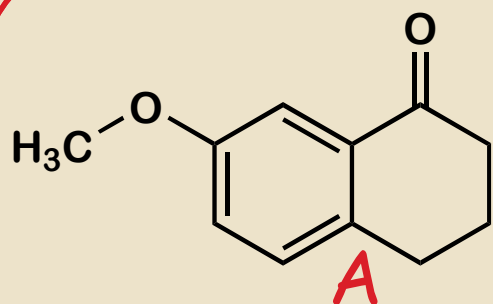


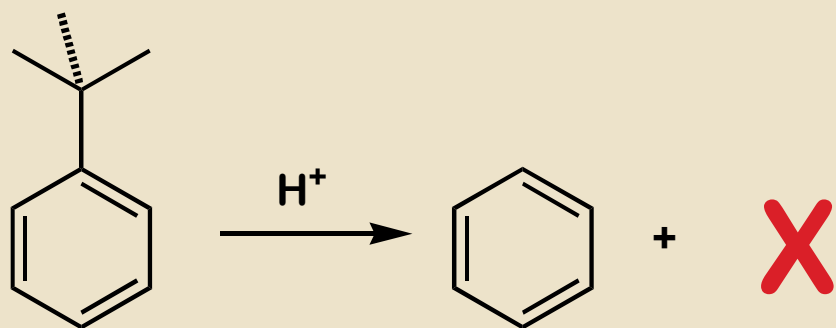
Draw a mechanism





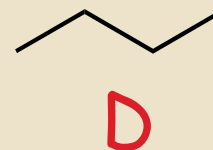
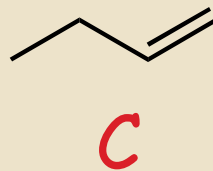
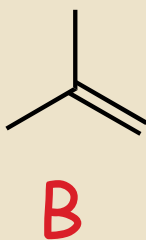
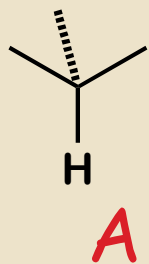
What is Z?

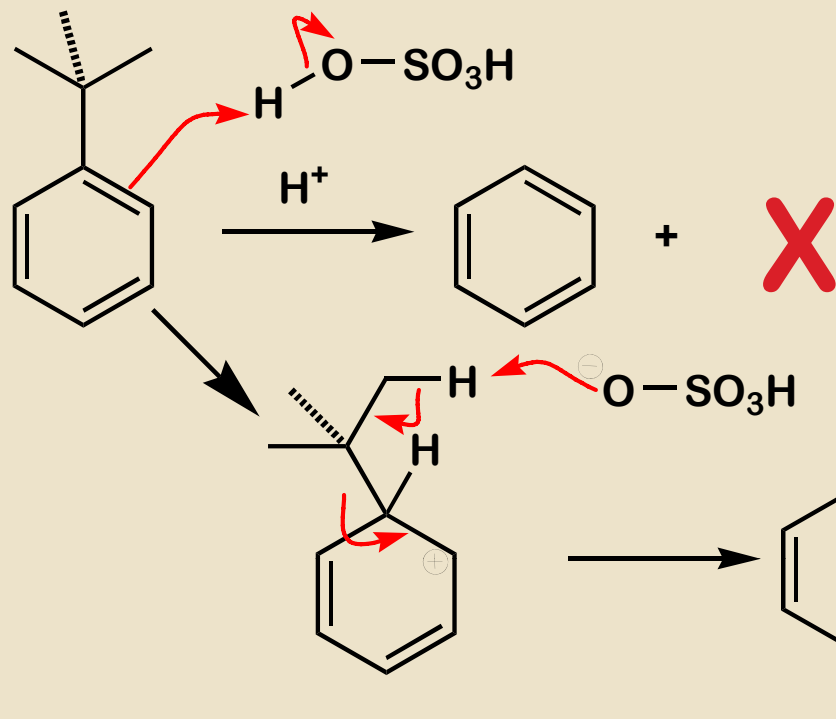




What is X?  
Write a mechanism.

What is X?





What is X?  
Write a mechanism.

What is the key intermediate?

