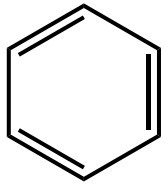
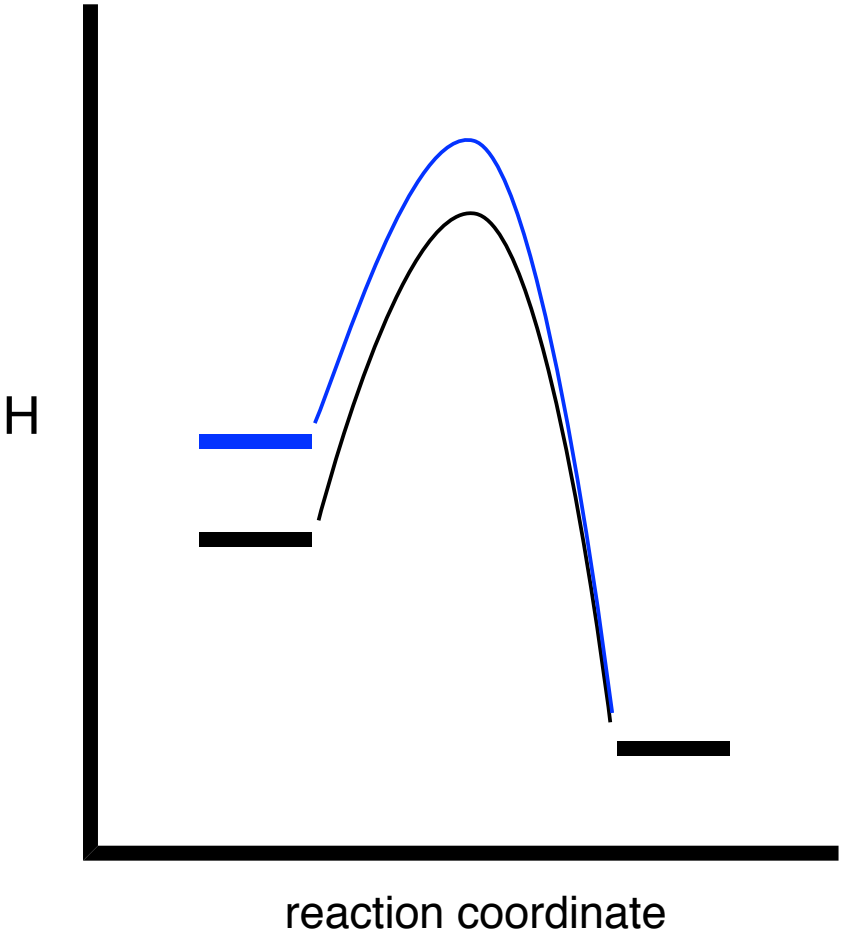
Benzene and resonance



Reactions that produce the same products can be used to compare the stabilities of the reactants



$\Delta H_{rxn} = H_{product} - H_{reactant}$

$\Delta H_{rxn} + H_{reactant} = H_{product}$

$\Delta H_{rxn} = H_{product} - H_{reactant}$

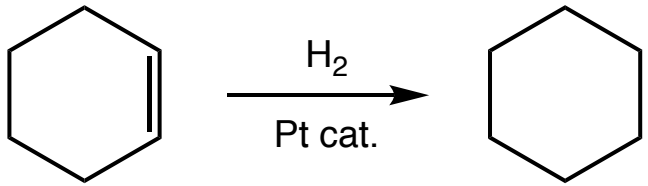
$\Delta H_{rxn} + H_{reactant} = H_{product}$

$\Delta H_{rxn} + H_{reactant} = \Delta H_{rxn} + H_{reactant}$

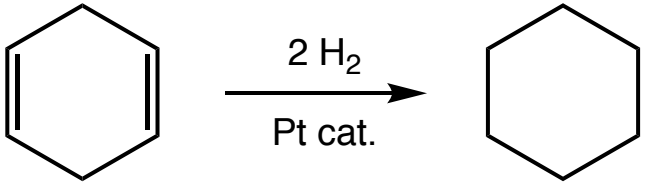
$\Delta H_{rxn} - \Delta H_{rxn} = H_{reactant} - H_{reactant}$

In other words, when two reactions end in the same place, the energy released or absorbed during the reaction can be used to compare the energies of the reactants.

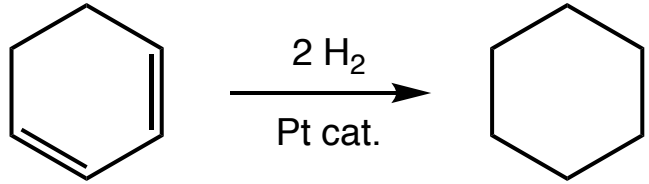
Aromaticity: a special kind of resonance/electron delocalization



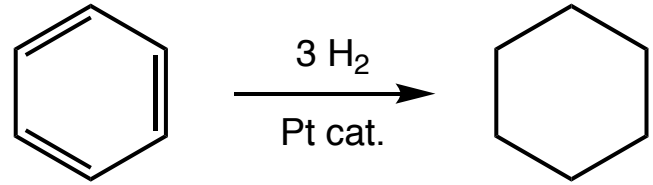
	$\Delta H_{reaction}$ (kcal/mol)	per bond (kcal/mol)
cyclohexene	–28.6	–28.6



1,4 cyclohexadiene	–57.4	–28.7

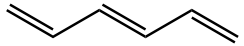


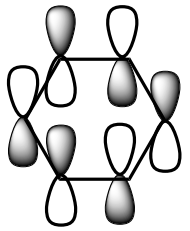
1,3-cyclohexadiene	–55.4	–27.7

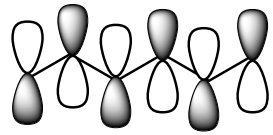


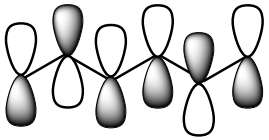
benzene	–79.8	

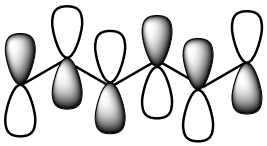
MO Basis for Aromaticity

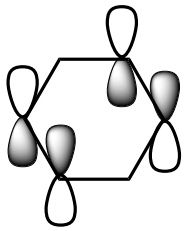


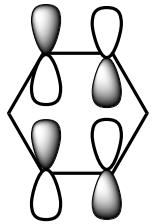


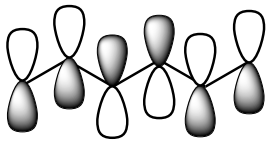


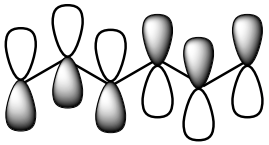


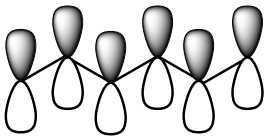


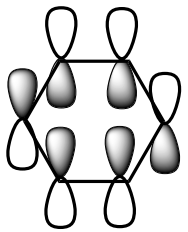


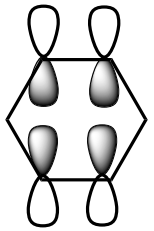


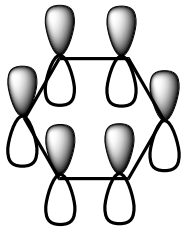






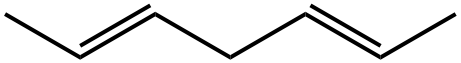




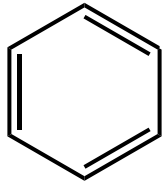


Aromatic, Antiaromatic, Resonance Stabilized, and None of the Above

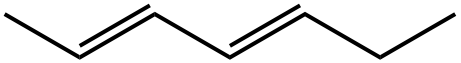
unconjugated π bonds



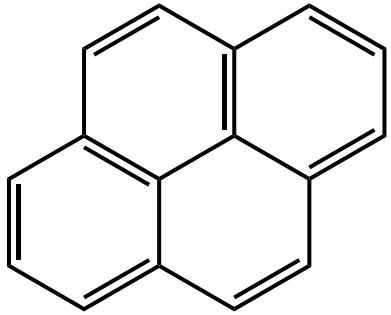
conjugated aromatic π bonds



conjugated π bonds



conjugated antiaromatic π bonds



Criteria for Aromaticity

1.Uninterrupted π cloud
- •cyclic
- •p orbital on every atom
- •planar

2. odd number of pairs of electrons or 4n+2 e^-'s

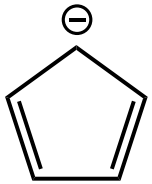
Criteria for Antiaromaticity

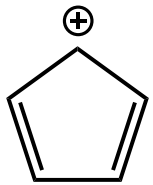
1. Uninterrupted π cloud
- •cyclic
- •p orbital on every atom
- •planar

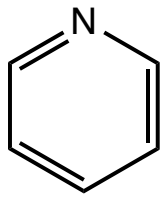
2. even number of pairs of electrons or 4n e^-'s in the π system

n is just a number not the number of C, H's or anything else

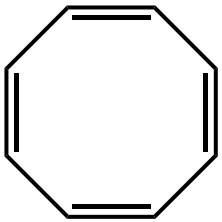
Aromatic, Antiaromatic, Resonance Stabilized, or None of the Above

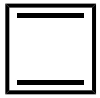


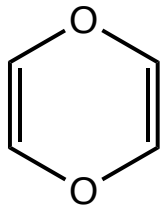




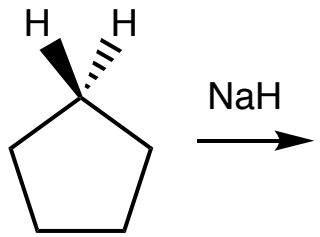
Aromatic, Antiaromatic, Resonance Stabilized, or None of the Above





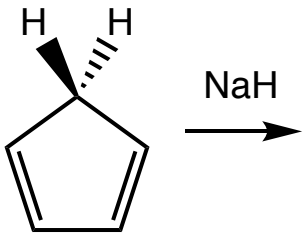


Aromaticity: encouraging and discouraging reactions



NaH

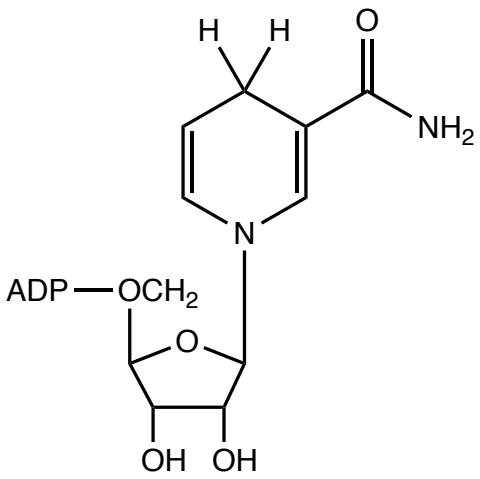
$pK_a > 50$



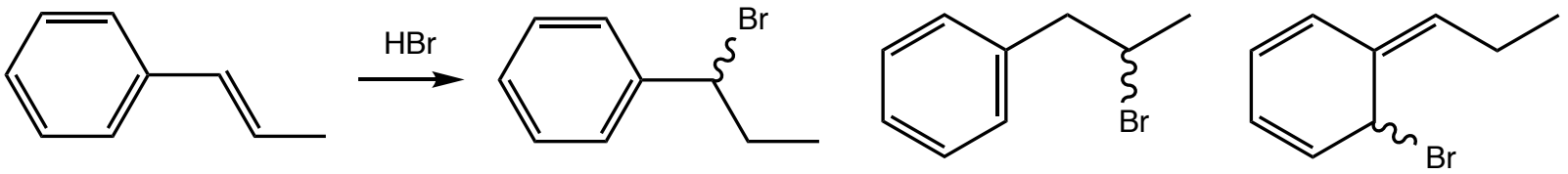
NaH

pK_a ~ 15 - 16

Aromaticity: encouraging and discouraging reactions

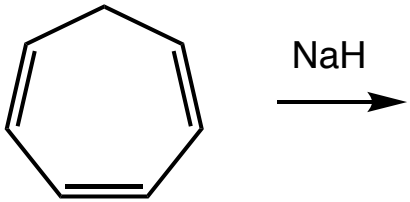


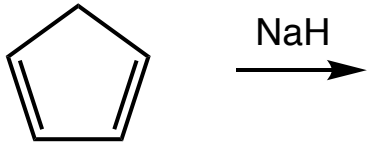
Aromaticity: encouraging and discouraging reactions



Aromaticity: encouraging and discouraging reactions

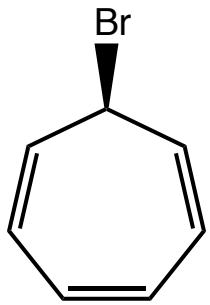
Sample question: Explain why NaH can deprotonate 1,3-cyclopentadiene but it cannot deprotonate 1,3,5-cylcoheptatriene.

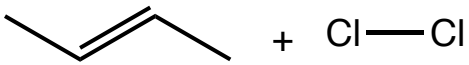


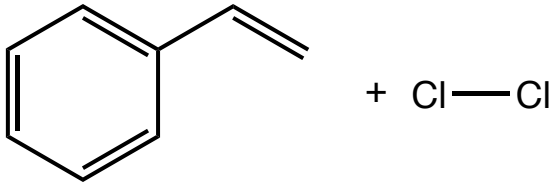


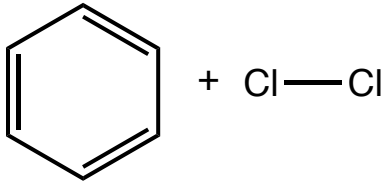
Aromaticity: encouraging and discouraging reactions

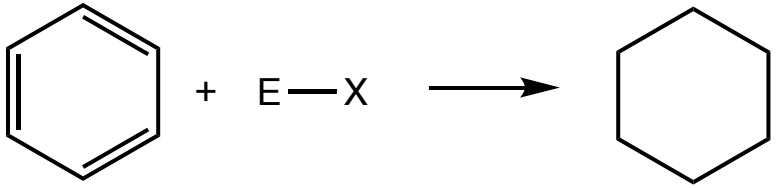
Sample question: Explain why solutions of 7-bromo-1,3,5-cycloheptatriene can conduct electricity when dissolved in polar solvents.

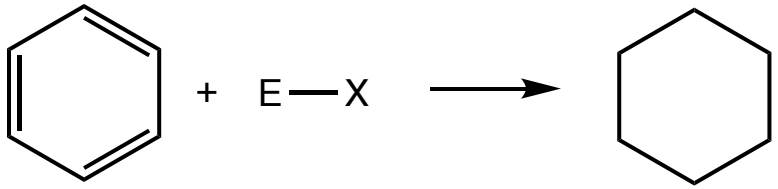


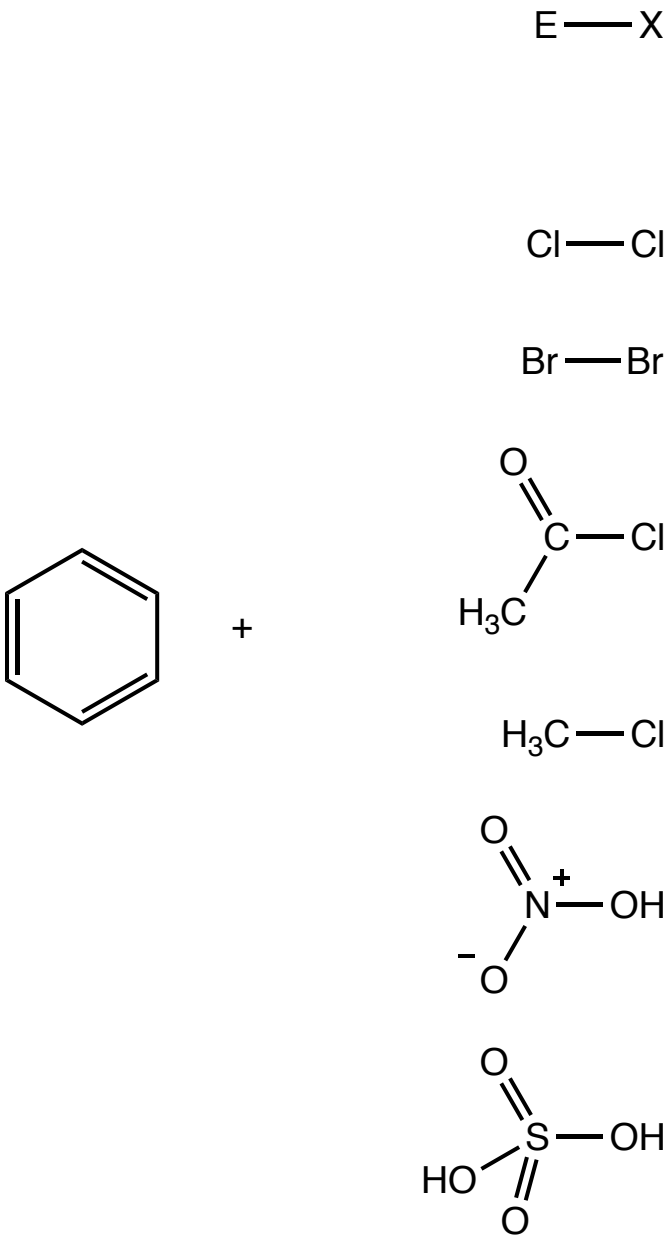

+ Cl—Cl

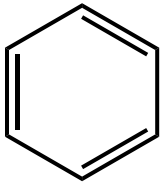

+ Cl—Cl


+ Cl—Cl

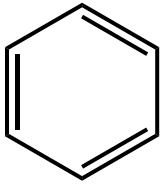

+ E—X


+
E
X

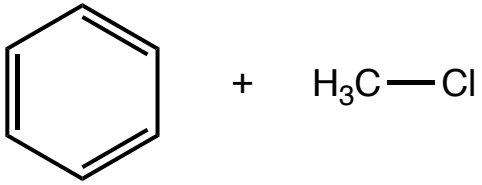

E — X
Cl — Cl
Br — Br
O
C — Cl
H3C
+
H3C — Cl
O
N+ — OH
-O
O
S — OH
HO
O

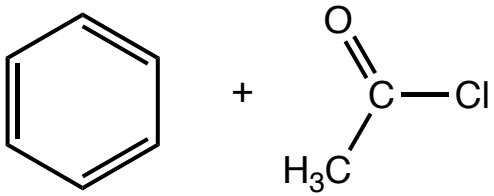


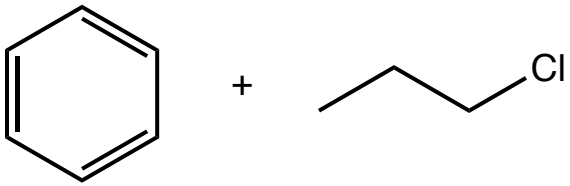
+ Br—Br

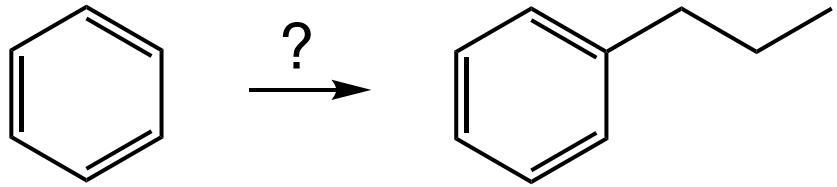


+ Cl—Cl

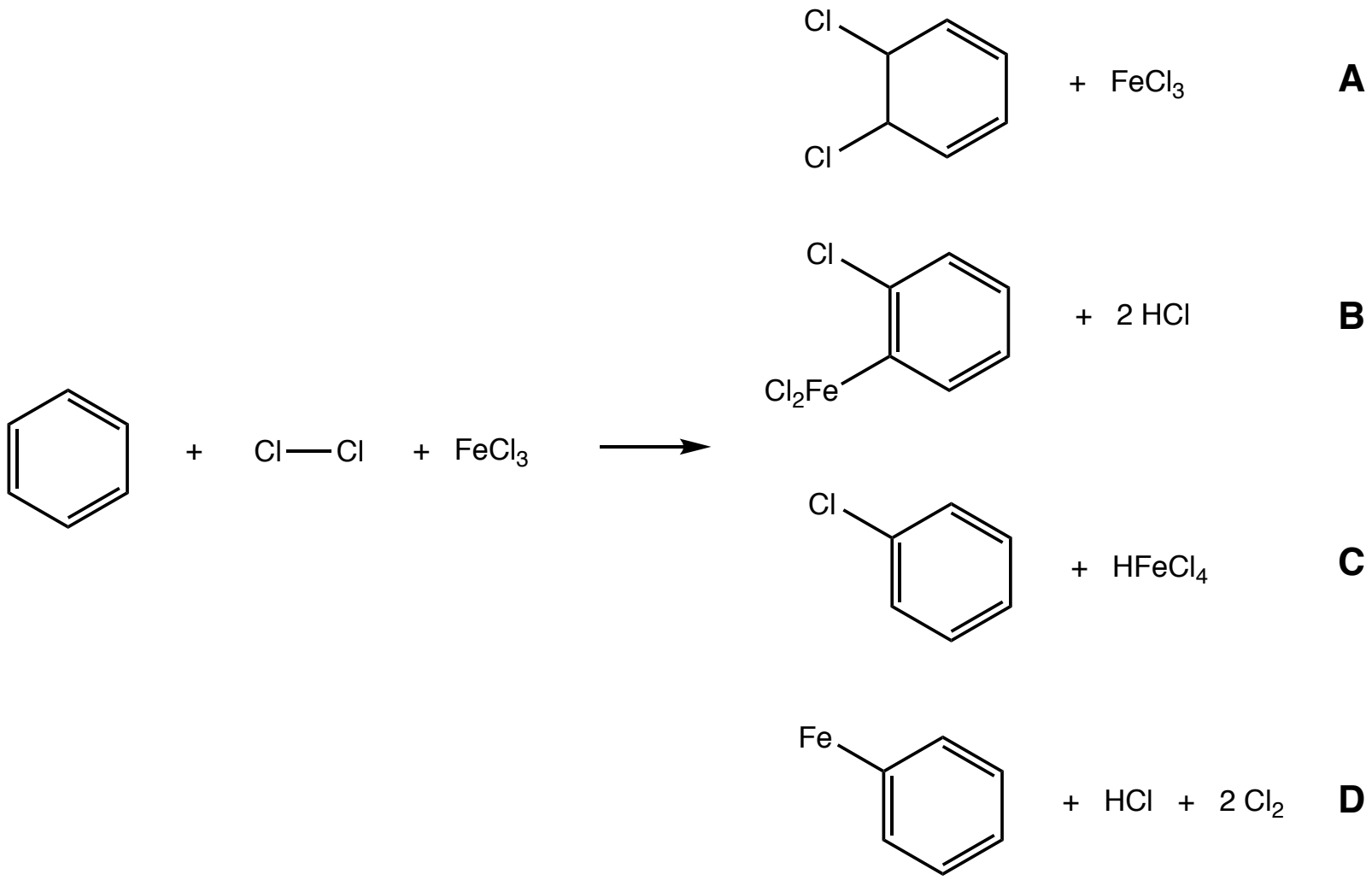

+
H3C
Cl


+
O
C
Cl
H3C

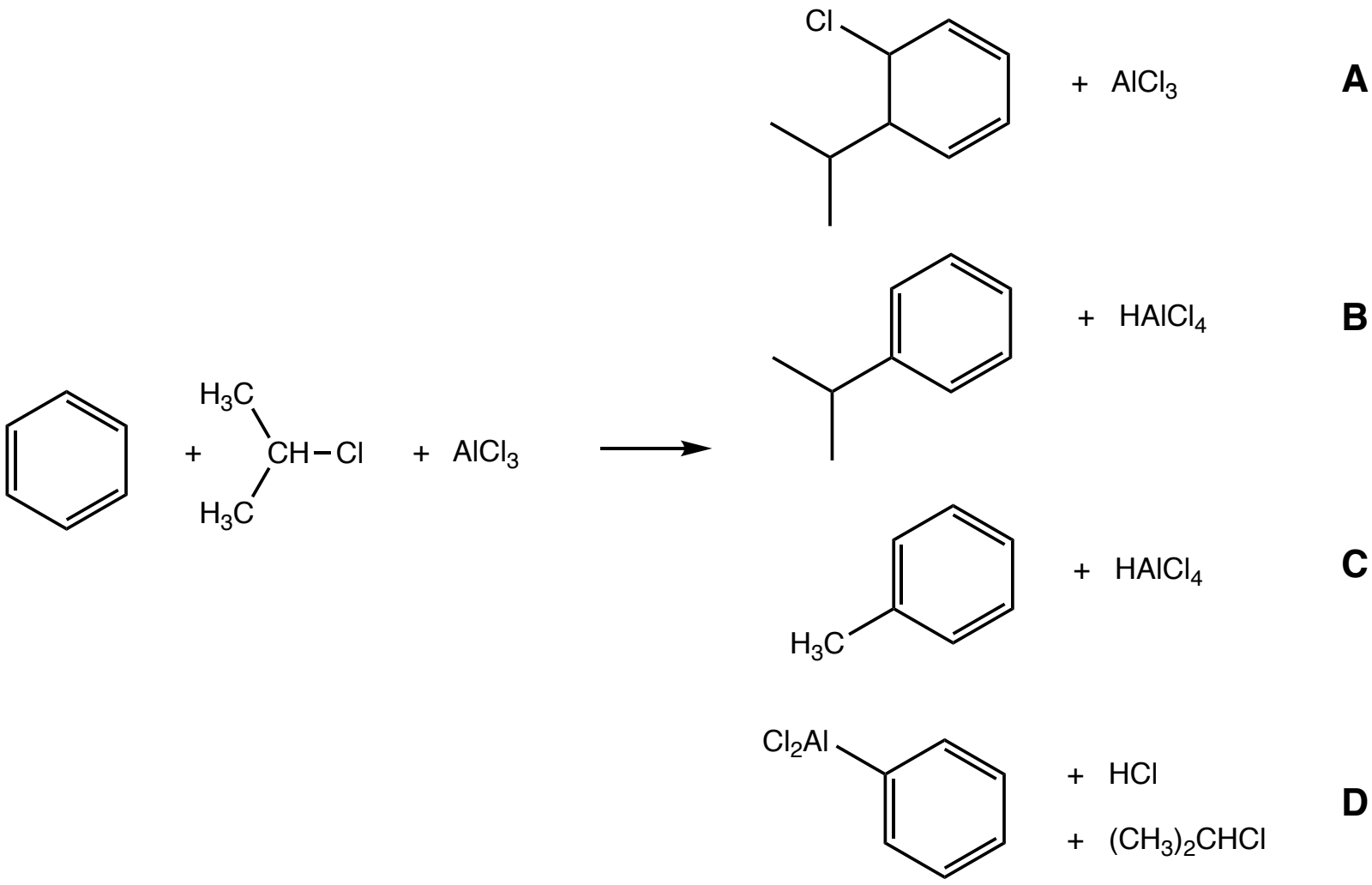

+
Cl



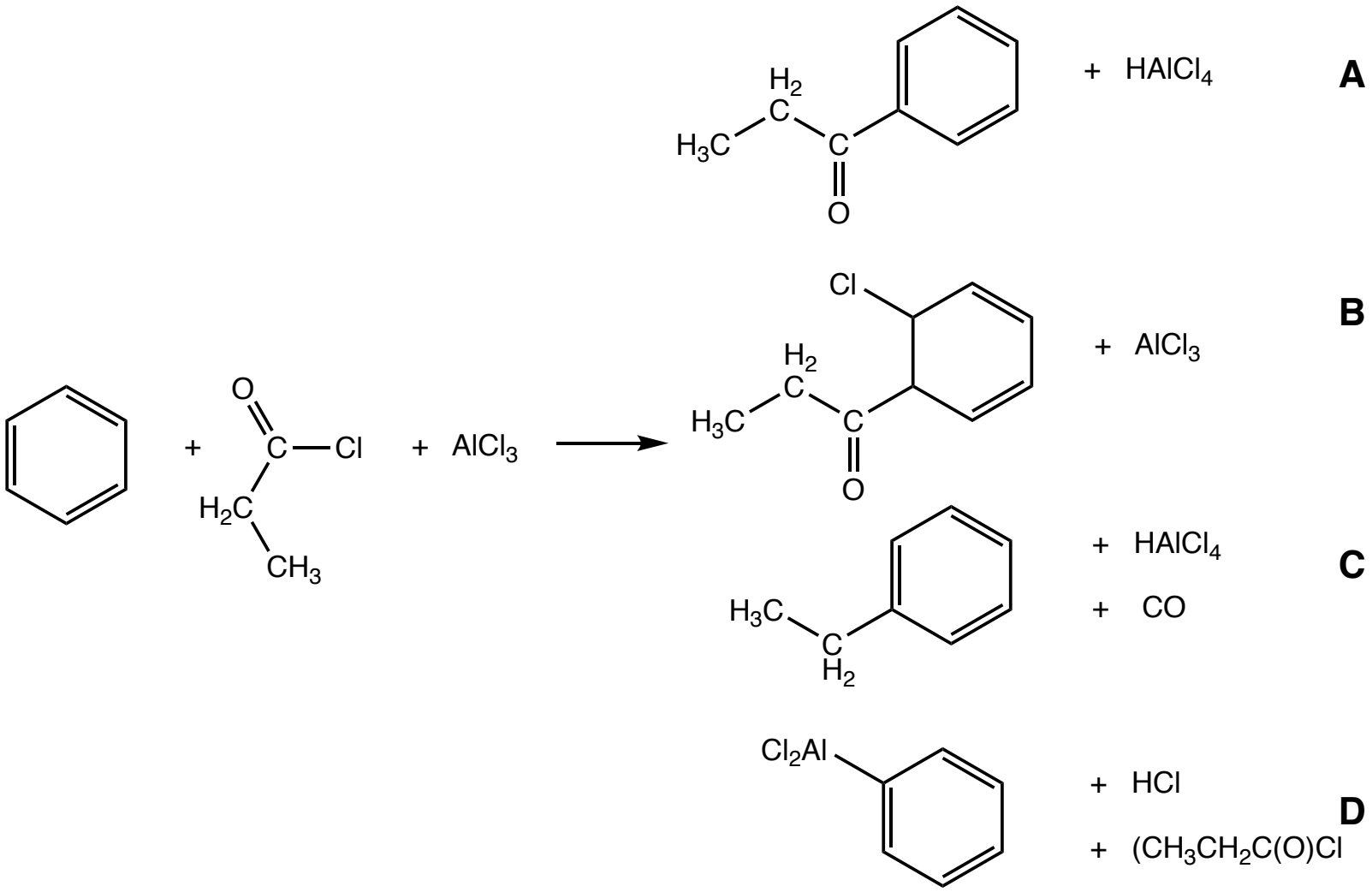
Review


Cl
Cl
+ FeCl3
A
Cl
Cl2Fe
+ 2 HCl
B
+ Cl—Cl + FeCl3
Cl
+ HFeCl4
C
Fe
+ HCl + 2 Cl2
D

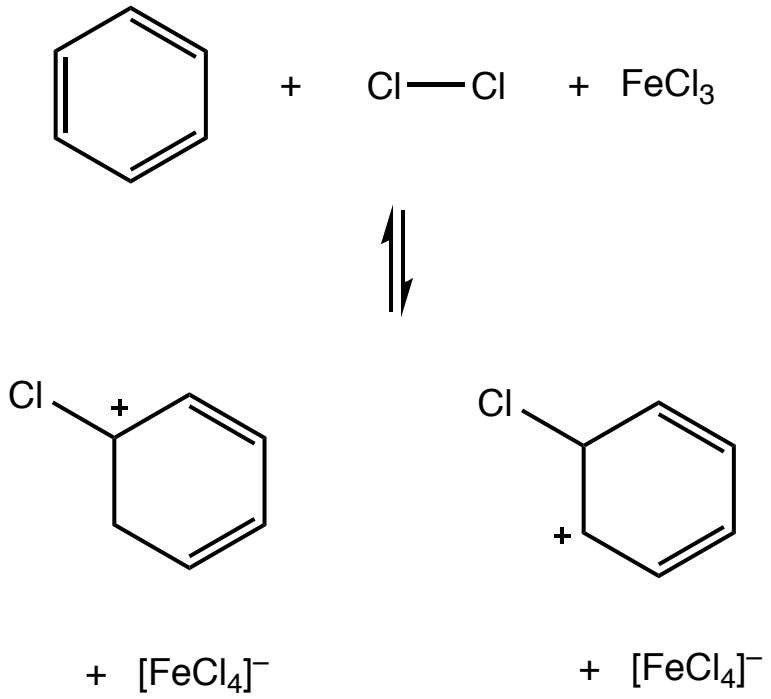
Review


Cl
+ AlCl3
A
H3C
+ CH – Cl + AlCl3
H3C
+ HAlCl4
B
+ HAlCl4
C
H3C
Cl2Al
+ HCl
+ (CH3)2CHCl
D

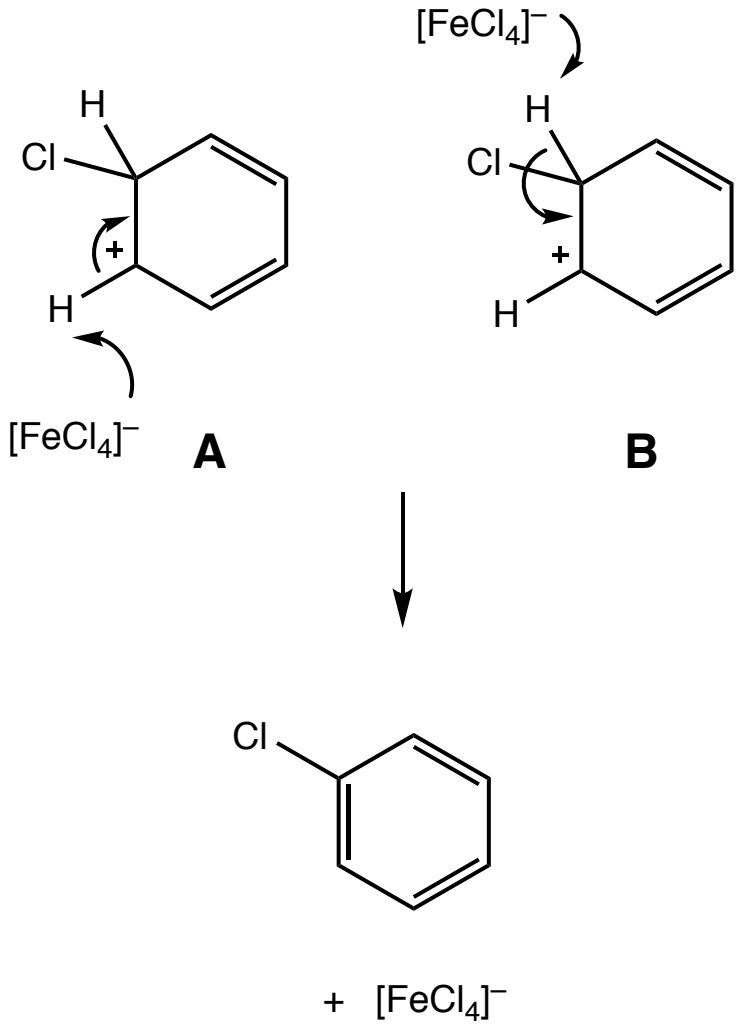
Review

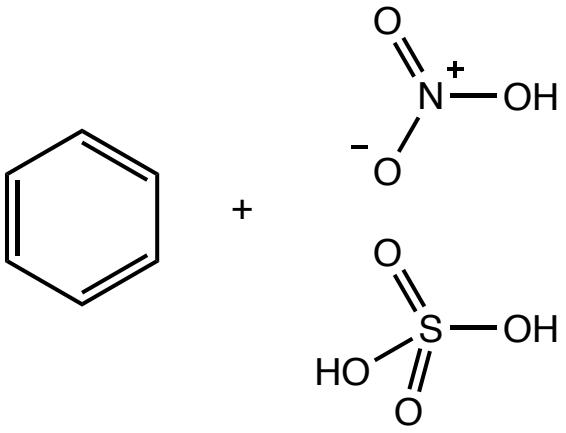

+ C(=O)Cl
H2C
CH3
+ AlCl3
H2
C
H3C
C
O
+ HAlCl4
A
Cl
+ AlCl3
B
+ HAlCl4
+ CO
C
Cl2Al
+ HCl
+ (CH3CH2C(O)Cl
D

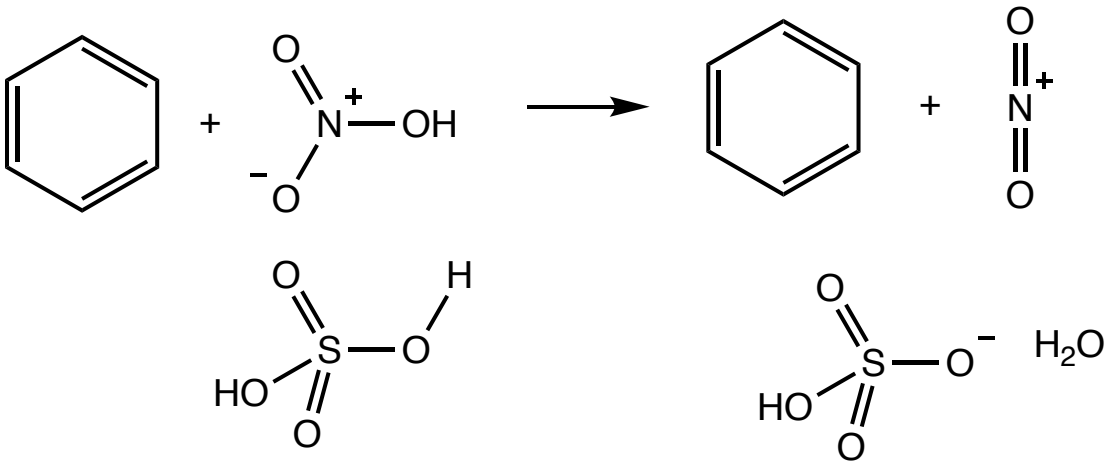
Review

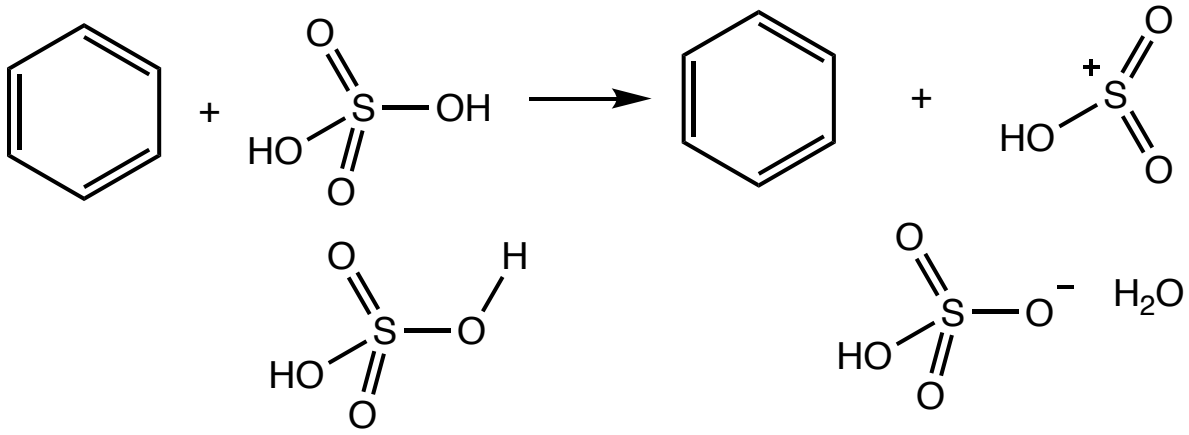


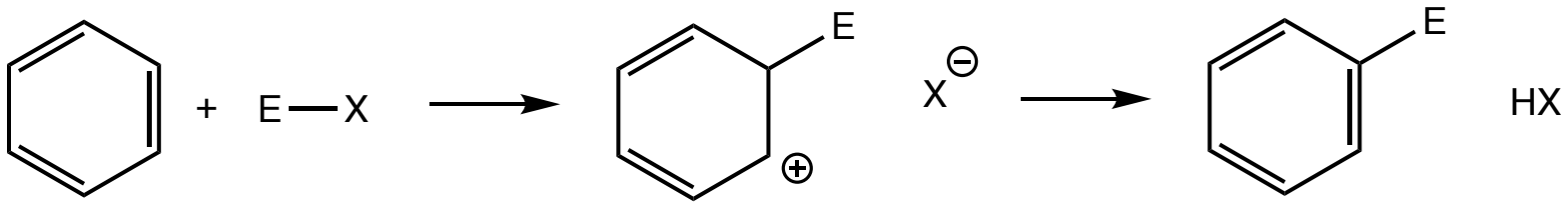
Review






O
N
OH
O
O
H
S
O
HO
O
O
N
O
O
S
O
HO
O
H_2O

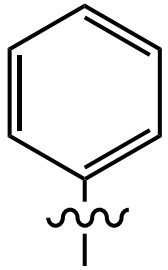

O
S
OH
HO
O
+
O
+
S
HO
O
O
H
S
O
HO
O
O
S
O
−
HO
O
H2O

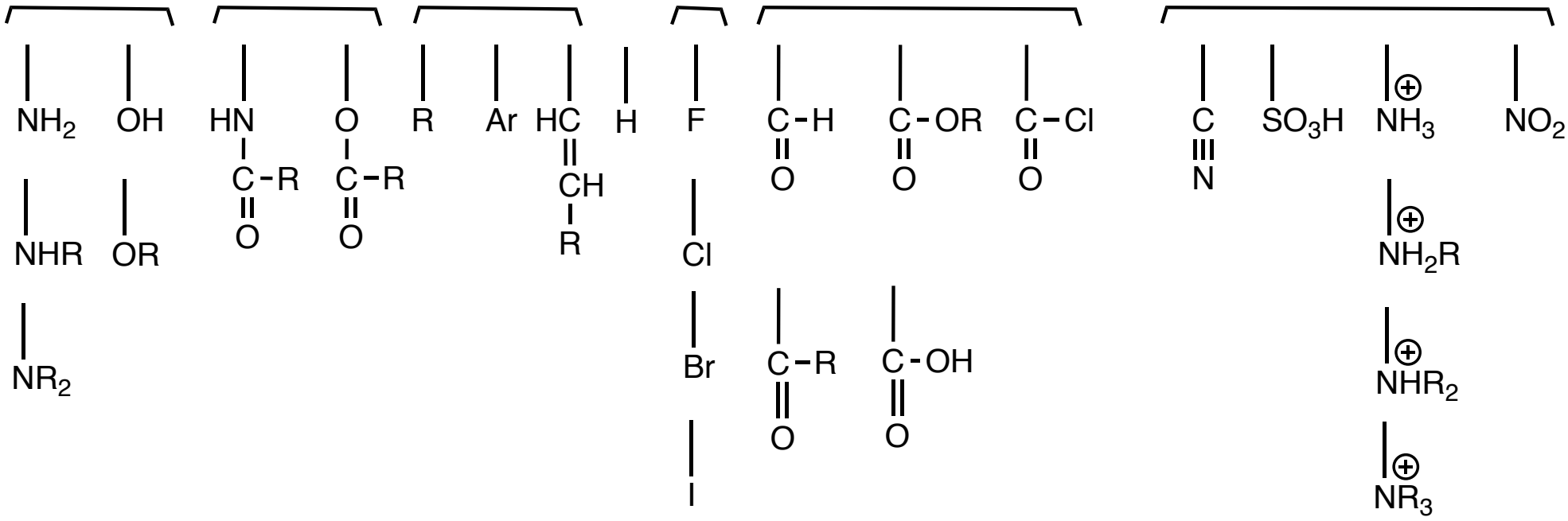


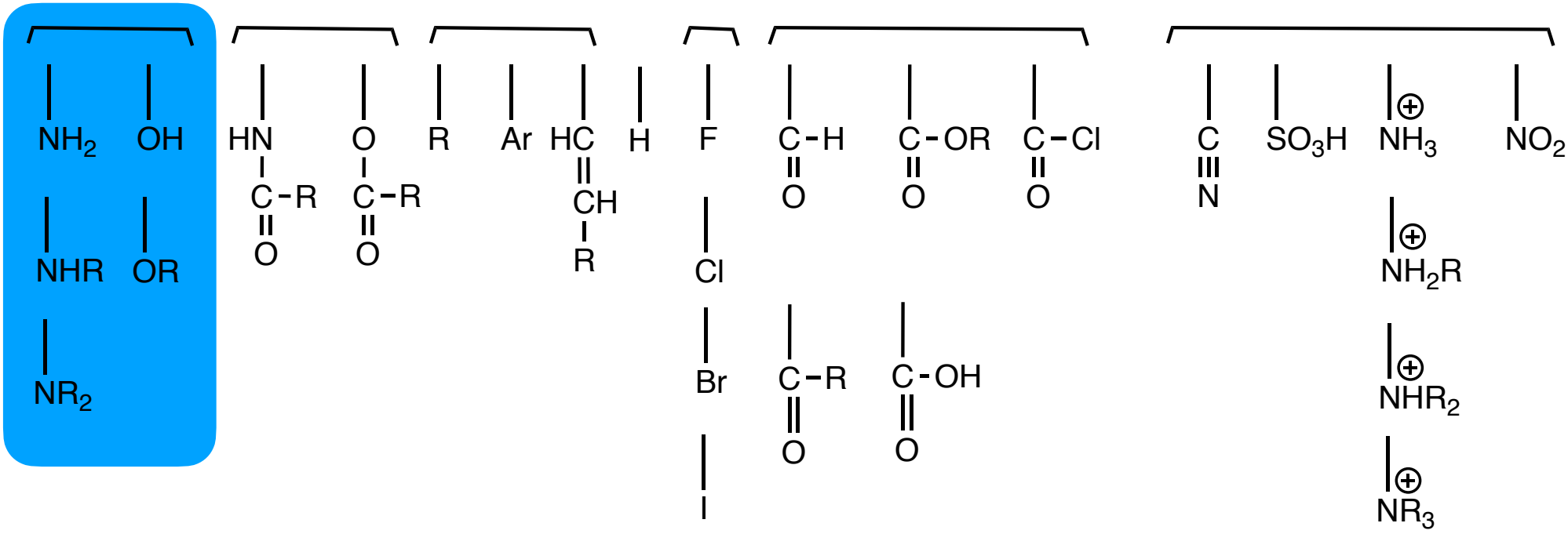
Increase election density to make the benzene ring more reactive toward electrophiles

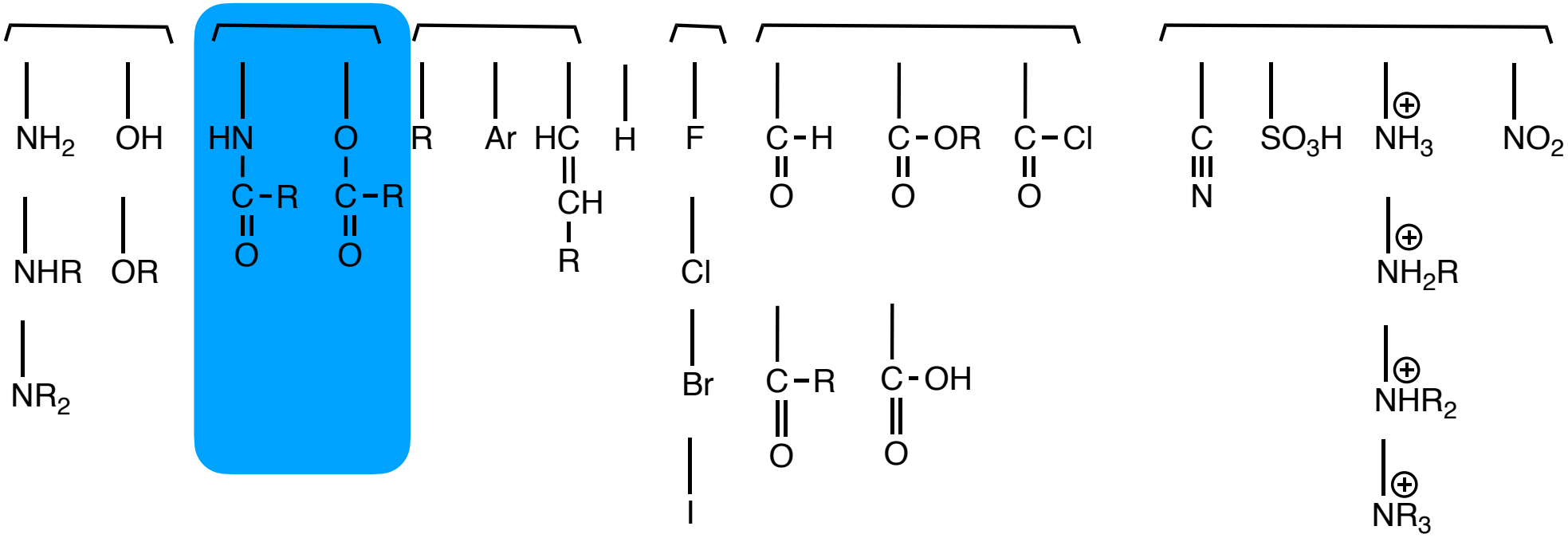
Stabilize the intermediate to make the reaction go faster

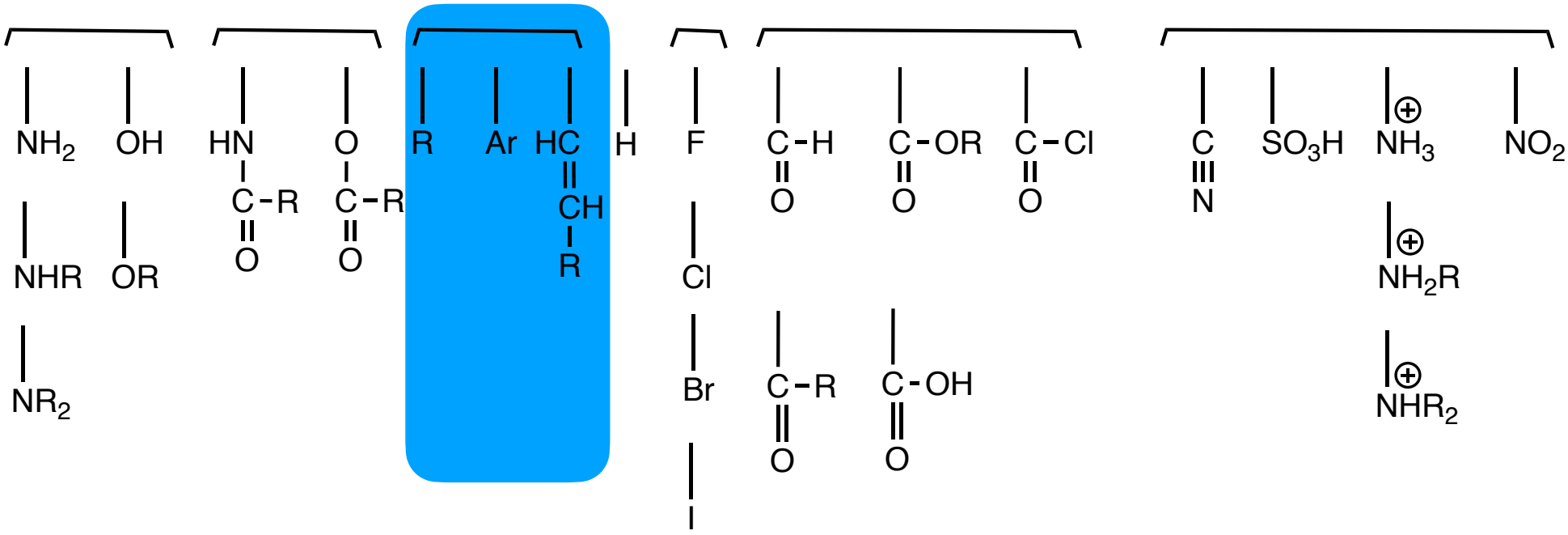
Move Electron Density Around Using....

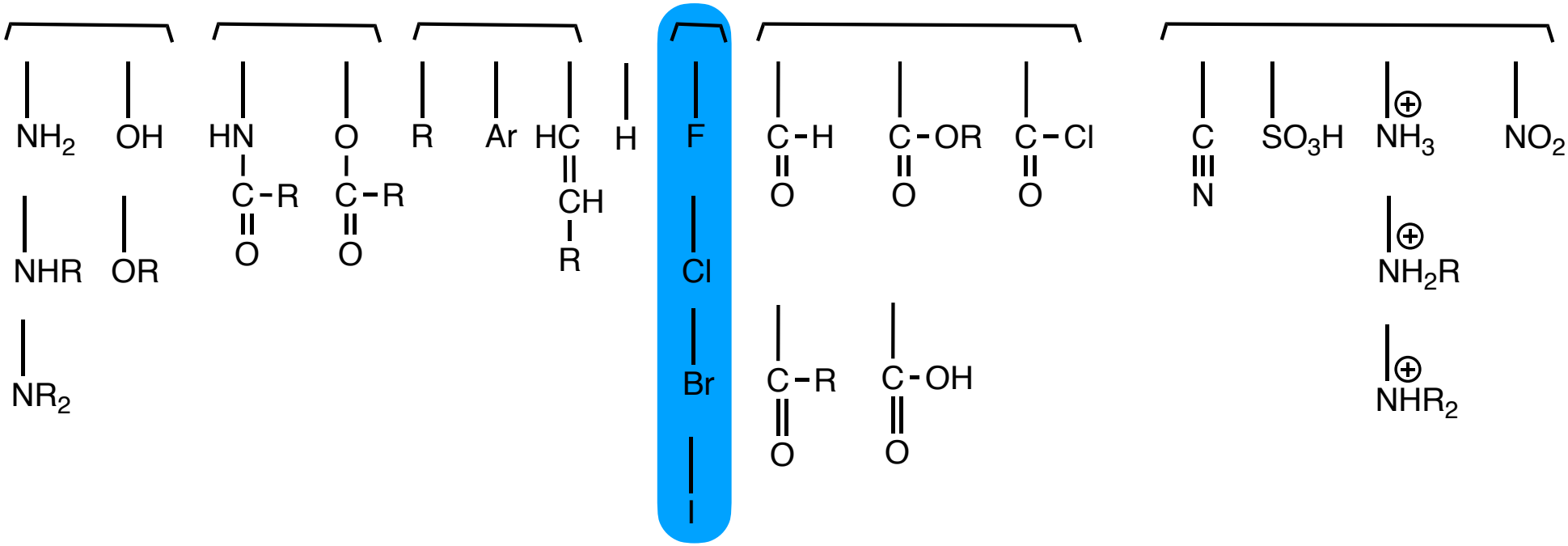


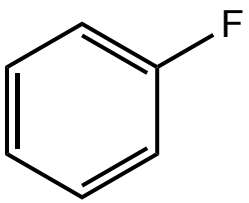

NH2
NHR
NR2
OH
OR
HN
C
R
O
O
C
R
O
R
Ar
HC
CH
R
H
F
Cl
Br
I
C
H
O
C
OR
O
C
Cl
O
C
R
O
C
OH
O
C
N
SO3H
NH3
NH2R
NHR2
NR3
NO2

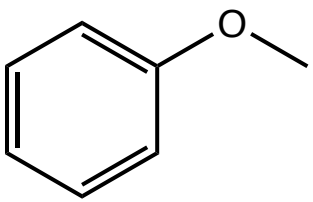

NH2
OH
NHR
OR
NR2
HN
C–R
O
O
C–R
O
R
Ar
HC
CH
R
H
F
Cl
Br
I
C–H
O
C–OR
O
C–Cl
O
C–R
O
C–OH
O
C
N
SO3H
NH3
NH2R
NHR2
NR3
NO2

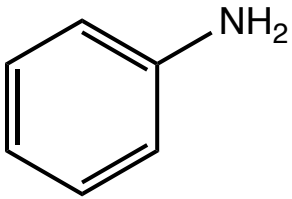

NH2
OH
HN
O
R
Ar
HC
H
F
C-H
C-OR
C-Cl
C
SO3H
NH3
NO2
C-R
O
CH
R
NHR
OR
Cl
Br
I
C-OH
NH2R
NHR2
NR3
NR2

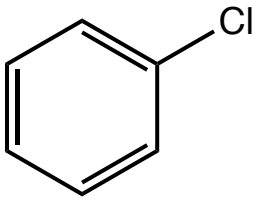

NH2
OH
NHR
OR
NR2
HN
C–R
O
O
C–R
O
R
Ar
HC
CH
R
H
F
Cl
Br
I
C–H
O
C–OR
O
C–Cl
O
C–R
O
C–OH
O
C
N
SO3H
NH3
NH2R
NHR2
NO2

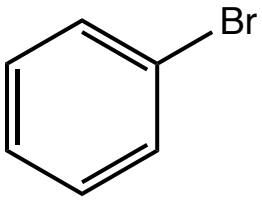

NH2
OH
NHR
OR
NR2
HN
C
R
O
O
C
R
O
R
Ar
HC
CH
R
H
F
Cl
Br
I
C
H
O
C
OR
O
C
Cl
O
C
R
O
C
OH
O
C
N
SO3H
NH3
NH2R
NHR2
NO2

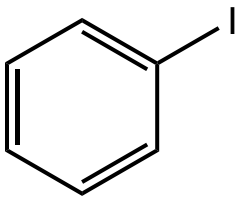

F

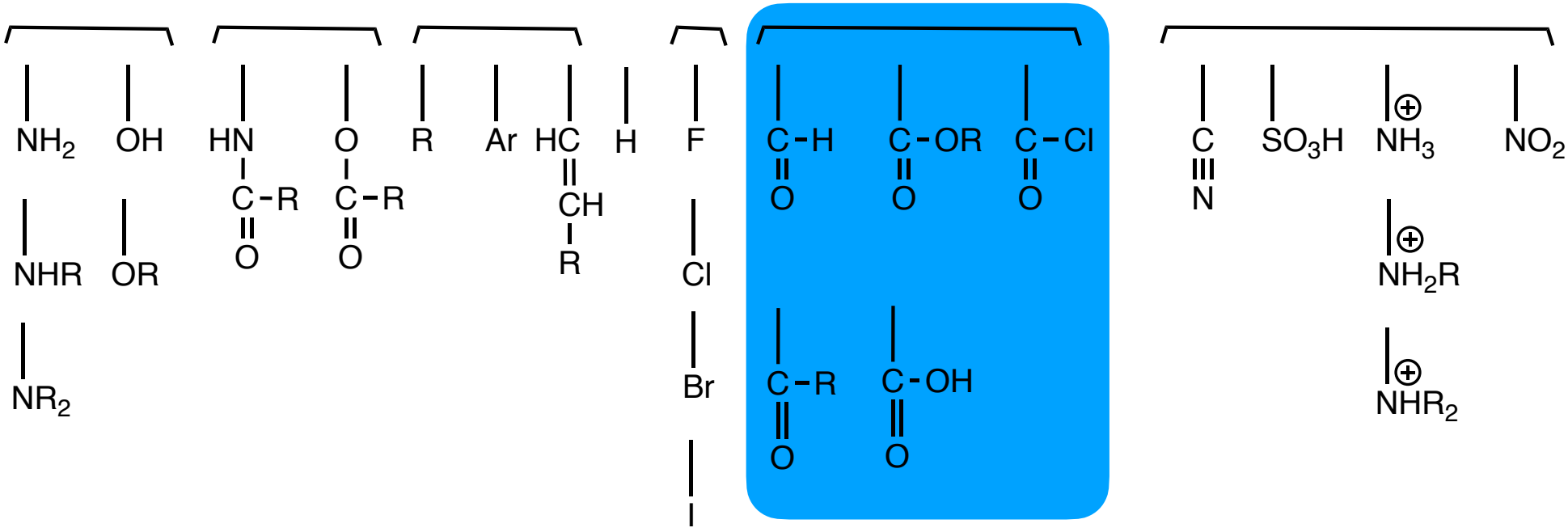

O

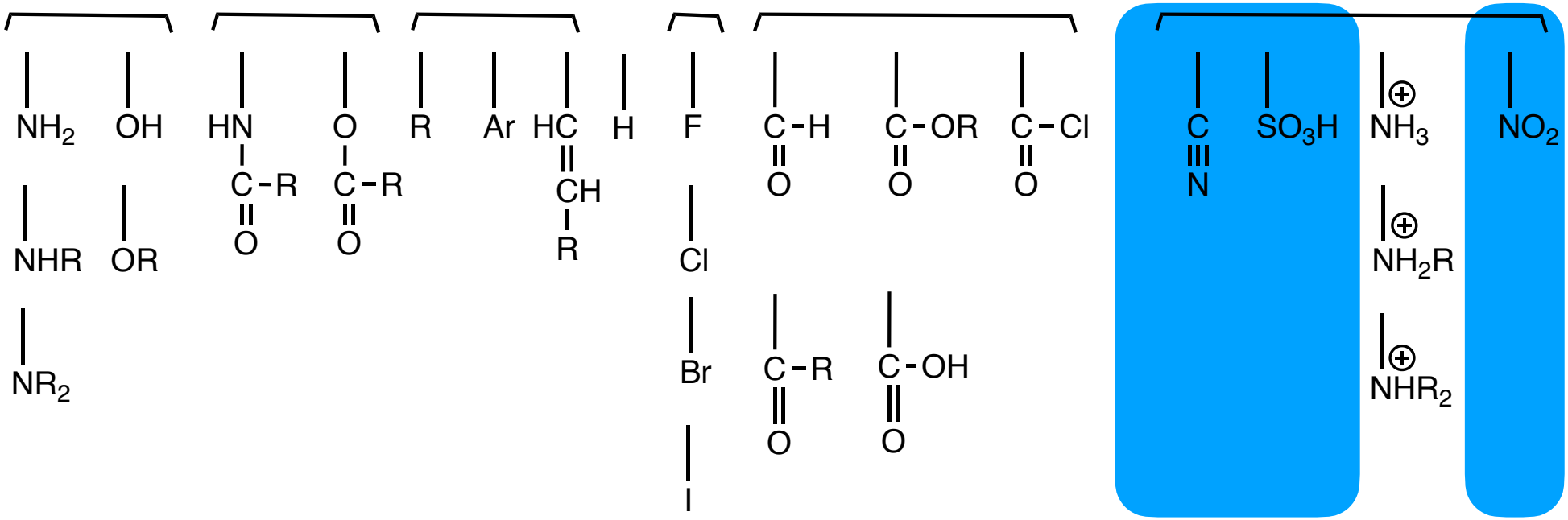

NH2

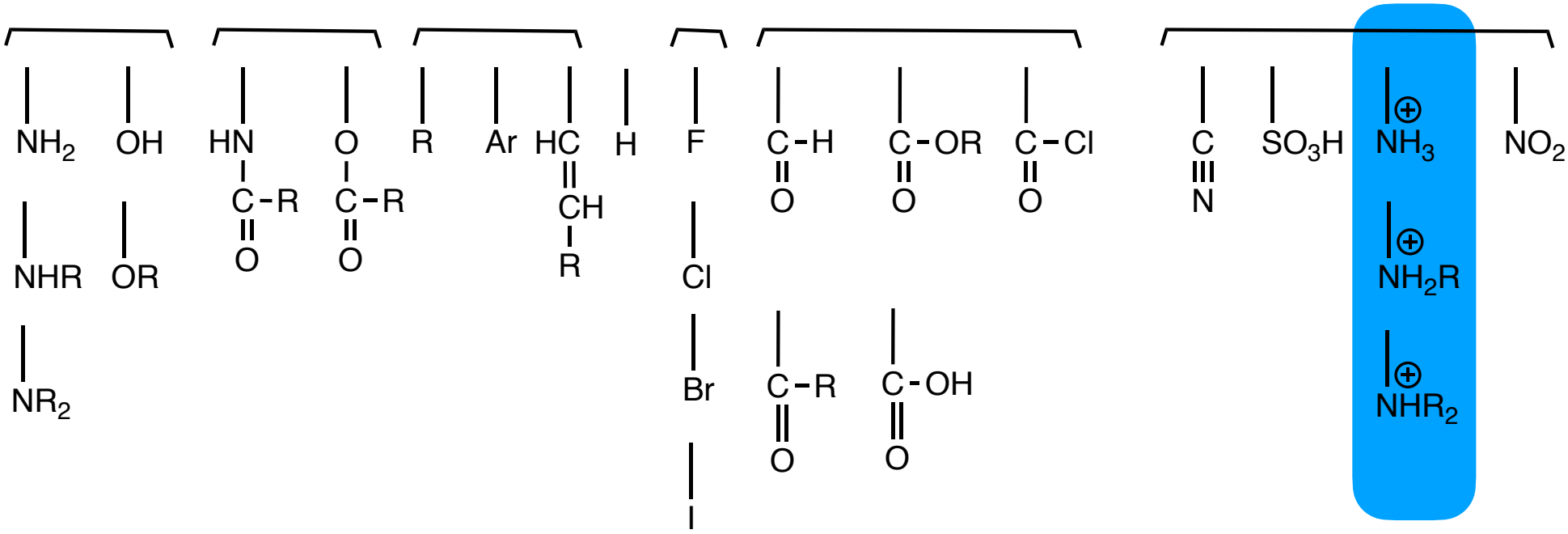

Cl

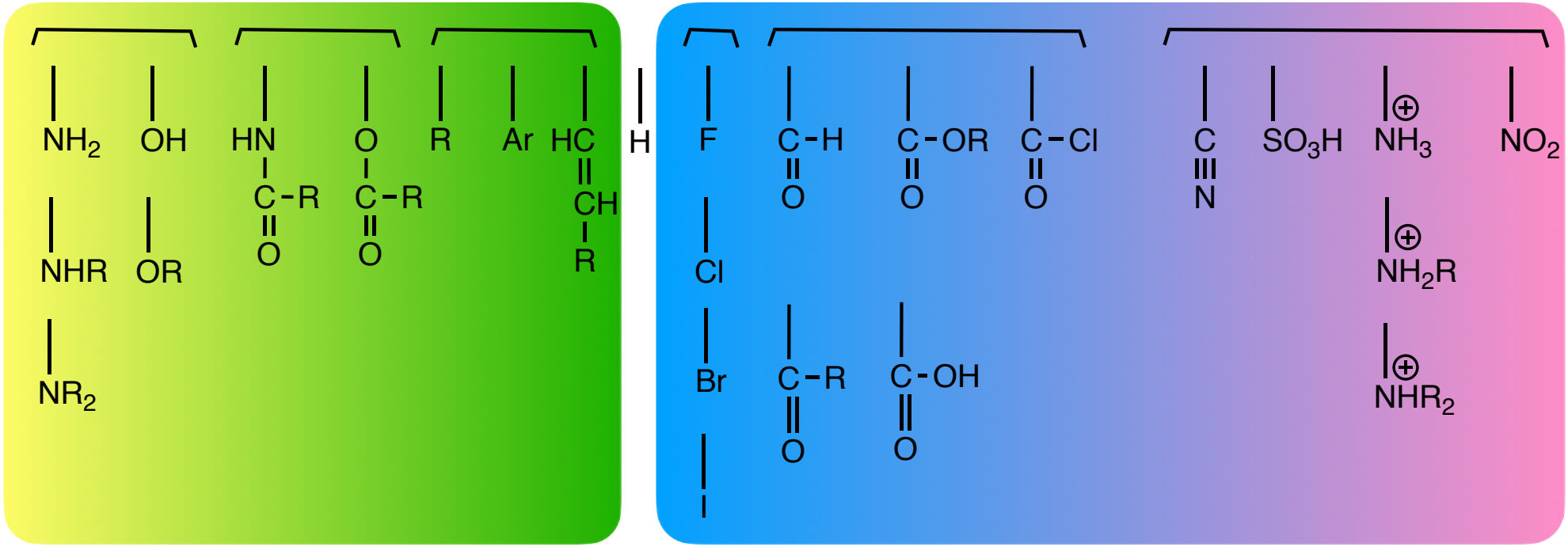

Br

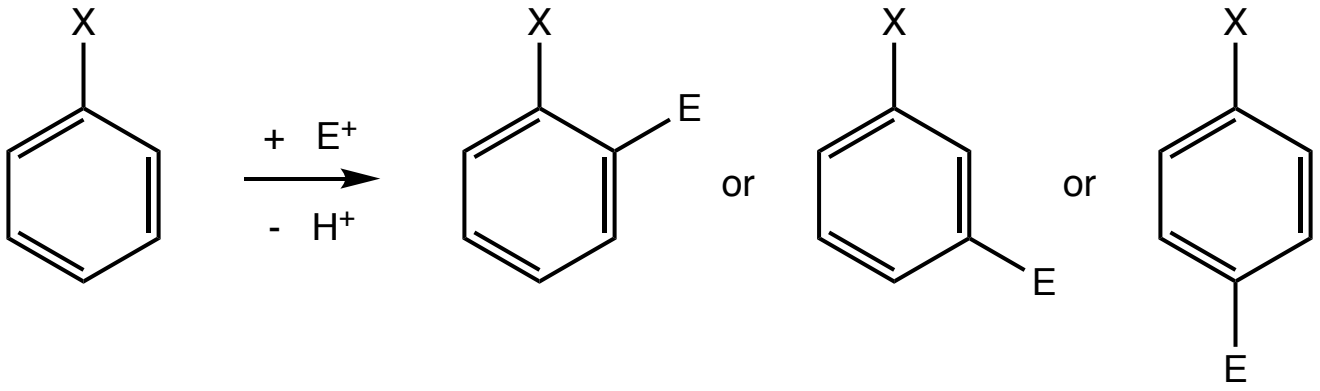

I

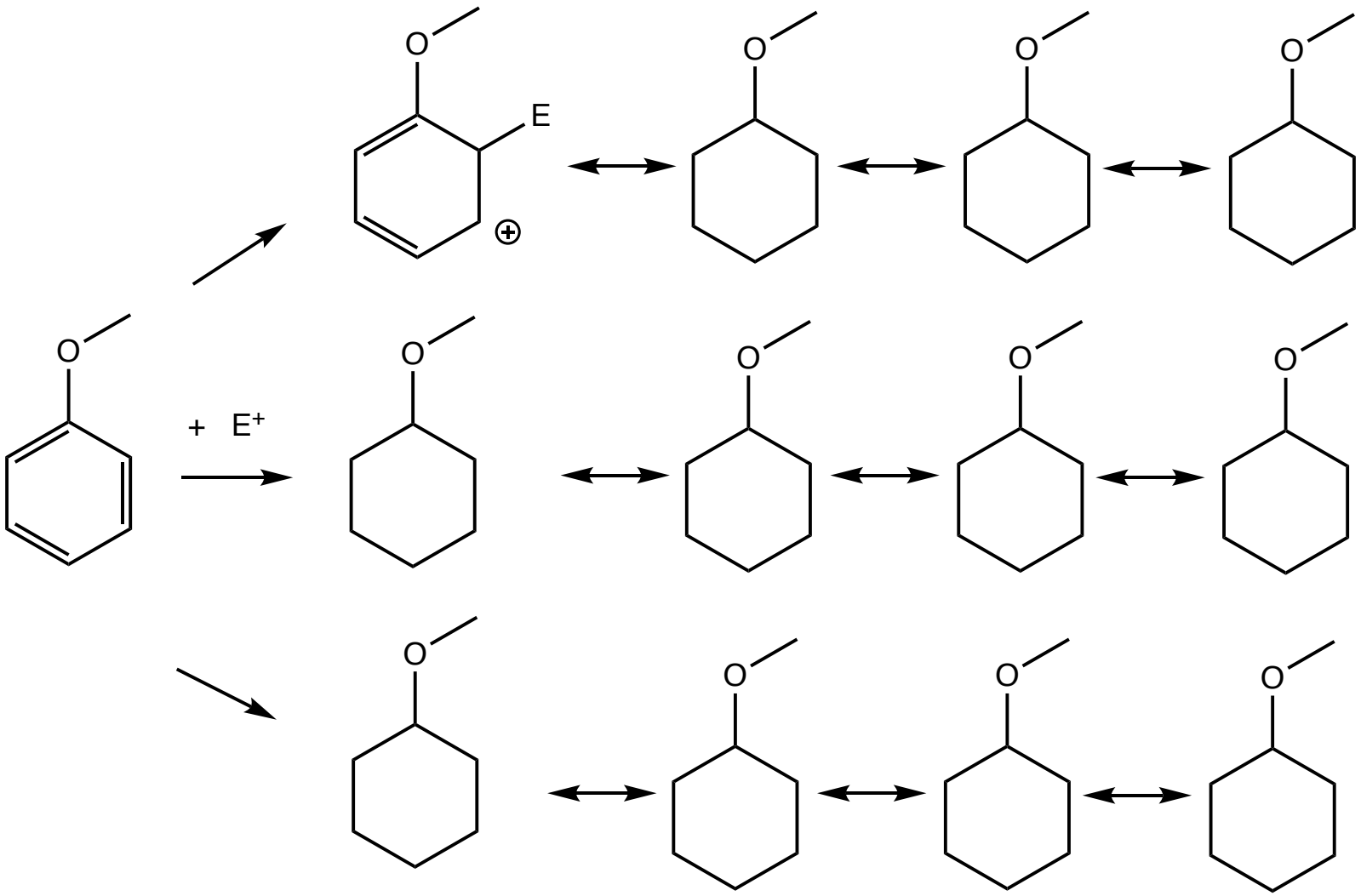

NH2
OH
NHR
OR
NR2
HN
C-R
O
O
C-R
O
R
Ar
HC
CH
R
H
F
Cl
Br
I
C-H
O
C-OR
O
C-Cl
O
C-R
O
C-OH
O
C
N
SO3H
NH3
NH2R
NHR2
NO2

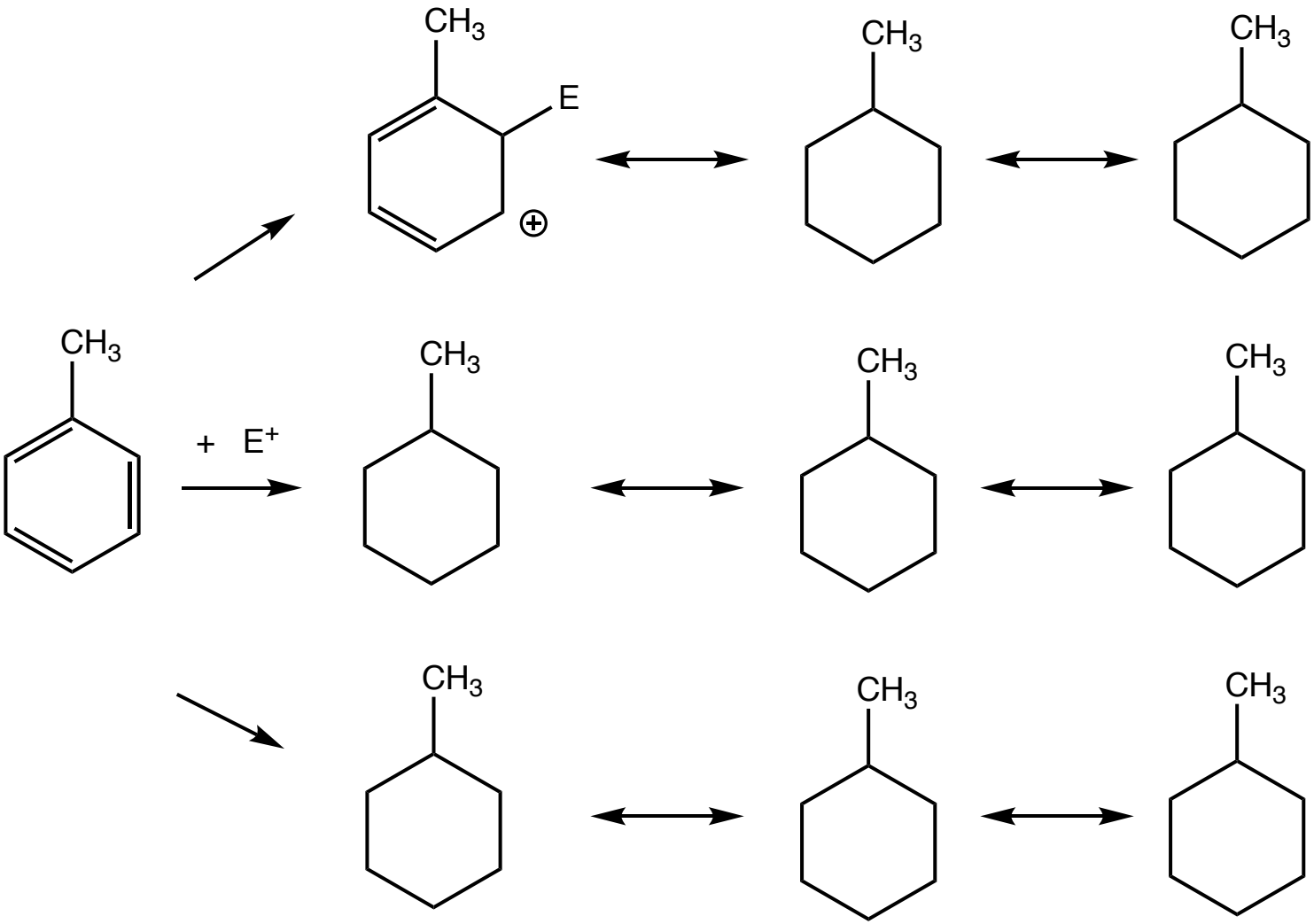

NH2
OH
NHR
OR
NR2
HN
C–R
O
O
C–R
O
R
Ar
HC
CH
R
H
F
Cl
Br
I
C–H
O
C–OR
O
C–Cl
O
C–R
O
C–OH
O
C
N
SO3H
NH3
NH2R
NHR2
NO2

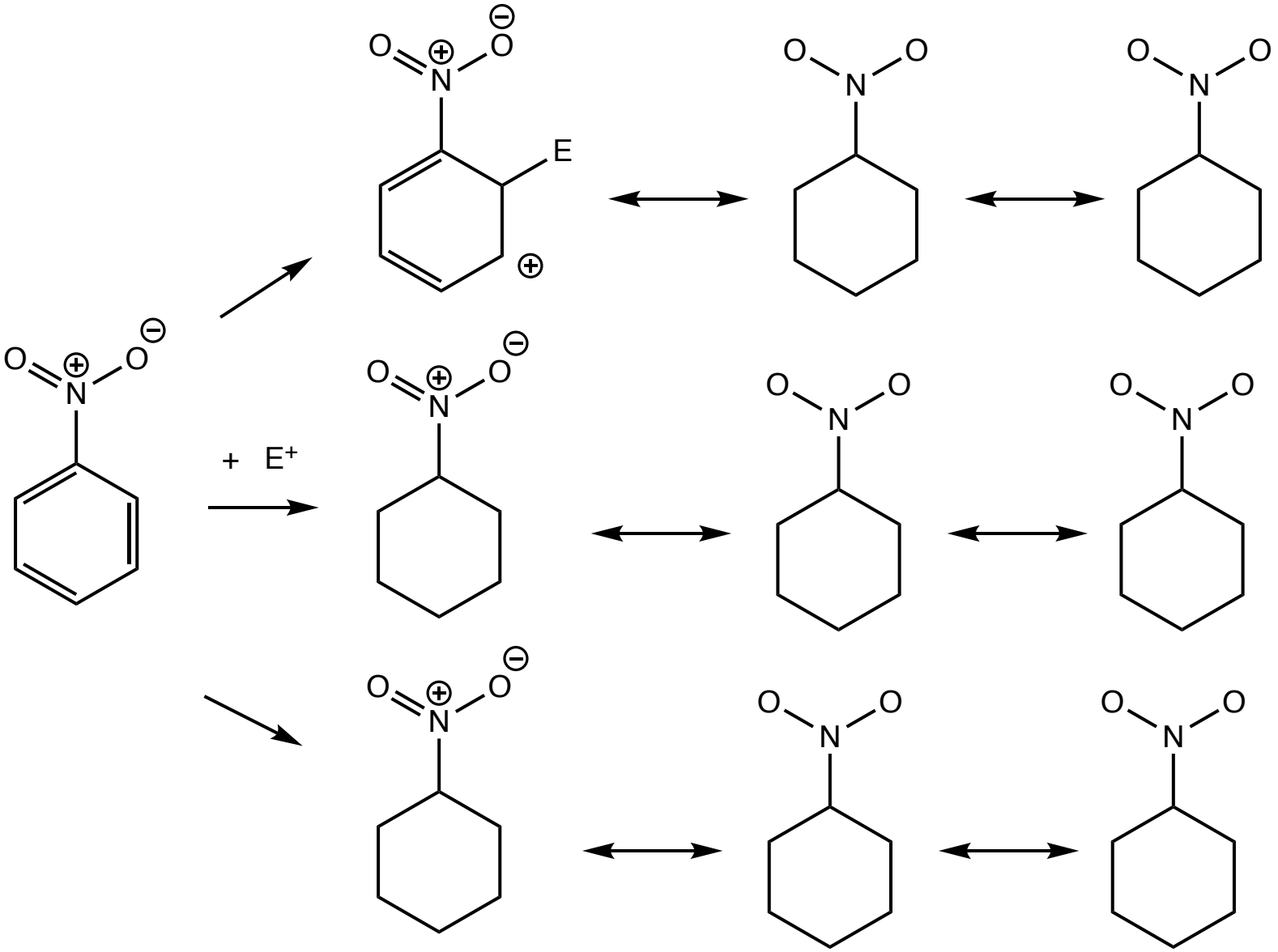

NH2
NHR
NR2
OH
OR
HN
C–R
O
O
C–R
O
R
Ar
HC
CH
R
H
F
Cl
Br
I
C–H
O
C–OR
O
C–Cl
O
C–R
O
C–OH
O
C
N
SO3H
NH3
NH2R
NHR2
NO2

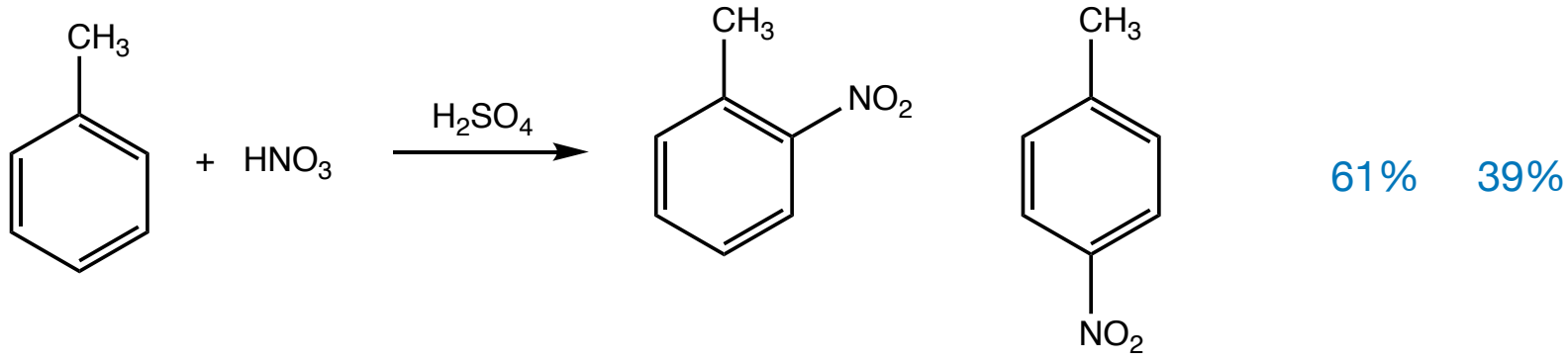

NH2
OH
HN
C-R
O
O
C-R
O
R
Ar
HC
CH
R
NHR
OR
NR2
H
F
Cl
Br
I
C-H
O
C-R
O
C-OR
O
C-OH
O
C-Cl
O
C
N
SO3H
NH3
NH2R
NHR2
NO2


X
+ E+
- H+
X
E
or
X
E
or
X
E

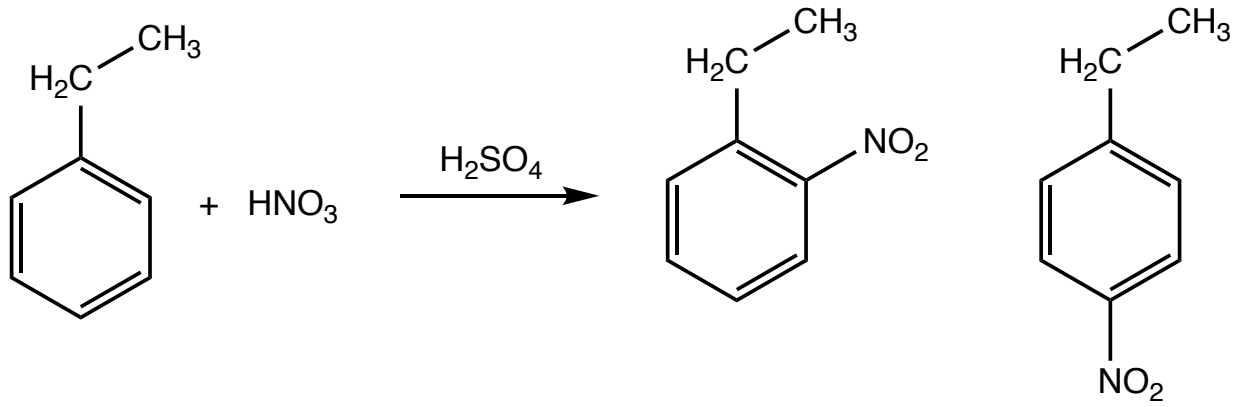

O
E
⊕
O
O
O
O
O
+ E+
O
O
O
O
O
O
O
O
O


CH3
E
⊕
CH3
CH3
CH3
CH3
+ E+
CH3
CH3
CH3
CH3
CH3
CH3
CH3

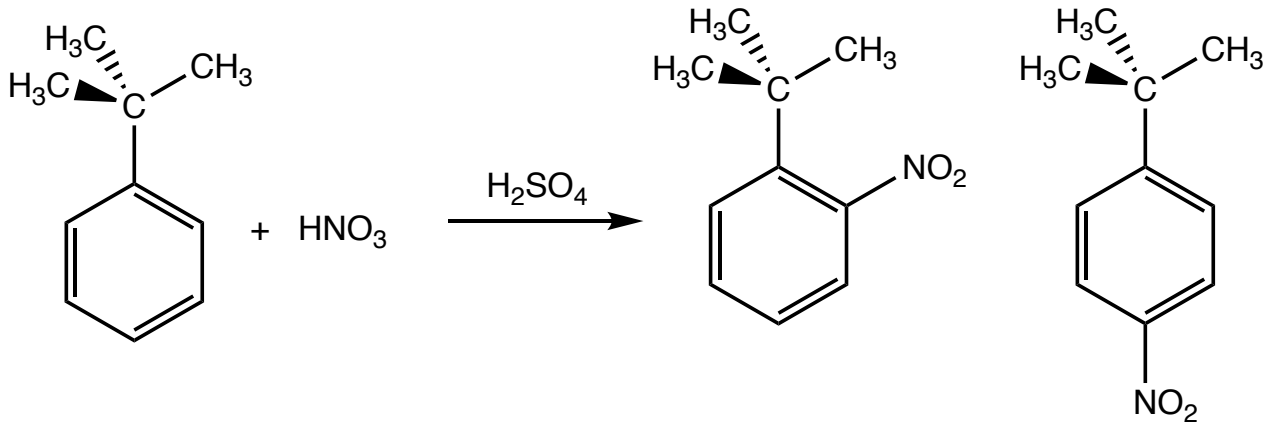

+ E+
E



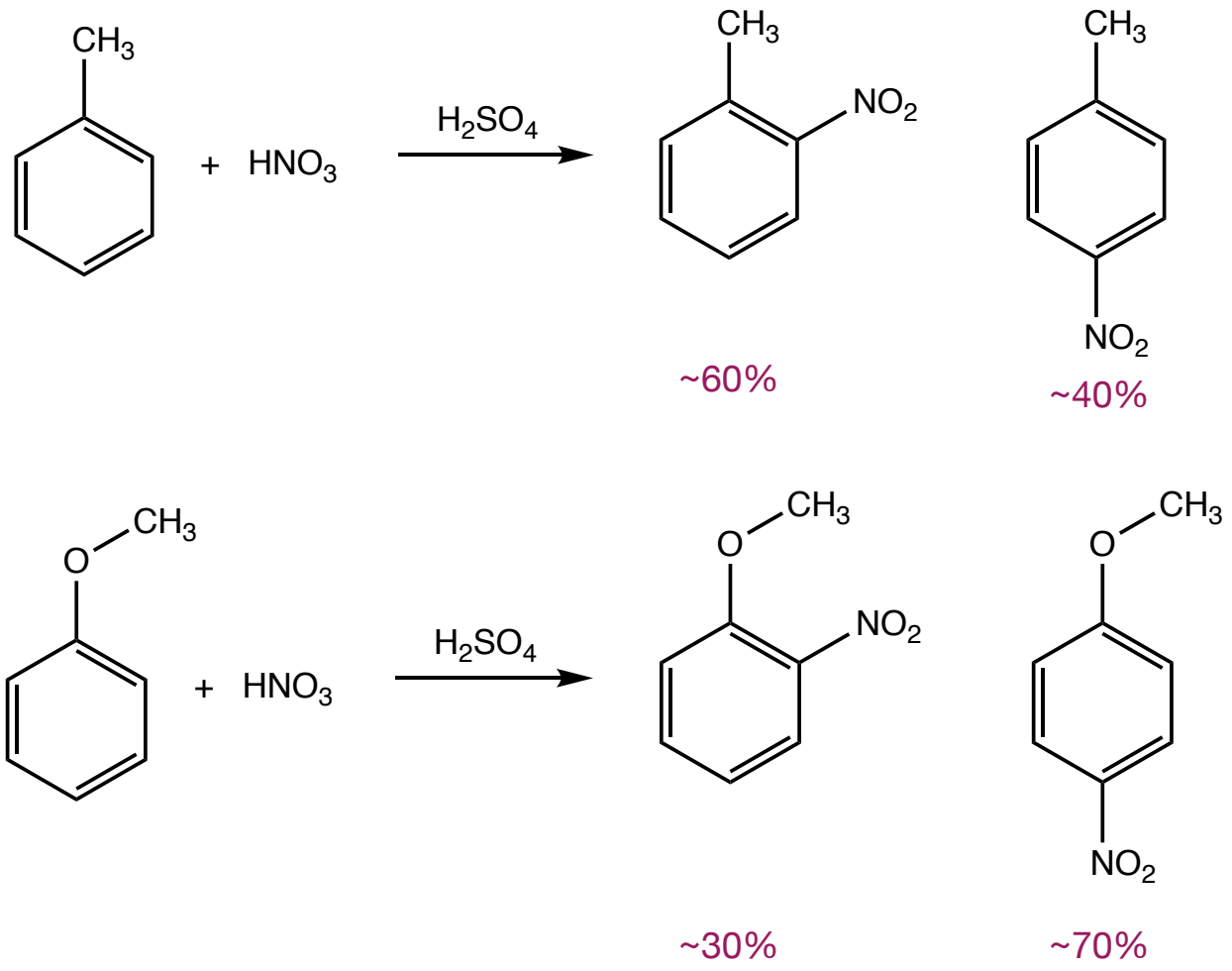
61% 39%



50% 50%



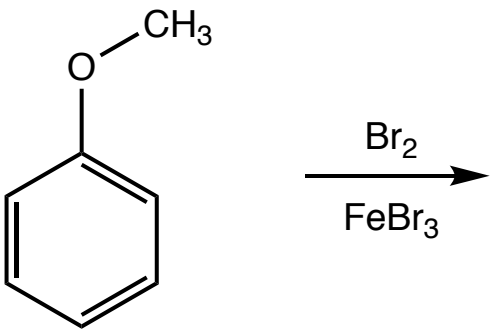
18% 82%

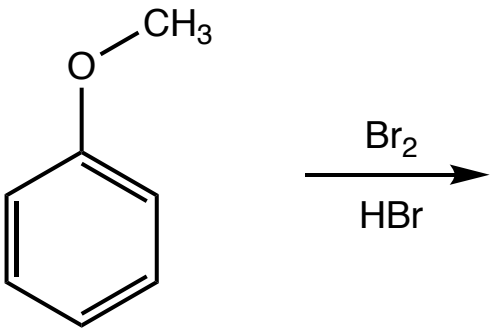


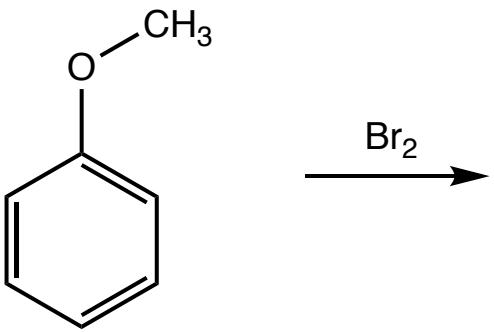
The *para* position has steric and electronic advantages

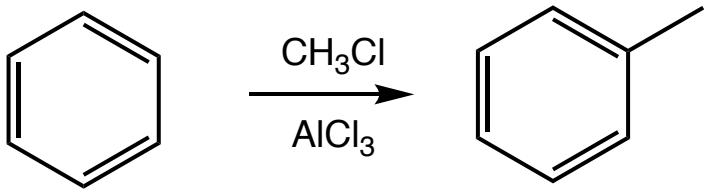
The *ortho* position has a statistical advantage

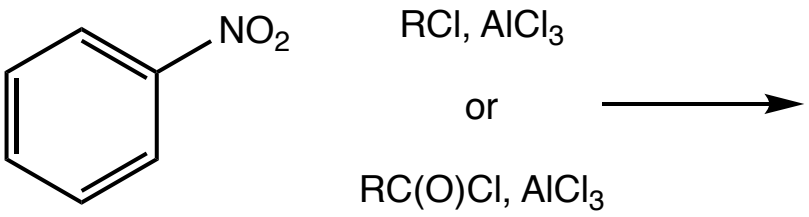
Mixtures of *o* and *p* isomers typically result


CH3
O
Br2
FeBr3

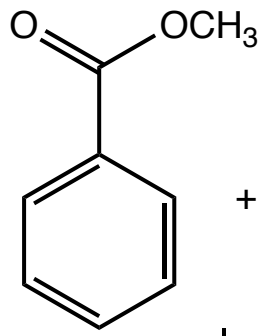

CH3
O
Br2
HBr


CH3
O
Br2


CH_3Cl
$AlCl_3$

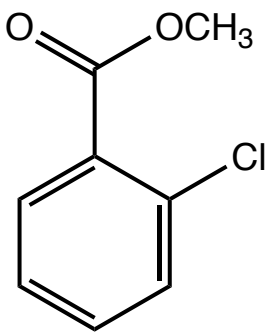

NO2
RCl, AlCl3
or
RC(O)Cl, AlCl3

Practice



+ Cl_2

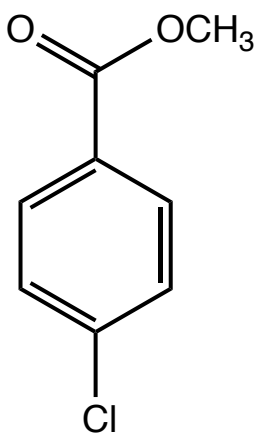
+ $FeCl_3$



+

$HFeCl_4$

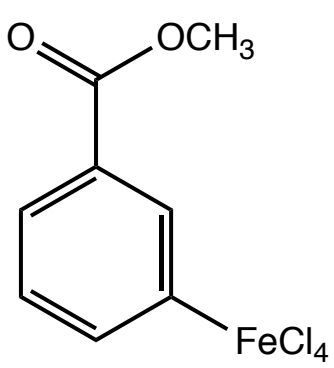
A



+

$HFeCl_4$

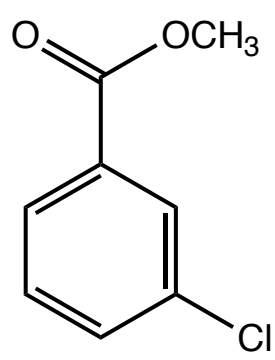
B



+

HCl

C

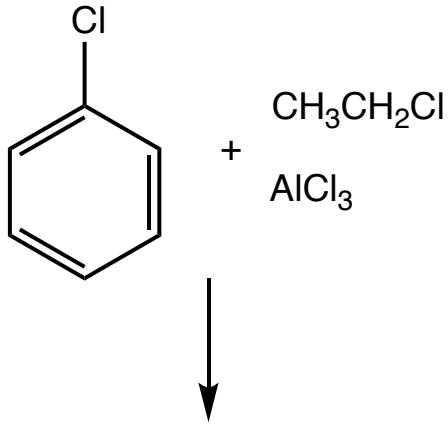


+

$HFeCl_4$

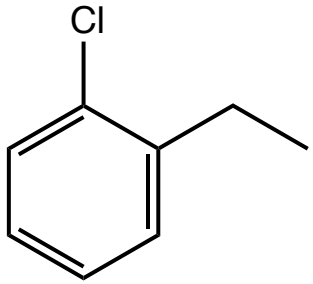
D

Practice



+ CH_3CH_2Cl

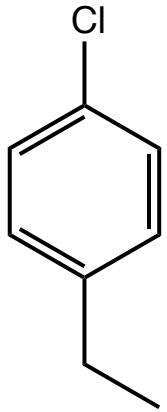
+ $AlCl_3$



+

$HAlCl_4$

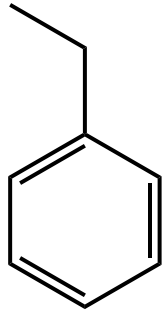
A



+

$HAlCl_4$

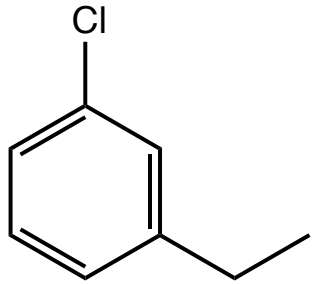
B



+

$Cl_2\ AlCl_3$

C



+

$HAlCl_4$

D