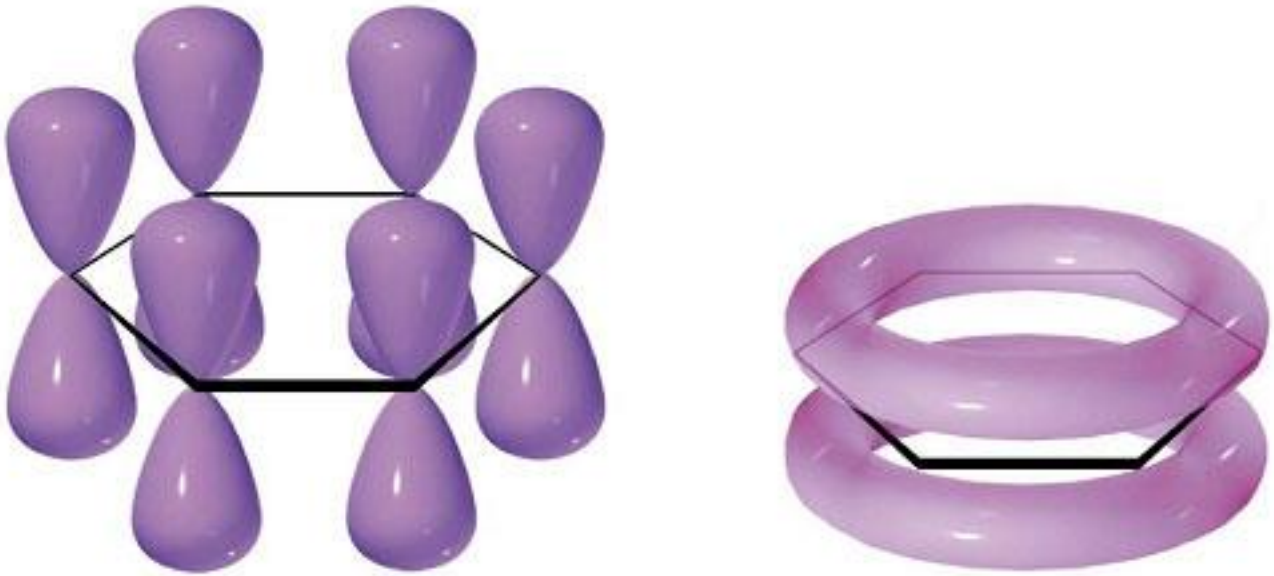
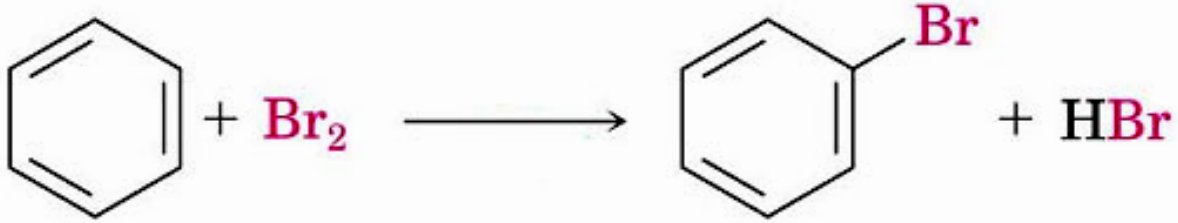
Organic Chemistry Concepts

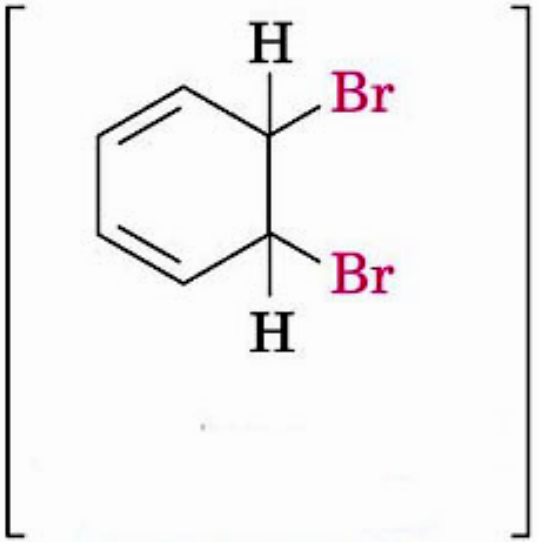
LOKT.09.051

Aromatic π-bond reactivity



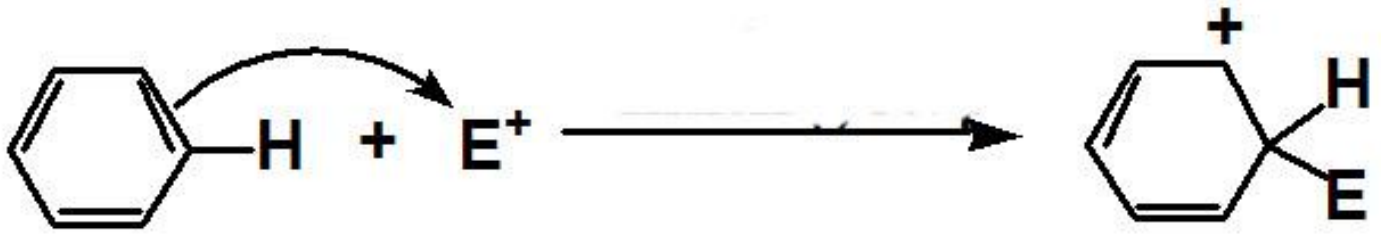
Not similar to alkene reactivity



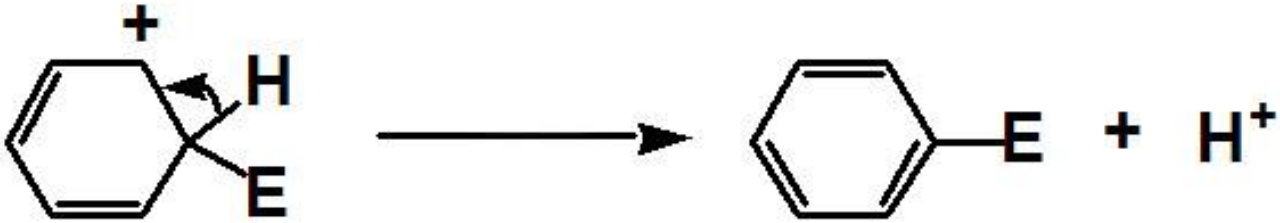


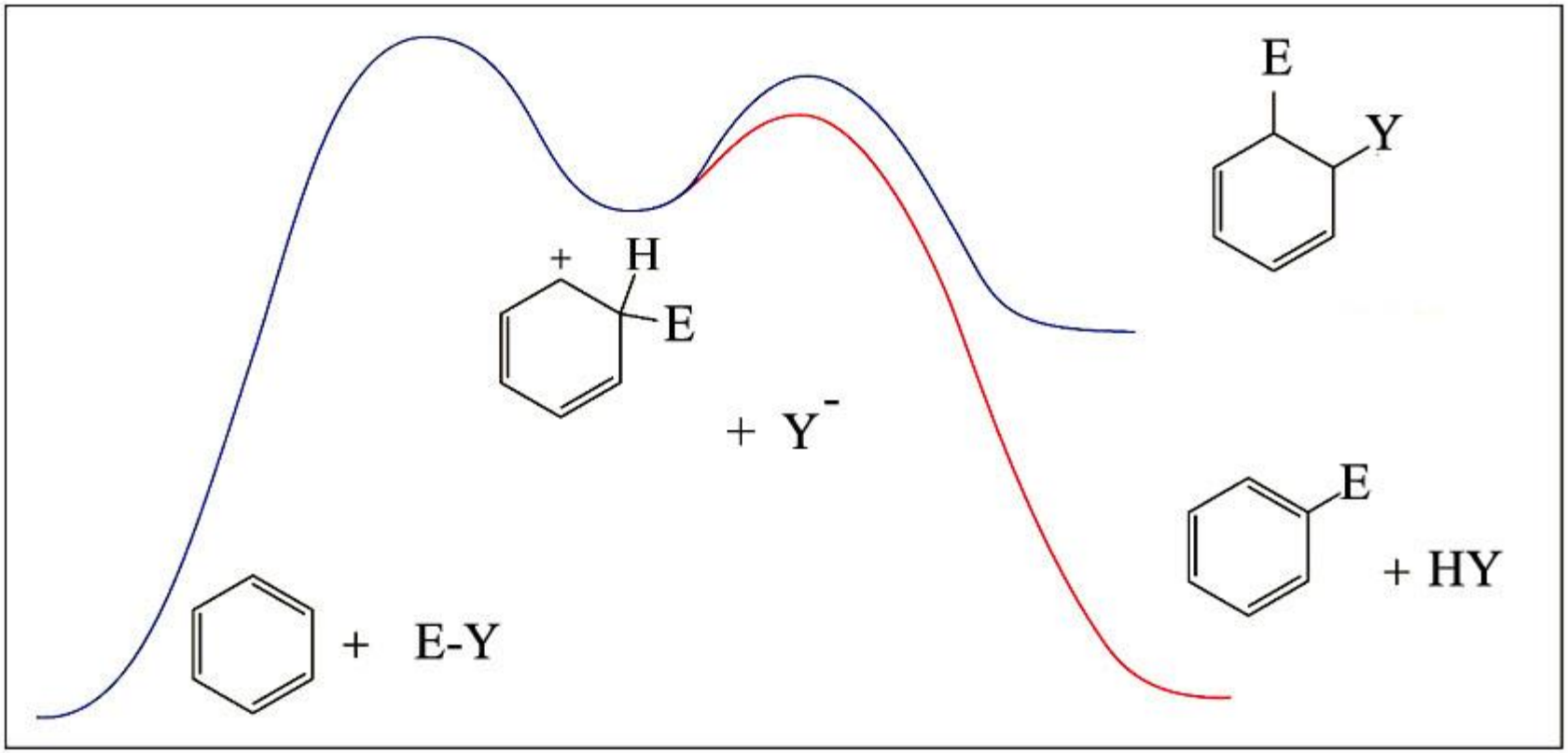
Not allowed

Electrophilic aromatic substitution, E^+

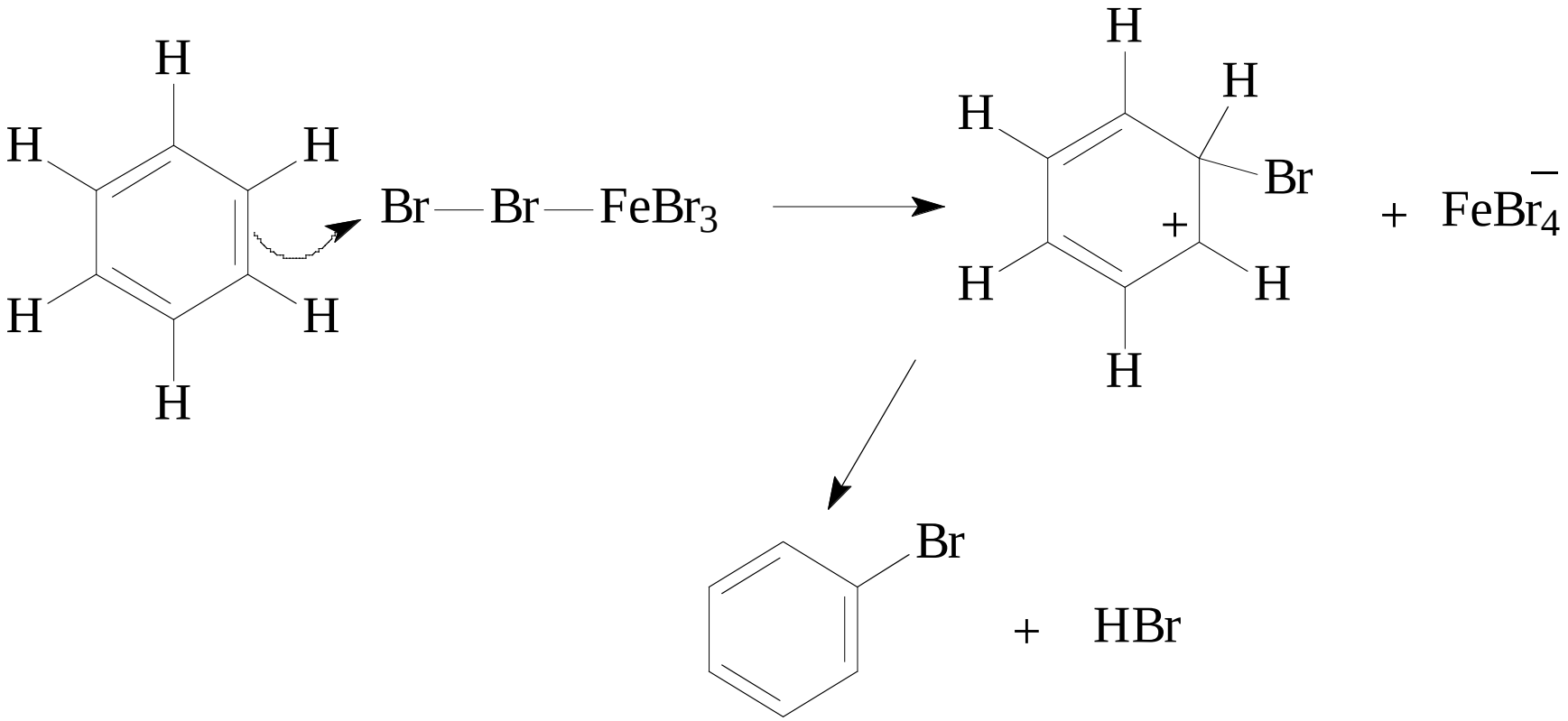


Wheland intermediate

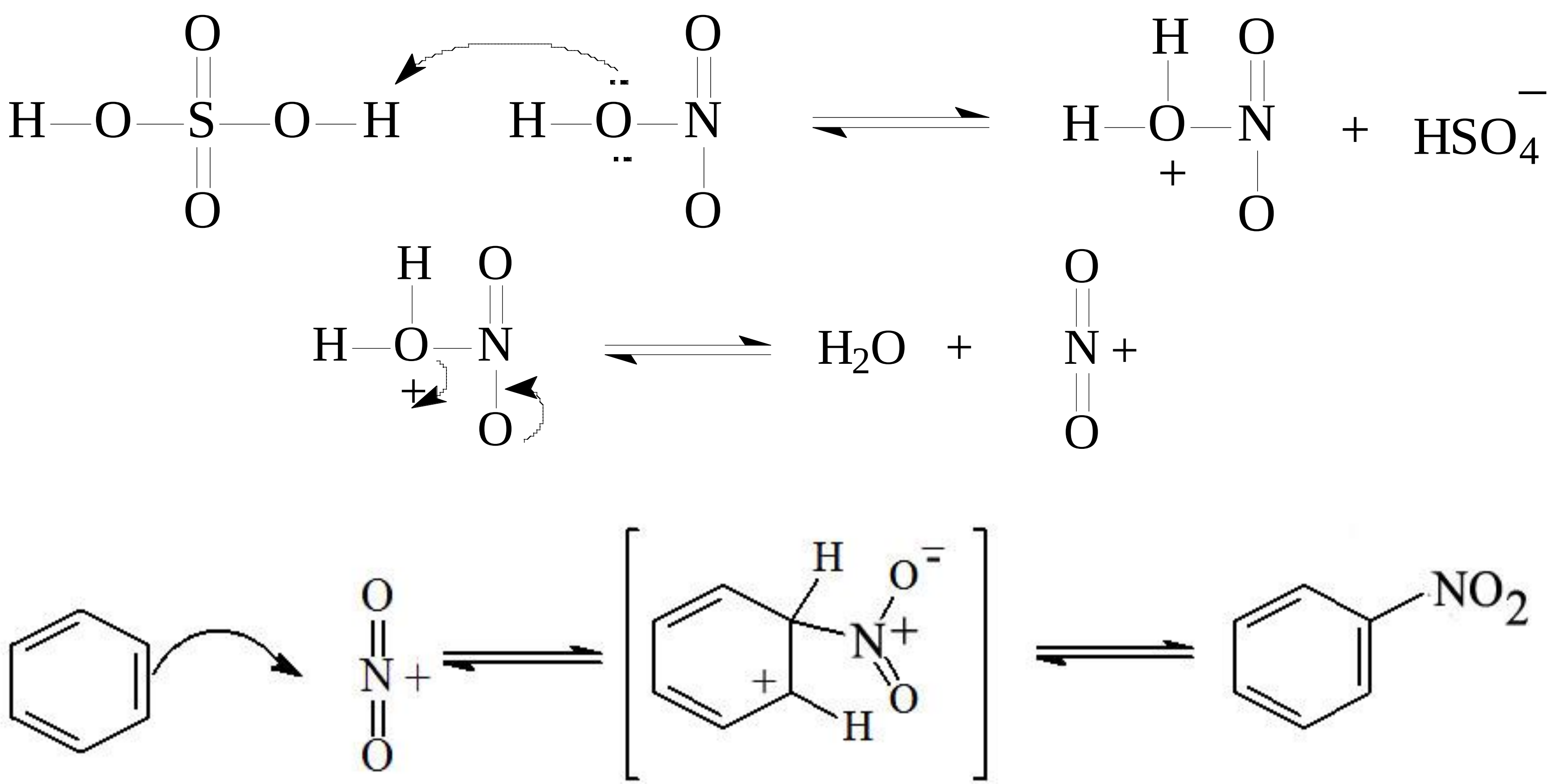



E
Y
+ H
E
+ Y-
E
+ HY
+ E-Y

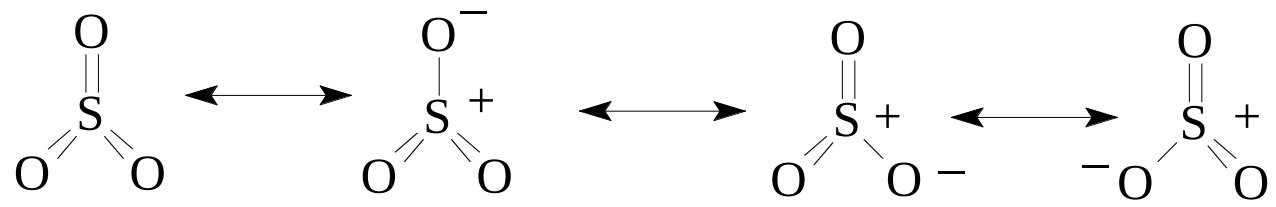
Bromination

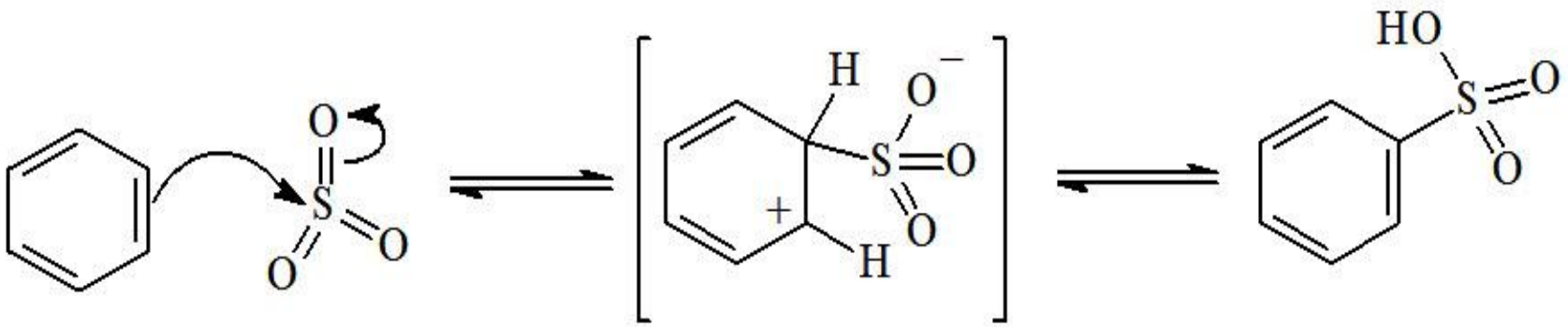


Nitration

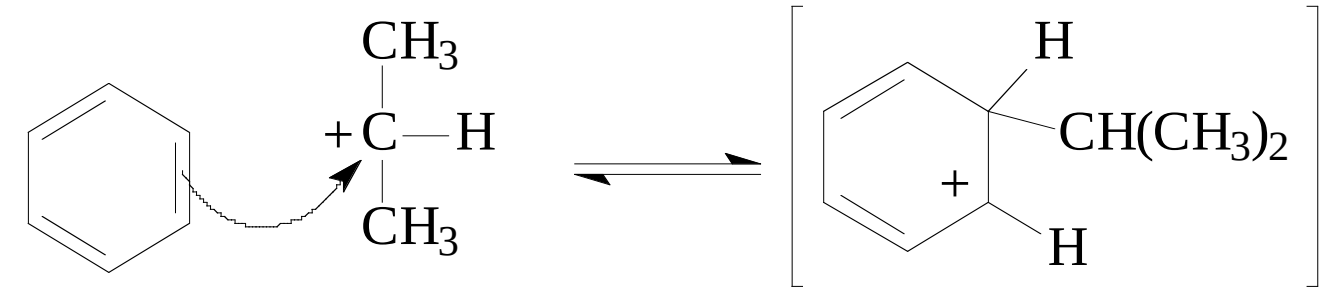


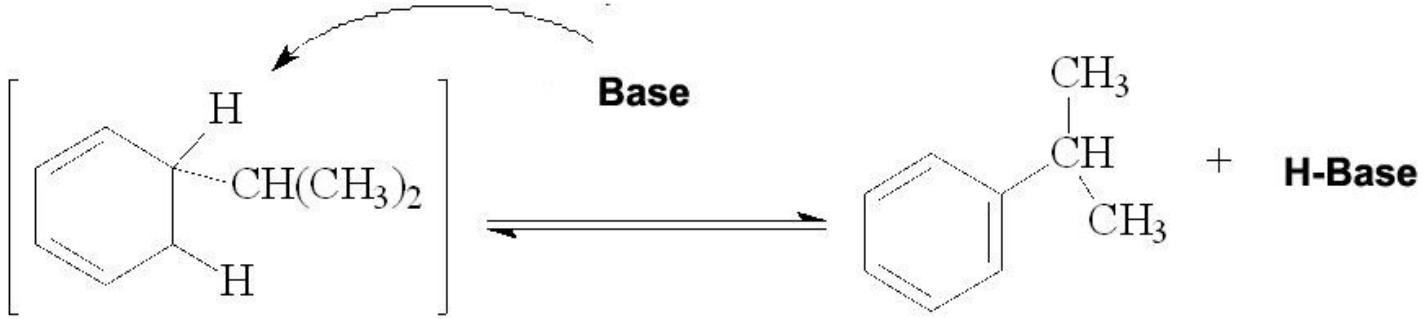
Sulfonation



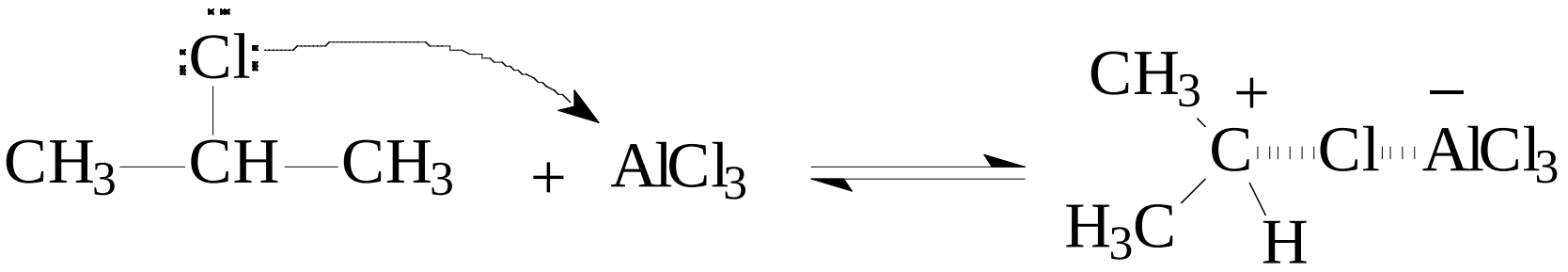


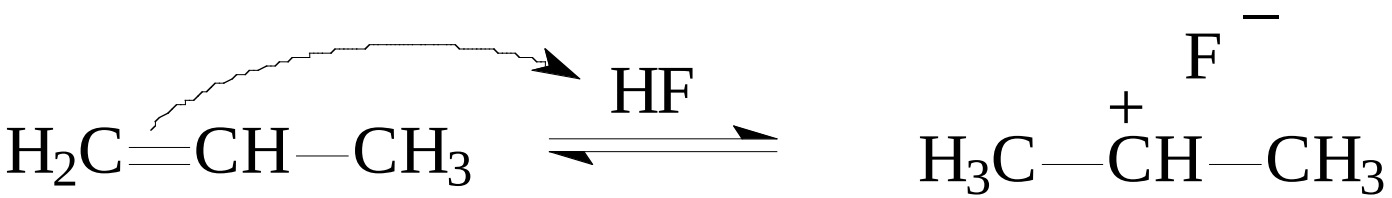
Alkylation



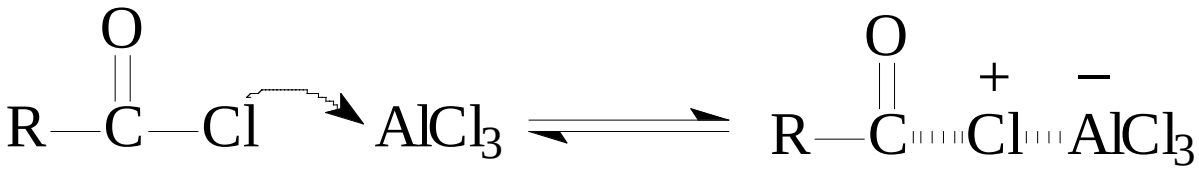


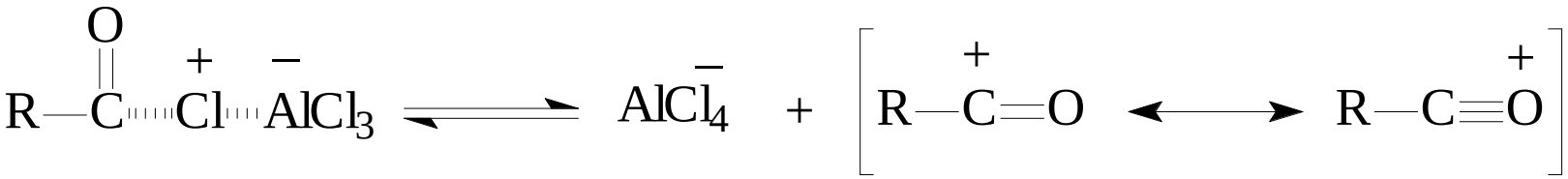
Carbonium ion formation

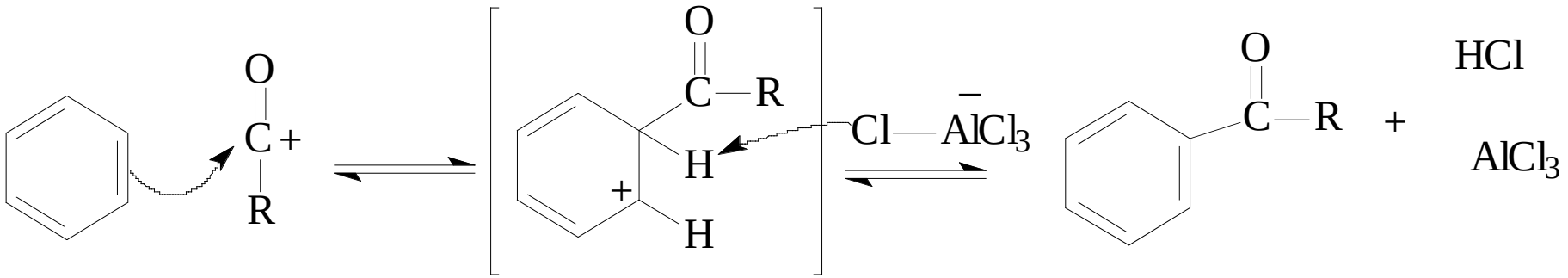




Acylation

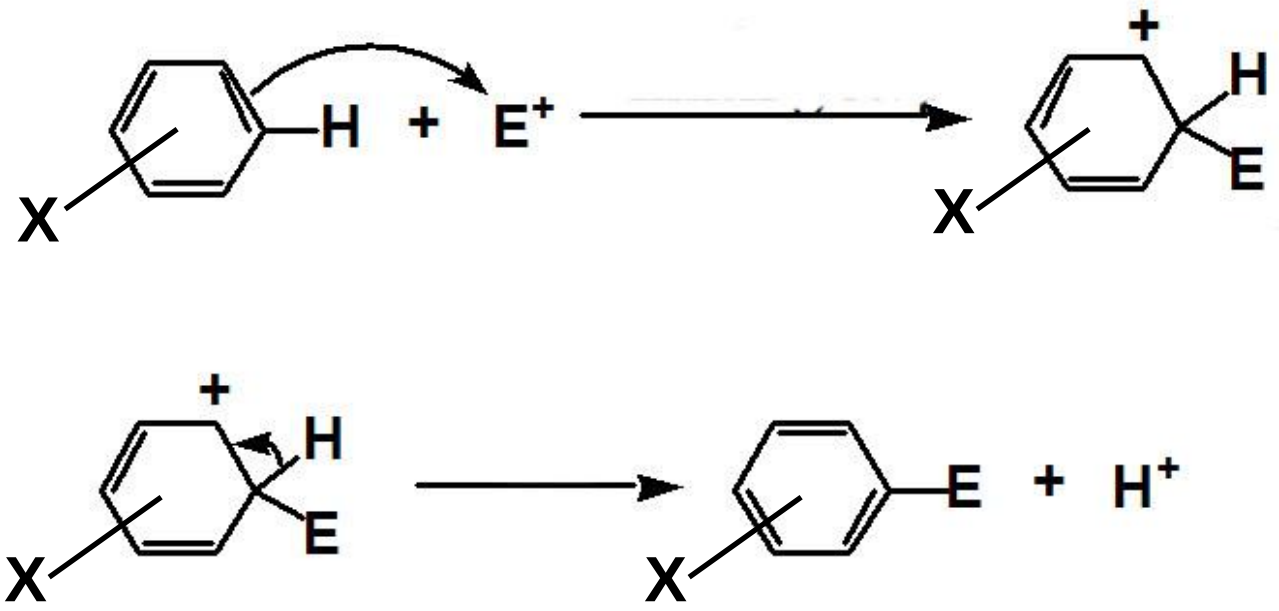




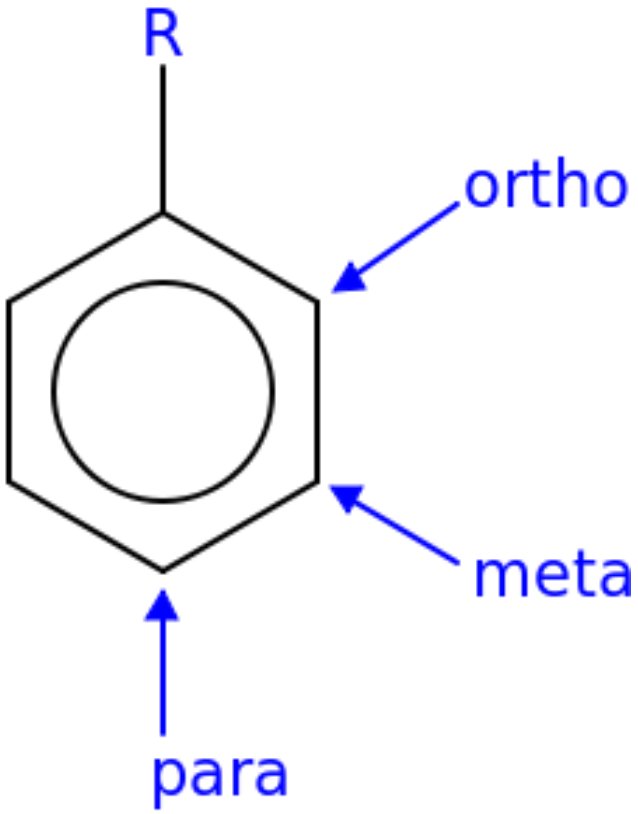


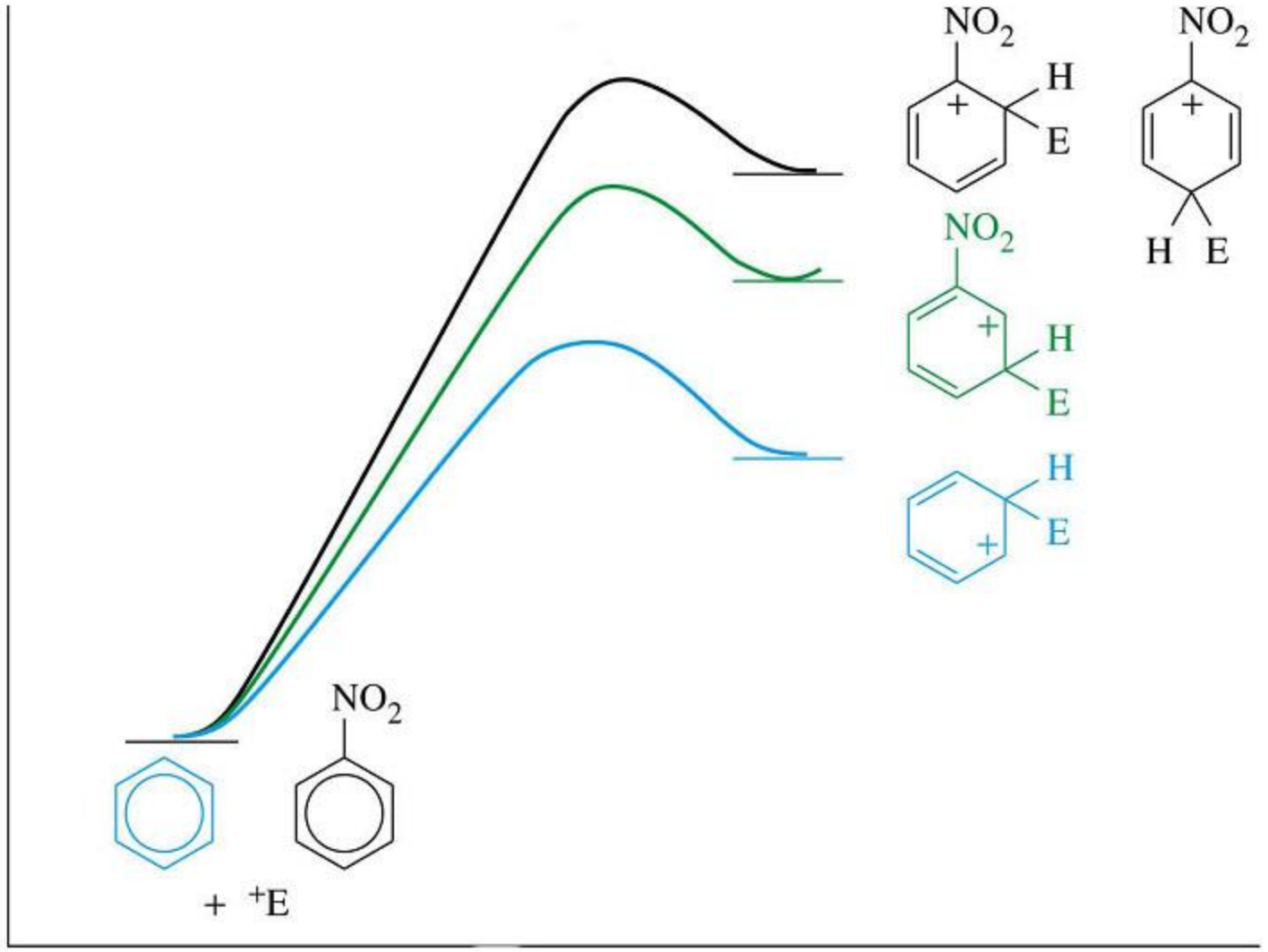
Acyl cation

Direction of aromatic substitution

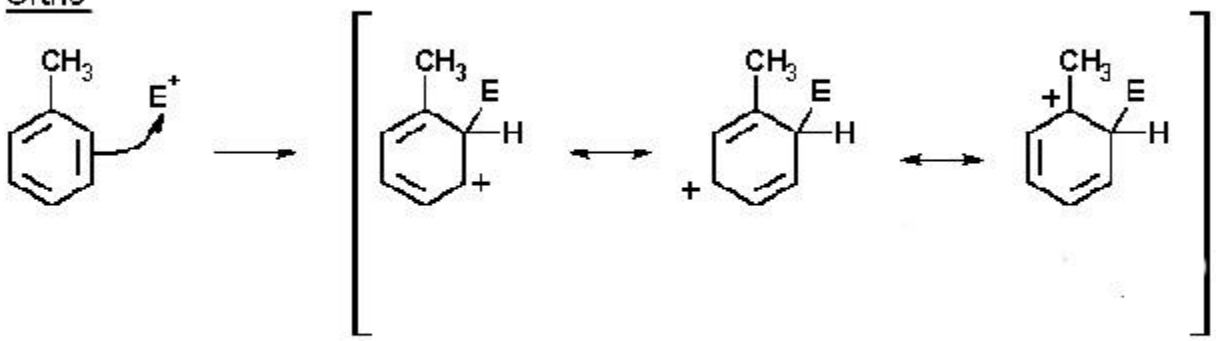


Electrophilic substitution pattern

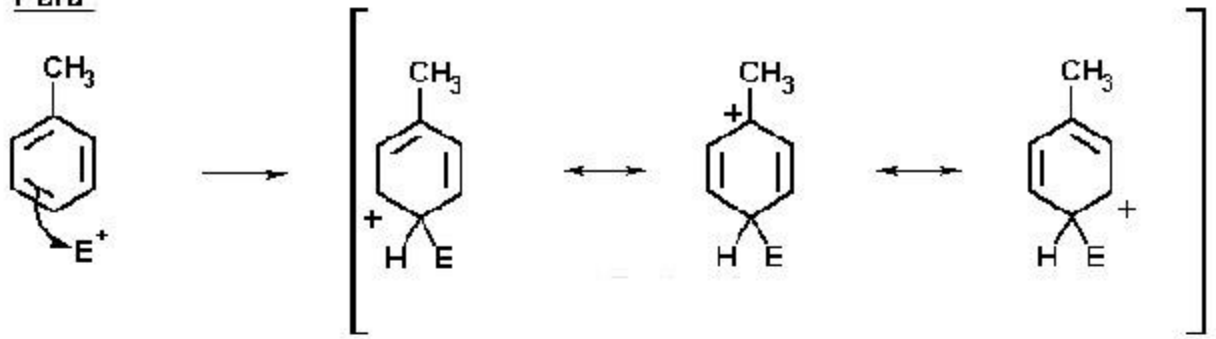



NO2
H
E
NO2
NO2
H
E
H E
NO2
H
E
NO2
+ +E

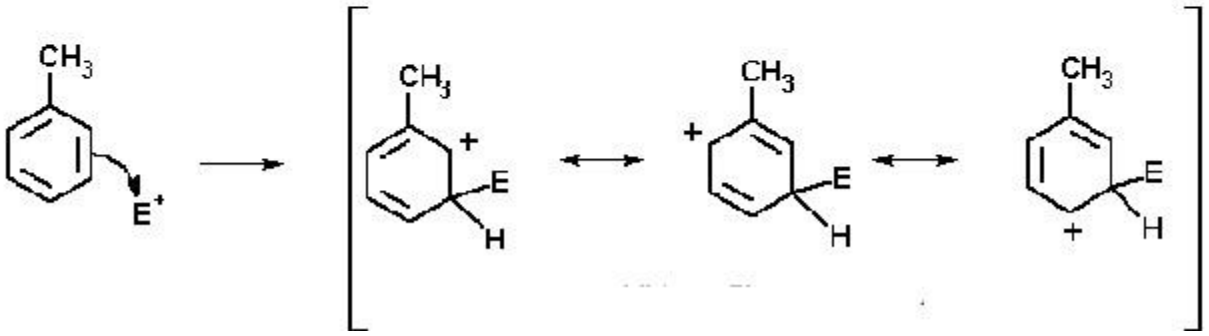
Ortho

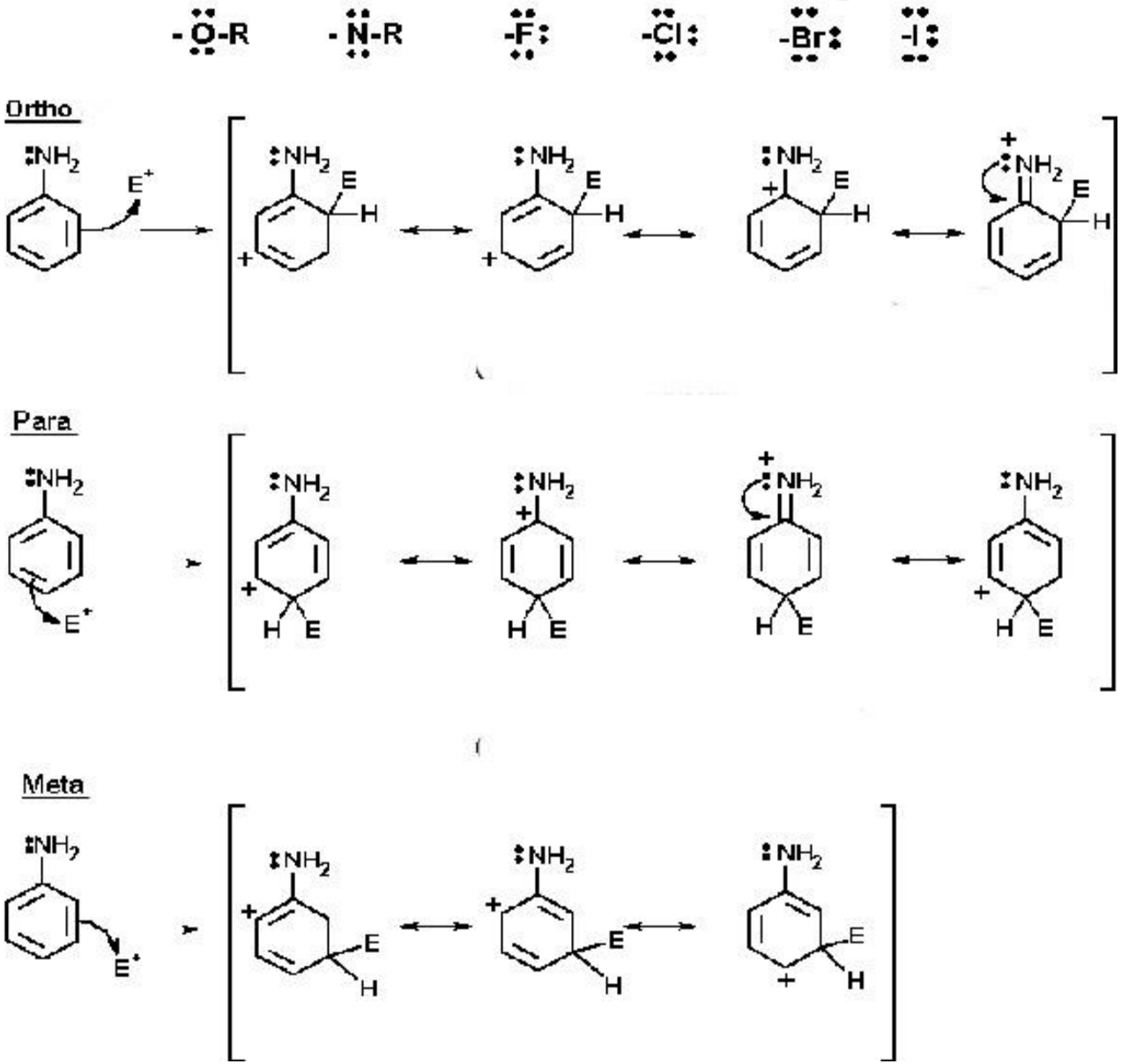


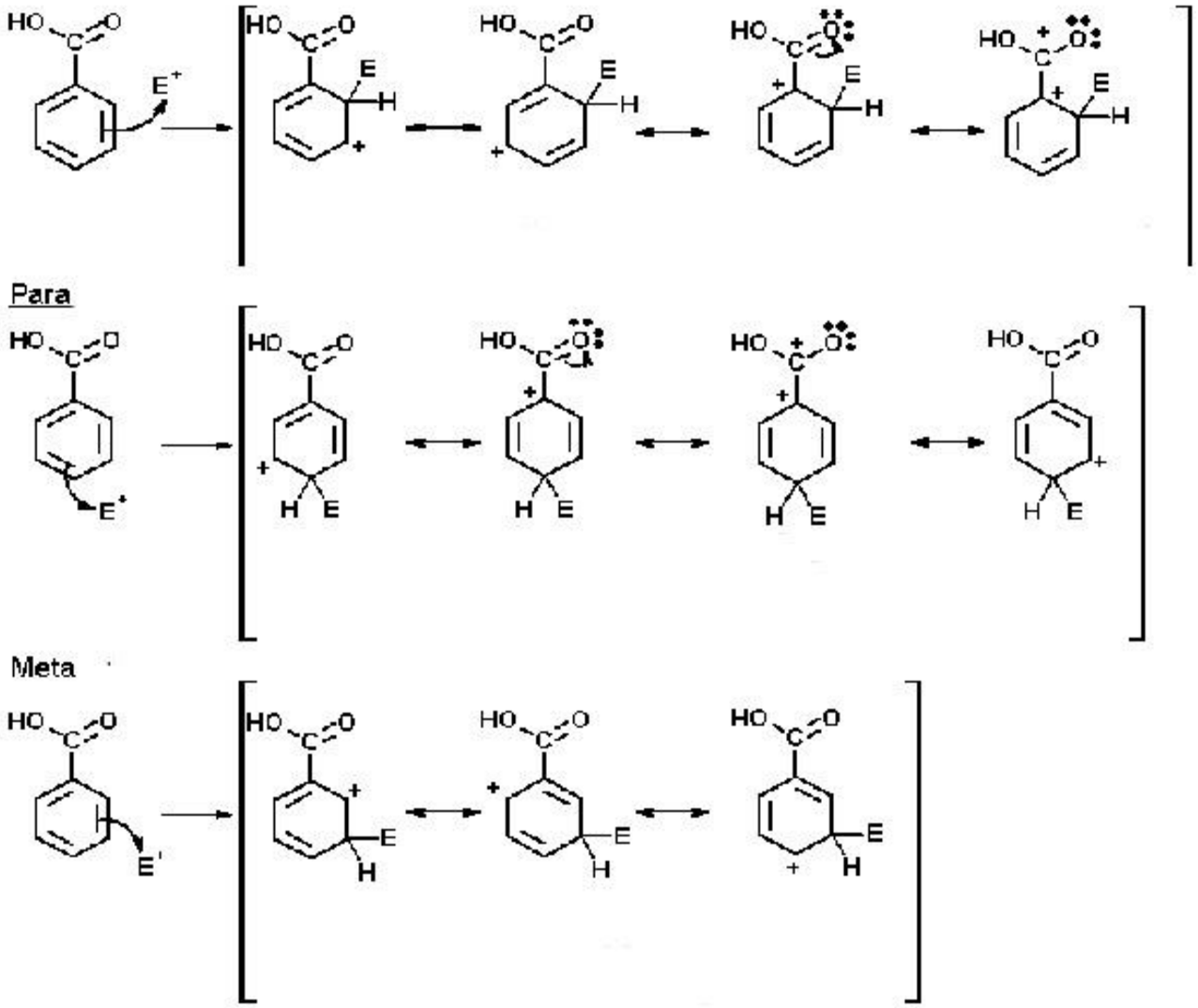
Para

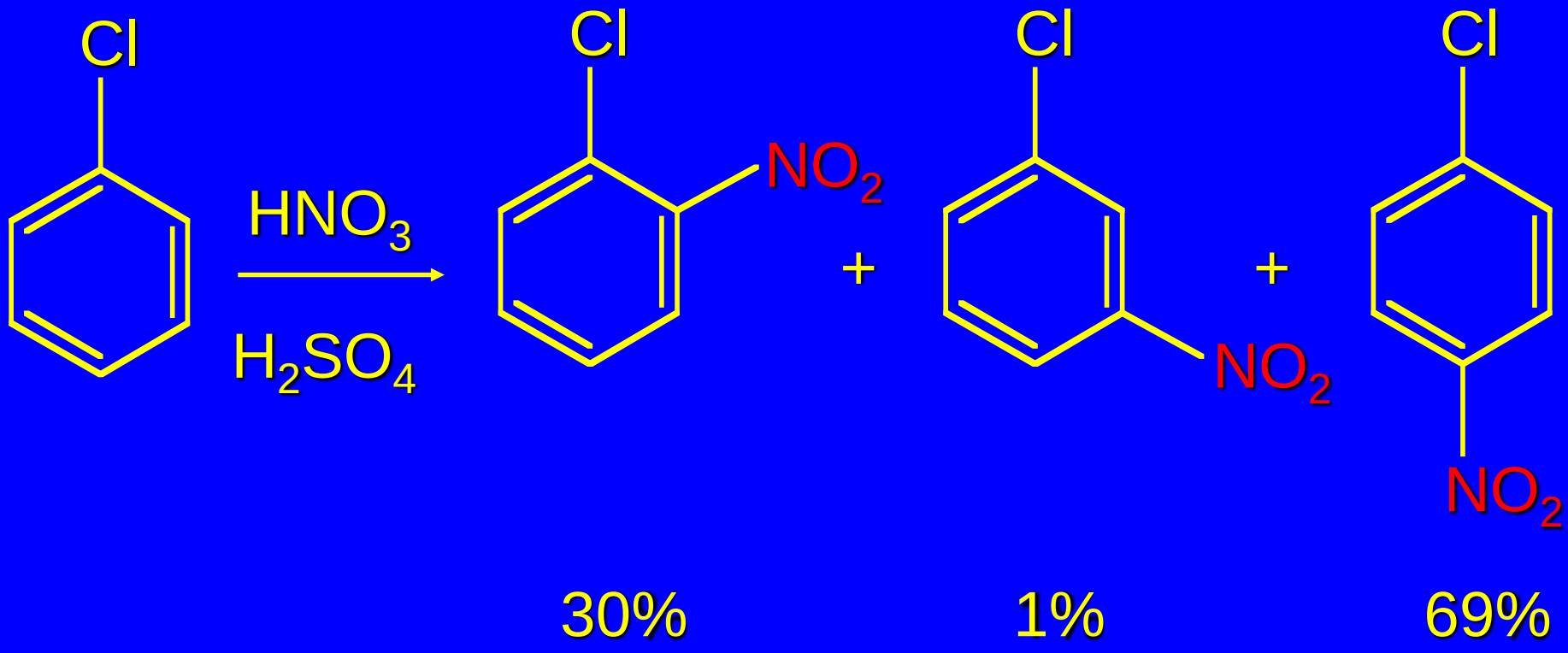


Meta

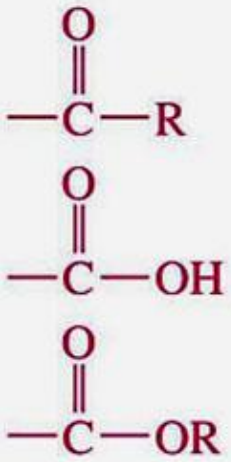



-O-R
-N-R
-F
-Cl
-Br
-I
Ortho
Para
Meta


Para
Meta


Cl
HNO3
H2SO4
Cl
NO2
+
Cl
+
Cl
NO2
NO2
30%
1%
69%

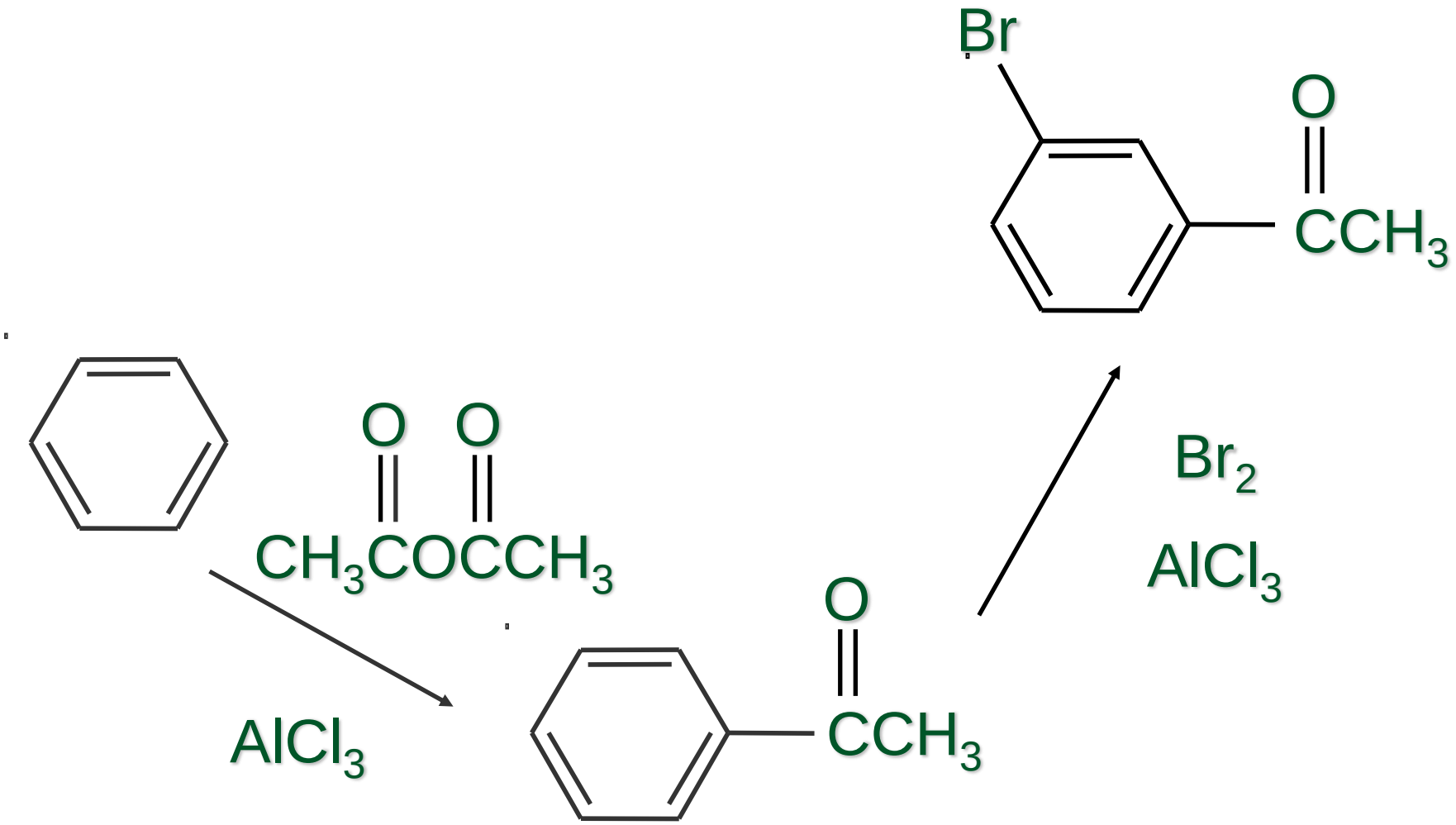
Summary

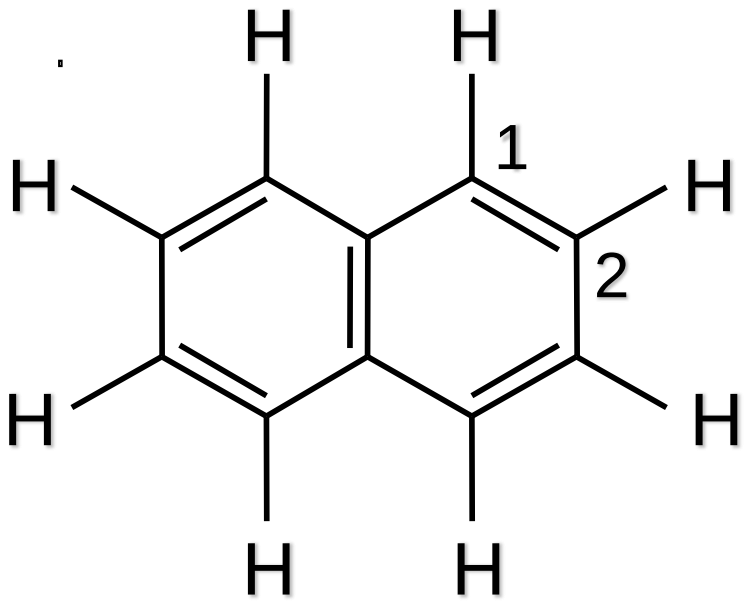
$-\ddot{N}H_2$ $-\ddot{O}H$ $-\ddot{O}R$ $-\ddot{N}HCOCH_3$	$-R$ (alkyl)  (aryl)	$-F$ $-Cl$ $-Br$ $-I$		$-SO_3H$ $-C\equiv N$ $-NO_2$ $-\overset{+}{N}R_3$

Orto and para

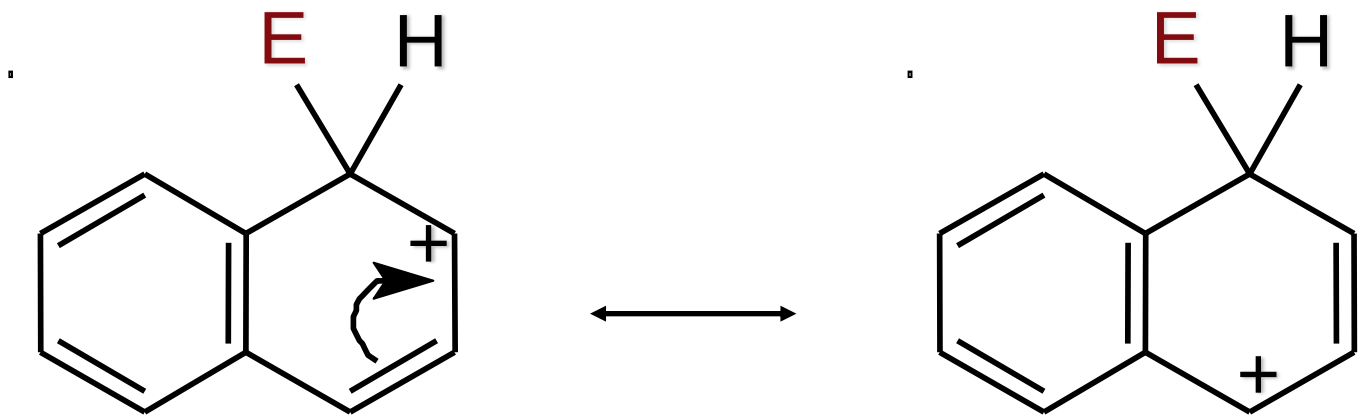
Meta

Meta-bromoacetophenone synthesis



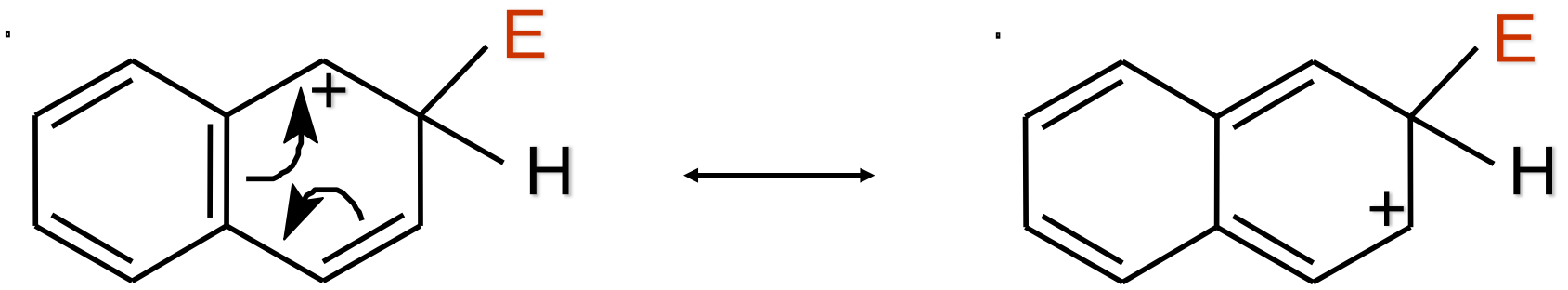


Different positions!!



-carbonium ion is stabilized

-stabile aromatic structure



-for carbonium ion stabilization the second ring loses its aromaticity