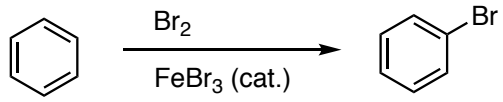
Electrophilic Aromatic Substitution: Bromination

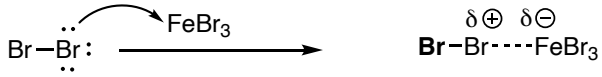
Benzene does not react with Br_2 alone, the way simple alkenes do.

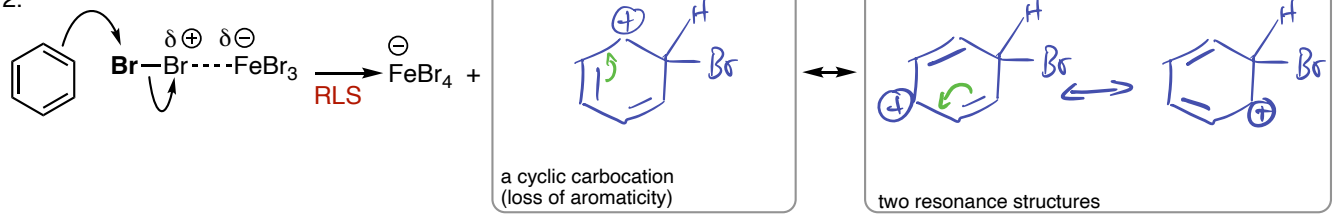
However, in the presence of $FeBr_3$, Br_2 forms a much more reactive complex, see step 1 in the mechanism below.

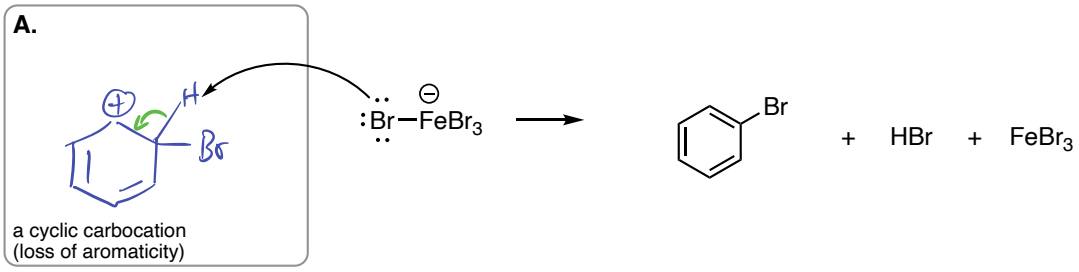
For this activity, draw the mechanism accounting for the formation of bromobenzene (see net reaction).

Net rxn: 

Mechanism:

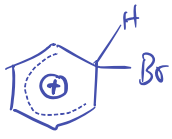
1. 

2. 

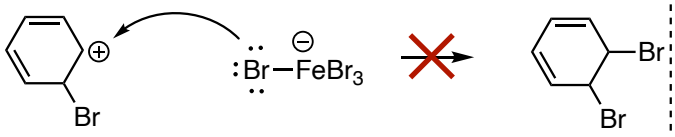
3. 

Draw the "hybrid" resonance structure in box **C**, which accounts for all carbocations in **A** and **B**.

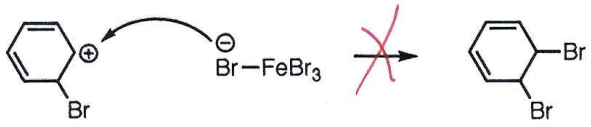
C.



Consider a possible step below in the mechanism. Why is the step below not observed?



Consider a possible step below in the mechanism.
Why is the step below not observed?



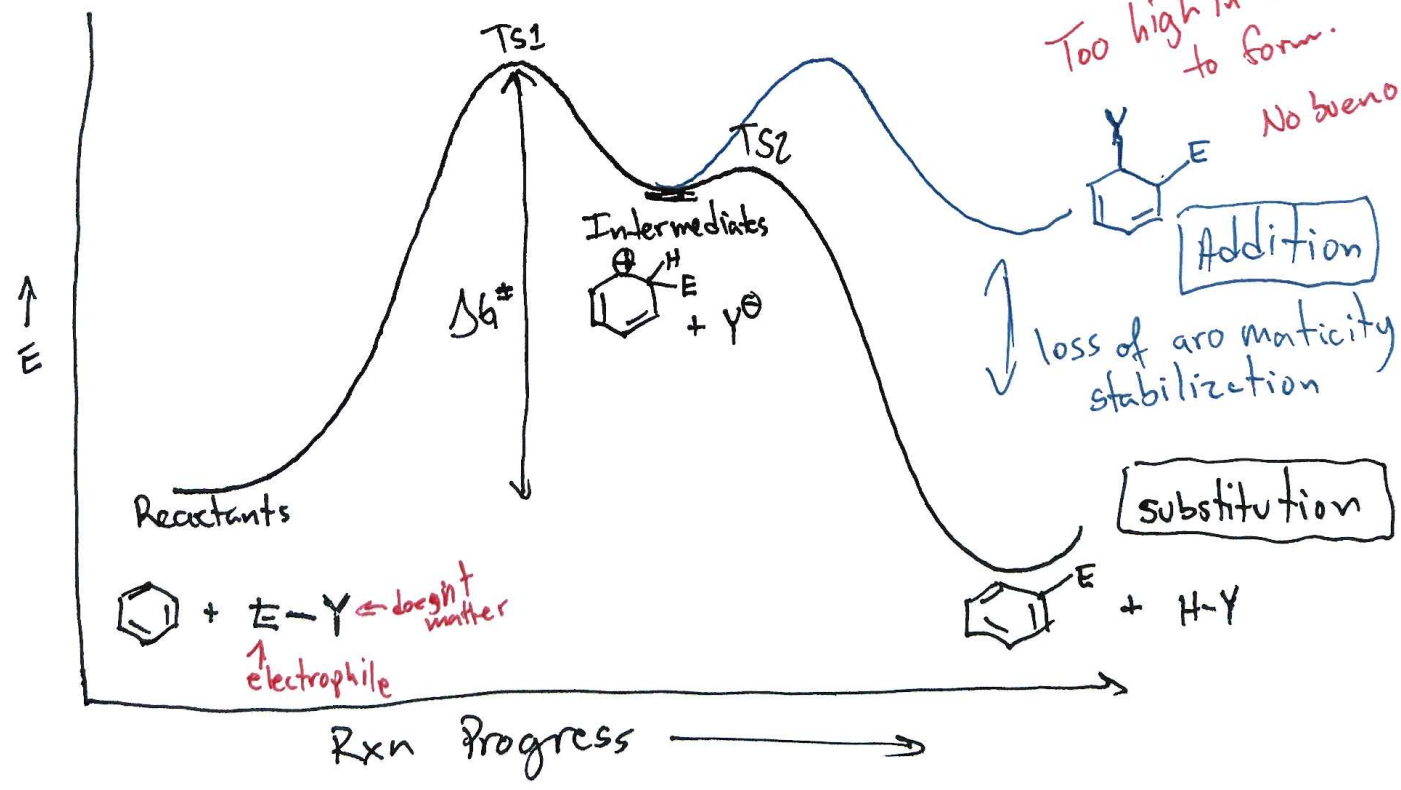
compound "X"

if this step was possible, the net reaction would be essentially Ionic Electrophilic ~~Addition~~ of Br_2.

← But this molecule is no longer aromatic.

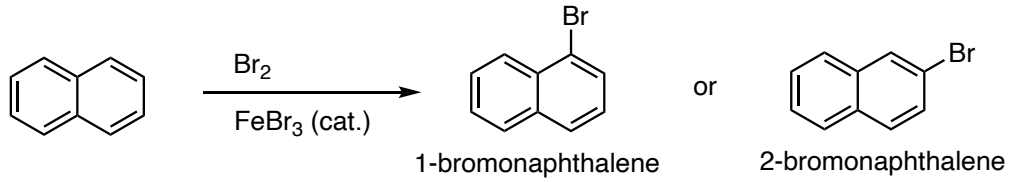
if Compound X was formed, there would be a large energetic penalty for the loss of aromaticity that benzene originally had. Such large energy penalty prevents the formation of X.

Consider the energy diagram:



Electrophilic Aromatic Substitution: Bromination of Naphthalene

The bromination of naphthalene yields one product. Considering the two possible products shown below, which compound is formed?

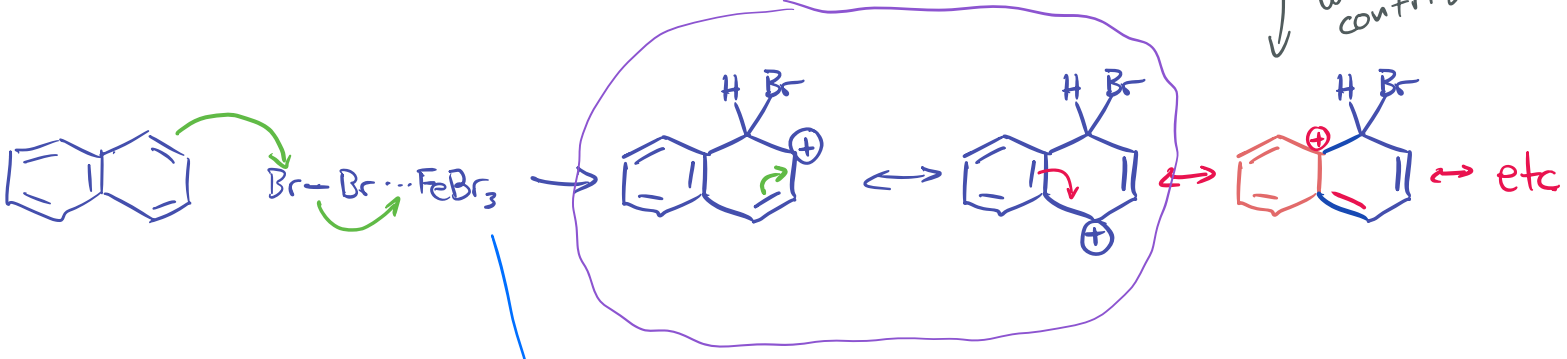


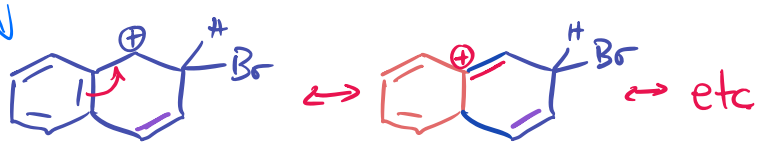
1-bromonaphthalene 2-bromonaphthalene

Hint: Draw the RLS for the generation of each isomer (wink, wink).

Forming 1-bromonaphthalene is favored since two resonance structures that do not "break" aromaticity

Breaks aromaticity "weak" resonance contributor



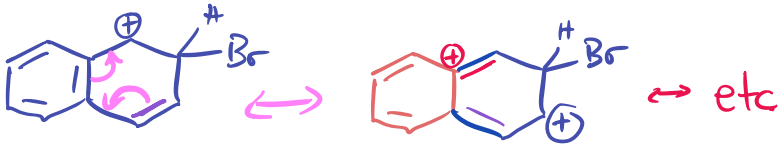


For 2-bromo....

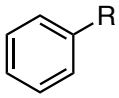
any resonance structure must break aromaticity.

Therefore, it is less favored since the carbocation shown is less stable than addition to the 1-position

or



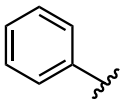
Friedel-Crafts Alkylation

Net rxn:  + R–Cl $\xrightarrow{AlCl_3}$  + HCl

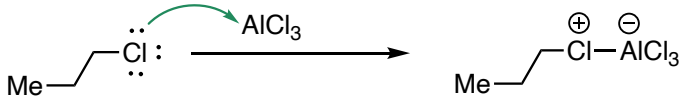
Alkyl halide Lewis Acid

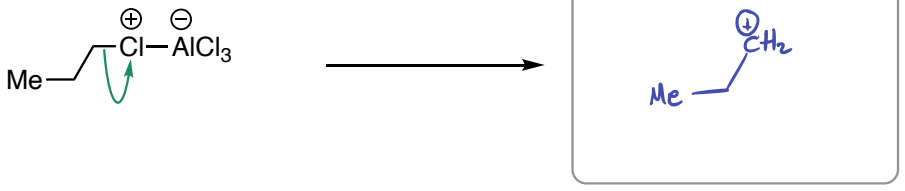
Works for: R-Cl, R-Br, R-I

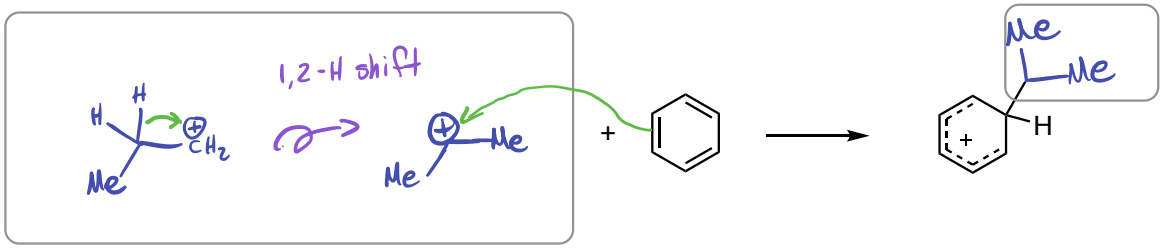
R = 3°, 2°, 1°, CH_3

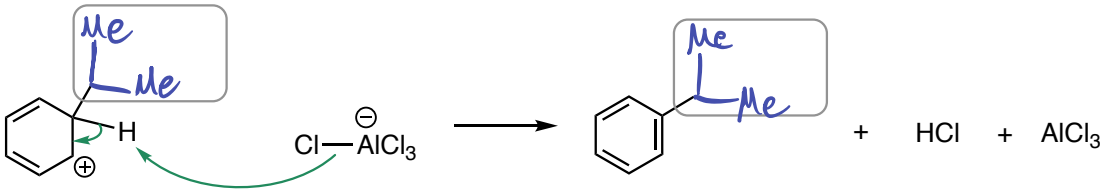
NOT  vinyl halides or aryl halides 

Mechanism:

1. 

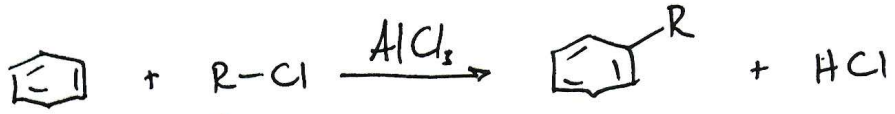
2. 

3. 

4. 

Friedel-Crafts Alkylation of Benzene

Net Rxn:



Alkyl group!

Works for: R–Cl, R–Br, R–I

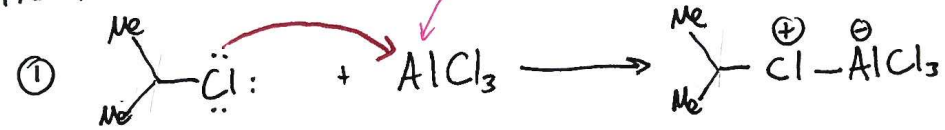
R = 3°, 2°, 1°, CH_3

Not  or 

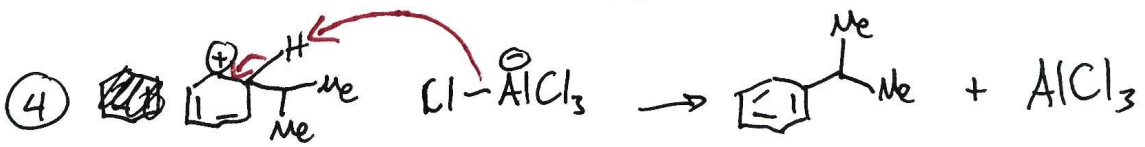
vinyllic Benzyllic

Mechanism:

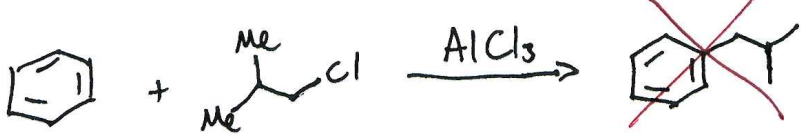
Lewis Acid



A carbocation is formed!
Rearrangements possible
!!
Strong Electrophile.

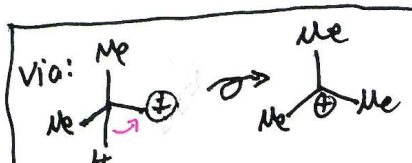


ex.



Not formed!

Via:



On your own: