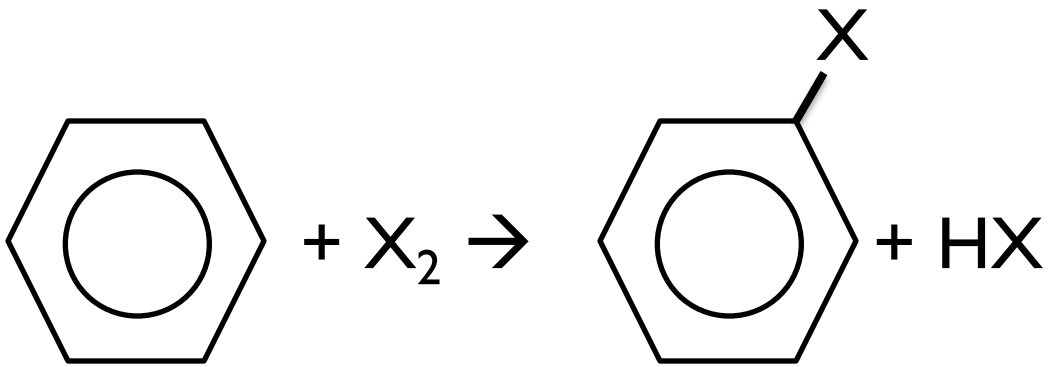
SUBSTITUTION & ELIMINATION REACTIONS

Substitution Reactions

Reactions where an atom or side-chain is replaced by a different atom or side-chain.

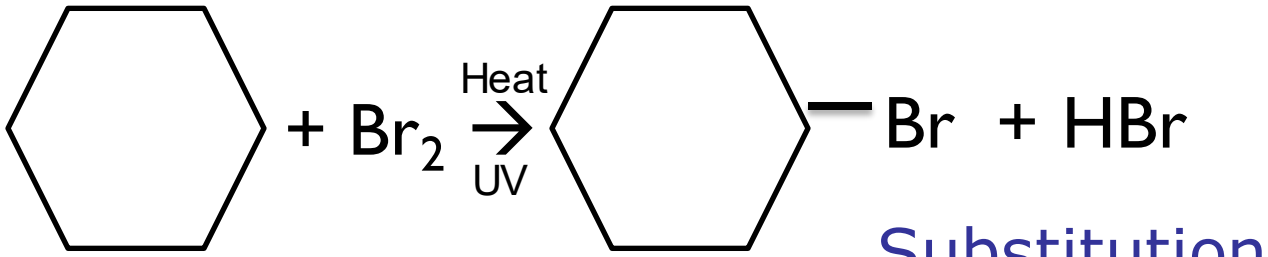
$$H_3C\text{-}X + H_2O \rightarrow CH_3OH + HX$$



SUBSTITUTION REACTIONS

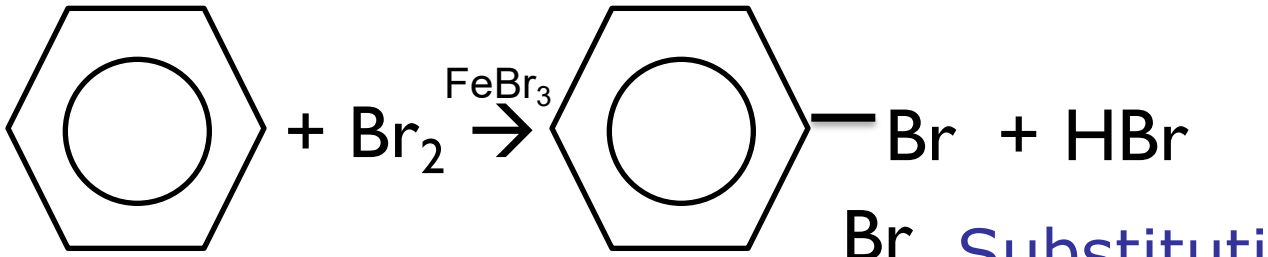
Identify the substitution reaction(s):

a)



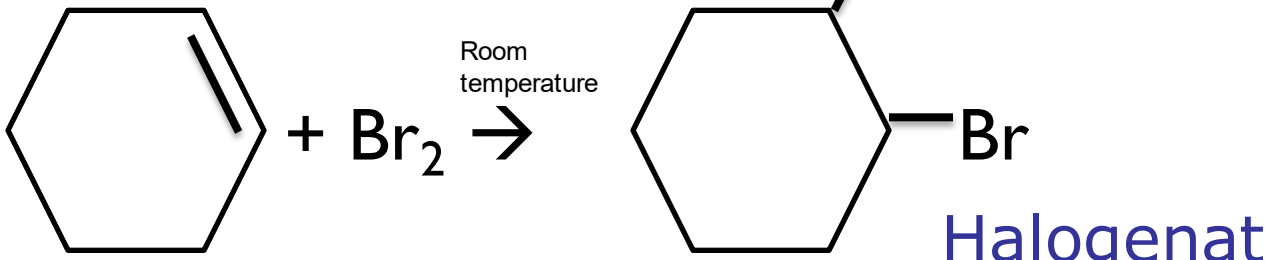
Substitution

b)



Substitution

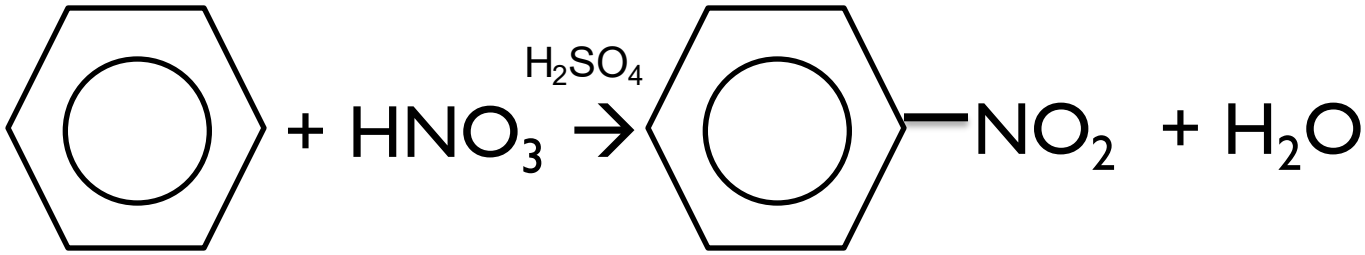
c)



Halogenation

Nitration of benzene

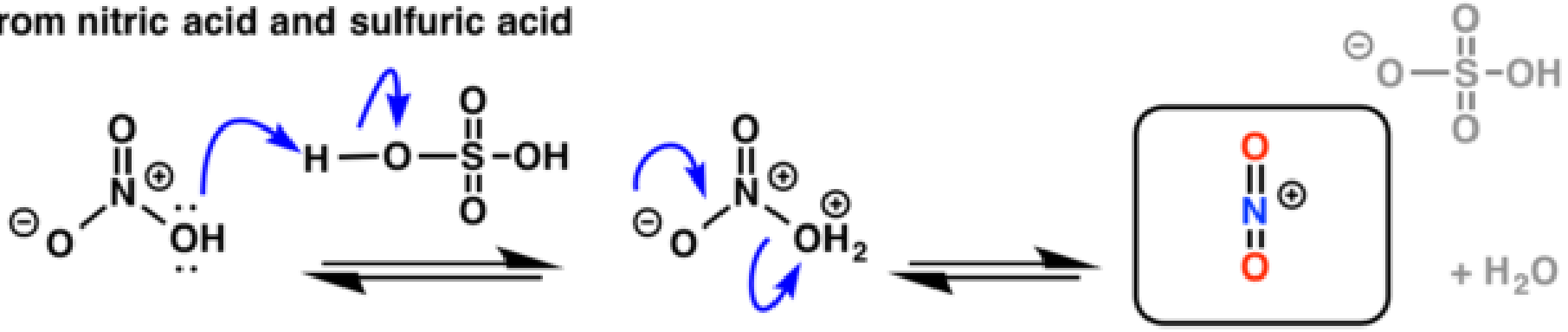
Nitric acid may react with benzene to substitute an H with a $-NO_2$ (nitro) group.



Nitration of benzene

Nitration of benzene

Step 1: Generation of the highly reactive electrophile, NO_2^+ (the nitronium ion) from nitric acid and sulfuric acid



Nitric acid, HNO_3

Sulfuric acid

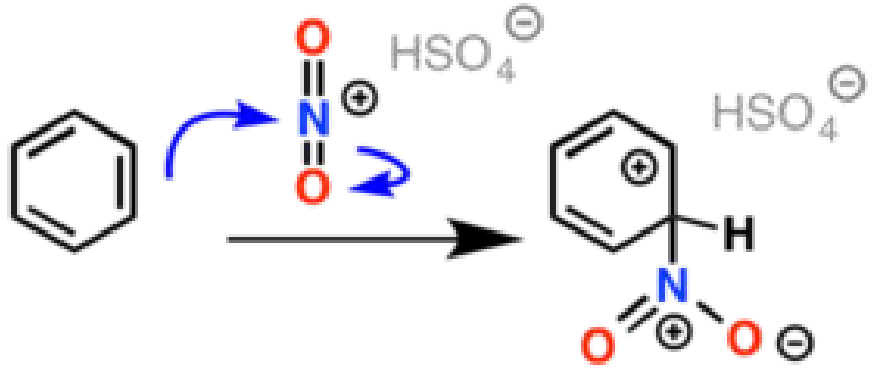
nitronium ion, NO_2^+

extremely reactive electrophile

SUBSTITUTION REACTIONS

Nitration of benzene

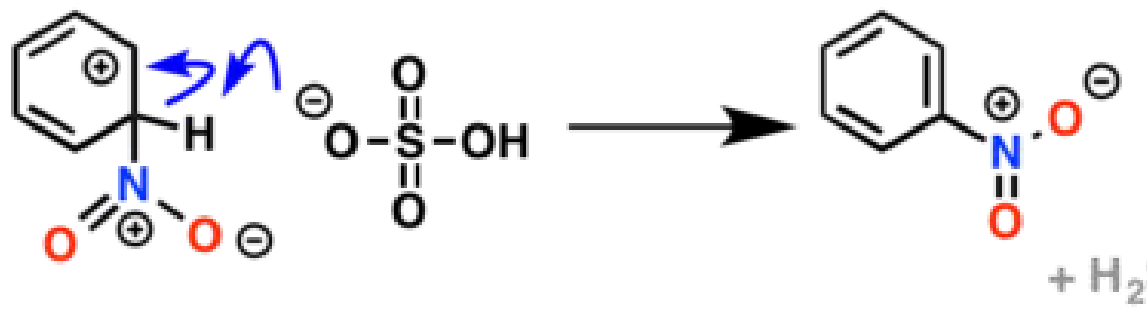
Step 2: Attack of electrophile by the aromatic ring (rate-determining step)



Bonds Formed	Bonds Broken
C–N	C–C (π)
	N–O (π)

Nitration of benzene

Step 3: Deprotonation



Bonds Formed

C–C (π)

O–H

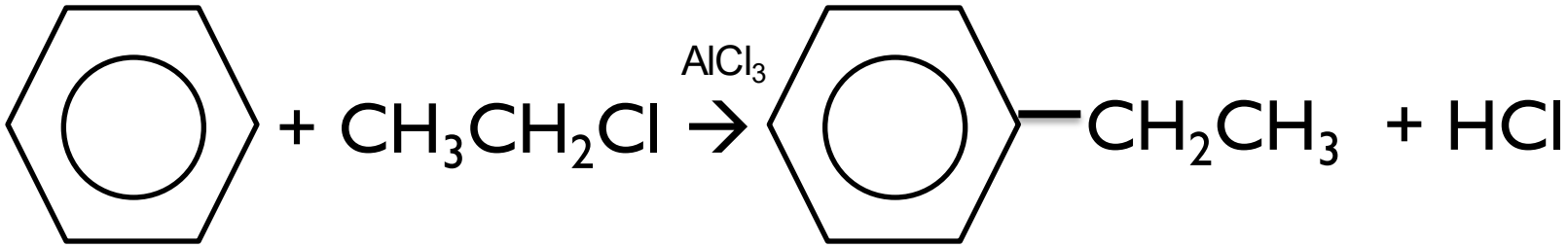
Bonds Broken

C–H

the base here can be the sulfonate ion (HSO_4^-) or water

Adding alkyl groups

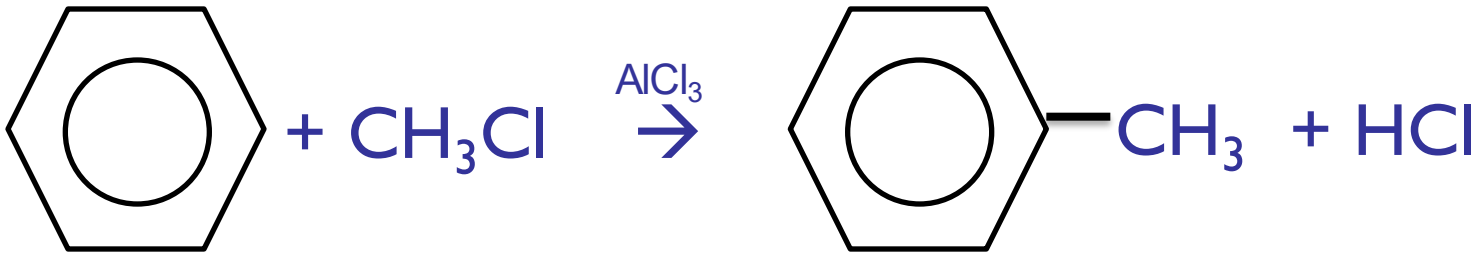
Alkyl groups may also be added to benzene groups.



SUBSTITUTION REACTIONS

Example #1

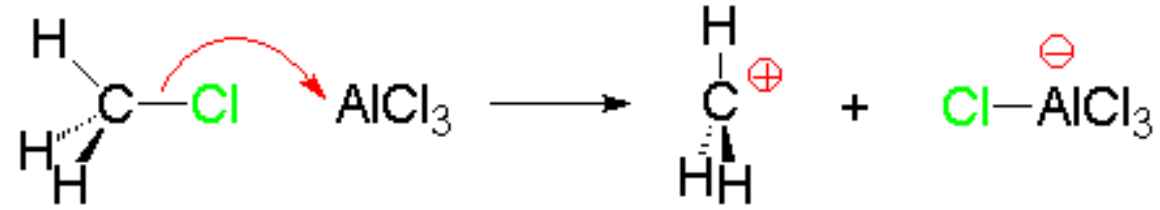
Predict the product formed when benzene reacts with chloromethane in the presence of $AlCl_3$ catalyst.

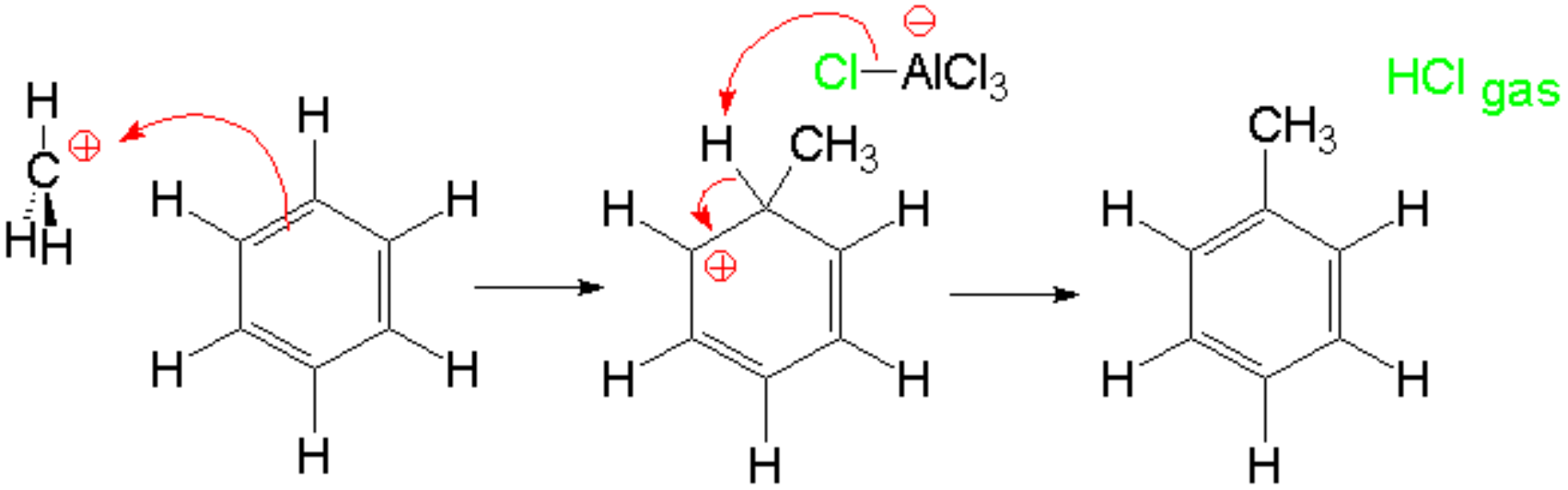


SUBSTITUTION REACTIONS

Example #1

Mechanism: benzene reacts with chloromethane in the presence of $AlCl_3$ catalyst.





Substitution Reactions

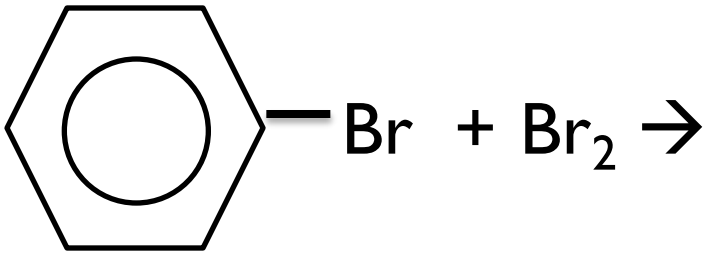
At first, only a single H group will be substituted in any reaction involving a cyclic or aromatic hydrocarbon.

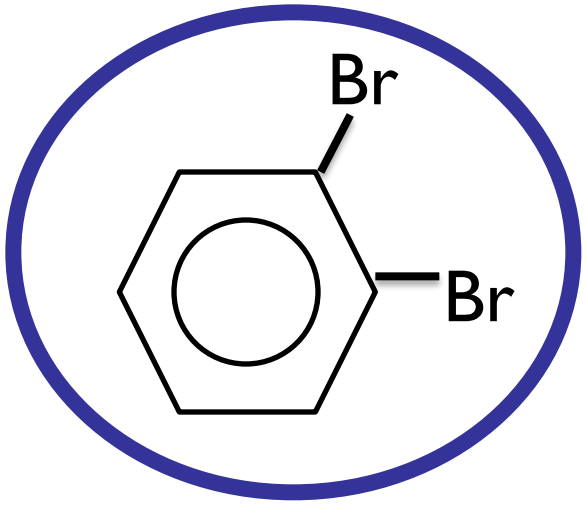
Additional substitutions on an aromatic ring will have preferences for location.

SUBSTITUTION REACTIONS

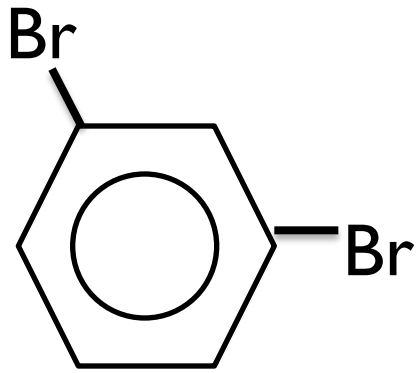
Second Aromatic Substitution

When another group is added to an aromatic ring, rules determine the preferred location of the second group.

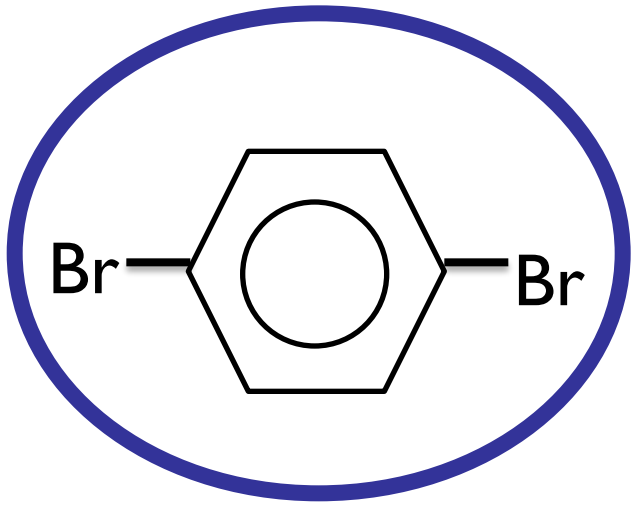




ortho



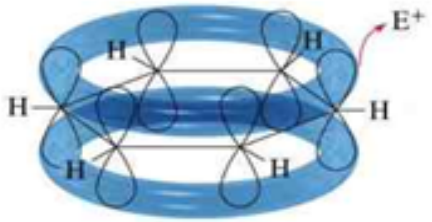
meta



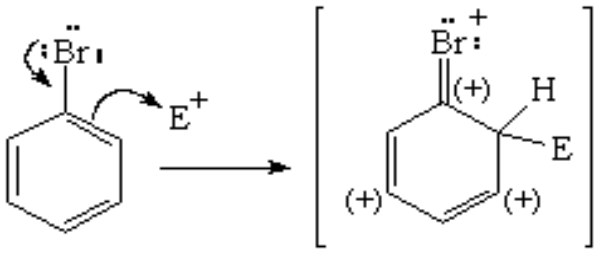
para

SUBSTITUTION REACTIONS

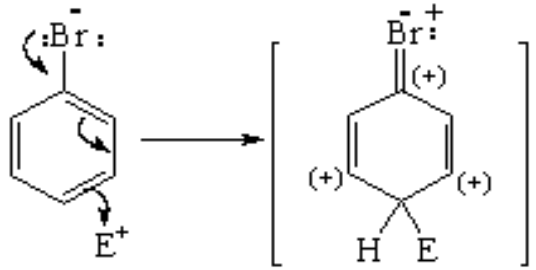
Sigma Complex for Bromobenzene



Ortho attack

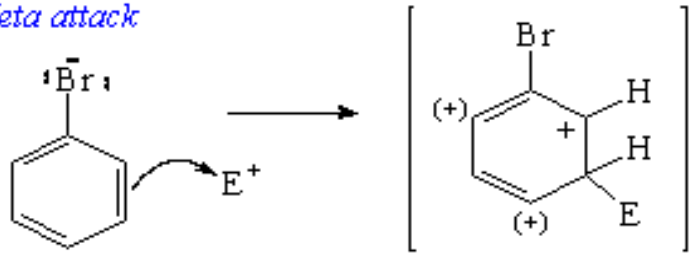


Para attack



Ortho and para attacks produce a bromonium ion and other resonance structures.

Meta attack

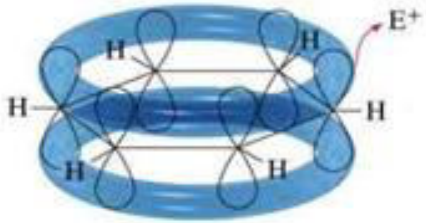


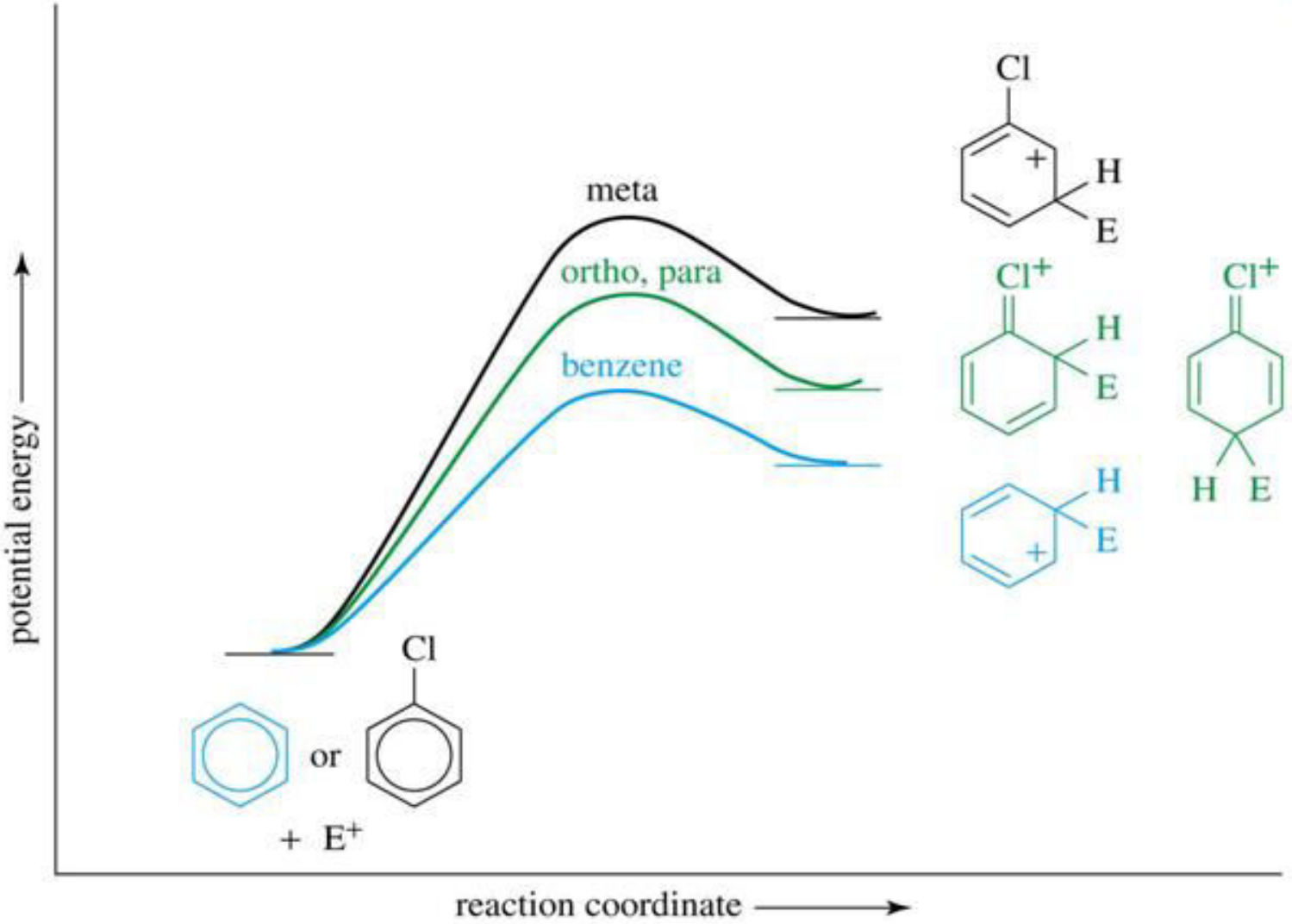
No bromonium ion possible with meta attack.

=>

SUBSTITUTION REACTIONS

Energy Diagram





SUBSTITUTION REACTIONS

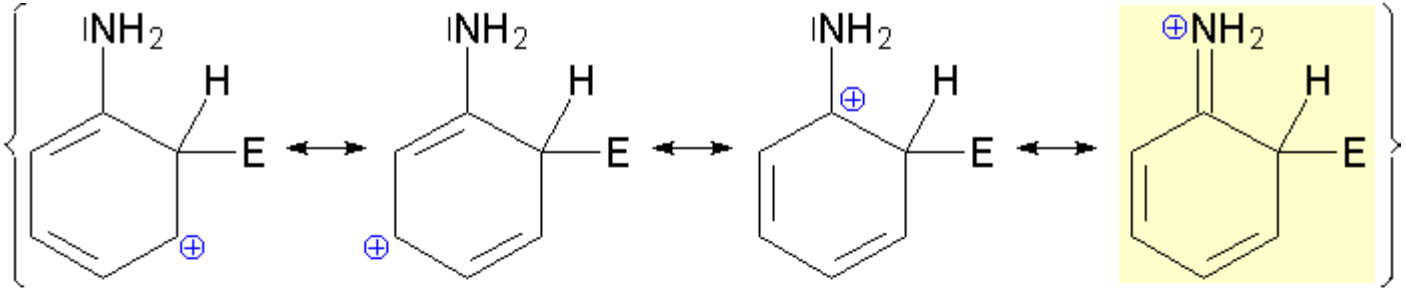
Position depends on the **substituent** involved

Y in C_6H_5–Y	Reaction	% Ortho-Product	% Meta-Product	% Para-Product
–O–CH_3	Nitration	30–40	0–2	60–70
–O–CH_3	F-C Acylation	5–10	0–5	90–95
–NO_2	Nitration	5–8	90–95	0–5
–CH_3	Nitration	55–65	1–5	35–45
–CH_3	Sulfonation	30–35	5–10	60–65
–CH_3	F-C Acylation	10–15	2–8	85–90
–Br	Nitration	35–45	0–4	55–65
–Cl	Chlorination	40–45	5–10	50–60

SUBSTITUTION REACTIONS

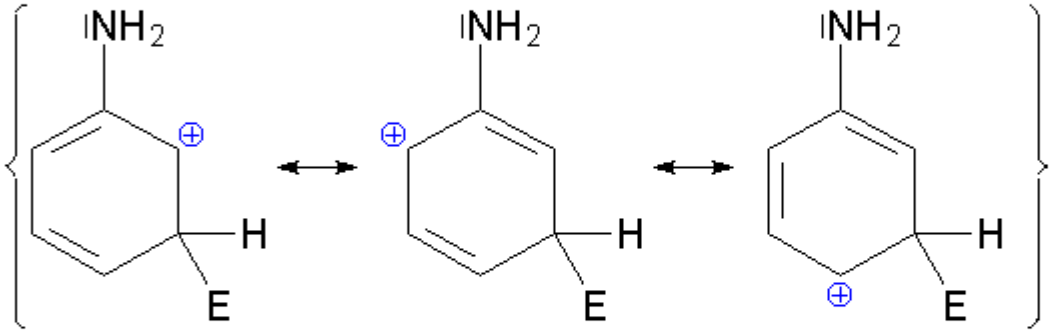
In the case of NH_2 as a substituent, **ortho** and **para** are favoured because of the stability of the reaction intermediate:

o:



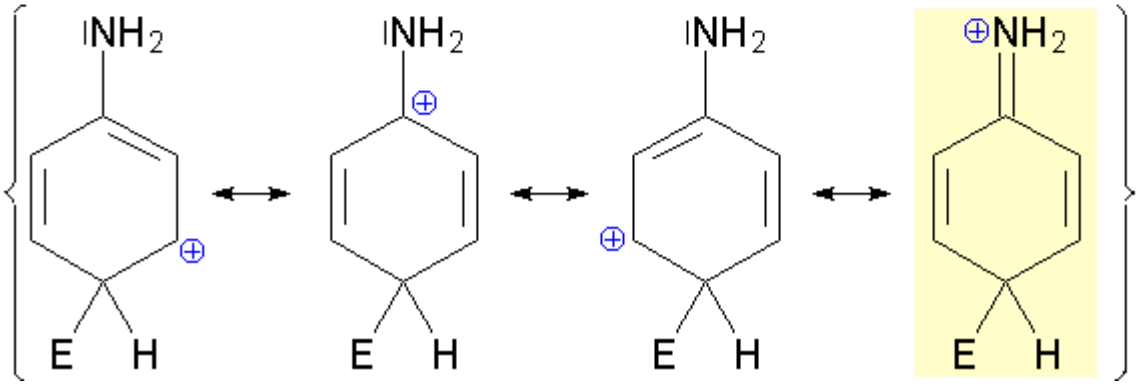
4 resonance structures

m:



3 resonance structures

p:

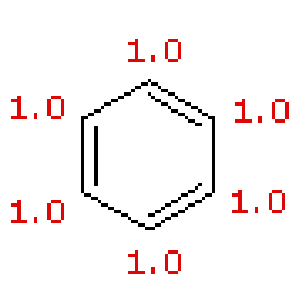


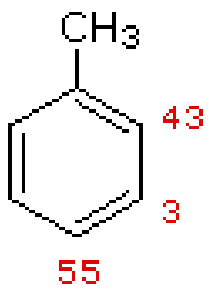
4 resonance structures

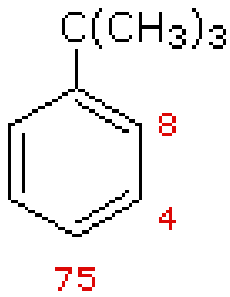
SUBSTITUTION REACTIONS

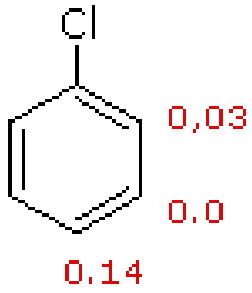
Position depends on the **substituent** involved

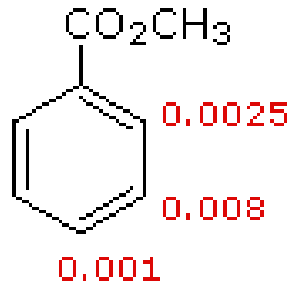
Rates of Nitration at Sites on the Benzene Ring











Total Rate	6.0	147	99	0.20	0.022
Relative Rate	1.0	24.5	16.5	0.033	0.004

The rate of substitution determines which product is favoured

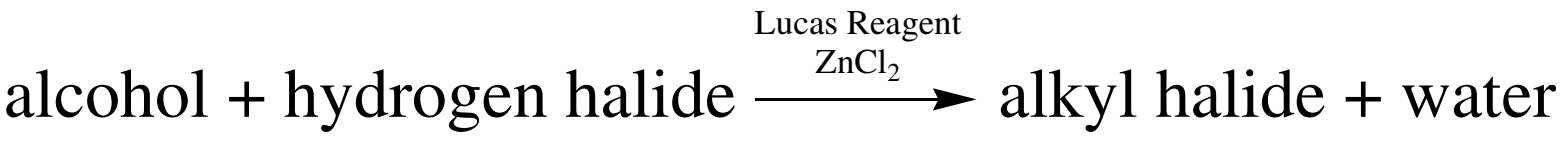
SUBSTITUTION REACTIONS

Amines are prepared by reacting alkyl halides with **NH_3**.

$$CH_3CH_2\text{-}I + NH_3 \rightarrow CH_3CH_2\text{-}NH_2 + HI$$

2° and 3° amines are produced with the addition of more alkyl halide reactants.

Substitution: Alcohols



This reaction with the Lucas Reagent ($ZnCl_2$) is a qualitative test for the different types of alcohols

The difference in rates of reaction is due to the solubility of the resulting alkyl halides:

- 3° ✹ turns cloudy immediately
- 2° ✹ turns cloudy after 5 minutes
- 1° ✹ longer than 5 minutes to turn cloudy

Substitution: Alcohols

With Sodium as a reactant

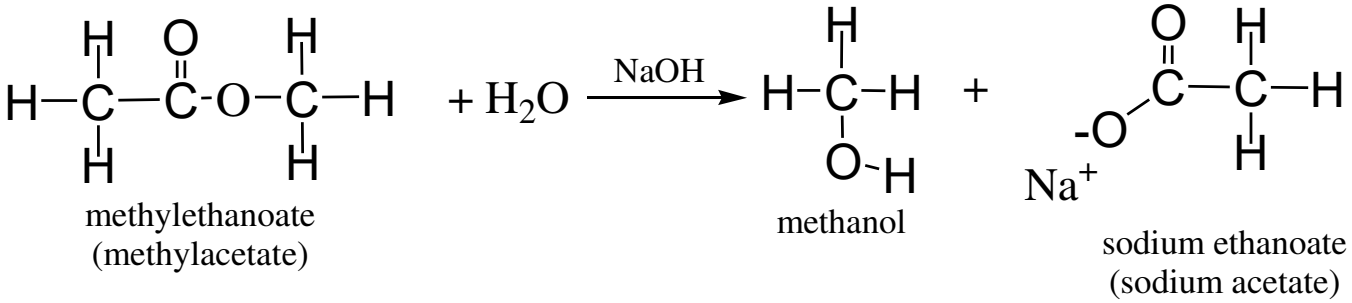
- When they react as an acid, the alkyl oxide ion ($R\text{-}CH_2O^-$) is formed:

ethanol + sodium ⟶ ethoxide ion + sodium ion + hydrogen

$$2\ CH_3CH_2OH\ +\ 2\ Na \longrightarrow 2\ CH_3CH_2O^-\ +\ 2\ Na^+\ +\ H_2$$

- This reaction also occurs to esters in a process called saponification

ester + water $\xrightarrow{\text{Basic Solution}}$ alcohol + carboxylate ion



methylethanoate (methylacetate)

methanol

sodium ethanoate (sodium acetate)

ELIMINATION REACTIONS

ELIMINATION REACTIONS

Two adjacent atoms or side groups are removed resulting in a double bond.

$$CH_3CHOHCH_3 \xrightarrow[H_2SO_4]{\text{Conc.}} CH_3CH{=}CH_2 + H_2O$$

The reverse reaction is an addition reaction.

HOMEWORK

Page 31 # 4, 6 (addition and substitution reactions)

Page 37 # 1, 2 (addition and elimination reactions)