

Lecture topics & readings

Today's class

- rxns of benzene: Ch. 14.8-15

Before next class

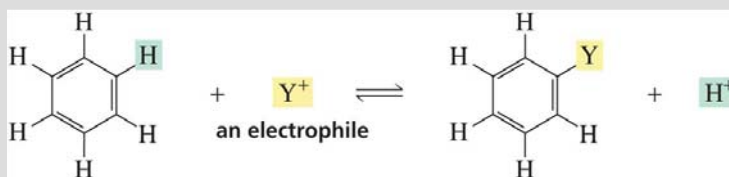
- master the basic electrophilic substitution mechanism
- learn the reagents used to functionalize benzene

Next class

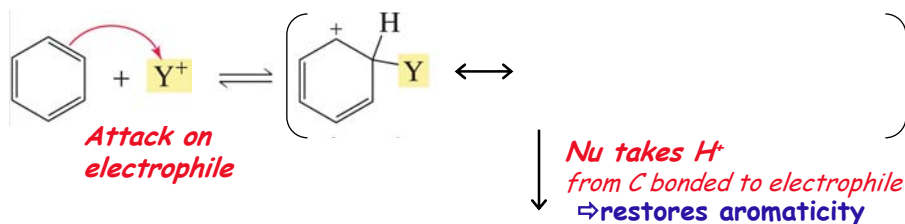
- finish rxns of benzene (Ch. 14)
- start rxns of substituted benzenes (Ch.15)

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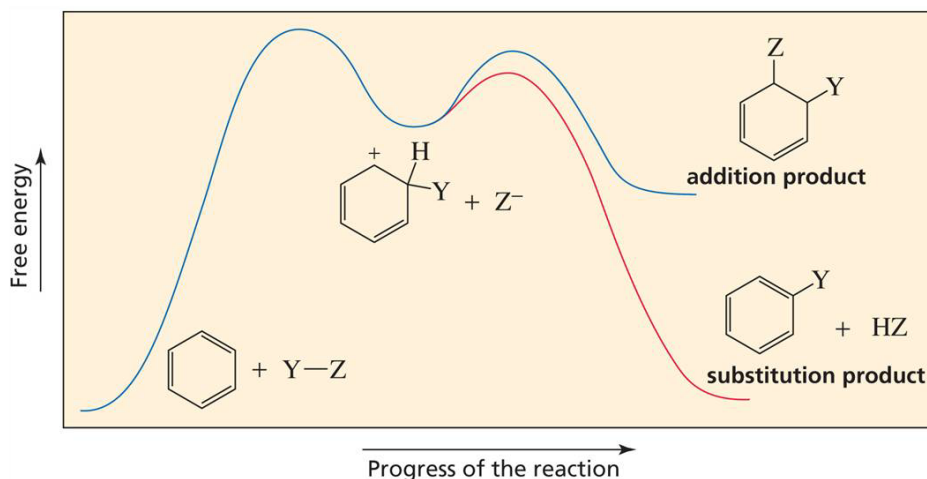
14.9 How benzene reacts: electrophilic aromatic substitution

Electron-rich
 π -system...reactive towards
strong E^+ s
(electrophiles)*Mechanism:*

benzene cation = a "sigma complex"

*If Nu adds to C^+ ...*(2) \Rightarrow aromaticity broken

The pathway yielding the aromatic product is favoured...

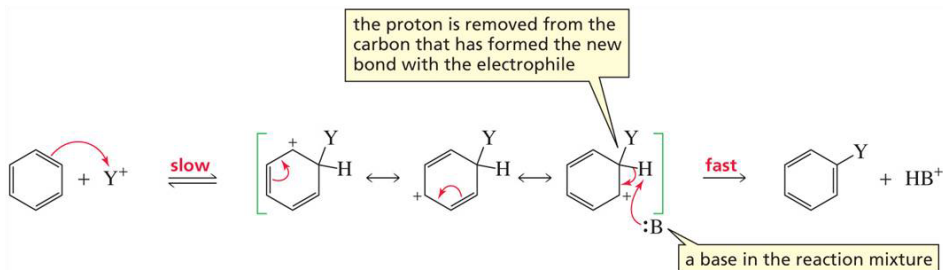


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14.10 Electrophilic aromatic substitution (S_E , not $S_N1/2$)

All follow same 2-step mechanism:

1. π -system attacks E^+ \Rightarrow σ -complex (resonance-stabilized C^+)
2. deprotonation \Rightarrow H^+ removed from $C-E^+$ \Rightarrow restores aromaticity



Common electrophilic subst'ns: replace H with...

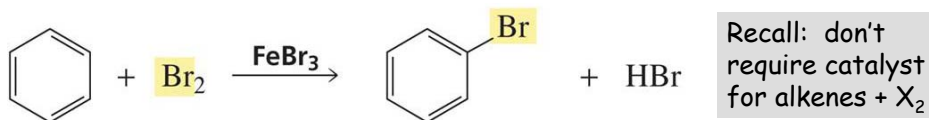
- | | |
|------------------------------|-------------|
| 1. Halogenation | Cl, Br or I |
| 2. Nitration | NO_2 |
| 3. Sulfonation | SO_3H |
| 4. Friedel-Crafts acylation | $RC=O$ |
| 5. Friedel-Crafts alkylation | R |

Reagents needed:

- | | |
|------------|-------------|
| Cl_2 | & $FeCl_3$ |
| HNO_3 | & H_2SO_4 |
| H_2SO_4 | & Δ |
| $RC(=O)Cl$ | & $AlCl_3$ |
| RCl | & $AlCl_3$ |

Benzene's stable π -system only reacts with REALLY STRONG E^+ s...

14.11 Halogenation of benzene: requires a Lewis acid catalyst



Attacking the Lewis acid activates Br₂...



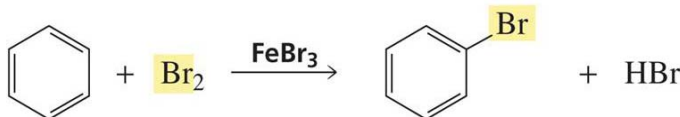
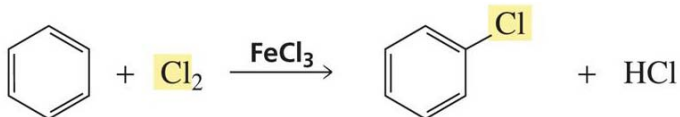
Mechanism of bromination using Br₂-FeBr₃ as E⁺:

Catalyst is regenerated:

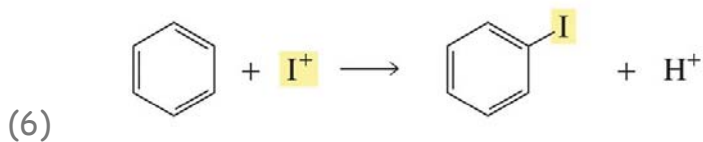
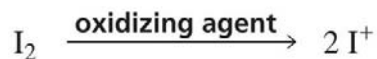


Halogenation of benzene: To make a sufficiently strong E⁺...

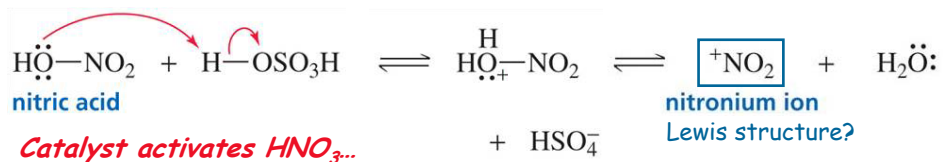
Use a Lewis acid catalyst to activate the halogen:



For iodination: use an oxidant instead (such as HNO₃)



14.12 Nitration of benzene: uses sulfuric acid as a catalyst



Mechanism of nitration: using $^+\text{NO}_2$ as E^+ ...

Catalyst is regenerated:

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Do this one on your own at home: direct analogy to nitration

14.13 Sulfonation of benzene: sulfuric acid = E^+ & catalyst

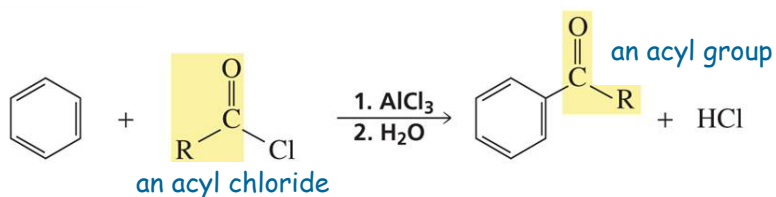


Mechanism of sulfonation: using $^+\text{SO}_3\text{H}$ as E^+ ...

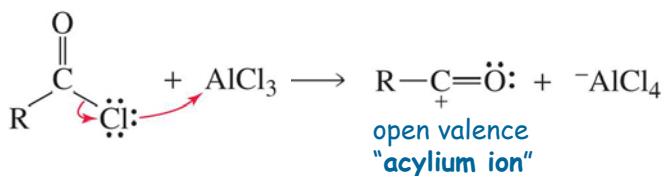
Catalyst is regenerated:

Note: Heat is required to drive the sulfonation reaction forward.

14.14 Friedel-Crafts acylation: uses AlCl_3 (not truly a catalyst here)



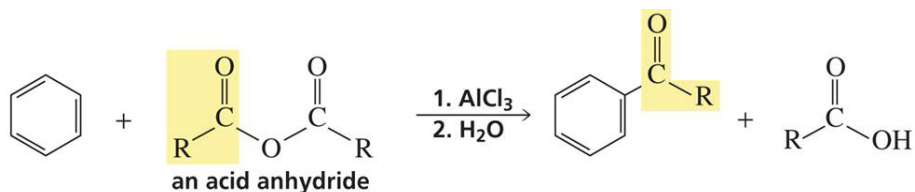
AlCl_3 activates acyl chloride: Al open valence... \Rightarrow strong E^+



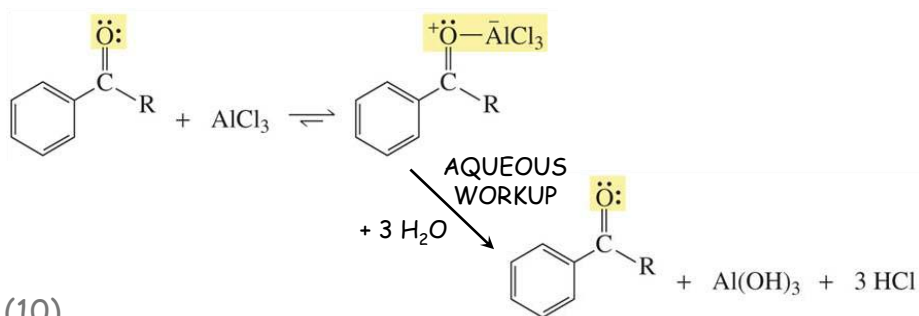
Mechanism of acylation: using $\text{RC}^+(\text{=O})$ as E^+ ...

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Friedel-Crafts acylation: can also use anhydrides as SM



Note: excess AlCl_3 is needed for all Friedel-Crafts acylations
WHY: carbonyl groups coordinate $\text{AlCl}_3 \Rightarrow$ prevents it from reacting



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14.15 Friedel-Crafts alkylation: also uses AlCl_3



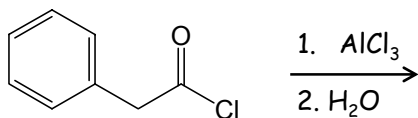
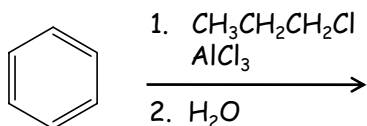
AlCl_3 activates alkyl chloride: to form "normal" carbocation which may rearrange...

On your own: Mechanism of acylation: using RC^+ as E^+ ...

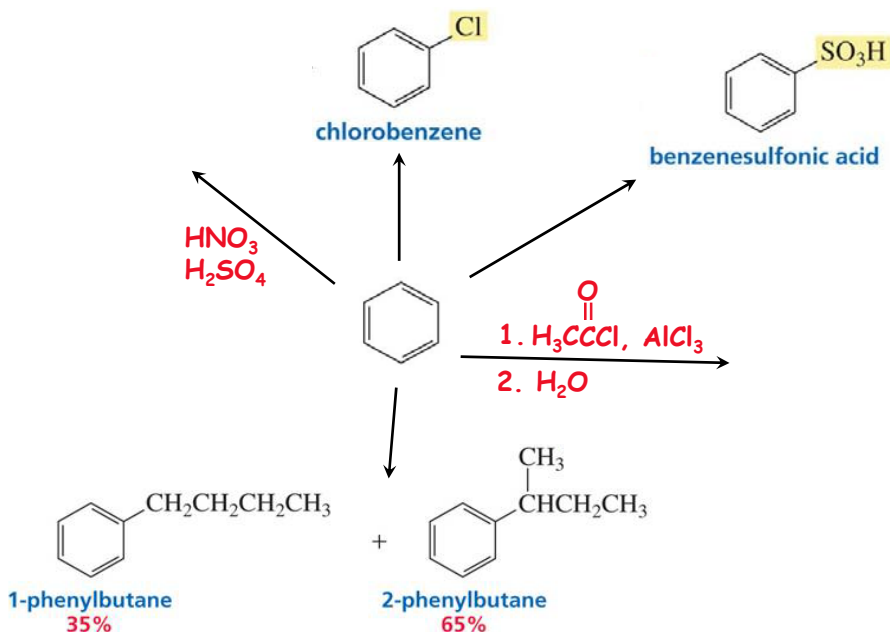
Important notes about Friedel-Crafts alkylation:

1. Low yield for attaching 1° alkyl groups: since 1°C^+ will rearrange
2. Alkylated Ph more reactive than benzene: must use excess benzene to avoid over-alkylation

What Friedel-Crafts product would we expect? (see Prob.26 & 37)

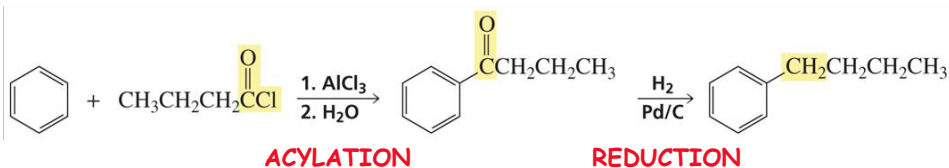


Identify the missing reagents & catalysts *OR* products...



14.16 Alkylation of benzene by acylation-reduction (skip 14.17)

- particularly useful for adding linear alkyl groups: no alkyl C^+ involved
- doesn't require huge excess of benzene: acyl-Ph less reactive than PhH



REDUCTION = conversion to lower oxidation state (reverse of oxidation)

HOW TO REDUCE CARBONYL GROUPS:

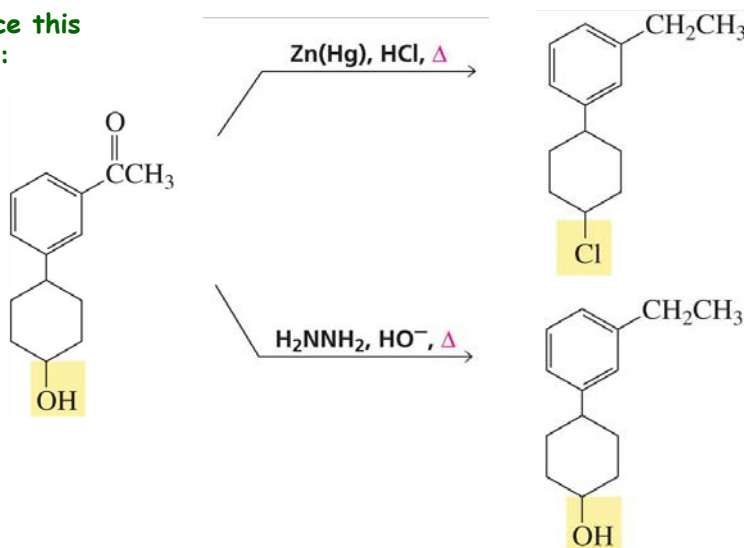
- Catalytic hydrogenation: H_2 , Pd/C (only for C=O groups on Ph ring)
- Clemmensen reduction: Zn-Hg amalgam, HCl, Δ (if tolerate acid)
- Wolff-Kishner reduction: H_2NNH_2 , HO^- , Δ (if tolerate base)

See 17.8 for mechanism

Remember: it is important to have more than 1 way to do a rxn...

14.17 Knowing >1 way to do a rxn is important for synthesis

To reduce this carbonyl:



Functional group compatibility: choose conditions carefully so other parts of your molecule will not undergo undesired rxns...