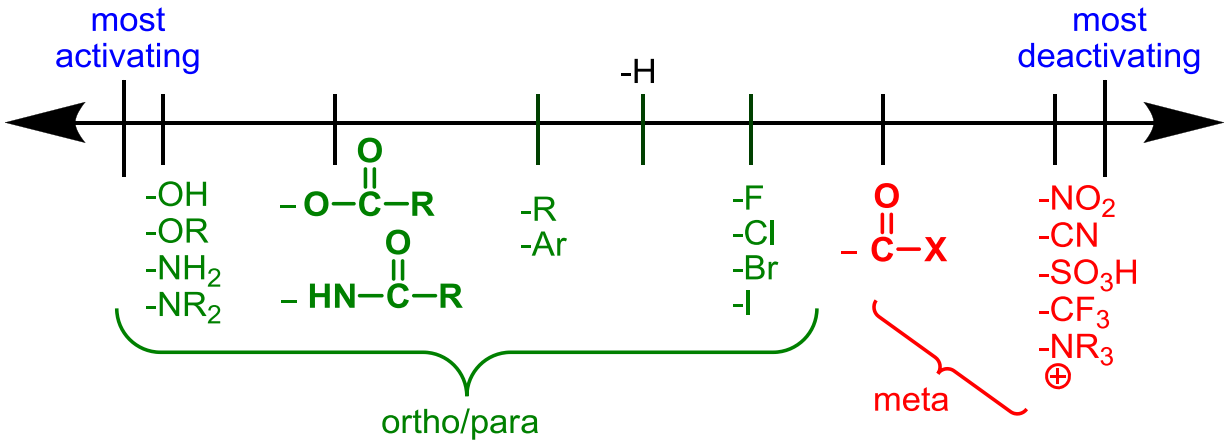
CHEM 242 – Lecture 19 28/02/2014

Overheads: - Outline

Quiz #3

Recap Wednesday: Directing Effects

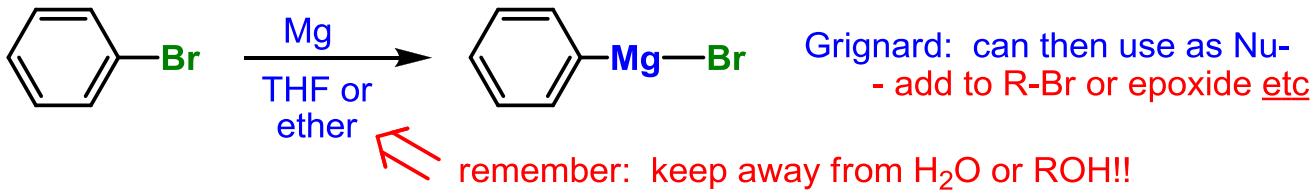


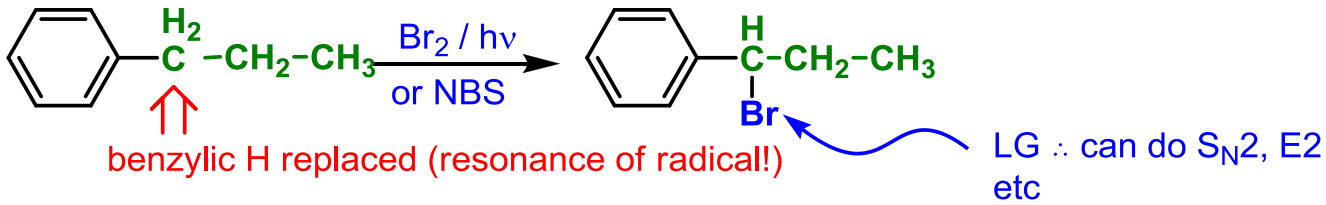
careful:

Reactions of Substituents on Benzene

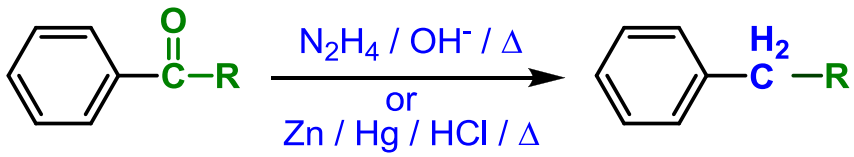
- how to add more than the "5 Electrophiles"

Some we already know:

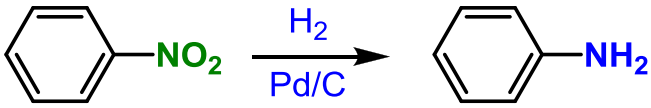




Reduction of C=O

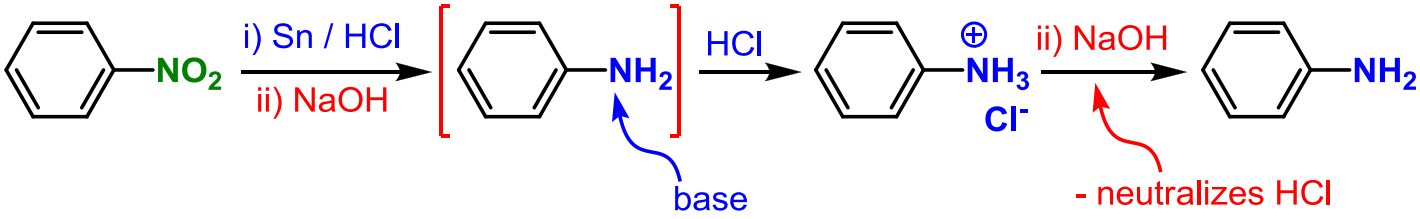


Reduction of NO_2 ($ArNO_2$ ⟶ $ArNH_2$) - 2 ways

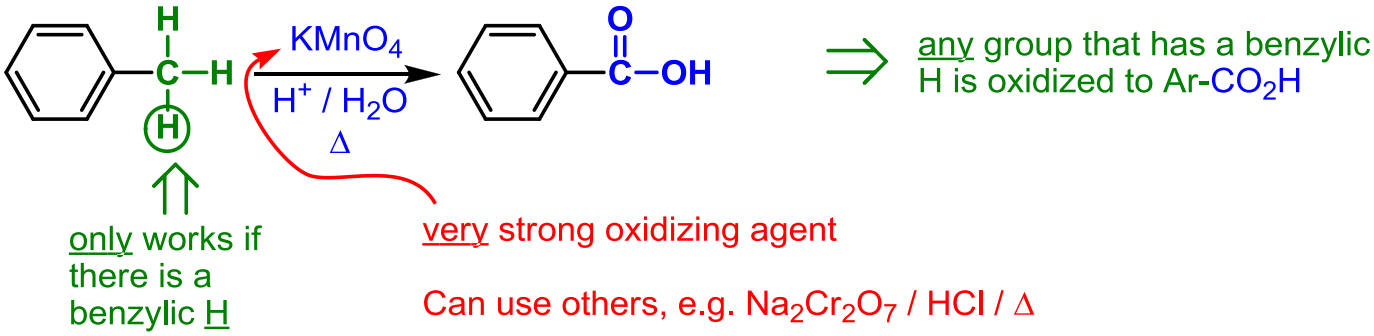


- similar to adding H_2 to C=C, but breaks N-O bonds

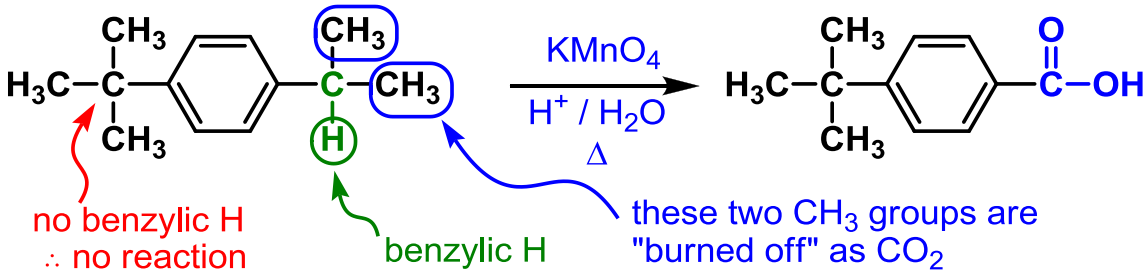
or



Oxidation of Alkyl Groups (⟶ more C-O bonds)

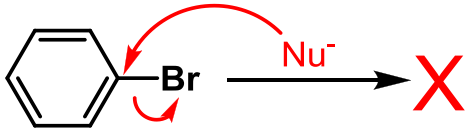


⇒ any group that has a benzylic H is oxidized to Ar-CO_2H



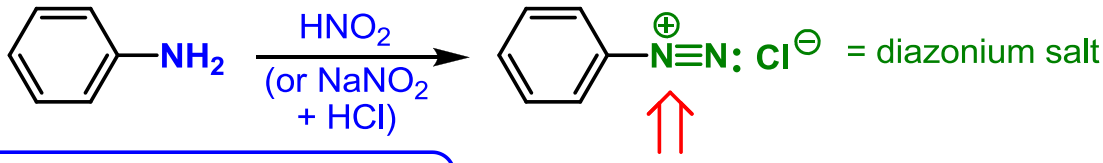
⇒ Formation of Diazonium Salts $R-\overset{\oplus}{N}\equiv N:\ Cl^{\ominus}$

Recall: normally can't do S_N1 or S_N2 on sp^2 C:



- can't do backside attack (no S_N2)
- C^+ very unstable (no S_N1)

But:

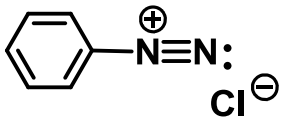


mechanism in Ch. 19.23 / 16.12
- don't need to know

e.g. $CH_3-NH_2 \xrightarrow[HCl]{NaNO_2} CH_3-\overset{\oplus}{N}\equiv N:\ Cl^{\ominus} \rightleftharpoons \boxed{CH_3^{\oplus}} + N_2\ (g)$

- very stable
- gas (∴ gone)

⇒ Can use Ar-N_2^+ to make many other groups:



- Cu^+Cl^- → Cl
- Cu^+Br^- → Br

} alternate way

- KI → I
- HBF_4 (~ H^+ F^- BF_3) → F

} recall: can't add these directly

- CuCN → CN
- H_3O^+, Δ → OH (phenol)
- H_3PO_2 → H ⇒ used to remove NO_2 or NH_2 group that's no longer needed

$H_3PO_2 + 2\ H_2O \longrightarrow H_3PO_4 + 4\ \boxed{H^-}$ ⇐ = Nu^-

Strategy: Ar-NO_2 → Ar-NH_2 → Ar-N_2^+ → Ar-X or Ar-H

- Ar-NO_2: use as meta-director
- Ar-NH_2: use as o/p-director
- Ar-X or Ar-H: replace or remove