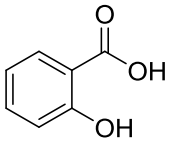
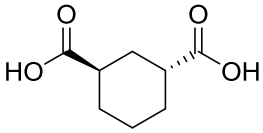
Nomenclature

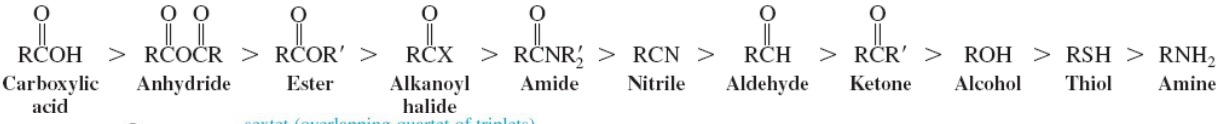


o-hydroxybenzoic acid or 2-hydroxybenzoic acid

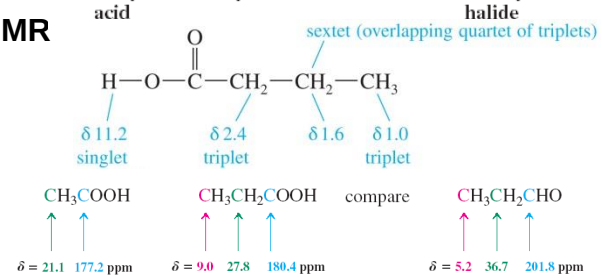


trans-1,3-cyclohexanedicarboxylic acid

Order of Precedence of Functional Groups



NMR



The H and C are deshielded.
Hydroxyl H very low field (δ = 10-13 ppm).

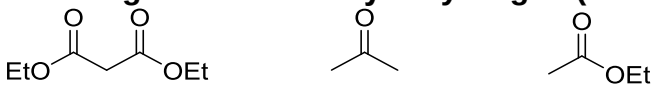
^{13}C NMR of CAs similar to aldehydes and ketones.

Acidity

Lower pK_a due to the electron-withdrawing effect of the positive carbonyl carbon and resonance
Electron-withdrawing substituents increase acidity.
- Due to inductive effect
- 3 EWG on α-carbon can result in pK_a near strong acids

Rank the following in increasing order of acidity α-hydrogen (lowest < highest).

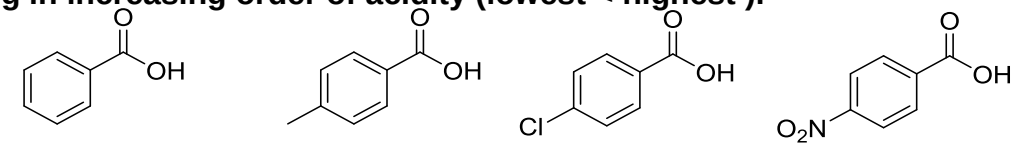
II < III < I



I **II** **III**

Rank the following in increasing order of acidity (lowest < highest).

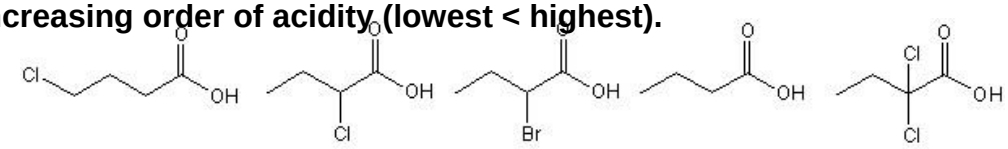
II < I < III < IV



I **II** **III** **IV**

Rank the following in increasing order of acidity (lowest < highest).

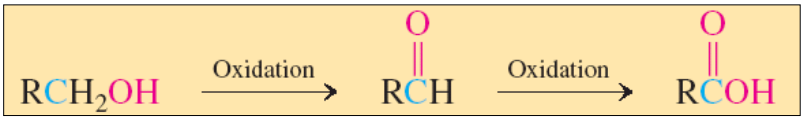
4 < 1 < 3 < 2 < 5

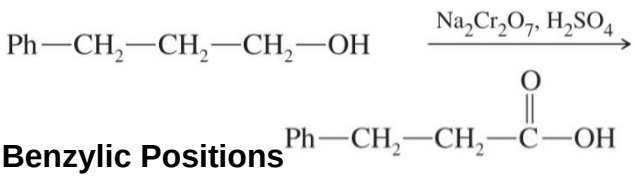


1 2 3 4 5

Introducing the Carboxy Group

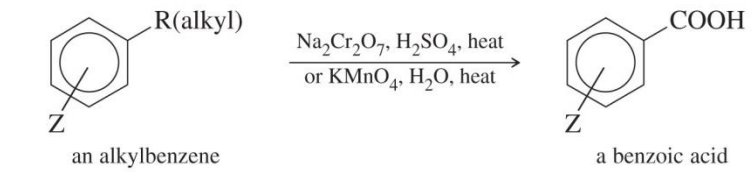
Primary alcohols → aldehydes → carboxylic acids.

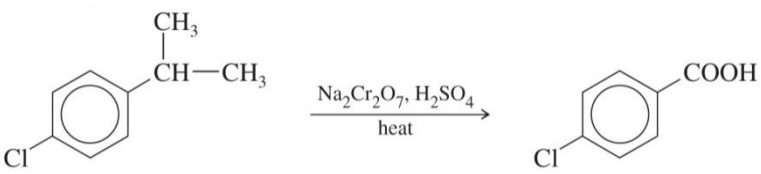




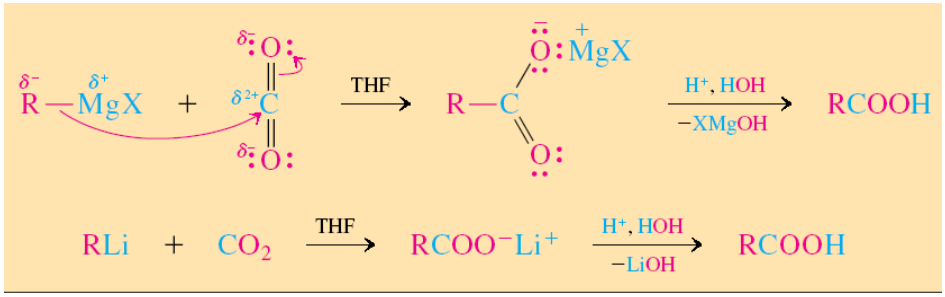
$Na_2Cr_2O_7$ (Jones), $KMnO_4$ and HNO_3.**Benzylic Positions**

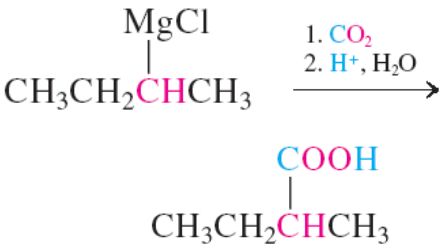
Replaces C-H bond with COOH



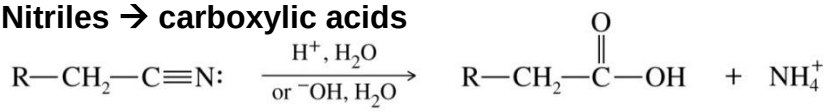


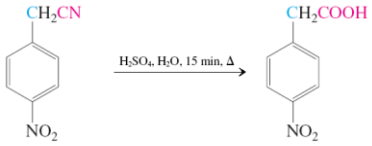
Organometallic reagents + CO_2 → carboxylic acids.





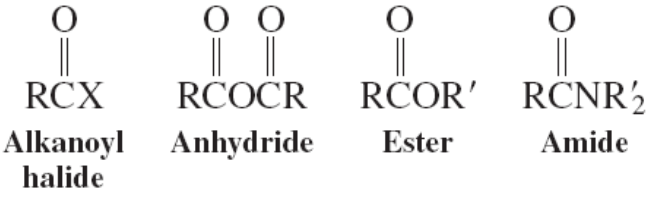
Nitriles → carboxylic acids

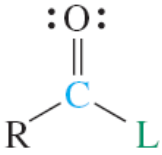




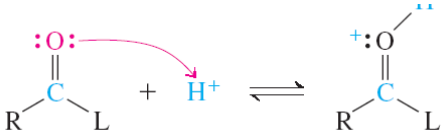
Preferable to Grignard if other functional groups compete with Grignard reagent (hydroxy or carbonyl)

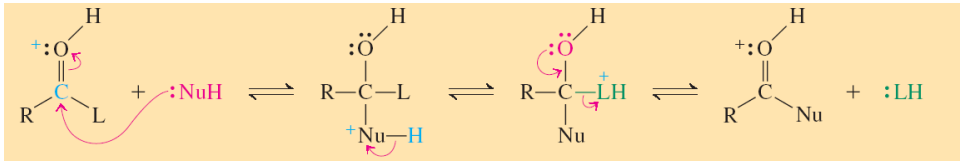
Substitution: Addition-Elimination
The carbonyl carbon is attacked by nucleophiles.



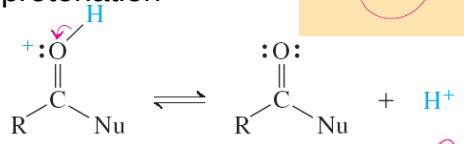


Acid mechanism
Step 1: Protonation
Step 2: Addition-elimination

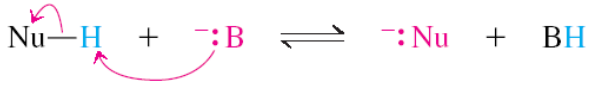




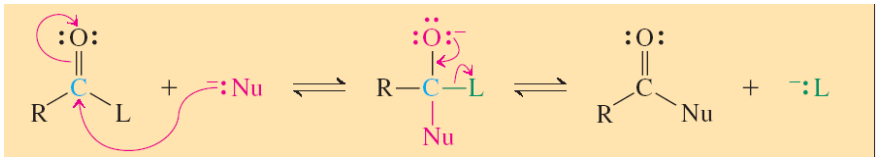
Step 3: Deprotonation



Base mechanism
Step 1: Deprotonation

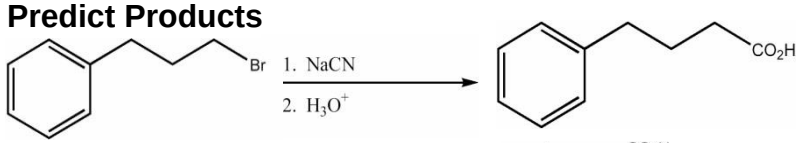


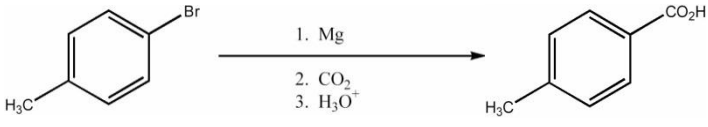
Step 2: Addition-elimination

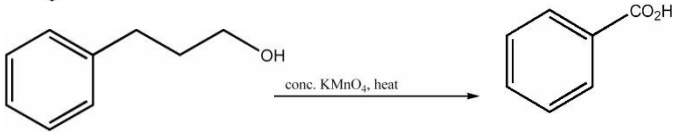


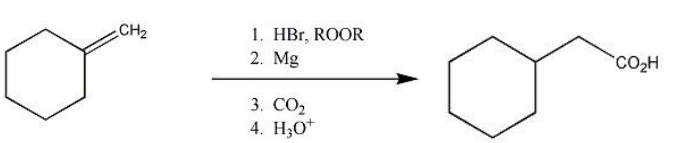
Step 3: Regeneration of Base.

Predict Products









Synthesis

1. BH_3·THF
2. H_2O_2, NaOH
3. $KMnO_4$, H_2O, Δ
4. H_3O+