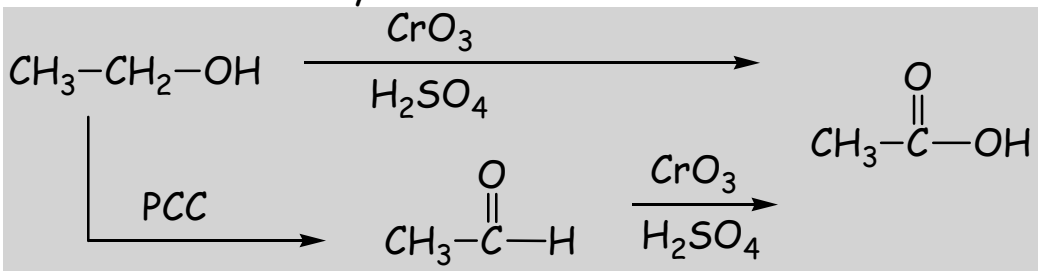
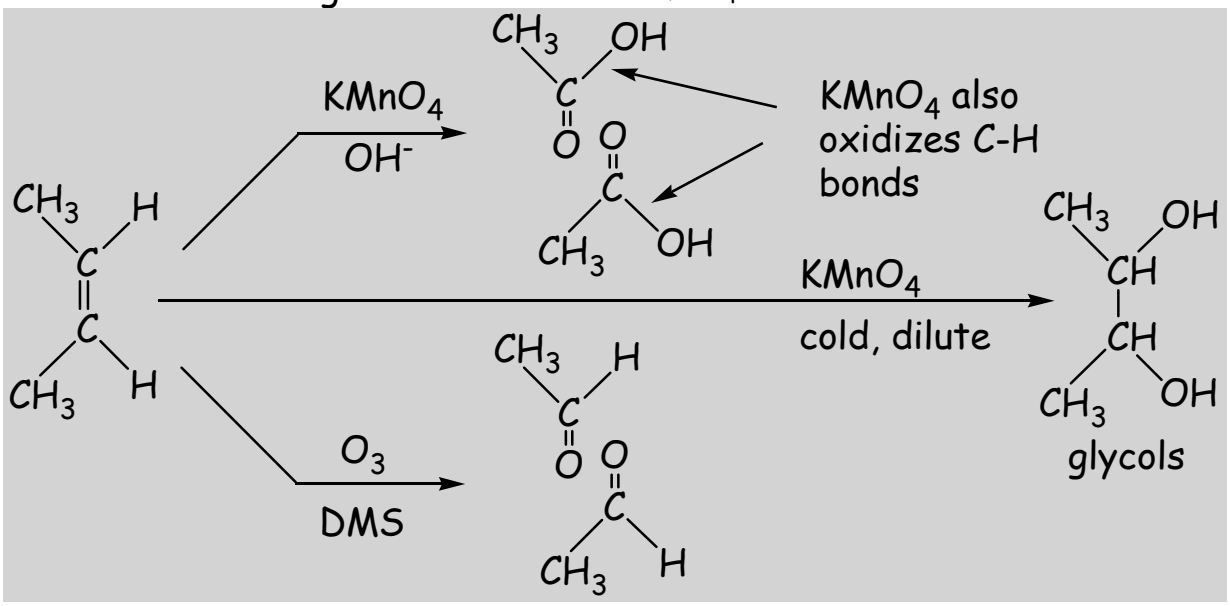
Synthesis of Carboxylic Acids:

1. Oxidation of aldehydes and alcohols (review)
2. Oxidative cleavage with ozone or $KMnO_4$ (review)
3. Benzylic oxidation of alkylbenzenes (review)
4. Carboxylation of Grignard reagents
5. Hydrolysis of cyanohydrins and nitriles

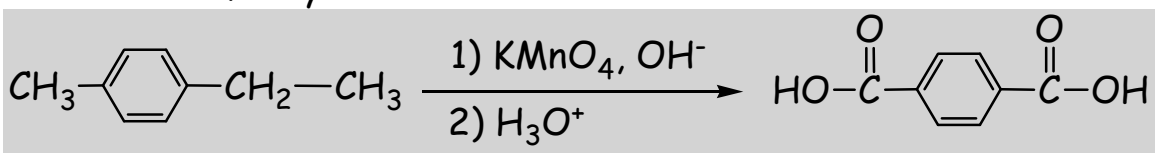
1. Oxidation of aldehydes and 1° alcohols



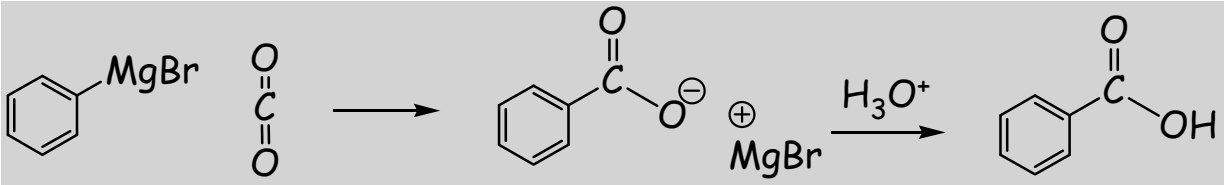
2. Oxidative cleavage with ozone or $KMnO_4$



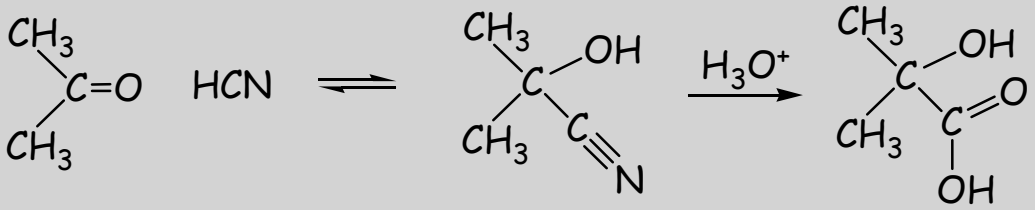
3. Oxidation of alkylbenzenes

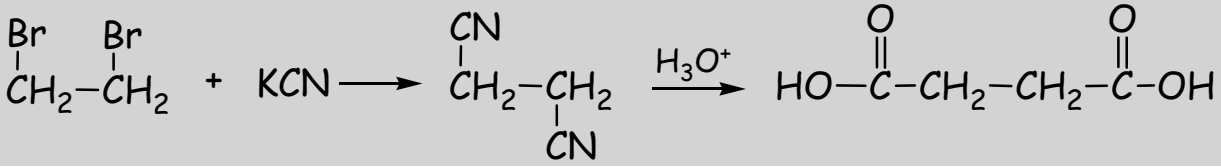


4. Carboxylation of Grignard reagents

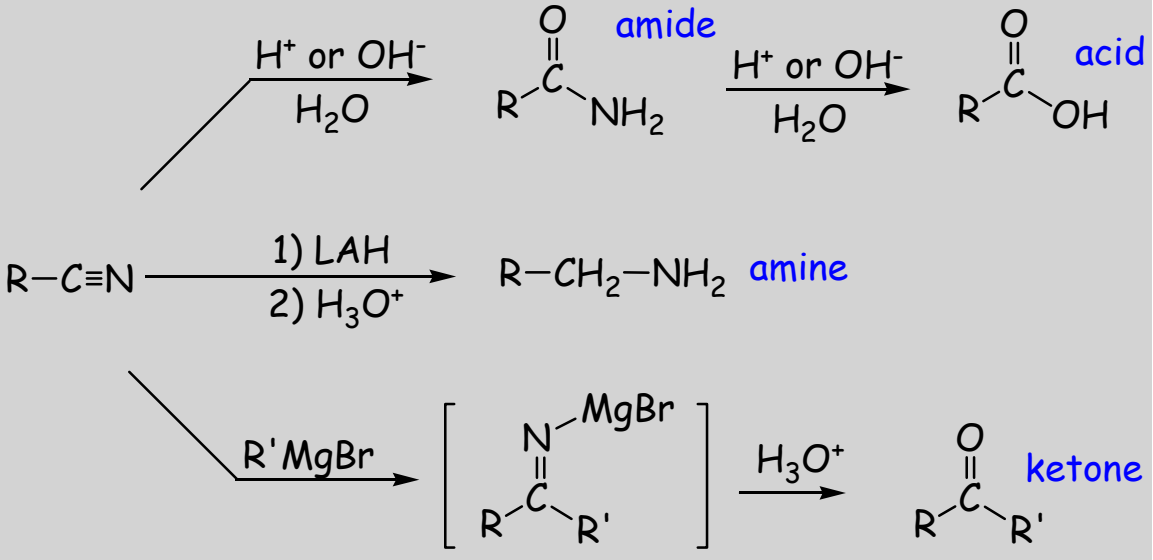


5. Hydrolysis of cyanohydrins and nitriles





Sidebar for cyano groups …



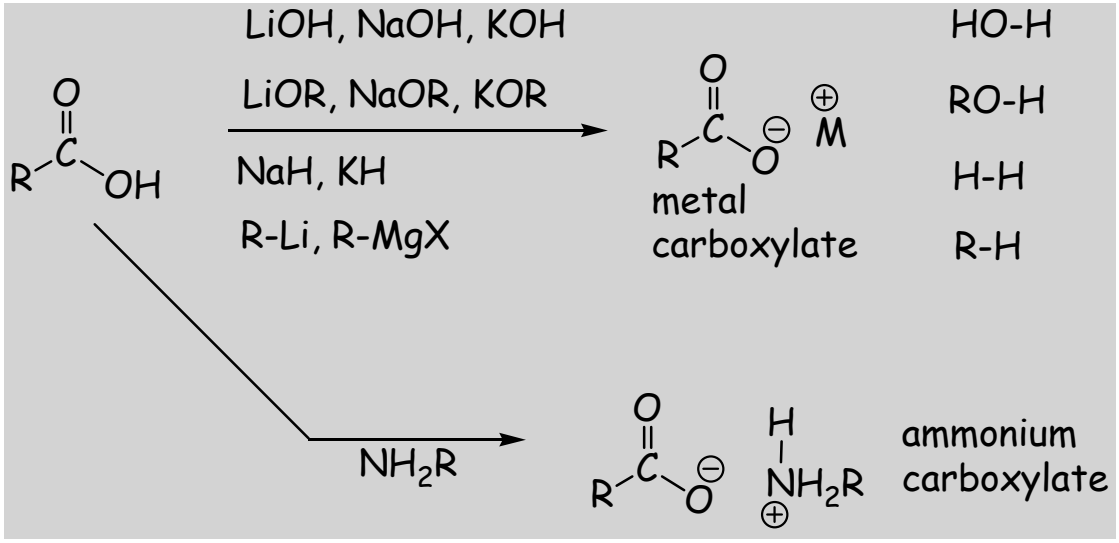
Reactions of Acids

1. Formation of carboxylates
2. Conversion to amides
3. Reduction
4. Conversion to ketones
5. Conversion to acid chlorides
6. Conversion to esters
   - Fischer Esterification
   - Diazomethane

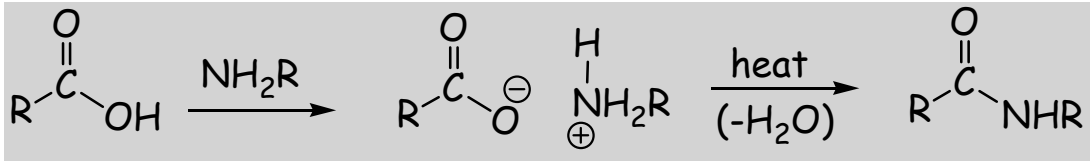
Hydrolysis of Esters

- Acid hydrolysis
- Base hydrolysis (saponification)

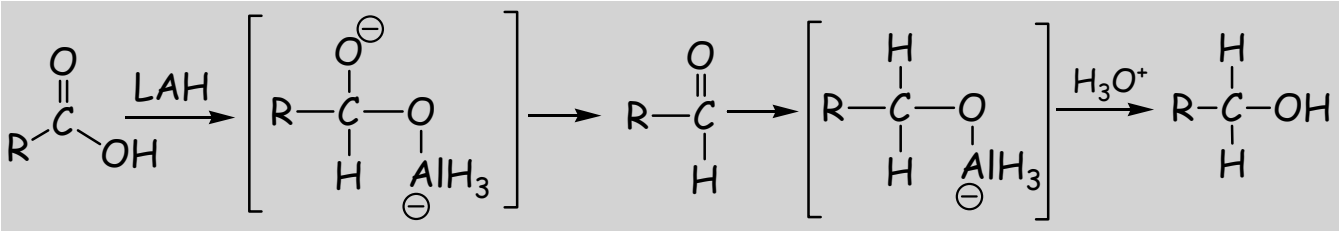
1. Formation of carboxylates



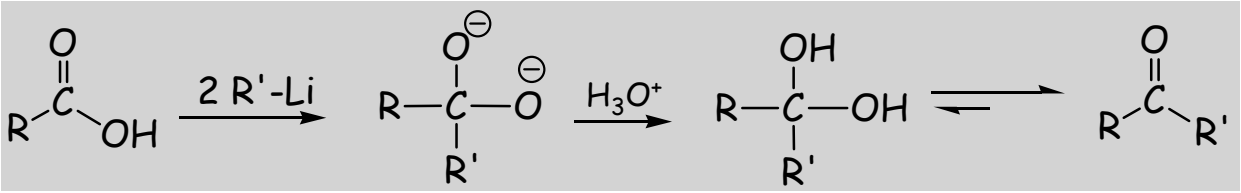
2. Conversion to amides



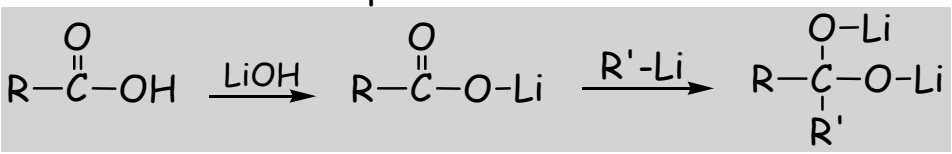
3. Reduction



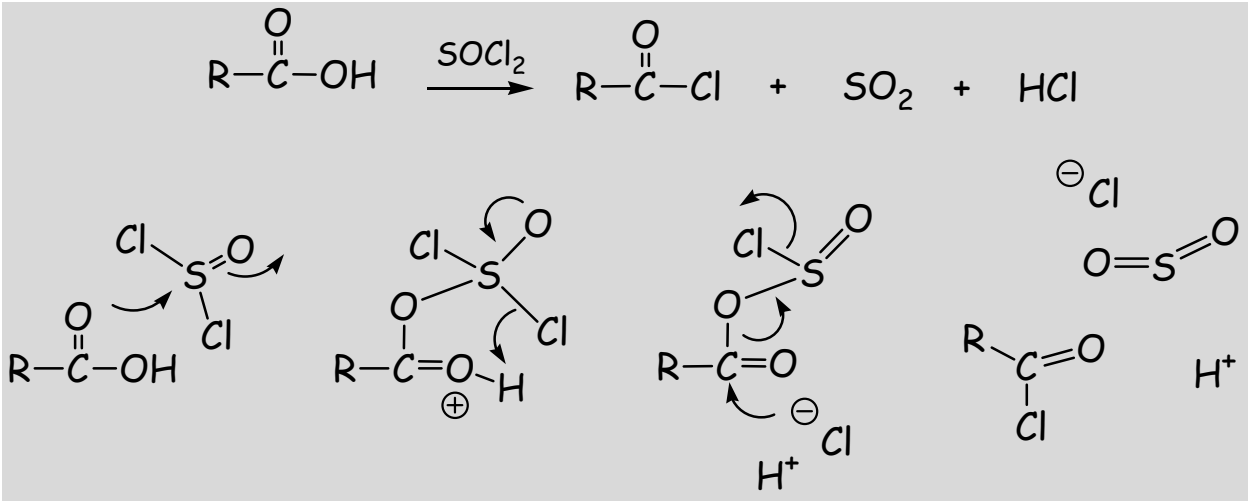
4. Conversion to ketones (via hydrolysis of ketone hydrate)



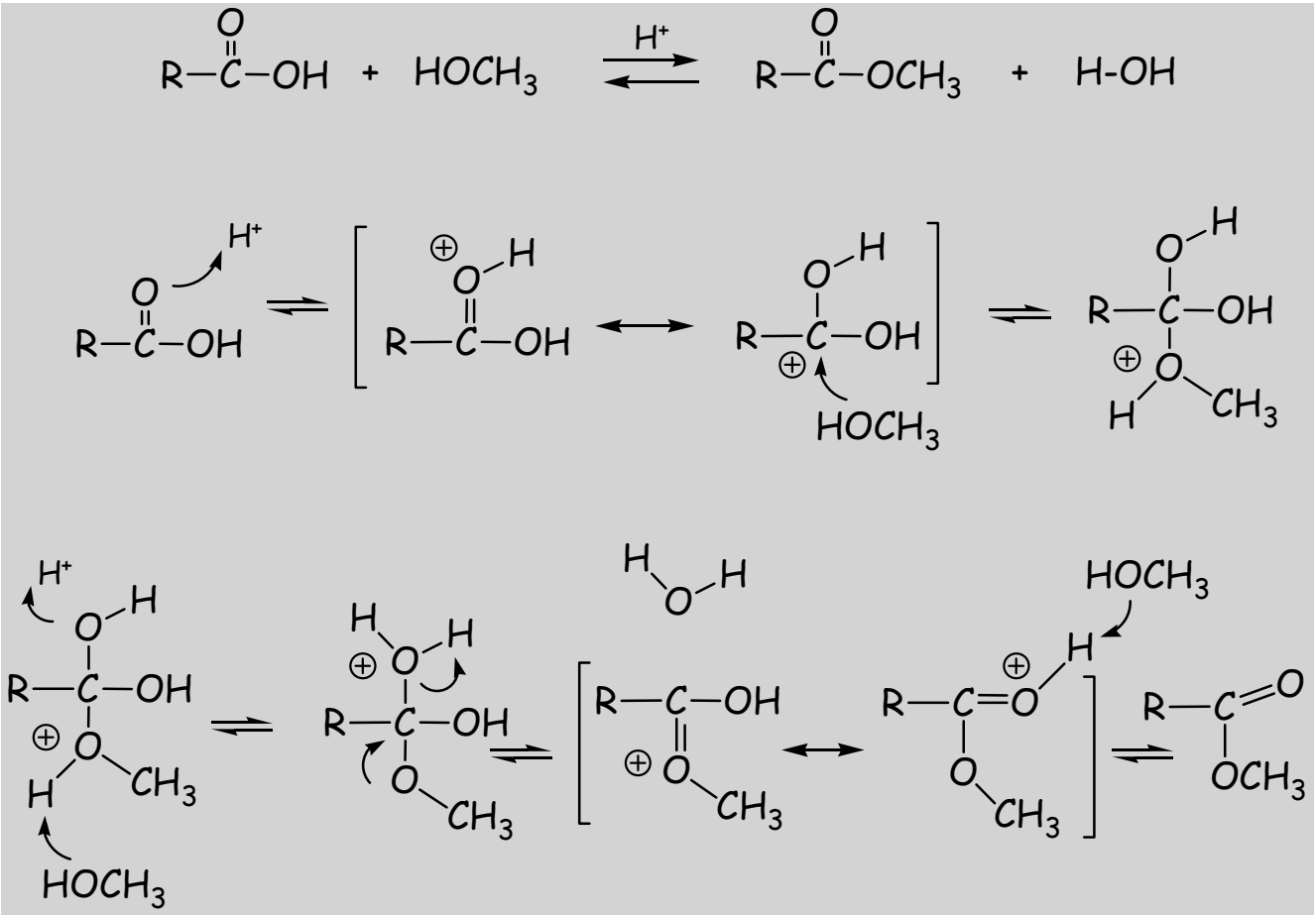
Better to use LiOH to deprotonate then use R-Li to add to carboxylate:



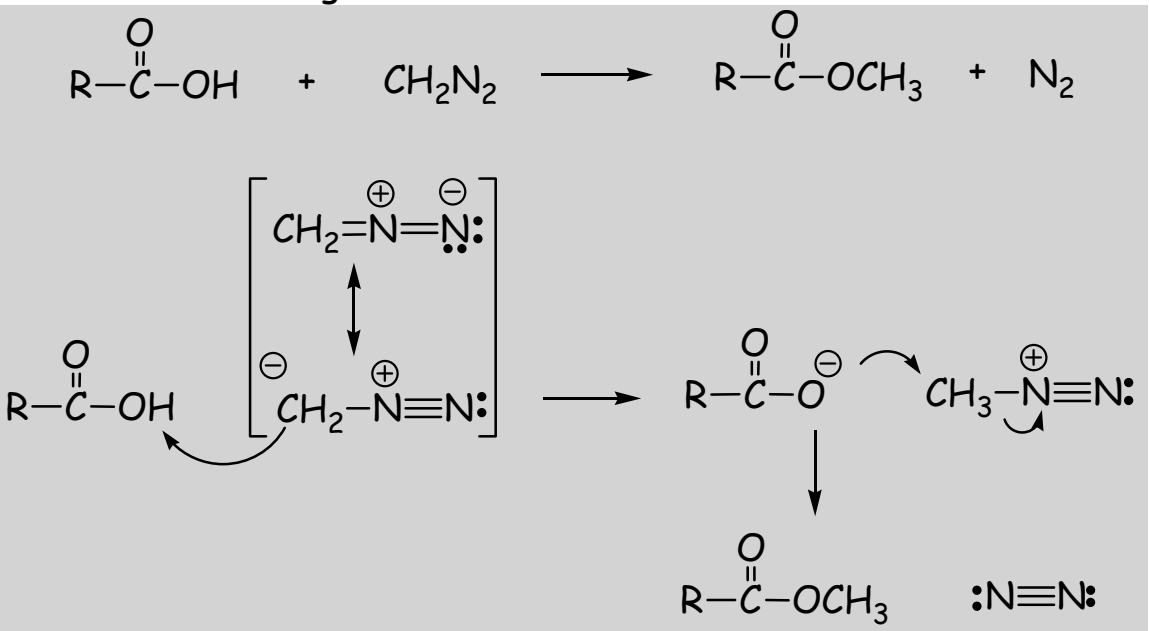
5. Conversion to acid chlorides



6. Conversion to esters (Fischer Esterification)



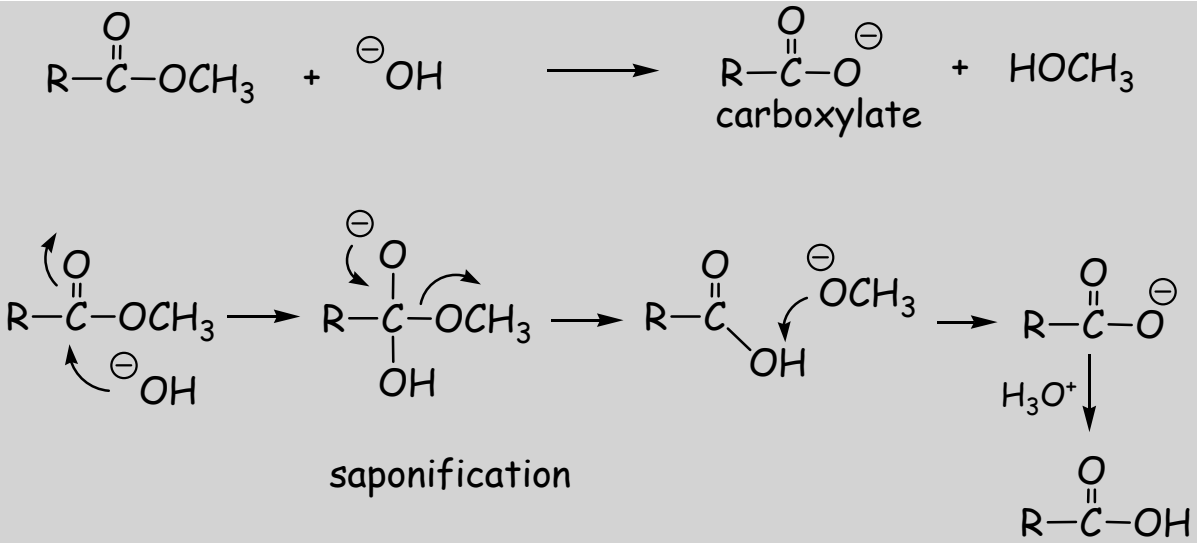
Esterification using diazomethane



Hydrolysis of Esters

Acid hydrolysis- reverse of Fischer esterification

Base hydrolysis (Saponification)

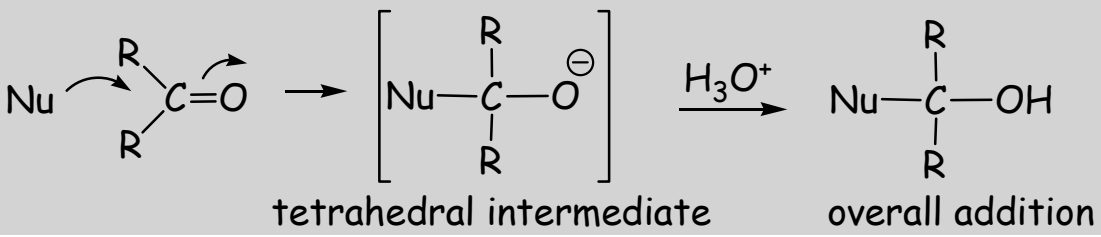


Hydrolysis under <u>acid</u> conditions provides <u>carboxylic acid</u>

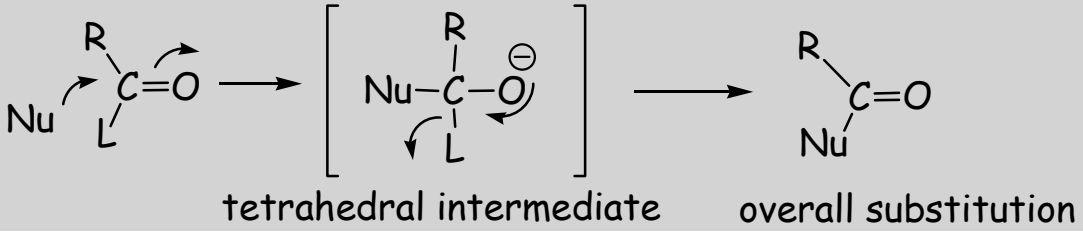
Hydrolysis under <u>basic</u> conditions provides <u>carboxylate ion</u>

Sidebar: Acyl Substitution

Aldehydes and ketones undergo <u>addition</u> to carbonyl:

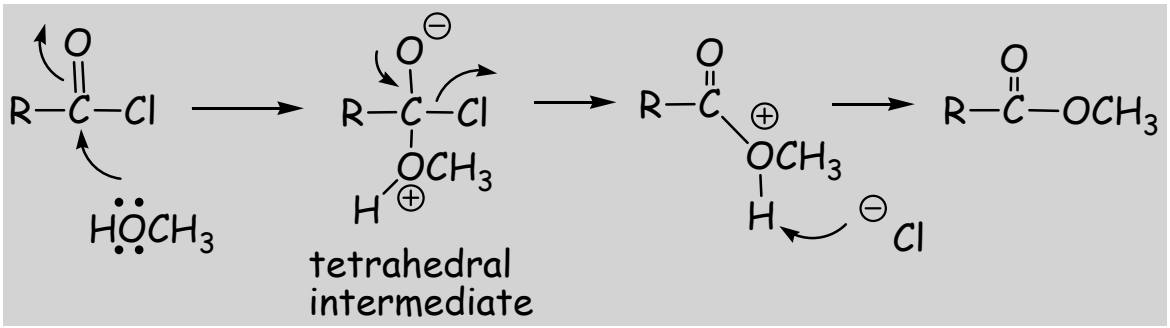


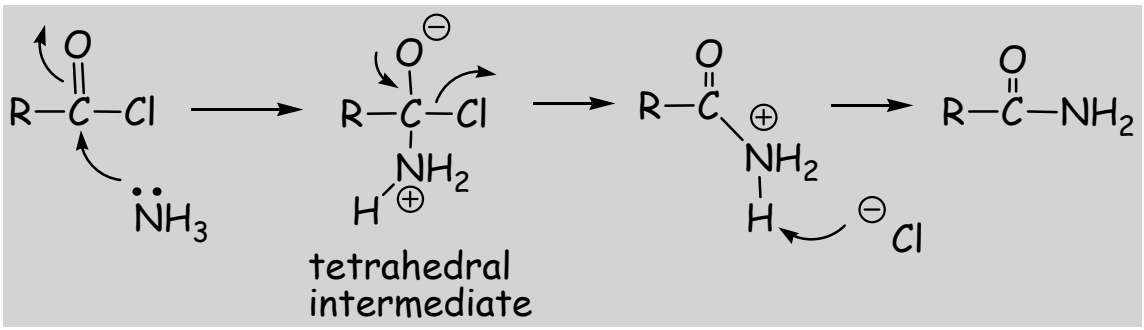
Acyl compounds undergo addition/elimination which is overall <u>substitution</u>:

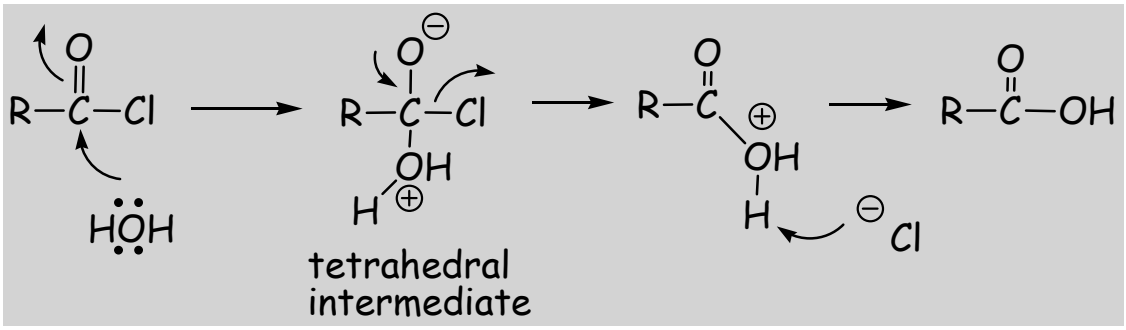


Acyl substitution is the process observed when acid chlorides are converted to other acid derivatives.

Acid chlorides react with alcohols, ammonia and water to provide esters, amides and acids:







Hydroxide and alkoxides are even better nucleophiles: