Carboxylic acid derivatives

Acyl Chlorides and Acid Anhydrides

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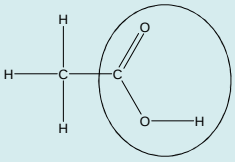
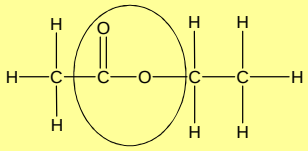
Chemrevise.org

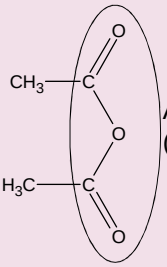
Carboxylic acid derivatives

carboxylic acid
(ethanoic acid)

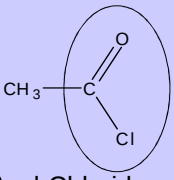




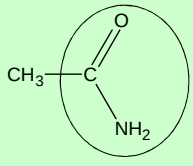
Ester
(ethyl ethanoate)



Acid Anhydride
(ethanoic anhydride)



Acyl Chloride
(ethanoyl chloride)

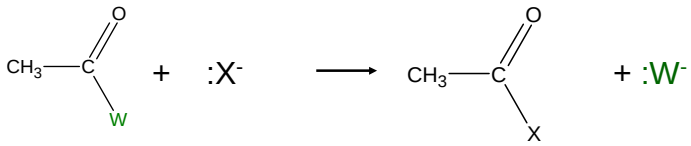


Amide
(ethanamide)

key

Comparing the reactivity of the acid derivatives

Many of the reactions of the carboxylic acid derivatives follow the pattern below with an attack by an nucleophile.



Where –W: and :W- can be –Cl and Cl- (acyl chlorides)
`or -OCH3 and OCH3- (esters)
`or -NH2 and NH2- (amides)

On a simplistic level, the stronger the electron attracting power of 'W', the more positive the carbon, and the more attractive the carbon is to nucleophiles.

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Comparing the reactivity of the acid derivatives

The relative attractive powers of the –W: are

-Cl > -OH > -OCH3 > -NH2

Therefore in the case of hydrolysis reactions, acyl chlorides are highly reactive and will be hydrolysed by weak nucleophiles such as water.

Amides and Esters contain only weak electron attracting W groups and need strong nucleophiles such as hydroxide ions in NaOH to hydrolyse.

This difference in reactivity is caused by a combination of the electronegativity of the Cl's, N's and O's causing electron density to be withdrawn from the carbon and delocalisation of the lone pairs on these atoms into the carbonyl system

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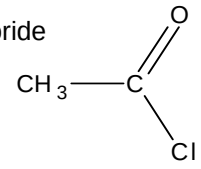
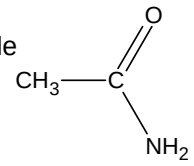
Comparing the reactivity of Acyl chlorides to amides

Acyl Chloride



Amide



Acyl chloride are more reactive than amides

Cl and N have similar electronegativities and so should attract electron density from the carbon by similar amounts, making the carbons equally positive

However, the lone pair on the nitrogen delocalises with the carbonyl group which decreases its reactivity

The Cl is too big to be able to delocalise. This difference in the ability to delocalise explains the difference in reactivity

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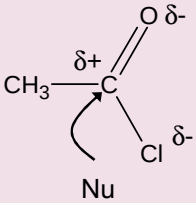
Reactions of Acyl Chlorides

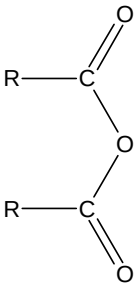
Acyl chlorides are much more reactive than carboxylic acids. The Cl atom is electronegative and attracts electrons from the carbon. The bond becomes polar . (Combined with the inability to delocalise unlike the OH group in carboxylic acids).

The carbon is therefore made positive and so is more attractive to nucleophiles than in carboxylic acids.
So less severe conditions are needed to bring about nucleophilic reactions in comparison to a carboxylic acid.

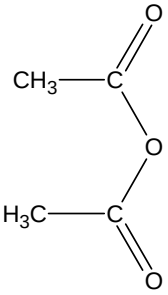


Acid Anhydrides

Generalised structure of acid anhydride



Ethanoic anhydride



Acid anhydrides have a similar reactivity to acyl chlorides and therefore bring about the same changes in functional groups.

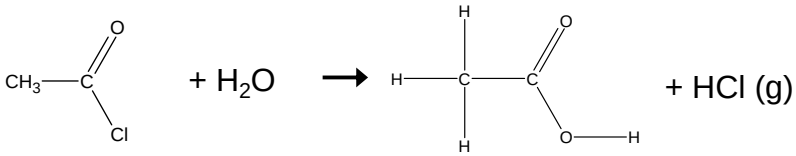
The main difference is the by-products. Acyl chlorides mostly give off HCl. Acid anhydrides give off RCOOH

Acyl chloride :Reaction with Water

Change in functional group: acyl chloride → carboxylic acid

Reagent: water

Conditions: room temp.



$RCOCl\ (l) + H_2O \rightarrow RCO_2H + HCl\ (g)$

Observation: Steamy white fumes of HCl are given off

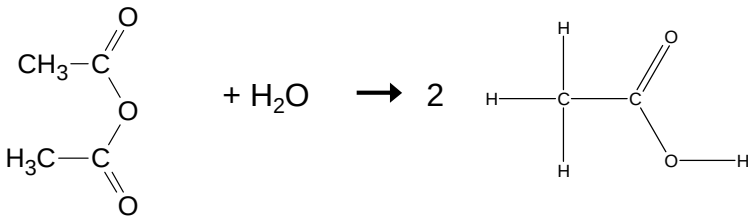
The nucleophile is the lone pair of electrons on the oxygen in the water molecule.

Type of reaction: addition-elimination

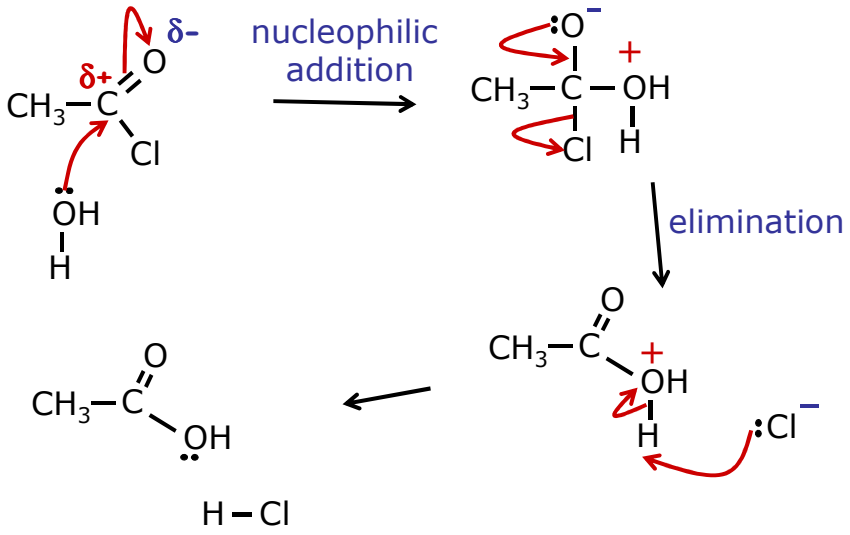
Acid anhydride: Reaction with Water

Change in functional group: acid anhydride → carboxylic acid
Reagent: water
Conditions: room temp.

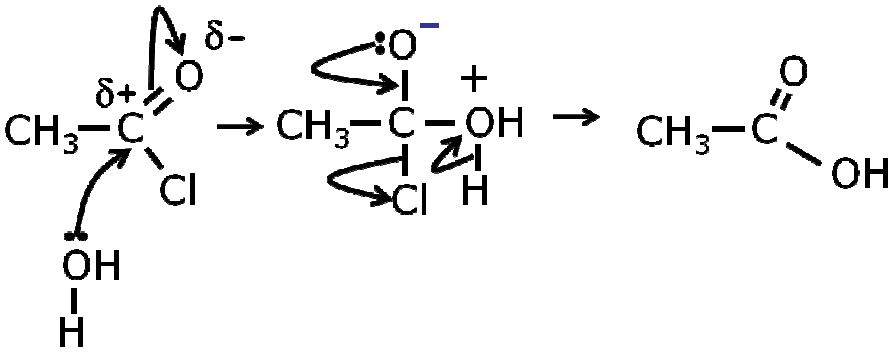
$$(RCO)_2O + H_2O \rightarrow 2RCO_2H$$



Nucleophilic Addition Elimination Mechanism



Nucleophilic Addition Elimination Mechanism Exam mark scheme version

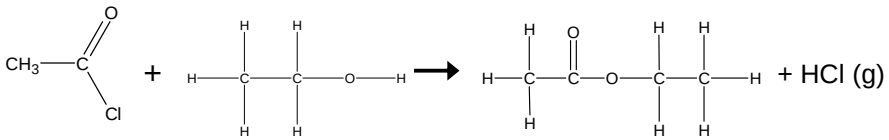


acyl chloride: reaction with alcohols

Change in functional group: acyl chloride → ester

Reagents: alcohol

Conditions: room temp (less severe conditions than esterification of a carboxylic acid where sulphuric acid catalyst is needed and heat under reflux)



Observation: Steamy white fumes of HCl are given off

$RCOCl\ (l) + CH_3CH_2OH \rightarrow RCO_2CH_2CH_3 + HCl$

The nucleophile is the lone pair of electrons on the oxygen in the alcohol molecule.

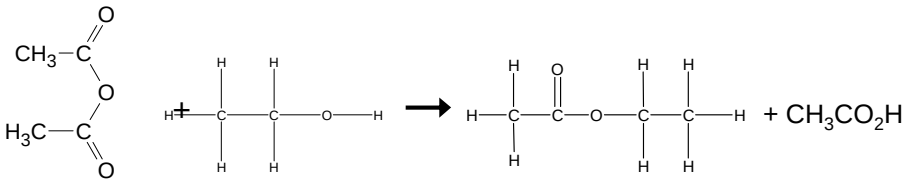
Acid anhydride: reaction with alcohols

Change in functional group: acid anhydride → ester

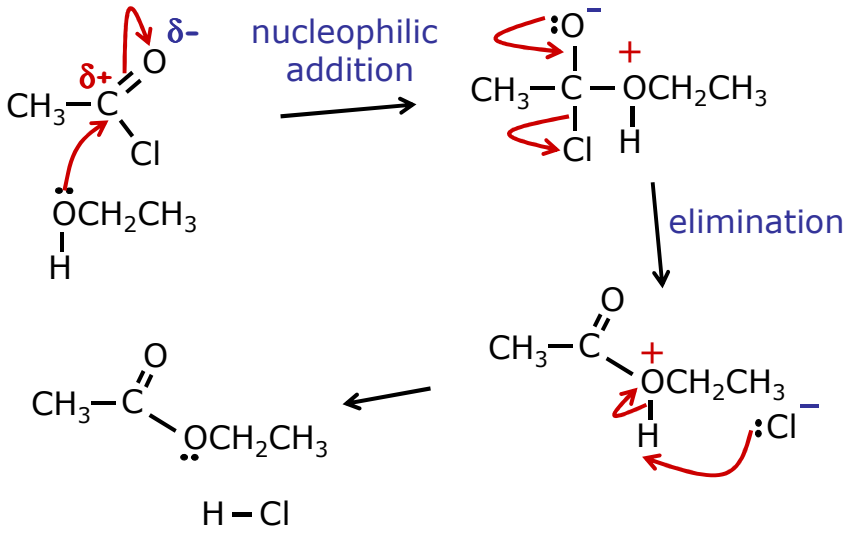
Reagents: alcohol

Conditions: room temp (less severe conditions than esterification of a carboxylic acid where sulphuric acid catalyst is needed and heat under reflux)

$(RCO)_2O + CH_3CH_2OH \rightarrow RCO_2CH_2CH_3 + RCO_2H$



Nucleophilic Addition Elimination Mechanism



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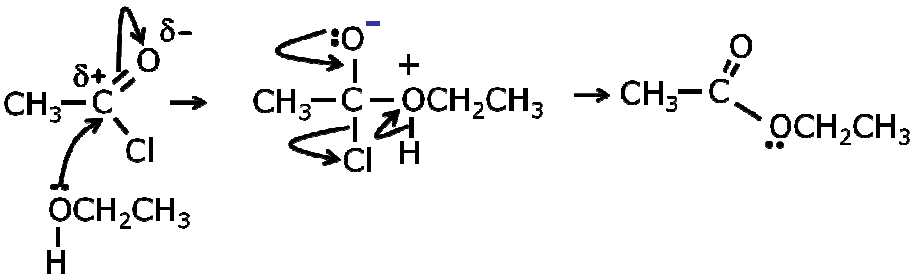
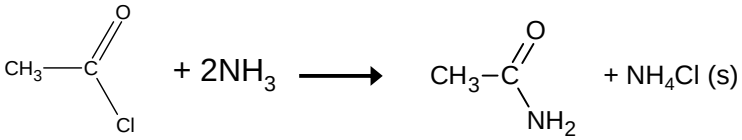


Acyl chloride :Reaction with ammonia

Change in functional group: acyl chloride → amide
Reagents: ammonia
Conditions: room temp



$RCOCl\ (l) + 2NH_3 \rightarrow RCONH_2\ (l) + NH_4Cl$

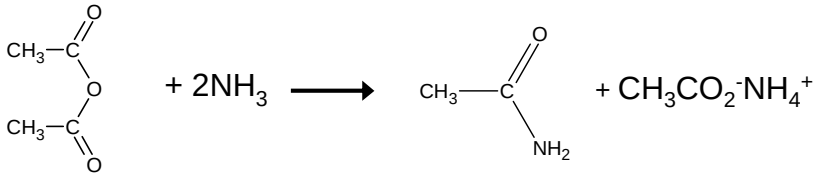
Observation: white smoke of NH_4Cl is given off

The nucleophile is the lone pair of electrons on the nitrogen in the ammonia molecule.

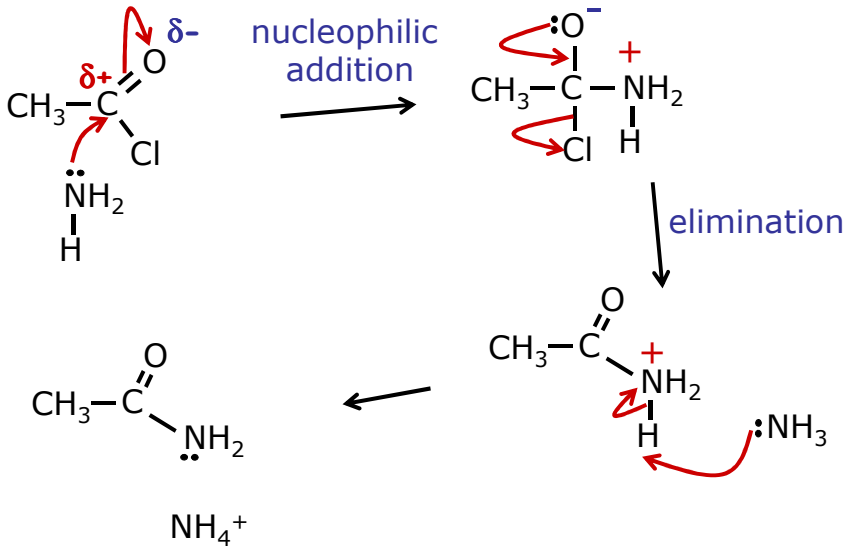
Acid anhydride :Reaction with ammonia

Change in functional group: Acid anhydride → amide
Reagents: ammonia
Conditions: room temp

$(RCO)_2O + 2NH_3 \rightarrow RCONH_2 + RCO_2^-NH_4^+$



Nucleophilic Addition Elimination Mechanism



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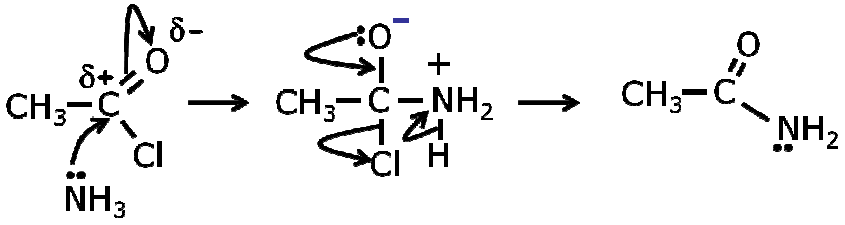
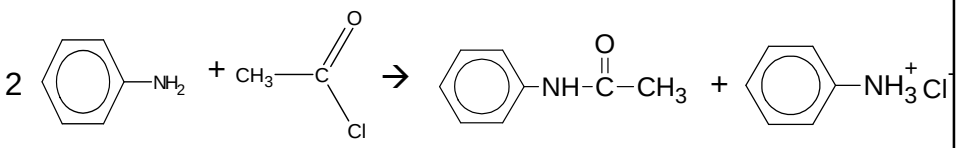
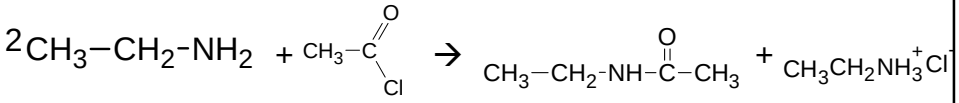


Reaction with amines

Reaction with acyl chloride

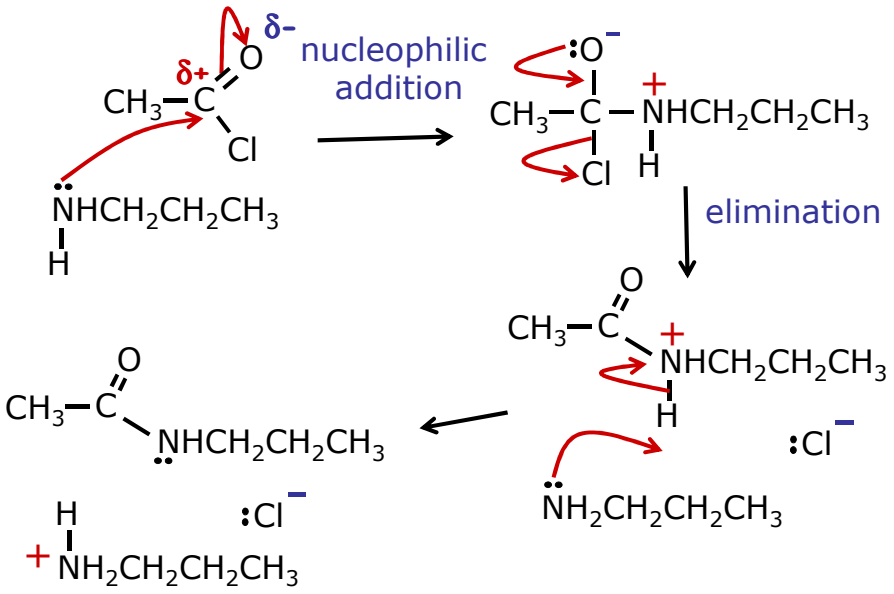


phenylamine ethanoyl chloride N-phenylethanamide



Ethylamine ethanoyl chloride N-ethylethanamide

Nucleophilic Addition Elimination Mechanism



Nucleophilic Addition Elimination Mechanism Exam mark scheme version