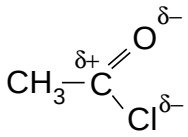
DERIVATIVES OF CARBOXYLIC ACIDS

ACYL (ACID) CHLORIDES - RCOCl

named from corresponding acid
remove *-ic* **add** *-yl chloride*

CH_3COCl ethanoyl chloride
C_6H_5COCl benzene carbonyl chloride

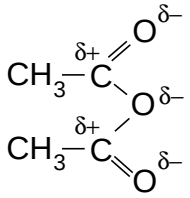


bonding in acyl chlorides

ACID ANHYDRIDES - $(RCO)_2O$

named from corresponding acid
remove *acid* **add** *anhydride*

$(CH_3CO)_2O$ ethanoic anhydride



bonding in acid anhydrides

Chemical Properties

- colourless liquids which fume in moist air
- **acyl chlorides are more reactive** than anhydrides
- attacked at the positive carbon centre by nucleophiles
- nucleophiles include water, alcohols, ammonia and amines
- undergo **addition-elimination** reactions

Uses of Acylation

Industrially Manufacture of **Cellulose acetate** - making fibres
Aspirin (acetyl salicylic acid) - analgaesic

Ethanoic anhydride is more useful
- cheaper
- less corrosive
- less vulnerable to hydrolysis
- less dangerous reaction

Laboratory Used to make **carboxylic acid, esters, amines, N-substituted amines**

Ethanoyl chloride is used as it
- is more reactive
- gives a cleaner reaction

Q.1 *Investigate how aspirin is made industrially and in the laboratory.*
Why are the reagents and chemicals different?
What properties of Aspirin make it such a useful drug?

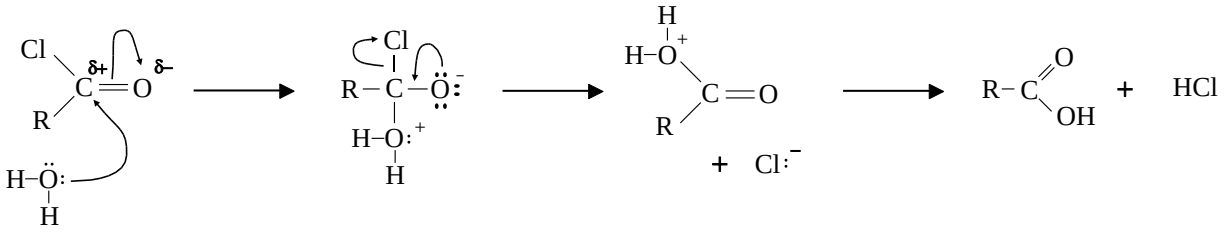
ADDITION ELIMINATION REACTIONS - OVERVIEW

Mechanism

- species attacked by nucleophiles at the positive carbon end of the C=O bond
- the nucleophile adds to the molecule
- either Cl or $RCOO^-$ is eliminated
- a proton is removed

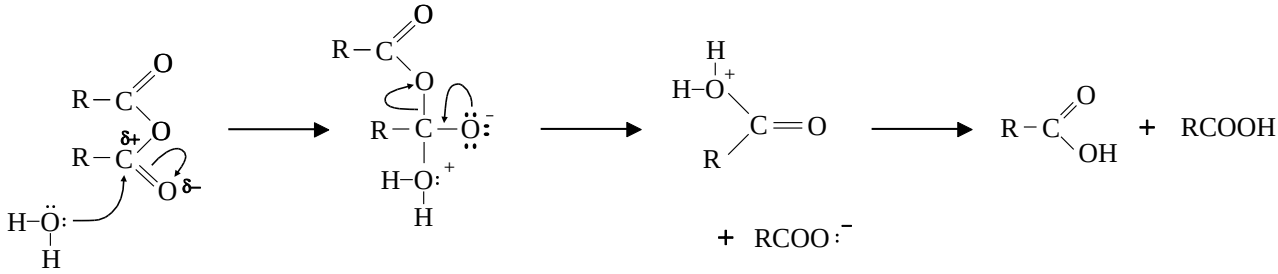
General example - with water

ACID CHLORIDES



RCOCl + H_2O ——> RCOOH + HCl

ACID ANHYDRIDES



$(RCO)_2O$ + H_2O ——> 2RCOOH

Use these mechanisms to help construct others in the spaces which follow

SYNTHETIC POSSIBILITIES

	PRODUCT WITH				*By-product*
	WATER	ALCOHOLS	AMMONIA	AMINES	
ACYL CHLORIDE	CARBOXYLIC ACID	ESTER	AMIDE	N-SUBSTITUTED AMIDE	HCl
ACID ANHYDRIDE	CARBOXYLIC ACID	ESTER	AMIDE	N-SUBSTITUTED AMIDE	CARBOXYLIC ACID

ADDITION ELIMINATION - the reactions

ACYL (ACID) CHLORIDES - RCOCl

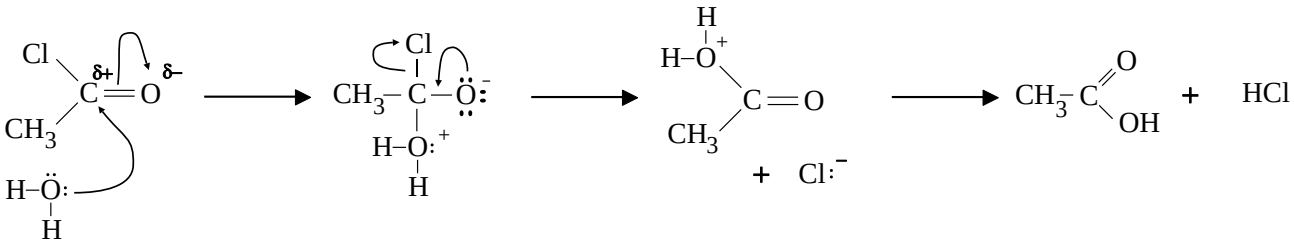
Water

Product(s) carboxylic acid + HCl (fume in moist air / strong acidic solution formed)

Conditions cold water

Equation **$CH_3COCl_{(l)} + H_2O_{(l)} \longrightarrow CH_3COOH_{(aq)} + HCl_{(aq)}$**

Mechanism addition-elimination



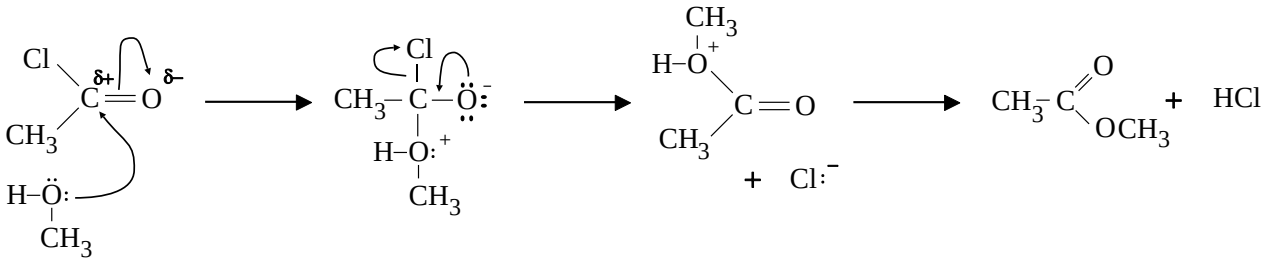
Alcohols

Product(s) ester + hydrogen chloride

Conditions reflux in dry (anhydrous) conditions

Equation **$CH_3COCl_{(l)} + CH_3OH_{(l)} \longrightarrow CH_3COOCH_{3(l)} + HCl_{(g)}$**

Mechanism addition-elimination



Q.2 *What organic product is formed when the following pairs react?*

- *C_3H_7COCl and H_2O*
- *C_2H_5COCl and C_2H_5OH*

Q.3 *How would you synthesis the following?*

- *methyl butanoate*
- *butyl methanoate*
- *$C_6H_5COOCH_3$*
- *$CH_3COOC(CH_3)_2$*

Ammonia

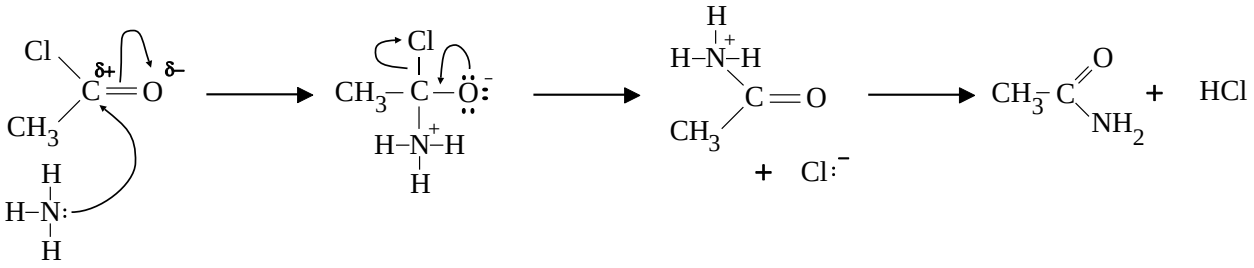
Product(s) Amide + hydrogen chloride

Conditions Low temperature and excess ammonia. Vigorous reaction.

Equation $\mathbf{CH_3COCl_{(l)} + NH_{3(aq)} \longrightarrow CH_3CONH_{2(s)} + HCl_{(g)}}$

or $\mathbf{CH_3COCl_{(l)} + 2NH_{3(aq)} \longrightarrow CH_3CONH_{2(s)} + NH_4Cl_{(s)}}$

Mechanism addition-elimination



Amines

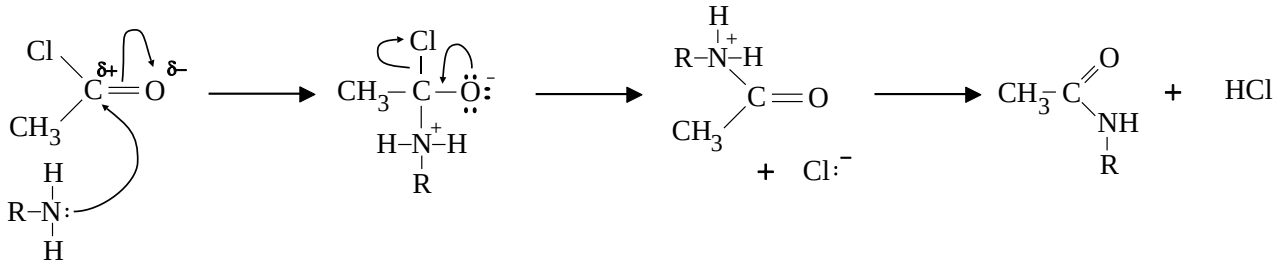
Product(s) N-substituted amide + hydrogen chloride

Conditions anhydrous

Equation $\mathbf{CH_3COCl_{(l)} + C_2H_5NH_{2(aq)} \longrightarrow CH_3CONHC_2H_{5(s)} + HCl_{(g)}}$

or $\mathbf{CH_3COCl_{(l)} + 2C_2H_5NH_{2(aq)} \longrightarrow CH_3CONHC_2H_{5(s)} + C_2H_5NH_3Cl_{(s)}}$

Mechanism addition-elimination - similar to that with ammonia



Q.4 *Why are two moles of ammonia (or amine) required in each equation?*

Q.5 *What pairs of chemicals would you use to synthesis the following?*

- *butanamide*
- $C_2H_5CONH_2$
- $CH_3CON(CH_3)_2$
- *N-phenylethanamide*

ACID ANHYDRIDES - $(RCO)_2O$

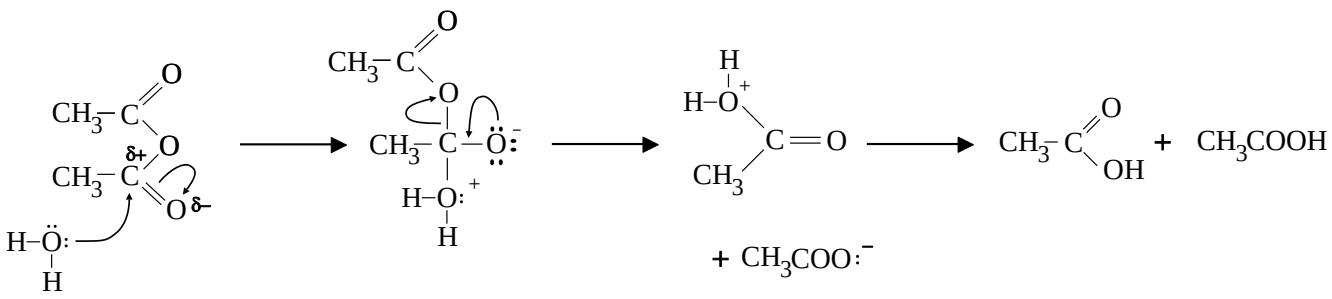
Water

Product(s) carboxylic acid (weak acidic solution formed)

Conditions cold water - but can be slow

Equation **$(CH_3CO)_2O_{(l)} + H_2O_{(l)} \longrightarrow 2CH_3COOH_{(aq)}$**

Mechanism



Alcohols

Product(s) ester + carboxylic acid

Conditions reflux in dry (anhydrous) conditions

Equation **$(CH_3CO)_2O_{(l)} + CH_3OH_{(l)} \longrightarrow CH_3COOCH_{3(l)} + CH_3COOH_{(aq)}$**

Mechanism

Q.6 *What organic product(s) is/are formed when the following pairs react?*

- *$(C_3H_7CO)_2O$ and H_2O*
- *$(CH_3CO)_2O$ and C_2H_5OH*
- *$(CH_3CO)_2O$ and $(CH_3)_2CHOH$*

Ammonia

Product(s) Amide + carboxylic acid

Conditions Low temperature and excess ammonia.

Equation $(CH_3CO)_2O_{(l)} + NH_{3(aq)} \longrightarrow CH_3CONH_{2(s)} + CH_3COOH_{(aq)}$

or $(CH_3CO)_2O_{(l)} + 2NH_{3(aq)} \longrightarrow CH_3CONH_{2(s)} + CH_3COO^-NH_4^+{}_{(s)}$

Mechanism

Amines

Product(s) N-substituted amide + carboxylic acid

Equation $(CH_3CO)_2O_{(l)} + C_2H_5NH_{2(aq)} \longrightarrow CH_3CONHC_2H_{5(s)} + CH_3COOH_{(aq)}$

or $(CH_3CO)_2O_{(l)} + 2C_2H_5NH_{2(aq)} \longrightarrow CH_3CONHC_2H_{5(s)} + CH_3COO^-NH_4^+{}_{(s)}$

Mechanism

Q.7 *What organic product(s) is/are formed when the following pairs react?*

- $(C_3H_7CO)_2O$ *and* NH_3
- $(CH_3CO)_2O$ *and* $C_2H_5NH_2$
- $(CH_3CO)_2O$ *and* $(CH_3)_2NH$