

Topic 5 – Carbonyl Compounds

Revision Notes

1. Introduction

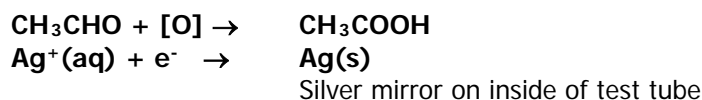
- Carbonyl compounds contain the group C=O
- The C=O bond is polar with the C being δ^+ and the O δ^- . Nucleophiles are attracted to the δ^+ C

2. Aldehydes and ketones

- The functional group in aldehydes is –CHO on the end of a chain e.g. ethanal CH₃CHO
- The functional group in ketones is C=O not at the end of a chain e.g. propanone CH₃COCH₃
- Position of C=O needs to be specified if ketone has five or more Cs i.e. butanone but pentan-2-one and pentan-3-one
- The characteristic reaction of aldehydes and ketones is nucleophilic addition (nucleophiles attracted to δ^+ C, addition due to double bond)

a) Oxidation

- Aldehydes react with mild oxidising agents such as Tollens' reagent and Fehling's solution
- Ketones do not react with Tollen's and Fehling's because they are not easily oxidised.
- Tollen's reagent is ammoniacal silver nitrate. The compound to be tested is warmed with Tollen's reagent.
- With Tollen's aldehydes produce a silver mirror e.g.



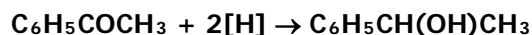
- Fehling's contains a blue copper (II) complex. The compound to be tested is warmed with Fehling's solution
- With Fehling's aldehydes produce a brick-red precipitate of copper (I) oxide, Cu₂O

b) Reduction

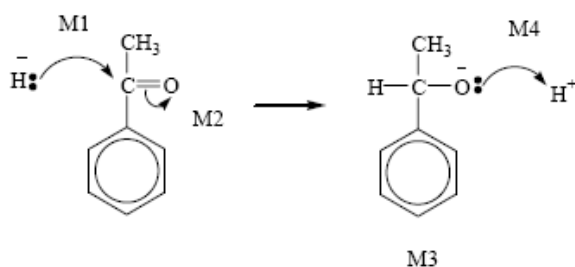
- Reduction, here, means addition of hydrogen
- A specific reducing agent for aldehydes and ketones is sodium borohydride, NaBH₄. In equations the reducing agent is represented by [H]
- Aldehydes are reduced to primary alcohols by NaBH₄ e.g.



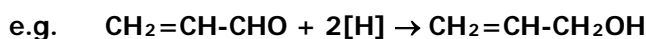
- Ketones are reduced to secondary alcohols by NaBH₄ e.g.



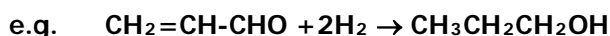
- The mechanism for this reaction is called nucleophilic addition. The nucleophile is H⁻ which is provided by NaBH₄



- NaBH_4 will reduce $\text{C}=\text{O}$ double bonds but it will not reduce $\text{C}=\text{C}$ double bonds

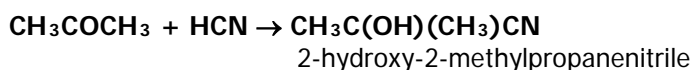
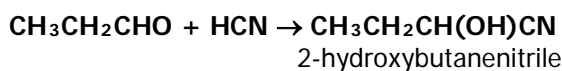


- To reduce both $\text{C}=\text{O}$ and $\text{C}=\text{C}$ use H_2 with Ni catalyst

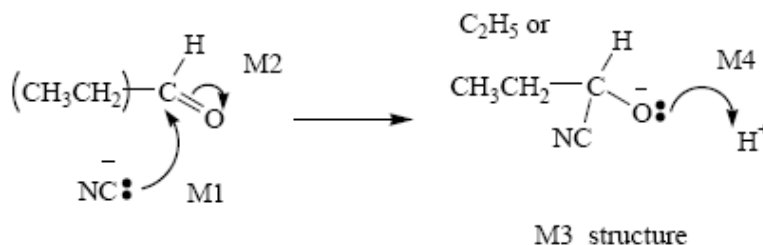


c) Addition of HCN

- Addition of HCN to an aldehyde or ketone produces a hydroxynitrile e.g.



- The aldehyde or ketone is refluxed with $\text{KCN}(\text{aq})$
- HCN and KCN are toxic
- The mechanism for this reaction is nucleophilic addition. The nucleophile is CN^-

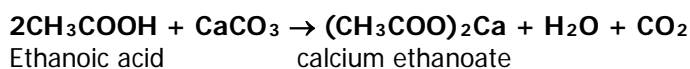


3. Carboxylic acids

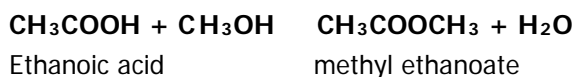
- The functional group in carboxylic acids is $-\text{COOH}$ on the end of a chain e.g. ethanoic acid CH_3COOH
- They are weak acids (H^+ donors). The acidic H is in the $-\text{COOH}$ group e.g.



- They react with carbonates and the fizzing produced can be used to distinguish carboxylic acids from other organic compounds



- Carboxylic acids react with alcohols to make an ester and water e.g.



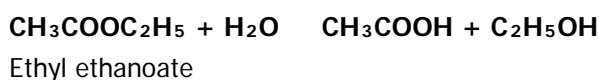
- This reaction is called esterification and requires a catalyst of concentrated H₂SO₄
- Note that C₆H₅COOH is called benzene carboxylic acid. Its salts are benzene carboxylates e.g. sodium benzene carboxylate

4. Esters

- Esters have the form RCOOR' where R and R' are alkyl groups such as CH₃, C₂H₅ etc
- Esters have pleasant smells and are used as flavourings in food and as solvents and plasticisers
- Esters can be hydrolysed by dilute acids and alkalis. This involves nucleophilic attack on the δ+ C of the carbonyl group by H₂O or OH⁻

a) Acid hydrolysis

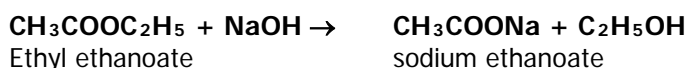
- This is the reverse of esterification



- For acid hydrolysis, heat the ester with a dilute acid such as HCl
- Fats and oils are tri-esters. Acid hydrolysis of fats produces long-chain acids (fatty acids) and glycerol (propane-1,2,3,-triol)

b) Alkaline hydrolysis

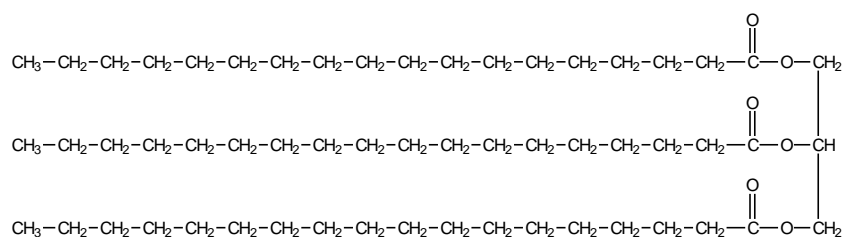
- This is similar to acid hydrolysis but produces the sodium salt of acid rather than acid itself. This is not reversible.



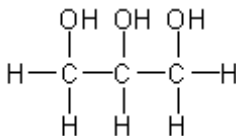
- For alkaline hydrolysis, heat the ester with dilute NaOH
- Alkaline hydrolysis of fats and oils produces glycerol and salts of fatty acids (soaps)

5. Fats and oils

- Animal fats and vegetable oils are tri-esters of glycerol and 3 fatty acids e.g.



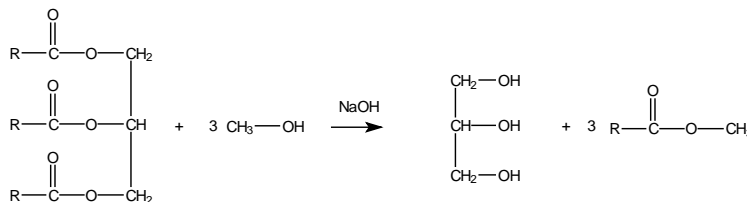
- Glycerol is propane-1,2,3-triol



- Acidic hydrolysis of animal fats and vegetable oils produces glycerol and long chain carboxylic acids (fatty acids)
- Alkaline hydrolysis of fats and oils produces glycerol and the sodium salts of fatty acids, which are used as soap

6. Biodiesel

- Biodiesel consists of the methyl esters of fatty acids
- Biodiesel can be made from cooking oil. The oil is mixed with methanol and potassium or sodium hydroxide is added as a catalyst

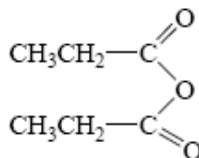


Source - <http://www.chemsheets.co.uk/>

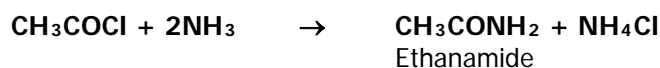
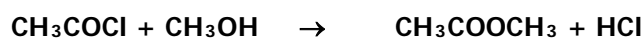
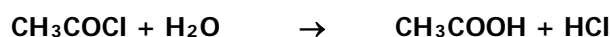
- The use of biodiesel is increasing because of reduced greenhouse gas emissions, deforestation and pollution compared with petro-diesel (made from crude oil)

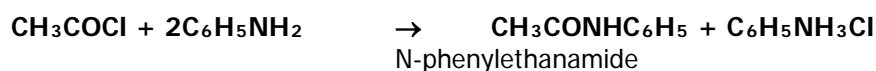
7. Acylation reactions

- The functional group in acyl chlorides is $-\text{COCl}$ on the end of a chain e.g. ethanoyl chloride CH_3COCl
- Acid anhydrides can be thought of as 2 molecules of acid that have lost a molecule of water e.g. propanoic anhydride, $(\text{CH}_3\text{CH}_2\text{CO})_2\text{O}$

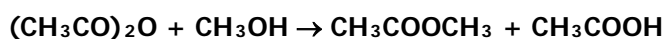


- Acyl chlorides react with water, alcohols, ammonia and primary amines in acylation reactions

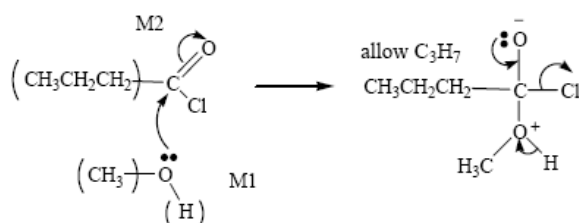




- These are vigorous reactions and white fumes are HCl are produced
- Water, alcohols, ammonia and primary amines are all nucleophiles. They have a lone pair on an O or N
- The reaction with an alcohol produces an ester. Compared with esterification (using a carboxylic acid), the acylation reaction has the benefits of not being reversible and not requiring a catalyst
- Acid anhydrides do the same reactions but the second product is ethanoic acid rather than HCl (so no white fumes are seen)



- A similar reaction is used to manufacture aspirin. Ethanoic anhydride is used rather than ethanoyl chloride because the anhydride is cheaper, less corrosive and less susceptible to hydrolysis
- The mechanism for acylation is called nucleophilic addition-elimination



M3 for structure
M4 for 3 arrows and lone pair
(only allow for correct M3 or close)

M2 not allowed independent of M1,
but allow M1 for correct attack on C⁺ if M2 shown as independent first.