ChemFactsheet

www.curriculum-press.co.uk Number 101

Organic Functionality and Structure – Part 2 (A2)

To succeed in this topic you need to:

- remember that carbon atoms form the backbone of all organic molecules
- understand why and how carbon atoms form four covalent bonds
- understand the properties and reactivity of simple functional groups like alcohols and alkenes
- be comfortable with the naming and testing of functional groups

After working through this Factsheet you will:

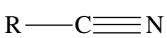
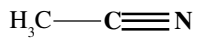
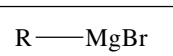
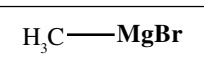
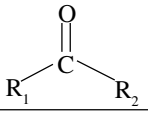
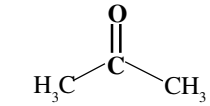
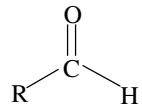
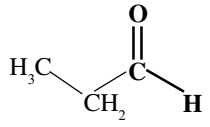
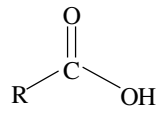
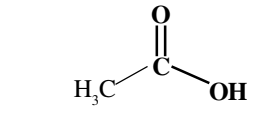
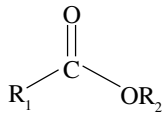
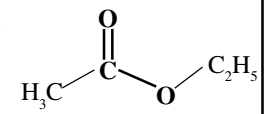
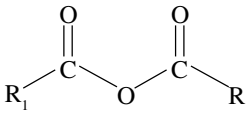
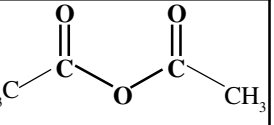
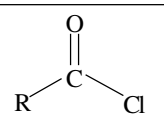
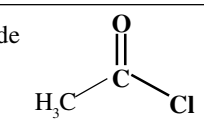
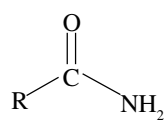
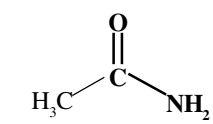
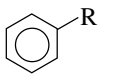
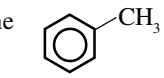
- be able to recognise the key functional groups in A2 Chemistry
- be able to predict chemical and physical properties of the key functional groups in A2 Chemistry

Not all A2 courses cover all the functional groups mentioned in this Factsheet, so make sure you have checked your notes and your syllabus to be clear about which ones you need to study.

In your AS Chemistry course you have developed some important skills of organic chemistry. You should now be able to look at the structure of any organic compound and pick out the key functional groups.
You should also be able to predict the chemical and physical properties of the compound based on those functional groups. In A2 Chemistry you meet a wider variety of functional groups, but you still need to be able to name them, describe tests, suggest ways of making them and predict their physical properties and chemical reactions.

Table 1 shows the functional groups that most commonly occur in A2 Chemistry, along with the suffix or prefix used in the systematic naming of the group. The functional groups are highlighted. Remember that the abbreviation R is used to show that a carbon-containing group, linking to the rest of the molecule, is attached to the atom we are interested in.

Table 1. A2 Functional groups

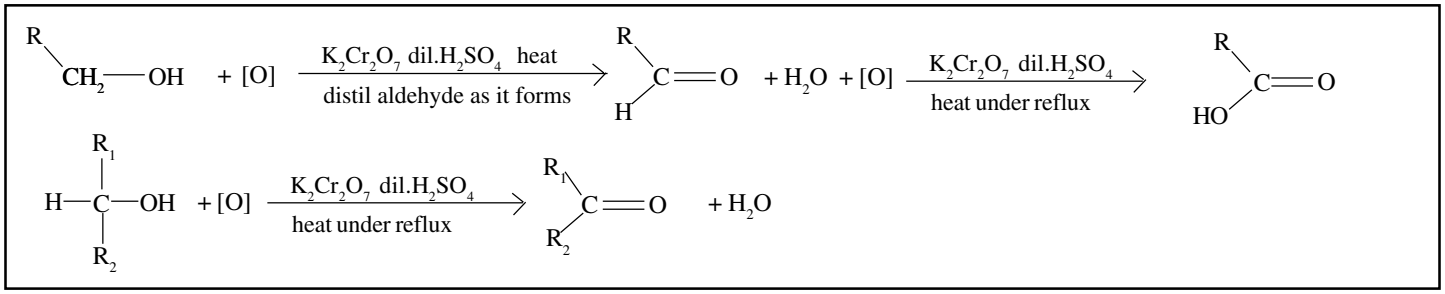
Name	Suffix or prefix*	Structure	Example
Nitrile	-nitrile		 Ethanonitrile
Grignard reagent	-magnesium iodide or bromide		 Methyl magnesium bromide
Ketone**	-one		Propanone 
Aldehyde**	-al		Propanal 
Carboxylic acid**	-oic acid		Ethanoic acid 
Ester**	-oate		Ethyl ethanoate 
Acid anhydride**	-oic anhydride		Ethanoic anhydride 
Acid chloride**	-oyl chloride		Ethanoyl chloride 
Amide**	-amide		Ethanamide 
Benzene ring	-benzene or phenyl-		Methyl benzene 

*** Naming of functional groups is covered in Factsheet 15. ** These functional groups contain the carbonyl group, C=O.**

Carboxylic acids, aldehydes and ketones

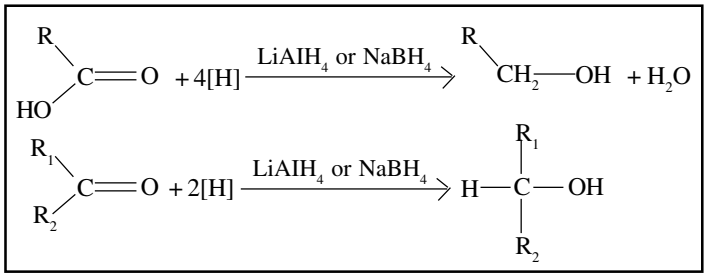
Carboxylic acids, aldehydes and ketones are made by oxidation of alcohols (Fig 1). The oxidising agent most commonly used is acidified potassium (or sodium) dichromate(VI), $K_2Cr_2O_7$ (or $Na_2Cr_2O_7$). Oxidation of a primary alcohol produces an aldehyde, which must be distilled off as it forms or it will be further oxidised to the carboxylic acid. Secondary alcohols produce ketones. Tertiary alcohols cannot be oxidised under these conditions since the carbon atom of the alcohol is not bonded to a hydrogen atom.

Fig 1. Oxidation of alcohols



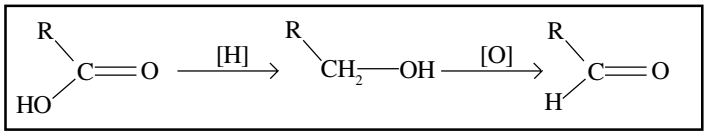
Carboxylic acids, aldehydes and ketones can be reduced back to their respective alcohols by reaction with reducing agents such as sodium tetrahydridoborate, $NaBH_4$, or lithium tetrahydridoaluminate, $LiAlH_4$. These reductions can be viewed as nucleophilic addition reactions because the metal hydrides are sources of nucleophilic H^- ions which attack the unsaturated δ^+ carbonyl carbon atom (Fig 2).

Fig 2. Reduction of carboxylic acids and ketones



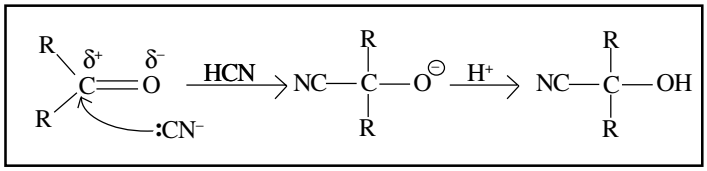
It is difficult to stop the reduction of a carboxylic acid at the aldehyde stage, so if this transformation is required, a more effective approach is to reduce to the primary alcohol and then re-oxidise to the aldehyde (Fig 3).

Fig 3. Conversion of a carboxylic acid to an aldehyde



Aldehydes and ketones react similarly with other nucleophiles, like hydrogen cyanide, HCN (Fig 4). These reactions are also nucleophilic additions where the unsaturated carbonyl group is transformed to a saturated single C-O single bond as a result of the nucleophilic CN^- ions attacking the unsaturated δ^+ carbonyl carbon atom. The nitrile group can be further manipulated to make carboxylic acids and amines.

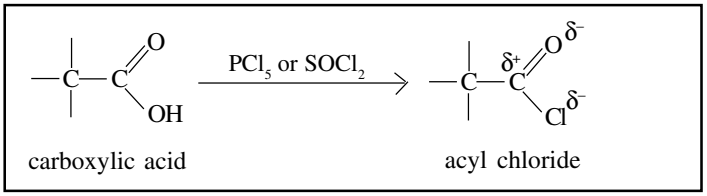
Fig 4. Nucleophilic addition of HCN to aldehydes and ketones



Acyl chlorides and acid anhydrides

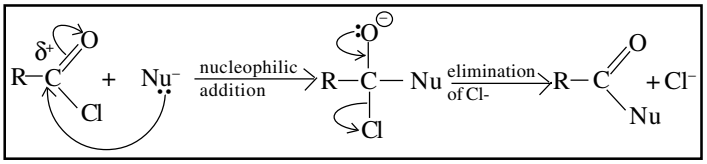
Acyl chlorides are synthesised from carboxylic acids by reaction with PCl_5 or $SOCl_2$ (Fig 5). Acyl chlorides are more reactive than carboxylic acids because the C-Cl bond is weaker than the C-OH bond of the carboxylic acid.

Fig 5. Synthesis of acyl chlorides



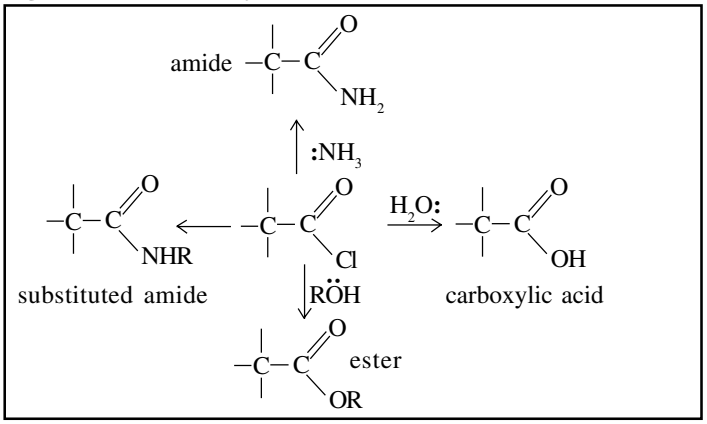
Thus, acyl chlorides also react with nucleophiles, as shown in Fig 6, which attack the δ^+ carbon atom, ultimately breaking the weaker carbon-chlorine bond, but leaving intact the unsaturated C=O bond.

Fig 6. Nucleophilic addition-elimination reactions of acyl chlorides



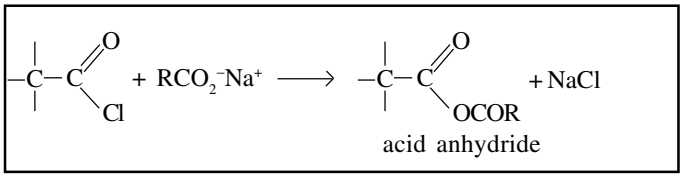
The nucleophiles commonly used in this reaction are species with lone pairs such as ammonia, amines, water and alcohols, which convert acyl chlorides into amides, substituted amides, carboxylic acids and esters respectively, as shown in Fig 7. Note that in each of these reactions, HCl is produced as well.

Fig 7. Reactions of acyl chlorides



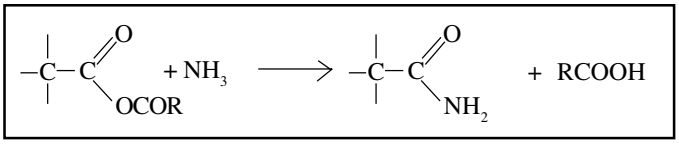
Acid anhydrides are synthesised from acyl chlorides by reaction with the sodium salt of a carboxylic acid (Fig 8). This is also a nucleophilic attack on the δ^+ carbonyl carbon by the alkanoate ion (RCO_2^-).

Fig 8. Synthesis of an acid anhydride from acyl chloride



Acid anhydrides are also more reactive than carboxylic acids and can be used in similar ways to acyl chlorides. The example (Fig 9) shows the synthesis of an amide by reaction with nucleophilic ammonia. Substituted amides, esters and acids can be made from amine, alcohol, and water nucleophiles respectively.

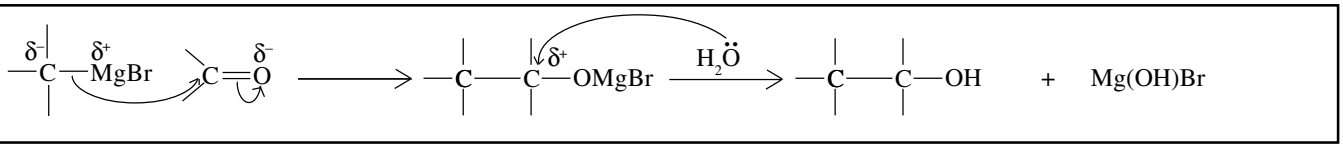
Fig 9. Reaction of an acid anhydride with ammonia



Grignard Reagents

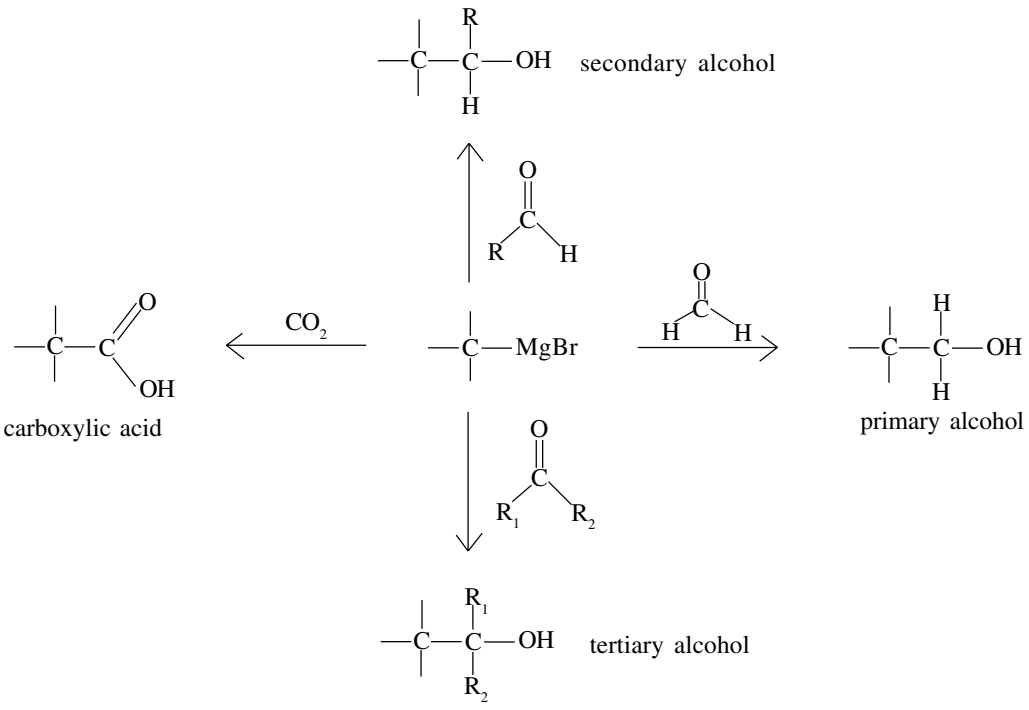
Grignard reagents contain a nucleophilic carbon atom because of the electropositive nature of the magnesium atom, which increases the electron density around the carbon atom. Hence, they also react with polar carbonyl groups by nucleophilic addition as shown in Fig 10.

Fig 10. Reactivity of a Grignard reagent



The resulting addition product can be hydrolysed to form various products depending on the nature of the original carbonyl molecule. Fig 11 shows some examples. Methanal produces a primary alcohol, other aldehydes produce secondary alcohols and ketones produce tertiary alcohols. They also react with the C=O bond in carbon dioxide to make carboxylic acids, and with water to make alkanes.

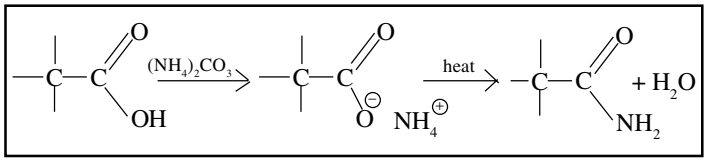
Fig 11. Nucleophilic reactions of Grignard reagents



Amides

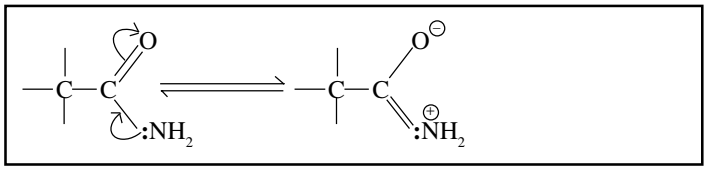
Amides, which also contain a carbonyl group, are a common feature of many biological molecules. They can be produced by the reaction of acyl chlorides with ammonia and amines (see Fig 7), or by hydrolysis of nitriles (see Fig 18). Another route to amides is the dehydration of the ammonium salt of a carboxylic acid, as seen in Fig 12.

Fig 12. Synthesis of an amide from a carboxylic acid



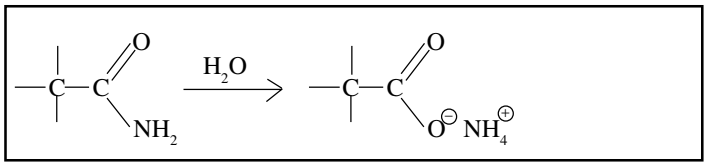
Unlike amines, amides are not basic since, as shown in Fig 13, the electron-withdrawing nature of the carbonyl group reduces the electron density of the nitrogen atom, making it less able to use its lone pair to accept a proton.

Fig 13. Reduced basic character of the amide nitrogen atom



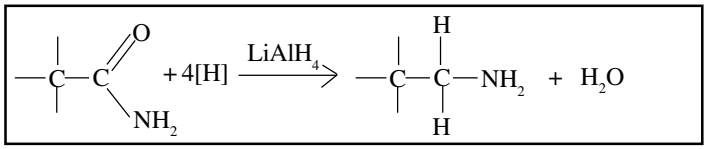
Like acyl chlorides and acid anhydrides, amides react by nucleophilic attack on the carbonyl carbon atom. As shown in Fig 14, they can be hydrolysed to carboxylic acid salts by reaction with either acid or base. In these processes, H_2O and OH^- are the nucleophiles.

Fig 14. Hydrolysis of an amide



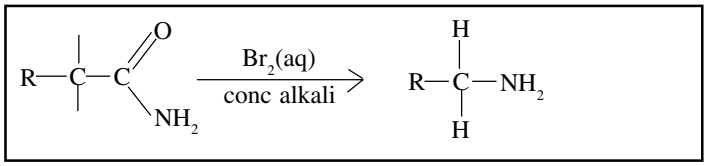
They can also be reduced to amines using lithium tetrahydridoaluminate. This is seen in Fig 15 and is analogous to the nucleophilic addition of hydride to aldehydes, ketones and acids (Fig 2).

Fig 15. Reduction of an amide



The Hofmann degradation (Fig 16) is another reduction reaction, this time producing an amine with one less carbon atom than the original amide.

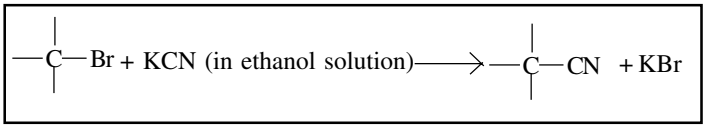
Fig 16. The Hofmann degradation reaction



Nitriles

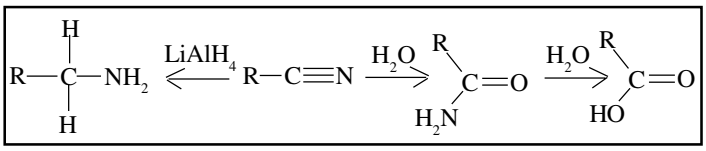
Reactive carbon atoms tend to be δ^+ since they are usually attached to electron-withdrawing halogens, oxygen or nitrogen. However, it is possible to reverse this reactivity and produce a nucleophilic carbon atom. The nitrile ion, CN^-, found in compounds like KCN, is an example of this reversed reactivity since the lone pair of the negatively charged carbon atom will attack the δ^+ carbon atoms of halogenoalkanes. This, as shown in Fig 17, is a nucleophilic substitution reaction.

Fig 17. Nucleophilic substitution of a halogenoalkane by a cyanide ion



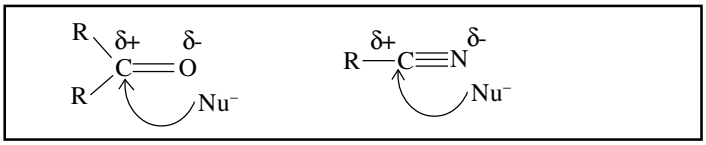
Nitrile groups extend the carbon chain by one atom. The group can then be reduced to an amine (again by reaction with lithium tetrahydridoaluminate, $LiAlH_4$) or hydrolysed under acidic or alkaline conditions to an amide and subsequently to a carboxylic acid, as shown in Fig 18.

Fig 18. Reactions of the nitrile group



These reactions all involve nucleophilic attack on the carbon of the CN group, which, due to the electron-withdrawing nature of the nitrogen atom, behaves in a similar way to the carbon of a carbonyl group (Fig 19). In the reduction, $LiAlH_4$ acts as a source of nucleophilic H^- ions, while in the hydrolysis, water is the nucleophile.

Fig 19. Nucleophilic attack on carbonyl and nitrile groups

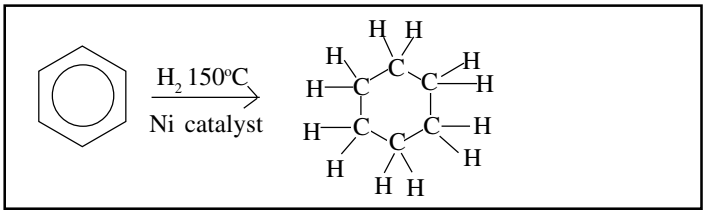


Reactions of the benzene ring

Benzene rings are a common feature of naturally occurring organic compounds. It is important, therefore, to have synthetic methods which can provide routes to the whole range of substituted rings.

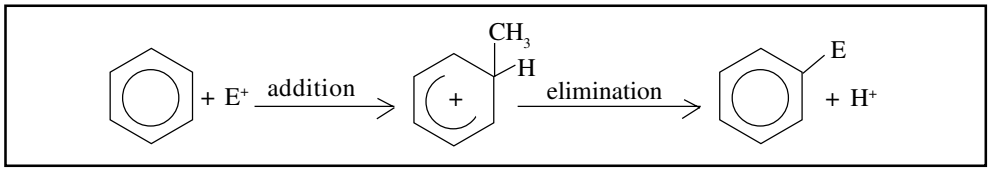
Benzene's stability means that, unlike alkenes, it does not readily undergo electrophilic addition reactions, but it can be forced to react with hydrogen by using a high temperature and nickel catalyst (see Fig 20). This is a free radical addition reaction and a reduction, since it involves the addition of hydrogen.

Fig 20. Reduction of benzene



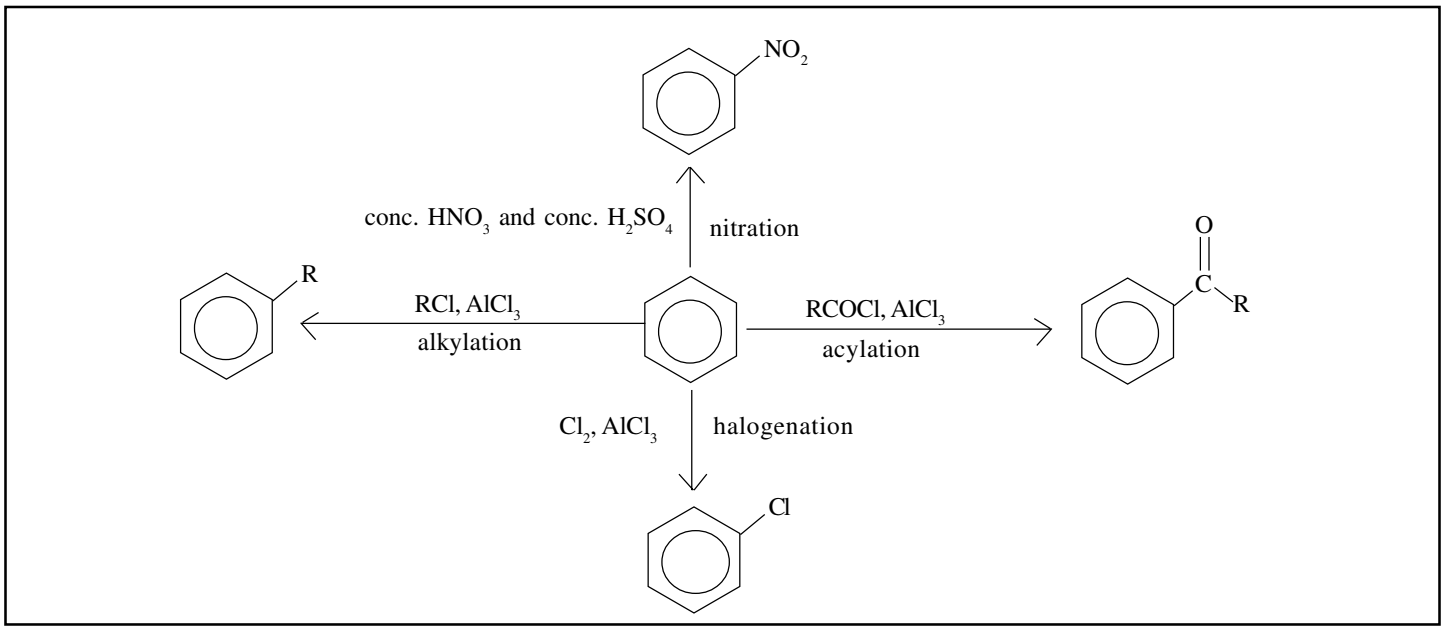
The benzene ring is most often involved in electrophilic substitution reactions (see Fig 21) which retain the stable benzene ring structure. After the initial electrophilic addition, an H^+ ion is eliminated, and so this process can be viewed as an addition-elimination reaction.

Fig 21. Electrophilic substitution of the benzene ring



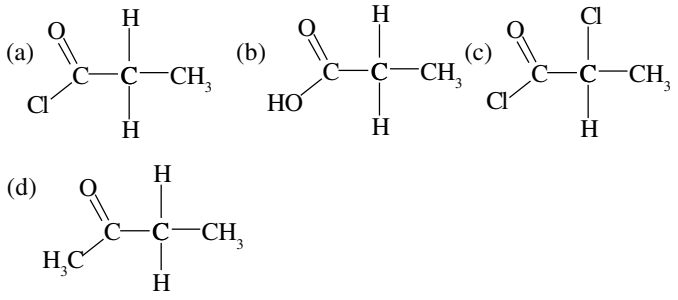
The benzene ring can be substituted by electrophilic halogens (e.g. Cl^+), NO_2^+, alkyl groups (e.g. CH_3^+) and carbonyl groups (e.g. CH_3C^+O). These are all generated in-situ as shown in Fig 22.

Fig 22. Electrophilic substitution reactions of the benzene ring

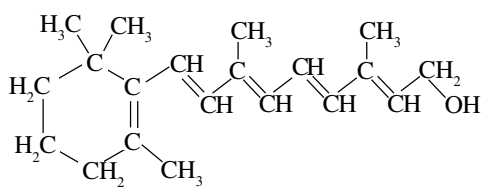


Questions

1. Put these molecules in order of reactivity with nucleophiles, least reactive first. Justify your choice.

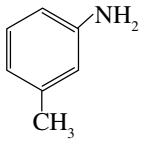


2. The diagram shows the structure of Vitamin A.



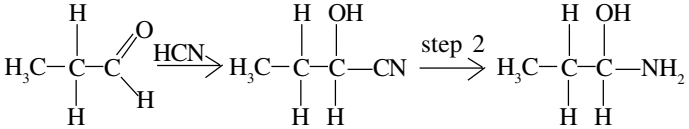
   (a) Draw the product that would be made on complete oxidation of this compound by dichromate(VI).
   (b) What conditions would you need to carry out this oxidation?
   (c) Partial oxidation of Vitamin A would produce an aldehyde. Draw this aldehyde.
   (d) Name and give the formula of a reagent that could be used to convert this aldehyde back to Vitamin A.

3. The diagram shows a substituted benzene compound.



   (a) Draw the organic product of the reaction of this compound with the acyl chloride CH_3CH_3COCl.
   (b) What is the other product?
   (c) Name and draw the mechanism of this reaction.
   (d) Which species in this reaction is behaving as a nucleophile? What feature of this species enables it to do so?

4. Look at the reaction sequence below.



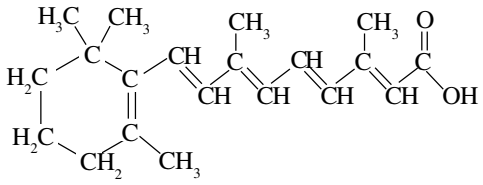
   (a) Name the starting aldehyde.
   (b) Is the second step a nucleophilic addition or substitution? Explain your answer.
   (c) Which species is acting as the nucleophile in this reaction?
   (d) Name and give the formula of a reagent which could be used to carry out Step 2.
   (e) What type of reaction is Step 2?

Answers

1. d – b – a – c

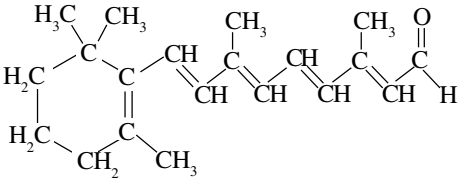
   The ketone is the least reactive, then the carboxylic acid, with its electron-withdrawing OH group, then the unsubstituted acyl chloride (a), with its weaker C-Cl bond. The most reactive is the chloro-substituted acyl chloride because the electronegative chlorine atoms withdraw electron density from the carbonyl carbon, enhancing its δ^+ charge.

2. (a)



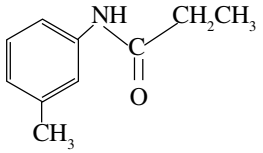
   (b) H_2SO_4 (aq), heat and reflux.

   (c)



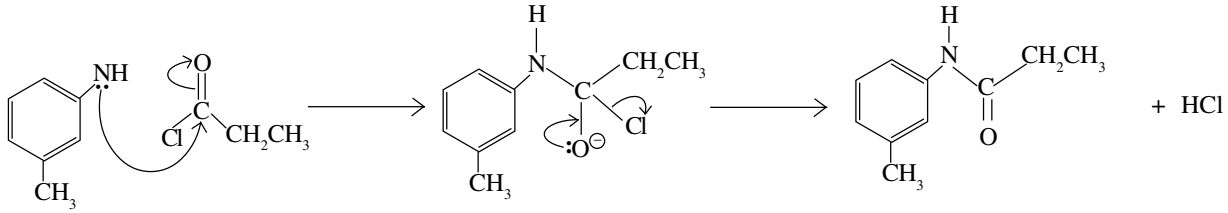
   (d) Lithium tetrahydridoaluminate, $LiAlH_4$
   or sodium tetrahydridoborate, $NaBH_4$.

3. (a)



   (b) HCl

   (c) The mechanism is a nucleophilic addition-elimination



   (d) The amine-substituted benzene is the nucleophile. It is the lone pair of the amine nitrogen atom which enables it to act in this way.

4. (a) Propanal
   (b) It is a nucleophilic addition because one product is made from the two starting materials.
   (c) The nucleophile is the CN- ion.
   (d) Lithium tetrahydridoaluminate, $LiAlH_4$ or sodium tetrahydridoborate, $NaBH_4$.
   (e) Step 2 is a reduction, or a nucleophilic addition of H^- ions.

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