Chem Factsheet

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Avoidable Errors in Reaction Mechanisms at A2-Level

The aim of this Factsheet is to enable 'A2' level candidates to score full marks when answering A2 questions on reaction mechanisms. Mechanisms must be written with care: curly arrows, dots, (representing unpaired electrons), electrical charges and covalent bonds have to be placed correctly to be certain that full marks will be gained.

The Factsheet on, "Avoidable Errors in Reaction Mechanisms at AS level" (No. 187), covers AS mechanisms and these mechanisms have not been repeated in this Factsheet even though they can be examined at A2.

The approach taken is to consider the correct mechanism and then follows a question regarding typical errors that students might make. However, first of all are the meanings of some important terms:

1. Types of Reaction

(a) **Addition:** a chemical reaction in which two (or more) molecules chemically combine to form a single molecule.

e.g. $CH_3CHO + H_2 \rightarrow CH_3CH_2OH$ (also a redox reaction)

(b) **Elimination:** a chemical reaction involving the removal of a small molecule (e.g. H_2O, HBr) from a molecule to leave an unsaturated molecule.

e.g. $CH_3CH_2OH \rightarrow H_2C{=}CH_2 + H_2O$

(c) **Substitution:** a chemical reaction where one atom or group of atoms is replaced by another atom or group of atoms.

e.g. $CH_4 + Br_2 \rightarrow CH_3Br + HBr$ (also a redox reaction)

2. Reacting Species

(a) **Electrophile:** an electron pair acceptor. e.g. $^+NO_2$. Electrophiles are attracted to an electron rich centre and form a new covalent bond by accepting a pair of electrons.

(b) **Nucleophile:** an electron pair donor. e.g. $^-$**:**CN or **:**NH_3 Nucleophiles donate a lone pair of electrons to an electron deficient centre ($C^{\delta+}$) so forming a (co-ordinate) bond with that centre.

3. Reaction Mechanism

A reaction mechanism is a theoretical stepwise description of how a chemical reaction occurs. A mechanism shows what happens to the bonding electrons and lone pairs. It shows which bonds break, which bonds form, changes in lone pairs and any intermediate species involved.

A curly arrow, ↷, shows the movement of an electron pair. The tail is placed at the electron pair (in a covalent bond or a lone pair) and the head shows where the electron pair is to be moved to form a NEW bond or a NEW lone pair.

The name of a type of reaction mechanism is (normally) obtained by combining the name of the type of attacking species with the type of reaction.

(a) Electrophilic Substitution Reactions of Arenes

Arenes (e.g. benzene) can react with reagents that can produce electrophiles. These include nitric acid, alkyl halides, acyl halides, fuming sulfuric acid and bromine. The mechanisms can be divided into four steps:

Step 1. Electrophile formation involving a catalyst.

Step 2. The electrophile attracts the delocalised electron density of the pi bonds of the benzene ring. The electrophile accepts an electron pair from the ring and so bonds with a carbon atom of the ring.

Step 3. Hydrogen ion loss from the carbon atom to which the electrophile is attached. The electron pair of the C-H bond goes into the ring and restores the number of delocalised electrons from four to six.

Step 4. The regeneration of the catalyst.

(i) Nitration: the introduction of a nitro group ($-NO_2$) into a molecule.

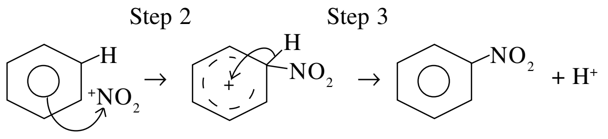
Reagents for benzene: concentrated nitric acid mixed with concentrated sulfuric acid as a catalyst at 60^0C.

Overall equation: $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$

Mechanism

Step 1: Generation of the nitronium ion ($^+NO_2$):

$HNO_3 + 2H_2SO_4 \rightarrow 2HSO_4^- + H_3O^+ + {}^+NO_2$



Note: The intermediate has + charge. Its partial delocalisation must be shown to extend fully from 2nd to 6th carbon atom.

Step 4: $H^+ + HSO_4^- \rightarrow H_2SO_4$

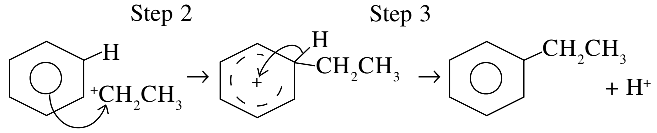
(ii) Friedel-Crafts Alkylation: the introduction of an alkyl group ($-C_nH_{2n+1}$) into a molecule.

Reagents for benzene: an appropriate halogenoalkane ($C_nH_{2n+1}X$; X usually Cl) along with anhydrous aluminium chloride catalyst at about 50^0C.

Overall equation for the formation of phenylethane:
$C_6H_6 + C_2H_5Cl \rightarrow C_6H_5CH_2CH_3 + HCl$

Mechanism

Step 1. $CH_3CH_2Cl + AlCl_3 \rightarrow [CH_3CH_2]^+ [AlCl_4]^-$



Note: Take care to draw the two curly arrows clearly and accurately. Penalties will result if your presentation is poor.

Step 4 $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

(iii) Friedel-Crafts Acylation: the introduction of an acyl group ($-COC_nH_{2n+1}$) into a molecule.

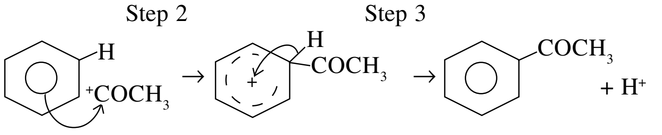
Reagent for benzene: an appropriate acyl chloride ($C_nH_{2n+1}COCl$) along with anhydrous aluminium chloride catalyst at about 40^0C.

Overall equation for formation of phenylethanone:

$C_6H_6 + CH_3COCl \rightarrow C_6H_5COCH_3 + HCl$

Mechanism

Step 1. $CH_3COCl + AlCl_3 \rightarrow [CH_3CO]^+[AlCl_4]^-$



Note: Step 3 in ALL these electrophilic substitution mechanisms produces a proton. Don't forget it!

(iv) Halogenation: the introduction of a halogen atom into a molecule.

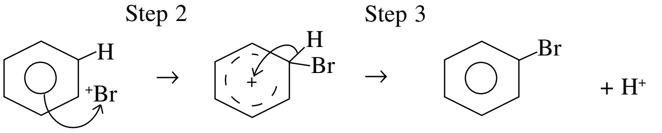
Reagent for benzene: liquid bromine with anhydrous iron(III) bromide catalyst at room temperature.

Overall equation for the formation of bromobenzene:

$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$

Mechanism

Step 1. $Br_2 + FeBr_3 \rightarrow Br^+[FeBr_4]^-$



Note: Remember ALL of the + charges – on the electrophile, the intermediate and the H^+ formed.

Step 4 $H^+ + FeBr_4^- \rightarrow FeBr_3 + HBr$

(b) Nucleophilic Substitution Reactions of Haloalkanes (Halogenoalkanes) with Amines.

The nucleophilic substitution reactions with the nucleophiles OH^-, CN^-, and NH_3 were considered in the AS Factsheet.

The mechanisms with primary, secondary and tertiary amines are analogous to that with ammonia.

The mechanism can be shown in two steps.

Step 1: The attack by the nucleophile on the electron deficient carbon atom and the heterolytic fission of the C-X bond (X usually Cl or Br).

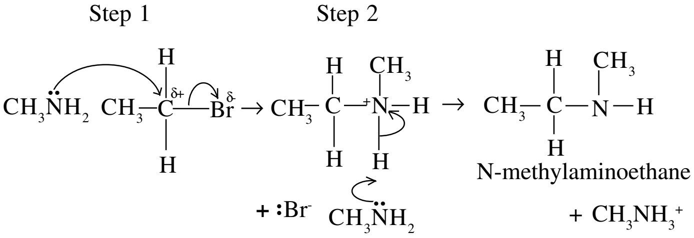
Step 2:The removal of a proton by another molecule of the amine which is now acting as a base, rather than a nucleophile.

e.g. the reaction of methylamine with bromoethane to form N-methylaminoethane.

Overall equation for the first reaction:

$2CH_3NH_2 + CH_3CH_2Br \rightarrow CH_3NH(CH_2CH_3) + CH_3NH_3^+Br^-$

Mechanism



Note: Curly arrows MUST begin at:
(i) lone pairs, i.e. N**:** or
(ii) the centre of a covalent bond, i.e. C-Br & N-H. Also, don't forget the + on the N!

The product, N-methylaminoethane (or N-methylethylamine), is a secondary amine and also a nucleophile since it has a lone pair of electrons on the N atom. Thus, with sufficient bromoethane, a tertiary amine can be formed by an analogous mechanism, (see Q2). The tertiary amine is also a nucleophile and so can react further forming the quaternary ammonium salt, triethylmethylammonium bromide.

(Note: Quaternary ammonium salts with a chiral N atom are possible.)

(c) Nucleophilic Addition Reactions of Carbonyls

Carbonyls have a polar $>C^{\delta+}=O^{\delta-}$. The mechanisms have two steps:

Step 1:`The electron deficient carbon atom ($C^{\delta+}$) accepts an electron pair from a nucleophile and the electron pair of the carbonyl pi bond transfers to the electron rich oxygen atom ($O^{\delta-}$).

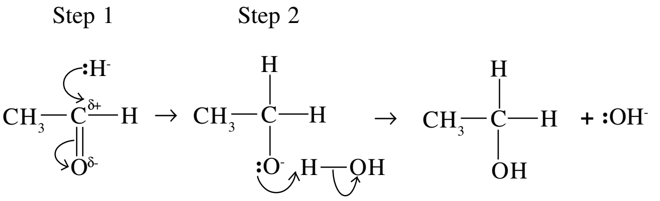
Step 2: The intermediate has an O^- with a lone pair and this gains a proton from water or acid to form the final addition product.

The electron deficient carbon atom is attacked by nucleophiles such as the hydride ion ($:H^-$) and the cyanide ion ($:CN^-$).

e.g. 1. Mechanism for the reduction of ethanal with sodium tetrahydridoborate(III), $NaBH_4$, in water to form ethanol.

Overall equation : $CH_3CHO + H_2 \rightarrow CH_3CH_2OH$

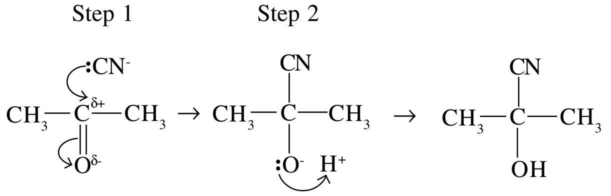
Mechanism



Note: Aldehydes are reduced to primary alcohols. Ketones are reduced to secondary alcohols. Unsymmetrical ketones produce a racemate since the nucleophile is equally likely to attack $C^{\delta+}$ from above or from below the planar >C=O group.

Note. $LiAlH_4$ in dry ether followed by acid hydrolysis is another suitable reducing agent.

e.g. 2. Mechanism for the addition of hydrogen cyanide to propanone.



Note: This reaction gives the product a side chain. Aldehydes and unsymmetrical ketones produce a 50:50 mixture of optical isomers. i.e. a racemate (racemic mixture).

(d) (Nucleophilic) Addition-Elimination Reactions.

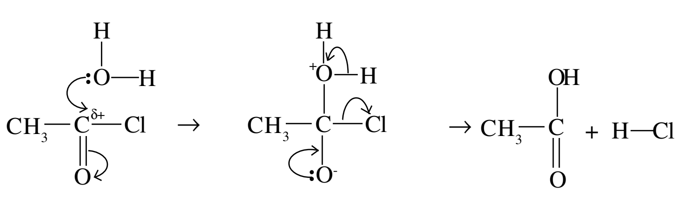
Acyl chlorides (RCOCl) react rapidly with nucleophiles containing O-H or N-H bonds such as water, alcohols, ammonia and amines to give carboxylic acids, esters, amides and N-substituted amides respectively.

The mechanisms can be written in two steps:

Step 1. As for carbonyls above.

Step 2: The carbonyl group reforms and a chloride ion and hydrogen ion are lost.

e.g. The mechanism for ethanoyl chloride reacting with water to produce a carboxylic acid.

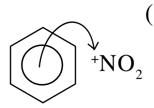


Curly arrows from a: lone pair becomes a bond pair, bond pair becomes a lone pair.

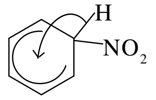
Practice Questions

1. Write each of the following correctly:
   (a) NO^+_2 (b) $CH_2CH_3^+$ (c) CH_3CO^+ (d) $^-AlCl_4$ (e) $CH_3CH_2^+$

(f)



(g)



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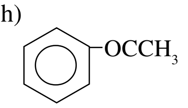
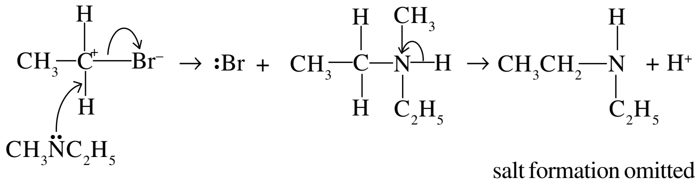
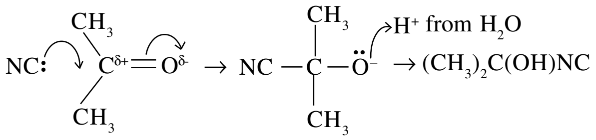


2. Criticise the following nucleophilic substitution mechanism:

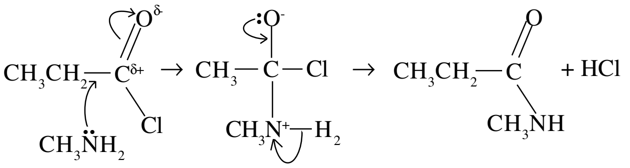


salt formation omitted

3. Criticise the following mechanism of the nucleophilic addition of HCN to propanone.



4. Criticise the following addition-elimination mechanism between propanoyl chloride and methylamine.

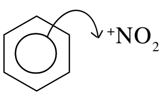


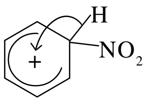
5. State the reagent(s) / catalyst (if any) /reacting species and then write mechanisms for the following conversions.
   (a) Nitrobenzene to 1,3-dinitrobenzene.
   (b) Benzene to 2-methyl-2-phenylpropane.
   (c) Benzene to benzenecarbaldehyde (C_6H_5CHO).
   (d) Methyl benzene to 4-bromomethylbenzene.
   (e) Chloromethane to methylamine.
   (f) Phenylethanone to 2-hydroxy-2-methylpropanenitrile.
   (g) Methanal to methanol.
   (h) Propanoyl chloride to propanamide.
   (i) Methanoyl chloride to ethyl methanoate.

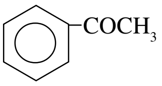
6. $CH_3CH_2—C^+=O$ is an example of an acylium ion. Write an equation showing the formation of this acylium ion from propanoyl chloride and one other substance. Name and outline the mechanism of how $CH_3CH_2C^+=O$ reacts with benzene. Include in your answer the reformation of the other substance.

7. Name and write the mechanism for the reaction of methylamine with bromoethane to form N-methylbromoethane.

Answers

1. (a) $^+NO_2$ (b) $^+CH_2CH_3$ (c) CH_3C^+O (d) $[AlCl_4]^-$ (e) $^+CH_2CH_3$ (f) 

(g) 

(h) 

2. (i) N's lone pair is going to the C—H covalent bond,
   (ii) C and Br have full charges,
   (iii) electrons from the C—Br bond are going to the – charge,
   (iv) negative charge missed off Br,
   (v) positive charge missed off N of intermediate,
   (vi) lone pair missed off N of product.

3. (i) No negative charge on the C atom of the cyanide group,
   (ii) the curly arrow from the C=O goes to δ-,
   (iii) the curly arrow goes from the negative charge on the O to the H^+,
   (iv) the product is $(CH_3)_2C(OH)CN$.

4. (i) CH_2 missed from the intermediate
   (ii) no curly arrow from C—Cl bond to Cl,
   (iii) N^+— H_2 is not H—N^+—H.

5. (a) Conc. HNO_3 / conc H_2SO_4 / $^+NO_2$
   (b) $(CH_3)_3CCl$ / $AlCl_3$ / $(CH_3)_3C^+$
   (c) $HCOCl$ / $AlCl_3$ / HC^+O
   (d) Br_2 / $FeBr_3$ / Br^+
   (e) Conc NH_3 / none / NH_3
   (f) HCN / none / ^-CN
   (g) $NaBH_4$ / none / H^-
   (h) Conc NH_3 / none / NH_3
   (i) CH_3CH_2OH / none / CH_3CH_2OH

   Mechanisms: see the example in the main text and the replace the attacking group by the one here.

6. $CH_3CH_2COCl + AlCl_3 \rightarrow [CH_3CH_2C^+{=}O]\ [AlCl_4]^-$.
   See Friedel-Crafts acylation in the main text.
   $CH_3CH_2C^+{=}O$ replaces $CH_3C^+{=}O$ in mechanism a) iii) of the main text.

7. See b) in the main text.

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