Chem Factsheet

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Organic Chemistry 2: Halogeno-compounds and Grignard Reagents

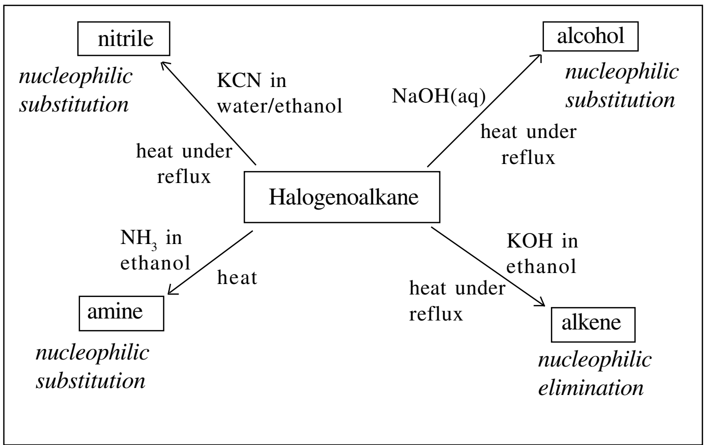
To succeed in this topic you need to:-
- **Have a good understanding of AS-level Organic Chemistry (Factsheets 15, 16, 17 and 27);**
- **Be confident in using organic nomenclature and structural formulae.**

After working through this Factsheet you will:-
- **Have reviewed the chemistry of the halogeno-compounds covered so far;**
- **Know how Grignard reagents are formed;**
- **Know how Grignard reagents are used in a variety of organic preparations.**

Halogeno-alkanes

Fig 1 below summarises the reactions of the halogeno-alkanes.

Fig. 1 Halogenoalkane reactions



Grignard Reagents

The main focus of this Factsheet is on the formation and use of a commonly examined set of reagents derived from the halogenoalkanes - Grignard reagents.

Preparation of Grignard Reagents

Grignard reagents are prepared by refluxing alkyl or aryl bromide or iodide compounds, dissolved in dry ether, with small magnesium turnings.

$$R{-}Br + Mg \rightarrow R{-}MgBr$$
'Grignard reagent'

The Grignard reagent cannot be isolated - it must remain in etheral solution for further reaction.

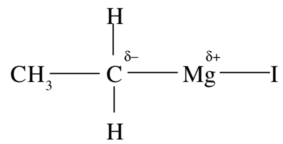
Example of Grignard reagent **preparation**:

$$C_2H_5I + Mg \rightarrow C_2H_5MgI$$

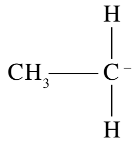
Reaction type: Addition
Conditions: Dry ether solvent
Reflux
Trace of iodine as catalyst

Reactions of Grignard reagents

The Grignard reagent is very reactive.



They contain a δ- carbon, which gives rise to the extremely reactive R^- species i.e. in the above example,



The R^- species is a strong **nucleophile**, which is capable of attacking δ+ carbons in other molecules - hence **carbon chain lengths can be increased.**

1. Reaction with water to form alkanes

$$R{-}MgI + H_2O \rightarrow R{-}H + Mg(OH)I$$

Reaction type: Substitution.
Mechanism: Nucleophilic.

This reaction shows why Grignard reagents must be prepared in dry conditions.

2. Reaction with methanal to form primary alcohol.

Methanal gas is passed into the solution of the Grignard, and the mixture is then hydrolysed with dilute hydrochloric acid.

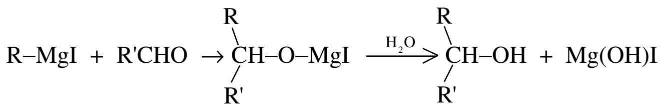
$$R{-}MgI + CH_2{=}O \rightarrow R{-}CH_2{-}O{-}MgI \quad \text{(Nucleophilic addition)}$$

Then:

$$R{-}CH_2{-}O{-}MgI + H_2O \rightarrow R{-}CH_2{-}OH + Mg(OH)I \quad \text{(Hydrolysis)}$$

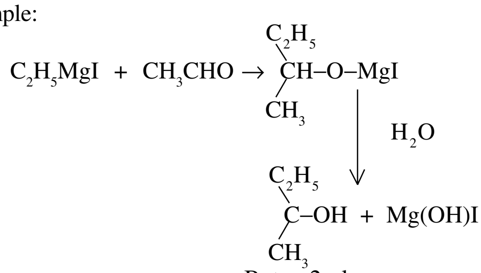
Reaction conditions: In dry ether, followed by addition of dilute acid for hydrolysis.

3. Reaction with other aldehydes to form secondary alcohols.



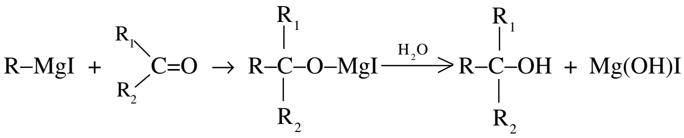
Reaction conditions: In dry ether, followed by addition of dilute acid for hydrolysis.

For example:



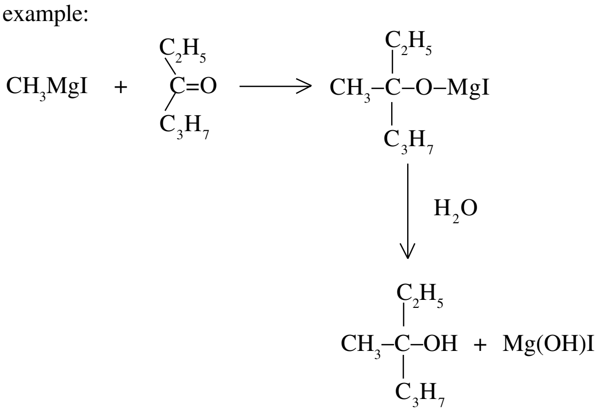
Butan-2-ol

4. Reaction with ketones to form tertiary alcohols.

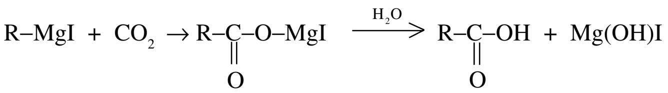


Reaction conditions: In dry ether, followed by addition of dilute acid for hydrolysis.

For example:



5. Reactions of Grignard with carbon dioxide to form carboxylic acid.
Carbon dioxide is bubbled through (or solid CO_2, 'dry ice', is added to) an etheral solution of a Grignard reagent.



Reaction conditions: In dry ether, followed by addition of dilute acid for hydrolysis.

Questions

1. Write the structural formulae of the following compounds:

   (a) 2-bromopropane

   (b) 1,2-dichlorobutane

   (c) 2,2-dibromo-1-chloro-3-methylhexane

2. Explain why Grignard reagents are very reactive.

3. Explain clearly how the Grignard reagent CH_3MgI would be formed from CH_3I.

4. This question relates to the following reaction scheme:

$$CH_3CH_2CH_2I \xrightarrow{\text{step 1}} CH_3CH_2CH_2MgI \xrightarrow{\text{step 2}} CH_3CH_2CH_2COOH$$

   Give the reaction equations and conditions for:
   (a) Step 1.
   (b) Step 2.

5. This question relates to the following reaction scheme:

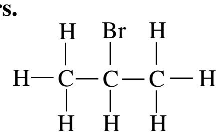
$$CH_3CH_2Br \xrightarrow{\text{step 1}} CH_3CH_2MgBr \xrightarrow{\text{step 2}} CH_3CH_2CHOHCH_3$$

   Give the reaction equations and conditions for:

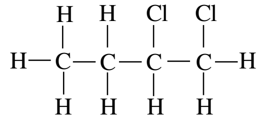
   (a) Step 1.
   (b) Step 2.

Answers.

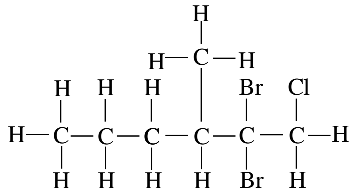
1. (a)



   (b)



   (c)



2. Because they contain a very unstable δ- carbon atom, an extremely strong nucleophile.

3. CH_3I should be dissolved in dry ether
   Magnesium turnings added
   Iodine catalyst
   Heat under reflux

4. (a) $CH_3CH_2CH_2I + Mg \rightarrow CH_3CH_2CH_2MgI$
   Conditions: Reflux in ether
   Iodine catalyst

   (b) $CH_3CH_2CH_2MgI + CO_2 + H_2O \rightarrow CH_3CH_2CH_2COOH + Mg(OH)I$
   Conditions: Addition of CO_2 in dry ether, then dilute acid for hydrolysis

5. (a) $CH_3CH_2Br + Mg \rightarrow CH_3CH_2MgBr$
   Conditions: Reflux in ether
   Iodine catalyst

   (b) $CH_3CH_2CH_2MgI + CH_3CHO + H_2O \rightarrow CH_3CH_2CHOHCH_3 + Mg(OH)Br$
   Conditions: Dissolved in dry ether, then dilute acid for hydrolysis.

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