Chem Factsheet

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Friedel Crafts Reactions

To succeed in this topic you need to:-
- Remember the chemistry of halogenoalkanes and acyl chlorides
- Remember that electrophilic attack on arenes results in substitution
- Be confident with the use of organic nomenclature and structural formulae
- Be familiar with the conventions used when representing organic mechanisms

After working through this Factsheet you will:-
- Understand that Friedel-Crafts reactions are important steps in organic synthesis pathways
- Understand the mechanism of Friedel-Crafts alkylation
- Understand the mechanism of Friedel-Crafts acylation
- Have tried practice questions to gain experience in how these ideas can be called upon in an examination

Friedel-Crafts reactions are used in both the *alkylation* and *acylation* of arenes. One of the most important applications of alkylation is in the preparation of phenylethene, which is, in turn, used in the production of poly(phenylethene) (polystyrene). Acylation reactions produce aryl ketones, which are used for a wide variety of syntheses, including the manufacture of some dyes.

Alkylation

Alkylation is when a hydrogen atom on the benzene ring is replaced by an alkyl group.

In the laboratory, benzene reacts with a halogenoalkane at room temperature, in the presence of an anhydrous aluminium chloride catalyst, to form a phenyl alkane (alkyl benzene).

e.g. $C_6H_6 + CH_3Cl \rightarrow C_6H_5CH_3 + HCl$

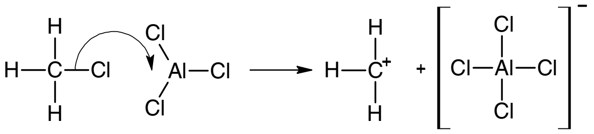
The $AlCl_3$ does not appear in the equation above, as it is a catalyst, but it could be written over the arrow if you wished.

The mechanism for this reaction is best thought of in three stages.

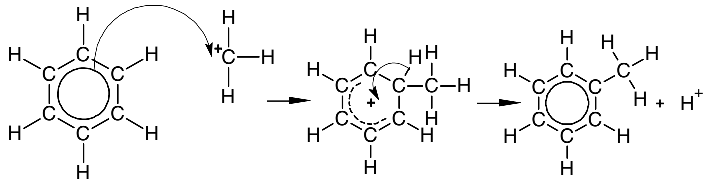
1. **Generation of the electrophile (e.g. $^{+}CH_3$)**
   $CH_3Cl + AlCl_3 \rightarrow {}^{+}CH_3 + [AlCl_4]^-$
2. **Electrophilic substitution of the benzene ring**
   $C_6H_6 + {}^{+}CH_3 \rightarrow C_6H_5CH_3 + H^+$
3. **Regeneration of the catalyst**
   $H^+ + [AlCl_4]^- \rightarrow HCl + AlCl_3$

The process can also be represented using the 'curly arrow' method. In fact, examiners will *expect* this sort of representation for stage 2!

1. Generation of the electrophile



2. Electrophilic substitution of the benzene ring



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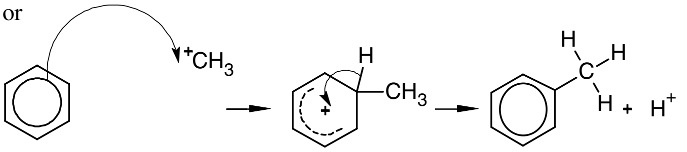
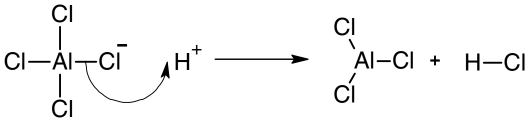
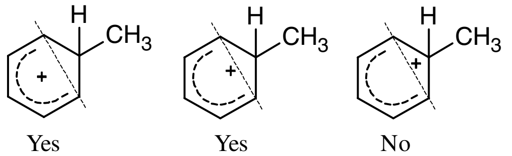


3. Regeneration of the catalyst



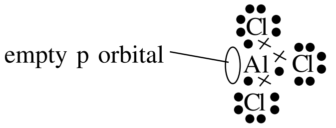
In an exam it is essential for you to pay careful attention to the 'fine detail' when representing mechanisms such as this if you want to access all the available marks. In particular remember the following points:

- A curly arrow represents the movement of a *pair of electrons* – either from a bond or a lone pair – to an electron deficient centre. The arrow **must** therefore start in the correct position. In the example above each arrow starts touching the line that represents the bond from which the pair of electrons comes.
- The intermediate in step 2 *represents* a species in which the delocalised electron system has been temporarily disrupted, as two of the six electrons that form the delocalised 'ring' are now being shared in the new C-C bond. The 'open' part of the partial ring **must point towards** the carbon that is now bonded to the attacking species ($^{+}CH_3$ in this case).
- The positive charge shown in the intermediate species of step 2 represents the temporary electron deficiency of the ring so must be drawn **in** the partial ring and **not on** the carbon atom. A rule of thumb used by examiners is to imagine a line joining the carbon atoms on either side of the carbon that bonds to the attacking species – the + sign must be the opposite side of this line from the carbon atom. Related to this, the dotted line is expected to cover the remaining 5 un-substituted atoms!



The role of the catalyst

An aluminium atom has the electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^1$. When it bonds to chlorine atoms to form $AlCl_3$ one of the 3s electrons is promoted to one of the vacant 3p orbitals, so that there are three unpaired electrons to share with the chlorines' electrons. This means that, in the $AlCl_3$ molecule, there is an empty p orbital in the outer shell of the aluminium atom.



It is the empty p orbital that makes this molecule capable of accepting a pair of electrons, forming a co-ordinate (dative) bond. This means that the aluminium chloride acts as a Lewis Acid in this reaction. (see Factsheet 122).

It is this bond formation with the $AlCl_3$ that 'helps' the C-Cl bond in the halogenoalkane to break, so reducing the activation energy and hence increasing the reaction rate.

Problems with the Friedel-Crafts alkylation

There are two main problems with Friedel-Crafts alkylation as a step in a synthesis:

- multiple substitutions
- rearrangements.

The second of these lies well outside the scope of A level courses but the first problem is due to the ring-activating nature of an alkyl group.

Alkyl groups are electron-releasing and so create a positive inductive effect (+*I*) when attached to a benzene ring.

This means that, with an alkyl group attached, a benzene ring will have a greater negative charge density than when there is no such group attached. If the negative charge density is greater then the ring will be more attractive to an electrophile and hence, more reactive. If the product of the reaction is more reactive than the starting material then the product will react in preference to the un-alkylated starting material and a mixture of mono-, di- and tri-alkylated (and even, possibly, tetra-, penta- and hexa- derivatives) will tend to be formed. This will inevitably reduce the yield of the desired product.

Acylation

Acylation is when a hydrogen atom on the benzene ring is replaced by an acyl group.

In the laboratory, benzene reacts with an acyl chloride at room temperature, in the presence of an anhydrous aluminium chloride catalyst, to form a phenyl alkyle keytone.

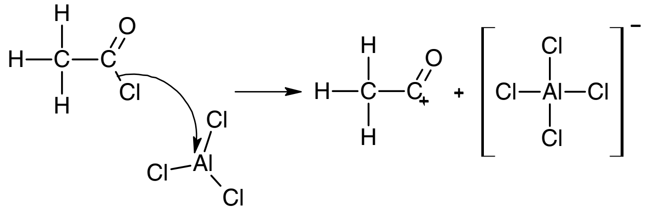
$C_6H_6 + CH_3COCl \rightarrow C_6H_5COCH_3 + HCl$

As in the alkylation reaction, the $AlCl_3$ does not appear in the equation, as it is a catalyst, but it could be written over the arrow. As before, the mechanism for this reaction is best thought of in three stages.

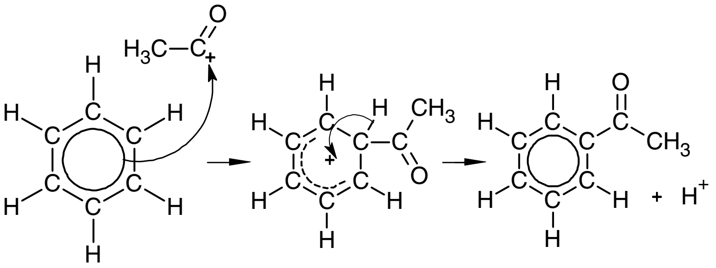
1. **Generation of the electrophile**
   $CH_3COCl + AlCl_3 \rightarrow {}^+COCH_3 + [AlCl_4]^-$
2. **Electrophilic substitution of the benzene ring**
   $C_6H_6 + {}^+COCH_3 \rightarrow C_6H_5COCH_3 + H^+$
3. **Regeneration of the catalyst**
   $H^+ + [AlCl_4]^- \rightarrow HCl + AlCl_3$

The 'curly arrow' mechanism looks very similar to that for alkylation, simply with a different electrophile.

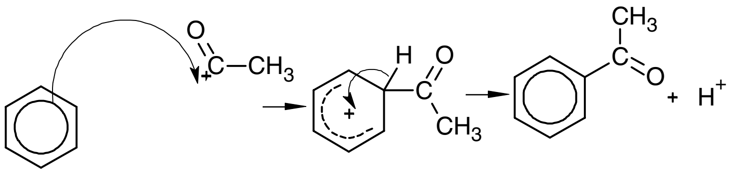
1. **Generation of the electrophile**



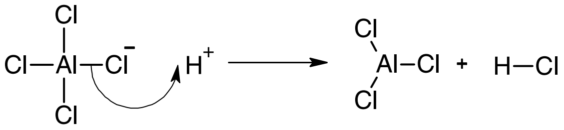
2. **Electrophilic substitution of the benzene ring**



As in the alkylation mechanism (or any mechanism involving benzene) it is again acceptable to use the abbreviated representation of the benzene ring (skeletal formula) when drawing out the mechanism.

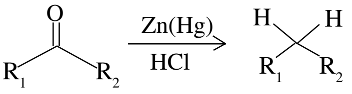


3. **Regeneration of the catalyst**



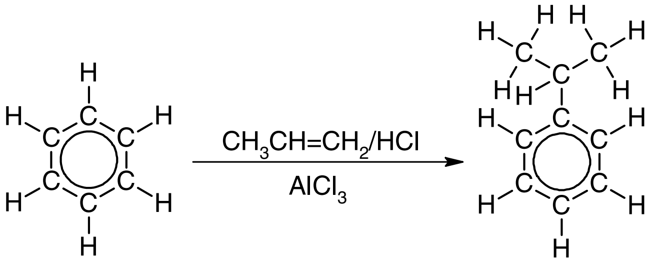
By comparison with the alkylation process, acylation has the advantage that there is very little chance of multiple substitutions reducing the yield of the required product. This is because the acyl side-chain deactivates the benzene ring i.e. it makes the ring less susceptible to further electrophilic attack than the original un-acylated molecule. The acyl group as a whole is electron-withdrawing, due to the electronegative nature of the oxygen atom, so the negative charge density of the ring is reduced; making it less attractive to electrophiles.

If the desired product is an alkyl benzene derivative it is possible to reduce the acyl group to the corresponding alkyl group by means of the Clemmensen Reduction with zinc amalgam and hydrochloric acid.



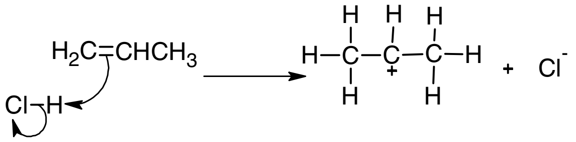
Industrial Applications

Friedel-Crafts reactions are used in a very wide variety of industrial synthesis processes related to situations as diverse as the manufacture of fragrances, dyestuffs and flavourings. The application most frequently quoted as an example at A level is the 'Cumene Process' for the manufacture of phenol (and propanone as a very usefulbi-product). The process is named after the non-systematic name of the intermediate compound formed by Friedel-Crafts alkylation.



2-propylbenzene
(Cumene)

In this reaction the first stage is the reaction between the propene and hydrogen chloride to form the 2-propyl carbocation. (Rem : this is more stable than the alternative 1-propyl carbocation.)



The Cl^- is immediately taken up by the $AlCl_3$ leaving the 2-propyl carbocation to attack the benzene ring as in the detailed mechanism above.

In practice, the industrial process increasingly makes use of Brønsted-Lowry catalysis with phosphoric(V) acid instead of the Lewis acid, $AlCl_3$.

The remainder of the process to form phenol and propanone involves a combination of oxidation and acid hydrolysis.

In an exam question about the reaction of benzene with propene you could be asked to suggest a second, minor, product. This is a reference to the fact that, during the electrophilic attack of the HCl on the propene, it is possible for either the primary carbocation $CH_3CH_2CH_2^+$ or the secondary carbocation $CH_3^+CHCH_3$ to be formed. The greater stability of the secondary carbocation means that its formation is more likely, but a small proportion of the primary carbocation will also be produced, leading to the formation of small amounts of $CH_3CH_3CH_2C_6H_5$ as well as the desired product, $CH_3CH(CH_3)C_6H_5$.

How to answer an exam question on Friedel-Craft's Reactions

1. *The term acylation can be applied to the reactions of ethanoyl chloride with ethylamine and ethanoyl chloride with benzene in the presence of a catalyst.*
   For each of these reactions, write an equation for the overall reaction and name the organic product. Name and outline a mechanism for each reaction and identify a suitable catalyst for the reaction with benzene. (15 marks)

'Free Response' questions of this nature often look more daunting than they actually are – especially as you will just have spent time answering 'Structured' questions where each question is broken down into little bits, each of which is answered in spaces on the question paper. In this case you may well be put off by the fact that there are 15 marks available all in one 'chunk'

The key to success, before you actually start writing an answer, is to break the question down into its component parts. Some of the clues in the question are fairly subtle but nonetheless important.

In the first sentence of this question it is worth noting the use of the plural – "reactions", which should immediately draw your attention to the fact that there will be at least two different things to talk about in your answer and the plan you produce should therefore start by identifying what these reaction are – I would write them down as column headings and then list everything that the question asks you to do under each heading (a likely breakdown of the marks available is shown in brackets).

ethanoyl chloride + ethylamine	**ethanoyl chloride + benzene**
write an equation (2)	write an equation (2)
name the organic product (1)	name the organic product (1)
name the mechanism (1)	name the mechanism (1)
outline a mechanism (3)	outline a mechanism (3)
	identify a suitable catalyst (1)

This list immediately makes it clear that there are nine separate headings under which your answer will be organised, which, in turn, makes the idea of earning 15 marks seem much less daunting.

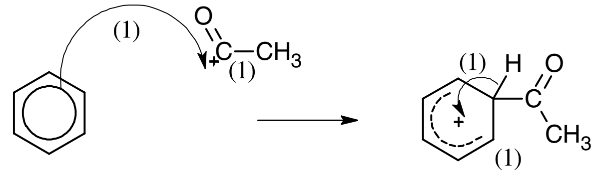
The mark scheme for the 'ethanoyl chloride + benzene' part of the question is given below:

$CH_3COCl + C_6H_6 \rightarrow C_6H_5COCH_3 + HCl$

(1 mark for formula of organic product and 1 mark if all the rest of the equation is correct)

organic product = phenylethanone (1)
Catalyst = anhydrous $AlCl_3$ (1)

Mechanism = electrophilic substitution (1)



i.e. 1 mark for curly arrow from ring
1 mark for formula of CH_3C^+O (NB '+' MUST be on the C)
1 mark for curly arrow from C-H
1 mark for structure of intermediate

So, overall, there are nine possible marks for this part of the question but only a maximum of eight will be awarded. This means that full marks for this section can be earned even if one of the points is overlooked in your answer.

2. *Write a balanced equation for the overall reaction of propanoyl chloride with benzene. Identify a suitable catalyst for this reaction. Write equations to show how this catalyst reacts and how it is regenerated. Name and outline a mechanism for the reaction involving benzene (8 Marks)*

The presentation of this question makes it slightly more 'user-friendly' than the previous one but, once again, the key is to recognise how the question breaks down into sections so that you make sure that you don't overlook any of the marking points in your answer.

$C_6H_6 + C_2H_5COCl \rightarrow C_6H_5COC_2H_5 + HCl$ (1)

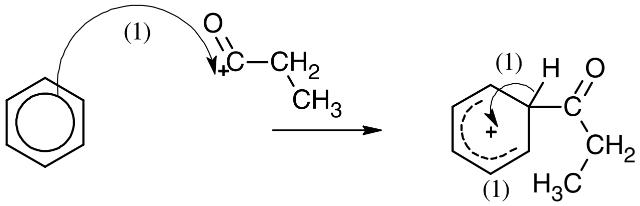
(Catalyst is) anhydrous $AlCl_3$ (or $AlBr_3$; $FeCl_3$; $FeBr_3$) (1)

$C_2H_5COCl + AlCl_3 \rightarrow C_2H_5CO^+ + AlCl_4$ (1)

(*curly arrows would be ignored unless they were drawn FROM the Al which would be penalised. The positioning of the '+' sign on the CH_3CO is not critical in this case).*

$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$ (1)

(Mechanism is) Electrophilic Substitution (1)



1st mark (M1) is for curly arrow from ring to electrophile
M2 is for structure of intermediate
M3 is for curly arrow from C-H of intermediate.

The guidance notes for examiners when applying the mark scheme would include comments such as the following:

- 'horseshoe' in intermediate must not extend beyond C2/C6 for M2
- '+' sign must not be too close to C1 (see guidance in notes above for advice on how to position this '+' sign) for M2
- The arrow for M3 must go into the ring
- The arrow for M1 must go to the C or the '+' sign on the C
- '+' sign in electrophile must be ON the C

Acknowledgements: *This Factsheet was researched and written by Tony Tooth.* ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ChemistryFactsheets*** *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.* ***ISSN 1351-5136***