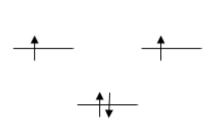
# <u>Tutorial 1</u>

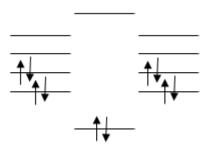
Question 1

a)



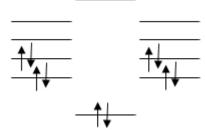
Antiaromatic.

b)



Aromatic.

c)



Aromatic.

c)

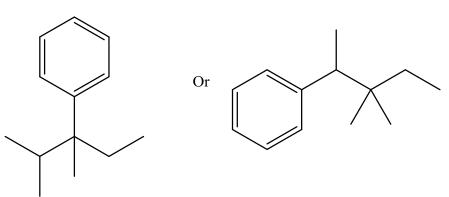
non-aromatic

d) non-aromatic

e) antiaromatic.

The nucleophilic susbsitution via an SN1 mechanism would more likely occur in the compound on the right. This forms an aromatic compound then the bromine is lost. The compound on the left forms an antiaromatic compound which is highly unfavourable.

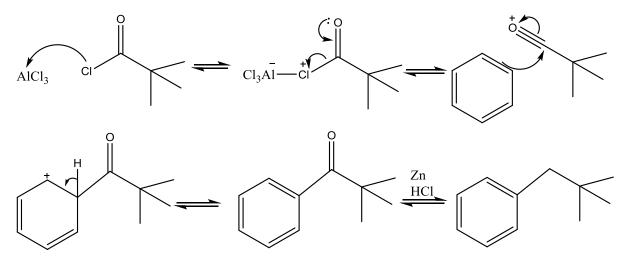
Question 3



The compound on the left will form in a greater quantity as the methyl migration will occur in this reaction. The compound on the right has a secondary carbocation formation which is much less stable than the tertiary carbocation produced in the right compound.

## Question 4

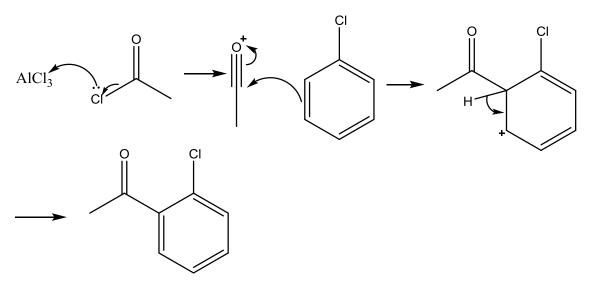
The importance here is avoiding the cationic exchange forming different species. This can be avoided by carrying out an acylation reaction.



Tutorial 2

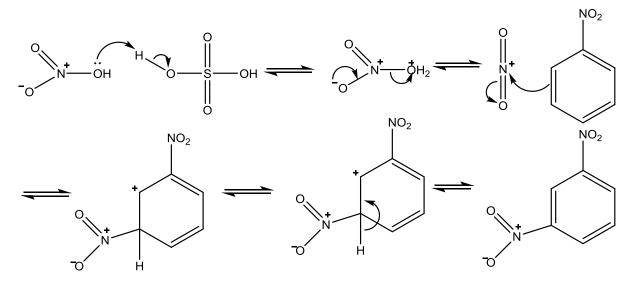
Question 1

a)



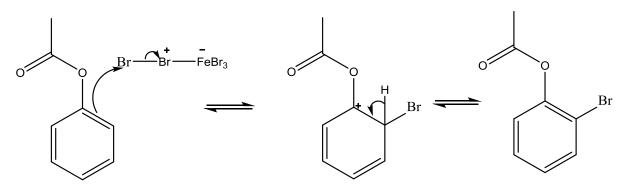
Chlorine is an electron withdrawing group but is an ortho/para directing group due to small amounts of resonance donation that occurs through the lone electrons in the p orbital.

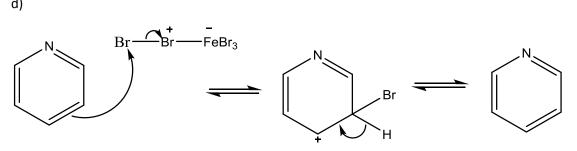
b)

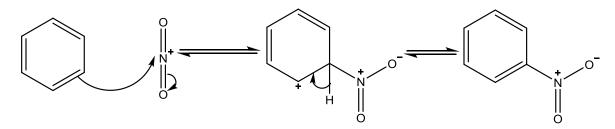


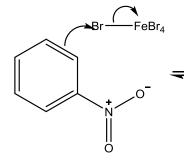
The nitrate group is heavily electron withdrawing and is therefore heavily meta directing. The electron withdrawing effects does cause there to be a lower electron density around the benzene ring making it progressively harder for electrophilic elimination to occur.

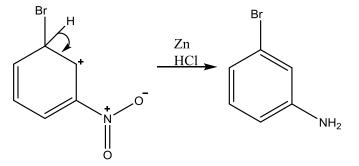
c)

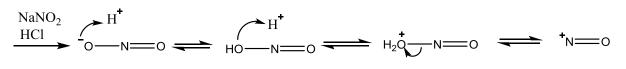


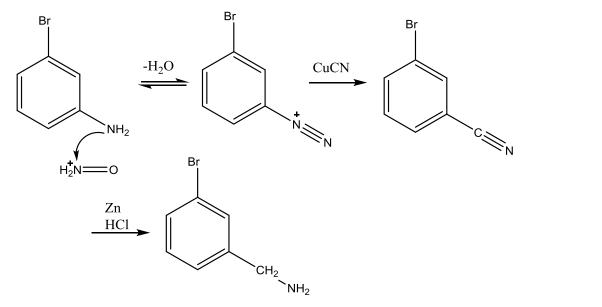










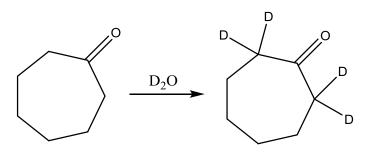


d)

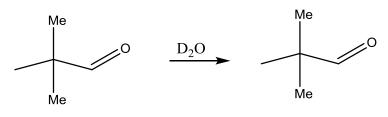
I'm quite sure that this reaction can be done quicker but this uses mechanisms that have definitely been covered.

## Question 3

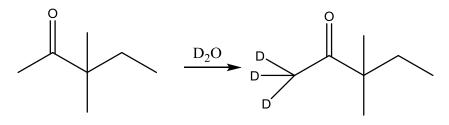
a)



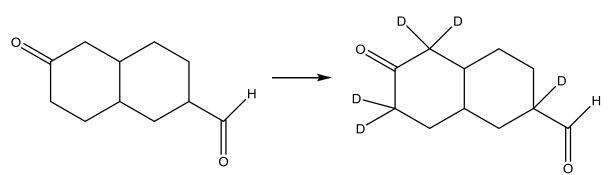
b)

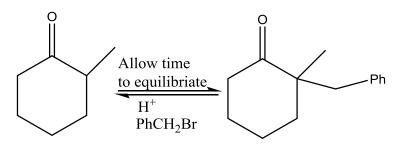


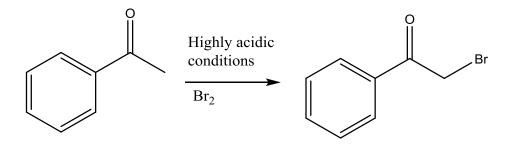
c)



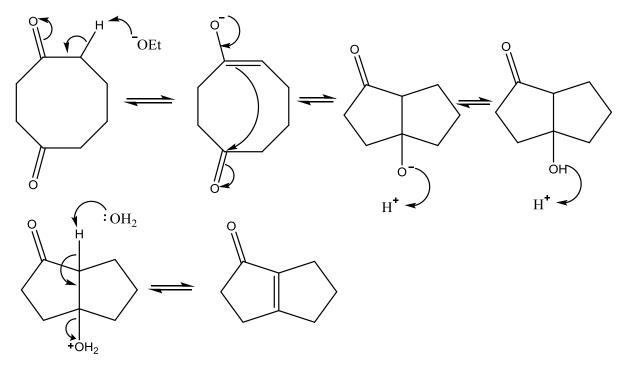
d)

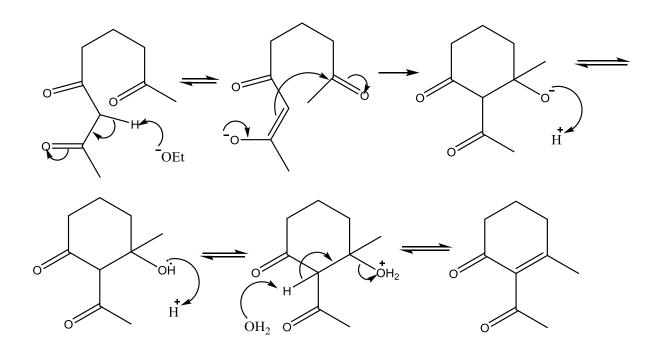


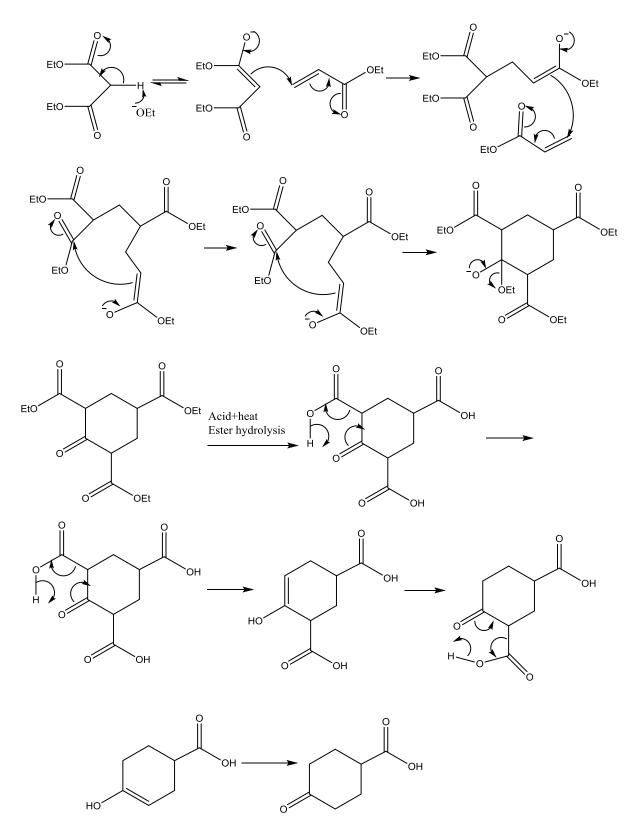




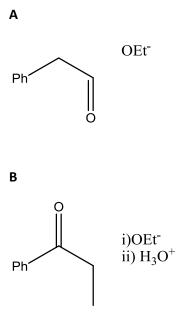
Tutorial 3



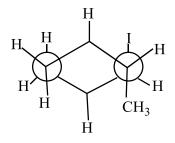




This reaction shows how intramolecular Claisen condensations can be used. This when used in ring formation is known as Dieckmann cyclisation.



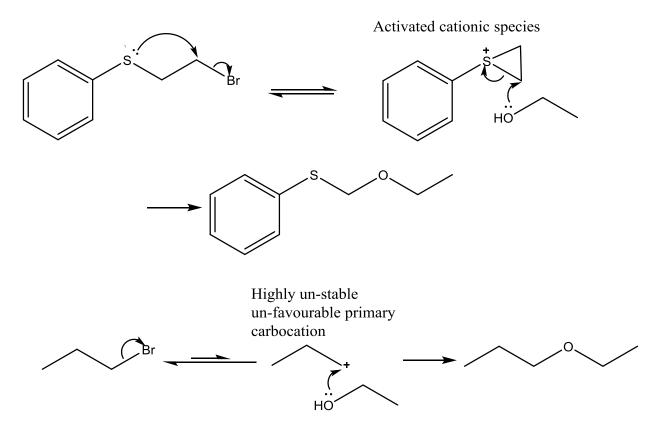
## Question 4



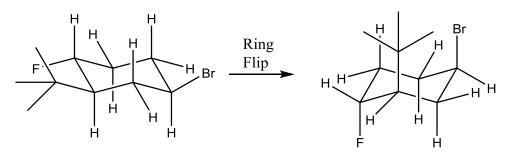
# Question 5

Conformation 1 is preferred due to the large steric strain that is present in the t-butyl group. When all of the species have been put into the equatorial position the steric strain is minimised which makes the formation highly favoured against the conformation where all of the groups are in the axial position.

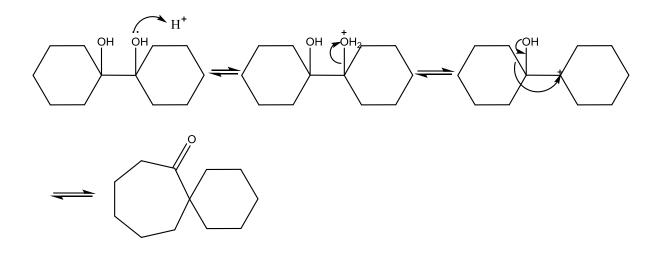
## Tutorial 4

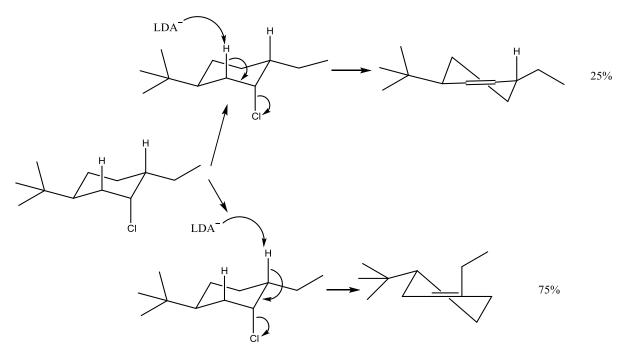


This shows an example of neighbouring group participation. This shows how the lone pair of electrons no the sulphur group can stabilise the carbon groups allowing the loss of the bromine. This then allows the relatively weak nucleophile of the alcohol group to react. This cannot occur in the bottom example due to the formation of a highly unstabilised primary carbocation.



The conformation on the left is the most stable due to the equatorial favourability of the tertbutyl group.





The difference in stabilisation is caused by the alkene being substituted in the bottom compound. This means that formation of this compound is much more favoured.

Compound **6** will not react as the chloride group is equatorial so orbital overlap cannot occur correctly to allow the loss of the chloride group.

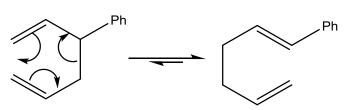
### Tutorial 5 answers

#### Question 1

Concerted:- the bond breaking and bond breaking occurs at the same time.

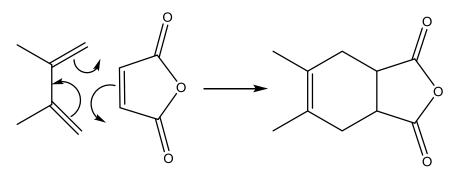
Pericyclic:- the reaction moves through a cyclic arrangement of electron density.

a)



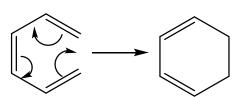
This reaction is a sigma tropic rearrangement as there is no change in the number of  $\sigma$  bonds present. The driving force of this reaction is the formation of a substituted alkene in the product on the right.

b)



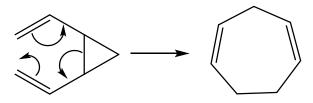
This reaction is a cycloaddition reaction. It is favoured due to an increased number of  $\sigma$  bonds over  $\pi$  bonds.

c)



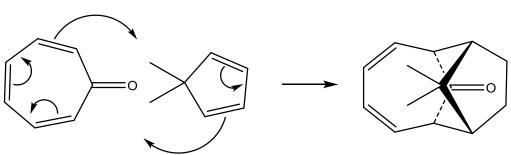
This reaction is an electrocyclic reaction as the number of  $\sigma$  bonds has increased and the number of  $\pi$  bonds has decreased.

d)



This is a sigmatropic reaction, the product has a lower angle strain so is favoured.

e)



This is a cycloaddition reaction, this reaction is favoured due to the increased number of  $\sigma$  bonds compared to  $\pi$  bonds.

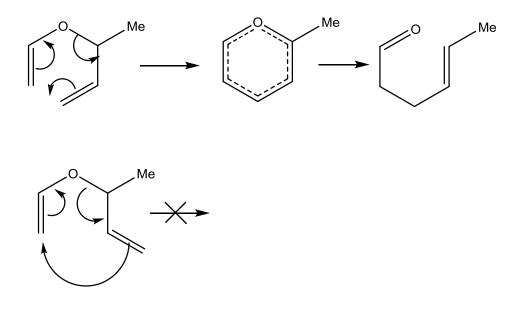
f)

This is an ionic rearrangement.

### Question 3

a)

The Claisen arrangement gives all E isomer due to the fact that a six membered ring needing to be formed. This means that the species need to be in close proximity to one another for the six membered ring to be formed. This is seen below with the following two reaction mechanisms one of these forming the E isomer and the other forming a Z isomer.

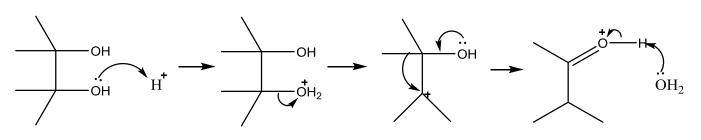


# b)

The photolysis of the compound (3) results in the compound (4). The formation of compound 4 would not normally occur due to the formation of an antiaromatic intermediate. This means that incorrect orbital overlap is present. This can occur when excited as the one of the orbitals is excited allowing overlap between a full and excited orbital.

### Answer 4

a)



b)

7

