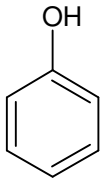
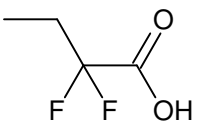
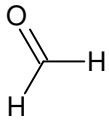
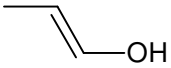
Organic Chemistry Practice Problems: Solutions

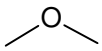
1.
   a. B, A
   b. D, B
   c. A, D
   d. D, A

2.
   a.  Resonance

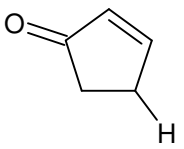
   b.  Electronegativity of fluorine atoms

   c.  Neither is very acidic, but the oxygen will help stabilise

   d.  Resonance

   e.  Electronegativity

   f. $CHCl_3$ Electronegativity

3.  The loss of the proton indicated gives more resonance forms. Make sure you have show this.

4. $CH_3CH_2Li > CH_3CH_2S^- > CH_3CH_2O^- > CF_3CH_2O^- > CH_3CO_2^- > (CH_3CH_2)_2O$

   Nucleophilicity depends on electron availability; and therefore the charge and electronegativity of the charge carrying atom. An organolithium is essentially a carbanion (why?) and very reactive. Sulphur and oxygen have similar electronegativities, but sulphur is more polarisable and so the electrons are more available. The electronegativity of the fluorines reduce electron density on the oxygen, but not as much as the resonance stabilised carboxylate. The ether oxygen comes in last.

1. $R\text{-}Br > R\text{-}O^+H_2 > RO_2CCH_3 > ROMe = ROH$
   (Don't know why? Think about their relative acidities)

2.

a. CH_3O^-
b. HI

3.
a. $C_6H_6CH_2OTs$
b. $CH_3CH_2OH_2^+$
c. CH_3Br

4.
a. Increase
b. Increase
c. Decrease

5. For initial reaction: $CH_3CH_2OCCH_3$
   a. $(CH_3)_3CH_2OCCH_3$
   b. $CH_3CH_2OCCH_3$
   c. CH_3CH_2OH
6. The first step is identifying the reaction. You need to think carefully about the chemistry involved. Out of the amide and the methyl iodide, which would make a better nucleophile or leaving group? You should know that $–NH_2$ groups are poor leaving groups (is NH_3^+ a strong acid? No.) and that the nitrogen has a lone pair that makes it a good nucleophile. Therefore – it a (S_N2 – make sure you know why) nucleophilic substitution of the methyl iodide.

   A good nucleophile has available electrons. Resonance would decrease their availability (they will now be stuck in the ring).

   Therefore: aniline is a poorer nucleophile and is therefore less reactive.

7. Firstly: S_N1, as there is hindrance to a backside attack.
   Secondly: a non-planar carbocation will destabilise the system

8.
a. 2-bromo-2-methylbutane > 2-bromopentane > 1-bromopentane
b. 2-bromo-2-methylbutane > 3-bromo-2-methylbutane > 1-bromo-3-methylbutane
c. 1-bromo-2,2-dimethylpropane > 1-bromo-2-methylbutane > 1-bromo-3-methylbutane > 1-bromobutane

9. Opposite to question 12 – you should be able to explain why.

10. ***STOP!*** Have you actually attempted this question? If not, ***go back and try it now!***

    Are you stuck? First hint: What is your nucleophile? How does it differ from your leaving group?

    Second hint: Does this mean that we might have a competing reverse reaction?

Third hint: What implications might that have on the eventual stereochemistry of the product? (Le Chatelier…)

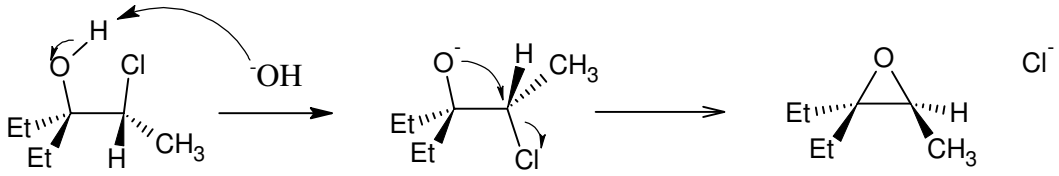
Fourth hint: Think about the reaction as if it were an S_N1. What would you expect? What about if it were S_N2?

Fine. I'll give you the solution.

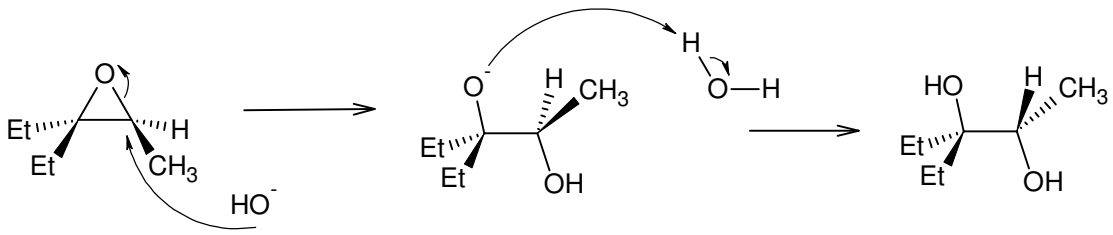
We expect this reaction to eventually produce a racemic mixture, as the Nu = Lg, so the reverse reaction is equally as likely. If the reaction is an S_N1, we will immediately see a racemate being formed, so the rate of iodide incorporation would equal the rate of racemisation. However, if it were S_N2, we would initially form one S molecule from one R. The S enantiomer would cancel out the rotation of *another* R starting material, so the rate of iodide incorporation would be half the rate of racemisation.

11. Woah. Haven't seen that before, right? Can't be S_N1, or we'd get a racemate and can't be S_N2, or we'd get inversion…tricky.

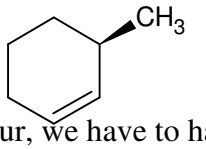
    Perhaps we could get two inversions? You've seen a reaction with Br_2 where something similar to this happens. The ^-OH may not act as a nucleophile, rather as a base to form RO^-, which is a very strong nucleophile (think of an E2 mechanism here).



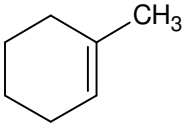
    All okay so far? Just like an elimination except we form an epoxide rather than a double bond. The epoxide can then be attacked by more ^-OH in a second S_N2 reaction at the less hindered position to give the product with the original configuration.



12. For the cis isomer (Br axial):

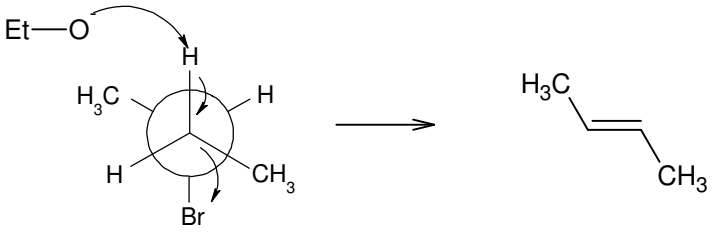
For the trans isomer:
This is the anti-Zaitzev product 

We get it because for E2 to occur, we have to have the H and leaving group in the antiperiplanar arrangement.

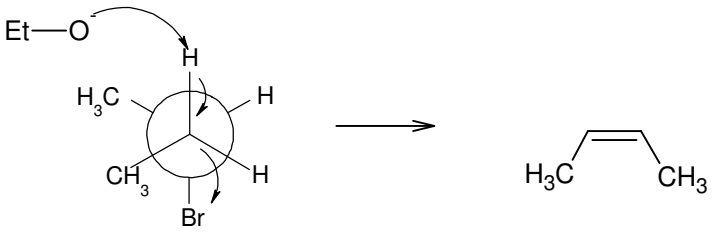
13. 

Note: why can OH act as a leaving group in this instance?

14. E2 reaction of an alkyl halide with a strong base.



This staggered conformation gives trans-2-butene

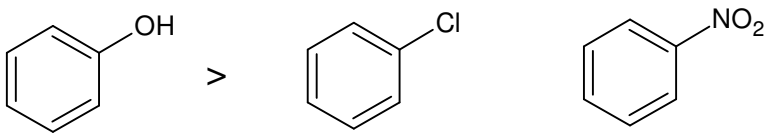


The gauche conformation is less stable, but leads to the cis-alkene.

(Which would be the major product?)

15. The lowest energy conformation of the first isomer has the chlorine atom in an equatorial position, so there is no antiperiplanar H and ring flipping is slow. However, in the second experiment, the lowest energy conformation has the Cl antiperiplanar to 2 protons, the major product is the more substituted alkene.

16. Phenol

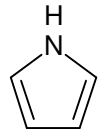
17. 

OH groups are strongly activating, halogens are weakly deactivating and NO_2 is strongly deactivating

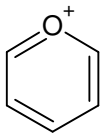
18. –OMe > -Me > $-CO_2Me$
The methoxy and methyl groups are electron donating, but the O on methoxy group makes it more electron donating. The CO_2Me group is electron withdrawing.

19. para > ortho > meta
The t-butyl group will sterically hinder the ortho position, making para the most favoured.

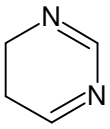
20.



Activated: there are 6π electrons over 5 atoms, which makes it more reactive



Deactivated: the positive charge will decrease reactivity towards electrophiles.

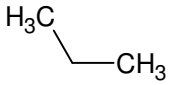
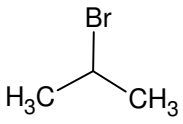
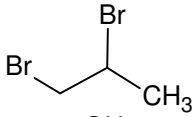
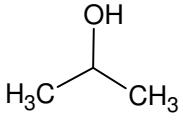


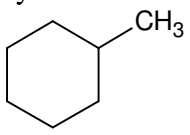
Deactivated: electronegative nitrogen atoms 'hold onto' electrons.

21.

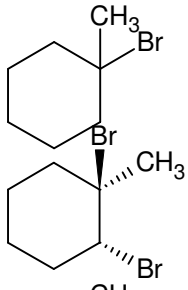
a. 1. $(CH_3)_2CHCl/AlCl_3$
   2. HNO_3/H_2SO_4
b. 1. $CH_3Cl/AlCl_3$
   2. HNO_3/H_2SO_4
   3. $Br_2/FeBr_3$

22.

a. Propene
   i. 
   ii. 
   iii. 
   iv. 

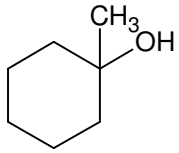
b. Methylcyclohexene
   i. 

ii.

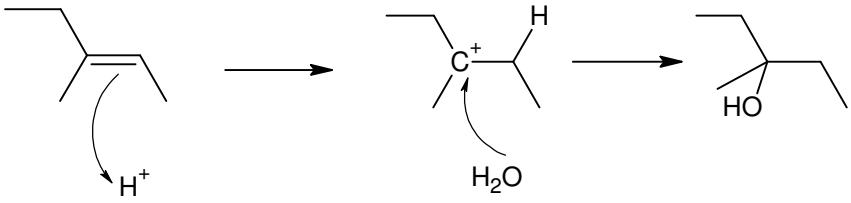


iii.

iv.

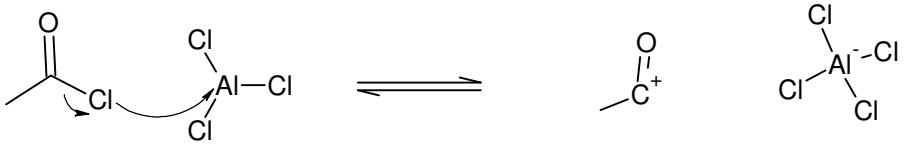


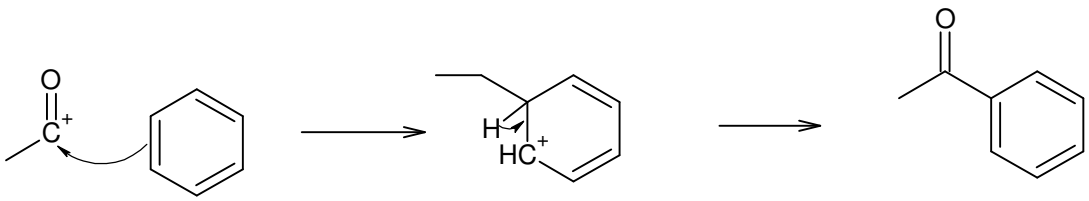
23.



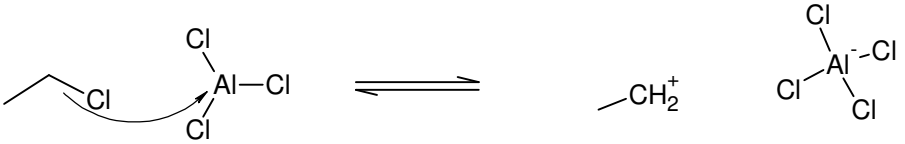
28.

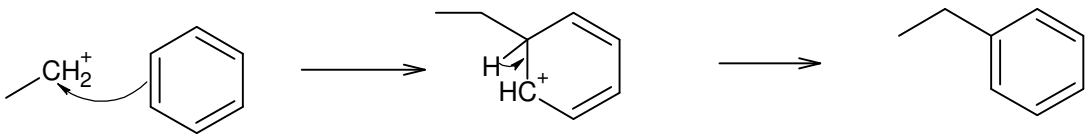
a. Friedel-Crafts acylation:



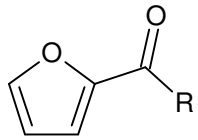


b. Friedel-Crafts alkylation:



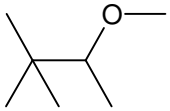


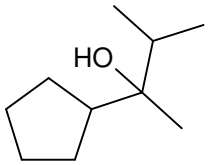
29. You should be able to work out the mechanism using your notes. The major product is this one:

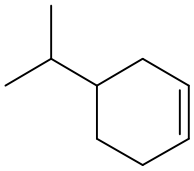


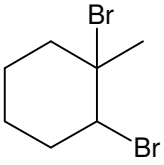
This due to more resonance forms during the reaction. Your mechanism should show you this.

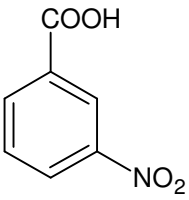
30.

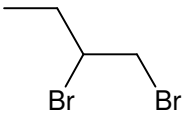
a. 

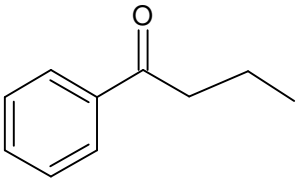
b. 

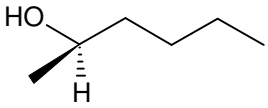
c. 

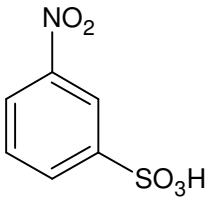
d. 

e. 

f. 

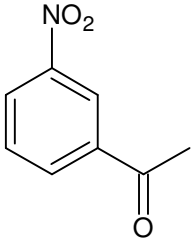
g. 

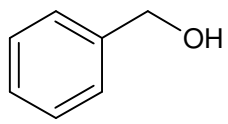
h. 

i. 

31.

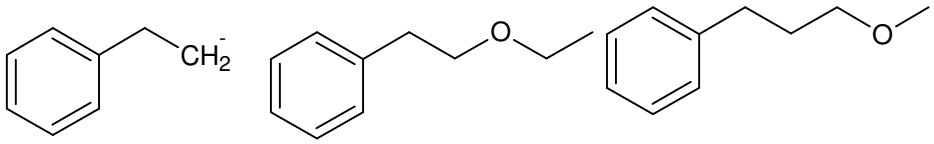
a. This is an addition to a double bond, with the proton going on the unsubstituted end. There are more detailed mechanisms in your notes.
b. S_N2

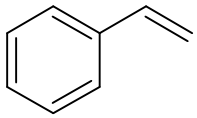
32. 

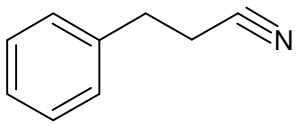
33. 

34. S_N1
35. I think you've probably done this question in your uni tutes. The key is an addition to a double bond that will lead to an amine.

36.

a. 

b. 

c. 

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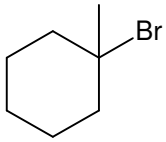
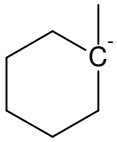
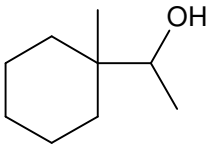
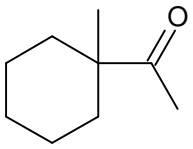
B: 

C: 

E: 

F: 

38.

a. NH_2
b. Alcohol to ester. Possibly NaH and $CH_3CH_2CH_2I$
c. Acid