

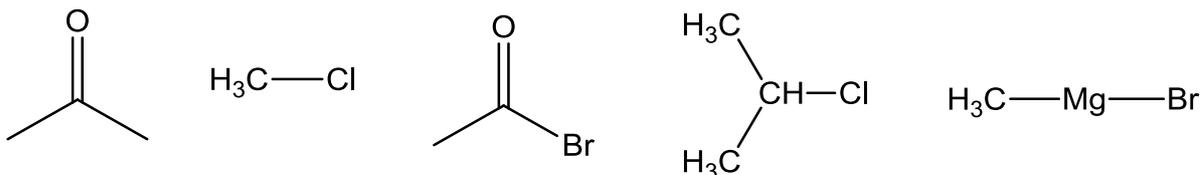
## CHEM1611 Worksheet 7: Addition and Substitution Reactions

### Model 1: Polar Reactions

In many covalent bonds, the electrons are not distributed evenly due to differences in the electronegativity of the two atoms involved. We use partial charges ( $\delta^+$ ,  $\delta^-$ ) to denote the resultant polarisation of the bond.

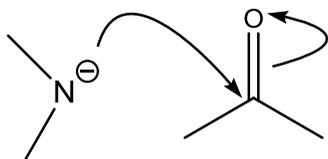
### Critical thinking questions

1. Determine the partial charges on the following molecules. In each case, do you expect the polarisation effect to be large or small?

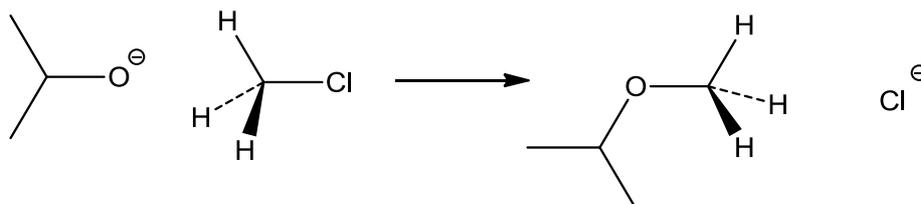


2. Given your knowledge of common organic molecules in chemistry, biochemistry and pharmaceutical science, do you think it is more common for the carbon atom in a functional group to have  $\delta^+$  or  $\delta^-$  partial charge?

We know that there is an attractive force between positively and negatively charged objects. With this in mind, it would seem sensible that the negatively charged nitrogen below would react with the slightly positive carbon of the carbonyl.



3. Draw the product of this reaction, making sure you include where the negative charge ends up.
4. The carbonyl C atom in the reactant is making 4 bonds. How many bonds does it make in the product?
5. Try using curly arrows to describe the movement of electrons in the reaction below. You may find it useful to write the partial charge on  $\text{CH}_3\text{Cl}$  first.

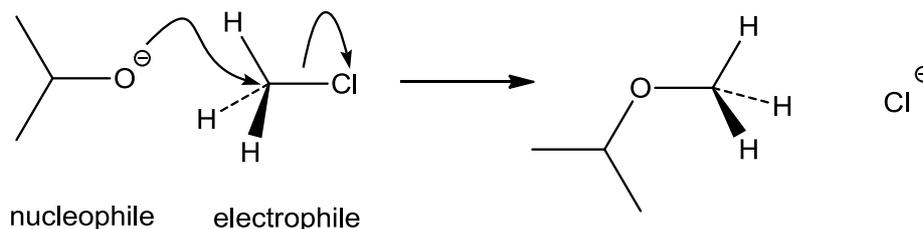


These are both examples of *polar reactions*, the most common type of reaction in organic chemistry. Polar reactions always involve the interaction between an electron rich component (**nucleophile**) and an electron deficient component (**electrophile**).

6. Identify the electrophile and the nucleophile in the two schemes above.

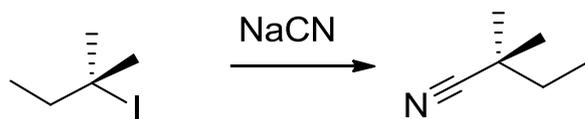
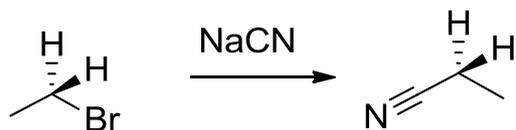
### Model 2: Nucleophilic Substitution

In Model 1, you practised drawing curly arrows in the reaction below in which *substitution* occurs.



### Critical thinking questions

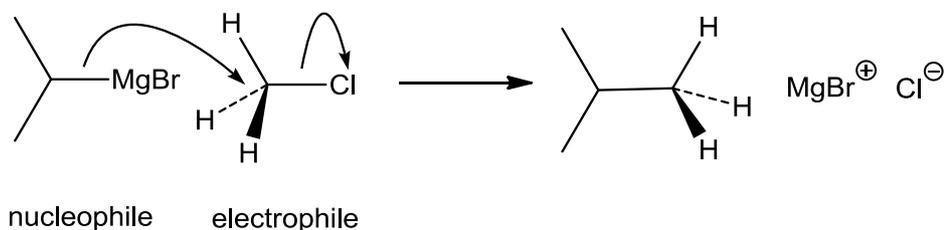
1. Describe *in words* what is happening to the C atom in the alkyl chloride above. (What type of reagent is it being attacked by? What is happening to the groups it is attached to?)
2. The reaction above has been drawn as a one step ('concerted') process. Can you draw an alternative two-step mechanism? (*Hint*: make sure you never draw *more* than 4 bonds to carbon so break a bond first. The first step will lead to a carbocation.)
3. The first mechanism is called  $S_N2$ , the second  $S_N1$ . Can you suggest what each component of these names might refer to?
4. Predict whether the following reactions would proceed via an  $S_N1$  or  $S_N2$  mechanism. To do this, you will need to consider (i) steric requirements (does crowding preventing attack) and (ii) the stability of any intermediates. (*Hint*: NaCN reacts like  $\text{Na}^+ \text{CN}^-$ ).



### Model 3: Using Grignard Reagents

As you noted in answering Model 1, carbon atoms in almost all naturally occurring functional groups have a  $\delta^+$  charge. Almost all organic and biochemical reactions involve nucleophiles reacting with electrophiles. This means that it is very hard to make new C-C bonds!

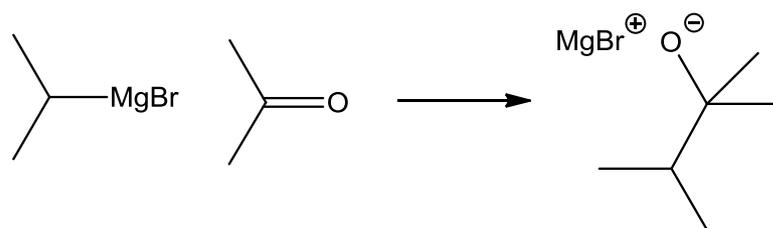
Grignard and related reagents are unusual as they have carbon bonded to a metal so that it has a  $\delta^-$  charge. It can now act as a nucleophile and react to form a C-C bond as in the example below.



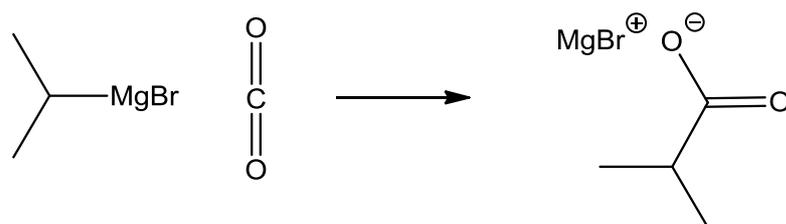
### Critical thinking questions

1. Draw on the partial charges ( $\delta^+$  or  $\delta^-$ ) on the atoms in the two reactants above.
2. Draw on the partial charges on the carbon atoms in the reactants below.

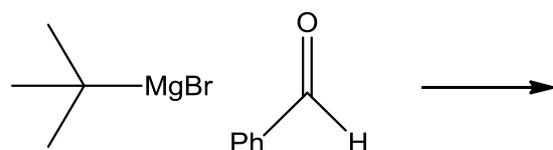
(a)



(b)



3. Add curly arrows to these reactions.
4. Predict the products for the reaction below and draw curly arrows to show how it is formed. (Ph =  $\text{C}_6\text{H}_5$ ).



5. Addition of acid to the products of these reactions leads to  $\text{H}^+$  being attached to the negatively charged oxygen atom. For each reaction above, draw the product that results from addition of  $\text{H}^+$ .

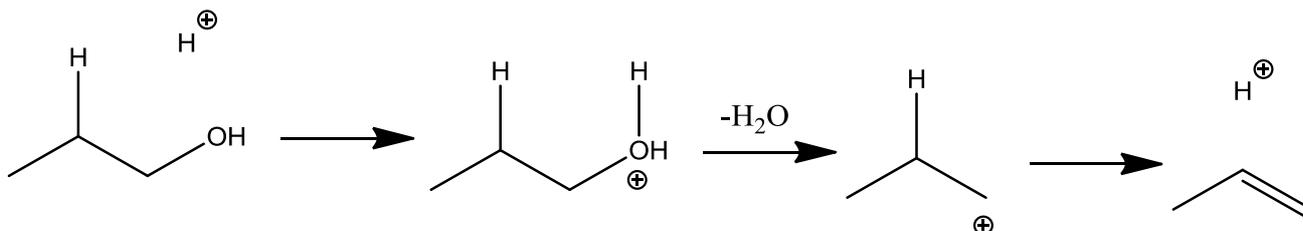
6. It is important to only add the acid *after* the Grignard reagent has reacted. Predict what would happen if acid were added to a Grignard reagent.

### Model 4: Elimination Reactions

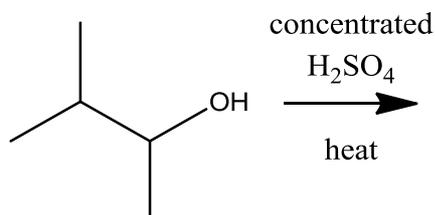
In Worksheet 6, you saw how the C=C bonds undergo electrophilic addition reactions in which a group is added to each end of the double bond and the  $\pi$  bond is lost. Elimination reactions are the opposite: a group is lost from each end of a C-C bond to form a C=C double bond. *Hydration* is a special example of addition:  $H^+$  is added to one end and  $OH^-$  added to the other of the C=C bond. *Dehydration* is the opposite and is a special example of elimination:  $H^+$  is removed from one end and  $OH^-$  removed from the other end of the C-C bond.

### Critical thinking questions

1. Complete the mechanism for the dehydration of 1-propanol to form propene by adding curly arrows.



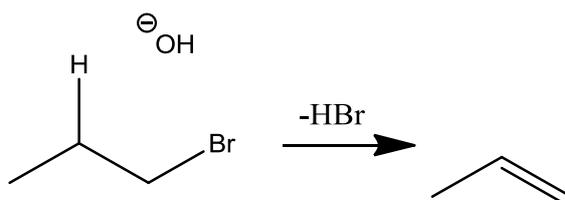
2. The first step involves protonation of the alcohol. Why is this step necessary?
3. What is the overall role of  $H^+$  in the reaction?
4. There are two possible alkenes formed in the elimination reaction below. Draw both.



5. *More* substituted alkenes are *more* stable. Indicate the likely *major* and *minor* products in Q4.

**This is an example of Zaitsev's rule: the major product of an elimination reaction will be the more substituted alkene**

The acid-catalysed dehydration reaction in Model 4 is a common way to make alkenes. A second way is through base elimination:



This is an example of an E2 reaction whereas the acid-catalysed elimination in Model 2 is an E1 reaction.

6. Complete the mechanism by adding curly arrows.
7. Explain the E1 and E2 nomenclature, using what you know about  $S_N1$  and  $S_N2$  reactions from Model 2.