Suggested solutions for Chapter 5

PROBLEM 1
Each of these molecules is electrophilic. Identify the electrophilic atom and draw a mechanism for a reaction with a generalised nucleophile Nu–, giving the structure of the product in each case.

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Purpose of the problem
The recognition of electrophilic sites is half the battle in starting to understand mechanisms.

Suggested solution
We have two cations, two carbonyl compounds and two compounds with σ bonds only. One of the cations has three bonds to a positively charged carbon so that is the electrophilic site as it has an empty orbital. The nucleophile will attack here.

The other cation has a three-valent oxygen atom that cannot be the electrophilic site. The nucleophile must attack the proton instead. Some nucleophiles might attack the carbon atom joined to the cationic oxygen.

The two carbonyl compounds will be attacked at the carbonyl group by the nucleophile. In general, π-bonds are more easily broken than σ-bonds and the negative charge goes on to the electronegative oxygen atom. These anions will not, of course, be the products of the reactions. The first will pick up a proton to give an alcohol but the second might decompose with the release of the stable carboxylate anion.
This type of substitution reaction is discussed in much more detail in chapter 10.

The remaining electrophiles have σ-bonds only, one of which must break. Chlorine is symmetrical so it doesn’t matter which end you attack. You have more choice with MeSCl but the stability of the chloride ion wins the day: attack occurs at sulfur.

PROBLEM 2
Each of these molecules is nucleophilic. Identify the nucleophilic atom and draw a mechanism for a reaction with a generalised nucleophile E⁺, giving the structure of the product in each case.

Purpose of the problem
The recognition of nucleophilic sites is the other half of the battle in starting to understand mechanisms.

Suggested solution
This time there are three anions but two of them (the alkyne and the sulfur anions) have lone pair electrons. We should start our arrows from the negative charges and they are the points of attachment of the electrophile in the product.
The third anion is like the borohydride anion discussed on p. 119 of the textbook. The negative charge does not represent a pair of electrons on Al: all the electrons are in the Al–H bonds and we must start our arrow from one of those. The nucleophilic site is a hydrogen atom.

The remaining nucleophiles have lone pairs. The nitrogen-containing molecule is hydrazine: both nitrogens are the same, and the product is positively charged, so it will lose a proton to become more stable.

The phosphorus compound has four atoms with lone pairs, the P and three O atoms. The lone pairs on oxygen are in lower energy orbitals than the one on phosphorus (P is lower down the periodic table and less electronegative than O), so it is the lone pair on P that reacts. The product is positively charged but this time it can’t lose a proton.

**PROBLEM 3**

Complete these mechanisms by drawing the structure of the product(s).

**Purpose of the problem**

Practice in interpreting curly arrows and drawing the products. Once the arrows are drawn, there is no more scope for decision making, so just draw the products.
Suggested solution

Just break the bonds that are broken and make the bonds that are being formed. Don’t forget to put in any charges and make sure you have neither created nor destroyed charge overall. You might straighten out the products a bit so that there are no funny angles.

![Chemical reaction diagram]

**PROBLEM 4**

Put in the curly arrows on these starting materials to show how the product is formed. The compounds are drawn in a convenient arrangement to help you.

![Chemical reaction diagram]

**Purpose of the problem**

To encourage you to be prepared to try and draw mechanisms for reactions you have never seen and to show you how easy it is.

**Suggested solution**

Just work out which bonds are lost and which are formed and draw arrows out of the one into the space for the other. Start your arrows on a source of electrons: an oxyanion in both these cases. End your arrows on an electronegative atom: oxygen in the first and bromine in the second example here.
Don’t worry if your arrows are not exactly the same as ours – so long as they start and finish in the right place they’re all right. The notes on the mechanisms are just to help you see what is going on: you would not normally include them. The second reaction looks more complicated than the first but it is actually easier: just move electrons through the molecule.