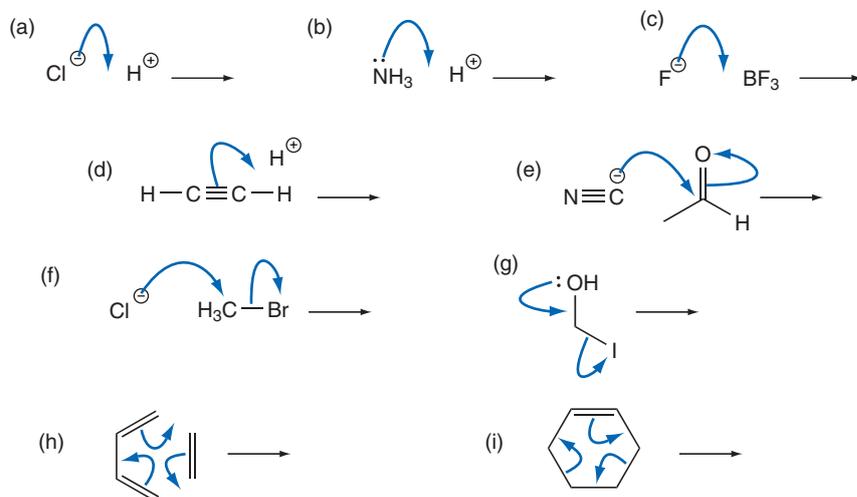
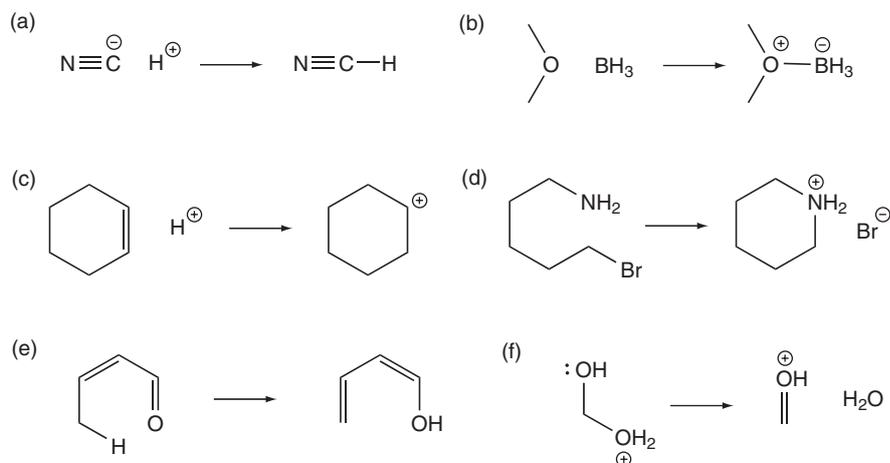


10 Describing reactions using orbitals

10.1 By following the implications of the curly arrows, determine the products of the following reactions

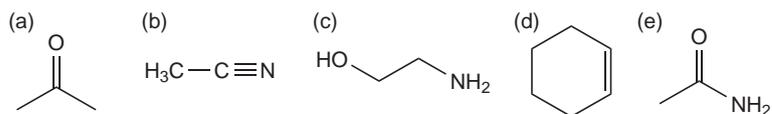


10.2 Draw the appropriate curly arrows for the following reactions (if your arrow originates from a lone pair, indicate this)

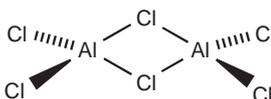


10.3 Explain why it is likely that the most favourable interaction between two molecules will be between the HOMO of one and the LUMO of the other.

Identify the HOMO in each of these molecules and hence suggest the position at which each would be most easily protonated. Draw a curly arrow mechanism for the protonation in each case.



- 10.4 Under normal conditions pure BF_3 is a gas, but it can be purchased from chemical suppliers as a solution in ethoxyethane (diethyl ether, Et_2O). Describe the interaction between BF_3 and the solvent, and draw a curly arrow mechanism for the interaction you suggest. Do you think that BH_3 might also be transported in this way?
- 10.5 At high temperatures in the gas phase aluminium trichloride exists as discrete AlCl_3 molecules which have a trigonal planar structure. At lower temperatures, a dimer Al_2Cl_6 is formed, and this species is also found in molten aluminium trichloride. The structure of the dimer is illustrated below (any formal charges are not shown)



Identify the HOMO and the LUMO in an AlCl_3 molecule and hence explain how a reaction between two such molecules can give rise to a dimer with the structure shown. Assign any formal charges required, and explain why the dimerization must be an exothermic process.

- 10.6 Protonation of cyclohexene gives an ion **A** which reacts with water to give a species **B**



Identify the HOMO in cyclohexene and hence determine the structure of **A**; draw a curly arrow mechanism for its formation. Consider the possible HOMO/LUMO interactions between **A** and H_2O , and hence predict the structure of **B**, drawing a curly arrow mechanism for its formation.

- 10.7 (a) Assuming the C and N to be sp hybridized, draw up a description of the bonding in CN^- and hence identify the HOMO.
 (b) By considering the likely orbital interactions, predict the initial product of the reaction between CN^- and methanal. Draw a curly arrow mechanism for your proposed reaction.
- 10.8 Cyanides (nitriles) $\text{R}-\text{C}\equiv\text{N}$ react hardly at all with H_2O , but under acid conditions their reactivity is greatly enhanced. By considering the orbitals involved, explain why protonation of a nitrile enhances its reactivity towards nucleophiles. In your answer be sure to specify the site of protonation, and give a curly arrow mechanism for the initial reaction of the protonated nitrile with H_2O .
- 10.9 Compound (a) is readily available and is stable under normal conditions, whereas compound (b) is not listed by any chemical supplier. Why is this?

