

## NOTES ON ARROW PUSHING (CURLY ARROWS)

These notes are intended to be used as a supplement to your 1<sup>st</sup> year lectures notes. Some important concepts are underlined, others which are treated only briefly here have been italicised; for more detailed coverage reference should be made to P. Sykes "A Primer to Mechanism in Organic Chemistry".

### **Introduction**

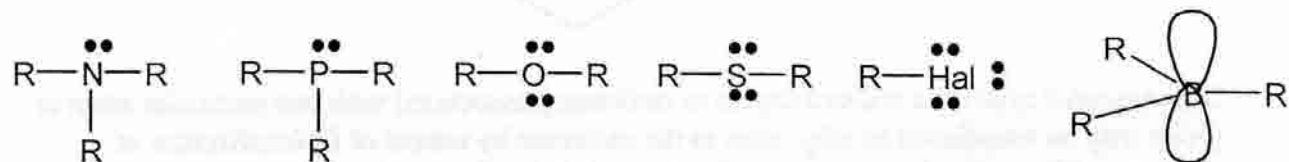
During reaction between organic molecules a number of covalent bonds are broken and formed. Since bonding is associated with electrons, the process of reaction may be considered as a redistribution of electrons between the molecules. The organic chemist uses 'arrow-pushing' to express the ways in which such electron redistribution may occur, i.e. he/she attempts to define possible mechanisms for the reactions. Subsequently the organic chemist tries to decide which of the many mechanistic possibilities is the most likely but this may require consideration other than simple 'arrow-pushing'. Before attempting to 'arrow-push', however, the organic chemist must have an idea of the electron distribution in the reactant molecules and how this distribution will influence reactivity.

### **Electron Distribution in Molecules**

Certain atoms in molecules may be considered as being relatively electron rich or electron poor and these atoms define Nucleophilic (nucleus seeking) or Electrophilic (electron seeking) centres respectively. Consider first that part of the Periodic Table which is of most concern to the organic chemist:

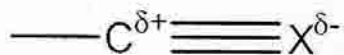
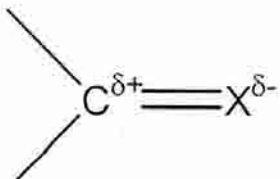
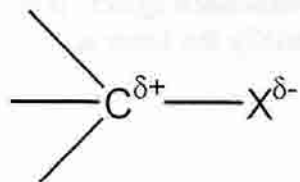
H						
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K						Br
						I

1. Elements to the right of those in Group IV bear lone pairs of electrons in their neutral compounds. These elements, therefore, represent electron rich centres in neutral molecules. Conversely, elements (except H) to the left bear low-lying, empty p-orbitals in their neutral compounds and these define electron poor centres.

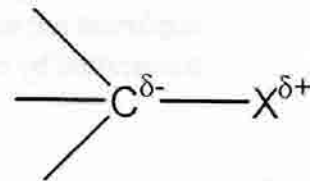


2. If 1. were the only criterion of electron 'density' then H and C (or Si) should be neither electron rich nor poor in their neutral compounds. However, they are made so by virtue of a property of the elements known as Electronegativity. This property determines to which atom bonding electrons will be most attracted and this resultant Bond Polarisation will define which atom is relatively electron deficient or rich:

X more electronegative than C or H



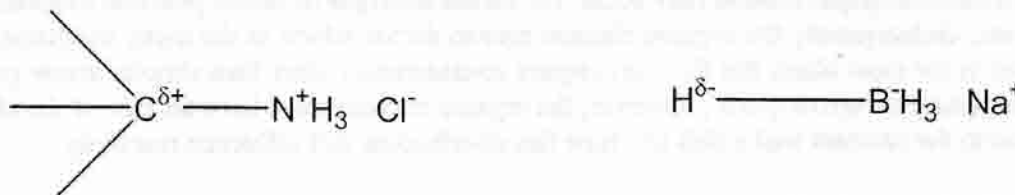
X more electropositive than C or H



This polarisation is known as the *Inductive Effect* of a particular atom and is usually represented either as above or as:



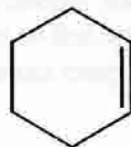
3. Atoms which are charged by virtue of dative covalent bonding are neither electron poor nor rich centres but induce a relative deficiency or excess in adjacent atoms:



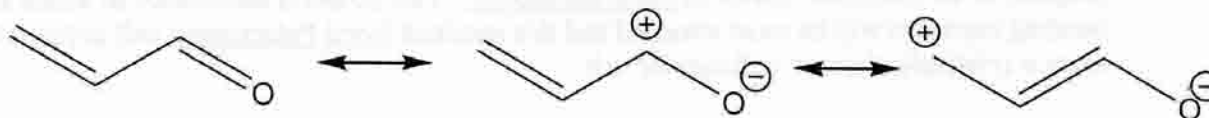
4. Atoms which are charged by virtue of removal of an adjacent atom with or without the bonding pair of electrons are electron poor or rich respectively:



5. Isolated  $\pi$ -bonds represent relatively rich electron centres because electrons in  $\pi$ -orbitals are less tightly bound to the atoms than are those in  $\sigma$ -orbitals. A  $\pi$ -bond is, therefore, an example of a nucleophilic centre not associated with one particular atom.




6. In *conjugated* systems a relative excess or deficiency associated with one particular atom or group may be transferred to other sites in the molecule by means of *Delocalisation* of electrons. The molecule is then considered as a hybrid of a number of structures each contributing to a different extent to the final form. This is the essence of *Valence Bond Theory*.



The resultant polarisation caused by this delocalisation is known as the *Resonance Effect*. It is important not to confuse this with the Inductive Effect (section 2). Essentially the latter is transmitted by  $\sigma$ -electrons and the former by  $\pi$ -electrons.

## Mechanics of Arrow-Pushing

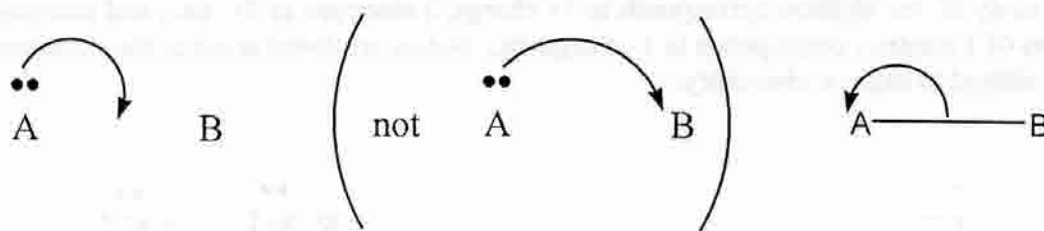
7. "Double-headed", curved or curly arrows () are used to denote the path of localised electron pair movement in reactions and, by definition, arrows point in the direction in which electrons are thought to be proceeding:



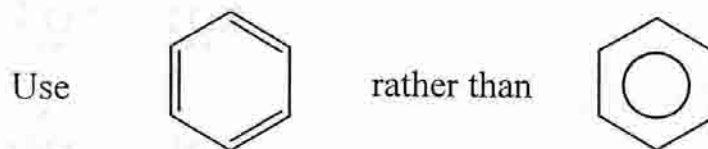
Other types of arrows are used in organic chemistry and curved (curly) arrows must not be confused with arrows to denote the following:



7. Curved arrows describe either formation or fission of covalent bonds. Almost all bonds in organic chemistry are of the 2-centre, 2-electron type i.e. the bonding of two atoms is defined by the presence of a pair of electrons between them. Therefore, the formation of such a bond must be denoted by an arrow whose head terminates in the space between the two atoms where the electrons will be bonding in the product; conversely, the fission of such a bond must be denoted by an arrow which begins at the bond between the atoms where the electrons are bonding in the reactant.
- Not all electron pairs are involved in bonding. These non-bonding, lone pairs are associated with particular atoms (section 1) and they may be used to form a new bond. Alternatively, they may be formed by fission of an old bond. Therefore, arrows may also begin and terminate on individual atoms.



8. In conjugated systems (e.g. benzene) where electron pairs are delocalised over more than two atoms, arrow pushing considers the system in terms of localised  $\pi$ -bonds, i.e. in terms of any valence bond structure (section 6). This is an obvious simplification but nevertheless the method works well in most cases.



9. In free radical reactions the electrons do not move as a pair but singly. The redistribution of single electrons is denoted by a single-headed, curved (curly) arrow.



These arrows obey the same rules as their double-headed counterparts, i.e. they must start or finish on atoms or between atoms. Therefore, formation and fission of bonds are again the dominant processes.

10. Since each electron is associated with one negative charge, any redistribution of electron pairs will result in the development of full charges whereas redistribution of single electrons will not. In order to understand this point consider covalent bond formation, A-B, from the electrons of its constituent atoms and subsequent bond fission. Each atom donated one electron to the formation of this bond and, considering the bond as a separate 2-electron entity, we may represent this as:



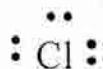
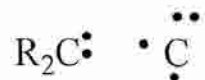
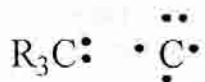
The movement of this bonding electron pair onto either A or B leaves a single + charge on the one atom and results in 2- + 1+ = 1- charge on the other. The arrow pushing for this process and its reverse is then:



However, in free radical processes there is no net transfer of an extra electron from one atom to the other and, therefore, no charge development. The arrow pushing for this process and its reverse is:

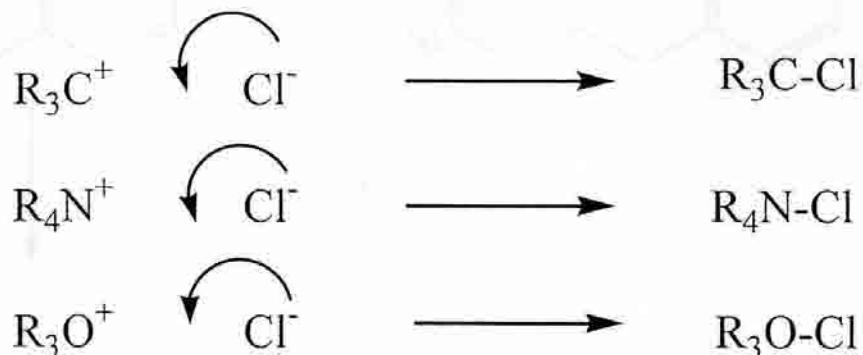


11. Now we need to decide whether a particular atom in any species should bear a charge. In order to do this, first replace the groups bound to that atom by one electron each i.e. by that atom's share in the covalent bond electrons. Then count the total number of electrons surrounding the atom, including lone pairs, and compare it to the number which the atom has in its atomic state. A deficiency of one electron corresponds to 1+ charge, 2 electrons to 2+, etc., and conversely, an excess of 1 electron corresponds to 1- charge etc. Below are listed some of the common species encountered in organic chemistry:





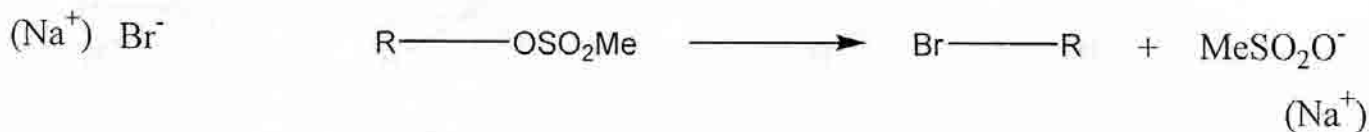
Note also the difference between  $^+CR_3$  and  $^+NR_4$  or  $^+OR_3$  species. The first has a total of 6 electrons around carbon (a carbenium ion or carbocation) whereas the last two both have 8 electrons around the central atom (ammonium, oxonium ions). As a consequence of the Octet Rule the first species will be attacked by species bearing an available lone pair to complete the octet (nucleophilic attack) whereas the last two will not suffer such attack:



12. Another consequence of the Octet Rule is that any nucleophilic attack on a 1<sup>st</sup> row element in a molecule which already has a share of 8 electrons must result in displacement of a pair of electrons which become associated with another atom i.e. bond formation and bond fission accompany each other during reaction in such cases:



15. When writing a mechanistic equation electroneutrality must be maintained i.e. all charges (including counterions) on both sides of the equation must balance out. If, as is often the case, the counterion is omitted, then each side of the mechanistic equation must maintain the same excess of the same charge e.g.:

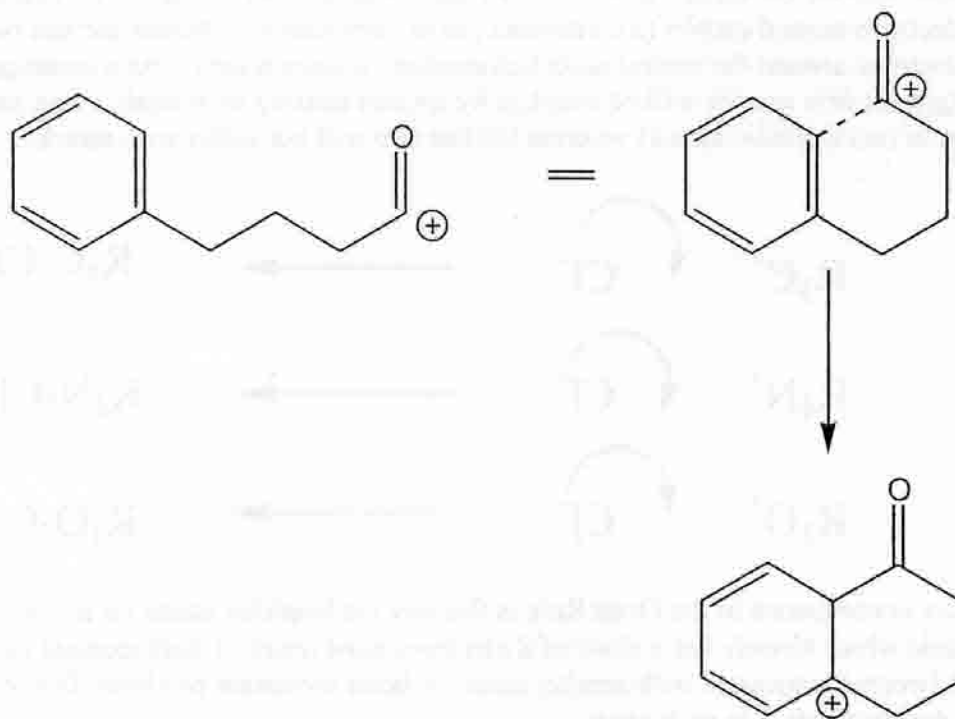


16. Where an arrow indicates movement of a pair of electrons onto or away from an atom the position of the head or tail of the arrow is obvious. However, in the formation of a new bond the terminus of the arrow head is sometimes difficult to determine. In these cases it is helpful to draw the formulae so that atoms which will become bonded in the product are close and then draw a dotted line between these atoms. The terminus of the arrow head is on the dotted line since this represents approximately the final position of the new bond e.g. :

Intermolecular

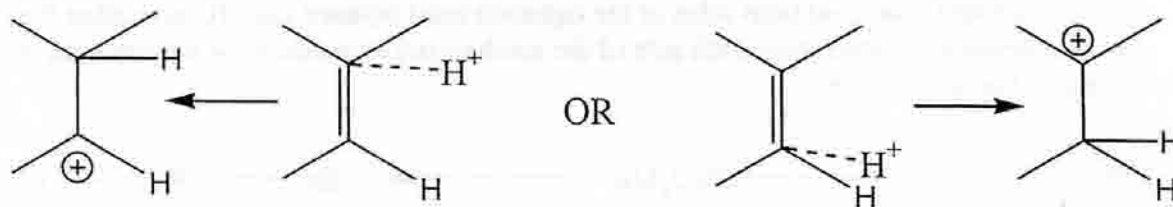


Intramolecular



## Other Factors to be Considered when Formulating a Mechanism

17. In a reaction between molecules containing a number of functional groups it may be possible to write down more than one set of curved (curly) arrows i.e. more than one mechanism. Which of these is closest to actuality depends on the relative rates of reaction for each mechanism. Since arrow pushing is mainly qualitative in nature it will probably not allow you to decide which mechanism is favoured.



18. Electrons are organised in orbitals. Since orbitals represent the directional aspect of electron density, any electron redistribution during reaction requires the correct spatial alignment of orbitals. This stereochemical electronic (*stereoelectronic*) factor must be remembered when considering possible arrow pushing alternatives.
19. Arrow pushing takes no account of the interaction of groups or atoms not involved at the reactive sites. In particular severe, non-bonded, repulsive forces between such groups as the molecules approach (Steric Hindrance) may be sufficiently high to prevent reaction even though a reasonable set of arrows may be drawn.
20. Some reactions (pericyclic reactions) do not involve any nucleophilic, electrophilic or radical centres and are associated with a cyclic redistribution of electrons. Such reactions are best dealt with by *Molecular Orbital Theory* (2<sup>nd</sup> year) rather than in Valence Bond terms.