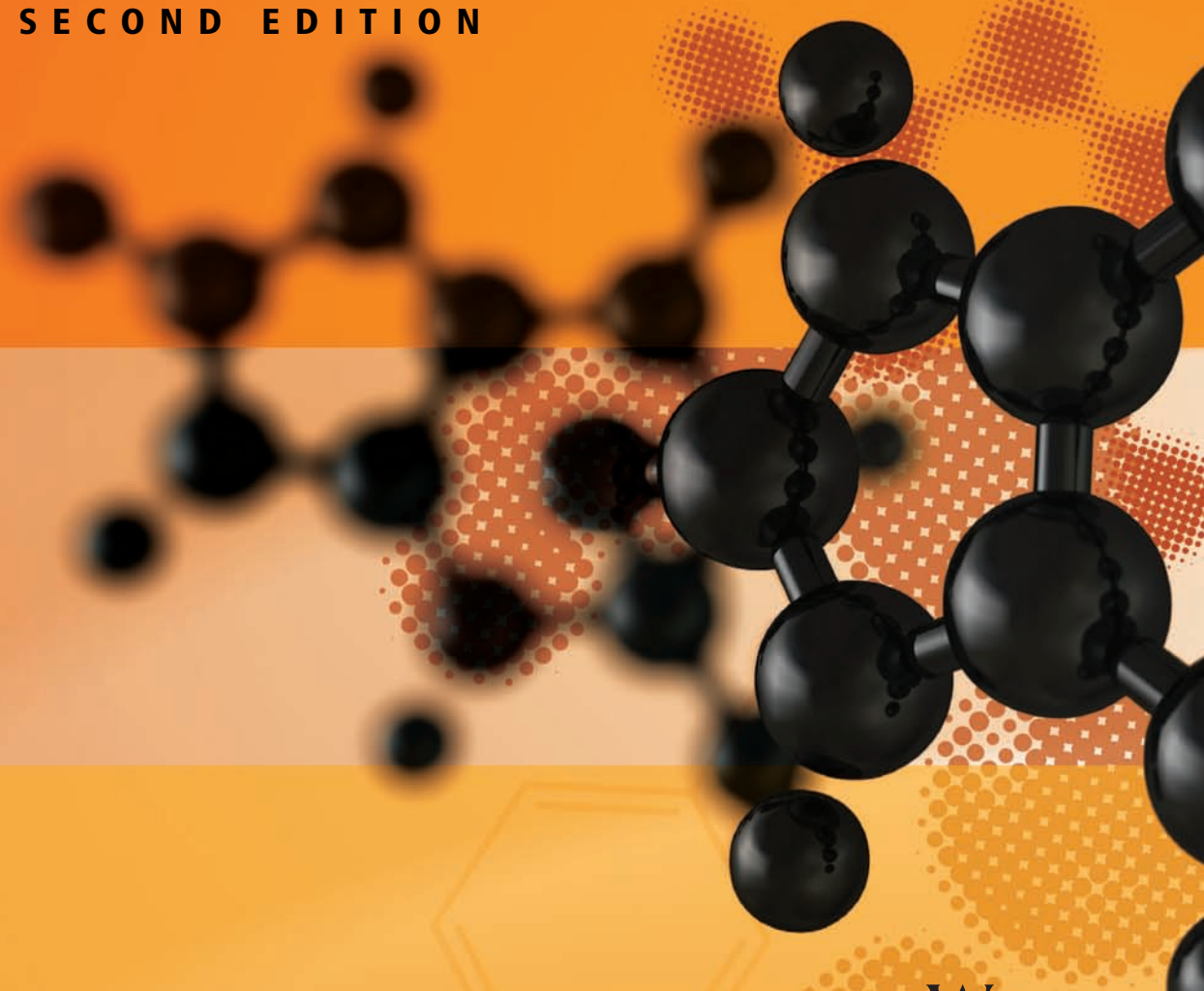


Andrew F. Parsons

KEYNOTES IN

Organic Chemistry

SECOND EDITION



WILEY

Keynotes in Organic Chemistry

Keynotes in Organic Chemistry

Second Edition

ANDREW F. PARSONS

Department of Chemistry, University of York, UK

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Preface

With the advent of modularisation and an ever-increasing number of examinations, there is a growing need for concise revision notes that encapsulate the key points of a subject in a meaningful fashion. This keynote revision guide provides concise organic chemistry notes for first year students studying chemistry and related courses (including biochemistry) in the UK. The text will also be appropriate for students on similar courses in other countries.

An emphasis is placed on presenting the material pictorially (pictures speak louder than words); hence, there are relatively few paragraphs of text but numerous diagrams. These are annotated with key phrases that summarise important concepts/key information and bullet points are included to concisely highlight key principles and definitions.

The material is organised to provide a structured programme of revision. Fundamental concepts, such as structure and bonding, functional group identification and stereochemistry are introduced in the first three chapters. An important chapter on reactivity and mechanism is included to provide a short overview of the basic principles of organic reactions. The aim here is to provide the reader with a summary of the 'key tools' which are necessary for understanding the following chapters and an important emphasis is placed on organisation of material based on reaction mechanism. Thus, an overview of general reaction pathways/mechanisms (such as substitution and addition) is included and these mechanisms are revisited in more detail in the following chapters. Chapters 5–10 are treated essentially as 'case studies', reviewing the chemistry of the most important functional groups. Halogenoalkanes are discussed first and as these compounds undergo elimination reactions this is followed by the (electrophilic addition) reactions of alkenes and alkynes. This leads on to the contrasting (electrophilic substitution) reactivity of benzene and derivatives in Chapter 7, while the rich chemistry of carbonyl compounds is divided into Chapters 8 and 9. This division is made on the basis of the different reactivity (addition versus substitution) of aldehydes/ketones and carboxylic acid derivatives to nucleophiles. A chapter is included to revise the importance of spectroscopy in structure elucidation and, finally, the structure and reactivity of a number of important natural products and synthetic polymers is highlighted in Chapter 11. Worked examples and questions are included at the end of each chapter to test the reader's understanding, and outline answers are provided for all of the questions. Tables of useful physical data, reaction summaries and a glossary are included in appendices at the back of the book.

New to this edition

A number of additions have been made to this edition to reflect the feedback from students and lecturers:

- A **second colour** is used to clarify some of the diagrams, particularly the mechanistic aspects
- **Reference notes are added in the margin** to help the reader find information and to emphasise links between different topics
- **Diagrams are included in the introductory key point sections** for each chapter
- **Additional end-of-chapter problems** (with outline answers) are included
- A **worked example** is included at the end of each chapter
- The information in the **appendices has been expanded**, including reaction summaries and a glossary

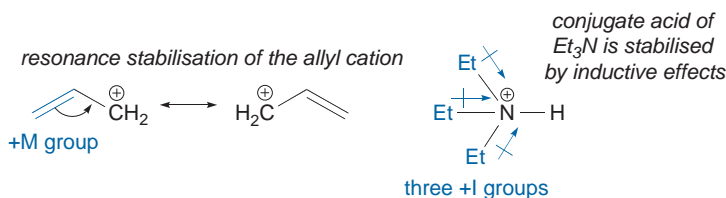
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There are numerous people I would like to thank for their help with this project. This includes many students and colleagues at York. Their constructive comments were invaluable. I would also like to thank my family for their support and patience throughout this project. Finally, I would like to thank Paul Deards and Sarah Tilley from Wiley, for all their help in progressing the second edition.

Dr Andrew F. Parsons
2013

Structure and bonding

Key point. Organic chemistry is the study of carbon compounds. *Ionic* bonds involve elements gaining or losing electrons but the carbon atom is able to form four *covalent* bonds by sharing the four electrons in its outer shell. Single (C–C), double (C=C) or triple bonds (C≡C) to carbon are possible. When carbon is bonded to a different element, the electrons are not shared equally, as *electro-negative* atoms (or groups) attract the electron density whereas *electro-positive* atoms (or groups) repel the electron density. An understanding of the electron-withdrawing or -donating ability of atoms, or a group of atoms, can be used to predict whether an organic compound is a good *acid* or *base*.

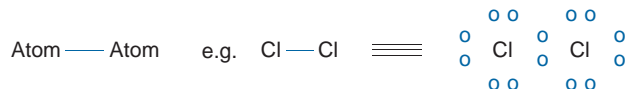


1.1 Ionic versus covalent bonds

- *Ionic bonds* are formed between molecules with opposite charges. The negatively charged anion will electrostatically attract the positively charged cation. This is present in (inorganic) salts.

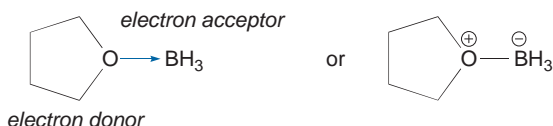


- *Covalent bonds* are formed when a pair of electrons is shared between two atoms. A single line represents the two-electron bond.



- *Coordinate (or dative) bonds* are formed when a pair of electrons is shared between two atoms. *One* atom donates both electrons and a single line or an arrow represents the two-electron bond.

The cyclic ether is tetrahydrofuran (THF) and BH_3 is called borane (Section 6.2.2.5)



- *Hydrogen bonds* are formed when the partially positive ($\delta+$) hydrogen of one molecule interacts with the partially negative ($\delta-$) heteroatom (e.g. oxygen or nitrogen) of another molecule.

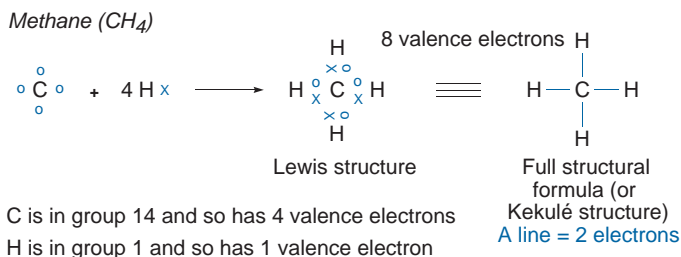
Intramolecular hydrogen bonding in carbonyl compounds is discussed in Section 8.4.1



1.2 The octet rule

To form organic compounds, the carbon atom shares electrons to give a stable ‘full shell’ electron configuration of eight valence electrons.

Methane is the smallest alkane – alkanes are a family of compounds that contain only C and H atoms linked by single bonds (Section 2.4)



Drawing organic compounds using full structural formulae and other conventions is discussed in Section 2.5

A single bond contains two electrons, a double bond contains four electrons and a triple bond contains six electrons. A lone (or non-bonding) pair of electrons is represented by two dots ($\bullet\bullet$).



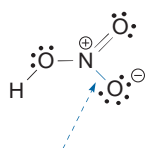
1.3 Formal charge

Formal positive or negative charges are assigned to atoms, which have an apparent ‘abnormal’ number of bonds.

Atom(s)	C	N, P	O, S	F, Cl, Br, I
Group number	14	15	16	17
Normal number of 2 electron bonds	4	3	2	1

$$\text{Formal charge} = \begin{array}{l} \text{group number} \\ \text{in periodic} \\ \text{table} \end{array} - \begin{array}{l} \text{number} \\ \text{of bonds} \\ \text{to atom} \end{array} - \begin{array}{l} \text{number of} \\ \text{unshared} \\ \text{electrons} \end{array} - 10$$

Example: Nitric acid (HNO_3)



Nitrogen with 4 covalent bonds has a formal charge of +1
Formal charge: $15 - 4 - 0 = +1$

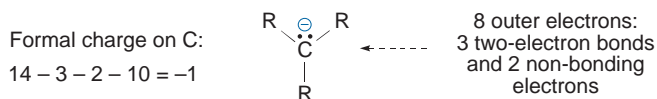
The nitrogen atom donates a pair of electrons to make this bond

Carbon forms four covalent bonds. When only three covalent bonds are present, the carbon atom can have either a formal negative charge or a formal positive charge.

Nitric acid is used in synthesis to nitrate aromatic compounds such as benzene (Section 7.2.2)

The stability of carbocations and carbanions is discussed in Section 4.3

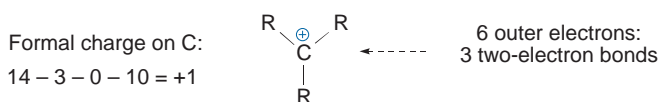
- *Carbanions*—three covalent bonds to carbon and a formal negative charge.



The negative charge is used to show the 2 non-bonding electrons

Carbanions are formed on deprotonation of organic compounds. Deprotonation of a carbonyl compound, at the α -position, forms a carbanion called an enolate ion (Section 8.4.3)

- *Carbocations*—three covalent bonds to carbon and a formal positive charge.



The positive charge is used to show the absence of 2 electrons

Carbocations are intermediates in a number of reactions, including $\text{S}_{\text{N}}1$ reactions (Section 5.3.1.2)

1.4 Sigma (σ -) and pi (π -) bonds

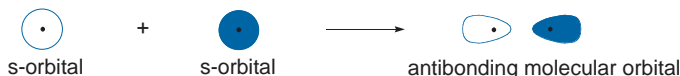
The electrons shared in a covalent bond result from overlap of atomic orbitals to give a new molecular orbital. Electrons in 1s and 2s orbitals combine to give sigma (σ -) bonds.

When two 1s orbitals combine *in-phase*, this produces a *bonding molecular orbital*.

Molecular orbitals and chemical reactions are discussed in Section 4.10

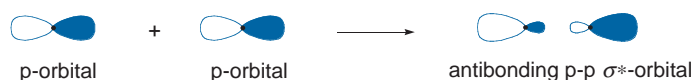
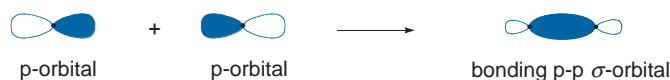


When two 1s orbitals combine *out-of-phase*, this produces an *antibonding molecular orbital*.



Electrons in p orbitals can combine to give sigma (σ) or pi (π) bonds.

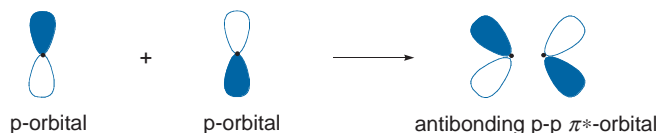
- *Sigma (σ -) bonds* are strong bonds formed by head-on overlap of two atomic orbitals.



Alkenes have a C=C bond containing one strong σ -bond and one weaker π -bond (Section 6.1)

All carbonyl compounds have a C=O bond, which contains one strong σ -bond and one weaker π -bond (Section 8.1)

- *Pi (π -) bonds* are weaker bonds formed by side-on overlap of two p-orbitals.

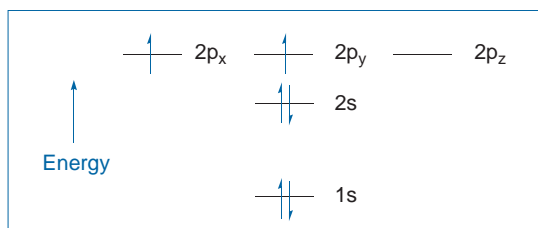


Only σ - or π -bonds are present in organic compounds. All single bonds are σ -bonds while all multiple (double or triple) bonds are composed of one σ -bond and one or two π -bonds.

1.5 Hybridisation

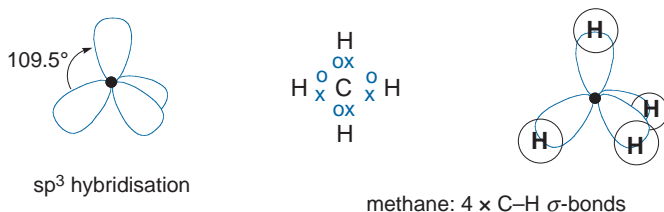
Hund's rule states that when filling up a set of orbitals of the same energy, electrons are added with parallel spins to different orbitals rather than pairing two electrons in one orbital

- The ground-state electronic configuration of carbon is $1s^2 2s^2 2p_x^1 2p_y^1$.
- The six electrons fill up lower energy orbitals before entering higher energy orbitals (Aufbau principle).
- Each orbital is allowed a maximum of two electrons (Pauli exclusion principle).
- The two 2p electrons occupy separate orbitals before pairing up (Hund's rule).



The carbon atom can mix the 2s and 2p atomic orbitals to form four new hybrid orbitals in a process known as *hybridisation*.

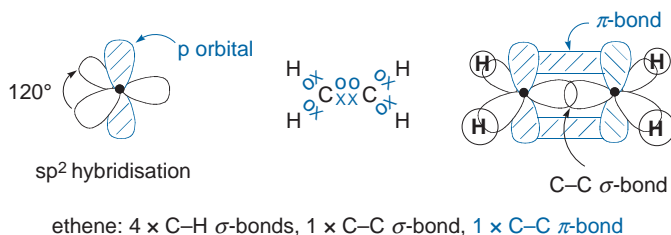
- *sp³ Hybridisation*. For four single σ -bonds – carbon is sp^3 hybridised (e.g. in methane, CH_4). The orbitals move as far apart as possible, and the lobes point to the corners of a tetrahedron (109.5° bond angle).



- *sp² Hybridisation*. For three single σ -bonds and one π -bond – the π -bond requires one p-orbital, and hence the carbon is sp^2 hybridised (e.g. in ethene, $\text{H}_2\text{C}=\text{CH}_2$). The three sp^2 -orbitals point to the corners of a triangle (120° bond angle), and the remaining p-orbital is perpendicular to the sp^2 plane.

Alkenes have a C=C bond containing one strong σ -bond and one weaker π -bond (Section 6.1)

All carbonyl compounds have a C=O bond, which contains one strong σ -bond and one weaker π -bond (Section 8.1)



- *sp Hybridisation*. For two single σ -bonds and two π -bonds – the two π -bonds require two p-orbitals, and hence the carbon is sp hybridised (e.g. in ethyne, $\text{HC}\equiv\text{CH}$). The two sp -orbitals point in the opposite directions (180° bond angle), and the two p-orbitals are perpendicular to the sp plane.

Alkynes have a $\text{C}\equiv\text{C}$ bond containing one strong σ -bond and two weaker π -bonds (Section 6.1)

