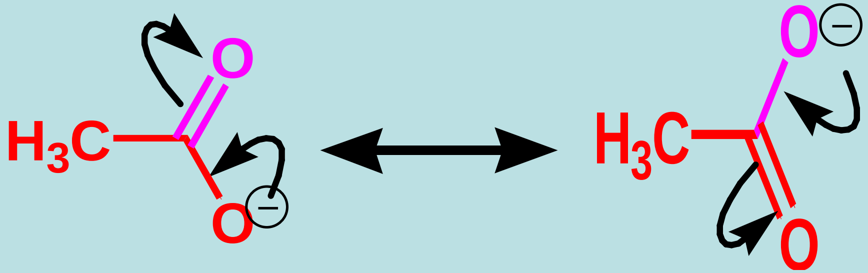
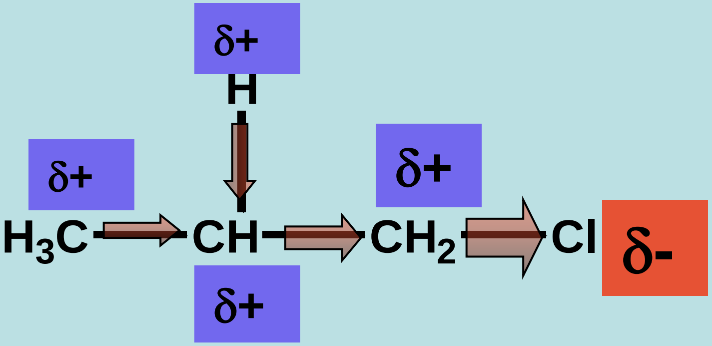
Part 1

CHM1C3

Resonance and Inductive Effects





Content of Part 1

Resonance

- Benzene Bond Lengths
- Resonance of Benzene
- The Resonance Arrow and its Physical Meaning
- Resonance Imparts Stability to Charged Structures
- Important Aromatic Resonance Structures
- General Structure that will Display Resonance of Charges and Lone Pairs

Inductive Effects:

- Electronegativity
- Short Range Nature of Inductive Effects
- Carbocation Stability

– Learning Objectives Part 1 –

Resonance and Inductive Effects

After completing PART 1 of this course you should have an understanding of, and be able to demonstrate, the following terms, ideas and methods.

(i) *Resonance* is the process whereby (generally) π-electrons can be delocalised by exchanging double bonds and single bonds.

(ii) Resonance can be used to delocalise both lone pairs of electrons and cationic charges which are adjacent to double bonds.

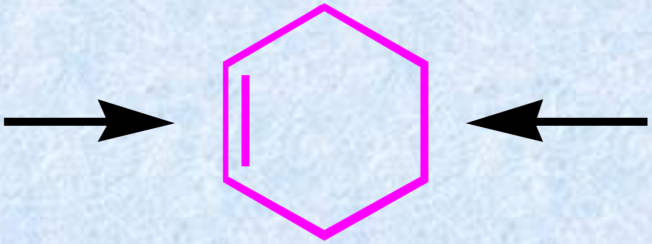
(iii) Delocalisation of positive and negative charges lead to relatively stable cations and anions, respectively.

(v) *Inductive effects* are caused by differences in electronegativity between bonded atoms, which leads to a polarisation of the bond.

(vi) The inductive effects are short range (unlike resonance effects) .

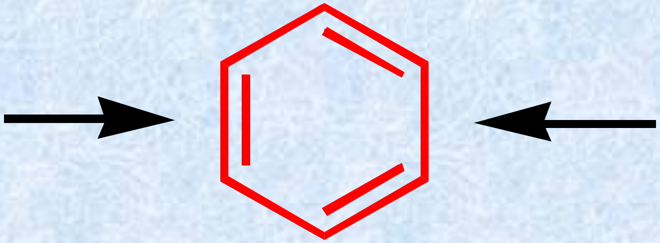
Resonance

Benzene Bond Lengths



1.33 Å

1.52 Å



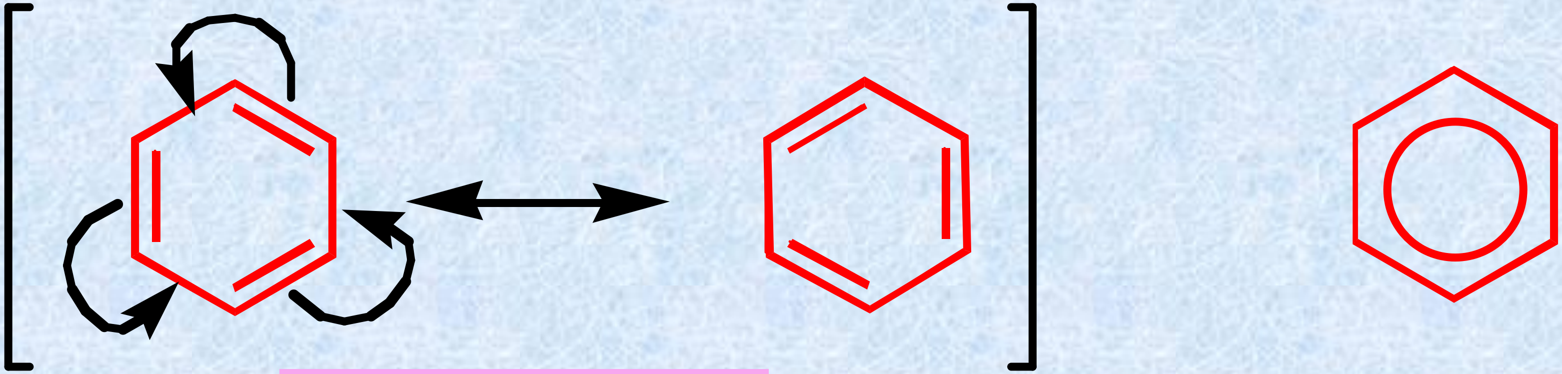
1.42 Å

1.42 Å

Resonance Structures of Benzene

The 6 π-electrons are able to flow (or resonate) continually around the π-molecular orbital formed from the six p atomic orbitals on each of the 6 carbon atoms on the ring structure. This is represented by the two resonance structures below (which are identical or degenerate).

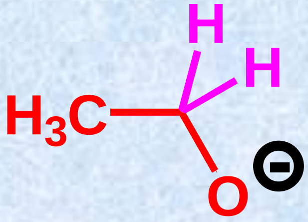
This flow of electrons leads to a very stable electronic structure, which accounts for benzenes low reactivity relative to alkenes. This stabilty is referred to as the *Resonance Stablisation Energy*.



Canonical structurtes

The π-electrons are referred to as being conjugated.

Resonance Imparts Stability to Anionic Structures (and Cationic Structures – See Questions 3 and 4)



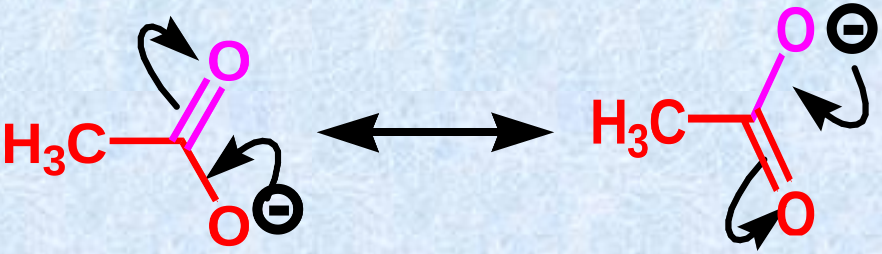
No adjacent double bond to
the oxygen lone pair

Relatively difficult to form

CH_2

Replaced by

C=O



Relatively easy to form

VERY IMPORTANT POINT

The ability to be able to delocalise (spread out) charge *via* resonance allows an assessment of

(i) the degree of ease of formation of the charged species, and

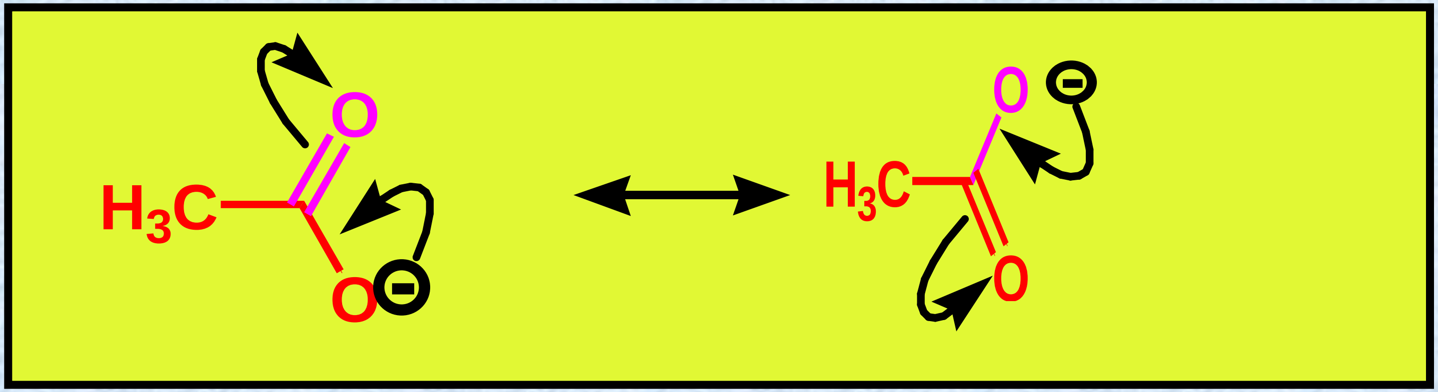
(ii) the stability of the charged species

Part 1 of this course will reinforce the importance of understanding resonance.

You must understand resonance. It will be a tool that you will use again and again…

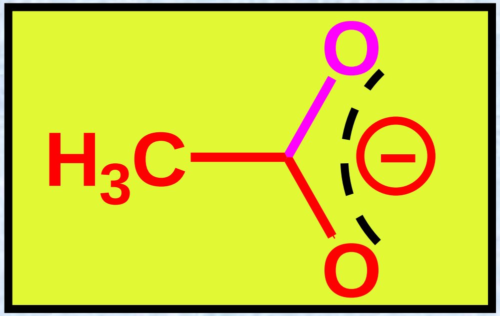
The Resonance Arrow and its Physical Meaning

The resonance arrow is not an equilibrium arrow



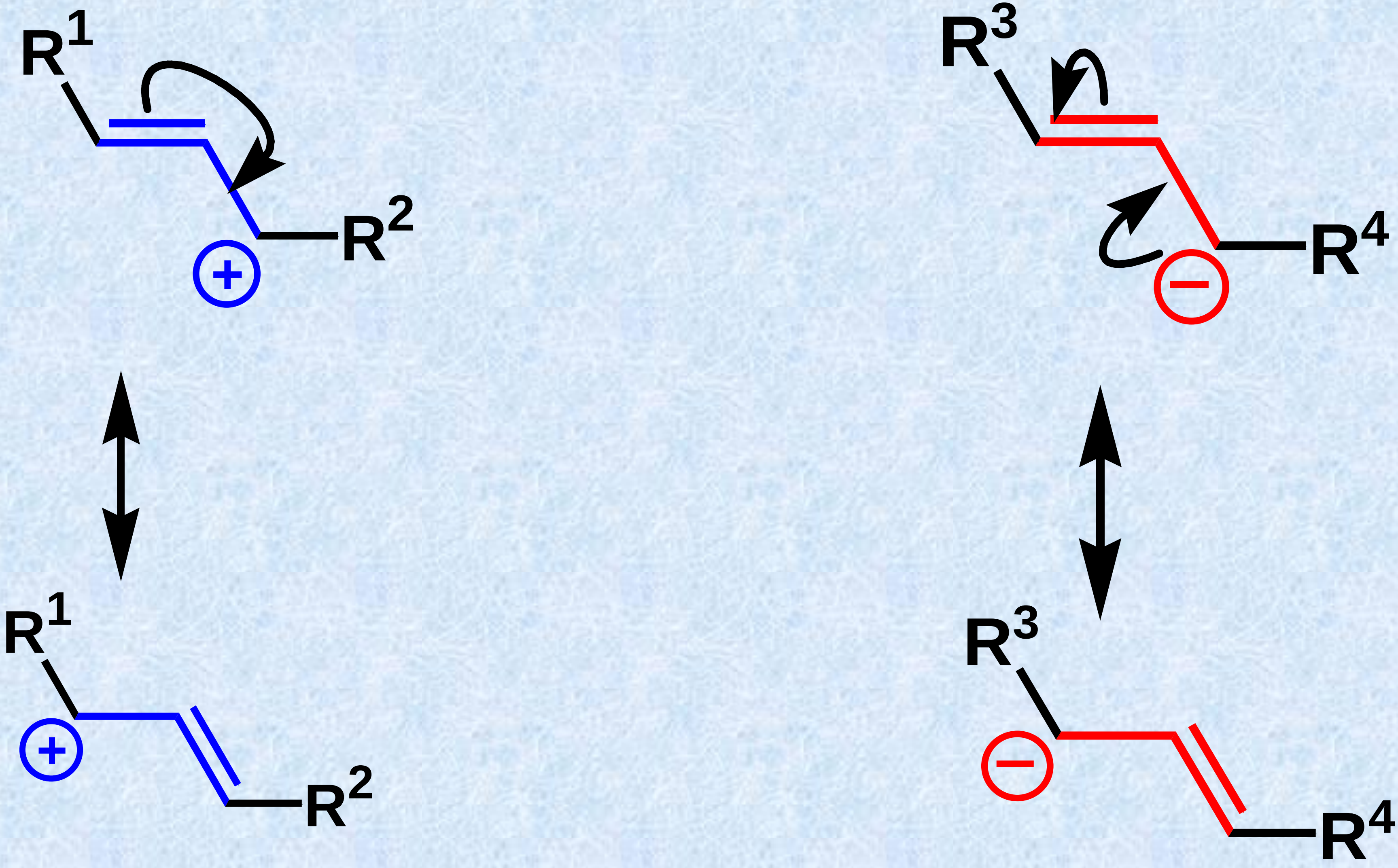
The resonance arrow shows only the distribution of electrons.

Thus, for the two degenerate structures above, the implication is that there is an even distribution of the two electrons between the two oxygen atoms, at all times.



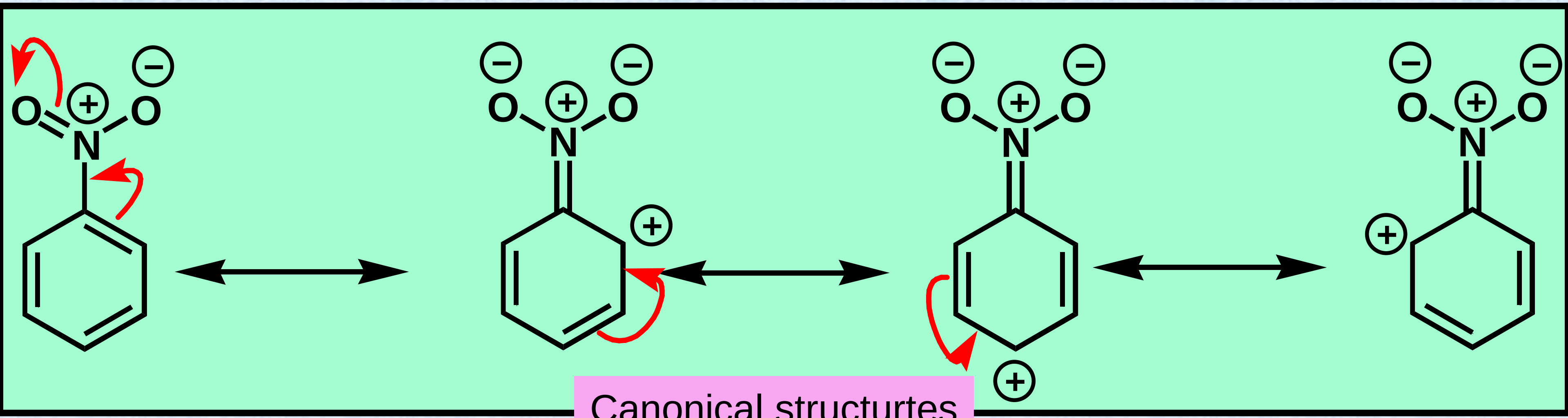
Experimentally it is found that both C-O bonds are the same length and are intermediate in length between the C-O single and double bond, as are the C-C bonds in benzene.

General Structure that will Display Resonance of Charges and Lone Pairs of Electrons

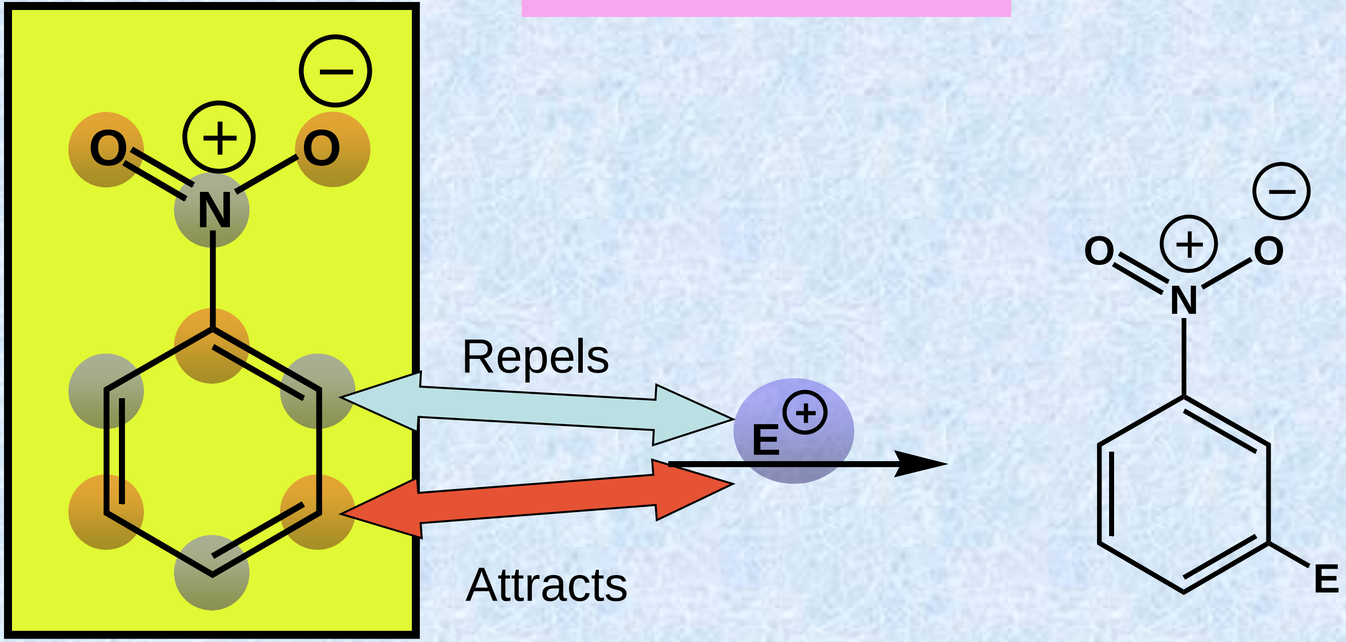


Some Important Aromatic Resonance Structures

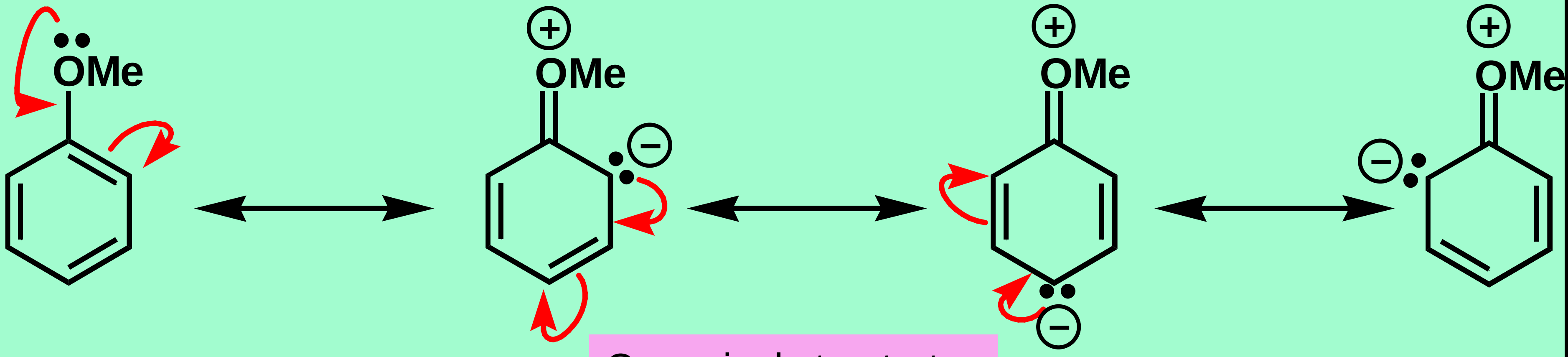
Nitro Group: An Electron Withdrawing Group



Canonical structurtes

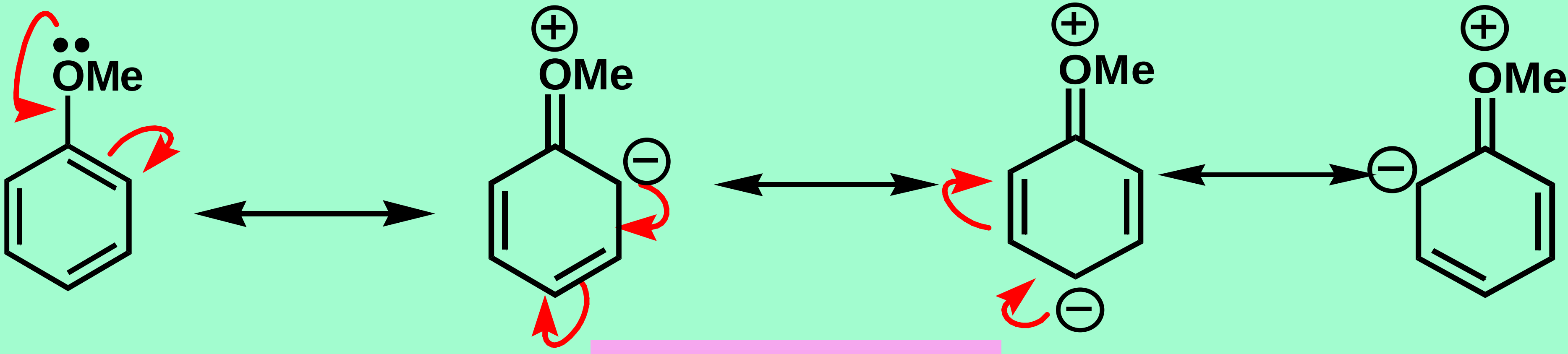


Methoxy Group: An Electron Donating Group



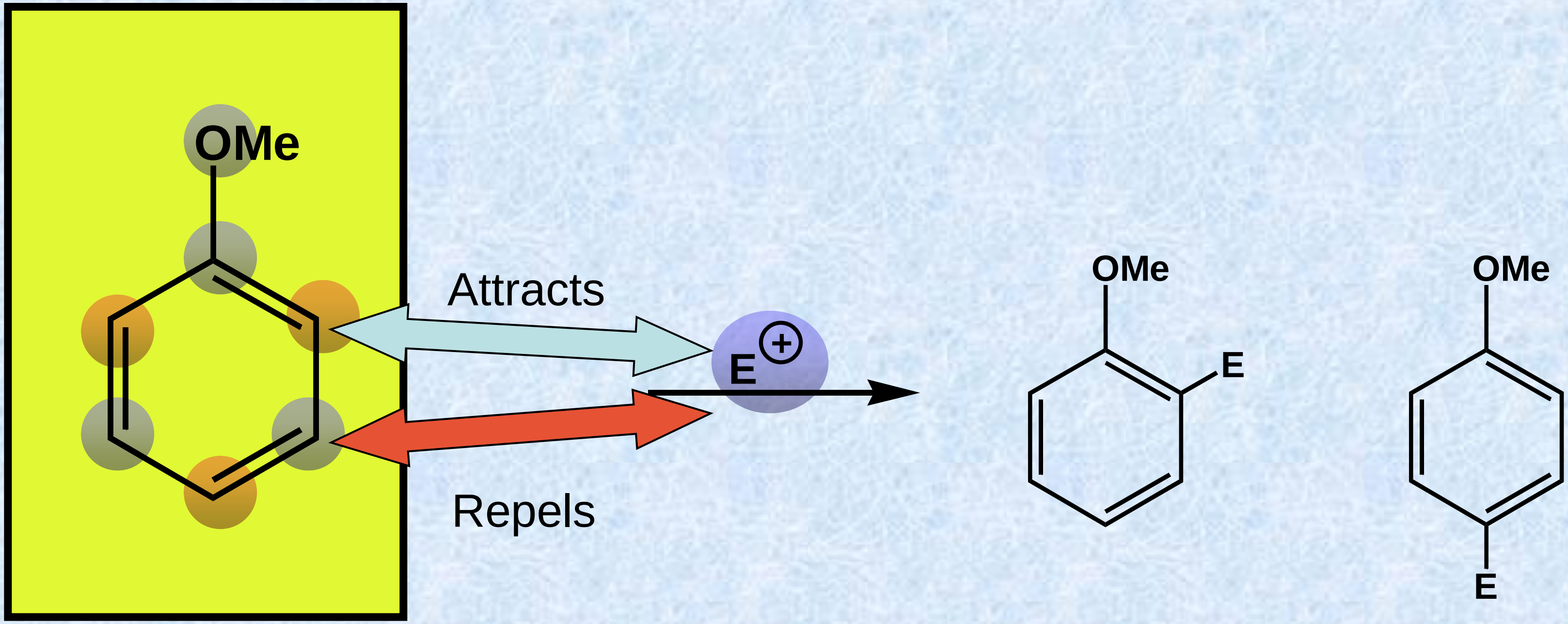
Canonical structurtes

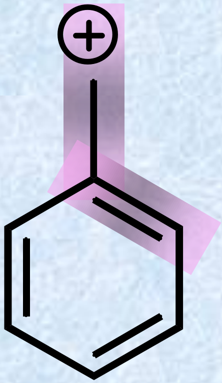
…Note in a reaction mechanism we would not show the lone pairs on the carbons carrying the –ve charge…

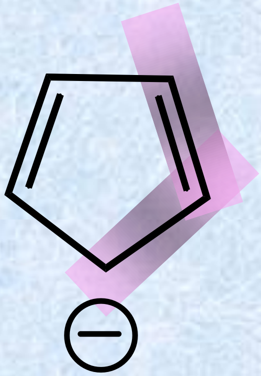


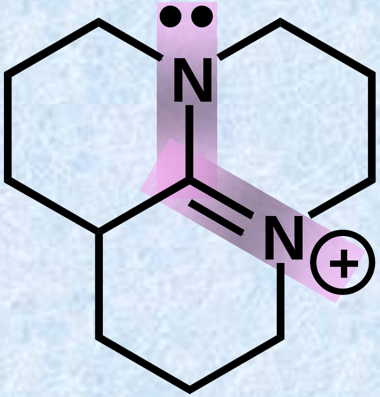
Canonical structurtes

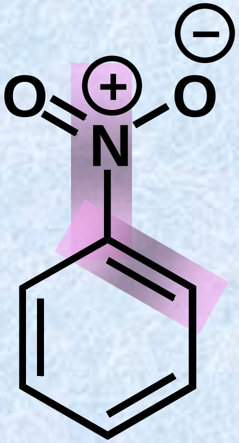
These resonance structures allow us to rationalise (and predict) reactivity

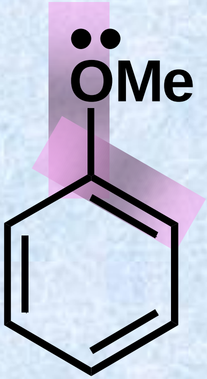






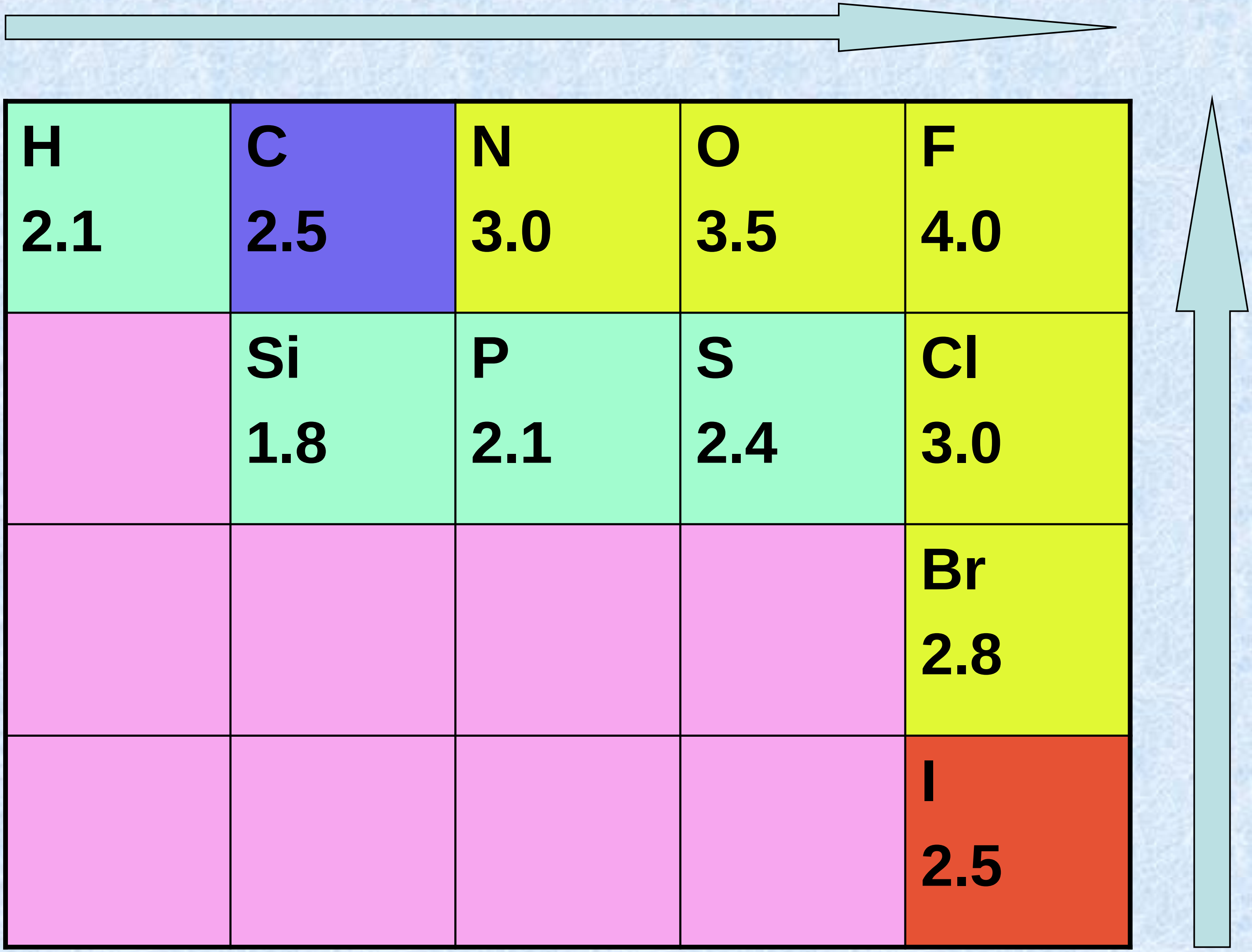

N
N


O
N
O


OMe

Inductive Effects

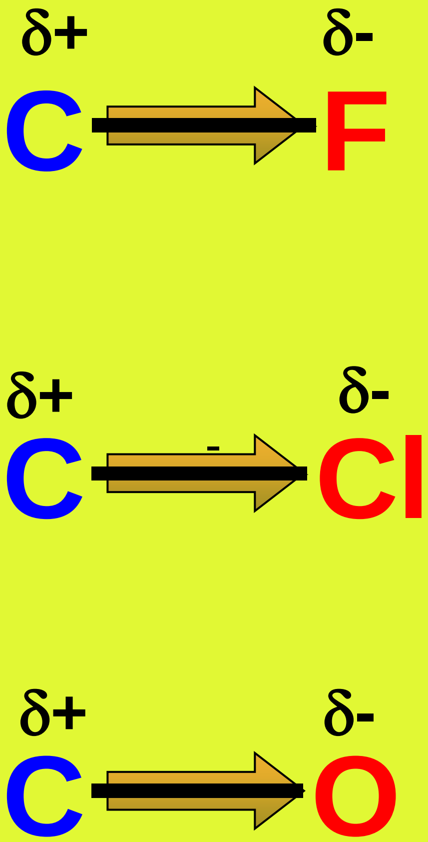
Electronegativity Values



H 2.1	C 2.5	N 3.0	O 3.5	F 4.0
	Si 1.8	P 2.1	S 2.4	Cl 3.0
				Br 2.8
				I 2.5

Bond Polarisation and Inductive Effects

-I Inductive Effects

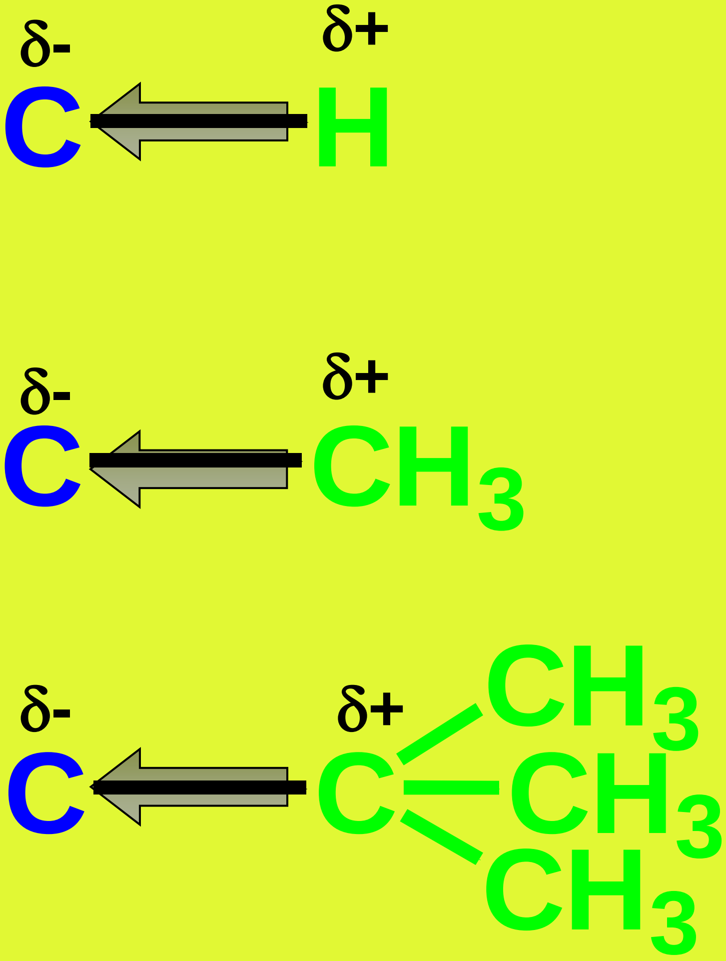


$\overset{\delta+}{C} \longrightarrow \overset{\delta-}{F}$

$\overset{\delta+}{C} \longrightarrow \overset{\delta-}{Cl}$

$\overset{\delta+}{C} \longrightarrow \overset{\delta-}{O}$

+I Inductive Effects



$\overset{\delta-}{C} \longleftarrow \overset{\delta+}{H}$

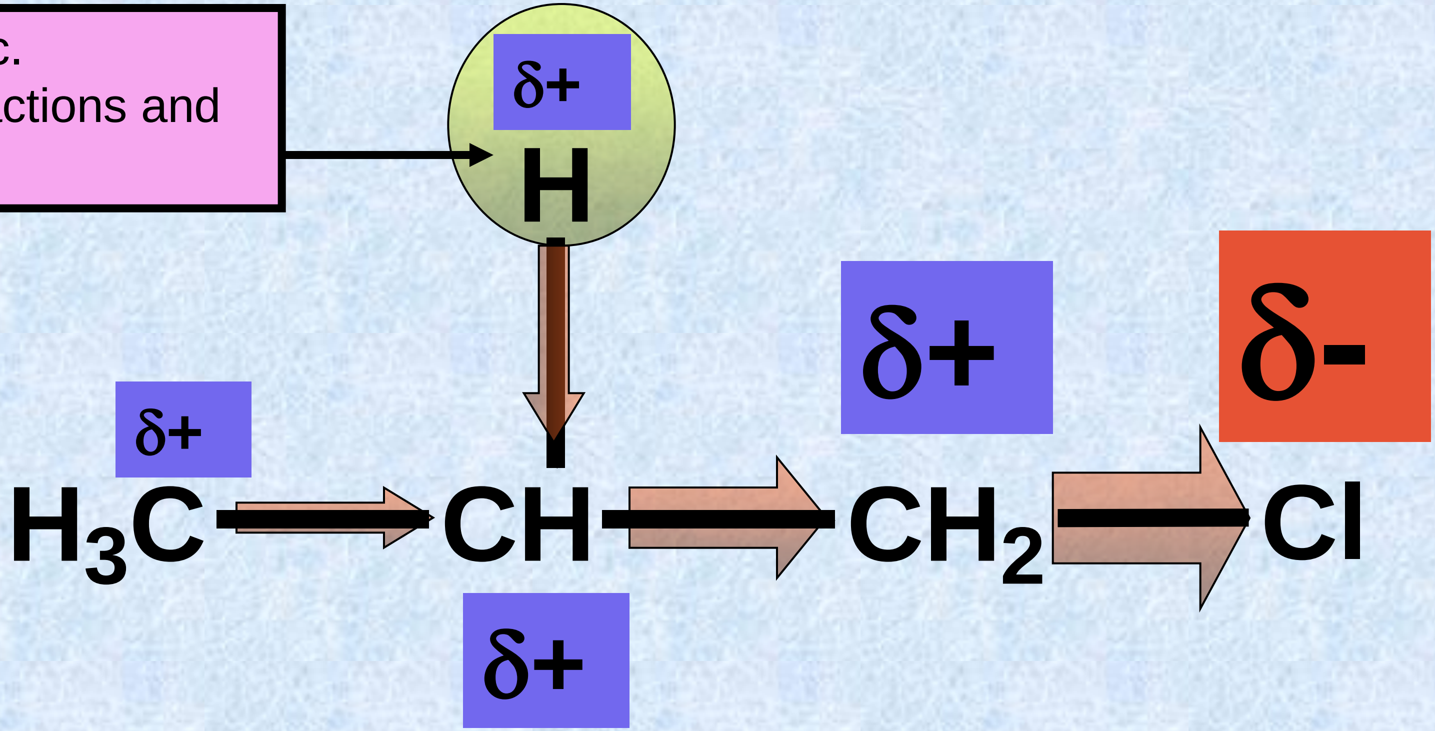
$\overset{\delta-}{C} \longleftarrow \overset{\delta+}{CH_3}$

$\overset{\delta-}{C} \longleftarrow \overset{\delta+}{C}(CH_3)_3$

Inductive Effects are Short Range

In Contrast to Resonance Effects

This proton is acidic.
See Elimination reactions and alkene formation.

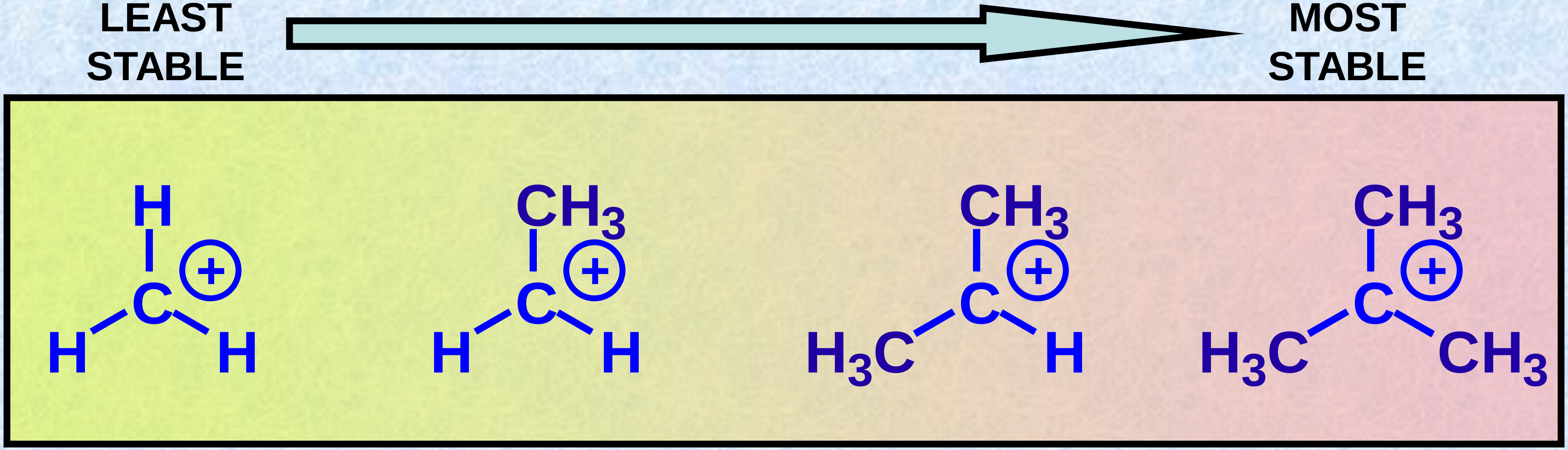


The polarised C-Cl bond transmits further polarisation through the σ-bond framework,

But effect drops off quickly…

Inductive Effects and Carbocation Stability

Important when considering substitution reactions in part 4 of this course



Methyl Carbocation

Primary Carbocation

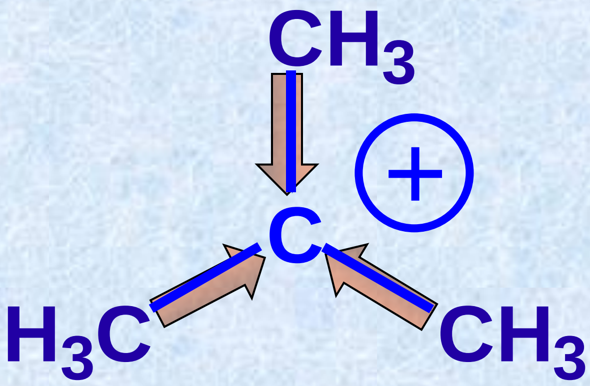
Secondary Carbocation

Tertiary Carbocation

Carbon atom is electron deficient (only has 6 electrons in its outer valence).

The methyl groups have +I inductive effects.

Thus, extra electron density is 'pushed' onto the carbocation, which stabilises the carbocation.



CHM1C3
– Introduction to Chemical Reactivity of Organic Compounds–

– Summary Sheet Part 1 –

Resonance and Inductive Effects

The redistribution of electrons in π-conjugated molecular systems is referred to as *resonance*.

The structures that result from this redistribution of electron density <u>should not</u> be thought of discrete structures. They should be viewed as a way of representing the <u>average distribution of electrons in the π-system</u>. They individual *canonical* structures should therefore be <u>hybridised</u> together to give a true view of the electron density, at any single point tin time.

However, consideration of the individual canonical structures can lead to <u>predictive capabilities</u> with respect to chemical reactivity and electronic properties (both optical and electronic). For example,

(i) when considering aromatic species which bear substituents, it is possible to predict where electrophiles will react on the aromatic rings by considering the canonical structures (you will examine this in detail in a later course), and

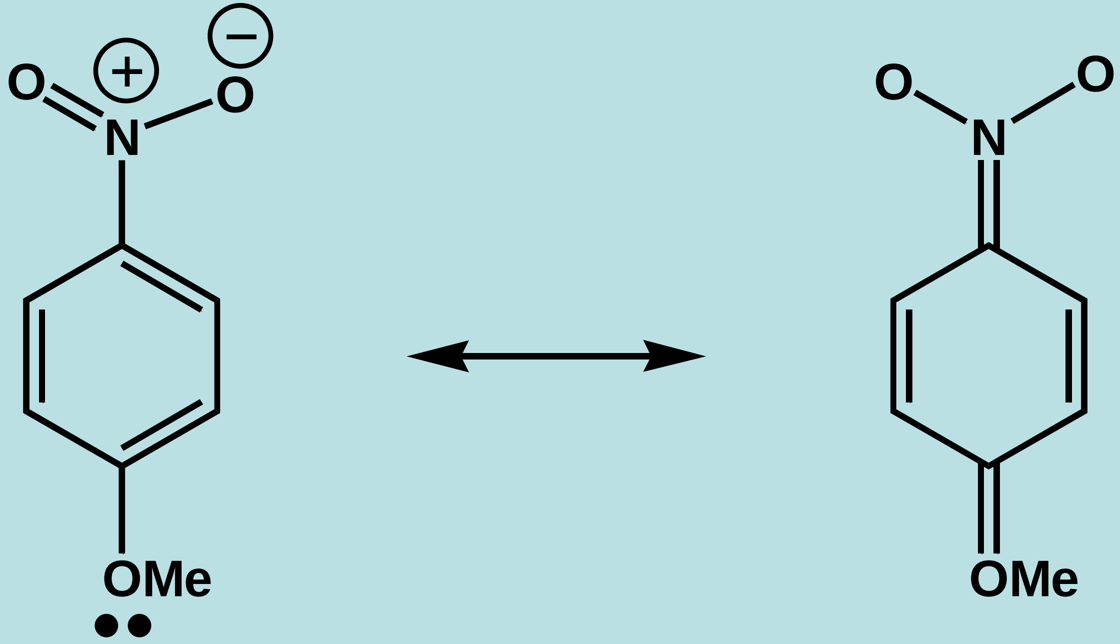
(ii) consideration of the canonical structures of structurally realated acids can aid with predicting which acids will be strongest and weakest, as we shall see in part 2 of the course.

The differences in <u>electronegativity</u> between bonded atoms leads to a <u>polarisation of the covalent bond</u> such the most electronegative atom has has a partial negative charge and the other atom has a partial positive charge. <u>The polarisation is transmitted to adjacent bonds, but the effect drops rapidly.</u>

Consideration of inductive effects allows qualitative predictions of orders of acidity in organic acids as we shall see in Part 2 of the course.

Question 1: Resonances

On structure A draw on the curly-arrows that will lead to the bonding in the resonance structure B. Then place charges on structure B.



A

B

Answer 1: Resonances

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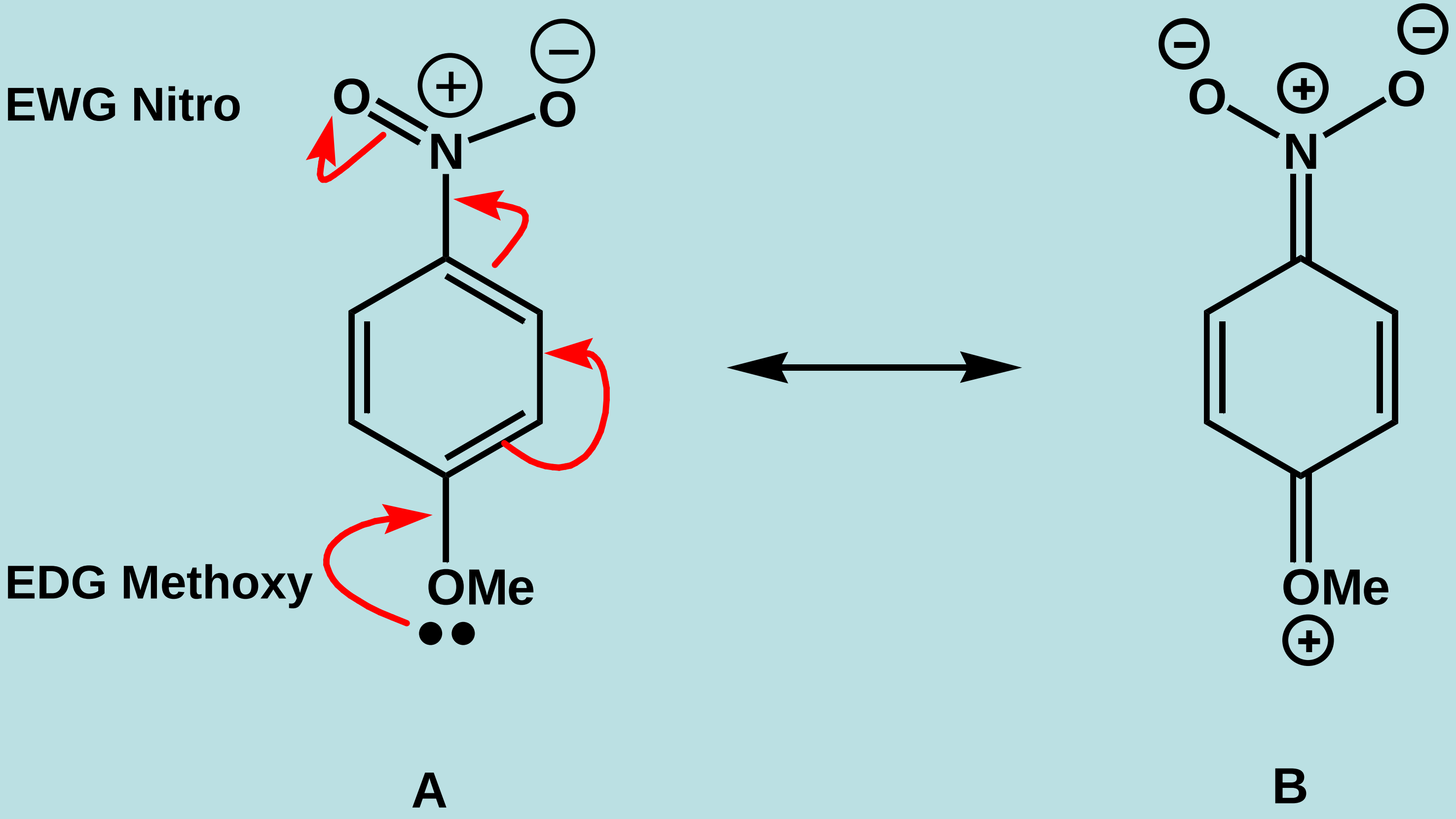
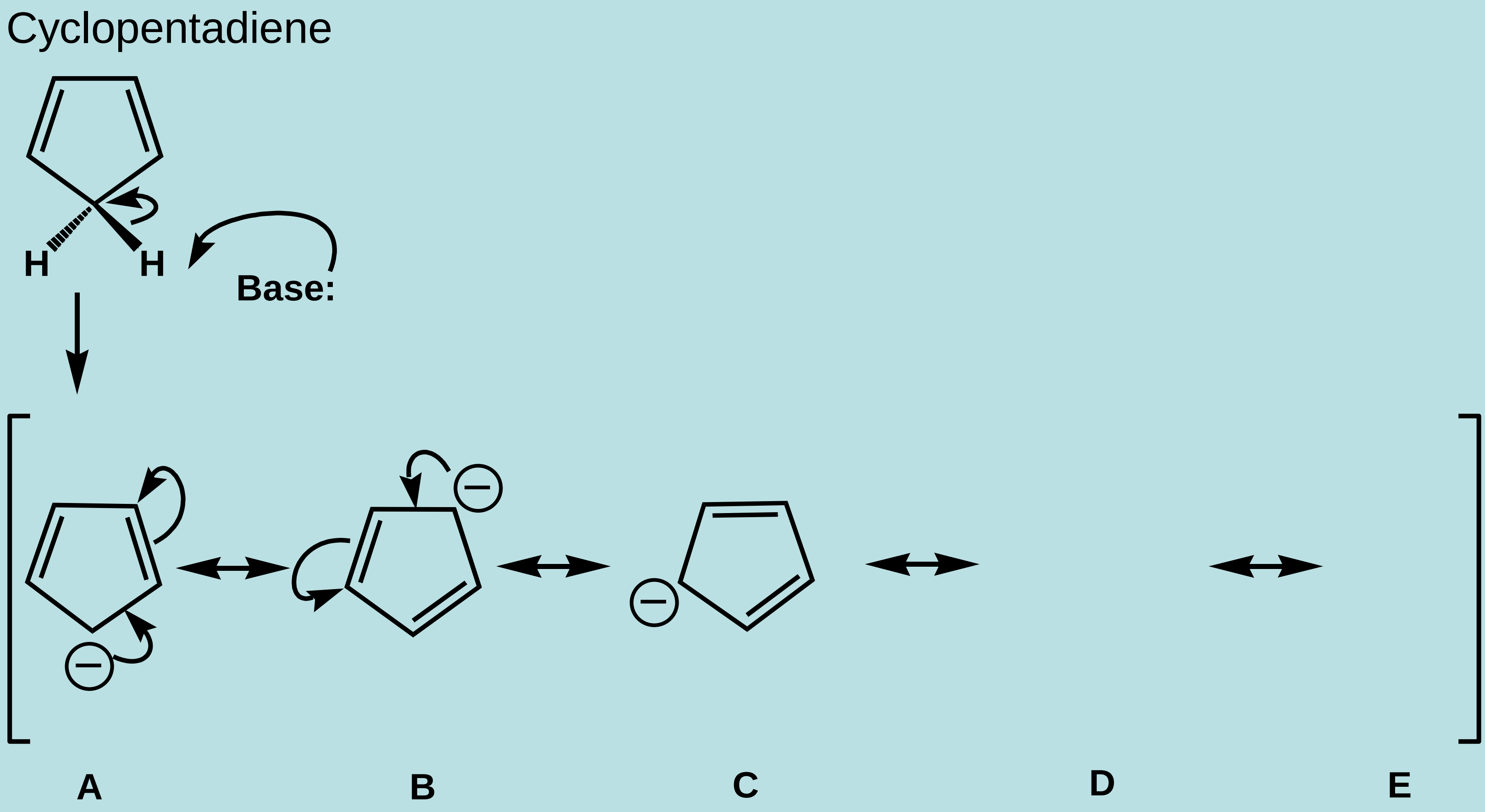


Question 2: Resonances

Cyclopentadiene can be deprotonated to the anion A. Anion A, the cyclopentadienyl anion, has 4 degenerate resonance structures. Complete the arrow pushing in C and identify structures D and E.



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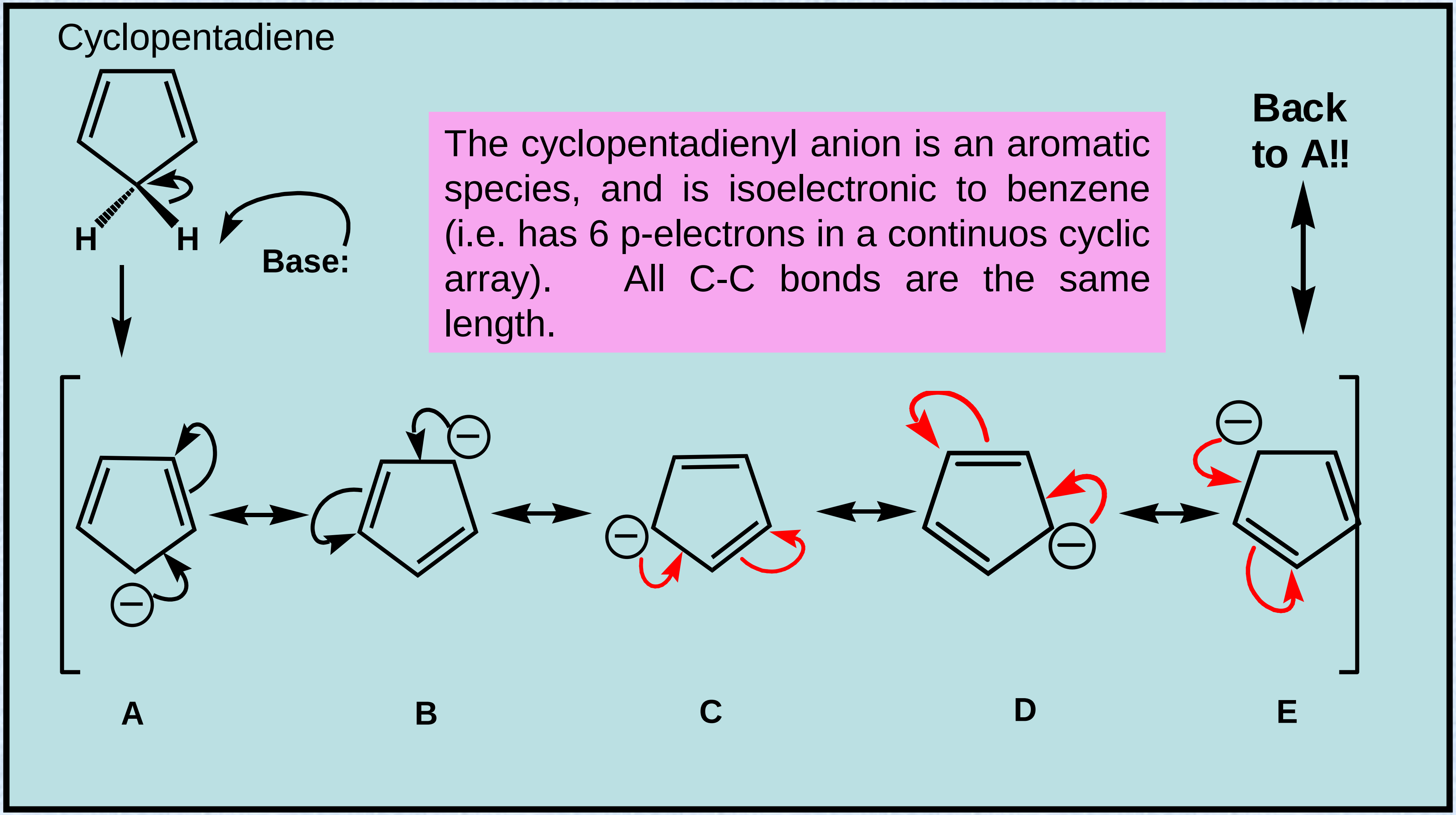
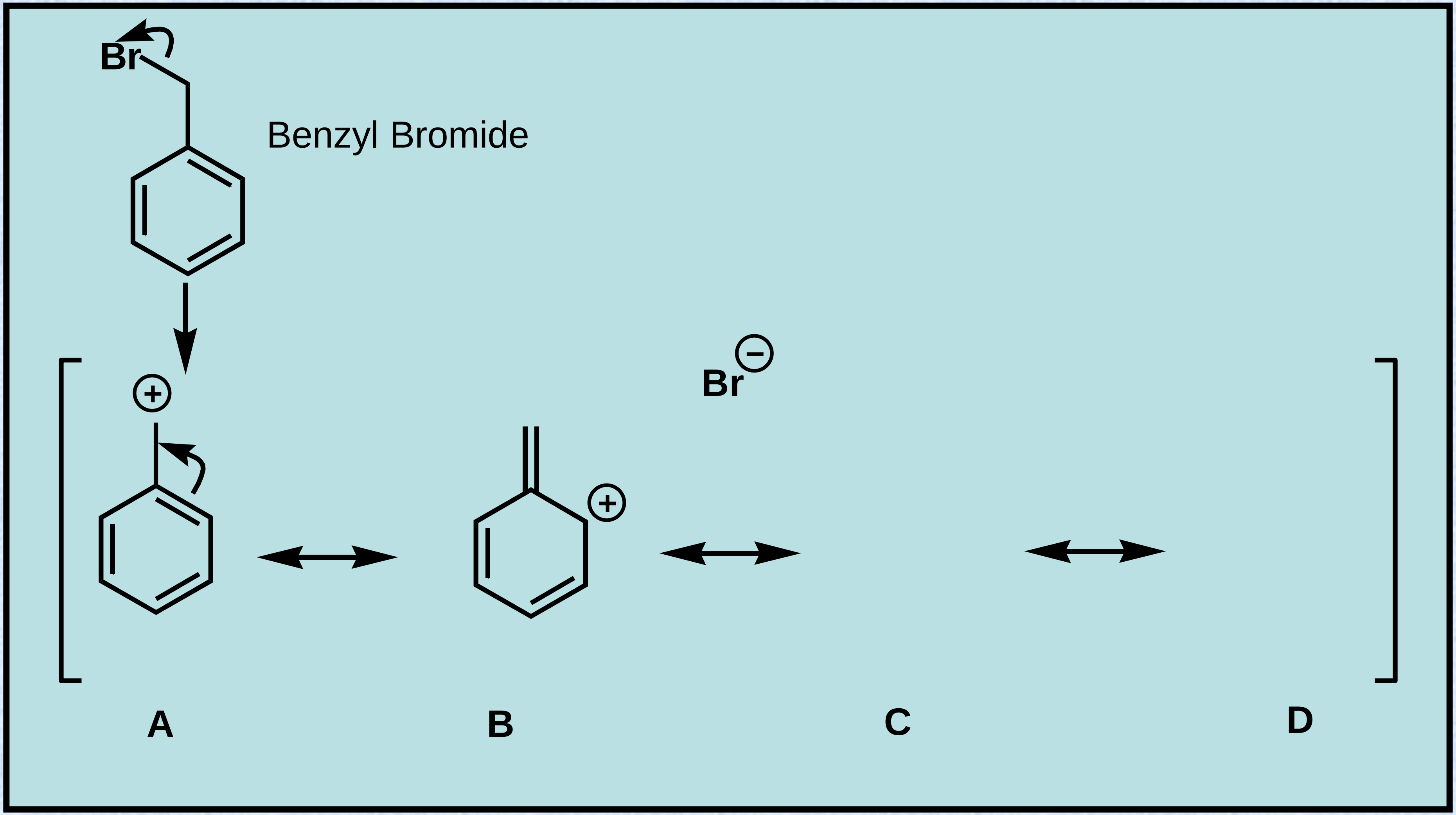


The cyclopentadienyl anion is an aromatic species, and is isoelectronic to benzene (i.e. has 6 p-electrons in a continuos cyclic array). All C-C bonds are the same length.

Question 3: Resonances

Benzyl bromide undergoes C-Br bond cleavage to generate the benzyl cation A. Through resonance the positive charge can be delocalised through the ring. Identify resonance structures C and D and draw in the curly-arrows.



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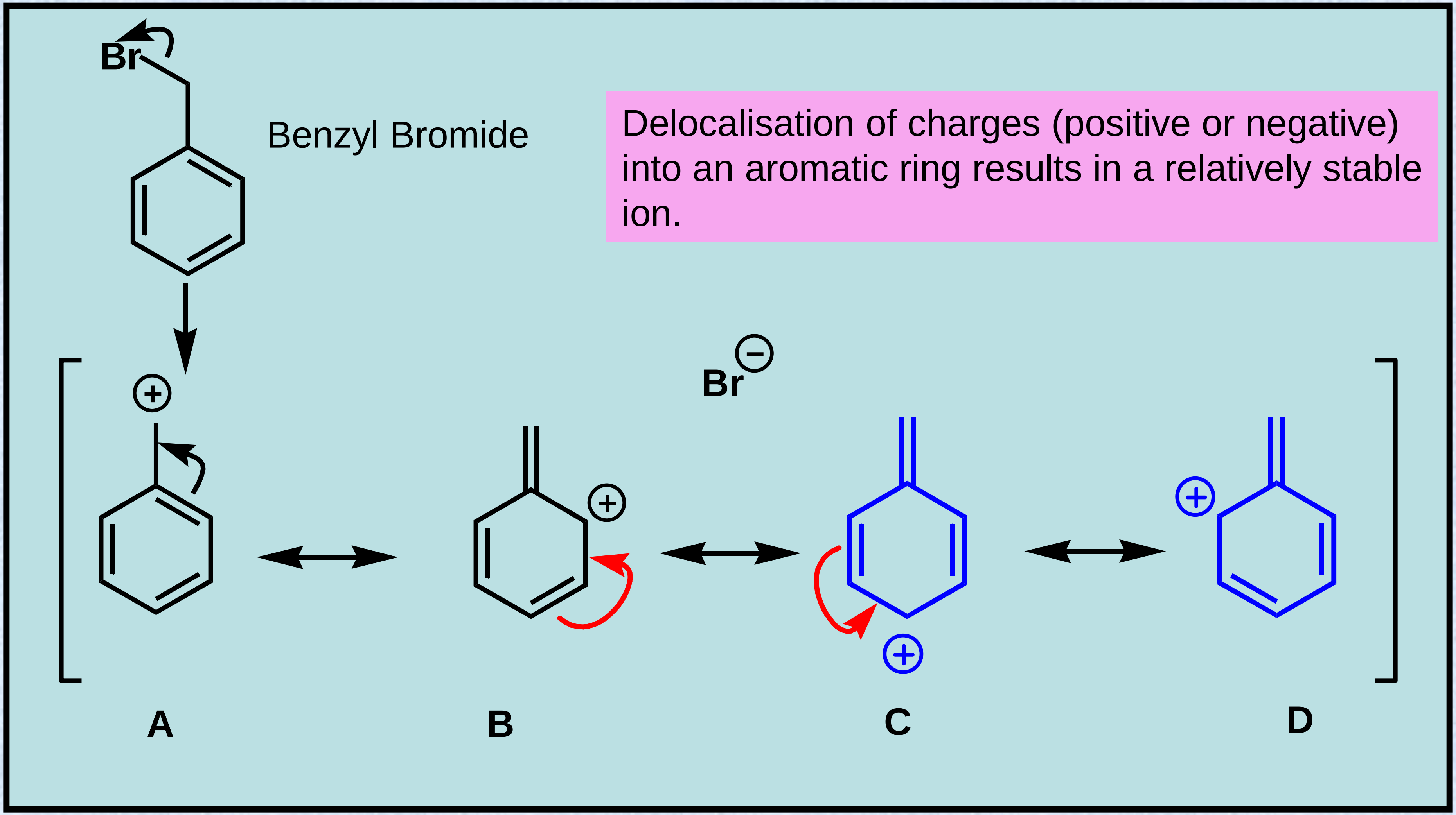
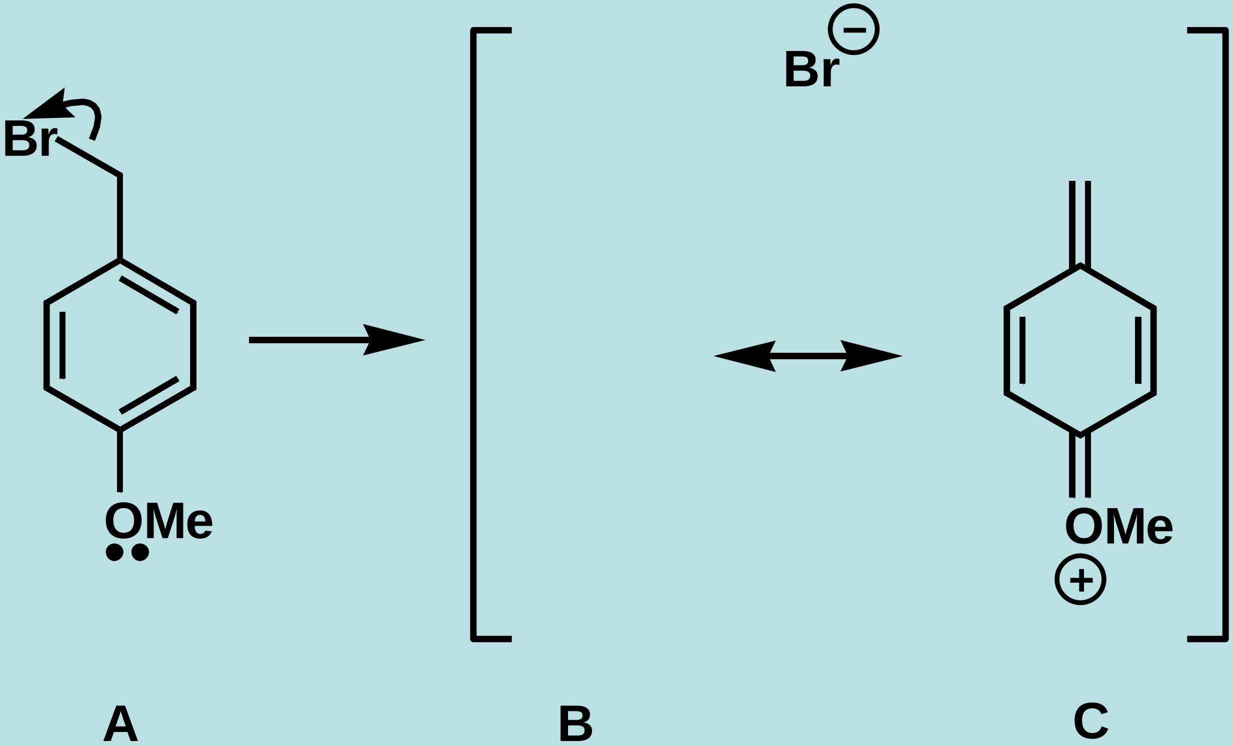


Delocalisation of charges (positive or negative) into an aromatic ring results in a relatively stable ion.

Question 4: Resonances

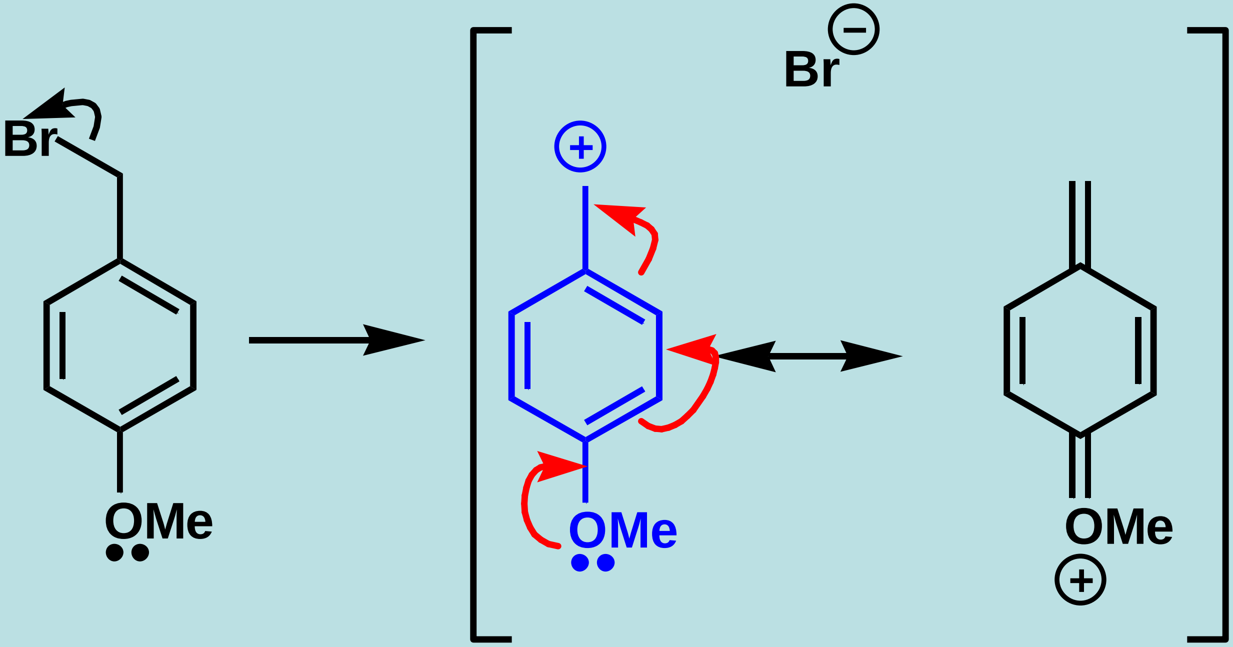
The 4-methoxybenzylic bromide A undergoes C-Br bond cleavage much more easily to generate the benzyl cation B, than does the C-Br bond in benzyl bromide in question 3. Indentify B and then draw in the curly arrows that lead to the resonance structure C.



Comment on why **A** undergoes C-Br cleavage more readily than the parent benzyl bromide from Q3.

Answer 4: Resonances

The benzylic bromide A undergoes C-Br bond cleavage very easily to generate the benzyl cation B. Indentify B and then draw in the curly arrows that lead to the resonance structure C.



A **B** **C**

The reason that the C-Br bond is cleaved so readily, is due to the positive charge being able to delocalise through the aromatic ring and onto the oxygen atom. i.e. the charge is spread out over many atoms leading to a stable electronic structure.