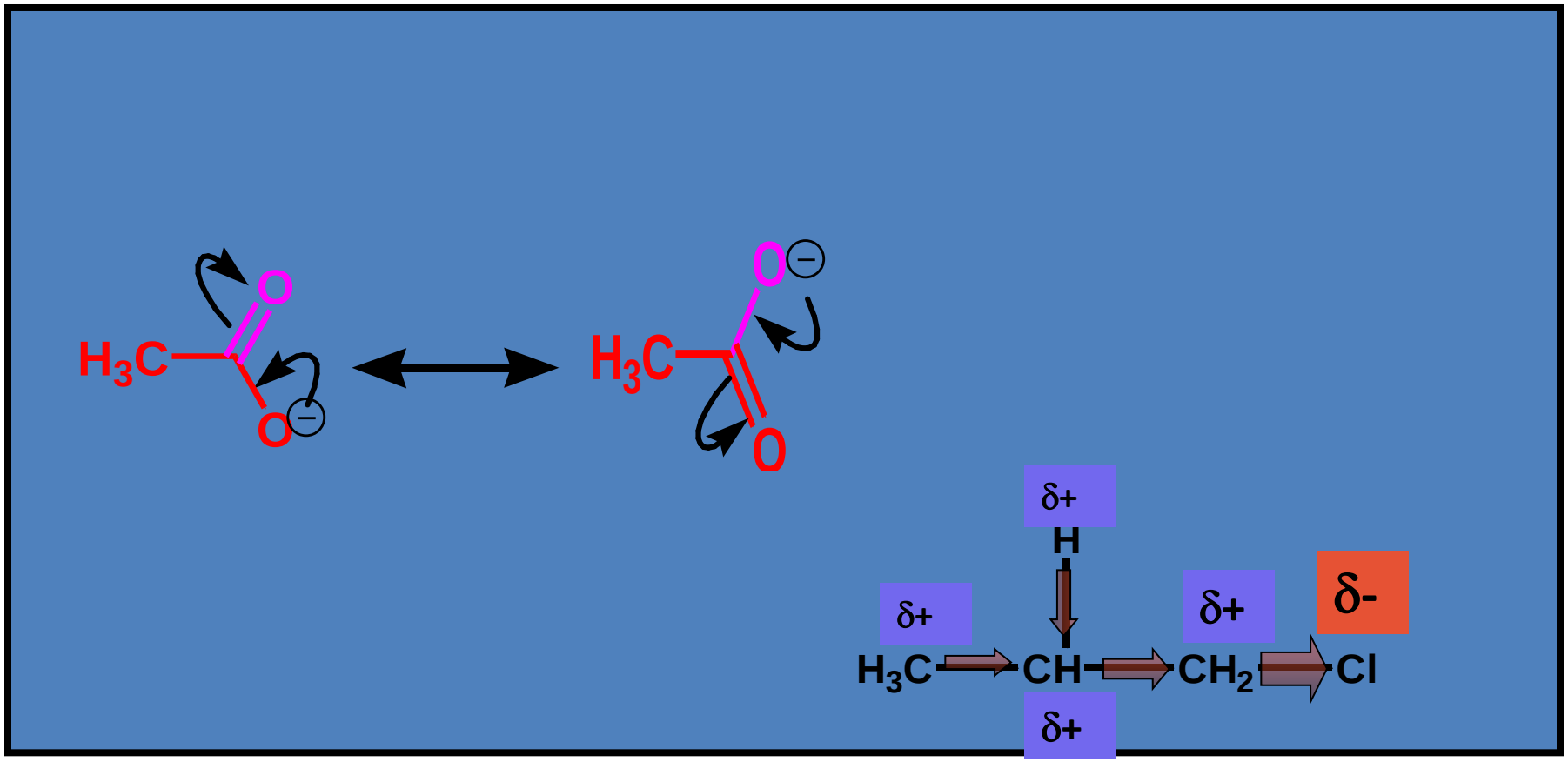
Paper II- Organic Chemistry

Chapter-I
Structure and Bonding

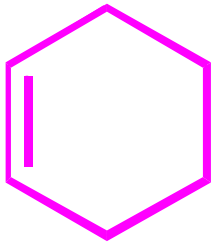
Mr. Chaudhar Uddhav N.
Assistant Professor,
Department of Chemistry,
Kalikadevi Arts, Commerce and Science College, Shirur Ka. Dist-Beed

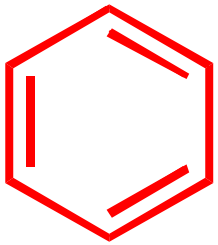
Resonance and Inductive Effects



Resonance Effect

Benzene Bond Lengths

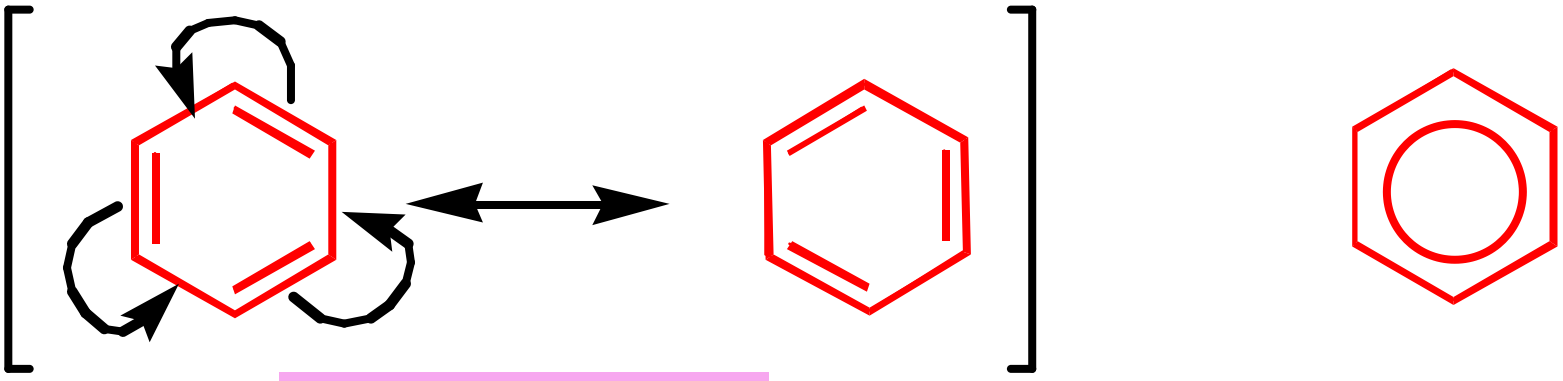
1.33 Å →  ← 1.52 Å

1.42 Å →  ← 1.42 Å

Resonance Structures of Benzene

The 6 π-electrons are able to flow (or resonate) continulally 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

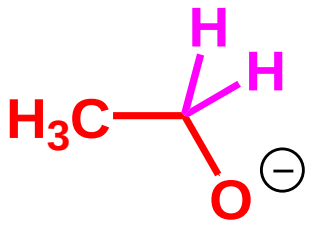
The π-electrons are referred to as being conjugated.

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

CH_2

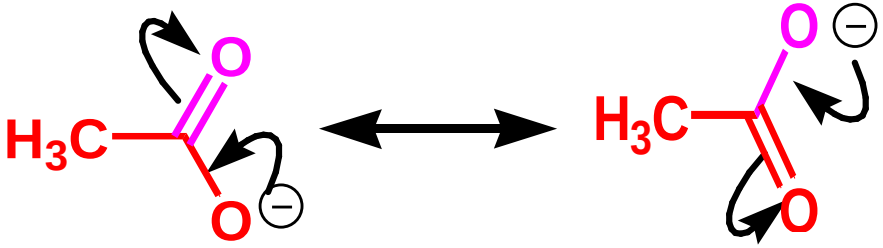
Replaced by

C=O



No adjacent double bond to the oxygen lone pair

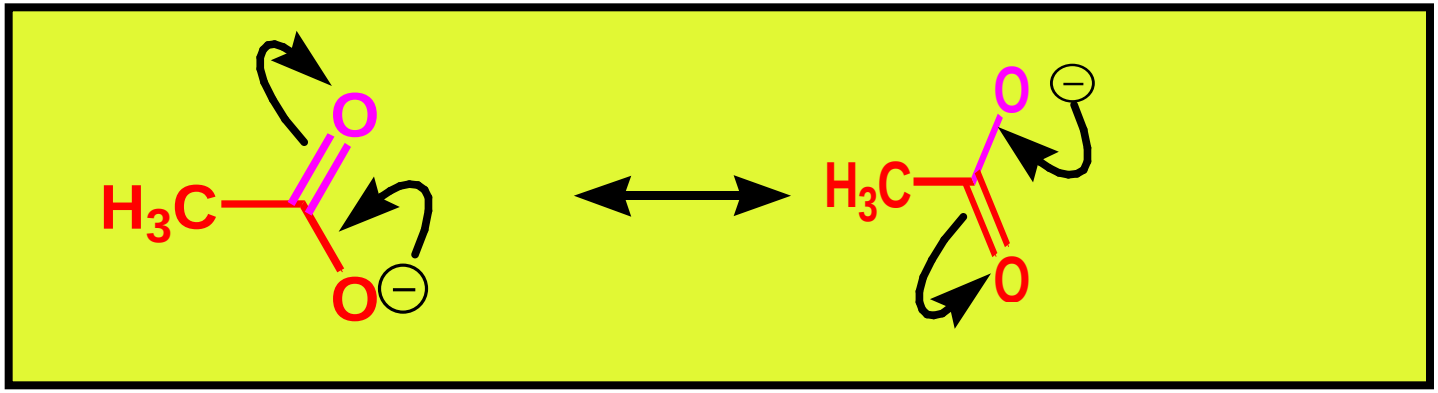
Relatively difficult to form



Relatively easy to form

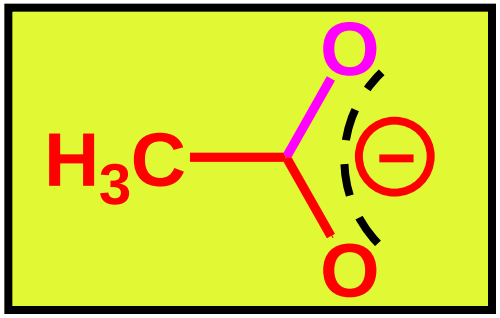
The Resonance Arrow and its Physical Meaning

The resonance arrow is not an equilibrium arrow



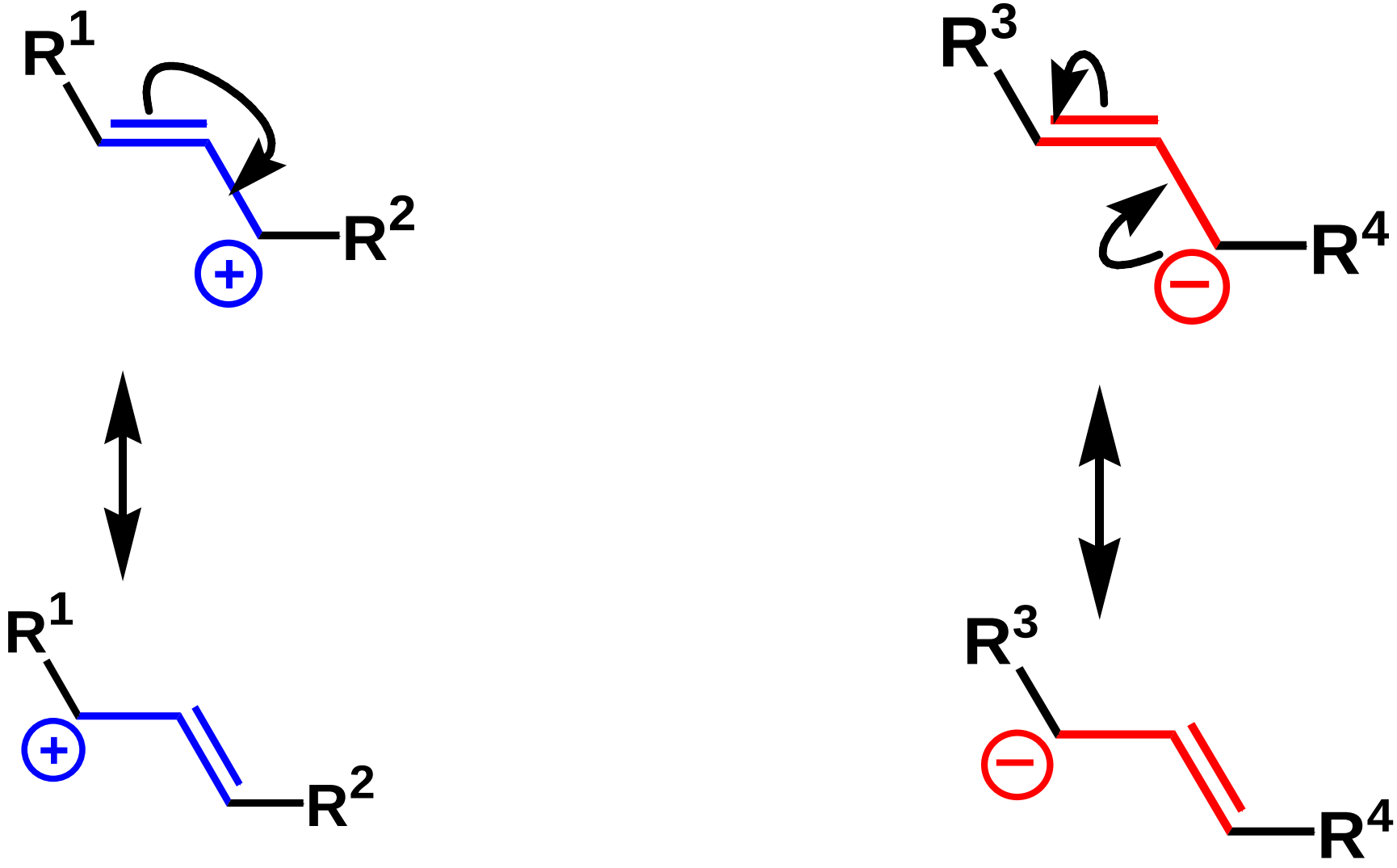
The resonance arrow shows only the distribution of electrons.

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.



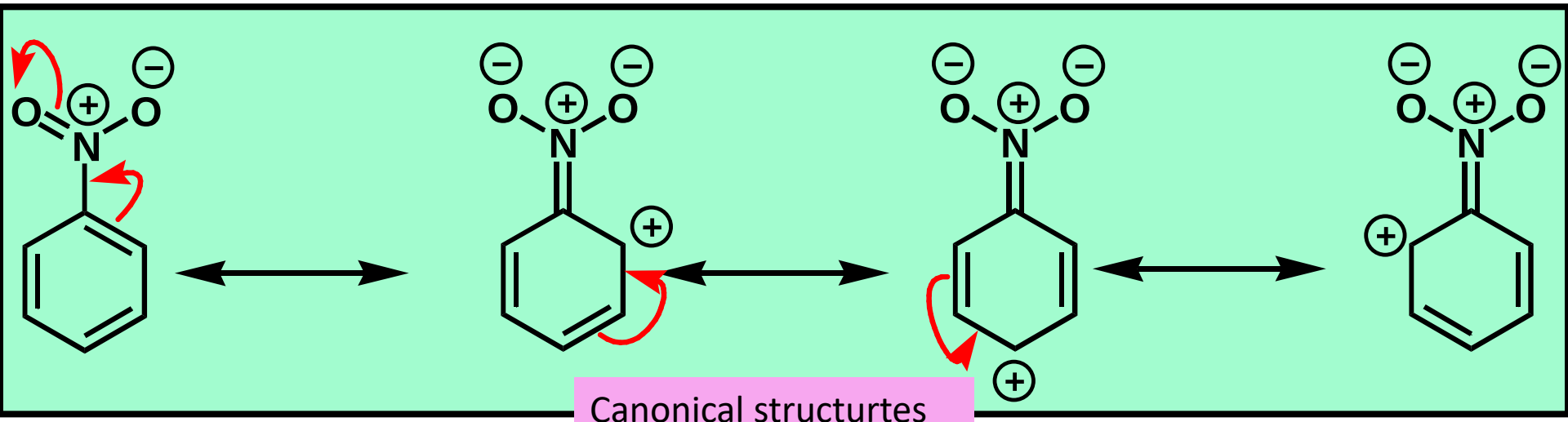
Experimentally it is found that both C-O bonds are the same length and are intermediate in length between the C-O single and double bond, as are the C-C bonds in benzene.

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

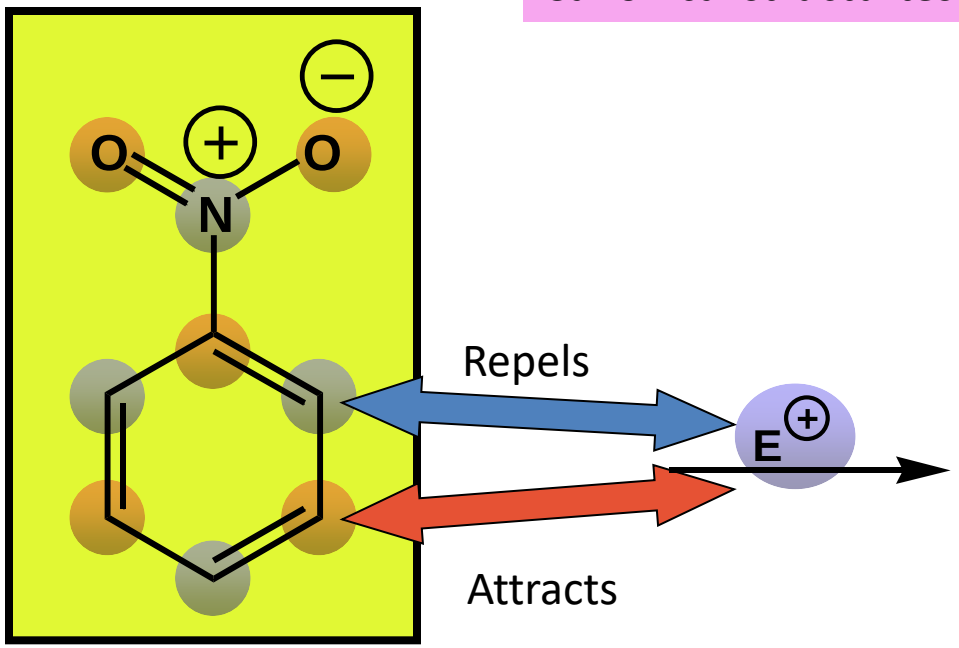


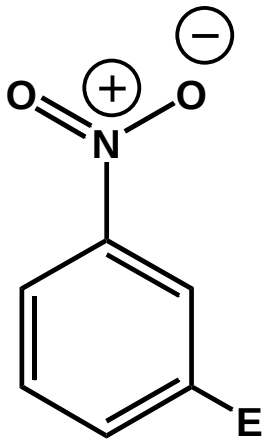
Some Important Aromatic Resonance Structures

Nitro Group: An Electron Withdrawing Group

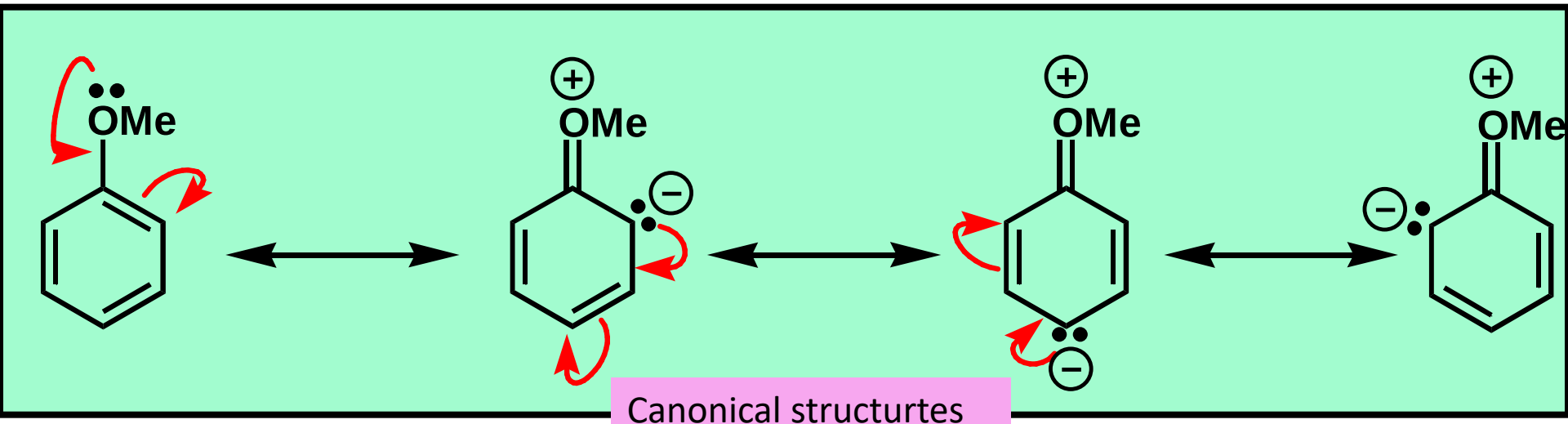


Canonical structurtes



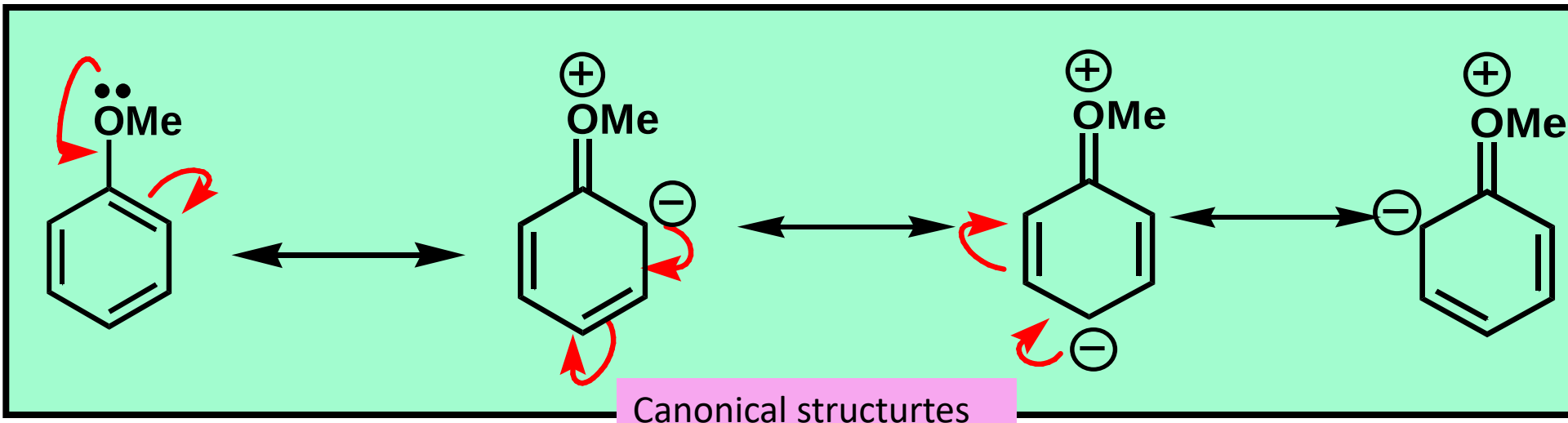


Methoxy Group: An Electron Donating Group



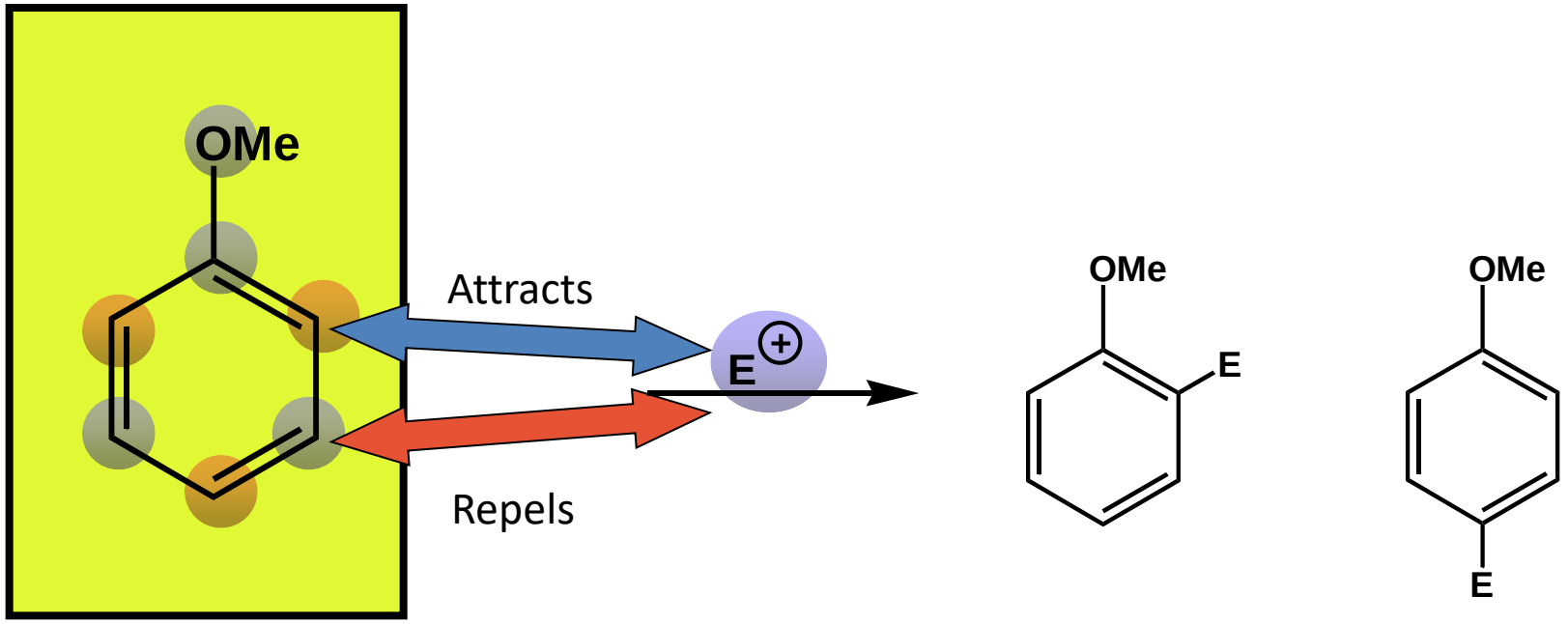
Canonical structurtes

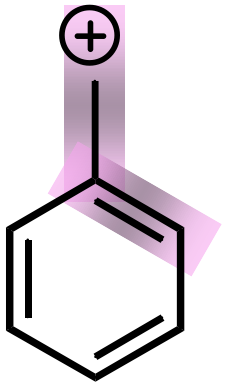
…Note in a reaction mechanism we would not show the lone pairs on the carbons carrying the –ve charge…

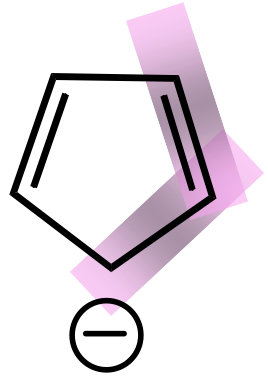


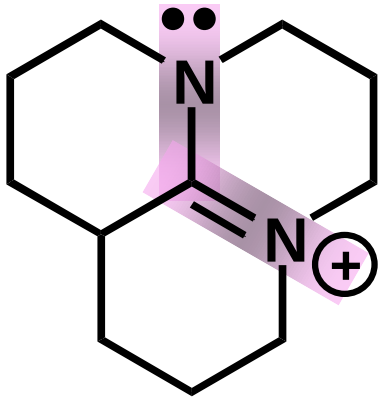
Canonical structurtes

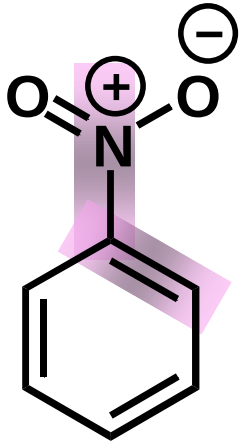
These resonance structures allow us to rationalise (and predict) reactivity

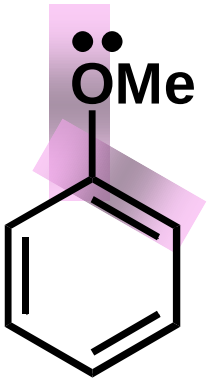






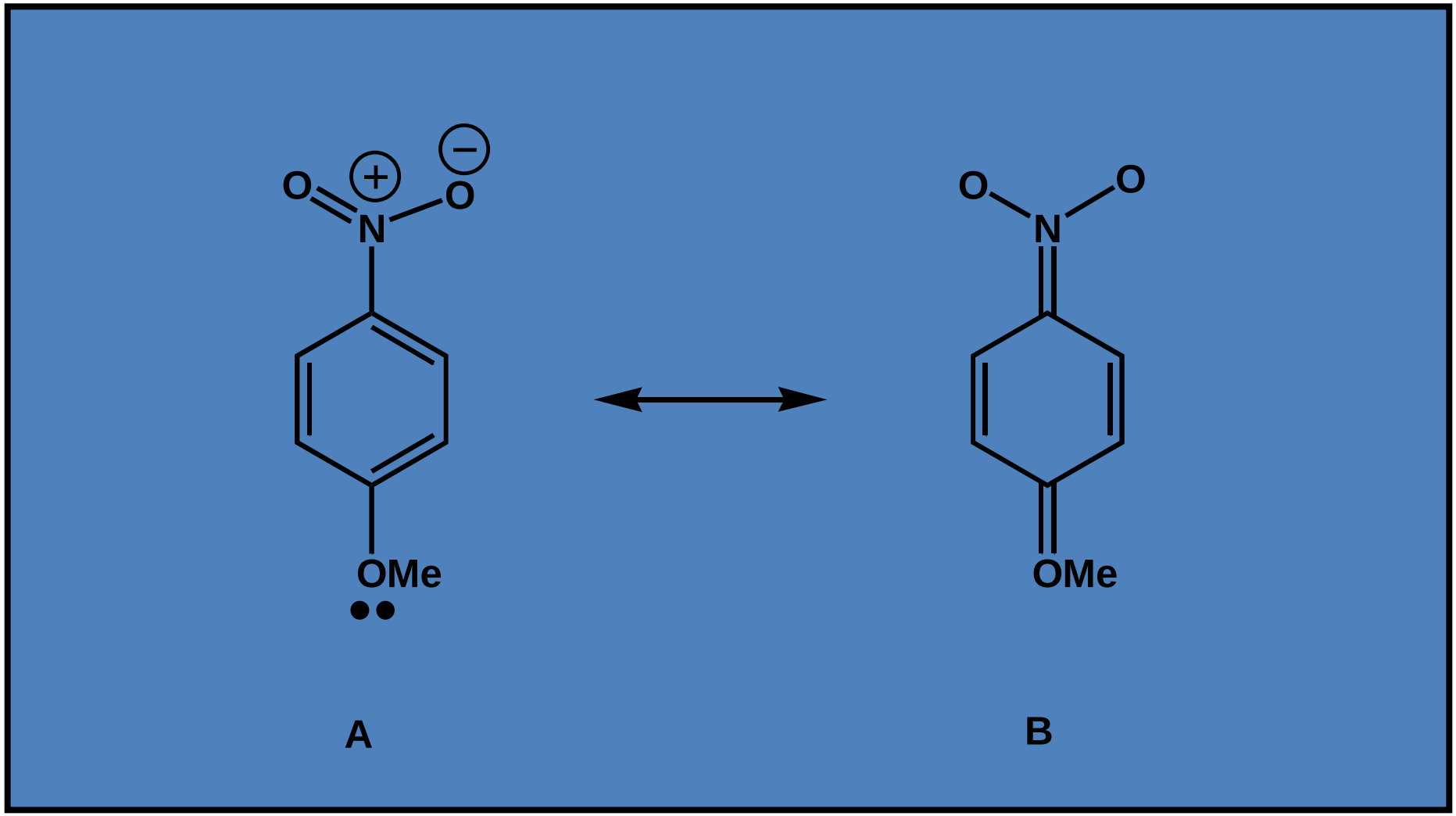

N
N


O
N
O


OMe

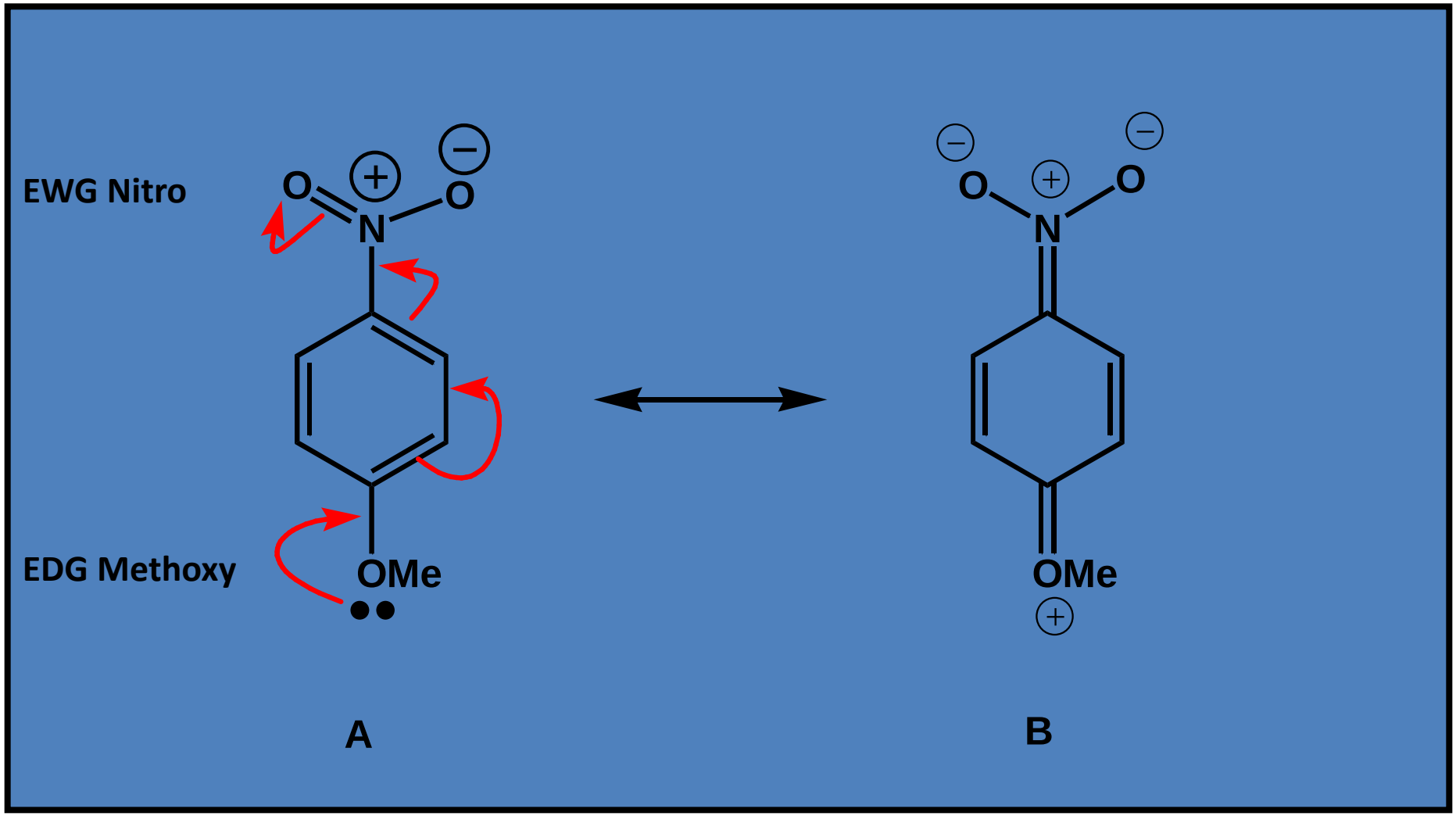
Question 1: Resonances

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.



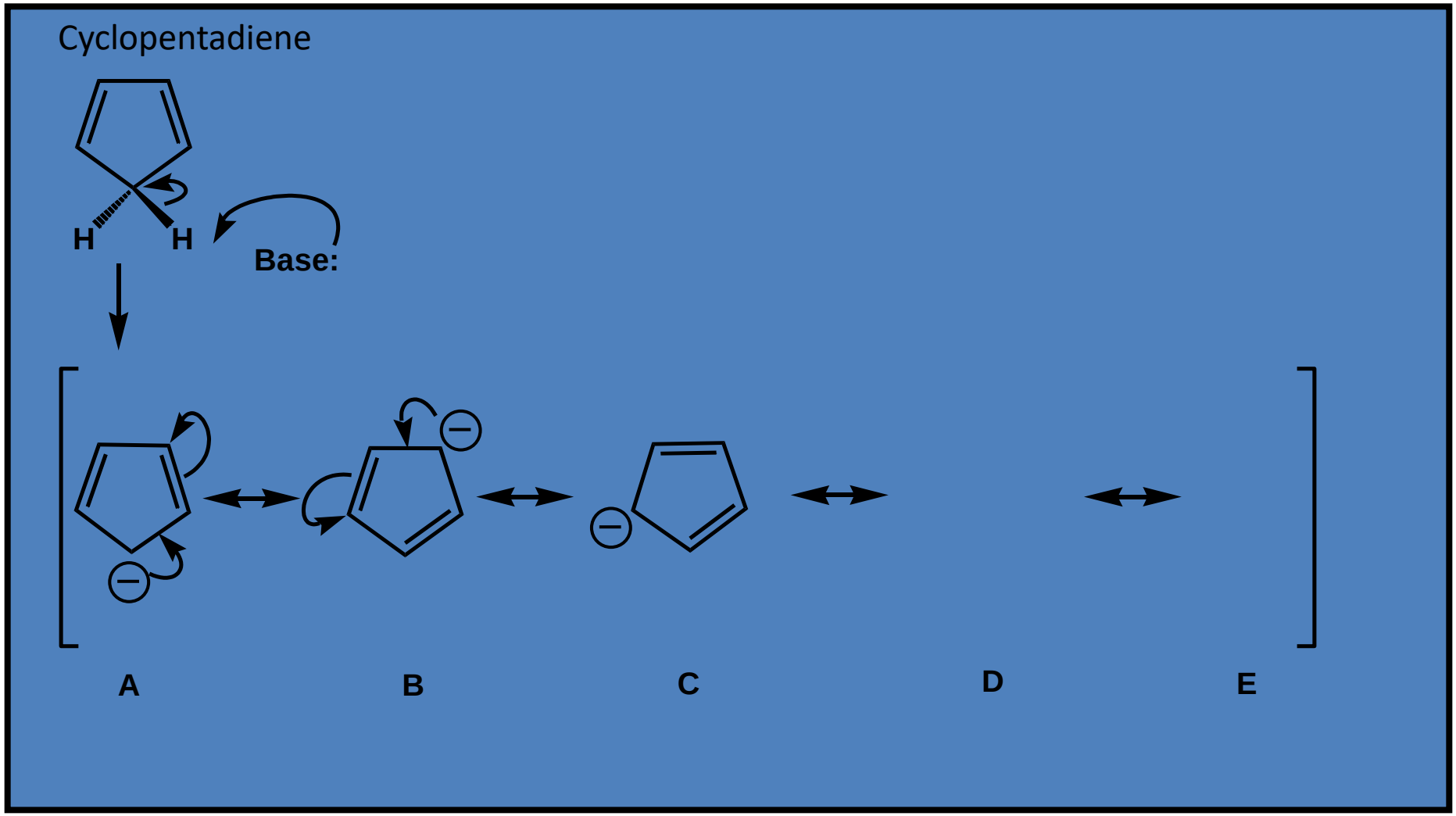
Answer 1: Resonances

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.



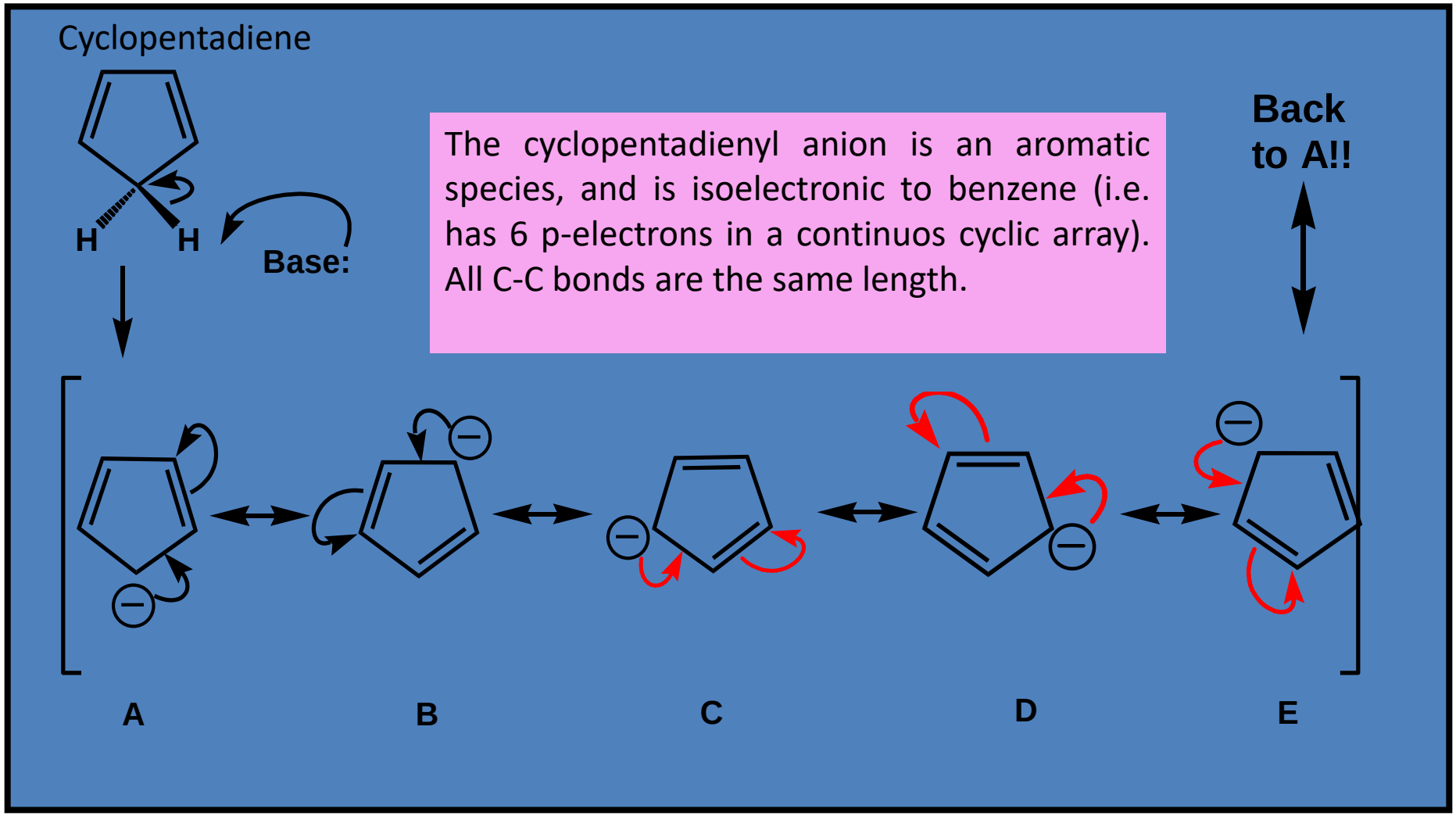
Question 2: Resonances

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.



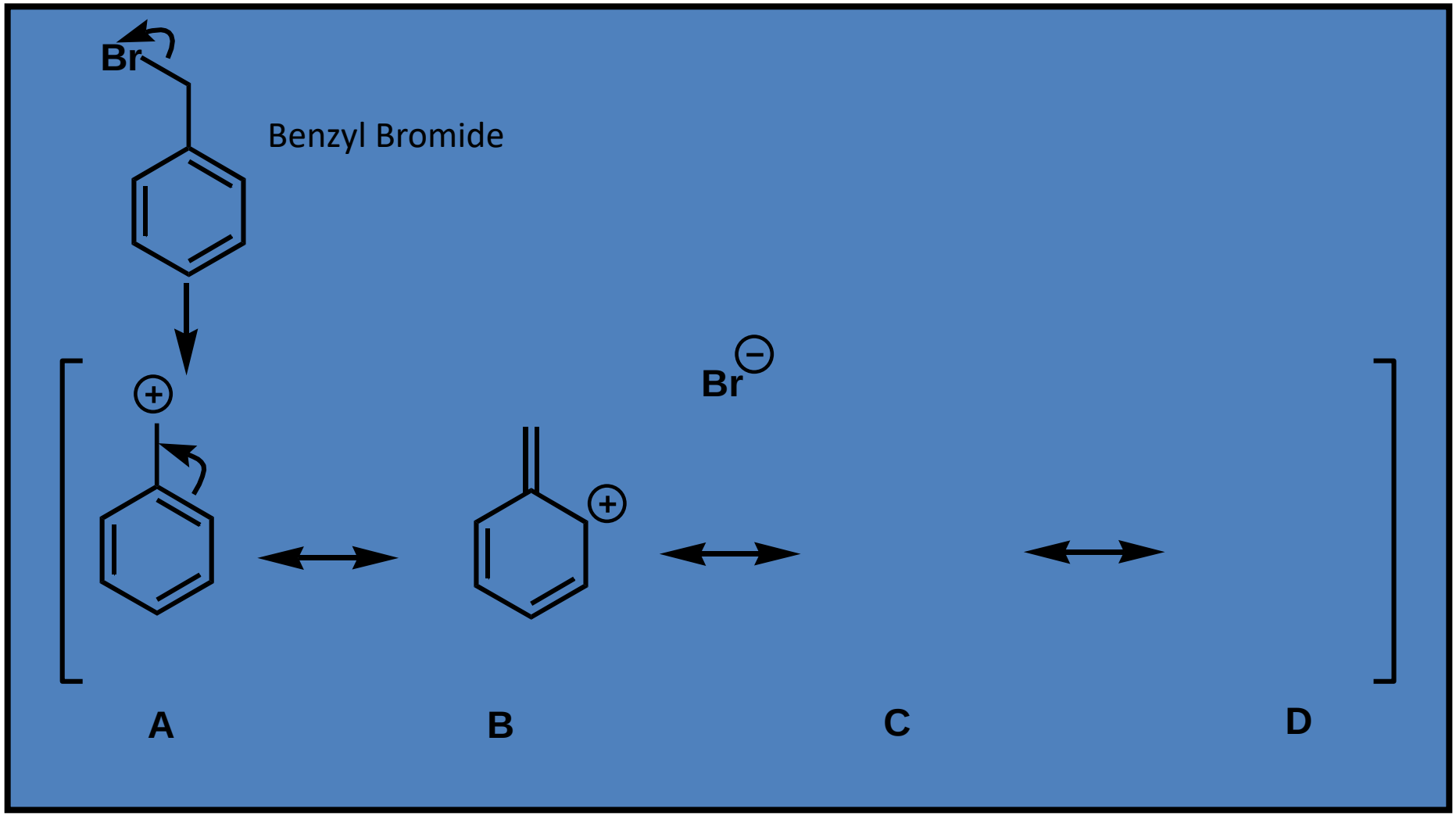
Answer 2: Resonances

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.



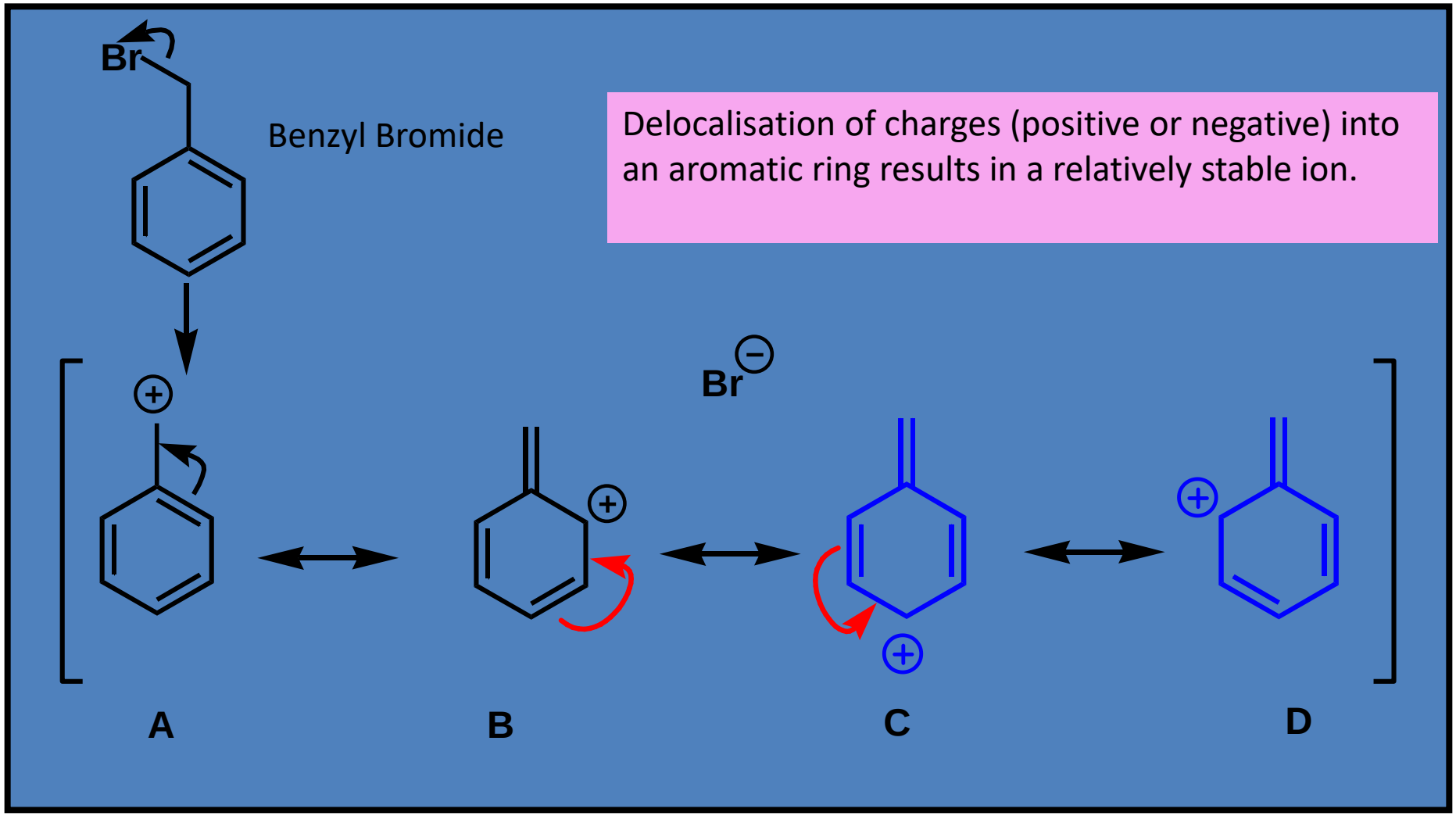
Question 3: Resonances

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.



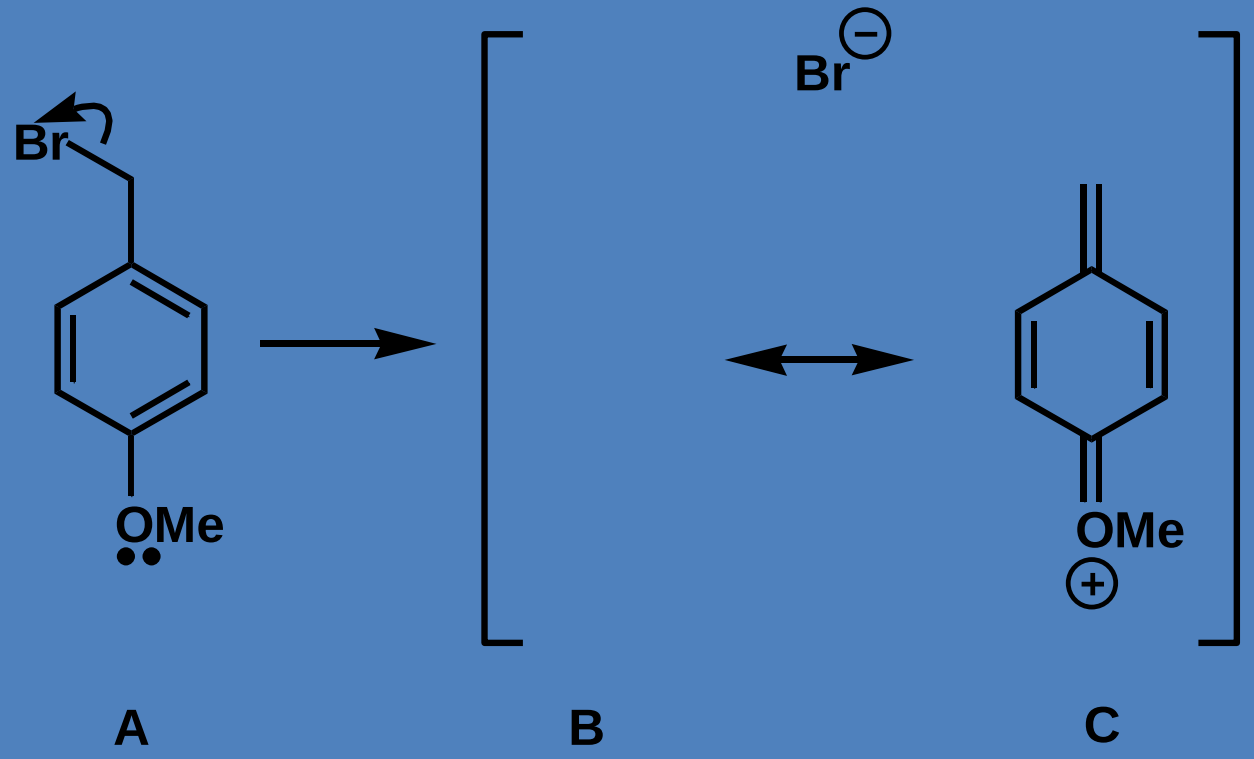
Answer 3: Resonances

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.



Question 4: Resonances

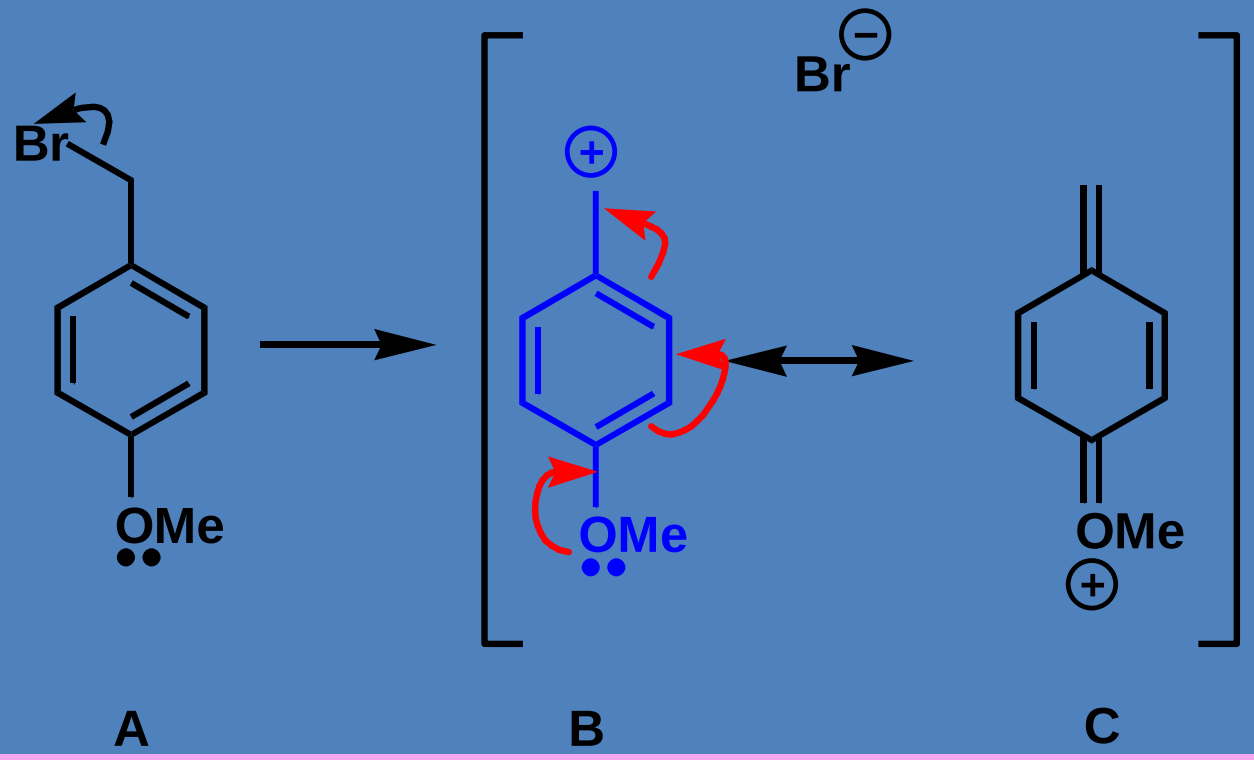
The 4-methoxybenzylic bromide A undergoes C-Br bond cleavage much more easily to generate the benzyl cation B, than does the C-Br bond in benzyl bromide in question 3. Indentify B and then draw in the curly arrows that lead to the resonance structure C.



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.

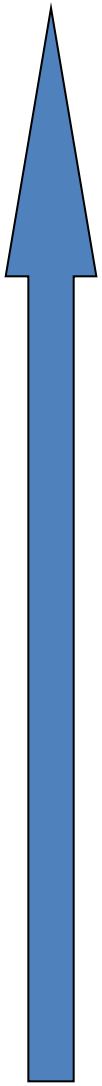


The reason that the C-Br bond is cleaved so readily, is due to the positive charge being able to delocalise through the aromatic ring and onto the oxygen atom. i.e. the charge is spread out over many atoms leading to a stable electronic structure.

Inductive Effects

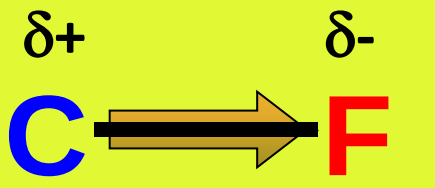
Electronegativity Values

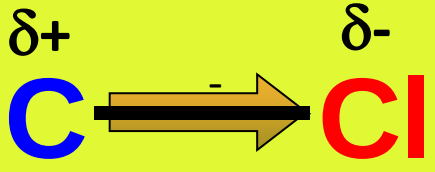
H 2.1	C 2.5	N 3.0	O 3.5	F 4.0
	Si 1.8	P 2.1	S 2.4	Cl 3.0
				Br 2.8
				I 2.5

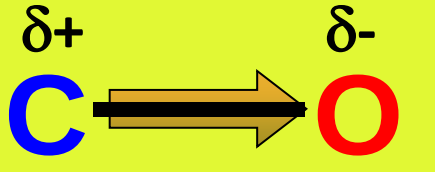


Bond Polarisation and Inductive Effects

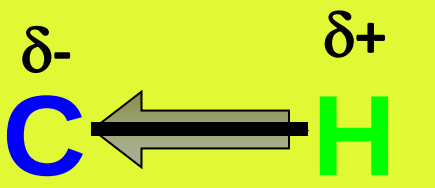
-I Inductive Effects

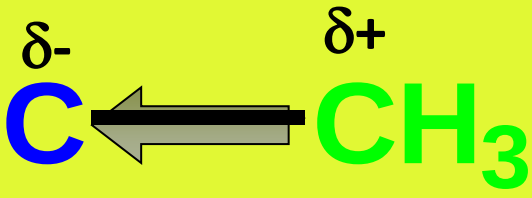


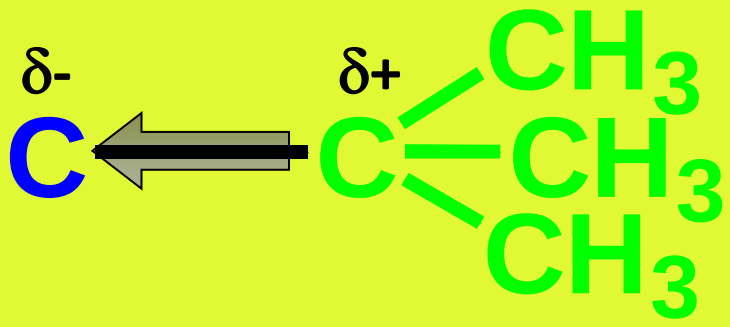




+I Inductive Effects



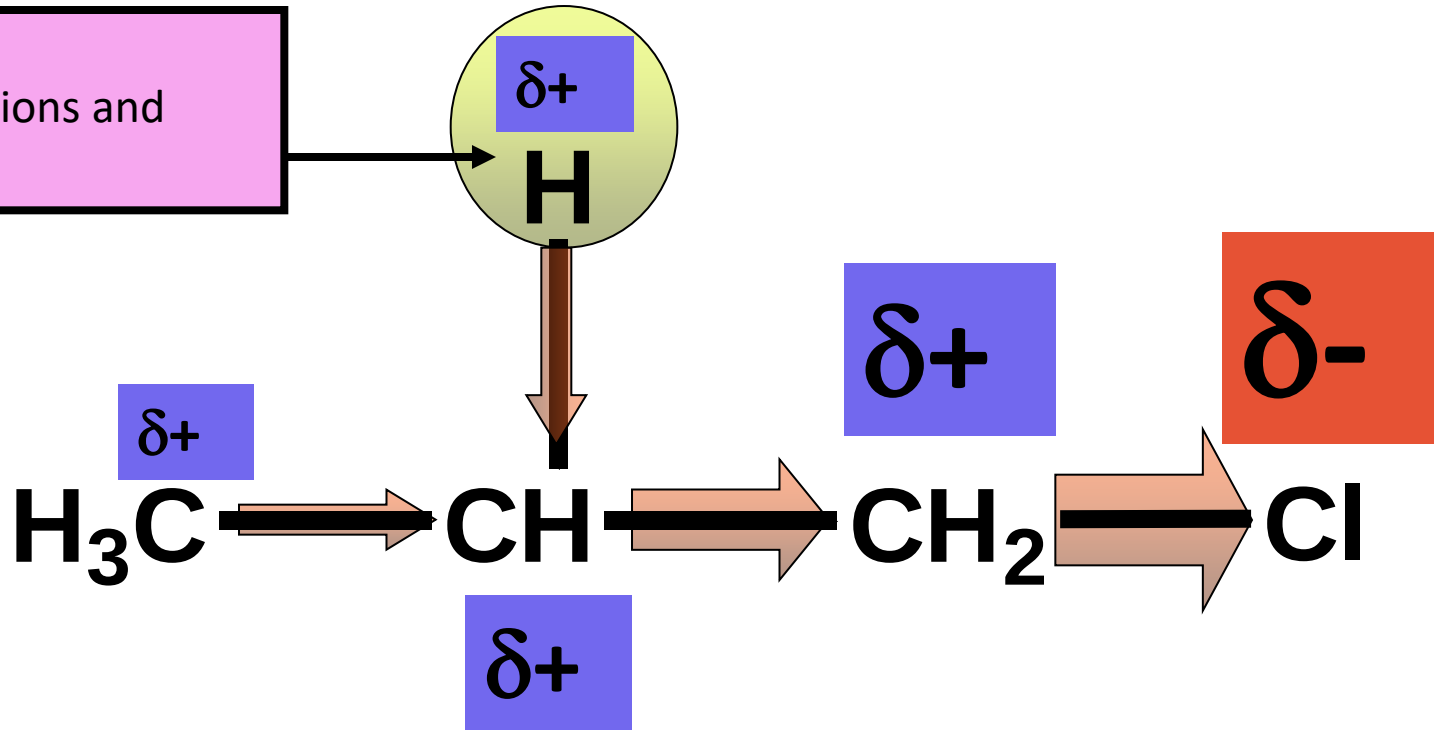




Inductive Effects are Short Range

In Contrast to Resonance Effects

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



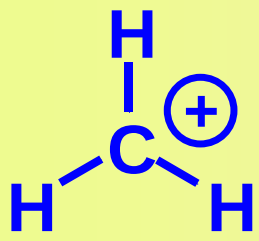
The polarised C-Cl bond transmits further polarisation through the σ-bond framework,

But effect drops off quickly…

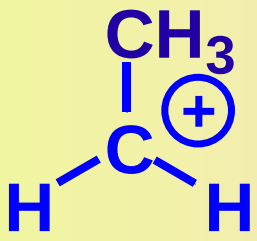
Inductive Effects and Carbocation Stability

Important when considering substitution reactions in part 4 of this course

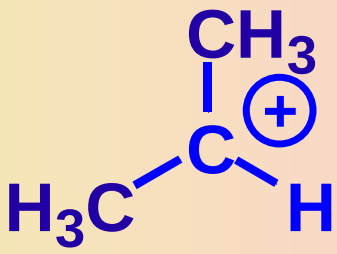
LEAST STABLE → MOST STABLE



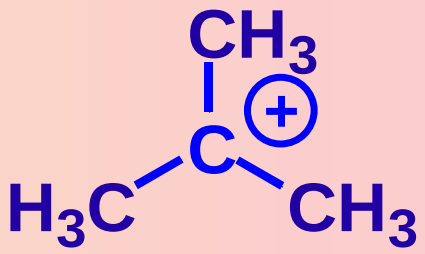
Methyl Carbocation



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.