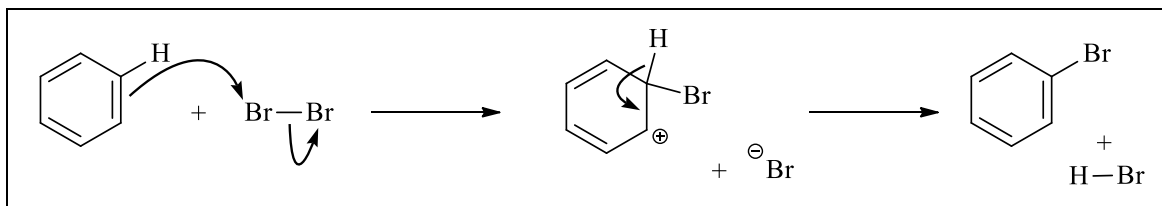


- Benzene can undergo an S_EAr reaction with bromine, Br_2 , as shown below. Demonstrate your understanding of this reaction by adding curly arrows to complete the mechanism.

Marks
9



Explain what each part of the abbreviation S_EAr means.

S = substitution

E = electrophilic

Ar = aromatic

Identify one nucleophile and one electrophile in the scheme above.

nucleophile

C=C in step (i). Br^- in step (ii)

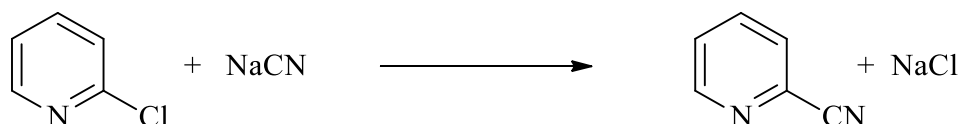
electrophile

Br_2 in step (i). Carbocation in step (ii).

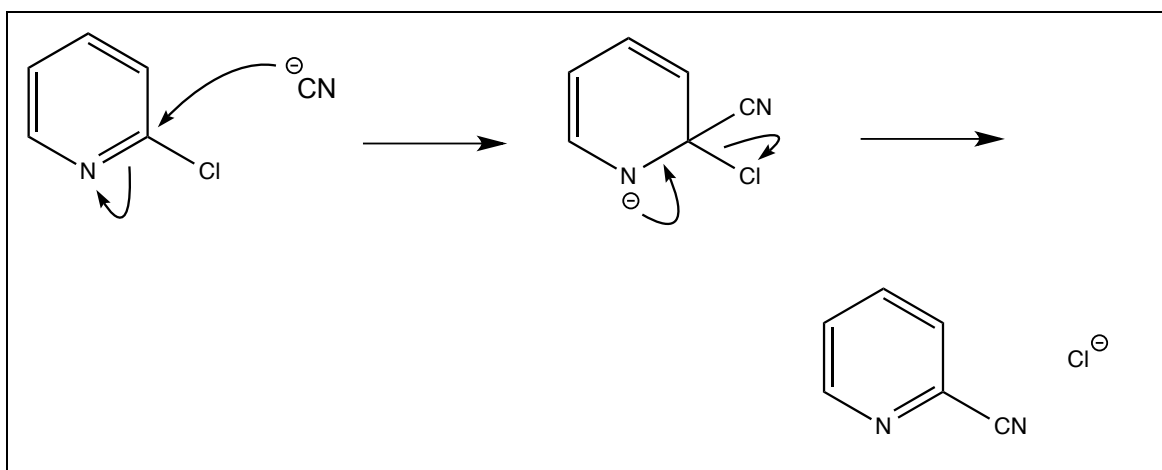
Iron(III) bromide, $FeBr_3$, is often added to the reaction shown above. Why?

It is a catalyst. Br_2 attaches weakly to it causing the non-polar Br-Br bond to become polarised with a partial positive charge on one end. This makes it more electrophilic.

2-Chloropyridine can undergo the following reaction with sodium cyanide.



This reaction also proceeds via a two-step mechanism and an ionic (*i.e.* charged) intermediate. Apply your understanding of organic reactions to propose a mechanism for this reaction.



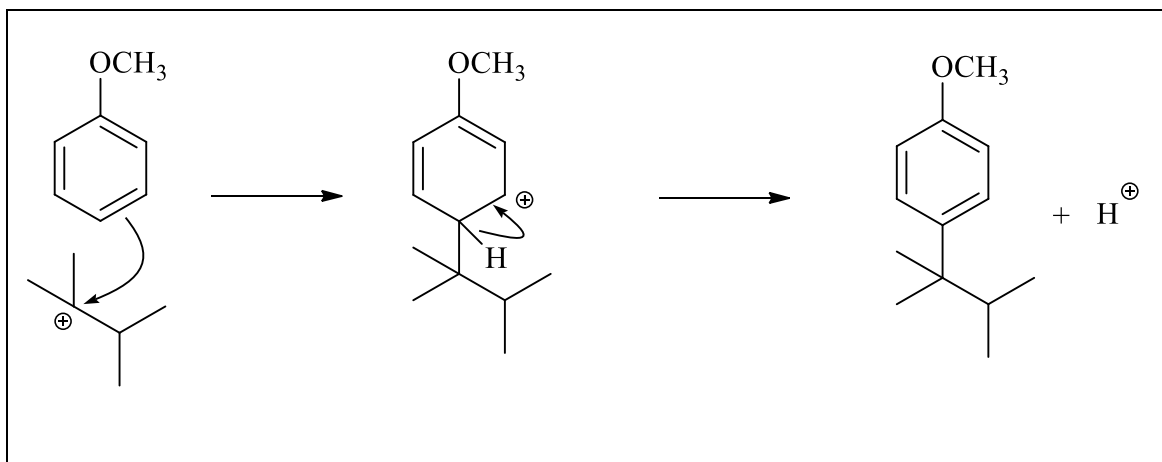
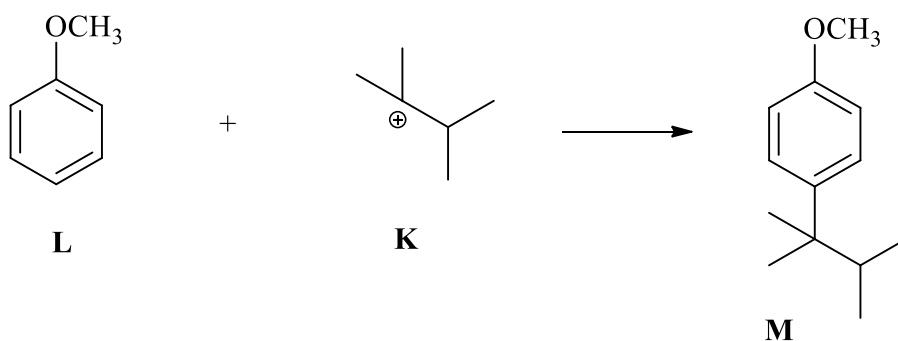
ANSWER CONTINUES ON THE NEXT PAGE

If the reaction of benzene shown above is S_EAr , how would you classify this reaction of chloropyridine?

S_NAr (nucleophilic)

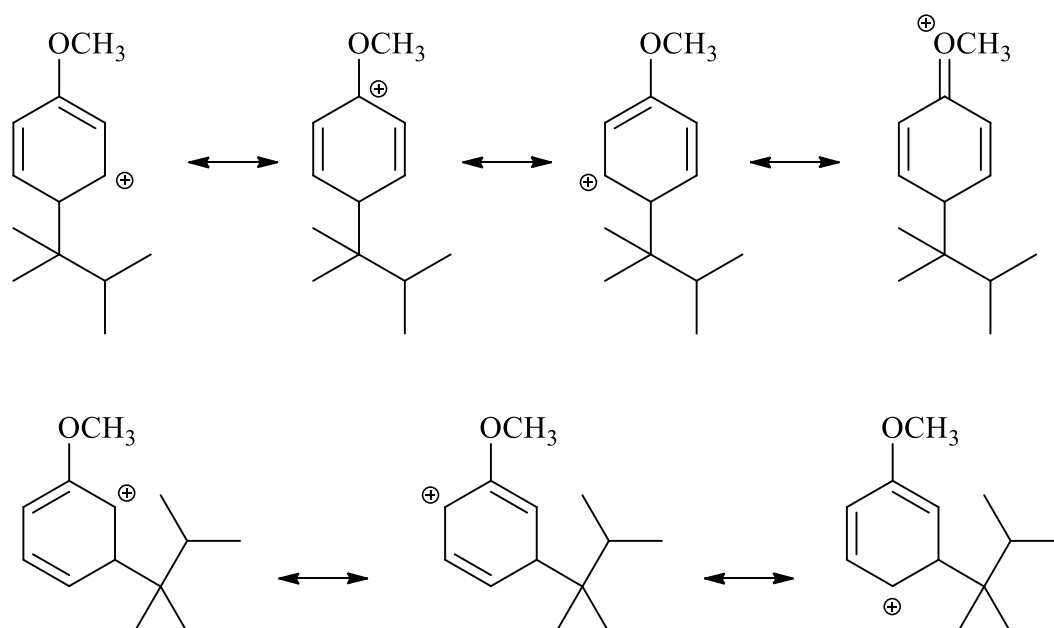
Reaction of **K** with anisole (methoxybenzene, **L**) gives **M** as the major product. Propose a mechanism for this transformation.

**Mark
s**
4



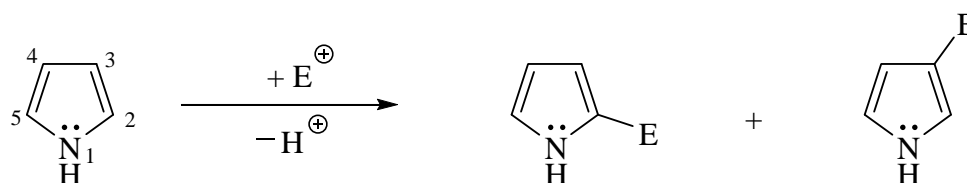
Briefly explain why the 4-substituted product **M** is formed preferentially.

Substitution at positions 2 and 4 is favoured over position 3 due to the relative stabilities of the Wheland intermediates. There are 4 resonance contributors for substitution at positions 4 (or 2), but only 3 for substitution at position 3. Position 4 is favoured over position 2 due to steric effects - the methoxy group attached to C1 physically blocks approach of the attacking carbocation./



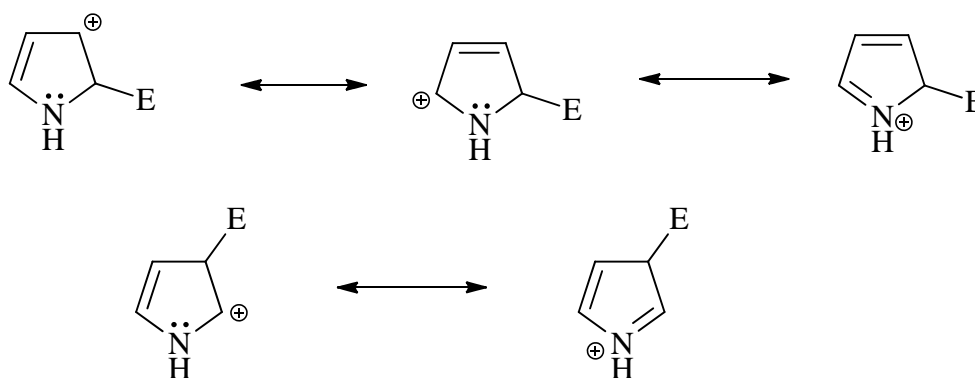
Marks
5

- In the electrophilic aromatic substitution (S_EAr) of pyrrole, the 2-substituted derivative is the major product.



Draw the cationic (Wheland-type) intermediate formed during reaction at the 2-position, and the equivalent intermediate formed during reaction at the 3-position. Using these structures, explain why reaction at the 2-position is faster, and leads to the major product.

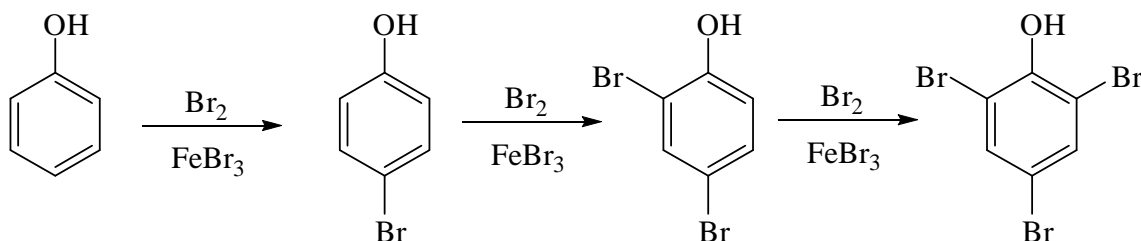
Substitution at position 2 gives 3 canonical forms for the Wheland intermediate, versus only 2 for the substitution at position 3.



The intermediate with the greater number of resonance structures is the more stable and leads to the major product.

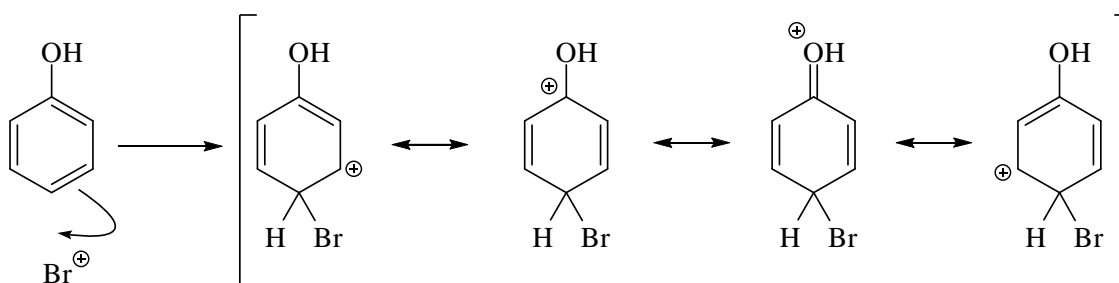
Marks
3

- The bromination of phenol proceeds as follows.



Show the Wheland intermediate for one of these steps and explain why bromination occurs at positions 2, 4 and 6, but not at positions 3 and 5.

Bromination at the 4 (or 2 or 6) position gives a Wheland intermediate that has four resonance contributors as the lone pair on the oxygen can be donated into the ring to help stabilise the charge.



Bromination at the 3 or 5 position gives a Wheland intermediate that has only three resonance contributors - the lone pair on the oxygen cannot participate in the resonance stabilisation.

