

1. June/2022/Paper\_41/No.4(d, e)

(d) The ligand bipyridine consists of two pyridine rings.

Pyridine,  $C_5H_5N$ , and benzene,  $C_6H_6$ , have similar planar, cyclic structures.



Fig. 4.2

By reference to the hybridisation of the carbon atoms and the nitrogen atom, and orbital overlap, suggest how the  $\sigma$  and  $\pi$  bonds are formed in a pyridine molecule.

.....

.....

.....

.....

[3]

(e) Pyridine reacts with  $Cl_2$  in the presence of  $AlCl_3$  as shown in Fig. 4.3.

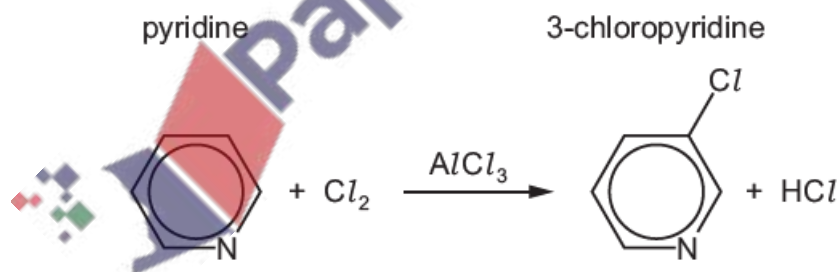


Fig. 4.3

The mechanism of this reaction is similar to that of the chlorination of benzene.  $AlCl_3$  reacts with chlorine to generate an electrophile,  $Cl^+$ .

Complete the diagram to show the mechanism for the reaction of pyridine with  $Cl^+$ . Include all relevant charges, dipoles, lone pairs of electrons and curly arrows as appropriate.



[3]

2. June/2022/Paper\_41/No.7

Procaine is used as an anaesthetic in medicine. It can be synthesised from methylbenzene in five steps as shown in Fig. 7.1.

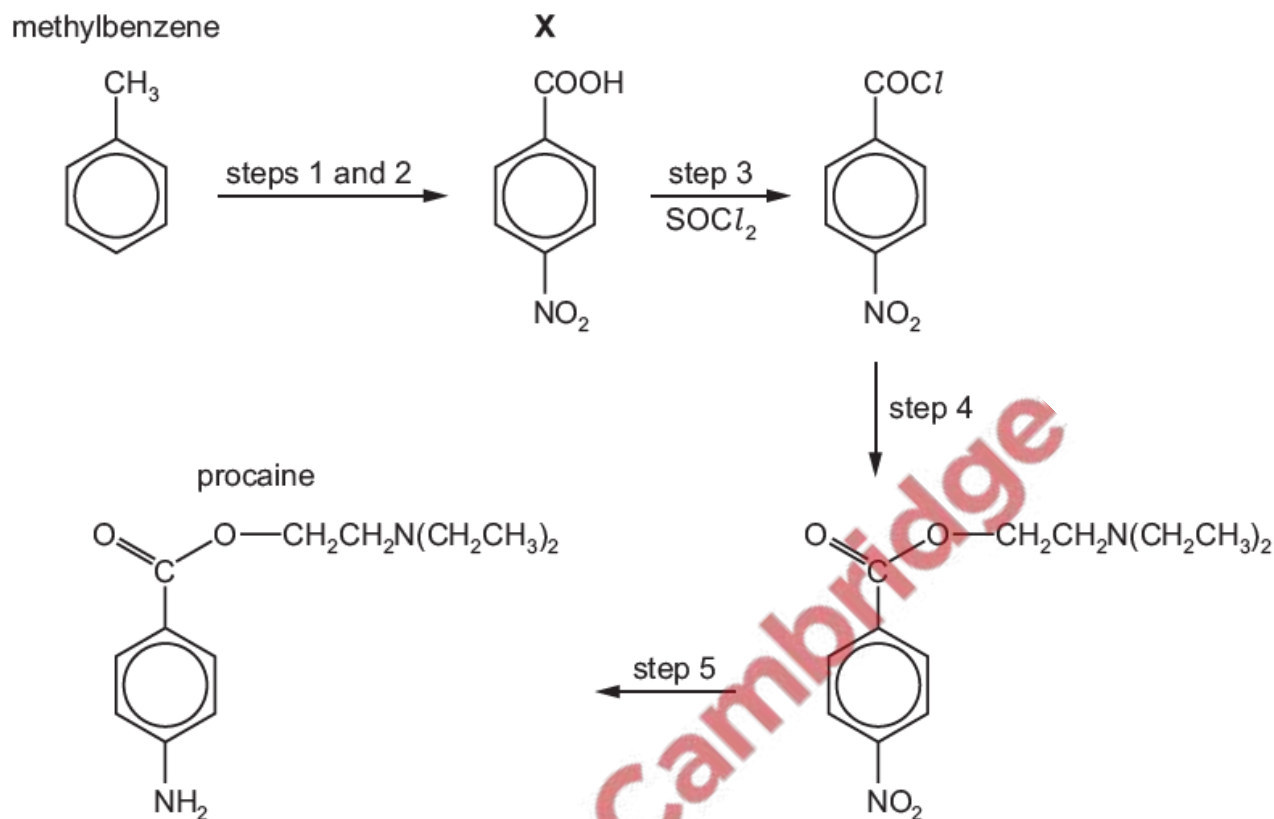


Fig. 7.1

(a) (i) Name all the functional groups present in procaine.

..... [1]

(ii) A molecule of procaine has 13 carbon atoms.

State the number of carbon atoms that are sp, sp<sup>2</sup> and sp<sup>3</sup> hybridised in procaine.

sp carbons = ..... sp<sup>2</sup> carbons = ..... sp<sup>3</sup> carbons = ..... [1]

(b) The proton (<sup>1</sup>H) NMR spectrum of procaine dissolved in D<sub>2</sub>O is recorded.

Predict the number of peaks observed.

..... [1]

(c) State why procaine can act as a base.

.....  
 ..... [1]

(d) Compound X can be synthesised in two steps from methylbenzene.

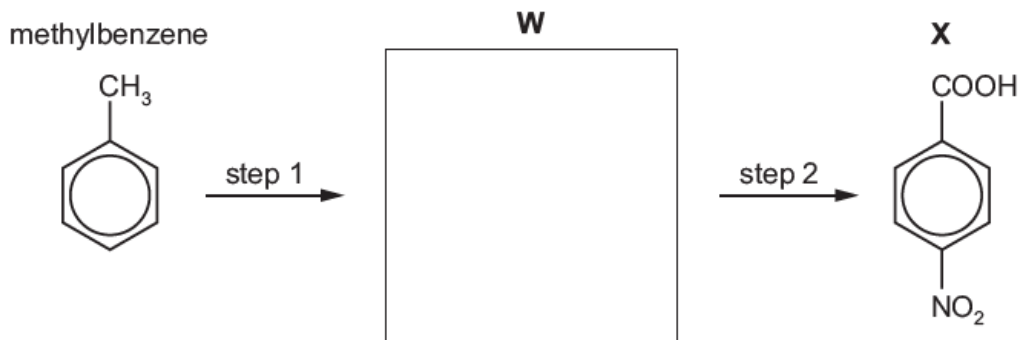


Fig. 7.2

(i) Draw the structure of compound W in the box provided. [1]

(ii) State the reagents and conditions for step 1 and step 2.

step 1 .....

step 2 .....

[2]

(e) Procaine is synthesised in three steps from X.

Suggest the reagents and conditions for step 4 and for step 5 in Fig. 7.1.

step 4 .....

step 5 .....

[3]

(f) (i) Explain what is meant by partition coefficient,  $K_{pc}$ .

.....

..... [2]

(ii) The partition coefficient of procaine between octan-1-ol and water is 1.77.

Octan-1-ol and water are immiscible. A solution containing 0.500 g of procaine in 75.0 cm<sup>3</sup> of water is shaken with 50.0 cm<sup>3</sup> of octan-1-ol.

Calculate the mass of procaine that is extracted into the octan-1-ol.

mass of procaine extracted = ..... g [2]

[Total: 14]

3. June/2022/Paper\_42No.6(a\_c)

- (a) The reagent and conditions required for the nitration of benzene, benzoic acid and phenol are shown in Table 6.1.

Table 6.1

compound	reagents and conditions for nitration
benzene	concentrated HNO <sub>3</sub> , 50 °C, concentrated H <sub>2</sub> SO <sub>4</sub> catalyst
benzoic acid	concentrated HNO <sub>3</sub> , 100 °C, concentrated H <sub>2</sub> SO <sub>4</sub> catalyst
phenol	dilute HNO <sub>3</sub> (aq), 20 °C

Concentrated HNO<sub>3</sub> reacts with concentrated H<sub>2</sub>SO<sub>4</sub> to generate the electrophile NO<sub>2</sub><sup>+</sup>.

- (i) Complete Fig. 6.1 to show the mechanism of the reaction between benzene and NO<sub>2</sub><sup>+</sup>. Include all relevant curly arrows and charges.

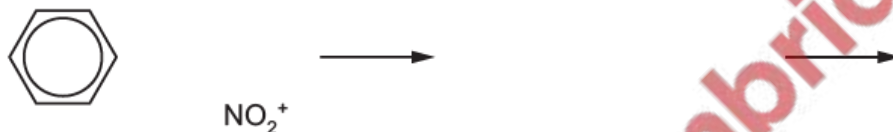


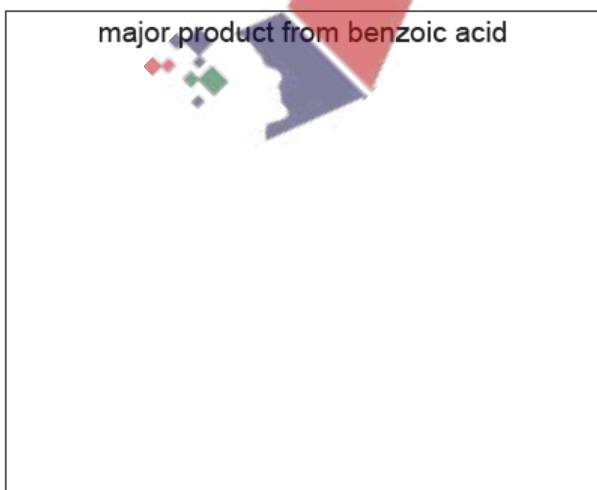
Fig. 6.1

[3]

- (ii) Write an equation to show how H<sub>2</sub>SO<sub>4</sub> is regenerated.

..... [1]

- (b) Draw the major products from the mononitration of benzoic acid and of phenol.



[2]

- (c) Compare the relative ease of nitration of benzene, benzoic acid and phenol. Explain your reasoning; include reference to the structures of the three compounds in your answer.

..... > ..... > .....

easiest  least easy

.....

.....

.....

.....

.....

[4]

