2014

CHEMISTRY

(Major)

Paper : 5.3

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

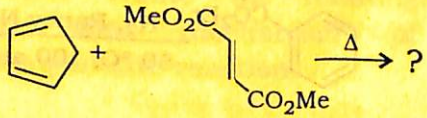
1. Answer the following questions : 1×7=7

(a) Arrange the following in order of increasing migratory aptitude in a pinacol rearrangement :

p-Chlorophenyl, *p*-tolyl, *p*-methoxyphenyl, phenyl

(b) How can you convert nitrobenzene to azobenzene?

(c) Write the product, taking care of stereochemistry :

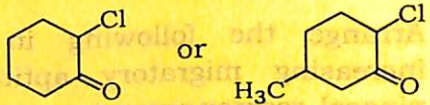


(d) Give one natural source each for pyrrole and pyridine.

(e) $C_3H_7NO_2$ is a nitroalkane. It reacts with nitrous acid to form a colourless compound which turns red when sodium hydroxide solution is added. What is the possible structure of the parent compound?

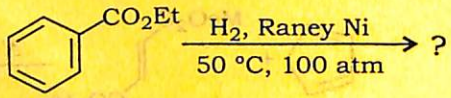
(f) Which is more acidic CH_3SH or CH_3OH? Why?

(g) Which one of the following two compounds will exhibit scrambling in a Favorskii rearrangement?

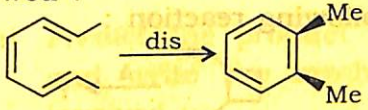


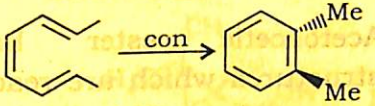
2. Answer the following questions (any *four*) : $2\times4=$

(a) What is Raney nickel? Write the appropriate product for the following reaction :



(b) State whether the given reactions are thermally allowed or photochemically allowed :

(i) 

(ii) 

(c) Which position(s) of quinoline undergo nucleophilic aromatic substitution?

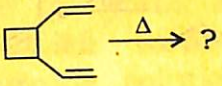
(d) 'Pyridinium ion' is about as strong an acid as carboxylic acid. Explain.

(e) What is mustard gas? What is the cause of its toxicity?

3. Answer any *three* of the following questions [any *one* from *(a)* and *(b)*, any *two* from *(c)*, *(d)* and *(e)*] : 5×3=15

(a) How can you convert acetic acid to propanoic acid, using a rearrangement reaction? Name the rearrangement. Write the mechanism of the rearrangement reaction. 2+1+2

(b) What will happen if 3-hydroxy-1,5-diene is heated? Propose a mechanism. Write the product(s) expected to be formed in the following reaction : 2+2+1



(c) (i) Acetoacetic ester has two structures which are readily inter-convertible. Write down the structures.

(ii) How is ethyl cyanoacetate prepared?

(iii) Write the reactions involved in the preparation of adipic acid from diethyl malonate.

(d) Account for the observation that *ortho-*, *para*-directing substituents on the 1-position of naphthalene directs substituents to 2- and 4-positions, whereas the same substituent on the 2-position directs substitution almost exclusively to the 1-position.

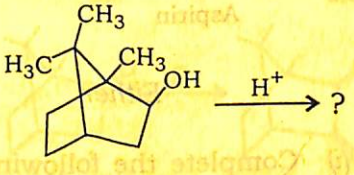
(e) (i) Write the sequence of reactions involved in the Skraup synthesis of quinoline.

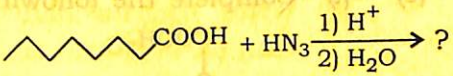
(ii) Which position of pyrrole undergoes aromatic electrophilic substitution easily and why?

4. Answer the following questions : 10×3=30

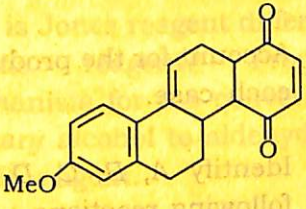
Either

(a) *(i)* Predict the product in each case and write the mechanistic steps involved : 2+3

(1) 

(2) 

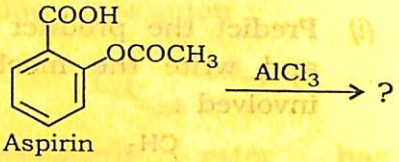
(ii) Diels-Alder reaction is stereo-selective. Explain. Work out the diene and dienophile components in the given compound : 4+1



Or

(b) *(i)* Use HOMO-LUMO approach to show that [4+2] cycloaddition is thermally allowed. 5

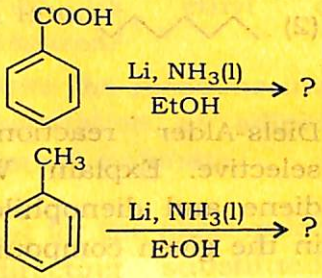
(ii) Give the product of the following reaction, name the rearrangement and propose a mechanism : 1+1+3



Aspirin

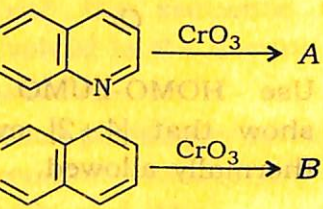
Either

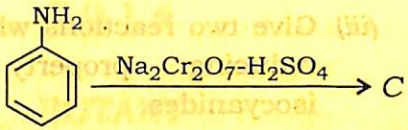
(c) (i) Complete the following reactions :



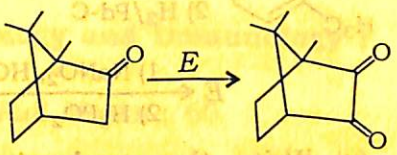
Account for the product obtained in each case. 2½+2½

(ii) Identify *A*, *B*, *C*, *D* and *E* in the following reactions : 1×5=5



(3) 

(4) 

(5) 

Or

(d) *(i)* Propose a general mechanism for catalytic hydrogenation which can account for different types of product obtained in such a hydrogenation reaction. 5

(ii) How is Jones reagent different from Collins reagent? Propose a mechanism for the conversion of a primary alcohol to aldehyde with a Cr(VI) reagent. 2+3

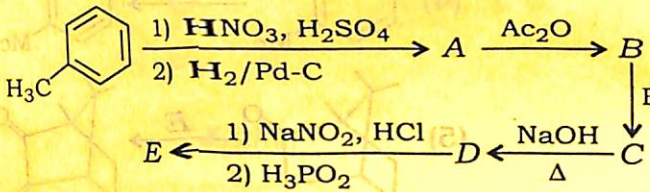
Either

(e) *(i)* Suggest a method for preparation of alkyl isocyanides. 2

(ii) Alkyl isocyanides are insoluble in water. Why? 1

(iii) Give two reactions which show the reducing property of alkyl isocyanides. 2

(iv) Identify *A*, *B*, *C*, *D* and *E* from the following : 2½

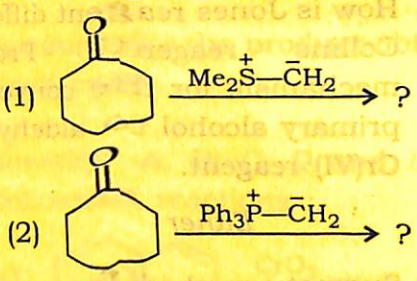


(v) Write the mechanism for diazotization of a primary amine. 2½

Or

(f) (i) Describe a method for synthesis of pyrrole. 3

(ii) Give the products in each of the following reactions : 2



(iii) What are stabilized and non-stabilized ylides? Propose a mechanism for Wittig reaction. 2+3

★ ★ ★