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M.Sc. RNLKWC-/CEM-302/22

2022

ADVANCE ORGANIC CHEMISTRY-I
M.Sc. Third Semester End Examination - 2022
PAPER - CEM-302

Full Marks : 40

Time : 2 hours

*The figures in the right-hand margin indicate marks.
Candidates are required to give their answers in their own
words as far as practicable.
Illustrate the answers wherever necessary.*

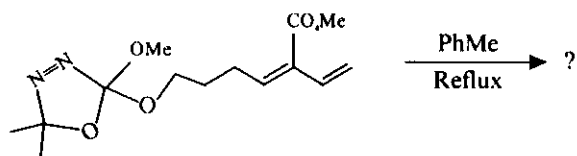
Group-A

- A. Answer any four of the following question. 4×2=8
1. What is linear and nonlinear approach in cheletropic reaction?
 2. A linear Hammett plot is obtained in the alkaline hydrolysis of p- and m-substituted benzoic acid esters while the Hammett plot of similar esters in 99.9% H₂SO₄ consists of two straight lines of positive and negative slopes meeting at zero. Explain.

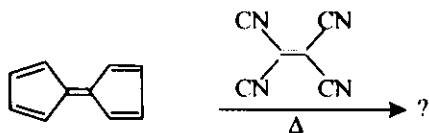
(Turn Over)

(2)

3. Show the catalytic cycle of Suzuki coupling with oxidation state of the metal properly marked.
4. The acid catalysed hydrolysis of ethyl benzoate has a ' ρ ' value (+0.144). What would be the effect of (-1) group on the rate of the reaction? Explain indicating the mechanism.
5. What is Petasis reagent? Show one special application of petasis reagent.
6. Find the product of the following considering cheletropic reaction.

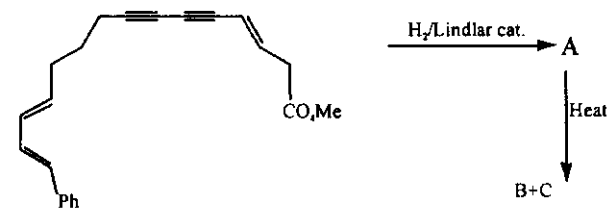


7. Write down the applications of organometallic polymers.
8. Predict the products in the following reactions indicating Frontier orbital interaction (F.O.I).

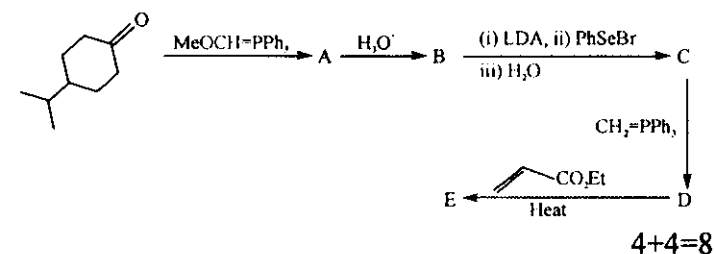


(3)

9. a) Find the products of the following reaction showing proper stereochemistry and mechanism with the help of electrocyclic ring closer and cycloaddition reaction.



- b) Fill in the blank with proper stereochemistry.



4+4=8

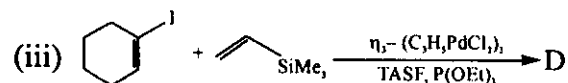
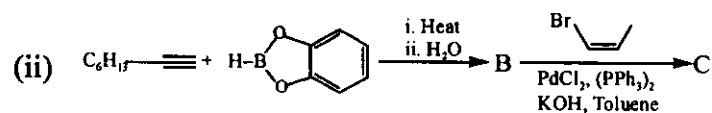
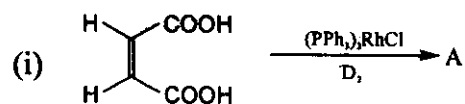
10. a) How Hammett equation was derived with reference to ionisation of benzoic acid as standard.
- b) The saponification of methyl benzoate has $\rho=2.229$. What would be the effect of introducing electron withdrawing group on the rate of the reaction? Show the rate determining step and transition state of the reaction. Do you expect a good linear Hammett plot or its deviation in presence of electron donating group? Explain with reason.

4+4=8

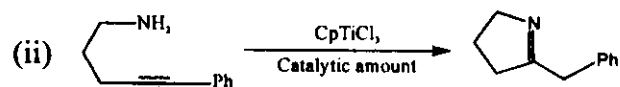
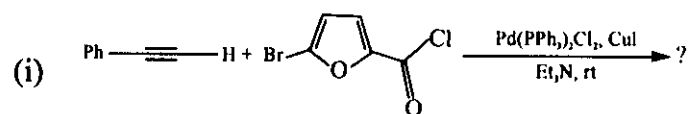
(4)

11. (a) Give example where hydropalladation-dehydropalladation can lead to alkene isomerisation.

(b) Write down the structure of the product (A to D) in the following reactions.



(c) Write down the product of the reaction with mechanism (any one)

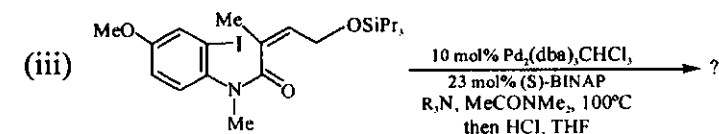
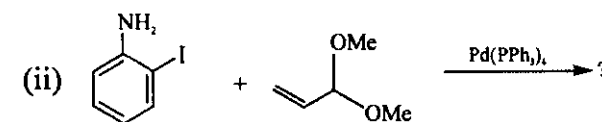
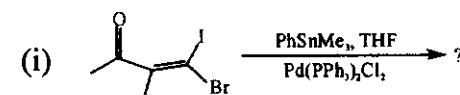


2+4+2=8

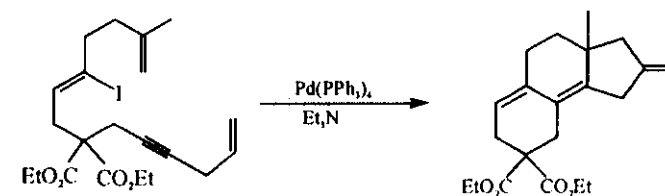
(5)

12. (a) What is migratory insertion? Give example.

(b) Predict the product(s) of the following reactions.



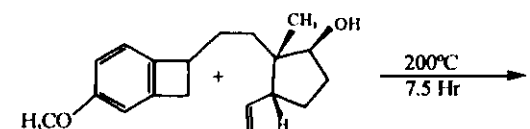
(c) Rationalize the following reactions.



(d) What is hapticity number?

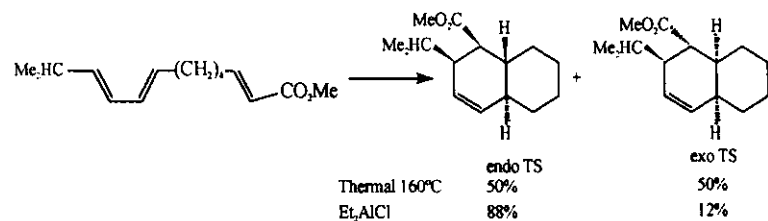
2+3+2+1=8

13. a) Find the product with proper stereochemistry



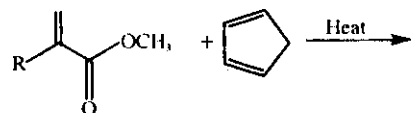
(6)

(b) Explain the role of Et_2AlCl in the following reaction.



(c) Acid hydrolysis of ethyl benzoate with (99.9% H_2SO_4) proceeds with electron withdrawing group having $\rho=+1.4$. Explain this statement indicating mechanistic pathway of the reaction. $3+3+2=8$

14. (a) Find the products with proper stereochemistry and comment on the product ratio when changing the R group from H to Me to Et.



(b) Show the FOI with regioselectivity of Diels-Alder reaction of the combination of electron deficient diene and electron rich dienophile.

(c) Find the products in the following reaction.

