

2022

M.Sc.

3rd Semester Examination

CHEMISTRY

PAPER – CEM-302 (Organic Special)

Full Marks : 50

Time : 2 Hours

(CEM 302-Advanced Organic Chemistry-I)

1. Answer any *four* bits:

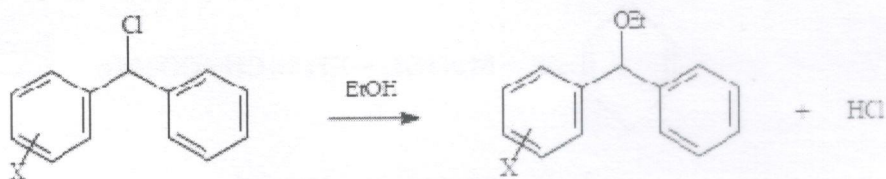
2×4 = 8

- What is ene reaction? Give example.
- Write down one synthetic application of organomercury compound.
- What do you mean by hapto number in organometallic complex?
- Give an example of insertion reaction of η^3 -allyl complex?
- What is chelotropic reaction? Give example.
- Define alternant hydrocarbon with examples.

2. Answer any *four* bits:

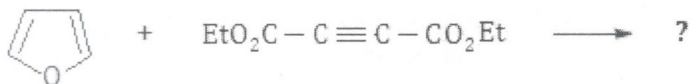
4×4 = 16

- The solvolysis of substituted diphenylcarbinyl chlorides was studied in ethanol at 25°C. A plot of $\log k$ versus σ^+ was linear with a slope of -5.1. Suggest a mechanism consistent with this observation and provide an explanation of the ρ value in terms of the *Hammond postulate*.



- Write down two synthetic applications with chemical reactions of organorhodium compound

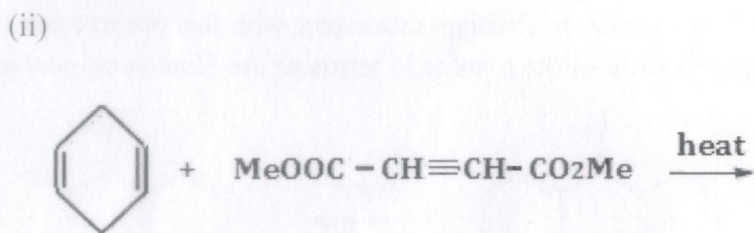
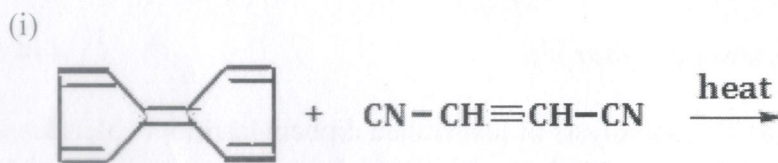
- (c) Explain the conceptual basis of Yukawa Tsuno equation.
 (d) Give an example of secondary interaction in cycloaddition reaction. Predict the product/s of the following reaction indicating F.O.I. 1 + 3



- (e) What is Heck reaction? Draw the catalytic cycle for Heck reaction.
 (f) Applying aromatic transition state theory predict the selectivity of electrocyclic reaction of $[4n + 2]$ pi electron system in thermal and photochemical condition.

3. Answer any *two* questions 2×8 = 16

- (a) Write down the product/s of the following reactions by showing F.O.I. 4 + 4



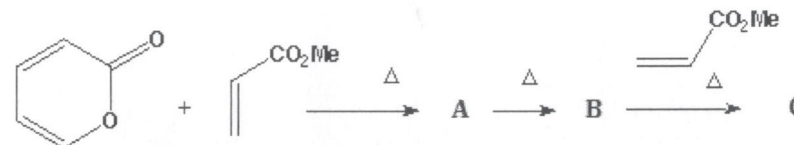
- (c) Define alternant hydrocarbon with examples. Write down the unique properties of alternant systems. Why the Hammett equation is called a linear free energy relationship? How does the Hammett reaction constant (ρ) vary with polarity of solvent? 2+2+2+2

- (c) (i) Draw the correlation diagram for the following conversion in the thermal and photochemical condition. 5



Indicate symmetry allowed path for each condition

- (ii) Identify A, B and C of the following reaction sequence. 3



- (d)i) Answer each of the following with reference to the corresponding substituent constants considering both inductive and resonance electronic contributions (σ_I and σ_R). Illustrate your answer showing resonance structures for substituted benzoic acids, where appropriate. 2 + 2

(a) The σ_{meta} and σ_{para} values for the $-\text{CO}_2\text{CH}_3$ group are both positive with $\sigma_{\text{para}} > \sigma_{\text{meta}}$

(b) The values of σ_{meta} for the methoxy substituent ($-\text{OCH}_3$) is positive, whereas the values for σ_{para} is negative.

ii) State and critically explain the Grunwald-Winstein equation. 4

Internal Assessment-10