

#### Damietta University

# جامحة دبباط Damietta University

## Faculty of Science

#### **Chemistry Department**

Fourth Year Chemistry Course: Pericyclic Reactions and Biochemistry (Chem 405)

Answer <u>all</u> questions: (135 Marks) **Date**: 15-01-2015 **Time**: 3hrs.

## Pericyclic Reactions (4 pages) (90 Marks)

(1) (a) Write the structures of the products for the photochemical electrocyclic reaction for compound (a) and show the terminal orbitals during the course of reaction. In addition, specify the type of rotation and write the names of the reactants and products? (8 marks)

**(b)** Based on the stereochemistry of the reactant and of the product, indicate if a **conrotatory or disrotatory** process is responsible for each transformation and specify whether they proceed **thermally or photochemically**. Mechanisms are not needed. (9 marks; 3 marks each)

(c) Define the type of the following pericyclic reactions. Specify whether the reaction takes place or not. If the reaction is *cycloaddition or sigmatropic* reactions, define the order of the reaction (e.g. [2 + 2]; [1,5] hydrogen shift). Mechanisms or explanations are not needed. (21 marks; 3 marks each)

(ii) 
$$2 \frac{hv}{hv}$$

(iii)  $\frac{Heat}{hv}$ 

(iii)  $\frac{CO_2Me}{hv}$ 

(iv)  $\frac{hv}{h}$ 

(v)  $\frac{hv}{hv}$ 

(vi)  $\frac{hv}{h}$ 

(vii)  $\frac{hv}{h}$ 

(viii)  $\frac{hv}{h}$ 

(d) For each of the following Diels-Alder reactions, **provide the structure** of the missing reagent(s) or product. To receive full credit, be sure to **include stereochemistry** when appropriate. <u>Mechanisms are not needed.</u> (20 marks)

(i) 1 + 2 
$$\xrightarrow{\text{Heat}}$$
  $\xrightarrow{\bar{c}}$   $\xrightarrow$ 

**2 (a) Complete** the following equations and **show the stereochemistry** when appropriate. Mechanisms are not needed. (20 marks; 3 marks each)

(i) 
$$H_3CO$$
  $\longrightarrow$   $N=N=N$   $+$   $H$   $CO_2Me$   $\longrightarrow$  1

(ii) 
$$H_2C = N = N + \square$$
 Heat  $\longrightarrow$  2

(iv) 
$$CH_3$$
  $OH$   $CH_3$   $OH$   $CH_3$   $OH$   $CH_3$ 

**(b)** Using curved arrows, **write** the mechanisms for the following reactions. <u>Do not combine steps.</u> Molecular orbital analysis <u>is not required</u>. (<u>6 marks</u>)

(i) 
$$CO_2Me$$
 +  $OCO_2Me$  +  $OCO_2Me$  CO $_2Me$ 

**(c) Propose** a structure for A, and show how it could have formed from the starting material. (6 marks)

(i) 
$$\stackrel{\text{H}}{ }$$
 O  $\stackrel{\text{CN}}{ }$  CN  $\stackrel{\text{CN}}{ }$  Heat  $\stackrel{\text{MeO}}{ }_{2}\text{C}$  CN  $\stackrel{\text{CN}}{ }$ 

With my best wishes

Dr. Ali El-Agamey