DEPARTMENT OF CHEMISTRY,

SCHOOL OF PHYSICAL SCIENCES,

FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA

FIRST SEMESTER EXAMINATION 2021/2022 SESSION

COURSE CODE: CHM 514 **UNITS: 2**

COURSE TITLE: PHOTOCHEMISTRY AND PERICYCLIC REACTIONS

TIME ALLOWED: 2 HOURS

INSTRUCTIONS: ANSWER ANY THREE (3) QUESTIONS

Q1. 2, 4, 5-Trimethylhexan-3-one can absorb a photon of light and undergo the following photochemical processes at the respective temperatures:

(i) Norrish Type I cleavage at 60^{o}C **(6½ marks)**

(ii) Norrish Type II cleavage at 32^{o}C **(7 marks)**

(iii) Intramolecular Hydrogen abstraction at 35^{o}C **(6½ marks)**

Assuming the molecule phosphorescences to ground state forming sp, sp^2 and sp^3 hybridized molecules;

a. Provide a suitable mechanism for each process
b. Name all molecules formed at every stage of each proposed mechanism and identify their type of hybridization.

Q2. (a). β- Carotene, the major phytochemical constituent that accounts for the orange colour in carrots absorbs light at 483 nm. Explain in details the process **(5 marks)**

b. Using 4-Methylpent-4-en-1-yn-3-one as a model:
   (i) Indicate the various types of bonding in all atoms of the molecule **(1 mark)**
   (ii) Give the distribution of electrons in each molecular orbital **(1 mark)**
   (iii) Give a detailed energy diagram of the distribution of all the electrons in their various molecular orbitals from 2 b (ii) above. Assuming the molecule observed both Grothus-Draper and Stark-Einstein laws (only 1 diagram required). **(13 marks)**

Q3. a. List TEN (10) similarities of singlet and triplet states of an organic molecules **(5 marks).**

b. Predict the type of energy transitions expected in the triplet states of the following molecules:

(i) Diethyl ether (ii) Butanamide (iii) 1-Acetyl-3-hydroxynaphthalene **(6 marks)**

c. With the aid of a Jablonski diagram only, give detailed photophysical processes that a molecule of But-3-en-1-yne will undergo. Considering the transitions that require the lowest energy only. **(DO NOT REPEAT THE SAME PROCESS TWICE) (7 marks)**

d. Rate the photophysical processes in (3c) above in order in which they will occur from the fastest to the slowest. **(2 marks)**

Q4. a. List FIVE (5) conditions required for the electrons of a molecule of 2-Methylbut-3-enal to undergo both radiative and non-radiative processes **(5 marks)**

b. 2, 3-Dichlorobut-2-ene can undergo photo-isomerization in the presence of propanone.

(i) Suggest a suitable mechanism for the reaction **(5 marks)**

(ii) Draw a suitable detailed energy diagram for the entire process **(5 marks)**

(iii) What is the importance of addition of propanone? **(5 marks)**