STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted from the academic year 2008–09)

SUBJECT CODE: CH/PC/OM24

M. Sc. DEGREE EXAMINATION, APRIL 2009
BRANCH IV- CHEMISTRY
SECOND SEMESTER

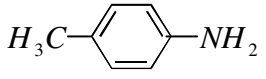
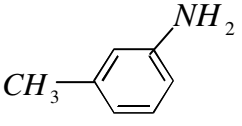
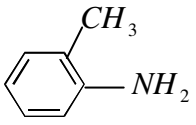
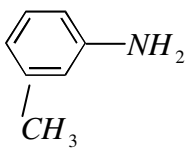
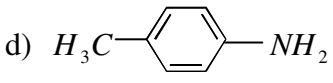
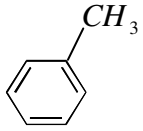
REG.NO …….

COURSE : MAJOR CORE
PAPER : ORGANIC REACTION MECHANISM
TIME : 30 MINUTES **MAX. MARKS: 20**

SECTION – A
TO BE ANSWERED ON THE QUESTION PAPER ITSELF.

Answer all the questions: **(20 x 1= 20)**
Choose the correct answer:

1. Claisen rearrangement is an example for
   a) 1,2 Sigmatropic shift b) 2,3 Sigmatropic shift
   c) 3,2 Sigmatropic shift d) 3,3 Sigmatropic shift
2. An example for a π excess aromatic compound is
   a) Cyclopentadine b) Cyclopentadienyl anion
   c) Cyclopropenium anion d) Tropylium cation
3. Internal conversion is
   a) $S_2 \rightsquigarrow S_1$ b) $S_1 \rightarrow T_1$ c) $S_1 \rightarrow S_0$ d) $T_1 \rightarrow S_0$
4. The Diel's Alder reaction of cyclopentadient occurs at the highest rate with
   a) Ethylene b) 2-Butene c) Succinic anhydride d) Maleic anhydride
5. The solvent that is commonly used in the Grignard reaction is
   a) Anhydrous ethanol b) Anhydrous acetic acid
   c) Anhydrous ether d) Anhydrous acetone
6. The partial reduction of benzene to 1,4 – Cyclohexadiene may be effected with
   a) H_2 / Lindlar catalyst b) $Na / NH_3 / EtOH$ c) $LiAlH_4$ d) $Na / EtOH$
7. The most suitable reaction for the synthesis of β -hydroxyesters is
   a) Wittig reaction b) Reformatsky reaction
   c) Friedel Craft's reaction d) Beckmann rearrangement
8. The reaction of p-bromotoluene with $NaNH_2$ / liq NH_3 gives

   a)  and 
   b) 
   c) 
   d)  and 

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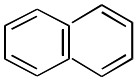
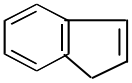
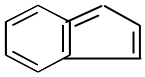
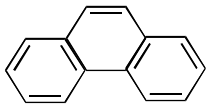
9. Among the following which has the highest dipolemoment

a)  b)  c)  d) 

10. Antiaromatic compounds are also known as
a) Paratropic b) Diatropic c) Anisotropic d) Nonaromatic

Fill in the blanks:

11. The reaction that is effectively used in the synthesis of caprolactum is _____.
12. An example for a π - deficient aromatic compound is _____.
13. The reagent used in Meerwein Pondroff Verley reduction is _____.
14. Fries rearrangement is a _____ rearrangement.
15. The metal used in Reformatsky reaction is _____.

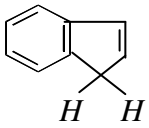
.

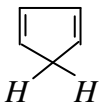
Give the answer in one or two lines:

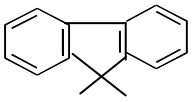
16. Give an example for a fluxional molecule.

17. $N-$ substituted amides $R-CO-NHR'$ do not undergo Hofmann rearrangement. Why?

18. Arrange the following compounds in the order of increasing acidity.







19. Dehydro [14] annulene with 16π electrons is aromatic. Why?

20. What is the sterochemical outcome of a reaction which proceeds by neighbouring group participation mechanism.

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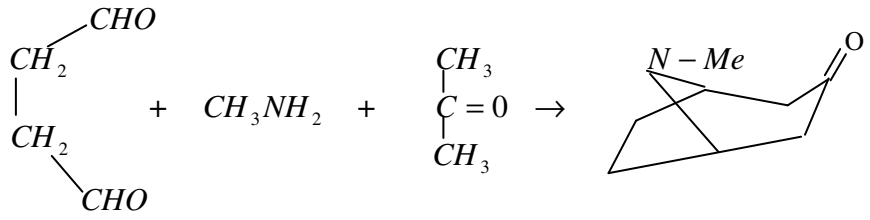
PAPER : ORGANIC REACTION MECHANISM
TIME : 2 HOURS & 30 MINS **MAX. MARKS: 80**

SECTION – B

ANSWER ANY FIVE QUESTIONS: **(5X8=40)**

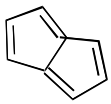
1. a) Predict the mechanism for the Mannich reaction given below

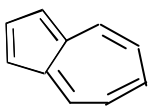


b) $C_6H_5CH_2-CO-\overset{Cl}{\overset{|}{C}}H_2$ and $C_6H_5-\overset{Cl}{\overset{|}{C}}H-CO-CH_3$ undergo Favorskii rearrangement on treatment with OH^- to give one and the same product. Explain.

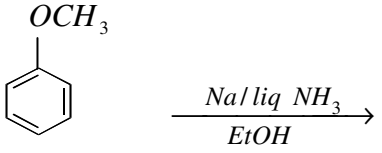
(5+3)

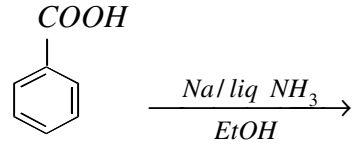
2. a) Explain with two examples how isotopic labeling studies help in the elucidation of reaction mechanism.
b) What is Craig's rule? Apply Craig's rule to pentalene and azulene to predict its aromatic character.


Pentalene


Azulene

3. a) Give the mechanism for Birch reduction. Predict the product for the following reaction

(i) 

(ii) 

(3+2)

b) The ρ value for the ionization of aromatic carboxylic acids is given below. Explain the data given below (3)

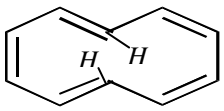
Acid	ρ
XC_6H_4COOH	1
$XC_6H_4CH_2COOH$	0.49
$XC_6H_4CH_2CH_2COOH$	0.21
$XC_6H_4CH=CHCOOH$	0.47

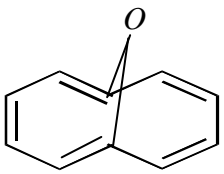
4. Discuss the stereochemistry and regioselectivity of Diel's Alder reaction. (8)

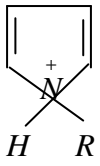
5. Write short notes on
   a) Paterno Buchi reaction (3)
   b) di-π- methane rearrangement (3)
   c) Aromaticity of C_{60} fullerenes (2)

6. a) Give two evidences to show that Claisen rearrangement involves allylic shift. (5)

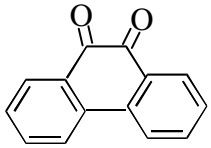
   b) Predict whether the following compounds are aromatic, antiaromatic or nonaromatic. (3)

(i) 

(ii) 

iii) 

7. Predict the product and give the mechanism for the following rearrangement reactions.

a)  $\xrightarrow{OR^-}$ (2½)

b) $C_6H_5\ CH_2\ CO\ NHNH_2 \xrightarrow{HNO_2}$ (2½)

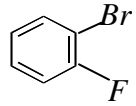
c) $C_6H_5\ CO\ CH_3 \xrightarrow{m-chloro\ perbenzoic\ acid}$ (3)

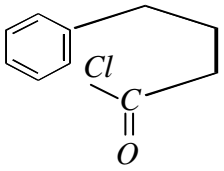
SECTION –C

ANSWER ANY TWO QUESTIONS: (2x20=40)

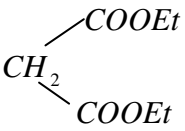
8. a) Write short notes on (4x3=12)
   (i) Norrish I cleavage reaction
   (ii) Norrish II cleavage reaction
   (iii) Homoaromatic compounds
   (iv) Chichibabin reaction

   b) Predict the product and name the reaction

(i)  $\xrightarrow{Mg/THF}$ A  B (2½)

(ii)  $\xrightarrow{AlCl_3}$ (2)

(iii) $C_6H_5-CO-CH_3 \xrightarrow{N_2H_4/alkali}$ (1½)

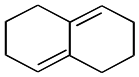
(iv)  $+ C_6H_5-CH=CH-CHO \xrightarrow{base}$ (2)

9. a) Account for the following

(i) Cyclo octatetraene is a tub shaped molecule (3)

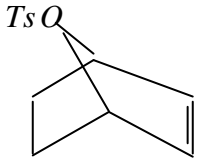
(ii) 2 – bromopropanoic acid reacts with a strong nucleophile like OH with inversion of configuration but with a weak nucleophile like Ag_2O with retention of configuration to give 2 – hydroxypropanoic acid . (4)

(iii) The following diene does not undergo Diel's Alder reaction. (2)

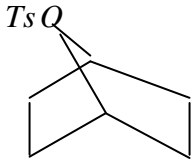


(iv) When the oxime of cinnamaldehyde is treated with P_2O_5, isoquinoline is formed. Why? (4)

(v) The acetolysis of 7-norbornyl tosylate (I) is 10^{11} times faster than that of its saturated analogue (II). (3)



(I)



(II)

b) Give the mechanism of photoreduction of benzophenone to give benzopinacol. (4)

10. a) Give the Benzyne mechanism for aromatic nucleophilic substitution reaction. Give two evidences in favour of the mechanism. (7)

b) What is Hammett equation? Explain the terms in it. (2+4)

c) Explain Jablonski diagram describing dissipation of energy from higher to lower energy states. (7)

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