

STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted from the academic year 2006 – 07)

SUBJECT CODE: CH/PC/OM24

M. Sc. DEGREE EXAMINATION, APRIL 2007
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.

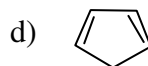
(20 x 1= 20)

Choose the correct answer:

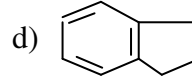
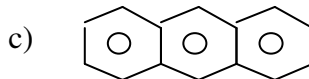
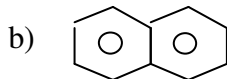
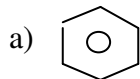
1. Which of the following is antiaromatic

a) cycloocta tetraene

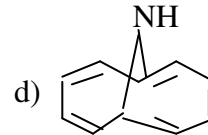
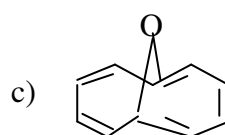
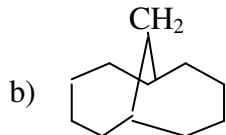
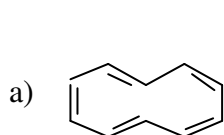
b) 1,3 – butadiene



2. In which of the following some C-C bonds have 75% = character and 25% single bond character and some other C-C bonds have 75% simple bond character and 25% double bond character?



3. Which of the following molecules is not planar?



4. Which of the following is not true?

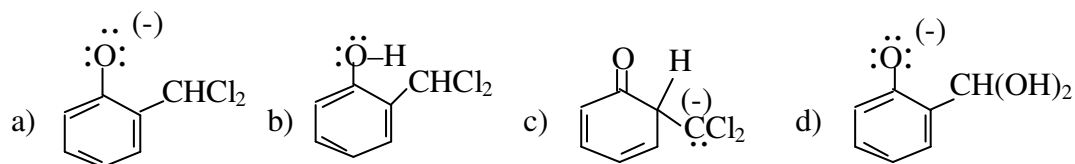
a) An einstein represents the energy of 6.02×10^{23} .

b) Only light absorbed by a molecule is effective in producing a chemical change.

c) Inherent phosphorescence life time is 10^{-9} to 10^{-6} sec and inherent fluorescence life time is 10^{-3} to 10 sec.

d) Benzophenone converts completely from S_2 to T_1 by ISC.

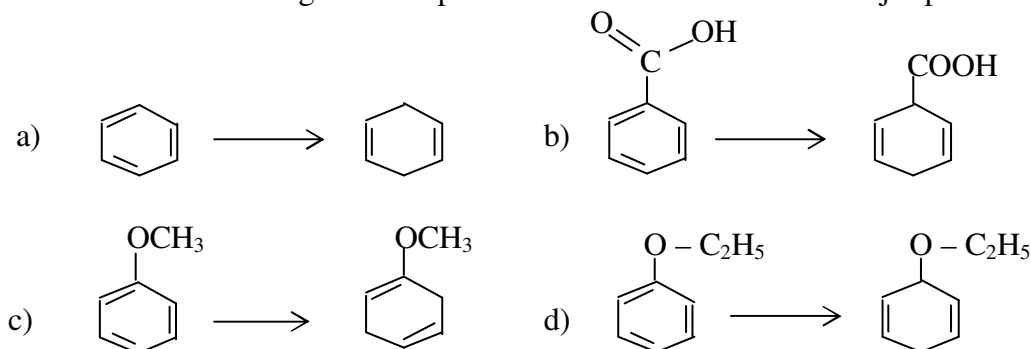
5. Which of the following is not an intermediate in Reimer-Tiemann reaction using CHCl_3 and aq. NaOH



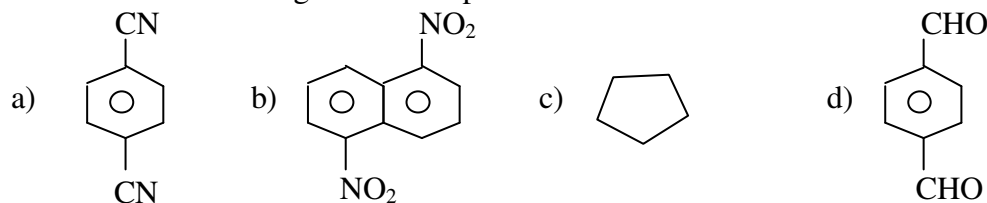
6. The starting materials for the formation of $\text{C}_6\text{H}_5 - \text{CH}_2 - \underset{\text{OH}}{\text{CH}} - \underset{\text{C}_2\text{H}_5}{\text{CH}} - \text{COOEt}$ by Reformatsky reaction are

- a) $\text{C}_6\text{H}_5\text{CHO}$ and $\text{C}_2\text{H}_5 - \text{CH}(\text{Br}) - \text{COOC}_2\text{H}_5$
 b) $\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CHO}$ and $\text{C}_2\text{H}_5 - \text{CH}(\text{Br}) - \text{COOC}_2\text{H}_5$
 c) $\text{C}_6\text{H}_5 - \text{CO} - \text{CH}_3$ and $\text{C}_2\text{H}_5 - \text{CH}(\text{Br}) - \text{COOMe}$
 d) $\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CHO}$ and $\text{C}_6\text{H}_5 - \text{CO} - \text{CH}_3$

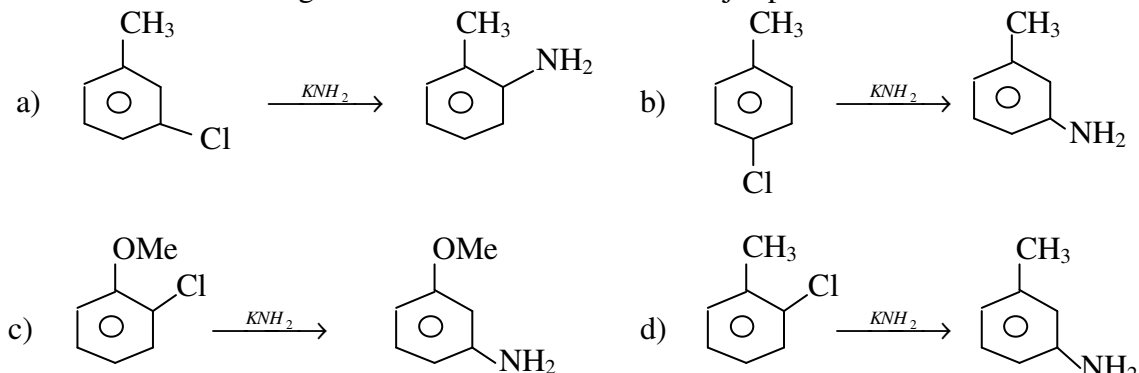
7. Which of the following do not represent correct Birch reduction major products?



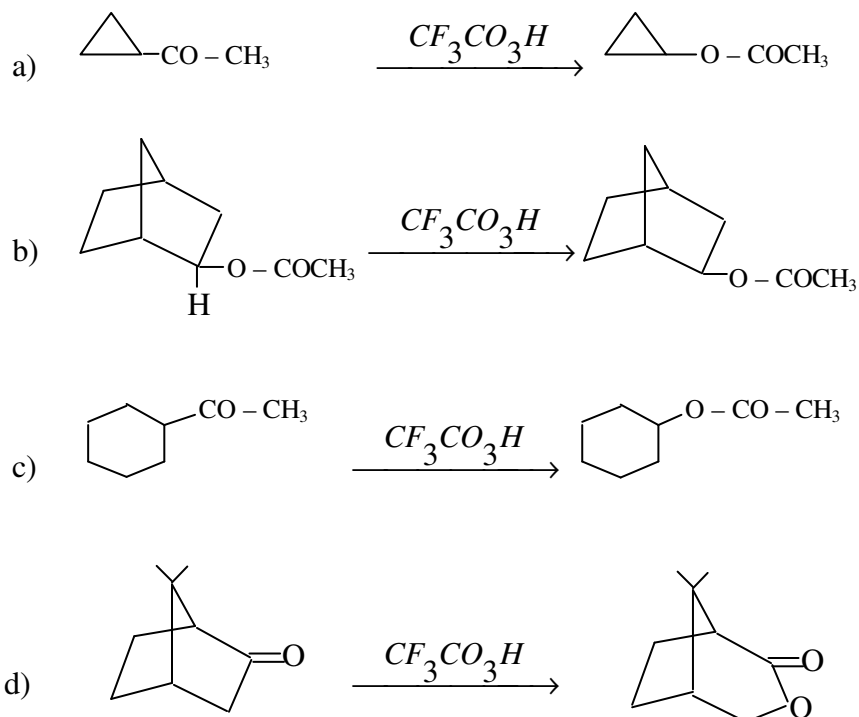
8. Which of the following has a net dipole moment?



9. Which of the following reactions does not show the major product?

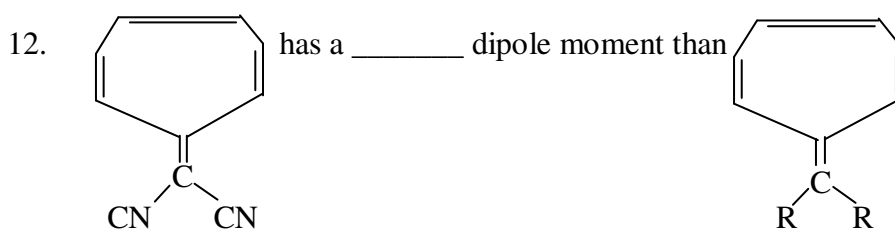


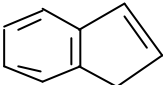
10. Which of the following does not show the major product?

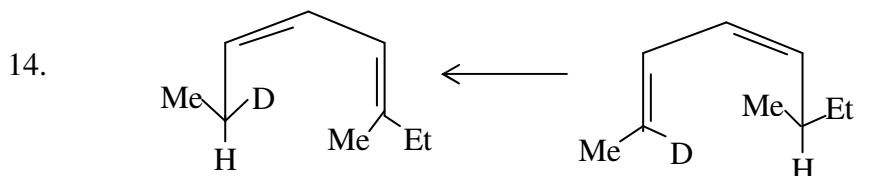


Fill in the blanks:


11. Structure of 18 – annulene is:



13. Indene  is _____ acidic than cyclopentadiene.

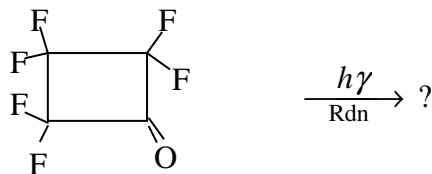


In the reaction shown there is a supra _____ shift.

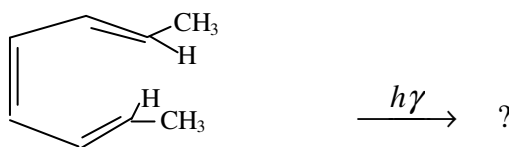
15. The product formed when  is treated with H^+ is _____

Give the answer in one or two lines:

16. Write the structure of product; what is the type of cleavage?



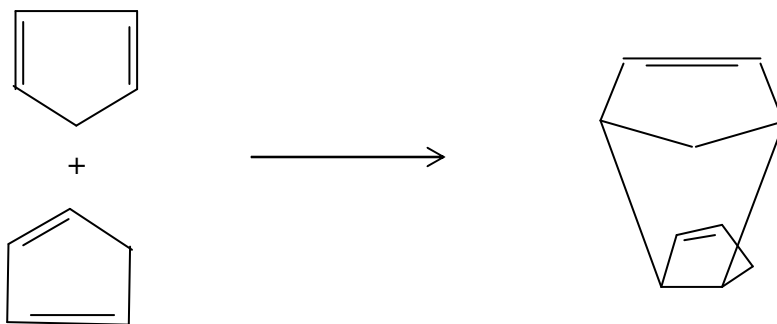
17. Write the structure of the product with proper stereochemistry.



18. Write the structure of the product when diethyladipate is treated with C_2H_5ONa .

19. Write the structure of the intermediate formed when mesitylene is treated with BF_3 .

20.



Classify this reaction as $(i + j)$ cycloaddition.

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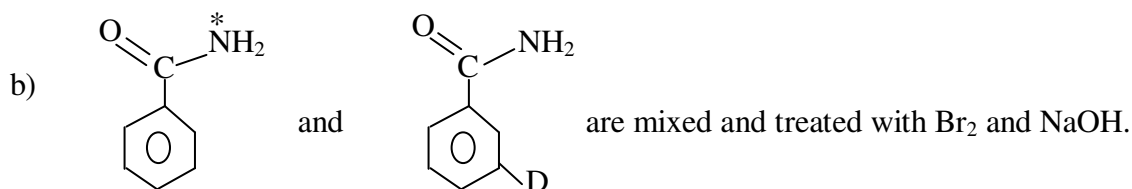
COURSE : MAJOR CORE
PAPER : ORGANIC REACTION MECHANISM
TIME : 2 HOURS & 30 MINS
MAX. MARKS: 80

SECTION – B

ANSWER ANY FIVE QUESTIONS: (5X8=40)

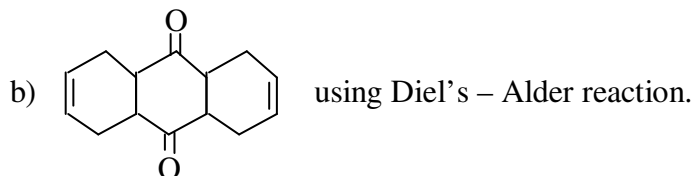
1. a) What is Hammett equation. Explain the terms. How is σ determined? (2)
b) For $-\ddot{O}-CH_3$ group $\sigma_m = +0.12$ and $\sigma_p = -0.27$; what does it signify. (2)
c) Predict ρ as +ve or -ve for the following reactions.
i) ionization of $(C_6H_5)_3C-Cl$ in liquid SO_2 at $0^\circ C$. Will a +R group aid the reaction? (2)
ii) addition of HCN to benzaldehyde in ethanol at $20^\circ C$. Will a -R group aid the reaction? (2)

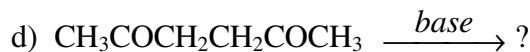
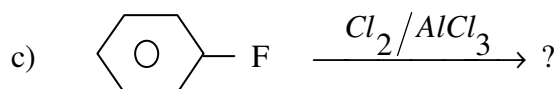
2. a) Explain:
 $C_6H_5-CH_2-CH_2-Br$ on treatment with C_2H_5ONa forms $C_6H_5-CH=CH_2$.
When C_2H_5OD was used as the solvent there was no isotopic exchange. Why?
Writing the mechanism explain the order. (4)



What are the products formed? What is the product NOT formed? What is the significance? (4)

3. How will you synthesise the following from suitable starting materials. (4x2=8)
a) $C_6H_5-CH=C(CH_3)_2$ using Wittig olefination.





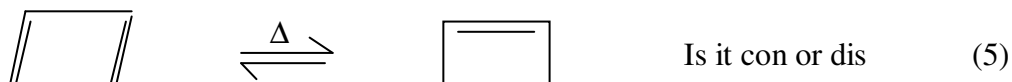
7. Explain with mechanism; give one example.
 a) Norrish Type II cleavage
 b) di-pimethane rearrangement

SECTION -C

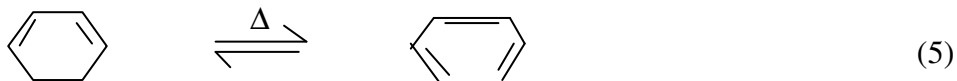
ANSWER ANY TWO QUESTIONS:

(2x20=40)

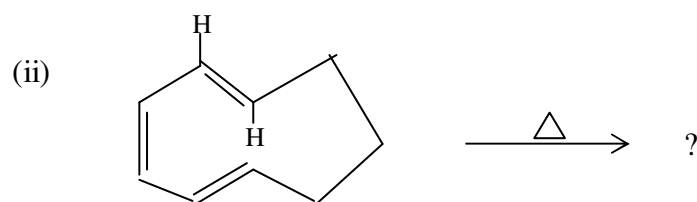
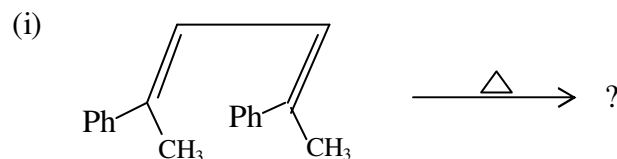
8. Giving the mechanism, explain the following reactions with one example.
 a) Paterno-Buchi reaction
 b) Wolff-kishner reduction
 c) Chichibabin reaction
 d) MPV reduction
 e) Curtius rearrangement (5x4=20)
9. a) Draw the molecular orbitals of 1,3,5 – hexatriene. Classify each orbital as symmetric and antisymmetric with respect to 'm' and C₂ symmetries. (6)
 b) Using FMO method explain the reaction



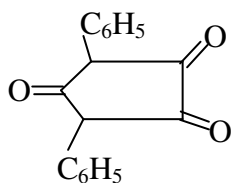
- c) Using correlation diagram explain the reaction. Is it con or dis?



- d) Predict the product with proper stereochemistry. (2+2=4)



10. a) Using FMO method explain that (4+2) cycloaddition is symmetry allowed thermally and the nature of addition is supra-supra. (5)
- b) Using correlation diagram explain the formation of \square from 2 $\text{CH}_2 = \text{CH}_2$. Is it thermally or photochemically symmetry allowed? (10)
- c) How will you synthesise the following from suitable starting materials. (5)



By Aldol type condensation.

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