

This question paper contains 8 printed pages]

ST—119—2022

FACULTY OF SCIENCE

M.Sc. (First Year) (First Semester) EXAMINATION

MAY/JUNE, 2022

(CBCS/New Pattern)

CHEMISTRY

Paper-I (CH-412)

(Organic Chemistry)

(Thursday, 30-6-2022)

Time : 9.30 a.m. to 1.15 p.m.

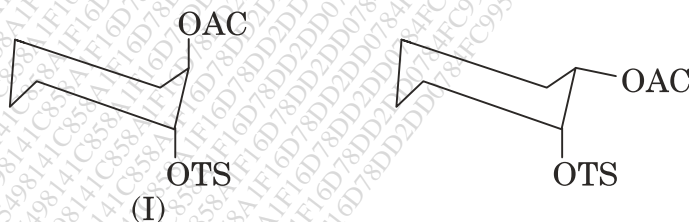
Time— 3.45 Hours

Maximum Marks—75

N.B. :— Attempt all questions.

1. Attempt any *three* of the following : 15

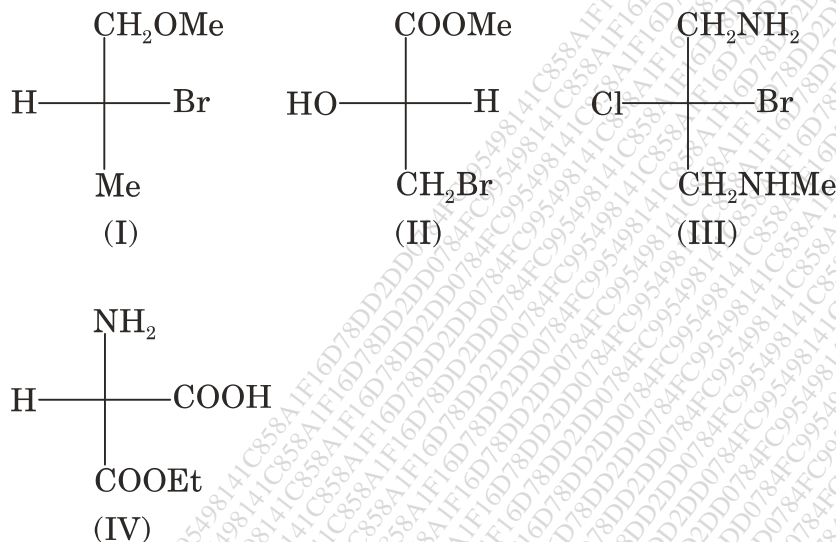
- (a) Why the trans isomer (I) undergoes acetolysis 670 times faster than the cis isomer (II) and that the product has the same cis stereochemistry in both cases ?



- (b) Explain Hammonds postulate for transition state structure in detail.
- (c) Explain the role of crossover experiment and kinetic isotope effect in determination of mechanism of organic reaction.
- (d) Draw the configuration and specify the R and S enantiomers of 2-chloropentane.

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(e) Designate structure I to IV as R or S.



2. Attempt any *three* of the following : 15

(a) Derive the Hammett equation and calculate the substituent constant of the following ethyl benzoate.

(Given data : PK_a value of substituted ethyl benzoate at M-Me = 4.26, P-H = 4.20, NO_2 = 3.49, P-OMe = 4.47, M-Br = 3.80 and $\text{PK}_a\text{H} = 4.20$)

Calculate :

$$\sigma_{\text{M-Me}} = ?$$

$$\sigma_{\text{M-NO}_2} = ?$$

$$\sigma_{\text{M-Br}} = ?$$

$$\sigma_{\text{P-H}} = ?$$

$$\sigma_{\text{P-OMe}} = ?$$

(b) Explain the terms homoaromaticity and antiaromaticity with suitable example.

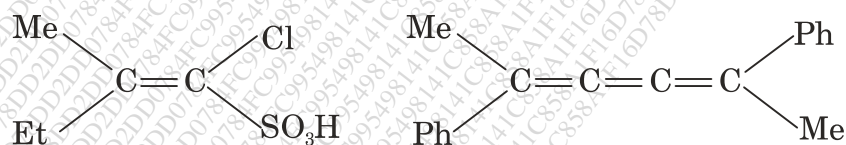
(c) Explain with examples neighbouring group participation.

- (d) Explain aromaticity in Benzenoid and Non-Benzenoid aromatic compound.
- (e) Nucleophilic substitution at chiral carbon by SN^2 mechanism is not accompanied by racemisation but by inversion.
3. (a) Write brief notes on : 7
- (i) Kinetically and thermodynamically controlled products.
- (ii) Role of cross over experiments in the determination of the mechanism of organic reactions.

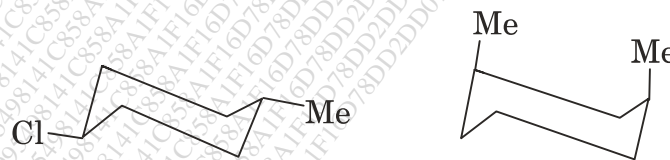
Or

Comment on the following :

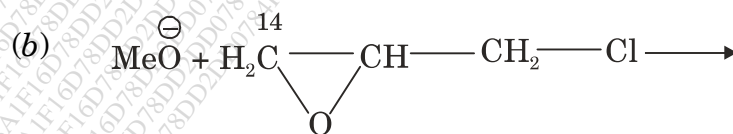
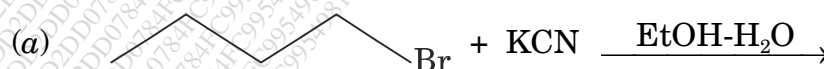
- (i) Assign E or Z configuration to the following :



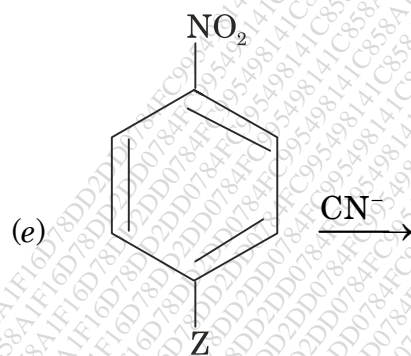
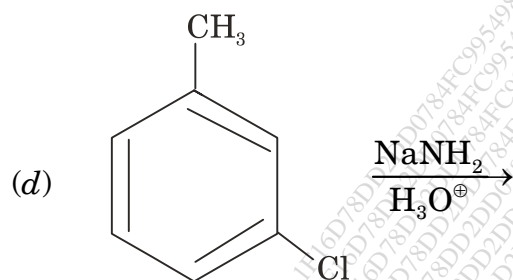
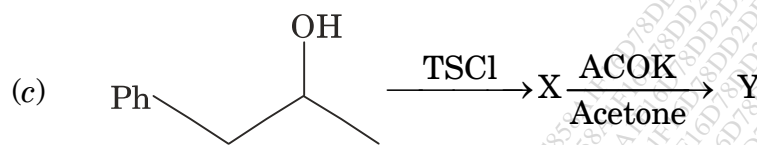
- (ii) List the following compounds as cis or trans and comment on their chirality :



- (b) Predict the product(s) with mechanism of the following : 8



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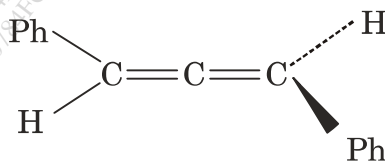


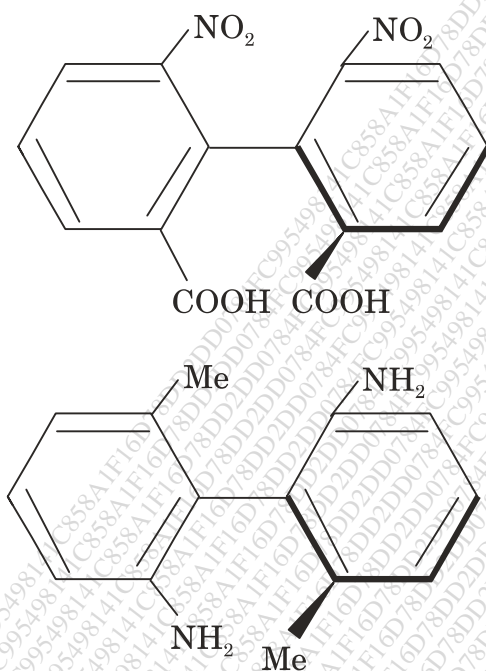
Z = electron withdrawing group.

4. (a) Taking an example of some cyclohexane derivative discuss the effect of conformation on chemical reactivity.

Or

Assign absolute configuration.





- (b) (i) What are annulenes ? Explain the aromaticity of [14] annulene.
(ii) Explain the stability of carbonion and free radical.

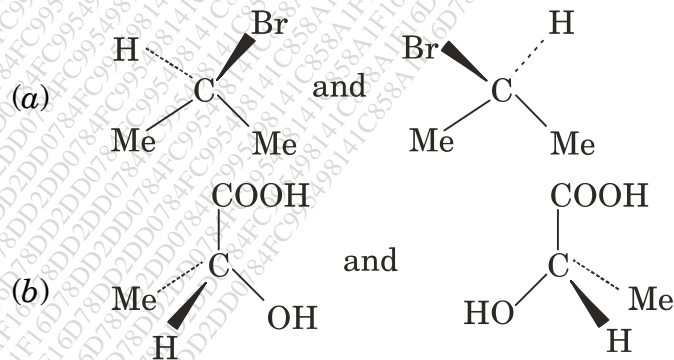
Or

- (i) Smiles Rearrangements.
(ii) SET Mechanism.

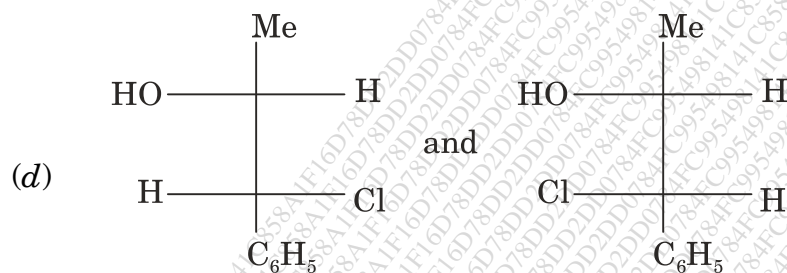
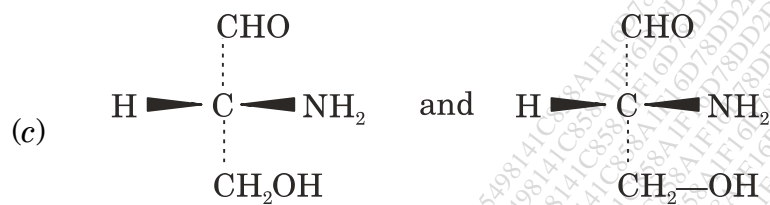
5. Multiple Choice Questions :

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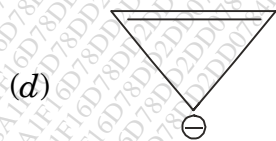
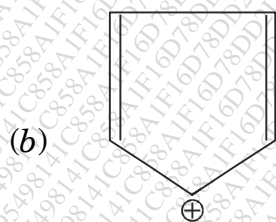
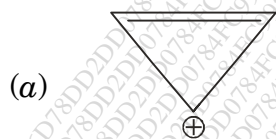
- (i) Which of the following pairs is diastereomers ?



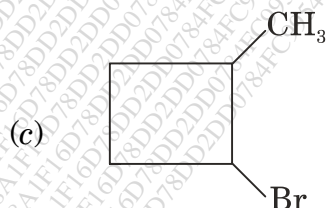
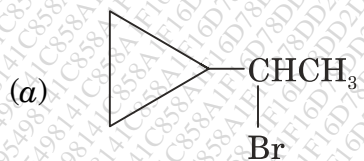
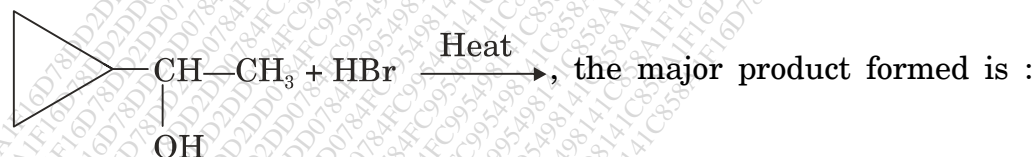
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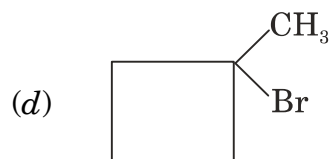
(ii) Among the following the aromatic compound is :



- (iii) 2-Bromobutane on heating with alcoholic alkali forms :
- α -Butylene only
 - β -Butylene only
 - 20% of β -Butylene + 80% of α -Butylene
 - 80% β -Butylene + 20% α -Butylene
- (iv) Unimolecular nucleophilic substitution [S_N1] involves.....steps, while bimolecular nucleophilic substitution involves.....steps :
- Two, one
 - One, two
 - Two, two
 - One, three
- (v) In the reaction :



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Write short notes on (any *two*):

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- (i) Homoaromaticity
- (ii) Taft equation
- (iii) Inclusion compounds.