This question paper contains 5 printed pages]

AI—80—2017

FACULTY OF SCIENCE

M.Sc. (First Year) (First Semester) EXAMINATION NOVEMBER/DECEMBER, 2017

(CBCS Pattern)

CHEMISTRY

Paper (CH-412)

(Organic Chemistry—I)

(Monday, 13–11–2017)

Time: 10.00 a.m. to 1.00 p.m.

Time—Three Hours

Maximum Marks—75

- N.B. := (i) Attempt all questions.
 - (ii) Figures to the right side indicate full marks.
 - (iii) Use of Logarithmic table and calculator is allowed.
 - (iv) Multiple choice questions (MCQs) should be attempted only once on page no. 3 of answer-book with complete answer.
- 1. Attempt any three of the following:

15

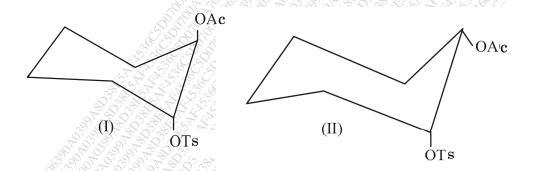
- (a) Why bromination of toluene is five times faster than that of t-butyl benzene?
- (b) Why cyclopentadiene is much more acidic than 1,3-cylohexadiene, while cyclopentadiene is much less acidic than an allylic compound?
- Nucleophilic substitution at chiral carbon by SN^2 mechanism is not accompanied by racemisation but by inversion.
- (d) What is the importance of photosensitizer in photochemistry? Which type of compounds behave as photosensitizer?
- (e) Discuss the photochemistry of 1,3-butadiene.

P.T.O.

2. Attempt any three of the following:

15

- (a) What are carbenes? How are they generated? Give the structures of singlet and triplet methylene.
- (b) What is aromaticity? Explain the aromaticity of benzenoid and non-benzenoid compounds.
- (c) 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:



- (d) Discuss the mechanism of the photoreduction of benzophenone leading to the formulation of benzopinacol.
- (e) Discuss the photochemical smog and PAN formation.
- 3. (a) Comment on the following:

7

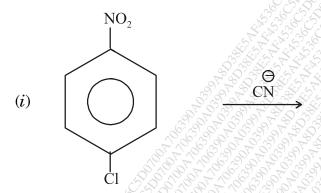
- (i) Kinetically and thermodynamically controlled products.
- (ii) Role of cross over experiments in the determination of the mechanism of organic reactions.

Or

Comment on the following:

- (i) Jablonski diagram
- (ii) Photochemistry of vision.

(b) Predict the product(s) with mechanism of the following (any four):



(ii)
$$+ C_6H_5 \stackrel{\bigoplus}{N} \equiv \stackrel{\stackrel{\longrightarrow}{N}}{\longrightarrow} ?$$

(iii)
$$Rac{\text{CCH}_3}{\text{Br}}$$
 $Rac{\text{KNH}_2}{\text{NH}_3(l)} ?$

(v)
$$C_6H_5$$
— $CHO + CH_3$ — $C \equiv C$ — $CH_3 \xrightarrow{hv} ?$

P.T.O.

$$(vi) \quad \begin{array}{ccc} CH_3 & CH_3 \\ C-CH_2-C-CH_2 & CH_3 \\ CH_3 & CH_3 \end{array} \xrightarrow{hv} ?$$

$$(vii) \qquad \qquad + CO + HCI \xrightarrow{AlCl_3} CuCl \qquad ?$$

4. (a) Explain photofries reaction and $n\pi - p\pi$ methane rearrangement. 7

Or

Explain with mechanism:

- (i) Smiles rearrangement
- (ii) SET mechanism.
- (b) Discuss the following:

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- (i) Orientation and reactivity in monosubstituted benzene in Aromatic electrophilic substitution.
- (ii) Effect of substrate and leaving group on aliphatic electrophilic substitution reaction.

Or

Comment on the following:

- (i) Stability of carbocations and carbanions.
- (ii) Cis-trans isomerisation of Alkene.

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	(a)	Select the <i>correct</i> answer from the given options for each of t following:										the 5		
		(i)	Geometry of trifluoromethyl free radical is:											
			(a) Planar (b) Pyramidal						97.75					
			(c)	V-sha	ped		(<i>d</i>)		etrahedı	ral.		0 40 0 00		
		(ii)	Which among the following anions is the best nucleofuge?											
			(a)	$Ac\overset{\Theta}{O}$	OF DO	332 V	(b)	C	Θ)H		2000	01. Y.		
			(c)	$\operatorname{Ts}\overset{\Theta}{\operatorname{O}}$	70000000	2 2 2 3 3 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	(d)	F	et O·					
		(iii)	Addition of bromine to cis 2-butene gives:											
			(a)	meso	form	2 2 4 0 C								
			(b) dl-pair of enantiomer											
			(c) both (a) and (b)											
			(d)	none	of the a	bove		00000 P	14000					
		(iv)	Which among the following undergoes nitration most readily?											
			(a)	Benze	ene		(b)	A	cetanilio	de				
			(c)	Aceto	phenone		(d)	C	hlorobei	nzene	9			
		(v)	Which of the ketone undergoes photoreduction?											
			(a)	Benzo	ophenone	330L	(<i>b</i>)	\mathbf{N}	Iicheler's	s keto	ones			
			(c)	Both	(a) and	(b)	(d)	N	Tone of t	these				
	(b)	Write short notes on any two:										10		
		(i)	Di-π methane rearrangement											
	01.7000 4000000000000000000000000000000000	(ii)	Aromaticity of Azulene											
	2100 OF	(iii)	Alternant and non-alternant hydrocarbons.											