Exercise-1

> Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Unimolecular elimination reaction (E1)

- Why dehydration of alcohol takes place in acidic medium generally but not in basic medium. A-1.
- A-2. 1º alcohols are poor starting material for synthesis of 1-Alkene. Explain ?
- Predict the major product of the acid catalysed dehydration of the following alcohols : A-3. (a) $(CH_3)_2C(OH)CH_2CH_3$ (b) CH₃CH₂CH₂CH(OH)CH₃ (c) (CH₃)₂C(OH)CH(CH₃)₂ (d) (CH₃)₃CCH₂OH
- A-4.2 When 1-Bromo-1-methylcyclohexane is heated in ethanol for an extended period of time, three products result: one ether and two alkenes. Predict the products of this reaction, and propose a mechanism for their formation. Also, mention the major elimination product.

Section (B) : Bimolecular elimination reaction (E2)

A halide with formula C₆H₁₃I is found to give two isomeric alkenes 2-methyl-2-pentene and 4-methyl-2-**R-1** pentene on dehydrohalogenation with alcoholic KOH. Suggest its structure.



Explain why more alkylated alkene is formed predominatly if base is CH₃CH₂O^O, while less alkylated alkene is obtained majorly when t-BuO base is used.

- Bromocyclodecane on heating with ethanolic KOH, produces two alkenes. Write the two products also B-3.🏊 mention the major one.
- Which alkyl chloride would yield following pure alkene on reaction with alcoholic KOH ? B-4. CH₃

(i) $CH_3 - C = CH_2$ (ii) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2$ (iii) $CH_3 - CH_2 - C = CH_2$ | CH_3

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- Predict all the alkenes that would be formed by dehydrohalogenation of the following alkyl halides with B-5. sodium ethoxide in ethanol and identify the major alkene : (ii) 2-Chloro-2-methylbutane (i) 1-Bromo-1-methylcyclohexane
 - (iii) 2, 2, 3-Trimethyl-3-bromopentane.



Give the major products of following reaction : B-6. CH₃ Br CH₃ Br $\xrightarrow{CH_3\dot{N}H_2}$? Et₃N (b) (a)



Section (C) : Unimolecular elimination by conjugate base (E1cB)

- C-1. What are the essential conditions for any reaction to show E1cB mechanism ?
- C-2.> If ethanol containing EtOD is used as solvent, then deuterium exchange take place in E1cB mechanism. Why ?
- C-3. If the mechanism is E1cB then the possible products will be :

$$\begin{array}{c} \longrightarrow \mathsf{CH}_2 - \mathsf{CH} - \mathsf{CH}_3 \xrightarrow{\mathsf{MeO}^{\Theta}} ? \\ \downarrow \\ \mathsf{Br} \end{array}$$

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Unimolecular eliminaiton reaction (E1)

A-1. Which of the following reaction is an example of elimination reaction :



A-7. A Identify the major product formed in the following reaction



A-8. Which of the following does not representing the correct product



Section (B) : Bimolecular elimination reaction (E2)

- B-1. Correct statement for E2 Reaction is :
 - (A) It is a two step process.
 - (C) Strong base favours

(B) It is an unimolecular reaction

(D) Intermediate is not Formed

- (D) Carbanion is formed during the reaction
- B-2. Intermediate of E2 reaction is -
 - (A) Carbocation
 - (C) Free radical













B-4. Which of the following cannot undergo E2 reaction ?







(B) Carbanion



B-5. 2-Chlorobutane on treatment with alcoholic KOH/ Δ gives major product :

(A) 2-Butene

(B) 1-Butene

- (C) 2-Butanol
- (D) 1-Butyne



PART - III : MATCH THE COLUMN

1. Match List I (Reaction) with List II (Type of reaction) and select the correct answer using the code given

below the lists :

	List I				List	: 11					
(P)	DBr	KSH >		(1)	S _N 1						
(Q)		H ₃ ••H <u>Alc. H</u>		(2)	S _N 2						
(R)	OH	H ₂ SO ₄	→	(3)	E1						
(S)	CI -	H ₂ O →		(4)	E2						
Codes	S:			1	1			_		_	_
(A) (C)	P Q 4 2 3 1	R 1 2	S 3 4			(B) (D)	P 2 2	Q 4 1	2	R 3 4	S 1 3

2. Match reactions written in List-I with their mechanism in List-II.

	List-I		List-II
(A)	Ph–CH ₂ –CH ₂ – Br $\xrightarrow{\text{aq. KOH}}$ Ph–CH–CH ₃ + Ph–CH=CH ₂ OH	(p)	S _N 1
(B)	$Ph-CH_2-CH_2-Br \xrightarrow{EtONa} Ph-CH_2-CH_2-OEt + Ph-CH_2CH_2$	(q)	S _N 2
(C)	Ph–CH ₂ –CH ₂ –Br $\xrightarrow{\text{EtO}/\text{EtOD}}$ Ph–CH=CH ₂	(r)	E1
(D)	Ph–CH ₂ –CH ₂ –Br $\xrightarrow{\text{EtO}/\text{EtOD}}$ Ph–CH=CH ₂ + Ph–CD ₂ –CH ₂ Br	(s)	E ₂
		(t)	E1cB

Exercise-2

> Marked questions are recommended for Revision.

PART - I : ONLY ONE OPTION CORRECT TYPE



 $(A) || > | > ||| \qquad (B) || > ||| > | \qquad (C) | > ||| > || \qquad (D) | > || > |||$



(C) 4 and $H_2C=CH_2$

(B) 2 and \checkmark (D) 3 and H₂C=CH₂

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

- 'X' is a smallest optically active alkanol. On dehydration it can form Y number of alkenes (including stereoisomers). On reaction with Lucas reagent it forms Z number of alkyl halides (including stereoisomers). Report your answer as Z Y.
- 2. If the starting material is labelled with deuterium as indicated, predict how many total deuterium atoms will be present in the major elimination product ?

٠D

Conc. H₂SO₄



- **3.** The total number of alkenes possible by dehydrobromination of 3-bromo-3-methylhexane using alcoholic KOH is :
- 4. In the given reaction : $CH_3-CH-CH_3 \xrightarrow{conc.H_2SO_4} Alkenes$

Total number of alkenes (Including stereo isomers) formed will be

5. Ph $\xrightarrow{\text{Alc. KOH}}$ Alkenes

the total number of possible alkenes in this elimination reaction is.

6. The difference of molecular weights of the major products P and Q form at the followng reactions is

(i)
$$(H_3 + CH_3 I \xrightarrow{KOH/\Delta} P$$
 (organic product)
(ii) $(H_3 + CH_3CH_2OH \xrightarrow{KOH/\Delta} Q$ (organic product)

7. Observe the following reaction sequence

$$\begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \\ & \end{array} \end{array} \xrightarrow{Ph} \xrightarrow{Conc. H_2SO_4, (boil)} \\ & \begin{array}{c} & \end{array} \end{array} (G) \xrightarrow{LiAlH_4} (H) \xrightarrow{H_3PO_4, \Delta} (I) \end{array}$$

Calculate molecular mass [W] of product I and report your answer as N , where N = W \div 3.

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Predict the products expected in given reaction 2-Bromo-1,1-dimethylcycopentane $\xrightarrow{C_2H_5OH}$

(A)
$$OC_2H_5$$





- 2. Which of the following order is/are correct for the rate of E2 reaction ?
 - (A) 5-Bromocycloheptene > 4-Bromocycloheptene
 - (B) 2-Bromo-1-phenylbutane > 3-Bromo-1-phenylbutane
 - (C) 3-Bromocyclohexene > Bromocyclohexane
 - (D) 3-Bromo-2-methylpentane > 2-Bromo-4-methylpentane



6. Which of the following statement (s) is/are correct

(A) E2 is a concerted reaction in which bonds break and new bonds form at the same time in a single step.

(B) Order of reactivity of alkyl halides towards E2 dehydrohalogenation is found to be 3° > 2° > 1°

(C) In E2 reaction both β hydrogen and leaving group should be antiperiplanar.

(D) In E2 elimination different stereoisomer (diastereomer) converts into different stereo product.

7. Following graph between ΔG and reaction progress in for/can be :



- (A) S_N1 reaction
- (B) E₁ reaction
- (C) Aromatic electrophilic substitution
- (D) Electrophilic addition reaction
- 8. Which observation/s will be correct about the major products X and Y of the following reaction.



9. In which of the following reaction, regioselectivity can be observed.

ĊH₃

What is / are true about above reaction ? (A) Major product is given by $S_N 1$ reaction.

(B) Through E1 mechanism 3 alkenes are formed.

(C) 3-Methylpentan-3-ol is also formed as one of the product.

(D) Fractional distillation of elimination products will give two fractions.

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension #1

10.2

Alcohols undergo acid catalysed elimination reactions to produce alkenes. Because water is lost in the elimination, this reaction is called dehydration reaction. Secondary and tertiary alcohols always give E1 reaction in dehydration. Primary alcohols whose β -carbon is branched also give E1 reaction. The reactivity of alcohol for elimination reaction is tertiary alcohol > Secondary alcohol > Primary alcohol.

1. Which of the following dehydration product (major) is incorrect ?



2. Identify the product in the given reaction :



Organic Reaction Mechanisms-IV Comprehension # 2 CH. $\begin{array}{c} \underline{\mathsf{Mel}} \\ \hline (1) \end{array} \longrightarrow \left[\begin{array}{c} \mathsf{Me}_{3} \overset{\bullet}{\mathsf{N}} & \overbrace{\mathsf{H}}^{2 \times 5} \\ & \mathsf{H}_{3} \end{array} \right] \overset{\bullet}{\mathsf{I}} \qquad \begin{array}{c} \overset{\bullet}{\mathsf{OH}}, \Delta \\ & \overset{\bullet}{\mathsf{OH}}, \Delta \\ \hline (2) \end{array} \right]$ (E) Elimination product Major Mel (3) [©]_{SH} (F) Substitution product (major) 3. The incorrect statement about step-1 is : (A) It is S_N2 reaction (B) Only one transition state is formed in this reaction (C) Walden inversion has occured at reactant 'X' (D) The reaction has molecularity two The product 'E' is % 4. (A) $CH_3-CH_2-CH_2-CH_2$ (B) $CH_3-CH_2-CH_3$ (C) $CH_2=CH_2$ (D) CH₃-CH=CH₂ The product 'F' is : 5.2 (B) $H \xrightarrow{} SH$ (C) CH_3SH C_2H_5 (D) HS- (A) C_2H_5SH

Comprehension # 3

Answer Q.6, Q.7 and Q.8 by appropriately matching the information given in the three columns of the following table.

Observe the three columns in which column-1 represents reactants, column-2 represents reaction conditions while column-3 represents products.

	Column-1	Column-2			Column-3		
(I)	HOOH	(i)	Zn dust / Δ	(P)	\bigcirc		
(II)	CI •CI	(ii)	Conc. H ₂ SO ₄	(Q)	CI		
(111)	OH	(iii)	HCI/ZnCl ₂	(R)	\bigcirc		
(IV)	OH	(iv)	Aqueous AgNO₃	(S)	$\langle \rangle$		

6.	The bimolecular reaction	n is represented by :		
	(A) (IV), (iii), (Q)	(B) (I), (ii), (S)	(C) (III), (ii), (P)	(D) (II), (i), (R)
7.	The dehydration reaction (A) (III), (ii), (R)	n is represented by : (B) (III), (iv), (P)	(C) (I), (ii), (S)	(D) (IV), (iii), (R)
8.	The unimolecular nucle (A) (II), (iii), (Q)	ophilic substitution is rep (B) (I) (iv), (S)	resented by : (C) (IV), (iv), (Q)	(D) (IV), (iii), (Q)

Exercise-3

* Marked Questions may have more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. Identify (X), (Y) and (Z) in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde (H_2C^*O) as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Mark the C* carbon in the entire scheme.

$$Ba\dot{C}O_{3} + H_{2}SO_{4} \longrightarrow (X) \text{ gas} [C^{*} \text{ denotes } C^{14}]$$

$$CH_{2}=CH-Br \xrightarrow[(ii)]{(ii)} X_{(iii)} X_{(iii)} H_{3}O^{+}} (Y) \xrightarrow{LiAIH_{4}} (Z)$$
[IIT-JEE 2001(M), 5/135]

2. Identify the set of reagents/reaction conditions 'X' and 'Y' in the following set of transformations. CH₃-CH₂-CH₂Br \xrightarrow{X} product \xrightarrow{Y} CH₃ - CH - CH₃ [IIT-JEE 2002(S), 3/150]

- (A) X = concentrated alcoholic NaOH, 80°C; Y = HBr acetic acid, 20°C (B) X = dil. aq. NaOH, 20°C, Y = HBr / acetic acid, 20°C
- (C) X = dil. aq. NaOH, 20°C, Y = $Br_2 / CHCl_3$, 0°C
- (D) X = conc. alc. NaOH, 80° C, Y = Br₂ / CHCl₃, 0° C
- 3.

4.

H ₃ C	- Сон	$\xrightarrow{H^+}$ [F] -	$\xrightarrow{\text{Br}_2/\text{CCl}_4}$	$\frac{C_4H_8Br_2}{5 \text{ such product}}$

How many structures of F is possible? (B) 5 (A) 2

∠CH₂

[IIT-JEE 2003(S), 4/144] (D) 3

Which is the best reagent to convert cyclohexanol into cyclohexene. [JEE-2005, 3/144] (A) conc. HCl (B) conc. HBr (C) conc. H₃PO₄ (D) HCl + ZnCl₂

(C) 6

5. Match the following (one term in column-I may match with more than one terms in column-II)

			[JEE-2006, 6/184]
	Column I		Column II
(A)	$CH_3 - CH - CD_3$ on reaction with $C_2H_5O^-$ gives $CH_2=CH-CD_3$	(p)	The reaction is E1
(B)	PhCH ₂ CH ₂ Br gives elimination faster than PhCD ₂ CH ₂ Br. The mechanism is	(q)	The reaction is E2
(C)	PhCH ₂ CH ₂ Br in presence of $C_2H_5OD/C_2H_5O^-$ gives good yield of PhCD ₂ CH ₂ Br along with alkene	(r)	The reaction is E1 cB
(D)	$Ph - CH - CD_3$ and $Ph - CH - CH_3$ on elimination, yield Br Br Br	(s)	The reaction is unimolecular
	alkene at the same rate		

Comprehension #1

In the following reaction sequence, product **I**, **J** and **L** are formed. **K** represents a reagent.





9. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is [JEE-2011, 4/160]

Comprehension # 2

An acyclic hydrocarbon \mathbf{P} , having molecular formula C_6H_{10} , gave acetone as the only organic product through the following sequence of reactions, in which Q is an intermediate organic compound.



Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the code given below the lists : [IIT-JEE-2013, 3/120]
 List I



(i) Hg(OAc)₂; (ii) NaBH₄
 NaOEt
 Et-Br
 (i) BH₃; (ii) H₂O₂/NaOH

S

4

1

R

1

4



Comprehension # 3

In the following reactions : $C_{8}H_{6} \xrightarrow{Pd-BaSO_{4}} C_{8}H_{8} \xrightarrow{i. B_{2}H_{6}} X$ $H_{2}O$ $H_{2}O$ $H_{3}SO_{4}, H_{2}SO_{4}$ $C_{8}H_{8}O \xrightarrow{i. EtMgBr, H_{2}O} Y$

14. Compound X is



15. The major compound Y is (A)





Q

2

2

[IIT-JEE-2015, 4/168]

[IIT-JEE-2015, 4/168]



16.

- The number of hydroxyl group(s) in Q is : H^{*} aqueous dilute KMnO₄ (excess) - O H /// heat 0°C HO H₃Ċ ČН
- 17. The desired product X can be prepared by reacting the major product of the reactions in LIST-I with one or more appropriate reagents in LIST-II. (Given, order of migratory aptitude: aryl > alkyl > hydrogen) [JEE(Advanced) 2018, 3/120]

[IIT-JEE-2015, 4/168]



18.

(R) (3) NaOMe OMe Br (S) (4) MeBr -ONa (5)

Match each reaction in LIST-I with one or more products in LIST-II and choose the correct option. (A) $P \rightarrow 1, 5$; $Q \rightarrow 2$; $R \rightarrow 3$; $S \rightarrow 4$ (B) $P \rightarrow 1, 4$; $Q \rightarrow 2$; $R \rightarrow 4$; $S \rightarrow 3$



(D) P \rightarrow 4, 5 ; Q \rightarrow 4 ; R \rightarrow 4 ; S \rightarrow 3, 4





(3)





9. The major product of the following reaction is



- **10.** The major product of the following reaction is : $CH_{3}CH_{2}CH-CH_{2} \xrightarrow[(i) KOH alc.]{(i) NaNH_{2}}$ Br Br in lig.NH₃
 - (1) $CH_3CH=C=CH_2$
 - (3) $CH_3CH_2C \equiv CH$



[JEE(Main) 2019 Online (12-01-19), 4/120]

[JEE(Main) 2019 Online (12-01-19), 4/120]

- (2) CH₃CH=CHCH₂NH₂
- (4) CH₃CH₂CH–CH₂ | | NH₂ NH₂
- **11.** The major product of the following reaction is: $\underline{C}H_2CH_3$



(3) CH₃CH₂C=CH₂ I CO₂CH₂CH₃



(2) $CH_3\dot{C}=CHCH_3$



[JEE(Main) 2019 Online (11-01-19), 4/120]

Answers

EXERCISE - 1

PART - I

- **A-1.** In basic condition very poor leaving group –OH will eliminate but in acidic medium –OH will be converted into $-\overset{\oplus}{O}H_2$ which is very good leaving group.
- **A-2.** 1° carbocation $R CH_2$ would rearrange and 2-alkene would result. Even if 1-alkene is also formed but, it would tend to rearrange in acidic medium to 2-alkene.



- **B-2.** t-BuO^o is bulky base so Hoffmann product is formed as major product.



Orga	nic Reaction N	/lechanism	s-IV						
	CH ³		CH₂						
B-6.	(a)		(b)						
C-1.	The compou	und must h	ave acidic β-h	ydrogen a	nd a relative	ely poor leavi	ng group.		
C-2.	In E1cB me	chanism c	arbanion is for	med as inf	termediate a	and 1st step is	s reversible.		
C-3.		:Н=СН–СН	, + (CH-CH-C	:H.				
				I I D Br					
				PA	RT - II				
A-1.	(B)	A-2.	(D)	A-3.	(A)	A-4.	(B)	A-5.	(A)
A-6.	(B)	A-7.	(B)	A-8.	(C)	B-1.	(C)	B-2.	(D)
B-3.	(A)	B-4.	(C)	B-5.	(A)	B-6.	(B)	B-7.	(A)
B-8.	(B)	C-1.	(B)	C-2.	(C)	C-3.	(B)	C-4.	(A)
				PAF	RT - III				
1.	(B)	2.	$(A \rightarrow p,r)$; ($B \rightarrow q,s);$	$(C \rightarrow s)$; (C	$D \rightarrow t$)			
				EXER	CISE -	2			
				PA	RT - I				
1.	(D)	2.	(D)	3.	(C)	4.	(D)	5.	(A)
6.	(A)	7.	(C)	8.	(B)	9.	(A)	10.	(C)
11.	(C)	12.	(C)	PΔ	RT - II				
1.	23	2.	6	3.	5	4.	5	5.	3
6.	32 [Molecul	ar Weights	(P – Q) = 114	- 82 = 32	2]	7.	78		
				PAF	RT – III				
1.	(ABCD)	2.	(BCD)	3.	(AD)	4.	(ABCD)	5.	(ABD)
6.	(ABCD)	7.	(ABCD)	8.	(BD)	9.	(CD)	10.	(ABC)
				PAF	RT - IV				
1.	(B)	2.	(C)	3.	(C)	4.	(A)	5.	(C)
6.	(D)	7.	(C)	8.	(D)				
				EXER	CISE -	3			
				PA	RT - I				
1.	$(X) = \overset{*}{C}O_2;$	(Y) = CH ₂	, = CH − Č− O − I	H;(Z) = C	$H_2 = CH - \dot{C}$	$\dot{C}H_2 - OH + H$	l ₂ 0	2.	(A)
	Ľ	- 4	 0		-	-			. ,
3.	(D)	4.	(C)	5.	(A) - q ; (E	B) - q ; (C) - r,	s ; (D) - p, s	6.	(D)
7.	(A)	8.	(C)	9.	5	10 .	(D)	11.	(B)
12.	(A)	13.	(A)	14.	(C)	15.	(D)	16.	(4)
17.	(D)	1 8.	(B)						

Orga	anic Reactior	n Mechanism	ns-IV						
				PA	RT - II				
			JEE	E(MAIN) OFF	LINE PRO	BLEMS			
1.	(2)	2.	(1)	3.	(3)	4.	(3)	5.	(3)
6.	(2)	7.	(1)	8.	(2)	9.	(3)	10.	(4)
11.	(1)	12.	(4)	13.	(4)				
			JE	E(MAIN) ON	LINE PROE	BLEMS			
1.	(2)	2.	(1)	3.	(3)	4.	(4)	5.	(1)
6.	(4)	7.	(1)	8.	(1)	9.	(4)	10.	(3)
11.	(2)								