

CHEMISTRY

BOOKS - CENGAGE CHEMISTRY (HINGLISH)

ORGANIC REACTION MECHANISM

Illustration

- **1.** Explain the effect of SN^2 rates for the following reactions :
- (a) Increasing the polarity of solvent.
- (b) Show the T. S with all partial charges for each reaction type.

$$\begin{array}{l} \text{(I)} \ Me_2\overset{\oplus}{S} - Me + NH_3 \rightarrow Me\overset{\oplus}{N}H_3 + Me_2S \\ \text{(II)} \ MeI + NH_3 \rightarrow Me\overset{\oplus}{N}H_3 + I^{\Theta} \\ \text{(III)} \ MeI + \overset{\Theta}{O}H \rightarrow MeOH + I^{\Theta} \\ \text{(IV)} \ Me_2S^{\oplus} - Me + \overset{\Theta}{O}H \rightarrow MeOH + Me_2S. \end{array}$$

2. Explain the order of the following nucleophiles in weakly polar aprotic solvents, e.g., acetone.

(a) LiI > LiBr > LiCI > > LiF

(b) CsF > RbF > KF > NaF > LiF

(c) $Bu_4N^{\,\oplus}CI^{\,\Theta} > Bu_4N^{\,\oplus}Br^{\,\Theta} > Bu_4N^{\,\oplus}I^{\,\Theta}.$

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3. Of the following pairs, which one is the stronger base and stronger

nucleophile ? (a) (I) MeO^{Θ} , (II) MeOH(b) (III) $\stackrel{\Theta}{OH}$, (IV) $\stackrel{\Theta}{CN}$ (c) (V) H_2O , (VI) $\stackrel{\Theta}{OH}$ (d) (VII) $\stackrel{\Theta}{NH}_2$, (VIII) NH_3 .

4. (a) Give the products of the following reactions :



(c) The reaction of C_2H_5OH with NaBr in the presence of H_2SO_4 is slow, but when trimethy1 sily1 chloride (Me_3SiC1) is added to it, reaction proceeds very fast. Why ?

5. Explain the reaction : (a) $ROH + NaBr \rightarrow$ (b) $ROH + HBr \rightarrow$ a. $ROH + NaBr \rightarrow$ b. $ROH + HBr \rightarrow$ c. $Me \frown Cl + NaNO_2 + EtOH \rightarrow$ d. $Me \frown O \frown Cl + NaNO_2 + EtOH \rightarrow$ e. Account for the rapid rate of ethanolysis of $Cl \frown O \frown Me$ (I), although it is a 1° halide.

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6. Give the organic products of the following reactions :

)



7. (I) Give the decreasing order of SN^2 reacivity of the following alkoxide nucleophile.

 $Me_3CO^{\Theta}, MeCH_2O^{\Theta}, Me_2CHO^{\Theta}$



8. Optically pure (+) - 2 -chlorooctane, $[\alpha] = +40^{\circ}$, reacts with aq. NaOH in acetone to give optically pure (-) - 2 -octanol, $[\alpha] = -12.0^{\circ}$. With partically racemised chloro compound whose $[\alpha] = +30^{\circ}$, the $[\alpha]$ of alcohal product is -6.0° . Calculate :

(a) The percentage optical purity of partially racemised chloro compound and alcohol.

(b) The percentage of inversion and racemisation.

(c) The percentage of front-side and back-side attacks.

(d) What interference can be drawn from the data in part (a) of the above example, about the mode of 2° alky1 halide.

(e) Give the rate expression.

In terms if the expression, decrease the experimental changes for encourage (i) SN^1 , (ii) SN^2 ,

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9. Explain the sterochemistry of the intermediates and products in the following reaction and give their R and S configurations.

$$n \Pr \xrightarrow{\text{CH}_{3}} \text{OH} \xrightarrow{\text{K}} (B) \xrightarrow{\text{C}_{2}\text{H}_{5}\text{OTs}} (C)$$

$$\xrightarrow{\text{H}} (R) \xrightarrow{\text{TsCl}} (D) \xrightarrow{\text{KOEt}} (E)$$

10. Predict the effect of increasing the percentage of H_2O in acetone

- $-H_2O$ solvent mixture in :
- (a) SN^1 solvolysis of Me_3C-Br
- (b) SN^2 reaction of K1 and EtC1.
- (c) Predict the relative yields of the product of Me_3CBr in

80 % EtOH and $20 \% H_2O$.

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- 11. Account for the following observations :
- (a) t BuF is solvolysed only in very acidic solution.
- (b) t BuC1 is solvolysed more slowly than 2-chloro-2,3,3,-trimethy1-

butane (A).

(c) t - BuC1 is solvolysed much faster than 2-chloro-1,1,1-trifluoro-2methy1 propane (B). (d) t-BuC1 is solvolysed more slowly in $90~\%~D_2O-10~\%~$ dioxane

than in $90~\%~H_2O-10~\%~$ dioxane solution.



(II) Predict the product and mechanism, E1, E2, or E1cB.



(III) Of the following pairs of structures, choose the componds that better fir the description.

(a) Gives more Saytzeff product in an E2 reaction



b. Reacts more rapidly with cold aqueous HBr.



c. Gives a mix of two alkenes by E1 reaction.



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13. Give all the possible major and minor products $(SN^1 \text{ and } E1)$ in the following. Explain.



(b) If t-pentyl shloride reacts with $25 \% H_2O$ and $75 \% C_2H_5OH$ in NaOH, what are the possible products formed ? Explain with mechanism.

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14. Give the product and find out which is faster ?

(a) (i)
$$CH_3CH_2I \xrightarrow{\Theta \\ OH}$$

(ii) $D_3C - CH_2I \xrightarrow{\Theta \\ OH}$

(b) Give the product and find out which is faster out of SN^1 and E1

(i)
$$(CH_3)_3 CC1 \xrightarrow{\Theta \\ OH}$$

(ii) $(CD_3)_3 C - C1 \xrightarrow{\Theta \\ OH}$



- 15. (a) Give the products of the reaction of KOH with
- (i) C_4H_9Br
- (ii) $C_2H_5CHBrCH_3$
- (iii) Me_3CBr
- (b) Give the reactivity order.
- (c) Give the factors that determine the major product.

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- **16.** (a) Why does $3^{\circ}RX$ rarely undergo E1 reaction ?
- (b) How can E1 be promoted ?
- (c) Give the products in the following reaction.

$$CH_{3}CHBrCH_{3} \xrightarrow[EtOH/NaOH]{EtOH} (A)$$
$$(B)$$

(d) Give the products of MeONa with



(ii) trans-2-Bromomethy1 cyclohexane.



17. (a) Compare the reactivity of $Me_3CO^{\Theta}K^{\oplus}$ and $EtNH_2$ in E2 reaction.

(b) Why is $Me_3CO^{\Theta}K^{\oplus}$ superior to EtO^{Θ} in E2 reaction ?

(c) Compare the effectiveness of $Me_3CO^{\Theta}K^{\oplus}$ in DMSO and

 Me_3COH as solvents.

(d) $Me_2CC1CH_2CH_3 \xrightarrow{Me_3CO^{\Theta}K^{+}}$ Major alkene.

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18. Complete the following and point out the mechanism as SN^2 , SN^1 , E1, E2, or none.

(a) $Me_2C = CHC1 + NaNNH_2$

(b) $CH_3CH_2Br+Pme_3$

(c) $BrCH_2CH_2CH_2Br + I^{\Theta}$

(d) $BrCH_2(CH_2)_2CH_2Br+Mg$ (ether)

(e) $Me_3CBr + HCOOH + HCOO^{\Theta}$ (small amount)

(f) $Me_3CBr + HCOOH$

(g) $CH_3CH_2CH_2Br + LiA1D_4$.

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19. Give the symbol SN^1 , SN^2 , E1, and E2 (more than one symbol may be used).

- (a) Rates are same.
- (b) Electrophilic catalysis is possible.
- (c) With a given substrate some pairs of these may be concurrent.
- (d) Rearrangement of the R skeleton may occur.
- (e) R1 reacts faster with RC1
- (f) R^{\oplus} are intermediates.
- (g) With saturated $R^{,s}$, a Saytzeff product is always formed.
- (h) Reactions are stereospecific.

- (i) Reactions are concerted.
- (j) Unhindered $1^{\circ}RX$ reacts with $NaOEt \mid EtOH$.
- (k) t BuBr reacts with $CH_3COOH + CH_3COO^{\Theta}Na^{\oplus}$ (small).
- (I) t BuBr reacts with CN^{Θ} .
- (m) t BuBr reacts in EtOH.
- (n) $2^{\circ} RC1$ reacts with $NaOEt \mid EtOH$.
- (o) $2^{\circ}RC1$ reacts with HCOOH and has high dielectric constant.
- (p) $2^{\circ} RC1$ reacts with I^{Θ} in acetone.
- (q) MeX cannot react.

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20. (a) When cis-2,3-dibromopent-2-ene is hydrogenated with H_2/Pt ,

The product is :

- (i) Meso-2, 3 -Dibromopentane
- (ii) (+)2, 3 -Dibromopentane
- (iii) (-)2, 3 -Dibromopentane
- (iv) $(\pm)2, 3$ -Dibromopentane

- (b) When trans-2,3-dibromopentane-2-ene is hydrogenated with
- H_2/Pt . The product is :
- (i) Meso-2,3 -Dibromopentane
- (ii) (+)2, 3 -Dibromopentane
- (iii) (-)2, 3 -Dibromopentane
- (iv) $(\pm)2, 3$ -Dibromopentane
- (c) When cis 2, 3 -dibromopent-2-ene is hydrogenated with Birch

reduction. The product is :

- (i) Meso-2,3-dibromopentane
- (ii) (+)2, 3 -Dibromopentane
- (iii) (-)2, 3- Dibromopentane
- (iv) $(\pm)2, 3$ -Dibromopentane
- (d) When trans-2,3-dibromopent-2-ene is hydrogenated with
- $Na+liq.\ NH_3$ + ethanol. The product is :
- (i) Meso-2,3-dibromopentane
- (ii) (+)2, 3 -Dibromopentane
- (iii) (-)2, 3 -Dibromopentane
- (iv) $(\pm)2, 3$ -Dibromopentane

(e) When 2-butyne is reduced with Lindlar's catalyst. The product is :

(i) cis-2-Butene

- (ii) trans-2-Butene
- (iii) Both (i) and (ii)
- (iv) None
- (f) When 2-Butyne is reacted with $Na + liq. NH_3 + C_2H_5OH$. The

product is :

- (i) cis-2-Butene
- (ii) trans-2-Butene
- (iii) Both (i) and (ii)
- (iv) None.

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Solved Example

1. (a) Explain how the sterochemistry of SN^1 and SN^2 differs.

(b) Explain the formation of $60~\%\,$ inverted and $40~\%\,$ racemic product

from a typical SN^1 reaction.

(c) Account for the following in terms of the rate of solvent in the above problem.

(i) The reaction is first order.

(ii) Under what conditions the rate expression is more than first order

?

(iii) What is the order and molecularity?

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2. (a) Define dielectric constant.

(b) How does dielectric constant affect SN^1 rates ?

(c) Explain why solvolyses are much faster in EtOH than in acetone

even though both solvents have the same dielectric constants.

3. (a) Show by enthalpy diagram the rate of solvolysis of t-BuCl on increasing the polarity of solvent.

(b) Give the equation of methanolysis of $[Me_3CSMe_2]^{\oplus}Br^{\Theta}$.

(c) Does the effect of solvent prevail for solvolysis of $\left[Me_3CSMe_2
ight]^\oplus$

?

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4. Hydrolysis of 2-bromo-3-methyl butane (2°) yields only 2-methy-2-

butanol (3°) , explain.

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5. Write structure for the solvolysis of $Et_3C - Cl$ with :

(a) MeOH

(b) MeCOOH

(c) *HCOOH*.



6. Explain the relative rates of RX with $H_2 \emptyset EtOH$ at $25\,^\circ C$ as given :

(i) MeBr(2140)

(ii) $MeCH_2Br(171)$

(iii) $Me_2CHBr(4.99)$

(iv) $Me_3CBr(1010)$

(b) Why is EtOH added to water ?

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7. Predict the order of nucleophicity of X^{Θ} in the following reaction :

$$(C_5H_{11})_4 N^{\textcircled{\bullet}} X^{\textcircled{\bullet}} (X^{\textcircled{\bullet}} = Cl, Br, I) \xrightarrow{\blacktriangle} (C_5H_{11})_3 N + C_5H_{11} X$$

8. Give the product of the following displacement reactions :

(a) $(R) - CH_3 CHBr CH_2 CH_3 + MeO^{\Theta}$

(b) $(S) - CH_3CHBrCH_2CH_3 + MeO^{\Theta}$

(c) rac, cis-lodo ethyl cyclohexane +OH

d.
$$(S) - Br + COEt + CN^{\ominus}$$

(d)





10. When 3-chlorocyclopropene (A) is treated with $SbCl_5$, it gives a stable salt (B), $C_3H_3SbCl_6$, which is highly polar. Further, when (A) is treated with $AgBF_4$, it gives a white precipitate of AgCl and a crystalline salt (C). Explain.

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11. Explain :

(a) An aq. Solution to troplylium bormide (C_7H_7Br) on treatment with $AgNO_3$ gives a pale yellow precipitate.

(b) Cycloheptatrienyl cation has a low π -electron energy than its open-chain counterparts.

(c) Cyclo-octatetraene reacts with 2 mol of potassium to yield a stable compound.

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12. Give the order of reactivity towards aqueous HCOOH of the

following.



13. Give the order of hydrolysis in SN^1 process for the following :



14. Give the order of (a) nucleophilicity (b) basic character, and (c)

fugacity of the following :

(i) *F* ^Θ

(ii) Cl^{Θ}

(iii) Br^{Θ}

(iv) I^{Θ} .



15. Give the most reactive substrate in each of the following pair with Θ OH ions under SN^2 conditions.

(a) C_2H_5I and C_2H_5Cl

- (b) $p-Br-C_{6}H_{4}CH_{3}$ and $PhCH_{2}Br$
- (c) CH_3Cl and CH_2Cl_2





16. Outline the synthesis of following compounds from suitable nucleophiles and an appropriate halide.



17. Give a suitable mechanism for the following :



18. Predict the order of reactivity of the following halides with (a) NaI

in acetone

(b) aq.alcoholic $AgNO_3$

(i) CH_3Br

(ii) C_2H_5Br





(iv)

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19. Explain :

(a) $ClCH_2OCH_3$ (chloromethyl methyl ether) undergoes SN^1

reaction.

(b) (+) - 4 -Bromo-2-pentene forms a racemic mixture on treatment

with NaI.

20. Write the products of the following SN reactions.



22. Bromobenzene can be dehydrobrominated to benzyne by three

possible routes. Explain. Which paths are desirable ?



23. Classify the following reactions as addition, elimination, substitution, condensation, rearrangement, geometric isomerisation, or oxidation/reduction.





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24. From the following elimination reactions, predict which one is

Hofmann or Saytzeff (Zaitev) type.



25. Which one is more reactive towards acidcatalysed hydration ? Predict the stereochemical alcohols formed form the compound.



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26. Which one hydrolyses at a faster rate by SN^1 mechanism ?





does (\pm) compounds. What are the respective alkenes formed ?





30. Mustard gas $(ClCH_2CH_2)_2 - S$ hydrolysed by water to $Cl(CH_2)_2S(Ch_2)_2OH$ much faster than expected for a primary halide. Offer an explanation.


31. Give the product, indicating stereo-chemistry of cyclohexene with :

(a) Br_2

(b) Br_2 inNaCl

(c) $Br_2 in CH_3 OH$

(d) $Br_2 {
m in} H_2 O$

(e) KI/H_3PO_4 .

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32. 1,2-Dimethylcyclohexene undergoes only trans-addition with HBr in non-polar solvents but both cis-and trans-additions occur with aq.

Acid. Explain.



33. Complete the following and state the relations between configurations of the reactant and products.

(i) $_{D-} MeCH(OH)Et + Ac_2O \rightarrow ?$

(ii) $._{D-} MeCH(Cl)COOH + 2NaOH \rightarrow$?

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Subjective

1. Complete the following and state the relations between configurations of the reactant and products.

(i) $_{L} - MeCH(OH)Et + HBr \rightarrow ?$

(ii)
$$._L - MeCH(OAc)Et + 2NaOH
ightarrow \ ?$$

(iii) $._L - MeEtPrCOMe + HI \rightarrow ?$

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2. What are the products and types of isomers when Br_2 adds to :



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4. Give the stereochemical products of the following :

(i)
$$CH\equiv CH+Br_{2}
ightarrow (A) \xrightarrow[KMnO_{4}]{Aq}$$





5. Give the products of the following organic reactions :



6. Of the following pairs, which is the faster SN^2 reactions ?



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7. Of the following pairs, which is the faster SN^1 reactions ?



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8. Which of the following would give a better yield of ether ?



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9. Give the decreasing order of SN^1 reactions of the following compounds in H_2O .



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10. Give the major product when the following compounds are reacted with C_2H_5ONa .



11. 2-Bromo pentane when treated with acl. KOH yields a mixture of three alkenes (A), (B), (C). Indentity them and find out which is predominant ?

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12. 2-Pentanol can coverted to 2-ethoxy pentane by two paths. In path I, configuration at chiral C is retained but at path II, configuration is inverted. Explain.





Tosyl (Ts) is

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13. When

reacts with alcoholic KCN, a mixture of isomeric products is obtained. Explain.



14. Give the stereochemical products of the following :



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15. Give the sterochemical products :

$$HC \equiv CH + 2NaNH_2 + 2EtBr
ightarrow (A) \xrightarrow{Cs\,, NH_3} (B) \xrightarrow{Br_2} (C).$$

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18. Explain the difference in the following reactions.



19. Predict the products with configurations in the following.

(a)
$$(+)2 - \text{Octanol} + PhSO_2Cl \rightarrow (A) \xrightarrow[NaOH]{Hot} (B)$$

(b) $(+)2 - \text{Octanol} + CH_3COCl \rightarrow (C) \xrightarrow[NaOH]{Hot} (D)$

(c)
$$CH_3O^*H + PhSO_2Cl \rightarrow (E) \xrightarrow[NaOH]{Hot} (F) + (G)$$

(d) $CH_3O^*H + CH_3COCl \rightarrow (H) \xrightarrow[NaOH]{Hot} (I) + (J).$

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Comprehension

1. The leaving group is that functional group which is ejected with \bar{e} 's of the σ -bond in a reaction. Better the leaving group, faster is the reaction. The relative leaving ability of the leaving group X in (R - X) is increased by :

- (i) The polarisability of (R X) bond.
- (ii) The stability of X^{Θ} .
- (iii) The degree of stabilisation through solvation of X.
- (iv) The strength of (R X) bond.
- The leaving group tendency is also called fugacity.
- Which statement is wrong?

A. In polar aprotic solvents such as DMSO, DMF, and DMA,

the fugacity order is $I^{\Theta} > Br^{\Theta} > Cl^{\Theta} > F^{\Theta}$.

B. Strong bases are good leaving groups.

C. The leaving group order of the following is :

$$\stackrel{\Theta}{OH} > RO^{\Theta} > CH \equiv C^{\Theta} > \stackrel{\Theta}{NH_2}.$$

D. Charges species are good leaving groups than neutral species.

Answer: B



2. The leaving group is that functional group which is ejected with \bar{e} 's of the σ -bond in a reaction. Better the leaving group, faster is the reaction. The relative leaving ability of the leaving group X in (R - X) is increased by :

(i) The polarisability of (R-X) bond.

(ii) The stability of X^{Θ} .

(iii) The degree of stabilisation through solvation of X.

(iv) The strength of (R - X) bond.

The leaving group tendency is also called fugacity.

Which statement is correct ?

A. Only SN^1 reaction depends on the nature of leaving group.

B. Only SN^1 reaction depends on the nature of leaving group.

C. Both SN^1 and SN^2 reactions depends on the nature of leaving

group.

D. All

Answer: C



3. The leaving group is that functional group which is ejected with \bar{e} 's of the σ -bond in a reaction. Better the leaving group, faster is the reaction. The relative leaving ability of the leaving group X in

(R-X) is increased by :

(i) The polarisability of (R - X) bond.

(ii) The stability of X^{Θ} .

(iii) The degree of stabilisation through solvation of X.

(iv) The strength of $\left(R-X
ight)$ bond.

The leaving group tendency is also called fugacity.

Which one of the followingd has the highest fugacity ?

A. Tosylate
$$\begin{pmatrix} \Theta \\ OTs \end{pmatrix}$$

B. Mesylate

C. Triflate
$$\left(F_3C-SO_3^{oldsymbol{\Theta}}
ight)$$

D. All are equal

Answer: C



4. The leaving group is that functional group which is ejected with \bar{e} 's of the σ -bond in a reaction. Better the leaving group, faster is the reaction. The relative leaving ability of the leaving group X in (R - X) is increased by :

(i) The polarisability of (R - X) bond.

(ii) The stability of X^{Θ} .

(iii) The degree of stabilisation through solvation of X.

(iv) The strength of (R - X) bond.

The leaving group tendency is also called fugacity.

Which of the following undergoes SN reaction easily ?

A. Vinyl bromide

B. Bromobenzene

C. p-Nitro bromobenzene



Answer: C

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- 5. The leaving group is that functional group which is ejected with \bar{e} 's of the σ -bond in a reaction. Better the leaving group, faster is the reaction. The relative leaving ability of the leaving group X in (R X) is increased by :
- (i) The polarisability of (R X) bond.
- (ii) The stability of X^{Θ} .
- (iii) The degree of stabilisation through solvation of X.
- (iv) The strength of (R X) bond.
- The leaving group tendency is also called fugacity.
- Which statement is correct ?
 - A. EtO^{Θ} is a strong base and therefore a good leaving group.

B. The amine group in $ArNH_2$ is converted into a good leaving

group be reacting $ArNH_2$ with $NaNO_2 + HCl$ at $0^{\circ}C$.

C. The (OH) group is converted into a good leaving group by

reacting alcohols with TsCl (p-toluene sulphonyl chloride)



D. The amine group in RNH_2 is converted into leaving group by

reacting RNH_2 with $NaNO_2 + HCl$ at $0^{\circ}C$.

Answer: C

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6. The leaving group is that functional group which is ejected with \bar{e} 's of the σ -bond in a reaction. Better the leaving group, faster is the reaction. The relative leaving ability of the leaving group X in

(R-X) is increased by :

(i) The polarisability of (R - X) bond.

(ii) The stability of X^{Θ} .

(iii) The degree of stabilisation through solvation of X.

(iv) The strength of (R - X) bond.

The leaving group tendency is also called fugacity.

Which of the following is the wrong order of fugacity?

A. $SbH_3 > AsH_3 > PH_3 > NH_3$ B. $F^{\Theta} > \stackrel{\Theta}{OH} > \stackrel{\Theta}{NH_2} > \stackrel{\Theta}{CH_3}$

C.

 $NH_3>NH_2-NH_2>MeNH-NH-Me>Me_2N-Nme_2$

$$ext{D. } CN > OH > MeO > CH_3.$$

Answer: D

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7. The rate of SN^2 reaction depends on the effectiveness of the nucleophile in ejecting the leaving group. Nucleophilicity is the affinity for C atom, while basicity is the affinity for proton.



In both cases, a new bond is formed. If a new bond is formed between the anion and proton, the specied acts as a base. If a new bond is formed between the anion and C atom, the species acts as nucleophile.

Which of the following statements is wrong ?

A. The nucleophilicity order in non-polar solvents (e.g., CCl_4, CS_2) of the followind is :

 $I^{\Theta} > Br^{\Theta} > Cl^{\Theta} > F^{\Theta}.$

B. The nucleophilicity order in polar protic solvents (e.g., H_2O) of

the following is :

$$I^{\,oldsymbol{ heta}} > Br^{\,oldsymbol{ heta}} > Cl^{\,oldsymbol{ heta}} > F^{\,oldsymbol{ heta}}$$

C. The nucleophilicity order in weakly polar protic solvents (e.g.,

nitro benzene, acetone) of the following is :

 $F^{\Theta} > Cl^{\Theta} > Br^{\Theta} > I^{\Theta}.$

D. The nucleophilicity order in polar aprotic solvents (e.g., DMSO, DMF) of the following is :

 $F^{\Theta} > Cl^{\Theta} > Br^{\Theta} > I^{\Theta}.$

Answer: C



8. The rate of SN^2 reaction depends on the effectiveness of the nucleophile in ejecting the leaving group. Nucleophilicity is the

affinity for C atom, while basicity is the affinity for proton.



In both cases, a new bond is formed. If a new bond is formed between the anion and proton, the specied acts as a base. If a new bond is formed between the anion and C atom, the species acts as nucleophile.

Which of the following statements is wrong ? Nucleophile order of the following in weakly polar aprotic solvents, e.g., acetone is :

A.
$$LiI > LiBr > LiCl > > LiF$$
.

B.
$$CsF > RbF > KF > NaF > LiF$$

C. $R_4 N^{\,\oplus} I^{\,\Theta} > R_4 N^{\,\oplus} Br^{\,\Theta} > R_4 N^{\,\oplus} Cl^{\,\Theta}$ (R = Butyl group)

D. All

Answer: C



9. The rate of SN^2 reaction depends on the effectiveness of the nucleophile in ejecting the leaving group. Nucleophilicity is the affinity for C atom, while basicity is the affinity for proton.



In both cases, a new bond is formed. If a new bond is formed between the anion and proton, the specied acts as a base. If a new bond is formed between the anion and C atom, the species acts as nucleophile.

Which of the following is wrong?

A. The decreasing basic order of the following is :

$$NH_3>PH_3>AsH_3>SbH_3$$

B. The decreasing basic order of the following is :

$$CH_3^{\Theta} > \overset{\Theta}{N}H_2 > \overset{\Theta}{O}H > F^{\Theta}.$$

C. The decreasing nucleophilic order of the following is :

$$\stackrel{\Theta}{C} H_3 < \stackrel{\Theta}{N} H_2 < \stackrel{\Theta}{O} H < F^{\,\Theta}.$$

D. The decreasing basic and nucleophilic order of the following is :

$$\stackrel{ extsf{def}}{O} CH_3 > H^{ extsf{def}} > \stackrel{ extsf{def}}{O} H > \stackrel{ extsf{def}}{O} Me > \stackrel{ extsf{def}}{C} N.$$

Answer: C

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10. The rate of SN^2 reaction depends on the effectiveness of the nucleophile in ejecting the leaving group. Nucleophilicity is the affinity for C atom, while basicity is the affinity for proton.



In both cases, a new bond is formed. If a new bond is formed between the anion and proton, the specied acts as a base. If a new bond is formed between the anion and C atom, the species acts as nucleophile.

Which of the following compounds gives SN^1, SN^2 , and SN^2 mechanisms ?



Answer: B



Which statement is wrong in the formation of (B) from (A).

A. It proceeds by SN^2 mechanism.

B. The configuration of product (B) is D form.

C. It proceeds by SN^1 mechanism

D. The Walden inversion occurs.

Answer: C





Which is correct in the formation of (c) from (A) ?

A. It proceeds by SN^1 mechanism.

B. Retention and racemisation take place.

C. The configurations of (c) are DL and L.

D. It proceeds by SN^i mechanism.

Answer: A



Which statement is wrong in the formation of (c) from (A) ?

A. The retention of configuration of (A) takes place.

B. The configuration of (c) is L form.

C. Due to the neighbouring group participation of (COO^{Θ}) group, the $\stackrel{\Theta}{OH}$ ion attacks from the same side and hence

retension occurs.

D. The reaction proceeds by $SN^{2'}$ mechanism.

Answer: D



14. In elimination reaction, the major product is either Saytzeff (moresubstituted alkene) or Hofmann product (less-substituted alkene) depending on the nature of the substrate and the nature of the base. Which statement is correct about the reactions ?



A. Both products (B) and (c) are Hofmann product.



B. Both products (B) and (c) are Saytzeff product.



C. product (B) is Hofmann and (c) is Saytzeff product.

D. Product (B) is Saytzeff and (c) is Hofmann product.

Answer: A

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15. In elimination reaction, the major product is either Saytzeff (moresubstituted alkene) or Hofmann product (less-substituted alkene) depending on the nature of the substrate and the nature of the base. Refer to Q.No.14 and find out which statement is correct ?

A. Both reactions proceeds by E2 mechanism.

B. Both reactions proceed by E1 mechanism.

C. Formations of (B) and (c) proceed by E1 and E2 mechanisms, respectively.

D. Formations of (B) and (c) proceeds by E2 and E1 mechanism,

respectively.

Answer: A

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16. In elimination reaction, the major product is either Saytzeff (moresubstituted alkene) or Hofmann product (less-substituted alkene) depending on the nature of the substrate and the nature of the base. Which statement is correct about the following reactions ?



A. The major product is (I) by E1 machanism.

B. The major product is (I) by E2 machanism.

C. The major product is (II) by E1 machanism.

D. The major product is (II) by E2 mechanism.

Answer: A

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17. In elimination reaction, the major product is either Saytzeff (moresubstituted alkene) or Hofmann product (less-substituted alkene) depending on the nature of the substrate and the nature of the base. Which statement is wrong about the given reaction.



A. The reaction proceeds by E1cB mechanism.

B. $EWG(-SO_3H)$ stabilities the carbanion formed in the first

step.

- C. The reaction in stereospecific but non-regioselective
- D. PhO^{Θ} is a stronger base than OH ion.

Answer: D

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18. In elimination reaction, the major product is either Saytzeff (moresubstituted alkene) or Hofmann product (less-substituted alkene) depending on the nature of the substrate and the nature of the base. Which statement is wrong about the given reaction ?



A. The reaction is called Cope reaction and proceeds by E1

mechanism.

- B. The reaction proceedsby syn-elimination.
- C. The reaction is stereospecific and stereselective.
- D. The reaction is non-stereospecific and regioselective.

Answer: D

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19. Consider the following reactions :



Which of the following are stereospecific reactions ?

A.(I),(II)

 $\mathsf{B.}\,(I),\,(II),\,(III)$

C.(III), (IV), (V)

D. All

Answer: D


20. Consider the following reactions :



Which of the following regioselective reactions ?

A. (I), (II), (V)B. (III), (IV), (VI)C. (I), (II), (IV)D. (III), (IV), (V)

Answer: A



21. Consider the following reactions :



Syn-addition takes place in :

A. (I), (II), (V)

 $\mathsf{B}.(III),(IV),(VI)$

C.(I), (II), (IV)

D.(III), (IV), (V)

Answer: A



22. Consider the following reactions :



Anti-addition takes place in :

 $\mathsf{B}.(III),(IV),(VI)$

 $\mathsf{C}.\,(I),\,(II),\,(IV)$

 $\mathsf{D}.\,(III),\,(IV),\,(V)$

Answer: B

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23. Consider the following reactions :



Meso-butan-2,3-diol is formed in :

A. (I), (II), (V)

 $\mathsf{B.}(III),(IV),(VI)$

 $\mathsf{C}.\,(I),\,(II),\,(IV)$

 $\mathsf{D}.\,(III),\,(IV),\,(V)$

Answer: A



24. Consider the following reactions :



Racemic-butan-2,3-diol is formed in :

A. (I), (II), (V)B. (III), (IV), (VI)C. (I), (II), (IV)D. (III), (IV), (V)

Answer: B



25. Consider the following reactions :



The name of structure of MMPP is :

A. Magnesium monoperoxy phthalate

$$\left(\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{array} \right)_2 Mg^{2+} (I)$$

- B. Megnesium perphthalate and structure (I)
- C. Methyl monoperoxy phthalate



D. Methyl perphthalate and structure (II).

Answer: A::B



26. Consider the following reactions :



Which of the following are stereospecific reactions ?

A.(I),(II)

 $\mathsf{B.}\,(I),\,(II),\,(III)$

 $\mathsf{C}.\,(III),\,(IV),\,(V)$

D. All

Answer: D



27. Consider the following reactions :



Which of the following regioselective reactions ?

A. (I), (II), (V)B. (III), (IV), (VI)C. (I), (II), (IV)D. (III), (IV), (V)

Answer: B



28. Consider the following reactions :



Syn-addition takes place in :

A. (I), (II), (V)

 $\mathsf{B}.(III),(IV),(VI)$

C.(I), (II), (IV)

D.(III), (IV), (V)

Answer: A



29. Consider the following reactions :



Syn-addition takes place in :

 $\mathsf{B}.(III),(IV),(VI)$

C.(I), (II), (IV)

D.(III), (IV), (V)

Answer: B





30.

Meso-tartaric acid is formed in :

B.(III), (IV), (VI)

C.(I), (II), (IV)

D.(III), (IV), (V)

Answer: B





31.

 (\pm) -Tartaric acid is formed in :

 $\mathsf{B.}\,(III),\,(IV),\,(VI)$

 $\mathsf{C}.\,(I),\,(II),\,(IV)$

 $\mathsf{D}.\,(III),\,(IV),\,(V)$

Answer: A

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32. Consider the following reactions :

$$IMe - \equiv (A) - Me \xrightarrow[EtOH]{Na+Liq.NH_3} (B)$$



Which statement is wrong about the reactions (i) and (ii) ?

A. The product (B) is trans-but-2-ene and (c) is cis-but-2-ene.

B. The product (B) is cis-but-2-ene and (C) is trans-but-2-ene.

C. The formation of (B) and (c) takes place by anti-and syn-addition

of H_2 , respectively.

D. In the formation of (B), one of the intermediate species is

radical anion.

Answer: B

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33. Consider the following reactions :

$$IMe - \equiv (A) - Me \xrightarrow[EtOH]{Na+Liq.NH_3} (B)$$



Which statement is wrong about the reactions (iii) and (iv) ?

A. Anti-addition takes place in both the reactions.

B. The product in both the reactions is racemic mixture.

C. Both the reactions are stereospecific and regioselective.

D. Both the reactions are EA (electrophilic addition) reaction.

Answer: C

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34. Consider the following reactions :

$$IMe - \equiv (A) - Me \xrightarrow{Na + Liq.NH_3} (B)$$



Which statement is wrong about the reaction (v) and (vi) ?

A. Syn-addition takes place in both the reactions.

B. The product in both reactions is racemic mixture.

C. The product (H) is (\pm)



Answer: A



35. Consider the following reactions :

$$IMe - \; \mathop{\equiv}\limits_{(A)} \; - Me \; {{Na + Liq \, . \, NH_3}\over {EtOH}} \; (B)$$



Which statement is wrong about the reactions (vii) and (viii) ?

A. The product (K) is trans-but-2-ene and product (L) is cis-but-2-

B. The product (K) is cis-bit-2-ene and product (L) is trans-but-2-

ene.

- C. Anti-elimination of Br_2 takes place in both the reactions.
- D. Both the reactions proceed by E2 mechanism.

Answer: B

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36. Consider the following reactions :

$$IMe - \equiv (A) - Me \xrightarrow[EtOH]{Na+Liq.NH_3} (B)$$



Which statement is wrong about the reactions (ix) and (x) ?

A. Both the reactions are stereospecific and stereoselective.

B. Reaction (ix) is sterospecific and stereoselective.

C. Reaction (x) is neither stereospecific nor stereoselective.

D. Reaction (ix) proceeds by singlet carbene and reaction (x) by

triplet carbene.

Answer: A

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Multiple Correct

1. Which of the following reactions are correct ?



$$\mathsf{D.}\,(A)(trans) \stackrel{H_2O}{\underset{SN^1}{\longrightarrow}} (C)(trans)$$

Answer: A::C



2. Which of the following reactions would give racemised and retention products ?



Answer: A::C::D

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3. Which of the following statements are correct statements ?

A. Carbocation is less \bar{e} deficient than alkyl radical.

B. Isomerisation of a less stable carbocation to more stable

carbocation by 1, 2 - Me shift is called Wagner-Meerwein rearrangement.

C. Isomerisation to a more stable carbocation is accompained by

decrease in potential energy.

D. Greater stability of benzyl, allyl, and 3° carbocation is due to

hyperconjugation.

Answer: A::C::D



4. In which of the following species containing both nucleophile and leaving group, intramolecular SN reaction occurs ?



Answer: A::B



5. Which of the following statements are correct?

A. The reaction of t-butyl chloride with OH follows first-order

kinetics.

B. An SN^1 reaction proceeds with the inversion of configuration.

C. An SN^2 reaction follows second-order kinetics.

D. An SN^2 reaction proceeds with stereochemical inversion.

Answer: A::C::D

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6. Which of the following are SN^2 reactions ?

A. Me
$$\xrightarrow{Me}_{Me}$$
 CI+KOH \rightarrow Me \xrightarrow{Me}_{Me} OH+KBr

B. $Me_3C - Br + KOH
ightarrow Mr_3C - OH + KBr$

 $\mathsf{C}.\, Et-I+EtONa \rightarrow Et-O-Et+NaI$

D.
$$Et - Cl + NaOH
ightarrow EtOh + NaCl$$

Answer: C::D

7. Vinyl bromide undergoes :

A. Addition reaction

B. Substitution reaction

C. Elimination reaction

D. Rearrangement reaction

Answer: A::C

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8. The halogen atom in RX can easily be replaced by nucleophiles

such as :

A. NO_2^{Θ}

B. RO^{Θ}

 $C.CN^{\Theta}$

D. None

Answer: A::B::C

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9. Which of the following statements are correct?

A. Polar protic solvents (e.g, MeOH, EtOH) form H-bonding to

nucleophile and stabilise it, thus rate of SN^2 reaction is

decreased.

B. Polar aprotic solvents (e.g., DMSO, DMF) raise the energy of

the nucleophile and thus the rate of SN^2 is increased.

P.E.

C. Reactivity of nucleophile in the presence of crown ether

(solvent) is increased for SN^1 and SN^2 reactions.

D. Reactivity nucleophile in the presence of crown ether (solvent)

is decreased for SN^1 and SN^2 reactions.

Answer: A::B::C

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10. Which of the following reactions represents SN reaction ?

- A. $EtCl + EtSNa \rightarrow EtSEt + NaCl$
- $B. EtCl + NaOH \rightarrow EtOH + KCl$
- C. $EtCl + AgCH
 ightarrow Et \overset{\oplus}{N} \equiv \overset{\Theta}{C} + AgCl$
- D. $EtCl+2H
 ightarrow C_2H_6+HCl$

Answer: A::B::C

11. Which of the following reactions are feasible ?



Answer: A::B



12. Which of the following transformations are feasible ?



Answer: A::B::C::D



13. In which of the following reactions, the intermediate species acyl

nitrene $\begin{pmatrix} O \\ || \\ R - C - \ddot{N} \end{pmatrix}$ and intermediate compound alkyl

isocyanate (R - N = C = O) are involved ?

A. a.
$$R = C = NH_2 \xrightarrow{Br_2 + KOH} ? \xrightarrow{H_2O} RNH$$

b. $R = C = NH = OH \xrightarrow{OH} ? \xrightarrow{OH} OH$
b. $R = C = NH = OH \xrightarrow{OH} ? \xrightarrow{OH} OH$
B. O



Answer: A::B::C::D

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14. Which of the following statements are correct?

A.
$$EtO^{\Theta}$$
 is a stronger nucleophile than $\stackrel{\Theta}{O}H$.
B. MeO^{Θ} is a stronger nucleophile than $\stackrel{\Theta}{O}H$
C. $RCOO^{\Theta}$ is a stronger nucleophile than ROH

D. MeO^{Θ} is a weaker nucleophile than OH.

Answer: A::C::D



15. Which of the following is//are the rate determining step (s) of the

given reaction ?







D. All

Answer: B


16. The products in the given reaction are :



Answer: B::C



17. Which of the following statements are correct about the addition

of HBr to buta-1,3-diene ?

Br (Me

A. 1,2-Addition product

, 3-bromobut-1-ene) is

the major product at lower temperature $(-80^{\,\circ}C)$ and is a

kinetic control or rate-controlled product.



B. 1,4-Addition product , 1-bromobut-2-ene) is

the major product at high temperature $(40^{\circ}C)$ and is a thermodynamic or equilibrium-controlled product.

C. In a non-polar solvent (e.g., hexane), 1,2-addition product is predominantly favoured.

D. In a polar solvent (e.g., acetic acid) 1,4-addition product is predominatly favoured.

Answer: A::B::C::D



18. Which of the following statements are correct ?



results in major addition to (C = O).

B. The nucleophilic addition of HCN to (I) results in major

addition (C = C)



results of 1,4-addition.



(Me CH=0)



D. The nucleophilic addition of PhMgCl to

(III) results in addition to (C = C).

Answer: B::C::D

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19. In which of the following reactions, rearrangement is possible ?

A. *E*1

B. SN^1

 $\mathsf{C}.\,SN^2$

D. E1cB

Answer: A::B::C

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20. Which of the following is an example of nucleophilic addition to acetaldehyde ?

A. Acetal formation

B. Cyanohydrin formation

C. Bisulphite adduct

D. Wolff-Kishner reaction.

Answer: A::B::C

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21. In which of the reactions, there is a migration of alkyl group to

carbene $(\ddot{C}H_2)$, i.e., rearrangement occurs ?

A. A.





Answer: A::B::C



22. Which of the following statements are correct ?



B. RS^{Θ} is less basic but a stronger nucleophile than RO^{Θ} .

C. NH_3 is both a stronger base and a stronger nucleophilic than

 H_2O

D. RO^{Θ} and OH are both stronger bases and stronger

nucleophile than ROH and H_2O .



23. Which of the following statements/reactions are correct ?

A. $SN^2/E2$ ratio is higher with RS^{Θ} than for those with RO^{Θ} .

B. $SN^2/E2$ ratio is highest for $1^\circ RX$ and least for $3^\circ RX$.

 $\begin{array}{c} \overset{Me}{\underset{Me}{\leftarrow}} Cl + EiO \overset{\Phi}{\underset{Me}{\leftarrow}} EiO \underset{Me}{\underset{Me}{\leftarrow}} H_2 + EiO \overset{Me}{\underset{More}{\leftarrow}} M_{e} \\ \textbf{C.} \\ (l) \\ (l) \\ (l) \\ (l) \end{array}$

 $\mathsf{D}.\, Me_3C-Br+KCN
ightarrow Me_3C-CN.$

Answer: A::B::C



24. Which of the following statements is//are correct ?

- A. Protic solvents solvate the nucleophile, lower enthalpy of nucleophiles, increase ΔG , and decrease the reaction rate of SN^2 reaction.
- B. SN^1 reactions are favoured in protic solvents.
- C. Crown ether increases the reactivity of nucleophile by solvating

its cation.

D. SN^2 reactions are more favoured in protic solvents.

Answer: A::B::C



25. Consider the following reactions :

$$egin{aligned} (I)Me &= &\equiv \ (A) &- Me \ rac{H_2+}{Pd+BaSO_4} & ? & rac{D_2/Pd/C}{(B)} \ \end{pmatrix} \ (C) \ (II)Me &= &\equiv \ (A) &- Me \ rac{Na+Liq.NH_3}{+EtOH} & ? & rac{D_2/Pt/C}{(D)} \ \end{pmatrix} \ \end{split}$$

Which of the following statements are correct ?

A. (B) is cis-but-2-ene and (D) is trans-but-2-ene.

B. (B) is trans-but-2-ene and (D) is cis-but-2-ene.

C. (c) is meso form and (E) is racemic form.

D. (C) is racemic form and (E) is meso form.

Answer: A::C

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26. Consider the following reactions :



Which of the following statements are correct ?



Answer: B::D



27. Consider the following reactions :



Which of the following statements are correct ?



Answer: B::C



28. Which of the following statements/reactions are correct ?



Answer: A::B::C







Answer: A::C::D



30. Which of the following reactions are both stereospecific and regioselective ?

A. cis-But-2-ene + $D_2 \xrightarrow{Pt}$

B. cis-But-2-ene + $OsO_4 + NaHSO_3
ightarrow$

C. cis-But-2-ene + $Br_2
ightarrow$

D. trans-But-2-ene + $PhCO_{3}H/H_{2}O$ ightarrow .

Answer: A::B::C





D. Both (b) and (c)

Answer: A

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bromide) undergoes alkaline hydrolysis by :

A. SN^1

 ${\rm B.}\,SN^2$

C. Both (a) and (b)

D. None

Answer: A

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3. Which of the following is the strongest nucleophile ?

A. EtO^{Θ}

 $\mathsf{B.}\,OH^{\,-}$

C. CN^{-}

D. $I^{\,-}$

Answer: A

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4. Rearrangement reactions are shown by :

A. Carbanion

B. Free radical

C. Carbene

D. Carbocation

Answer: D

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5. Equal amount of an $RCl(C_4H_9Cl)$ is reacted at the same temperature with equal volume of 0.2M and 0.4M solution of KOH, respectively, in two separate experiments. The time taken for the reaction of 50% of (C_4H_9Cl) was found to be same, the alkyl halide is :



Answer: B



6. Which of the following statements is correct about the following

reactions ?



A. (B) is obtained by elimination reaction.

B. (c) is obtained by substitution reaction.

C. The molecular formula of (B) is C_3H_6 and that of (c) is C_3H_8O

D. (B) is an isomer of ethyl methyl ether, while (c) is the

dehydrated compound of (B).

Answer: D

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Which statement is correct about the above reaction ?



C. Product (B) is (I) by SN^2 mechanism.

D. product (B) is (II) by SN^1 mechanism.

Answer: D

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8. In SN^2 , solvolysis RX in which the solvent is a nucleophile, what is

the order and molecularity of the reaction ?

A. First order , unimolecular

B. First order , bimolecular

C. Second order , bimolecular

D. Pseudo first-order , bimolecular

Answer: D

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9. A partially racemised (+) - 2-bromo-octane $(2^{\circ}RX)$ on reaction with aq. NaOH in acetone gives an alcohol with 80% inversion and 20% racemisation. What is the percentage of back-side attack ?

A. 0.4

B. 0.1

C. 0.9

D. 0.8

Answer: C

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10. Refer to Q.No. 9 above and find out the percentage of front-side attack.

A. 0.1

B. 0.2

C. 0.4

D. 0.8

Answer: A

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11. Refer to Q.No. 9 above and find out the rate expression of the reaction.

A. Rate
$$= K_1[2^\circ RX] egin{bmatrix} \Theta \ OH \end{bmatrix}$$

B. Rate $= K_2[2^\circ RX]$

$$\begin{array}{l} \mathsf{C. Rate} \ = K_1[2^\circ RX] \begin{bmatrix} \mathsf{\Theta} \\ OH \end{bmatrix} + K_2[2^\circ RX] \\ \\ \mathsf{D. Rate} \ = K_1[2^\circ RX] \begin{bmatrix} \mathsf{\Theta} \\ OH \end{bmatrix} + K_2[2^\circ RX] \end{array}$$

Answer: C

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12. Refer to Q.No. 9 above and find out under what condition the reaction would follow SN^1 mechanism.

A. Low concentration of $\stackrel{\Theta}{OH}$

B. High concentration of OH

C. Low concentration of $2^{\,\circ}\,RX$

D. High concentration of $2^{\circ} RX$.

Answer: A

13. Refer to Q.No. 9 above and find out under what condition the reaction would follow SN^2 mechanism.

A. Low concentration of $\stackrel{\Theta}{OH}$

B. High concentration of OH

C. Low concentration of $2^{\,\circ}\,RX$

D. High concentration of $2^{\circ} RX$.

Answer: B



14. Which of the compound in each of the following pairs will react $$\Theta$$ faster in SN^2 reaction with OH

(A) MeBr(I) and MeI(II)



Answer: D

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15. Which statement is correct about the following reactions ?

$$Me \xrightarrow{Me} Br + MeO^{\textcircled{o}} \longrightarrow Product$$



D. None

Answer: A



16. Which statement is correct about the following reactions ?





A. Product is

B. Product is

by elimination reaction.



- C. Product is (II) by SN^1 reaction
- D. Both (a) and (b).

Answer: B



17. Which statement is correct about the following reactions ?





mechanism.

- C. Major product is (II) and minor product is (I) by SN^1 mechanism.
- D. Major product is (II) and minor product is (I) by SN^2 mechanism.

Answer: A



18. The decreasing order of dehydrohalogenation of the following compounds is :



A.
$$(I) > (II) > (III) > (IV)$$

B. $(IV) > (III) > (I) > (I)$
C. $(II) > (I) > (II) > (IV)$
D. $(IV) > (III) > (II) > (I)$

Answer: B

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19. The decreasing order of nucleophilicities of the following is :

- (I) $Br^{\,\Theta}$
- (II) MeO^{Θ}
- (III) Me_2N^{Θ}
- (IV) Me_3C^{Θ} .

$$\begin{array}{l} {\sf A.}\,(I)>(II)>(III)>(IV)\\\\ {\sf B.}\,(IV)>(III)>(II)>(I)\\\\ {\sf C.}\,(IV)>(III)>(I)>(I)>(II)\\\\ {\sf D.}\,(II)>(I)>(I)>(III)>(IV) \end{array}$$

Answer: B



20. The decreasing order of nucleophilicities of the following is :

(I) H_2O

(II)
$$EtOH$$

(III) $MeCOO^{\Theta}$
(IV) $\stackrel{\Theta}{OH}$
(V) EtO^{Θ} .
A. $(V) > (IV) > (III) > (II) > (I)$
B. $(I) > (II) > (III) > (IV) > (V)$
C. $(IV) > (V) > (III) > (II) > (I)$
D. $(I) > (II) > (III) > (V) > (IV)$

Answer: A

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21. The decreasing order of the basic character of the following is :

(V)

(I) F^{Θ}

(II) NO_3^{Θ}

(III) H_2O

(IV) CH_3OH .

A.
$$(II) > (I) > (IV) > (III)$$

B. $(III) > (IV) > (I) > (II)$
C. $(I) > (II) > (III) > (IV)$
D. $(IV) > (III) > (II) > (I)$

Answer: C

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22. The decreasing order of nucleophilicities in DMSO (dimethylsulphoxide) is :

A.
$$F^{\Theta} > Cl^{\Theta} > Br^{\Theta} > I^{\Theta}$$

B. $I^{\Theta} > Br^{\Theta} > Cl^{\Theta} > F^{\Theta}$
C. $F^{\Theta} > Cl^{\Theta} > I^{\Theta} > Br^{\Theta}$

$$\mathsf{D}.\,I^{\,\Theta} > Br^{\,\Theta} > F^{\,\Theta} > Cl^{\,\Theta}$$

Answer: A

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23. In which of the following reactions, SN^2 rate increases on changing the solvent from (95 % acetone + 5 % H_2O) to (80 % acetone + 20 % H_2O)?

A.
$$Me_2 - \stackrel{\oplus}{P} - Me + NH_3 \rightarrow Me \stackrel{\oplus}{N}H_3 + Me_2P$$

B. $MeI + PH_3 \rightarrow Me \stackrel{\oplus}{P}H_3 + I^{\Theta}$
C. $MeBr + \stackrel{\Theta}{O}H \rightarrow MeOH + Br^{\Theta}$
D. $Me_2 - \stackrel{\oplus}{S} - Me + \stackrel{\Theta}{O}H \rightarrow MeOH + Me_2S$

Answer: B

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24. In which of the following reactions, retention of configuration takes place ?



Answer: B

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25. Refer to Q.No. 24 and find out in which of the reactions the inversion of configuration takes place.

A. (I), (III) B. (I), (II) C. (III), (IV)

 $\mathsf{D}.\,(I),\,(IV)$

Answer: C

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26. Refer to Q. No.24 and find out which of the reactions proceeds by

 SN^i mechanism.

 $\mathsf{A.}\,(I),\,(III)$

 $\mathsf{B.}\,(I),\,(II)$

C.(III),(IV)

 $\mathsf{D}.\,(I),\,(IV)$

Answer: B

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27. Refer to Q.No. 24 and find out which of the following reactions proceeds by SN^2 mechanism.

A. (I), (III)

B.(I), (II)

C.(III),(IV)

 $\mathsf{D}_{\cdot}\left(I\right),\left(IV\right)$

Answer: C

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28. Necessary conditions for Fiels-Alder reactions are :

A.(I), (II), (III)

 $\mathsf{B.}\,(I),\,(II),\,(IV)$

C.(II),(III)

 $\mathsf{D}.\,(II),\,(IV)$

Answer: A

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29. Which of the following compounds would undergo Diels-Alder reaction with dienophile (e.g., Maleic anhydride) ?

A.
$$HC \equiv C - C \equiv CH$$

$$\mathbf{b}. \bigcirc \mathbf{C} \mathbf{H}_2$$



Answer: D



30. Which of the following reaction would undergo Diels-Alder reaction ?



A. All

 $\mathsf{B.}\,(II),\,(III),\,(IV)$

 $\mathsf{C.}\,(III),\,(IV)$

 $\mathsf{D.}\left(II\right)$

Answer: C

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31. The decressing order of reactivity towards SE (substitution by electrophile) of the following is :

(I) Nitrobenzene

(II) Chlorobenzene

(III) Toluene

(IV) Benzene.

 $\begin{array}{l} \mathsf{A.}\,(I)>(II)>(III)>(IV)\\\\ \mathsf{B.}\,(IV)>(III)>(II)>(I)\\\\ \mathsf{C.}\,(III)>(IV)>(II)>(I)\\\\ \mathsf{D.}\,(I)>(II)>(IV)>(IV)>(III) \end{array}$

Answer: C

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32. Which of the following is a free radical substitution reaction ?

A. Benzene +
$$Me-Cl \stackrel{ ext{Anhyd.}}{\longrightarrow} Ph-CH_3$$

B. ^{b.} Ph $Cl + AgNO_2 \rightarrow Ph$ NO_2

C. ^{c.} $Ph - CH_3 + Cl_2 \xrightarrow{hv} Ph \frown Cl$

D. d. $\stackrel{Me}{H} \rightarrow O + MeOH \xrightarrow{H^{\oplus}} H^{Me} \rightarrow H^{OMe}$

Answer: C





Reagent I and II, respectively, are :

A. $OsO_4 / NaHSO_3, MMPP / H_2O$

B. Cold alkaline $KMnO_4, OsO_4 \, / \, NaHSO_3$

C. $PhCO_{3}H/H_{2}O$, Cold alkaline $KMnO_{4}$

D. $MMPP/H_2O, HCO_3H/H_2O$

Answer: C





Which product is racemic in the above reaction ?

A. Product B

B. Product C

C. Both

D. None

Answer: C



35. Consider the following reactions.



Answer: D

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36. Which of the following is a non-aromatic compound ?









Answer: A



37. The decreasing order of reactivity towards ArSN reaction of the

following with NaOMe is :



A. (I) > (II) > (III) > (IV)B. (IV) > (III) > (II) > (I)C. (II) > (I) > (II) > (IV)D. (IV) > (III) > (I) > (II)

Answer: C

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38. Consider the following reaction :



The product is :

A. o-Toluidine

B. m-Toluidine

C. p-Toluidine

D. All

Answer: D

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39. Refer to Q.No. 38 and find out which of the following statements is wrong ?

A. The reaction is ArSN (addition-elimination reaction)

B. The reaction is ArSN (elimination-addition reaction) via

benzyne mechanism.

C. One product is obtained by direct substitution.

D. Two products are obtained by cine-substitution.

Answer: A

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40. Which of the following is not a rearrangement reaction ?

A. a.
$$Me \longrightarrow N \xrightarrow{OH} H^{\oplus}$$

A. b. $Me \longrightarrow O \xrightarrow{Mg/Hg} H_{2O}$



Answer: B

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41. Arrange the following in the reactions order of NA (nucleophilic

addition) reaction.

(I) MeCOMe

(II) PhCOMe

(III) PhCOPh

(IV) $PhCH_2COMe$.

 $\mathsf{A.}\left(I\right)>\left(II\right)>\left(III\right)>\left(IV\right)$

B.(IV) > (III) > (II) > (I)

 $\mathsf{C.}\left(IV\right)>(I)>(II)>(III)$

Answer: C

42. Arrange the following in the decreasing order of nucleophilic acyl substitution reaction.

$$\begin{array}{ccccc}
O & O & O \\
\parallel & \parallel & \parallel \\
(I) R - C - Cl & (II) R - C - O - C - R \\
O & \parallel \\
(III) R - C - OR & (IV) R - C - NH_2
\end{array}$$

A.
$$(I) > (II) > (III) > (IV)$$

B. $(IV) > (III) > (II) > (I)$

 $\mathsf{C}.\left(I\right)>\left(III\right)>\left(II\right)>\left(IV\right)$

$$\mathsf{D.}\left(IV\right)>(II)>(III)>(I)$$

Answer: A Watch Video Solution

43. Which of the following reactions will not give Hofmann alkene?



Answer: C



44. Which of the following is the best method for the preparation of compound cyclopentyl cyanide from cyclopentyl chloride ?

D. All

Answer: A



Which statement is correct about the above reaction ?

- A. Both products (B) and (C) are optically active.
- B. Both products (B) and (c) are optically inactive.
- C. Product (B) is optically inactive but product (c) is optically active.
- D. Product (B) is formed by anti-addition but product (c) is

formed by syn-addition of H_2 .

Answer: C

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46. An alkyl halide of formula $C_6H_{13}Br$ on treatment with potassium t-butoxide gives two isomeric alkenes dimethy butane. Isomeric alkene are :





Answer: A





(A) and (B) are :





D. None of these

Answer: B



48. Which of the following reactions would give trans-alkene?



 $\mathsf{A.}\left(I\right)$

B.(II)

 $\mathsf{C}.\,(I),\,(III)$

 $\mathsf{D}.\,(II),\,(IV)$

Answer: C

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49. Which of the following reactions is Hofmann elimination ?



 $\mathsf{B.}\,(I),\,(III)$

C.(II),(III)

 $\mathsf{D}.\,(II),\,(IV)$

Answer: D

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50. In which of the following α -elimination occurs ?



 $\mathsf{A.}\,(I),\,(II)$

 $\mathsf{B.}\,(I),\,(IV)$

 $\mathsf{C.}\,(II),\,(III)$

 $\mathsf{D}.\,(II),\,(IV)$

Answer: B

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Assertion Reasoning

1. 1° allylic halides are more reactive than $1^{\circ}RX$ in SN^1 reaction. Allylic carbocation intermediate is stabilished by resonance.

A. If both (A) and (R) are true, but (R) is the correct explanation

of (A)

B. If both (A) and (R) are true, but (R) is not the correct

explanation of (A).

C. If (A) is true but (R) is false.

D. If (A) is false but (R) is true.

Answer: A

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2. Walden inversion takes place in SN^2 reaction.

Half-life period of SN^2 reaction is inversely proportional to the concentration of the substrate or nucleophile or both.

A. If both (A) and (R) are true, but (R) is the correct explanation

of (A)

B. If both (A) and (R) are true, but (R) is not the correct

explanation of (A).

C. If (A) is true but (R) is false.

D. If (A) is false but (R) is true.

Answer: B

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3. Chlorination of allylic hydrogen is difficult than vinylic hydrogen.

Allyl radical is stabilished by resonance.

A. If both (A) and (R) are true, but (R) is the correct explanation

of (A)

B. If both (A) and (R) are true, but (R) is not the correct explanation of (A).

C. If (A) is true but (R) is false.

D. If (A) is false but (R) is true.

Answer: D



4. Heavy metal ions Ag^+ or Pb^{2+} decrease SN^1 reactivity. They aid ionisation of RX.

A. If both (A) and (R) are true, but (R) is the correct explanation of (A)

B. If both (A) and (R) are true, but (R) is not the correct

explanation of (A).

C. If (A) is true but (R) is false.

D. If (A) is false but (R) is true.

Answer: D

5. Crown ether acts as phase transfer catalysis and increases SN^2 reactivity.

They strongly complex cation and leave anion (nulceophile) with increased reactivity.

A. If both (A) and (R) are true, but (R) is the correct explanation

of (A)

B. If both (A) and (R) are true, but (R) is not the correct

explanation of (A).

C. If (A) is true but (R) is false.

D. If (A) is false but (R) is true.

Answer: A

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6. RS^{Θ} is a stronger nucleophile and a better leaving group than RO^{Θ} .

 RS^{Θ} is a weaker base than RS^{Θ} .

A. If both (A) and (R) are true, but (R) is the correct explanation of (A)

B. If both (A) and (R) are true, but (R) is not the correct

explanation of (A).

C. If (A) is true but (R) is false.

D. If (A) is false but (R) is true.

Answer: A





The product (B) results by SN^2 mechanism and product (c) results by SN^2 ' mechanism.

A. If both (A) and (R) are true, but (R) is the correct explanation

of (A)

B. If both (A) and (R) are true, but (R) is not the correct

explanation of (A).

C. If (A) is true but (R) is false.

D. If (A) is false but (R) is true.

Answer: A

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 $egin{aligned} & 60\,\%\, ext{actone} \ & +40\,\%\,H_2O \ & H_2O \ \end{pmatrix} MePH_3 & \stackrel{\oplus}{\longrightarrow} MePH_3 + I^{\,\Theta} \ & (II)Mel + PH_3 & \stackrel{H_2O}{\longrightarrow} MePH_3 + I^{\,\Theta} \end{aligned}$

Increase in solvent polarity stablilises the T. S., lowers E_{act} , and increases the rate.

A. If both (A) and (R) are true, but (R) is the correct explanation

of (A)

B. If both (A) and (R) are true, but (R) is not the correct

explanation of (A).

C. If (A) is true but (R) is false.

D. If (A) is false but (R) is true.

Answer: A

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9. ElcB` reaction is favoured by stabilisation of carbanion and poor leaving group.

The reaction is kinetically of the second order and unimolecular.

A. If both (A) and (R) are true, but (R) is the correct explanation

of (A)

B. If both (A) and (R) are true, but (R) is not the correct

explanation of (A).

C. If (A) is true but (R) is false.

D. If (A) is false but (R) is true.

Answer: B





machanism is fast.

Carocation is stabilised by resonance.

A. If both (A) and (R) are true, but (R) is the correct explanation

of (A)

B. If both (A) and (R) are true, but (R) is not the correct

explanation of (A).

C. If (A) is true but (R) is false.

D. If (A) is false but (R) is true.

Answer: A

11. Phenol is more reactive than benzene towards electrophilic substitution reaction.

In case of Phenol, the intermediate carbocation is more resonance stabilised.

A. Statement I is true, Statement II is true , Statement II is the

correct explanation of Statement I.

B. Statement I is true , Statement II is true , Statement II is not

the correct explanation of Statement I

- C. Statement I is true , Statement II is false.
- D. Statement I is false , Statement II is true.

Answer: A



12. Addition of bromine to trans-2-butene yields meso-2,3dibromobutane.

Bromine addition is an electrophilic addition.

A. Statement I is true, Statement II is true , Statement II is the

correct explanation of Statement I.

B. Statement I is true , Statement II is true , Statement II is not

the correct explanation of Statement I

C. Statement I is true, Statement II is false.

D. Statement I is false , Statement II is true.

Answer: B

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1. The formation of cyanohydrin from ketone is an example of :

A. Electrophilic addtion

B. Nucleophilic addtion

C. Nucleophilic substitution

D. Electrophilic substitution

Answer: B

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2. Which of the following has the highest nucleophilicity ?

A. F^{Θ} B. OHC. CH_3 Θ

D. NH_2

Answer: C



3. As S_{N^2} reaction at an asymmetric carbon of a compound always gives:

A. An enantiomer of the substrate

B. A product with opposite optical rotation

C. A mixture of diastereomers

D. A single stereoisomer.

Answer: B


4. Identify the correct of reactivity in electrophilic substitution reaction of the following compounds.

(1) Benzene

(2) Toluene

(3) Chlorobenzene,

(4) Nitrobenzene.

A. (1) > (2) > (3) > (4)B. (4) > (3) > (2) > (1)C. (2) > (1) > (3) > (4)D. (2) > (3) > (1) > (4)

Answer: C

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5. 4-Methyl benzene sulphoic acid reacts with sodium acetate to give :





Β.



C.



Answer: A



6. The number of stereoisomers obtained by bromination of trans-2-

butene is :

A. 1 B. 2 C. 3 D. 4

Answer: A

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7. The order of leaving group ability is :

A.
$$(i) > (ii) > (iii) > (iv)$$

$$\texttt{B.}\,(iv)>(iii)>(i)>(ii)$$

 $\mathsf{C.}\left(iii\right)>(ii)>(i)>(iv)$

$${\sf D}.\,(ii)>(iii)>(iv)>(i)$$

Answer: B



8. During debromination of meso-dibromobutane, the major compound formed is :

A. n-Butane

B. 1-Butene

C. cis-2-Butane

D. trans-2-Butene

Answer: D

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1. Lodide is a better nucleophile than bromide.

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|--|
| |
| 2. During SN^1 reactions, the leaving group leaves the molecule |
| before the incoming group is attached to the molecule. |

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Analytical And Descriptive

1. Draw the stereochemical structures of the products in the following

reactions.



2. Write down the structure of the stereoisomers formed when cis-2-

butene is treated with bromine.

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3. Optically active 2-iodo burtane on treatment with NaI in acetone

gives a product which does not show optical activity. Explain briefly.

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6. Among the following, the total number of compound soluble in aqueous NaOH is :

