

Old bonds

New bonds

A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism. Reactants are of two types substrate and reagent.

Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent. If both reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called substrate.

3.0 CONCEPTS TO UNDERSTAND REACTION MECHANISM :

(1) Bond cleavage (2) Attacking reagent (3) Reaction intermediate (4) Electronic effect

3.1 TYPE OF BOND CLEAVAGE :

(a) Heterolytical cleavage/fission : Cleavage in which unequal distribution of electrons takes place during the bond cleavage is known as heterolytical cleavage. Due to unequal distribution of electrons, ions are formed. That's why it is also known as ionic cleavage or heterolytical cleavage.

(b) Homolytical cleavage/fission : Cleavage in which equal distribution of e-s takes place during the chemical reaction, is known as homolytical cleavage.

Due to equal distribution of electrons, without charge unpaired electron containing species are formed, which are known as free radicals and cleavage is known as unionic cleavage/homolytical fission.



3.2 TYPES OF ATTACKING REAGENTS

These are of two types :

(a) Electrophilic reagent or electrophiles: Electrophilic (electro + philic)

(electron + loving)

The reagent which attacks on the negative part of the molecule or having attraction for electrons are called electrophiles.

Electrophiles may be positively charged or neutral.

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(i)	Positively charged electrophiles : $\stackrel{\oplus}{H} \stackrel{\oplus}{SO_3}H \stackrel{\oplus}{NO_1} \stackrel{\oplus}{NO_2} \stackrel{\oplus}{X} \stackrel{\oplus}{R} R - \stackrel{\oplus}{C_6} H_5 - \stackrel{\oplus}{N_2}$			
(ii)	Neutral electrophiles :- central atom e ⁻ deficient			
	(a) All Lewis acids as :			
	BF ₃ , A1Cl ₃ , SO ₃ , ZnCl ₂ , BeCl ₂ , FeCl ₃ , SnCl ₂ , CO ₂ , SnC ₁₄ .			
	(b) Free radicals, carbenes and nitrenes act as electrophiles			
(b)	Nucleophilic reagent or nucleophiles.			
	Which attacks on the positive site of the substrate or loves nucleus or having attraction			
	towards nucleus.			
	Nucleophilic (Nucleo + philes)			
	\downarrow			
	(Nucleus + loving)			
	Nucleophiles may be negatively charged ions or posses a lone pair of electron or πe^{-1} .			
(i)	Negatively charged nucleophiles.			
	$H, OH, OR, CN, X, R, R - COO, NH_2, SH$			
(ii)	All Lewis base which contains lone pairs or πe^{-1} .			
	HOPOHRORNH R NH CH-CH CH-CH			
	$\Pi_2 \cup K = \bigcup_{i=1}^{n} K = \bigcup_{i=1}^{n} K$, $\Pi_1 = \bigcup_{i=1}^{n} (\Pi_1 = $			
(:::)				
(111)	$K - Mg - \Lambda$, LIAI Π_4 , Nad Π_4			

The star (*) indicates the atom which donates electrons to the substrate.

Ambident nucleophile :- Nucleophiles which have two sites of electron rich centre or in which two or more atoms bear a lone pair of electrons.

Examples :- $K^{\oplus\Theta}O-N=O$, NH_2-OH , NaCN

3.3 REACTION INTERMEDIATE

Carbocation :

Cation in which positive charge is present on carbon atom is called carbocation.

- Due to electron deficiency it acts as an electrophile and always attack on electron richer site.
- It is incomplete octet species because it has six electron in outer most shell.
- All electrons are paired.

Carbanions : Anion in which negative charge is present on carbon atom is called carbanion.

- It has eight electron in outermost shell so it is complete octet species.
- It is an electron richer species because it has extra electron.
- Due to presence of non bonding electrons it acts as a nucleophile.

Free Radical :

• Electrically neutral species in which unpaired electron is present on carbon atom is known as carbon free radical.

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	• It has seven electron or odd electron in outermost shell of unpaired electron containing carbon.								
	• It is electron deficient species due to incomplete octet.								
	Cl Ca Carber atoms	rbenes (CH₂:): nes are neutral or groups and o It behaves as a It is neutral.	carbon species carries two non an electrophile.	s in whi bonded	ich the electror	carbon atom 1s. 6 e ⁻ in oute 4 e ⁻ are boi	n is bonded ermost shell. nded and two	to two monov o are non bonde	alent d e⁻.
	Cl Nit Nitren or grou	renes (– N :) es are neutral r up and carries f It is monovale It is neutral.	nitrogen species our non-bonded ent radical.	s in whi l electro	ich the n ons. 6 e [−] in Two ar	nitrogen is b outermost s re bonded ar	bonded to or hell nd four are no	ne monovalent a	atom rons.
			BEC	GINNE	R'S BO	X-1			
1.	Which (1) NH	of the followin I ₂ OH	ng is ambident i $(2) \operatorname{NCO}^{\Theta}$	nucleop	hile :- (3) NO	02	(4) All o	f these	
2.	CH ₃ C	H ₂ -Cl undergoe	es homolytic fis	sion to	produce	e:-			
	(1) CH	$\mathbf{H}_{3}\mathbf{\dot{C}H}_{2}$ and $\mathbf{\dot{C}l}$			(2) CH	${}_{3}\dot{\mathbf{CH}}_{2}$ and (C ⁰		
	(3) CH	$H_3 \overset{\oplus}{C} H_2$ and Cl^{\oplus})		(4) CH	$^{\odot}_{3}$ $^{\odot}_{CH_{2}}$ and (Cl⊕		
3.	Which (1) Ca	of the followin rbocation	ng intermediate (2) Carbanion	has cor	nplete o (3) Fre	octet:- e radical	(4) Carb	ene	
3.4	ELEC There (1) Inc (3) Hy	CTRONIC EFF are four effects luctive effect perconjugation	FECTS : which affect th	ne chem	ical rea (2) Me (4) Ele	ction due to someric effe ctromeric ef	transfer of e ect ffect	lectron	
3.4.1	INDU	CTIVE EFFE	CT (I-EFFEC	Г):					

Polarity induced in non polar a bond due presence of adjacent polar bond is known as indt.ctive effect.

GOLDEN KEY POINTS

- In I-effect there is partial displacement of e^{Θ} . •
- After 3 or 4 C-atom I-effect is considered to be zero. •
- Inductive effect decreases on increasing distance. •

So Maginitude of I effect $\propto \frac{1}{\text{distance}}$

I-effect of hydrogen is considered as zero. •

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–I groups $-OH > -OR > -C \equiv CH > -NH_2 > Ph > -CH = CH_2 > H(I \approx O)$ —X > +I groups $\begin{array}{c} \overset{\Theta}{-\mathrm{NH}} > -\overset{\Theta}{\mathrm{O}} > -\mathrm{COO}^{\Theta} > \overset{I}{-\mathrm{CH}} -\mathrm{CH}_{3} > -\mathrm{CH}_{-\mathrm{CH}_{3}} > -\mathrm{CH}_{2} -\mathrm{CH}_{3} > -\mathrm{CH}_{3} \\ \overset{I}{-\mathrm{CH}_{3}} \qquad \overset{I}{-\mathrm{CH}_{3}} > -\mathrm{CH}_{3} > -\mathrm{CH}_{3} > -\mathrm{CH}_{3} > -\mathrm{CH}_{3} > -\mathrm{CH}_{3} \\ \end{array}$ $-CD_{a} > -CH_{a} > T > D > H(I \approx O)$ **APPLICATION OF I-EFFECT** (1) **Stability of carbocation :** Energy \propto charge $\propto \frac{1}{\text{stability}}$ Stability of carbocation $\propto \frac{+\text{Ieffect}}{-\text{Ieffect}}$ Stability order : (1) $CH_3 \rightarrow C_4 \rightarrow$ **Example :** Reason : More no. of +I group. more stable carbocation. so stability order 1 > 2 > 3 > 4. (2) **Stability of carbanion :** Stability of Carbanion $\propto \frac{-\text{Ieffect}}{+\text{Ieffect}}$ Example: (1) $CH_3 - C_{I_3} = C_{I$ More No. of +I group. Less stable carbanion. So stability order 4 > 3 > 2 > 1Example: (1) $\overset{\Theta}{CH_2}$ - CH--CH₂--CH₃ (2) $\overset{\Theta}{CH_2}$ - CH₂--CH₂--CH₃ (3) $\overset{\Theta}{CH_2}$ - CH₂--CH Minimum distance of –F. Maximum –I of –F.

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	Basic strength ∞ + I effec	$t \propto \frac{1}{-I \text{ effect}}$				
	Ex.: (1) CH_3NH_2 (2) C	$C_2H_5NH_2$	(3)	C ₃ H ₇ NH ₂	$(4) C_4 H_9 N H_2$	
	Ans. 4 > 3 > 2 > 1	Maxim	num +I			
		so max	kimum b	asic		
		BEGINNE	R'S BO	X-3		
1.	Which of the following is r	most acidic :				
	(1) Cl_3C -COOH (2) C	Cl ₂ CH–COOH	(3) ClC	COOH	(4) CH_3COOH	ł
2.	Which of the following is r	most acidic :				
	(1) $CH_2 - COOH$		(2) CH	$_2 - COOH$		
	Ė		Cl			
	$(3) \operatorname{CH}_2 - \operatorname{COOH}$		(4) CH	$_2 - COOH$		
	Br		i			
3	Which is most basic among	g the following :				
5.	(1) CH_2CH_2 -NH ₂	g the following .	$(2) Cl_{-}$	CH ₂ CH ₂ NH ₂		
	$(3) O_2N-CH_2CH_2-NH_2$		(2) - 0 - (4) - (4) - 0 - (4) - (4	CH ₂ CH ₂ CH ₂ -NH	[2	
					-2	

3.4.2 RESONANCE OR MESOMEIDC EFFECT

Delocalization of πe^- is called as resonance or complete transfer of πe^- from one shell to another shell is called as **Resonance**.

Conditions For Resonance

(1) If there are two π bonds in conjugation then e^- of one π bond are transferred towards another π bond.

Ex. (i)
$$CH_2 = CH + CH = CH_2 \leftrightarrow CH_2 - CH = CH - CH_2 \leftrightarrow CH_2 - CH = CH - CH_2 \leftrightarrow CH_2 - CH = CH - CH_2$$

(i) $CH_2 = CH + C - H \leftrightarrow CH_2 - CH = C - H$
(ii) $CH_2 = CH + C - H \leftrightarrow CH_2 - CH = C - H$
 O^{0}

(2) If there is lone pair or a negative charge and n bond are in conjugation the lone pair of e⁻ or negative charge are transferred towards n bond.

Ex. (i)
$$CH_2 = CH \xrightarrow{\oplus} OH \longleftrightarrow OH_2 - CH \xrightarrow{\oplus} OH$$

ii)
$$CH_2 = CH \stackrel{\frown}{-} CH_2 \longleftrightarrow OH_2 - CH = CH_2$$

(3) If there is positive charge (vacant orbital) and 1t bond are in conjugation then e- of 1t bond are transferred towards positive charge.

Ex.
$$CH_2 = CH - CH_2 \longleftrightarrow CH_2 - CH = CH_2$$

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(4) If there is free e^- and π bond are in conjugation.

Ex.
$$CH_2 \xrightarrow{\ell} CH \xrightarrow{\ell} \dot{C}H_2 \longleftrightarrow \dot{C}H_2 \longrightarrow \dot{C}H_2 - CH = CH_2$$

(5) If there is lone pair or negative charge and positive charge (vacant orbital) are in conjugation then e⁻ of lone pair or negative charge are transferred towards positive charge.

Ex.
$$\overset{\oplus}{\operatorname{CH}}_2 \xrightarrow{\bullet} \overset{\oplus}{\operatorname{OH}} \longleftrightarrow \operatorname{CH}_2 \xrightarrow{\oplus} \overset{\oplus}{\operatorname{OH}}$$

GOLDEN KEY POINTS

- In resonance only e⁻ are delocalised not atoms.
- The number of e⁻ or number of unpaired or paired e⁻ in all resonating structures should be same.
- It is permanent effect.
- All the resonating or canonical structures must follow the Lewis structures

Draw resonating structures :



- **M-effect :** Delocalisation of electron in conjugated system (due to presence of EWG or EDG) is known as 'M' effect.
- (1) +M effect :- Group that donates the electron pair to conjugated system is known as +M effect exerting groups and the phenomena is known as +M effect.

(2) -M effect :- Group, that withdraws electron pair from the conjugated system, is known as -M effect exerting groups and the phenomena is known as -M effect.

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(negative charge on more EN) (negative charge on less EN)

(5) Aromaticity (Huckel's rule) : Cyclic, planar and completely conjugated system with $(4n+2)\pi$ electrons (where n = 0, 1, 2, 3, ...) is known as aromatic compounds, these compound gains extra stability which is known as aromaticity.

Note : $[4n + 2]\pi$ electrons. (Odd number of 1t electron pairs) means

n = 0	2π electrons	or 1 pair
n = 1	6π electrons	or 3 pairs
n = 2	10 π electrons	or 5 pairs
n = 3	14π electrons	or 7 pairs

If

S.No	Compound	Cyclic	Plannar	Cyclic	Huckel	Aromatice
				Resonance	Rule	Yes/No
					(4n+2) πe ⁻	
1.	$\overset{\oplus}{\sim}$	\checkmark	~	~	2πe ⁻	Yes
2.		~	×	\checkmark	4πe ⁻	No
3.	(I)	~	× ·	~	4πe ⁻	No
4.	Î.	✓	~	V	6πе ⁻	Yes
5.		~	~		6πe ⁻	Yes
6.		~	×	×	$4\pi e^{-}$	No
7.	•		~	✓	6πе ⁻	Yes
8.	ÿ		\checkmark	~	6πe ⁻	Yes
9.	ÿ	\checkmark	\checkmark	\checkmark	6πe ⁻	Yes
10.	N H	✓	✓	\checkmark	6πe ⁻	Yes
11.		✓	~	\checkmark	6πе ⁻	Yes

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12.		\checkmark	~	~	10πe ⁻	Yes
13.		~	✓	\checkmark	14πe ⁻	Yes
14.	°Z	~	~	\checkmark	6πe ⁻	Yes
15.	°	~	×	×	6πе ⁻	No
16.	$\bigcirc - \bigcirc$	~	\checkmark	\checkmark	бπе ⁻ + 6πе ⁻	Yes

BEGINNER'S BOX-4

- Which of the following is nonaromatic 1.
 - (1)(3)
- 2. Which 'of the following compounds are aromatic in nature
 - $\ddot{N}H_2$ (c) (d) (a) (3) a,b, d (1) only a (2) a and b (4) all of these
- 3. Which of the following is. not aromatic compound



(Acidic strength \propto stability of conjugate base (anion) $\propto \frac{-M, -I}{N}$) Acidic strength: **(a)**

$$\frac{1}{M} \propto \frac{1}{+M,+I}$$

Illustrations

Illustration 1. Carboxylic acids are more acidic than phenols, why?

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Solution.

2, equal R.S. more stable anion so corresponding acid is more acidic. Here, carboxylate ion is more stable than phenoxide ion.



5, unequal R.S. less stable anion since –ve charge is being shared by oxygen is less electronegative carbon.

Note: The molecule having equivalent R.S. has more stability than the molecule having non equivalent R.S.

Illustration	2. Phenol is more acidic the	han alcohols why?		
	Ph-OH		R—OH	
Solution.	$\downarrow -H^{\oplus}$ PhO ^{\oplus} (Phenoxide ion)		H^{\oplus} R $-O^{\oplus}$ (Alko	oxide ion)
	anion stable by resonan	ice	no resonanc	e.
	So, corresponding acid	is more acidic	less stable a	nion

(b) **Basic strength order :-**Tendency to donate the electron pair by an atom or group is known as its basic strength. Compounds in which electron pair is delocalised will be less basic while, Those in which electron pair is localised will be more basic.

(Basic strength $\propto H^{\oplus}$ accepting tendancy $\propto l.p.$ donating tendency $\propto \frac{+M, +I}{-M, -I}$)

Ex. Give basic strength order :





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Reason : Due to intramolecular H-bonding in ortho nitrophenol, it is less acidic than para nitrophenol.





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(3) 3

(4) All are equally basic

3. Which is strongest base ?

2

(1) pyrole

(1) 2

(2) Aniline

(2) 2

(3) Pyridine

Î

4. Which is weakest base :

(1) C₆H₅--CH₂--NH₂

 $(3) O_2 N - CH_2 - NH_2$

 $(2) C_6H_5-CH_2-NH-CH_3$ $(4) CH_3-NH-CHO$

3.4.3 HYPERCONJUGATION EFFECT (H-EFFECT)

Complete transfer of e^- of C–H σ bond towards π bond or positive charge or free electron is called as H-effect (permanent effect). It is also called as No bond resonance (given by Nathen and Baker).

CONDITIONS OF H-EFFECT :

1. If there is C-H σ bond and positive charge are in conjugation Carbon which is attached to positively charged carbon is called as α -C and H which is attached to α -C is called as α -H. So if number of α -H are more, then there will be more number of hyperconjugating structures, so more stable will be the carbocation.

$$H \xrightarrow{\alpha} C \xrightarrow{\oplus} CH_{2} \longleftrightarrow H \xrightarrow{-C} CH_{2} \longleftrightarrow H \xrightarrow{-C} CH_{2} \longleftrightarrow H \xrightarrow{-H} C \xrightarrow{-C} CH_{2} \longleftrightarrow H^{\oplus} C \xrightarrow{-C} CH_{2} \longleftrightarrow CH_{2} \longleftrightarrow CH_{2} \longleftrightarrow CH_{2} \longleftrightarrow CH_{2} \longleftrightarrow CH_{2} \bigoplus CH_{2}$$

all are called as hyperconjugating structures or canonical structures.

2. If there is C–H σ bond and free e⁻ are in conjugation then there will be H-effect. Carbon, which is attached to C having unpaired e⁻, is called as α –C and H which are attached to α –C are called as α –H.



3. If there is C–H σ bond and π bond are in conjugation then there will be H-effect. sp³ carbon which is attached to double bonded C is called as α –C and H attached to α –C is called as α –H.

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Note : If there is C-H σ bond and negative charge in conjugation then there will be no Heffect.



no shifting of C–H σ bond, because anion is having complete octet (8e⁻)

APPUCATION OF H-EFFECT Stability of carbocation / Free Radical / Alkene

Stability oc No. of canonical structures \propto No. of α H. **Example :** Give stability order for :



 $R-CH=CH_2 + H_2 \longrightarrow R-CH_2-CH_3 + \Delta H$ (Heat of hydrogenation) Heat evolved when any unsaturated hydrocarbon is hydrogenated is called heat of hydrogenation (Δ H)

(If alkene is more reactive towards hydrogen then it will evolve more ΔH)

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	So, Heat of hydrogenation $\propto \frac{1}{\text{stabil}}$	$\frac{1}{\text{lity of alkene}} \propto \frac{1}{\text{number of}}$	$f \alpha - H$						
	BEGI	NNER'S BOX-6							
1.	Which of the following alkene is most	stable ($R = CH_3$).							
	(1) $R_2C=CR_2$ (2) $R-CH=CR_2$	(3) R-CH=CH-R	$(4) R-CH=CH_2$						
2.	Which of the following has minimum l	heat of hydrogenation~							
	(1) ethane (2) Propene	(3) cis-2-butene	(4) trans-2-butene						
3.	 Which of the following is most stable. (1) Conjugated alkadiene (CH₂=CH–CH=CH₂) (2) Isolated alkadiene (CH₂=CH–CH₂–CH=CH₂) (3) Cumulated alkadiene (CH₂=C=CH₂) (4) All are equal. 								
4.	What is the order of acidic strangth of OH OH OH $OH(I) OH CH_3 (II) OH CH_3(1)$ $I > II > III > IV(2)$ $IV > II > III > II > I$	given molecules OH OH OH OH OH OH OH OH							

3.4.4 ELECTROMERIC EFFECT : (E Effect)

Complete transfer of a shared pair of π -electrons from one atom to another atom in presence of attacking reagent, is known as 'E' effect.

(i) **Positive Eelctromeric Effect** (+ **E effect**) : In this effect the π -electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :



(ii) **Negative Electrometric Effect** (-**E effect**) : In this effect the 1t- electrons of the multiple bond are transferred to that atom, to which the attacking reagent does not get attached. For example.



Shifting of π electrons :

(i)
$$CH_{2} \stackrel{\text{reagent}}{\longrightarrow} \stackrel{\oplus}{C}H_{2} \stackrel{\oplus}{\longrightarrow} \stackrel{\oplus}{C}H_{2}$$

(ii) $CH_{3} - CH \stackrel{\oplus}{=} CH_{2} \stackrel{\text{reagent}}{\longrightarrow} CH_{3} - \stackrel{\oplus}{C}H \stackrel{\oplus}{\longrightarrow} \stackrel{\oplus}{C}H_{2}$
(iii) $CH_{3} - \underset{(b)}{C} \stackrel{\oplus}{=} C - CH_{3} \stackrel{\text{reagent}}{\longrightarrow} CH_{3} - \stackrel{\oplus}{C} \stackrel{\oplus}{=} \stackrel{\oplus}{C} - CH_{3}$ or $CH_{3} - \stackrel{\oplus}{C} \stackrel{\oplus}{=} \stackrel{\oplus}{C} - CH_{3}$
(iv) $CCl_{3} - CH \stackrel{\oplus}{=} CH_{2} \stackrel{\text{reagent}}{\longrightarrow} CCl_{3} - \stackrel{\oplus}{C}H - \stackrel{\oplus}{C}H_{2}$
 $-I$

3.5 TAUTOMERISM OR DESMOTROPISM

- Tautomers have same molecular formula but different structural formula due to migration of active hydrogen from one polyvalent atom to another polyvalent atom. This pnenomena is known as tautomerism.
- Desmotropism means bond turning. [Desmos = Bond ; Tropos =Turn]

$$\begin{array}{c} CH_{2} - C - H \\ H \\ H \\ O \\ \alpha - Hydrogen \text{ or active } H \end{array} \alpha - H \text{ of carbonyl compound is active } H \\ \hline H \\ \mathbf{Ex.} \qquad H - C - C - H \\ H \\ H \\ O \\ \mathbf{C} - C - C - H \\ H \\ H \\ O \\ \mathbf{C} - H \\ \mathbf{C} \\ \mathbf{C} - C - H \\ \mathbf{H} \\ \mathbf{C} \\ \mathbf{C}$$

- (I) Condition for Tautomerism :
- (a) For carbonyl compounds:- Carbonyl compounds having at least one active-H (α -H) show tautomerism

(i)
$$CH_3 - C - H$$
 3 α H, shows tautomerism.
(ii) $CH_3 - C - CH_3$ 6 α H, shows tautomerism
 0

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(c) H-C=N and $H-N \rightarrow C$ are tautomers [also Functional isomers] while R-C=N and $R-N \rightarrow C$ are only Functional isomers.

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H–C≡N $\frac{1}{2}$ † C \leq N–H Active H

(d)
$$H = N_{N}^{O}$$
 and $H = O = N = O$ are toutomers.

Õ

Note : Nitro compounds with at least one a-H are soluble in NaOH.

GOLDEN KEY POINTS

- More active the H, more will be its participation in tautomerism.
- Stability of enol form depends on (i) Resonance and (ii) H Bond (iii) Aromaticity.

BEGINNER'S BOX-7

1. Which of the following does not show keto enol tautomerism.



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4. In which of the following reaction most stable enol is present.





ANSWER KEY										
				BEGIN	NER'S I	BOX-1				
1	(4)	2	(1)	3	(2)	DOA-1			/	
1.	(+)	4.	(1)	5.	(2)					
				REGIN	JFR'S I	ROX-2				
1	(1)	2	(1)	DEGIN		DOA-2	_			
1.	(1)	2.	(1)							
				BEGIN	NER'S I	BOX-3				
1	(1)	2	(1)	3	(4)					
1.	(1)	4.	(1)	DECINI						
	4 1	-		DEGIN	IEN SI	DUA-4				
1.	(4)	2.	(4)	3.	(3)					
				BEGINN	NER'S I	BOX-5				
1.	(3)	2.	(2)	3.	(4)		4.	(4)		
					. ,					
	BEGINNER'S BOX-6									
1.	(1)	2.	(4)	3.	(1)		4.	(3)		
BEGINNER'S BOX-7										
1.	(3)	2.	(3)	3.	(4)		4.	(4)		