CHAPTER

16

Hyperconjugation

HYPERCONJUGATION

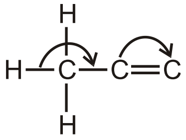
Hyperconjugation involves delocalisation of electrons through overlapping of '*p*' orbitals of a double bond and orbital of the adjacent single bond (conjugation). The structures are called ***hyperconjugative structures***. Since there is no bond between C and H , it is also called ***no bond resonance***. The free proton here is quite firmly bound to the electron cloud and is not free to move.

It is also evident that hyperconjugation occurs through H — atoms present on the carbon next to the double bond, that is, -hydrogen atoms. Naturally, the larger the number of such hydrogen, the more the hyperconjugative structures and greater the hyperconjugation effect. Thus, the order of this effect is

$$CH_3— \quad CH_3—CH_2— \quad (CH_3)_2CH— \quad (CH_3)_3C—$$

When (C — H) sigma electrons are in conjugation to pi bond, this conjugation is known as (C — H), conjugation, No bond resonance or -bond resonance or hyperconjugatioon.

BAKER-NATHAN EFFECT (1935)



As we have seen, the general inductive effect of alkyl groups is $Me_3C \quad Me_2CH \quad MeCH_2 \quad Me$. This inductive order has been used satisfactorily to explain various physical data, etc. In some reactions, however, the inductive order is reversed, the -electrons of the H — C bond become less localised by entering into partial conjugation with the attached unsaturated system. *i.e.,* , -conjugation :

Structural requirement for hyperconjugation :

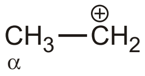
(A) Compound should have at least one sp^2-hybrid carbon of either alkene, alkyl carbocation or alkyl free radical.

(B) -carbon with respect to sp^2 hybrid carbon should have at least one hydrogen.

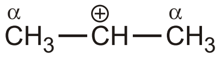
If both these conditions are fulfilled then hyperconjugation will take place in the molecule.

Hyperconjugation is of three types :

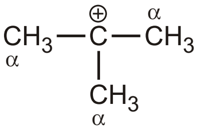
(i) (C — H), positive charge conjugation : This type of conjugation occurs in alkyl carbocation.



$\underset{\alpha}{CH_3}-\overset{\oplus}{C}H_2$



$\overset{\alpha}{CH_3}-\overset{\oplus}{CH}-\overset{\alpha}{CH_3}$



$\underset{\alpha}{CH_3}-\overset{\oplus}{\underset{\underset{\alpha}{CH_3}}{C}}-\overset{\alpha}{CH_3}$

Sigma Bonding + Empty *p*-orbital

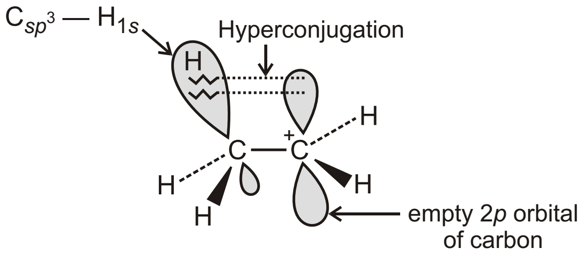
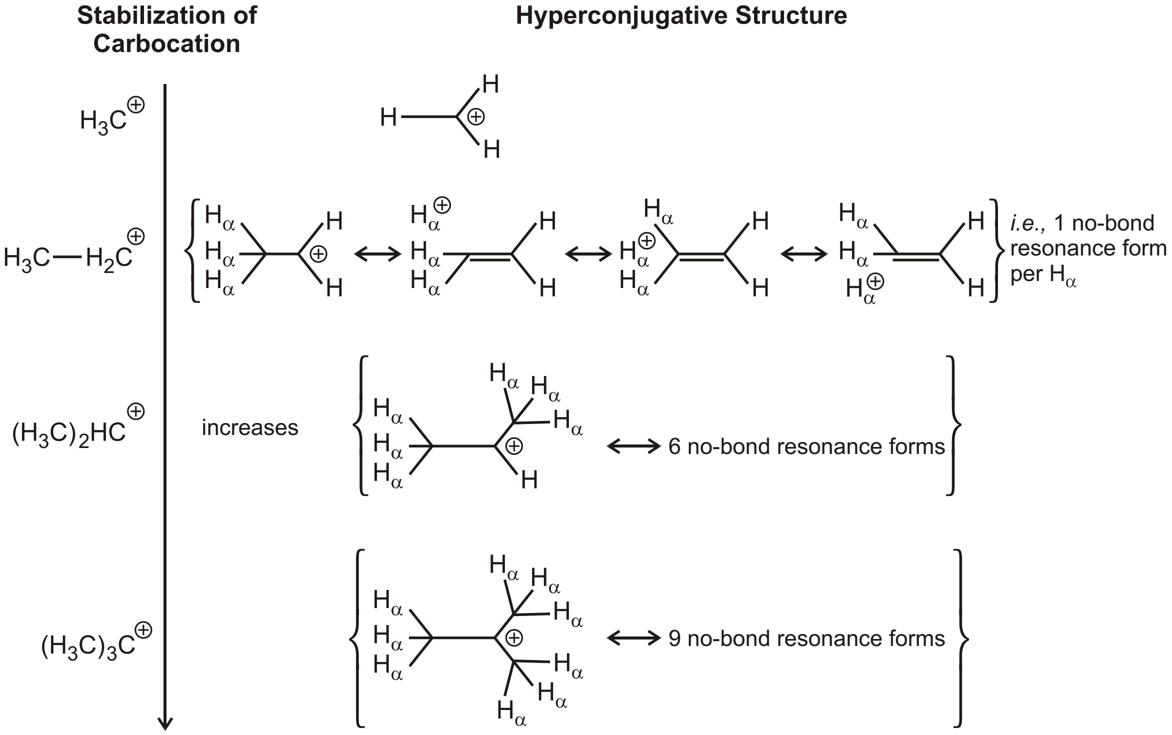
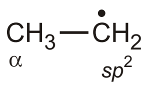


Figure : Orbital diagram showing hyper conjugation in ethyl cation

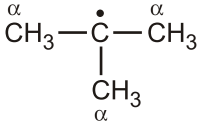
Table : Stabilization of Trivalent Carbenium Ion Centers by Methyl Substituents : Experimental Findings and Their Explanation by Means of no-bond Resonance Theory



(ii) (C — H), odd electron conjugation : This type of conjugation occurs in alkyl free radicals -



$\underset{\alpha}{CH_3}-\underset{sp^2}{\overset{\bullet}{C}H_2}$

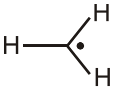
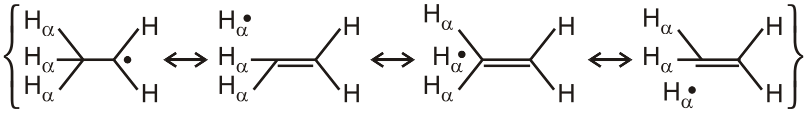
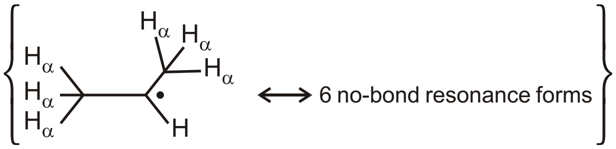
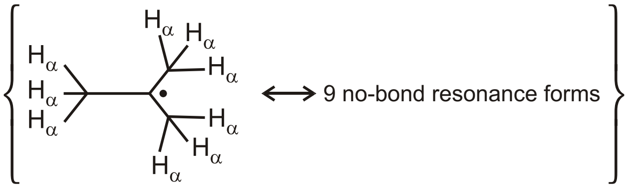


$\overset{\alpha}{CH_3}-\overset{\bullet}{\underset{\underset{\alpha}{CH_3}}{C}}-\overset{\alpha}{CH_3}$

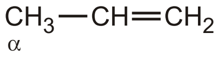
Figure : Some substrantes and products of radical substitution reactions

A primary radical is 6 kcal/mol more stable, a secondary radical is 9 kcal/mol more stable, and a tertiary radical is 12 kcal/mol more stable than the methyl radical.

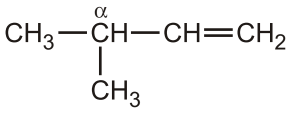
Table : Stabilization of Radicals by Alkyl Substituents

	DE kcal/mol	**Hyperconjugative structure formulation of the radical R**
H_3C-H	104	
H_3C-H_2C-H	98	 *i.e.,* 1 no-bond resonance form per H
$(H_3C)_2HC-H$	95	
$(H_3C)_3C-H$	92	

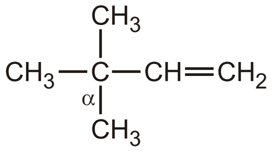
(iii) (C — H), conjugation : This type of conjugation occurs in alkenes.



$\underset{\alpha}{CH_3}-CH=CH_2$



$CH_3-\overset{\alpha}{\underset{CH_3}{CH}}-CH=CH_2$



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2$

Resonating structures due to hyperconjugation may be written involving "no bond" between the alpha carbon and hydrogen atoms.

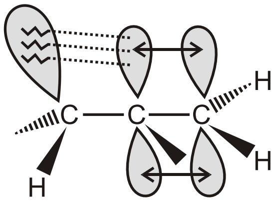
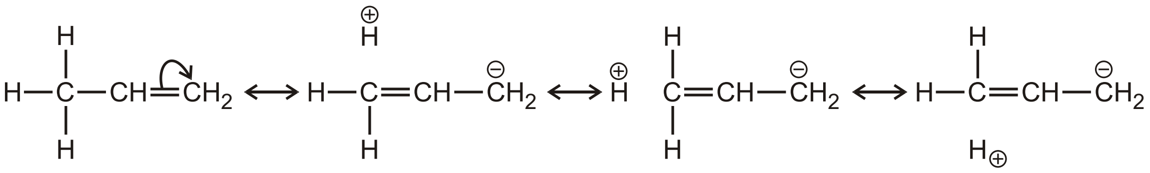


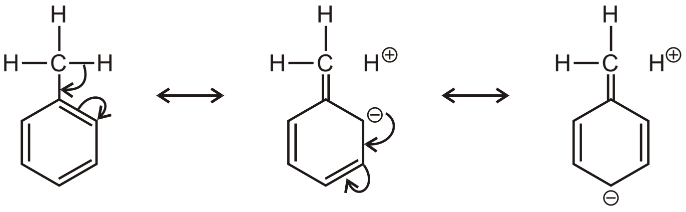
Figure : Orbital diagram showing hyper conjugation in propene

sigma-bond of (C — H) will delocalised in antibonding molecular orbital of -bond (*).

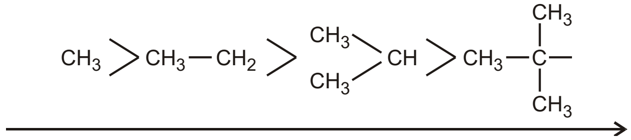


In the above resonating structures there is no covalent bond between carbon and hydrogen. From this point of view, hyperconjugation may be regarded as **"no bond resonance"**.

(C) Electron releasing (or donating) power of R in alkyl benzene : CH_3 — (or alkyl group) is +H group, ortho-para directing group and activating group for electrophilic aromatic substitution reaction because of the hyperconjugation.



- ⋆ The electron donating power of alkyl group will depends on the number of resonating structures, this depends on the number of hydrogens present on -carbon. The electron releasing power of some groups are as follows -



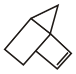
$$CH_3 > CH_3-CH_2 > \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CH > CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}- \longrightarrow$$

Electron donating power in decreasing order due to the hyperconjugation

- ⋆ Thus there is conjugation between electrons of single and those of multiple bonds. This type of conjugation is known as hyperconjugation, and is a permanent effect (this name was given by Mulliken, 1941).

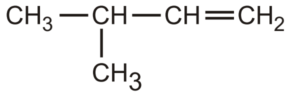
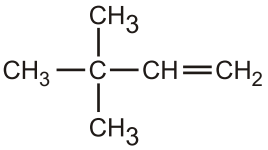
BREDT'S RULE

''Bredt's Rule is an empirical observation in organic chemistry that states that a double bond cannot be placed at the bridgehead of a bridged ring system, unless the rings are large enough. The rule in named after Julius Bredt.'' The German chemist J. Bredt proposed in 1935 that bicycloalkenes such as 1-norbormene, which have a double bond to the bridgehead carbon, are too strained to exist. (Making a molecular model will be helpful.)

e.g.,  No hyperconjugate due to Bredt's Rule.

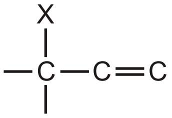
(A) **Carbon-carbon double bond length in Alkenes :** As we know that the more is the number of resonating structures, the more will be single bond character in carbon-carbon double bond. Thus, bond length between carbon-carbon double bond number of resonating structures.

Examples are :

Structures	**Number of -hydrogens zero**	**Number of hyperconjugation structures**	**Carbon-carbon double bond length in Å**
$CH_2 \quad CH_2$	zero	zero	1.34 Å
$CH_3 - CH \quad CH_2$	3	3	1.39 Å
$CH_3 - CH_2 - CH \quad CH_2$	2	2	1.37 Å
 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-CH=CH_2$	1	1	1.35 Å
 $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{\vert}{\underset{\vert}{C}}}}-CH=CH_2$	zero	zero	1.34 Å

REVERSE HYPERCONJUGATION

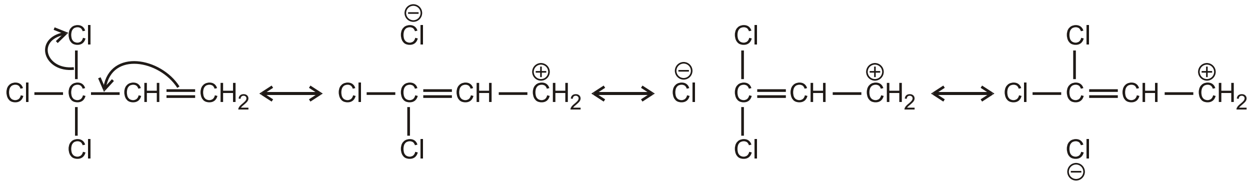
The phenomenon of hyperconjugation is also observed in the system given below :



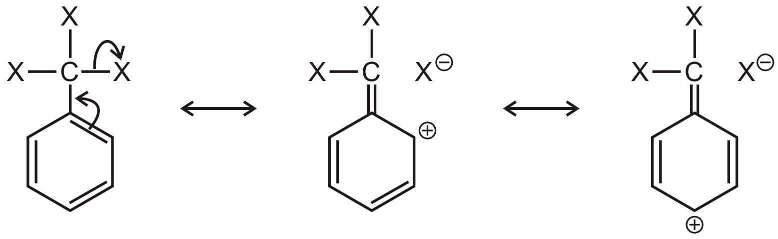
$$-\overset{X}{\underset{|}{\overset{|}{C}}}-C=C$$

where X - halogen

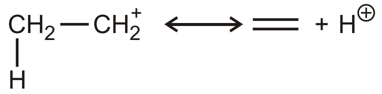
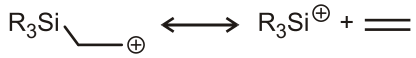
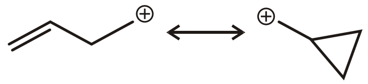
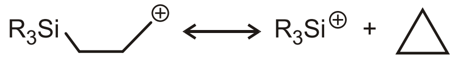
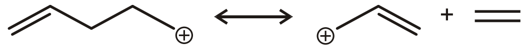
In such system the effect operates in the reverse direction. Hence the hyperconjugation in such system is known as reverse hyperconjugation.



The meta directing influence and dectivating effect of CX_3 group for electrophilic aromatic substitution reaction can be explained by this effect.



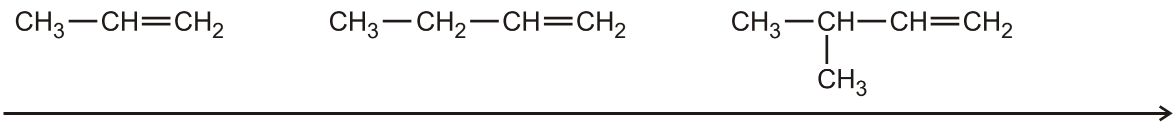
Types of hyperconjugation :

Valence Structures	Abbreviation	Name
		Sacrificial hyperconjugation
		Hyperconjugation
		Homoconjugation
		Homohyperconjugation
	/	Hyperconjugation/conjugation
	/	Double hyperconjugation

APPLICATION OF HYPERCONJUGATION

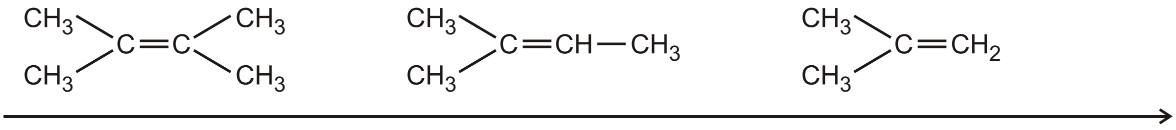
(A) Stability of Alkenes : Hyperconjugation explains the stability of certain alkenes over other alkenes :

(i) Stability of alkenes Number of alpha hydrogens Number of resonating structures



$CH_3-CH=CH_2$ $CH_3-CH_2-CH=CH_2$ $CH_3-\underset{CH_3}{CH}-CH=CH_2$

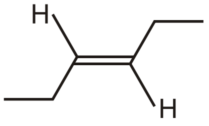
Stability in decreasing order



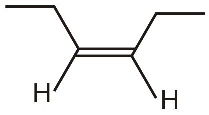
Number of alpha hydrogens in decreasing order stability of alkenes in decreasing order

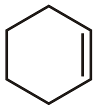
Solved Example

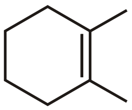
- Count those compounds having odd number of   -hydrogen.

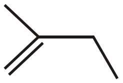
(a) 

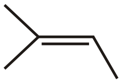
(b) 

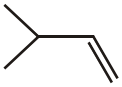
(c) 

(d) 

(e) 

(f) 

(g) 

(h) 

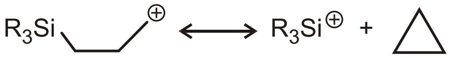
Bridt's rule

Ans. 3

EXERCISE

SINGLE CHOICE QUESTIONS

1. What is the type of conjugation for the given reaction?

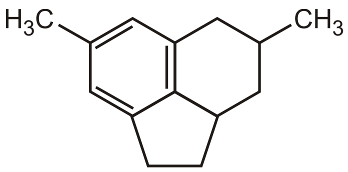


(A) Hyperconjugation
(B) Simple Conjugation
(C) Homoconjugation
(D) Homohyperconjugation

2. What is the type of conjugation for the given reaction?

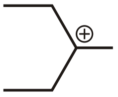
(A) Hyperconjugation
(B) Simple Conjugation
(C) Homoconjugation
(D) Double hyperconjugation

3. Number of Benzylic carbons in the given compound are :



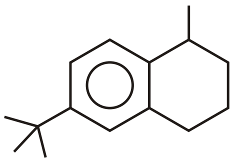
(A) 4
(B) 3
(C) 1
(D) 2

4. Number of   -   conjugation in the given compound is :



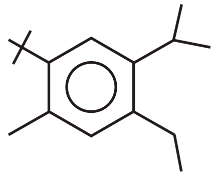
(A) 4
(B) 6
(C) 7
(D) 8

5. Number of   -hydrogen in given compound are :



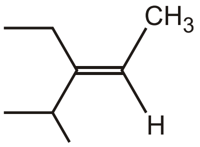
(A) 2
(B) 3
(C) 4
(D) 5

6. Number of -hydrogen in given compound are :



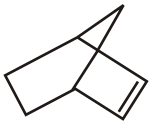
(A) 5 (B) 6 (C) 7 (D) 8

7. Number of -hydrogen in given compound are :



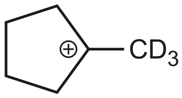
(A) 5 (B) 6 (C) 7 (D) 8

8. Number of hyperconjugating structure in given compound are :

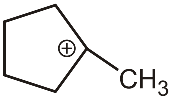


(A) 0 (B) 1 (C) 2 (D) 3

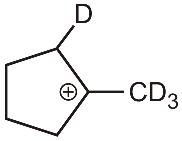
9. Rank the following according to stability (most stable to least stable).



(a)



(b)



(c)

(A) a > b > c (B) a > c > b (C) c > b > a (D) b > a > c

10. The type of delocalisation involving sigma bond orbitals is called :

(A) inductive effect (B) hyperconjugation (C) electromeric effect (D) mesomeric effect

11. The allyl radical has how many bonding -molecular orbitals?

(A) 1 (B) 2 (C) 3 (D) 4 (E) 5

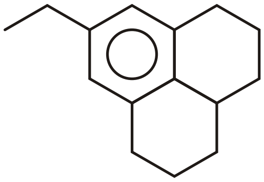
MULTIPLE CHOICE QUESTIONS

1. Which of the following alkene is more stable than 1-butene :

(A) cis-2-butene (B) trans-2-butene (C) Iso-butene (D) ethene

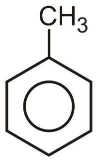
INTEGER TYPE QUESTIONS

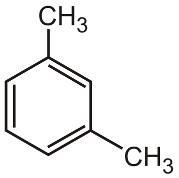
1. X Total number of -hydrogen in the below compound?

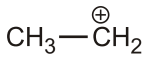


Find value of X?

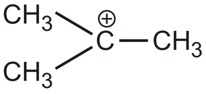
2. How many compounds have -hyperconjugation?

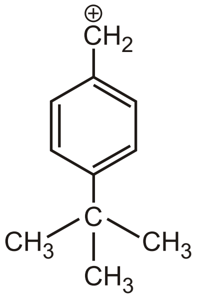


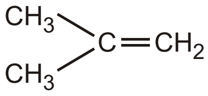




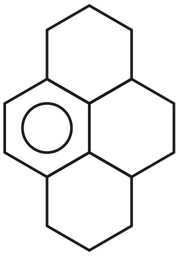
$\mathrm{CH_3{-}\overset{\oplus}{C}H_2}$



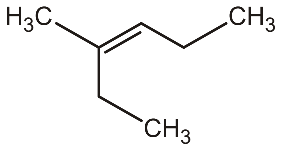
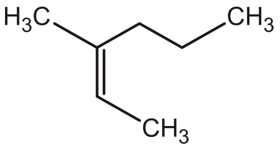
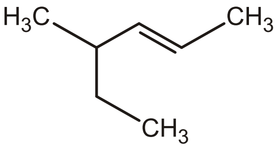
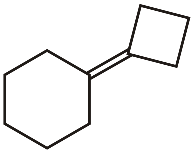
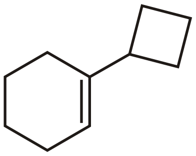
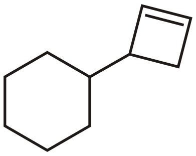
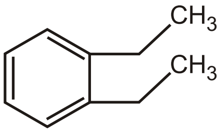
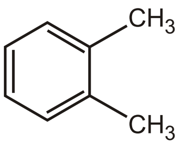
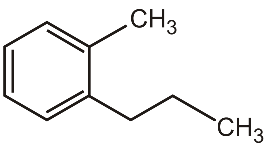
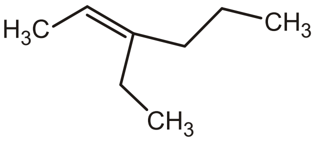
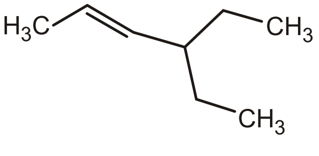
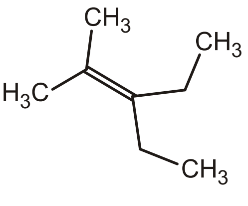
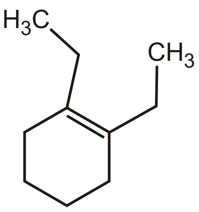
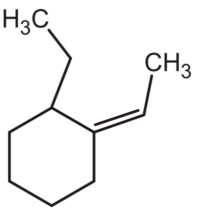
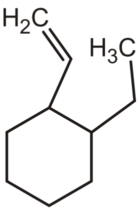


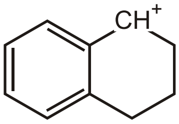
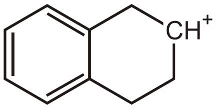
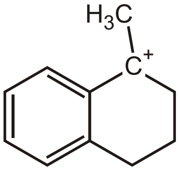
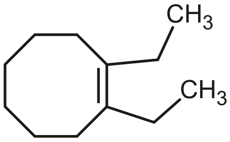
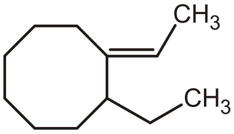
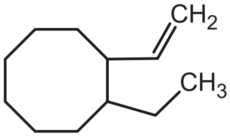
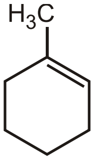
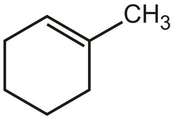
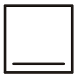


3. Total number of -hydrogen in the given compound is :



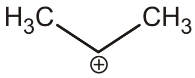
WORK SHEET - 1

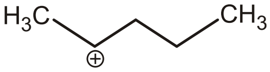
S.No.	Compound	Relative Stability
1.	  	
2.	  	
3.	  	
4.	  	
5.	  	

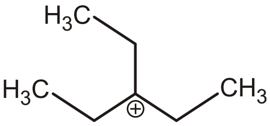
6.	  	
7.	  	
8.	 	
9.	 	

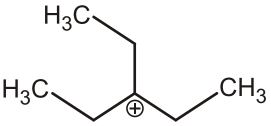
WORK SHEET - 2

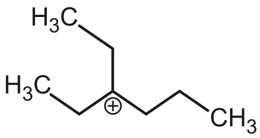
1. Write Number of -hydrogen in given carbocation in bracket :

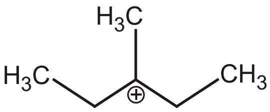
(1) 

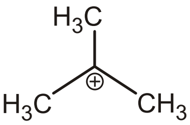
(2) 

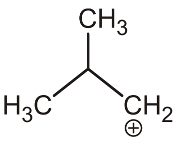
(3) 

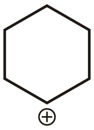
(4) 

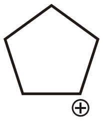
(5) 

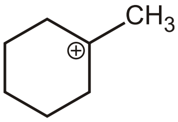
(6) 

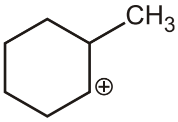
(7) 

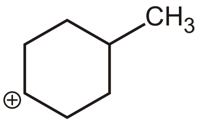
(8) 

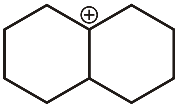
(9) 

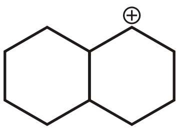
(10) 

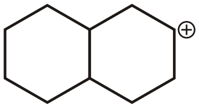
(11) 

(12) 

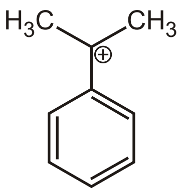
(13) 

(14) 

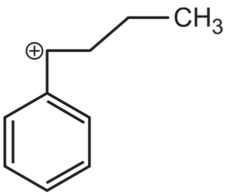
(15) 

(16) 

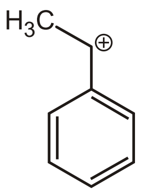
(17)



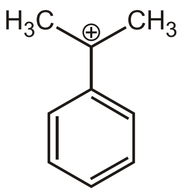
(18)



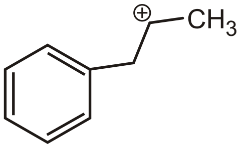
(19)



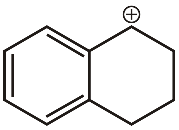
(20)



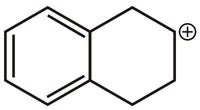
(21)



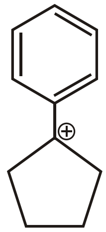
(22)



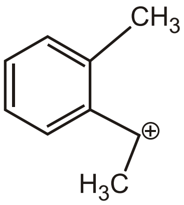
(23)



(24)



(25)

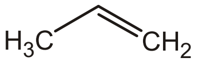


WORK SHEET - 3

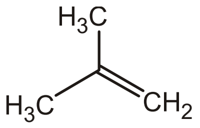
1. Write number of -Hydrogen in given compounds in the bracket :

(1) H_2C CH_2

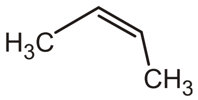
(2)



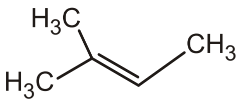
(3)



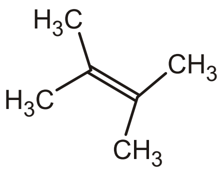
(4)



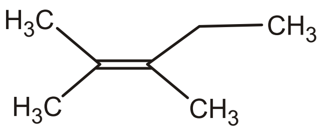
(5)



(6)



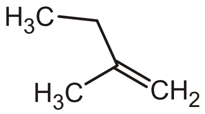
(7)



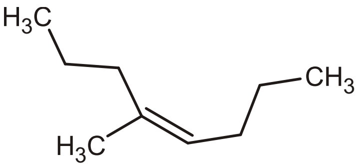
(8)

(9)

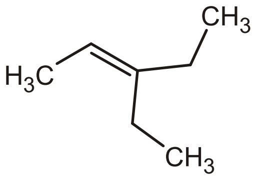
(10)



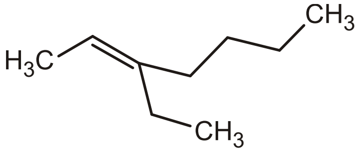
(11)



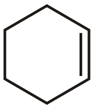
(12)



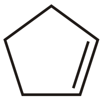
(13)



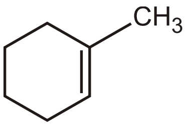
(14)



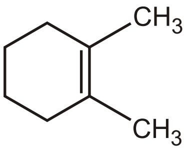
(15)



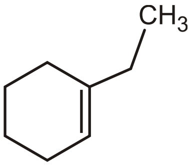
(16)



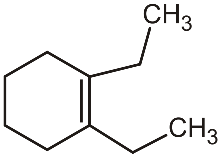
(17)



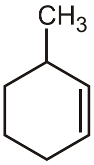
(18)



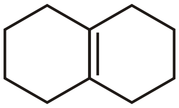
(19)



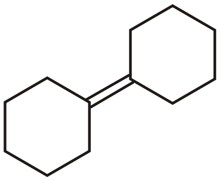
(20)



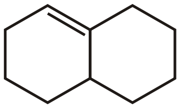
(21)



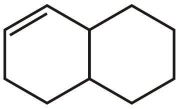
(22)



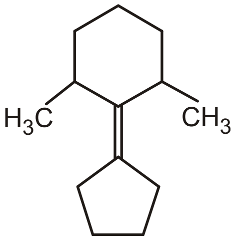
(23)



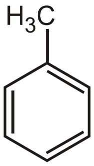
(24)



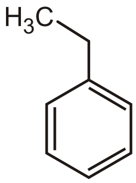
(25)



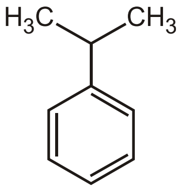
(26)



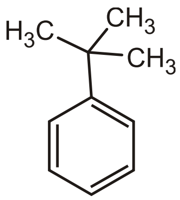
(27)



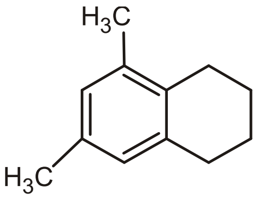
(28)



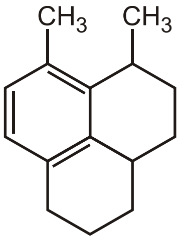
(29)



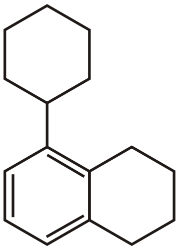
(30)



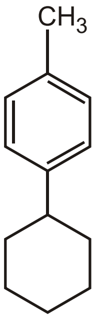
(31)



(32)



(33)



Answers

Single Choice Questions

1.	(D)	**2.**	(D)	**3.**	(A)	**4.**	(C)	**5.**	(B)	**6.**	(B)	**7.**	(B)	**8.**	(A)
9.	(D)	**10.**	(B)	**11.**	(A)										

Multiple Choice Questions

1. (A, B, C)

Integer Type Questions

1.	7	**2.**	2	**3.**	6

Work Sheet - 1

1. ii > i > iii **2.** i > ii > iii **3.** ii > iii > i **4.** iii > i > ii **5.** i > ii > iii **6.** iii > i > ii **7.** i > ii > iii **8.** i = ii **9.** i > ii

Work Sheet - 2

1.	6	**2.**	5	**3.**	6	**4.**	6	**5.**	6	**6.**	7	**7.**	9	**8.**	1
9.	4	**10.**	4	**11.**	7	**12.**	3	**13.**	4	**14.**	5	**15.**	3	**16.**	4
17.	6	**18.**	2	**19.**	3	**20.**	6	**21.**	5	**22.**	2	**23.**	4	**24.**	4
25.	3														

Work Sheet - 3

1.	0	**2.**	3	**3.**	6	**4.**	6	**5.**	9	**6.**	12	**7.**	11	**8.**	2
9.	5	**10.**	5	**11.**	7	**12.**	7	**13.**	7	**14.**	4	**15.**	4	**16.**	7
17.	10	**18.**	6	**19.**	8	**20.**	3	**21.**	8	**22.**	8	**23.**	5	**24.**	3
25.	6	**26.**	3	**27.**	2	**28.**	1	**29.**	0	**30.**	10	**31.**	7	**32.**	5
33.	4														

❑❑❑