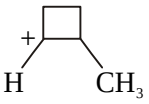
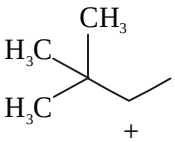
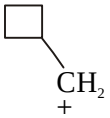
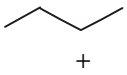
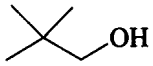
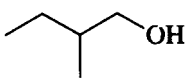
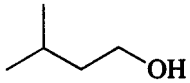
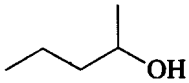
REARRANGEMENT OF CARBOCATIONS

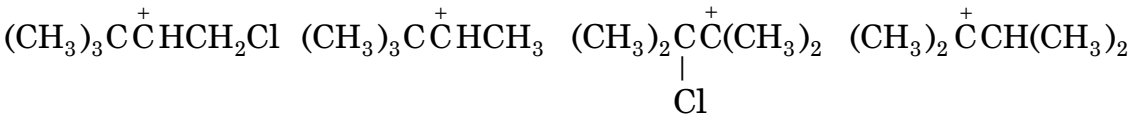
Q.1 Which of the following is most likely to undergo a favorable hydride shift ?

(A)  (B)  (C)  (D) 

Q.2 Which of the following alcohols would be most likely to undergo dehydration with rearrangement by a process involving a methyl migration (methyl shift) ?

(A)  (B)  (C)  (D) 

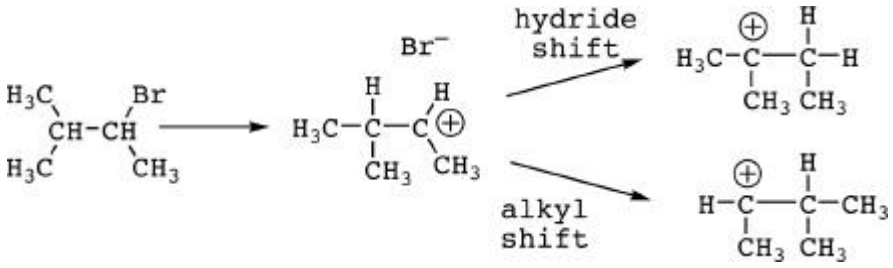
Q.3 Addition of HCl to 3, 3-dimethyl-1-butene yields two products, one of which has a rearranged carbon skeleton. Which of the following cations are intermediates in that reaction ?



1 2 3 4

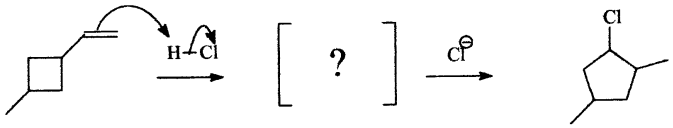
(A) 1, 3 (B) 1, 4 (C) 2, 3 (D) 2, 4

Q.4 Why does the carbocation intermediate formed in the following (partial) S_N1 reaction rearrange via a hydride shift rather than an alkyl shift ?



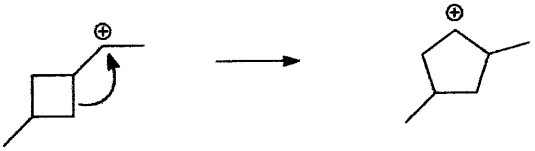
(A) Because the hydride is smaller than the alkyl group
(B) Because the alkyl shift forms a 2° carbocation
(C) Because the hydride ends up substituting for the $Br^{\ominus}$
(D) To make things more complicated and annoying

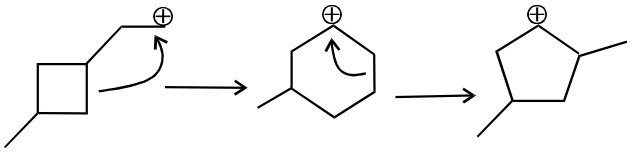
Q.5 Write mechanism best accounts for the transformation in the brackets?



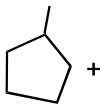
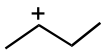
(A) 

(B) 

(C) 

(D) 

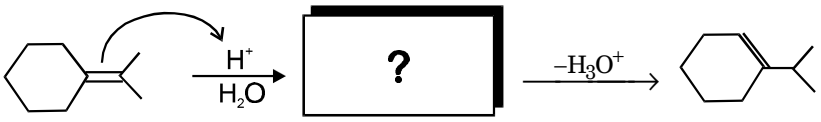
Q.6 Which of the following carbocations would not likely rearrange to a more stable carbocation?

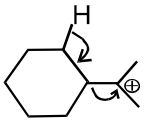
(A)  (B)  (C)  (D) 

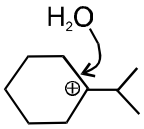
Q.7 A less stable carbonium ion rearranges to a more stable carbonium ion. During this rearrangement, the migrating atom or group leaves as a

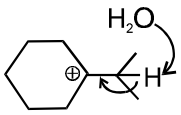
(A) Free radical
(B) Carbene
(C) Positively charged ion
(D) Negatively charged ion.

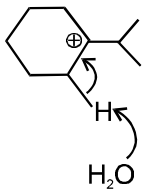
Q.9 Consider the following rearrangement. Select the structure of the intermediate that has correct mechanistic arrows accounting properly for the transformation.



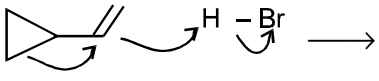
(A) 

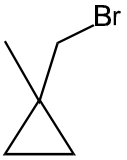
(B) 

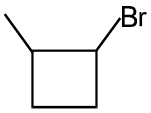
(C) 

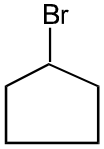
(D) 

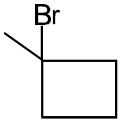
Q.9 Vinylcylopropane reacts with HBr to produce a rearranged alkyl bromide. Based on the mechanistic arrows in the following sequence, what is the organic product?



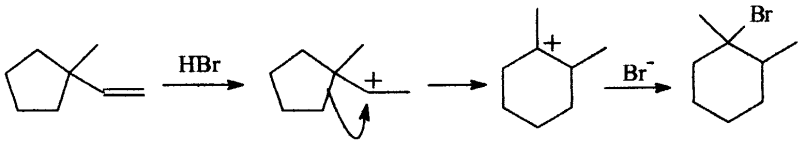
(A) 

(B) 

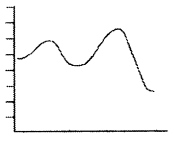
(C) 

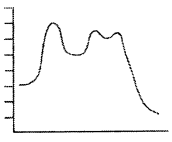
(D) 

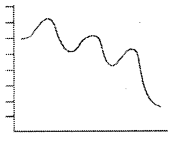
Q.10 Consider the following rearrangement reaction :

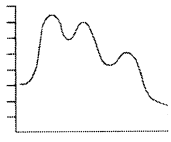


Which of the following reaction coordinates best represents the overall reaction ? (Note : the units are arbitrary)

(A) 

(B) 

(C) 

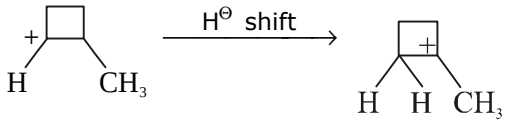
(D) 

ANSWER KEY

Q.No.	1	2	3	4	5	6	7	8	9	10
Ans.	A	A	D	B	C	B	D	D	B	D

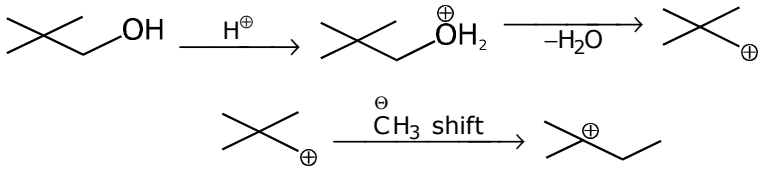
SOLUTIONS (REARRANGEMENT OF CARBOCATIONS)

Ans.1 In (A) Hydride shift results in formation of more stable carbocation.



2º carbocation 3º carbocation

Ans.2 In (A) Methyl shift results in formation of more stable carbocation.



1º carbocation 3º carbocation

Ans.3 $H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH=CH_2 \xrightarrow{H^{\oplus}} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{\oplus}{C}H-CH_3$

(2)

$H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{\oplus}{C}H-CH_3 \xrightarrow{CH_3^{\ominus}\text{ shift}} CH_3-\underset{\displaystyle \oplus}{\overset{\displaystyle CH_3}{\overset{|}{C}}}-\underset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3$

(4)

(2) & (4) are intermediates

Ans.4 Hydride shift results in formation of more stable 3º corbocation while alkyl shift results in less stable 2º carbocation.

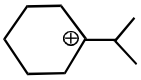
Ans.5 Intermediate carbocation (4-membered ring) undergoes RING EXPANSION to form more stable ring i.e. 5-membered.

Ans.6 (A) & (D) can undergoes Hydride shift to form more stable carbocation.

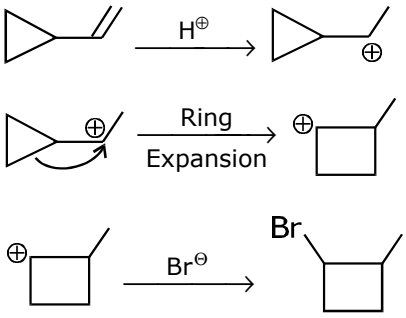
(c) can undergoes Ring expansion to form more stable 4-membered Ring.

In (B) Hydride shift or methyl shift results in formation of either the same carbocation or less stable carbocation respectively.

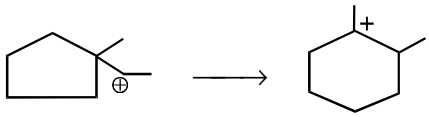
Ans.7 Migrating atom or group leeves by taking both the electrons of its bond with itself hence it is –vely charged.

Ans.8 Intermediate formed above is  which loses $H^{\oplus}$ from β-position to form π-bond.

Ans.9



Ans.10 There are two intermediates in the reaction.



I II

II is moe stable than I so its energy is lower than that of intermediate I in the graph.