ORGANIC CHEMISTRY

DPP

DAILY PRACTICE PROBLEMS

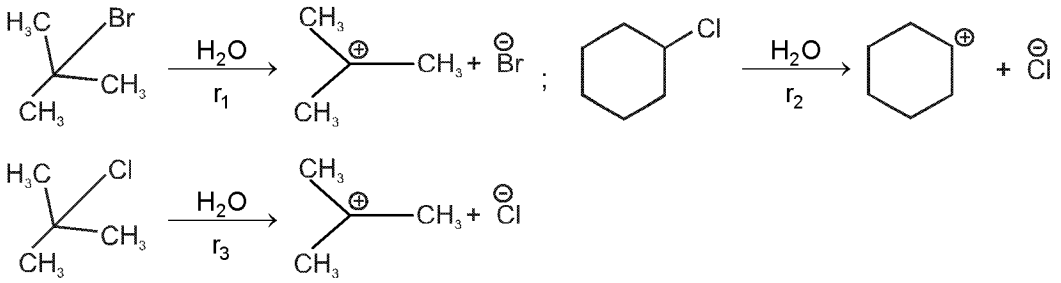
DPP No. 20

Total Marks : 32

Max. Time : 32 min.

Topic : Alcohols, Phenols and Ethers (Reaction Mechanism)

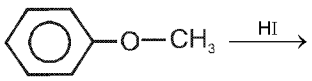
Type of Questions		M.M., Min.
Single choice Objective ('–1' negative marking) Q.1 to Q.5	(3 marks 3 min.)	[15, 15]
True or False (no negative marking) Q.6	(2 marks 2 min.)	[2, 2]
Comprehension ('–1' negative marking) Q.7 to Q.10	(3 marks 3 min.)	[15, 15]

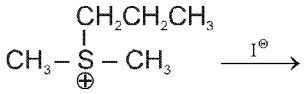
1. 

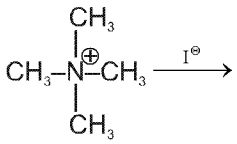
The rates r_1 , r_2 and r_3 are in the order :

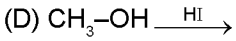
(A) $r_1 > r_2 > r_3$ (B) $r_3 > r_1 > r_2$ (C) $r_1 > r_3 > r_2$ (D) $r_2 > r_1 > r_3$

2. In which reaction methyl iodide is formed with fastest rate ?

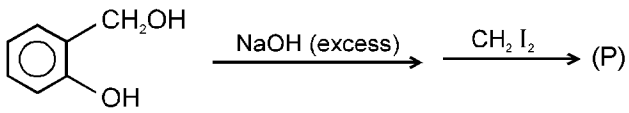
(A) 

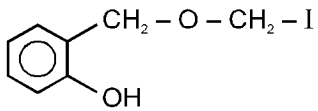
(B) 

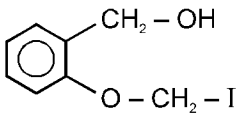
(C) 

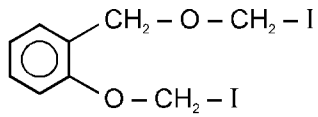
(D) 

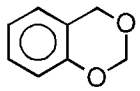
3. The product 'P' of the following reaction is :



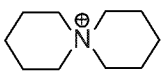
(A) 

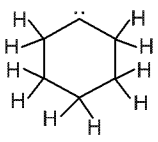
(B) 

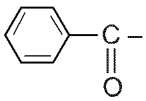
(C) 

(D) 

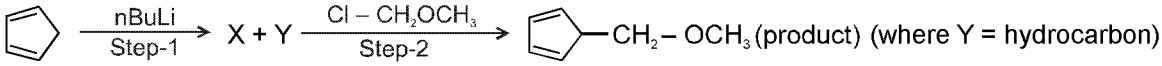
4. The correct order of true / false statements is :

(1)  has electrophilic 'N' atom.

(2)  is a nucleophile.

(3)  is an electrophile.

(A) TTF (B) TFT (C) TFF (D) FFT

5. 

(where Y = hydrocarbon)

In the above reaction which of the following statement is correct ?

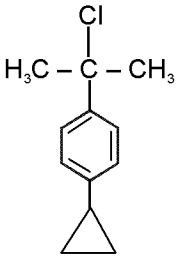
(A) Step-1-is an S_N2 reaction

(B) The hydrocarbon product of step-1 is $CH_3(CH_2)_2CH_3$.

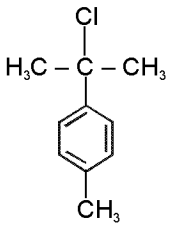
(C) X = cyclopentadiene

(D) the nucleophile in 2nd reaction is cyclopentadienyl anion

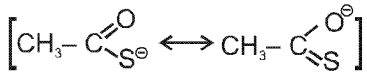
6. **(a)** Rate of solvolysis of (I) is faster than (II).



(I)



(II)

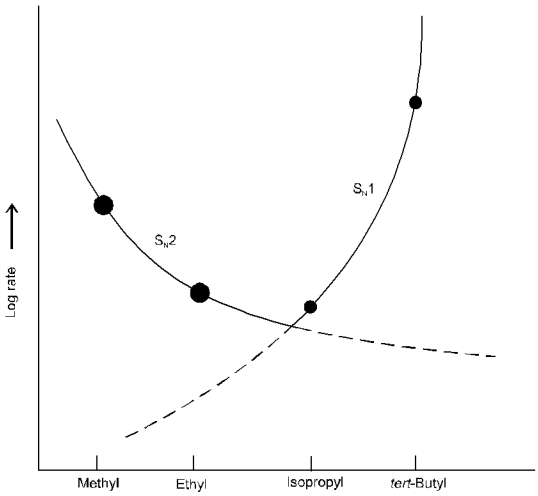
(b) When 

attacks on CH_3–Br, the nucleophilic site is oxygen atom to give major product.

Comprehension # 1 (Ques. 7 to 9)

In 1935, E.D. Hughes and Christopher Ingold took these two sets of facts-kinetic order and relative reactivity and on them built a broad theory of nucleophilic aliphatic substitution. The keystone of their theory was this: that nucleophilic aliphatic substitution can proceed by two different mechanisms. These mechanism, for reason that will become clear, they named S_N2 and S_N1. Different substrates react by different kinetic orders because they are reacting by different mechanisms : some, like methyl, by S_N2; others, like tert-butyl, by S_N1.

Reactivity passes through a minimum with secondary substrates because the mechanism changes at this point, from S_N2 to S_N1. The occurrence of a minimum or maximum in a property-reactivity, acidity, etc. as one proceeds along a logical series, suggests the working of opposing factors. Here, Hughes and Ingold proposed, the factors are the opposing reactivity sequences for the two different mechanisms. As one passed along the series, reactivity by the S_N2 mechanism decreases from CH_3 to 1° and at 2° is so low that the S_N1 reaction begins to contribute significantly, reactivity, now by S_N1 rises sharply to 3° (figure).



(Halide substrates)

S_N2 Vs S_N1 RX = $\xleftarrow{S_N2 \text{ increases}}$ CH_3 1° 2° 3° $\xrightarrow{S_N1 \text{ increases}}$

7. Which of the following gives fastest S_N1 ?

(A) Methylchloride (B) Ethylchloride

(C) Isopropyl chloride (D) tert-Butyl chloride

8. Which of the following gives fastest S_N2 ?
(A) Methyl iodide (B) Ethyl iodide
(C) Isopropyl iodide (D) tert-Butyl iodide

9. Which can show both S_N1 and S_N2 equally good ?
(A) Methyl iodide (B) Ethyl iodide
(C) Isopropyl iodide (D) tert-Butyl iodide

Comprehension # 2

10. Metal Hydrides

(a) **$NaBH_4$** Sodium borohydride is a milder reducing agent. It reduces aldehydes, ketones and acid chlorides to alcohols and alkyl halides to alkanes. It does'nt affect C=C, C≡C.

(b) **$LiAlH_4$** (LAH) Lithium aluminium hydride is stronger reducting agent than $NaBH_4$. It reduces almost all functional groups and generally does'nt affect C=C/C≡C.

Write Yes or No

	Reduction Reaction	**Recuction is possible by**	
		$LiAlH_4$	**NaBH4**
(i)	$R-CH=O \longrightarrow R-CH_2-OH$	Yes	Yes
(ii)	$R-\underset{\underset{O}{\|\|}}{C}-OH \longrightarrow R-CH_2-OH$	Yes	No
(iii)	$R-\underset{\underset{O}{\|\|}}{C}-Cl \longrightarrow R-CH_2-OH$	.....	.....
(iv)	$\begin{matrix}R\\R\end{matrix}\!\!>\!C=O \longrightarrow \begin{matrix}R\\R\end{matrix}\!\!>\!CH-OH$	.....	.....
(v)	$R-\underset{\underset{O}{\|\|}}{C}-OR' \longrightarrow R-CH_2OH + R'OH$	.....	.....
(vi)	$\begin{matrix}R\\R\end{matrix}\!\!>\!CH-Cl \longrightarrow \begin{matrix}R\\R\end{matrix}\!\!>\!CH_2 + HCl$	.....	.....
(vii)	$R-C\equiv N \longrightarrow R-CH_2-NH_2$	.....	.....
(viii)	$R-\underset{\underset{O}{\|\|}}{C}-NHR' \longrightarrow R-CH_2-NHR'$	.....	.....
(ix)	$R-NO_2 \longrightarrow RNH_2$	.....	.....
(x)	$R-CH=CH-R \longrightarrow R-CH_2-CH_2-R$	.....	.....

Answer Key

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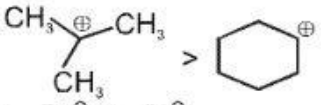
1.	(C)	**2.**	(B)	**3.**	(D)	**4.**	(D)	**5.**	(B,D)
6.	**(a)** True		**(b)** False	**7.**	(D)	**8.**	(A)	**9.**	(C)
10.	(iii) Yes, Yes (vii) Yes, No		(iv) Yes, Yes (viii) Yes, No		(v) Yes, No (ix) Yes, No		(vi) Yes, Yes (x) No, No		

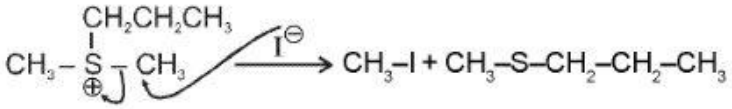
Hints & Solutions

DPP No. # 20

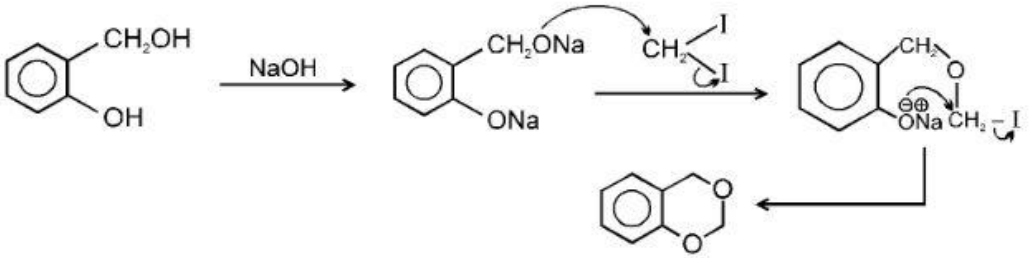
1. Carbocation Stability  >

leaving group ability is $Br^{\ominus} > Cl^{\ominus}$

over all reaction order $r_1 > r_3 > r_2$

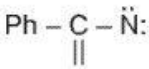
2. 

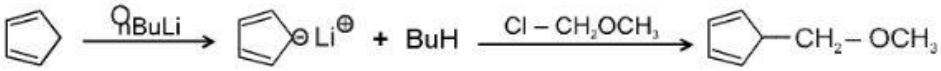
Me_2S is the best leaving group (Leaving group ability order is $Me_2S > H_2O > CH_3OH > (CH_3)_3N$).

3. 

4. (1)  The 'N' atom does not have vacant orbitals.

(2) It is an electron deficient species, carbene (electrophile)

(3)  It is electron deficient species, Nitrene (electrophile)

5. 

6. **(a)** The carbocation intermediate of (I) formed in solvolysis reaction is more stable due to formation of CPM C^+