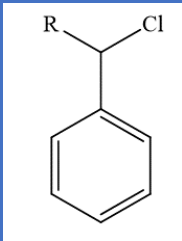1.   Explain the relative rates of the following compounds in the SN1 reaction based on MO approach.

	R	Relative rate
	CH_3	540
	CH_3CH_2	125
	$(CH_3)_2CH$	27
	$(CH_3)_3C$	1

Ans. For the benzyl carbocation, the stability through σ-conjugation will be maximum with R= CH_3, since 3 C-H bonds are available for interaction with the empty p-orbital [MO diagram needs to be shown].

The number of available C-H bonds decreases in going down the series and becomes nil with R= $(CH_3)_3C$.
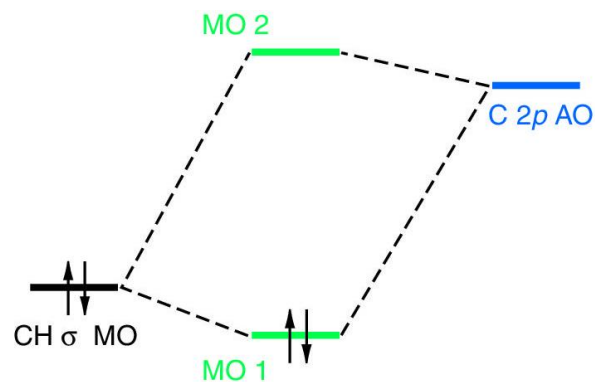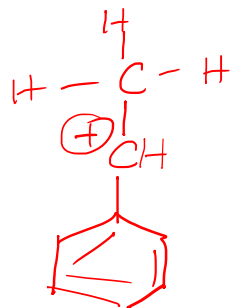
2. The reaction of cyclopentyl bromide with sodium cyanide to give cyclopentyl cyanide proceeds faster if a small amount of sodium iodide is added to the reaction mixture. Can you suggest a reasonable mechanism to explain the function of sodium iodide?

Cyclopentyl bromide → Cyclopentyl cyanide
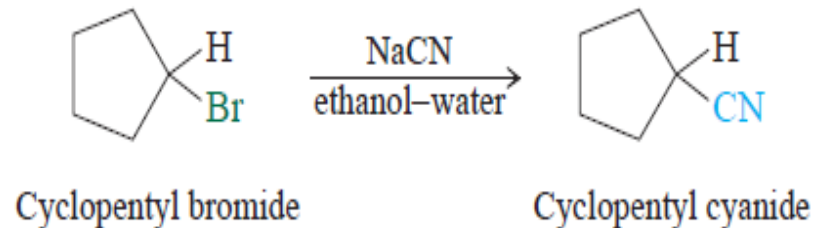
Ans. Iodide is a better nucleophile than cyanide and is also a very good leaving group. So, when a small amount of iodide is added to the aforementioned reaction, it reacts faster and displaces the bromide. Subsequently, cyanide displaces iodide to give the product. Although an extra step is added in this way, the rates of both the reactions are quite fast and hence the reaction is accelerated. Iodide here acts as a nucleophilic catalyst (k_1, k_2 and k_3 are rate constants).

$$k_2, k_3 > k_1$$
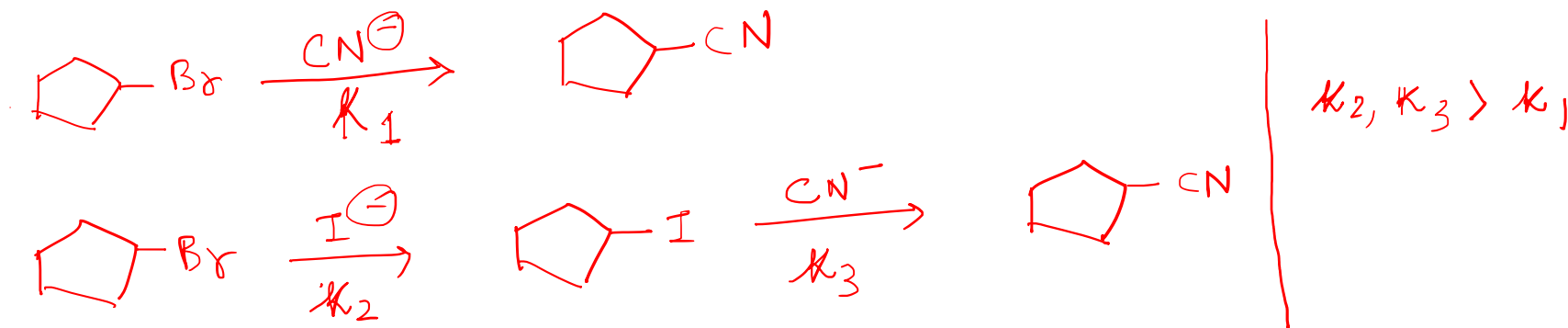
3.   The Relative rates (water = 1) of reaction of nucleophiles with MeBr in EtOH are provided below. Explain the observed trend.

| Nucleophiles	Relative rate
PhO⁻	2×10^3
EtO⁻	6×10^4
PhS⁻	5×10^7

Ans. Since the electrophile is MeBr, it will undergo S_N2 reaction with the nucleophiles.

Now, between PhO- and EtO-, the HOMO in EtO- is at a higher energy since in PhO-, the charge is more delocalized. Hence, the rate is higher for EtO-.

Between EtO- and PhS-, the HOMO in PhS- is energetically higher since S has a lower electronegativity than O. Although, in this case, delocalization is possible, the data shows that the HOMO in PhS- is still at a higher energy than EtO-.

4.   The relative rates of reactions of different nucleophiles with the following substrate are given in the table. Explain why the rate is practically the same for the first 3 nucleophiles whereas it increases for OH- and Ph-.

Nucleophile	Relative Rate
AcO-	1.02
Cl-	1.05
PhO-	1
OH-	20
PhS-	28
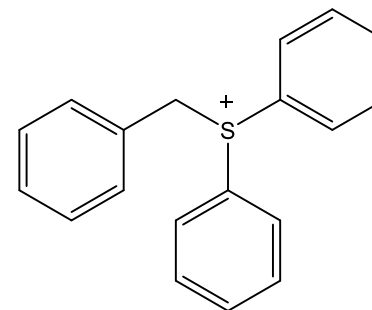
Ans. This is an interesting example in which there is a change in reaction mechanism depending on the nucleophile used. The substrate is a benzyl derivative and hence undergoes both S_N1 and S_N2 well. For AcO-, Cl- and PhO-, the reaction follows S_N1 and hence the rate is essentially the same. For OH- and PhS-, the reaction goes through S_N2 and hence the rate is higher for PhS- since the HOMO is at higher energy than OH-.

$$Ph-CH_2 \overset{\oplus}{\underset{\uparrow}{-SPh_2}} \xrightarrow{S_N 1} Ph\overset{\oplus}{CH_2} + Ph_2S$$

$$Ph-CH_2 \overset{\oplus}{\underset{\uparrow}{-SPh_2}} \xrightarrow[S_N 2]{N\overset{\ominus}{u}} Ph-CH_2-Nu + Ph_2S$$