

## Assignment: Rearrangement of Carbocation

### Concept

**Carbocation** can undergo rearrangement to gain stability. Rearrangement can take place via

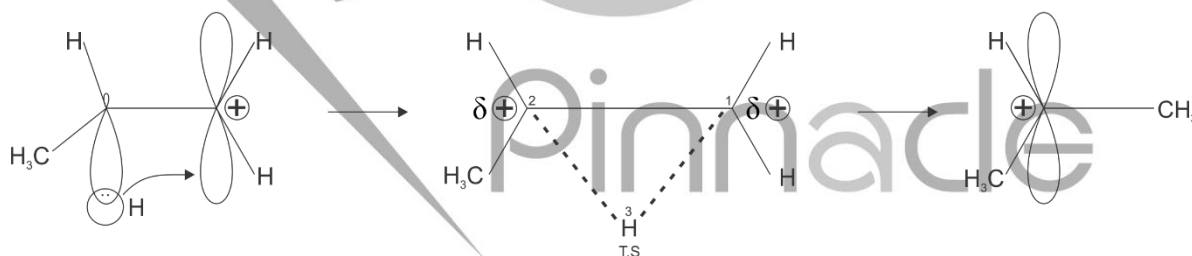
- 1, 2-  $\text{H}^-$  (Hydride) shift
- 1, 2-  $\text{Ph}^-$  (Phenyl) shift
- 1, 2-  $\text{R}^-$  (Alkyl) shift

#### Rules for Rearrangement

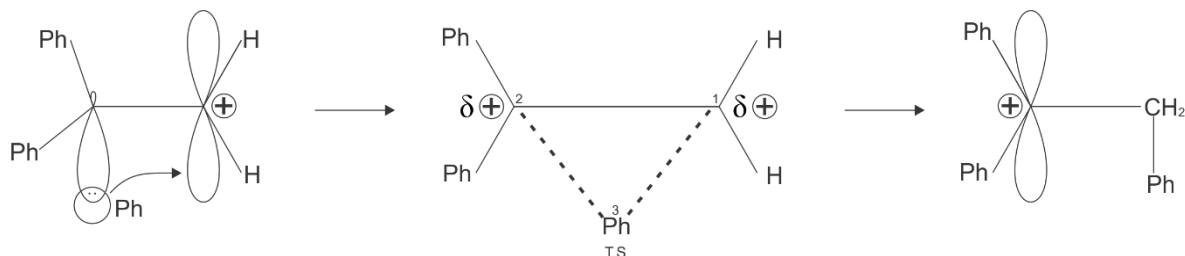
- Carbocation rearrangement takes place in between two consecutive carbon atoms
- In each rearrangement step, stability of carbocation should increase.
- The driving force responsible for more carbocation rearrangement is formation of more stable carbocation.
- If stability increases than shifting of carbocation take place
- if equal or less than shifting of carbocation is not possible

#### Hydride Shift ( $\text{H}^-$ Shift):

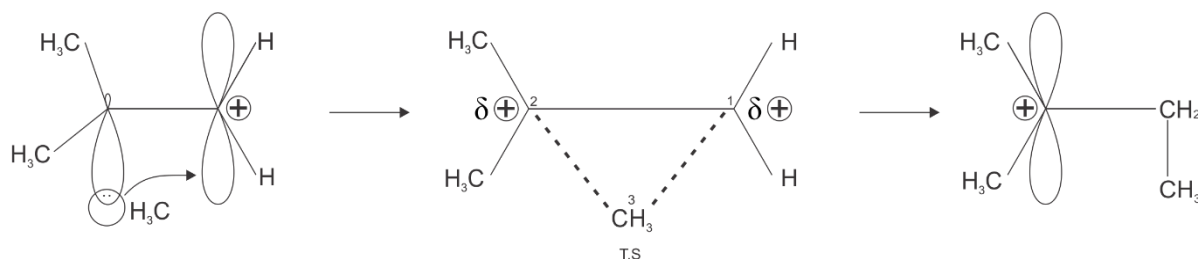
Example:  $\text{CH}_3 - \text{CH}_2 - \overset{\oplus}{\text{CH}}_2 \leftrightarrow \text{CH}_3 - \overset{\oplus}{\text{CH}} - \text{CH}_3$



#### Phenyl Shift ( $\text{Ph}^-$ Shift):



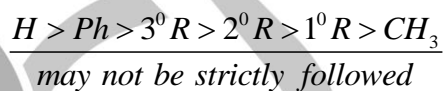
### Alkyl Shift ( $R^-$ Shift):



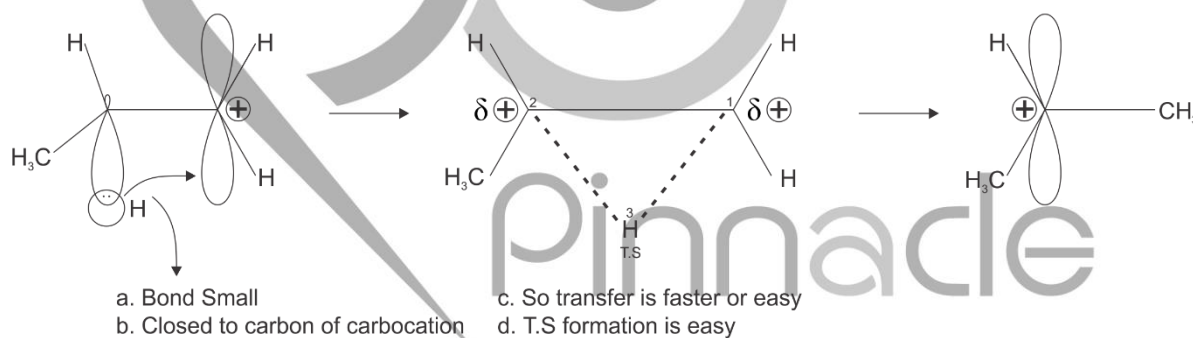
### MIGRATORY APTITUDE: (Rate associated with these type of group)

Depends on two factors

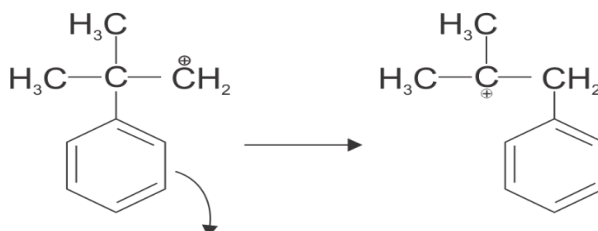
- Electron density
- Steric hindrance
- **Migratory aptitude**  $\propto$  Electron density in a group
- After considering all the factors, overall order is



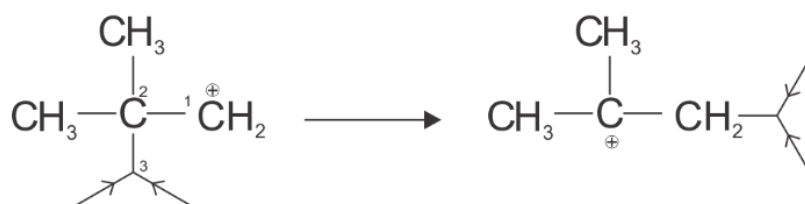
- Migratory aptitude of H is greater because of lower atomic mass & least steric hindrance.
- H- (Hydride) shift > Ph- (Phenyl) shift > R- (Alkyl) shift



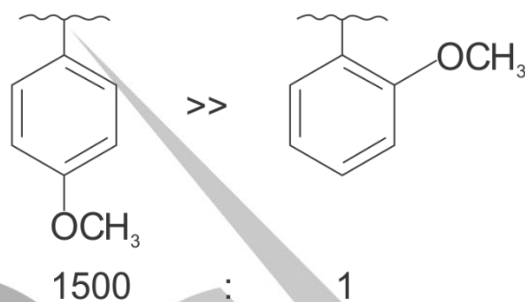
- **Isotopic Effect:**  $H > D > T$  (Reason: Bond energy increases in order  $H > D > T$ )
- **Better electron donor are better migrator**



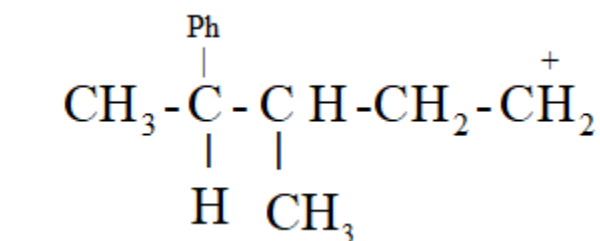
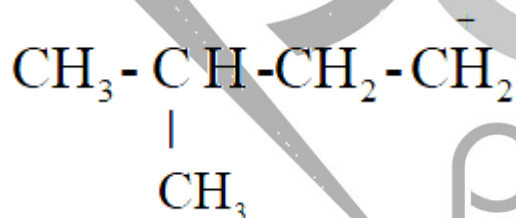
- $\pi e^-$ s (Electron rich)
- Strong attraction for positive charge
- Not based on the stability of carbocation
- Based on rate of rxn

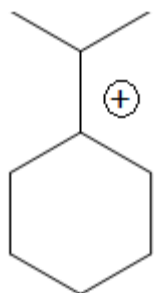


- Migratory aptitude is affected by steric hindrance

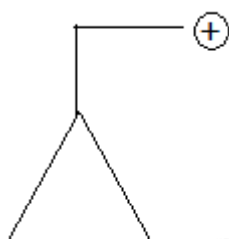


### Practice: Rearrangement of Carbocation

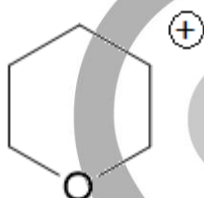




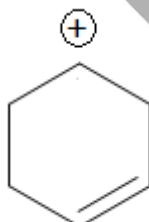
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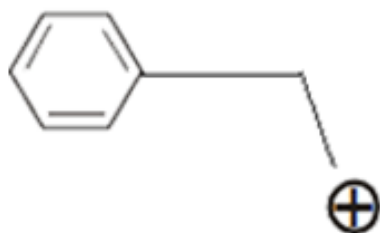
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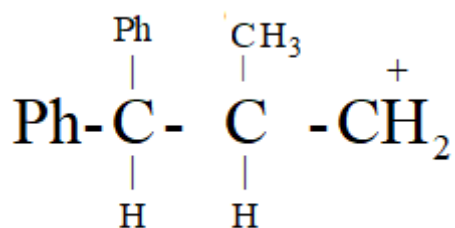
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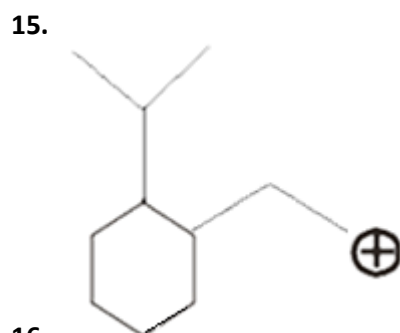
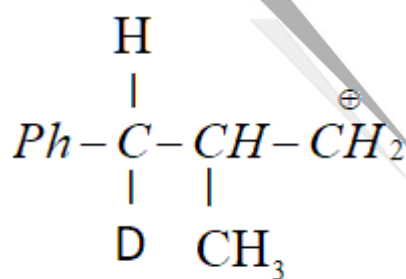
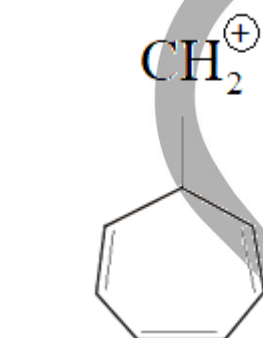
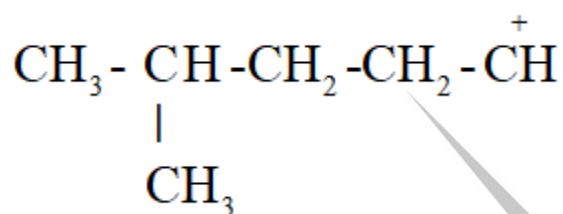
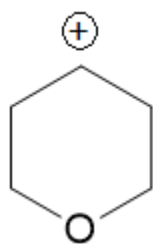
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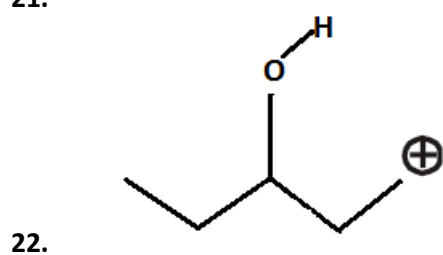
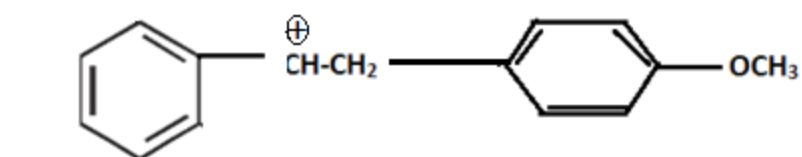
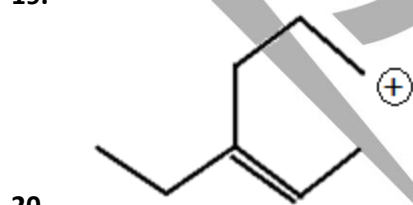
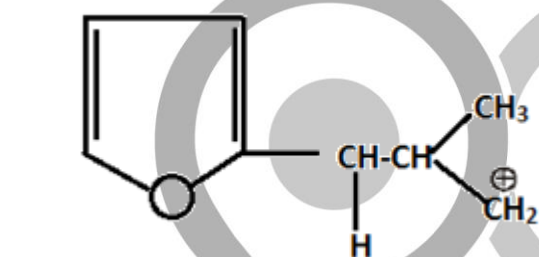
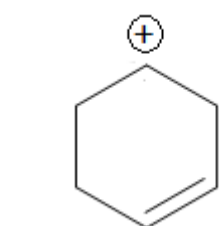
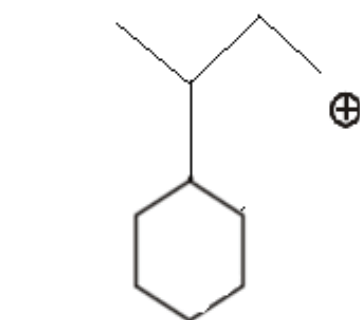


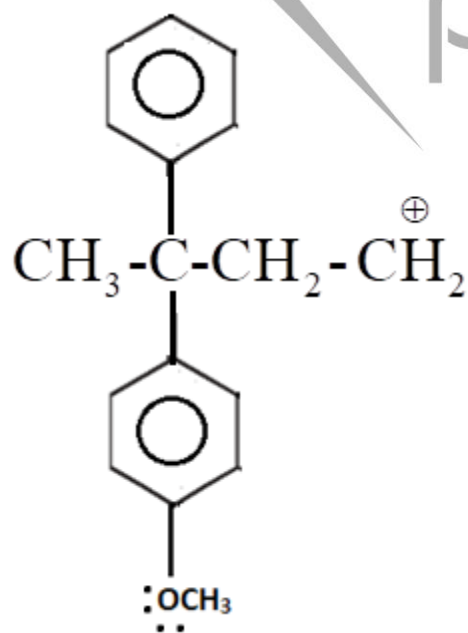
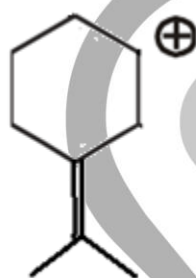
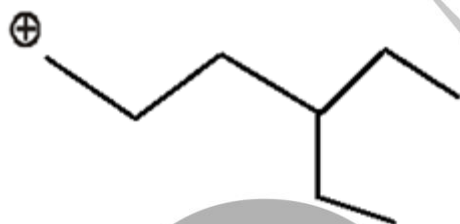
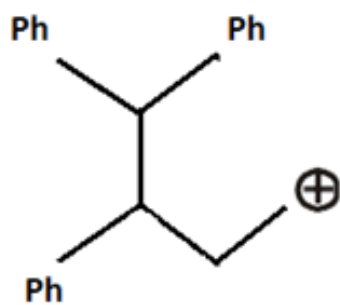
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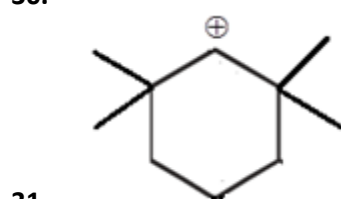
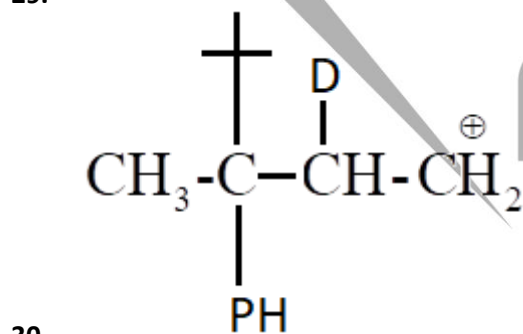
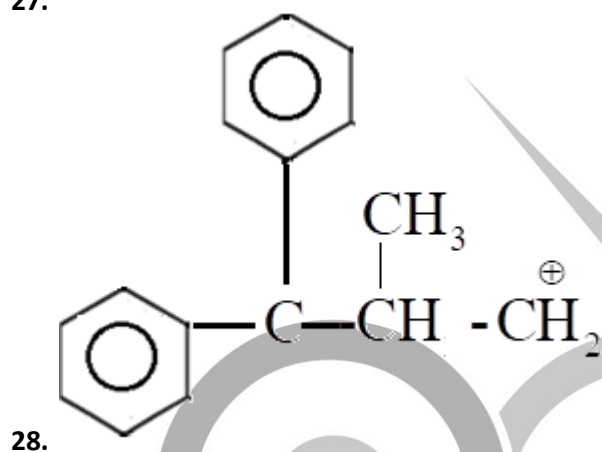
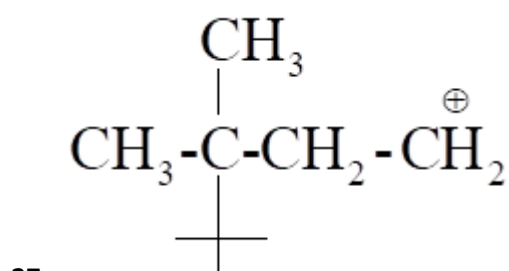


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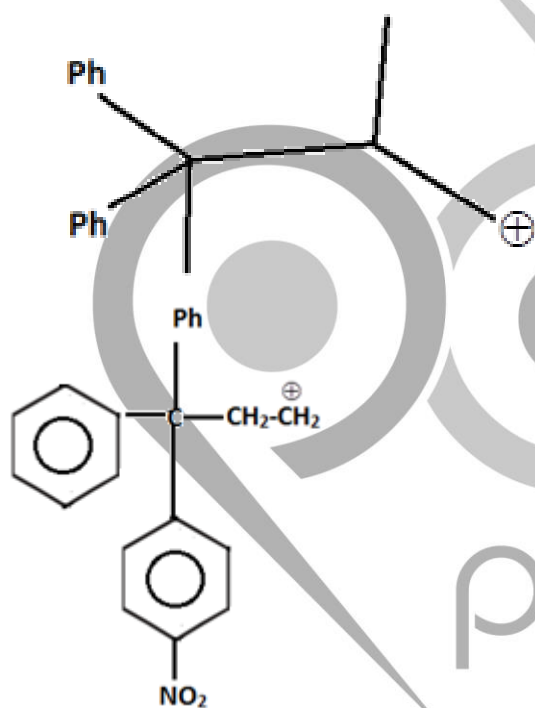
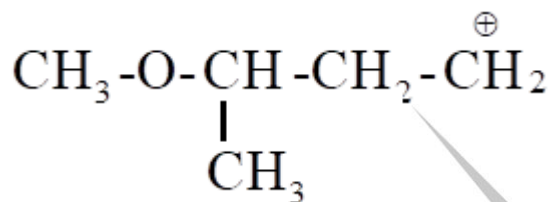
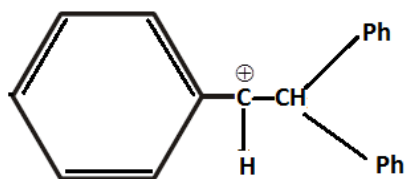












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