

UPSC Mains Chemistry Optional Paper-II Syllabus

1. Delocalised Covalent Bonding:

Aromaticity, anti-aromaticity; annulenes, azulenes, tropolones, fulvenes, syndones.

2 (i) Reaction mechanisms: General methods (both kinetic and non-kinetic) of study of mechanisms of organic reactions: isotopies, method cross-over experiment, intermediate trapping, stereochemistry; energy of activation; thermodynamic control and kinetic control of reactions.

(ii) Reactive intermediates: Generation, geometry, stability and reactions of carbenium ions and carbanions, free radicals, carbenes, benzyne and nitrenes.

(iii) Substitution reactions: $S_N 1$, $S_N 2$, and $S_N i$, mechanisms; neighbouring group participation; electrophilic and nucleophilic reactions of aromatic compounds including heterocyclic compounds—pyrrole, furan, thiophene and indole.

(iv) Elimination reactions: E1, E2 and E1cb mechanisms; orientation in E2 reactions- Saytzeff and Hoffmann; pyrolytic syn elimination-acetate pyrolysis, Chugaev and Cope eliminations.

(v) Addition reactions: Electrophilic addition to $C=C$ and $C\equiv C$; nucleophilic addition to $C=O$, $C=N$, conjugated olefins and carbonyls.

(vi) Reactions and Rearrangements:

(a) Pinacol- pinacolone, Hoffmann, Beckmann, Baeyer-Villiger, Favorskii, Fries, Claisen, Cope, Stevens and Wagner-Meerwein rearrangements.

(b) Aldol condensation, Claisen condensation, Dieckmann, Perkin, Knoevenagel, Wittig. Clemmensen, Wolff-Kishner, Cannizzaro and von Richter reactions; Stobbe, benzoin and acyloin condensations; Fischer indole synthesis, Skraup synthesis, Bischler- Napieralski, Sandmeyer, Reimer-Tiemann and Reformatsky reactions.

3. Pericyclic reactions: Classification and examples; Woodward-Hoffmann rules- electrocyclic reactions, cycloaddition reactions [2+2 and 4+2] and sigmatropic shifts [1, 3; 3,3 and 1,5], FMO approach.

4. (i) Preparation and Properties of Polymers: Organic polymers polyethylene, polystyrene, polyvinyl chloride, Teflon, nylon, terylene, synthetic and natural rubber.

(ii) Biopolymers: Structure of proteins, DNA and RNA.

5. Synthetic Uses of Reagents:

OsO_4 , HIO_4 , CrO_3 , $Pb(OAc)_4$, ScO_2 , NBS, B_2H_6 , Na- Liquid NH_3 , $LiAlH_4$, $NaBH_4$, $n-BuLi$, MCPBA.

6. Photochemistry: Photochemical reactions of simple organic compounds, excited and ground states, singlet and triplet states, Norrish-Type I and Type II reactions.

7. Spectroscopy: Principle and applications in structure elucidation:

(i) **Rotational**-Diatomic molecules; isotopic substitution and rotational constants.

(ii) **Vibrational**-Diatomic molecules, linear triatomic molecules, specific frequencies of functional groups in polyatomic molecules.

(iii) **Electronic**-Singlet and triplet states. $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions; application to conjugated double bonds and conjugated carbonyls Woodward-Fieser rules; Charge transfer spectra.

(iv) **Nuclear Magnetic Resonance (¹H NMR):** Basic principle; chemical shift and spin-spin interaction and coupling constants.

(v) **Mass Spectrometry:** Parent peak, base peak, metastable peak, McLafferty rearrangement.

