

**DISCIPLINE SPECIFIC CORE COURSE -8 (DSC-8): Carbonyls, Carboxylic acids, Amines, Nitro compounds, Nitriles, Isonitriles and Diazonium salts**

**CREDIT DISTRIBUTION, ELIGIBILITY AND PRE-REQUISITES OF THE COURSE**

Course title & Code	Credits	Credit distribution of the course			Eligibility criteria	Pre-requisite of the course (if any)
		Lecture	Tutorial	Practical/ Practice		
<b>Carbonyls, Carboxylic Acids, Amines, Nitro Compounds, Nitriles, Isonitriles and Diazonium salts (DSC-8)</b>	04	03	0	01	Passed Class 12 <sup>th</sup> with Physics, Chemistry, Mathematics	NIL

**Learning objectives**

The objectives of this course are as follows:

- To infuse students with the details of the chemistry of aldehydes, ketones, carboxylic acids and their derivatives, nitro, amines and diazonium salts.
- To make students aware of the chemical synthesis, properties, reactions and key applications of the listed classes of compounds and develop understanding of detailed mechanistic pathways for each functional group to unravel the spectrum of organic chemistry and the extent of organic transformations.
- To aid in the paramount learning of the concepts and their applications.

**Learning outcomes**

By studying this course, students will be able to:

- Explain the chemistry of oxygen and nitrogen containing compounds.
- Use the synthetic chemistry learnt in this course to do functional group transformations.
- Propose plausible mechanisms for the reactions under study.

**SYLLABUS OF DSC-8**

**UNIT – 1: Carbonyls, Carboxylic acid & their derivatives**

**(27 Hours)**

Carbonyl Compounds: Reaction of carbonyl compounds with ammonia derivatives, Aldol and Benzoin condensation, Knoevenagel condensation, Claisen-Schmidt, Perkin, Cannizzaro and

Wittig reaction, Beckmann and Benzil-Benzilic acid rearrangements, haloform reaction and Baeyer Villiger oxidation,  $\alpha$ -substitution reactions, oxidations and reductions (Clemmensen, Wolff Kishner,  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ , MPV, PDC), addition reactions of  $\alpha,\beta$ -unsaturated carbonyl compounds: Michael addition.

Carboxylic acids and derivatives: Effect of substituents on acidic strength on carboxylic acids, HVZ reaction, typical reactions of dicarboxylic acids and hydroxy acids. Comparative study of nucleophilic acyl substitution for acid chlorides, anhydrides, esters and amides, Mechanism of acidic and alkaline hydrolysis of esters, Dieckmann and Reformatsky reactions, Hoffmann-bromamide degradation and Curtius rearrangement.

Active methylene compounds: Keto-enol tautomerism. Preparation and synthetic applications of diethyl malonate and ethyl acetoacetate.

## **UNIT – 2: Nitro Compounds, Amines, Diazonium salts, Nitriles and Isonitriles (18 Hours)**

Nitro compounds: General methods of preparation: from alkyl halides, alkanes, oxidation of amines and oximes. Henry reaction, Nef reaction, Reduction-electrolytic reduction, reaction with nitrous acid, reduction in acidic, basic and neutral medium (for aromatic compounds)

Amines: Preparation, chirality in amines (pyramidal inversion), Basicity of amines: Effect of substituents, solvent and steric effects, distinction between Primary, secondary and tertiary amines using Hinsberg's method and nitrous acid, Gabriel Phthalimide synthesis, Carbylamine reaction, Mannich reaction, Hoffmann's exhaustive methylation, Hofmann-elimination reaction and Cope elimination.

Diazonium Salts: Synthetic applications of diazonium salts including preparation of arenes, haloarenes, phenols, cyano and nitro compounds; Coupling reactions of diazonium salts (preparation of azo dyes).

Nitriles: Preparation using following reactions: Dehydration of amides and aldoximes, substitution reaction in alkyl halides and tosylates, from Grignard reagents and from dehydrogenation of primary amines. Properties: Physical properties, discussion on the following reactions with mechanism: Reaction with Grignard reagent, hydrolysis, addition reaction with  $\text{HX}$ ,  $\text{NH}_3$ , reaction with aqueous  $\text{ROH}$ , Reduction reactions-catalytic reduction and Stephen's reaction, Condensation reactions-Thorpe Nitrile Condensation.

Isonitriles: Preparation from the following reactions: Carbylamine reaction, substitution in alkyl halides and dehydrogenation of N-substituted formamides. Properties: Physical properties, discussion on the following reactions with mechanism: Hydrolysis, reduction, addition of  $\text{HX}$ ,  $\text{X}_2$  and sulphur, Grignard reaction, oxidation and rearrangement.

## **Practical component (30 Hours)**

**(Laboratory periods:15 classes of 2 hours each)**

1. Preparation of oximes for aldehydes/ketones (like benzaldehyde, ethyl methyl ketone, cyclohexanone etc.)
2. Preparation of semicarbazone derivatives for aldehydes/ketones (like benzaldehyde, ethyl methyl ketone, cyclohexanone etc.)
3. Hydrolysis of amides/esters.
4. Selective reduction of *m*-dinitrobenzene to *m*-nitroaniline.
5. Preparation of S-benzylisothiuronium salts for water soluble and water insoluble carboxylic acids.
6. Systematic qualitative analysis of the given organic compounds containing monofunctional groups (aromatic hydrocarbons, alcohols, phenol) and preparation of one suitable derivative.

Students should be exposed to preparative routes for the synthesis of 3,5-dinitrobenzoate, benzoates, acetate derivatives.

**Note:** The above derivatives should be prepared using 0.5-1.0 g of the organic compound. The solid samples must be collected and may be used for recrystallization, melting point and compound analysis.

### Essential/recommended readings

#### Theory:

1. Morrison, R. N., Boyd, R. N., Bhattacharjee, S.K. (2010), **Organic Chemistry**, 7<sup>th</sup> Edition, Dorling Kindersley (India) Pvt. Ltd., Pearson Education.
2. Finar, I.L. **Organic Chemistry** Volume 1, Dorling Kindersley (India) Pvt. Ltd., Pearson Education.
3. Finar, I.L. **Organic Chemistry** Volume 2, Dorling Kindersley (India) Pvt. Ltd., Pearson Education.
4. Solomons, T.W.G., Fryhle, C.B.; Snyder, S.A. (2017), **Organic Chemistry**, 12<sup>th</sup> Edition, Wiley.

#### Practical:

1. Vogel, A.I. (2012), **Quantitative Organic Analysis**, Part 3, Pearson Education.
2. Mann, F.G., Saunders, B.C. (2009), **Practical Organic Chemistry**, Pearson Education.
3. Furniss, B.S., Hannaford, A.J., Smith, P.W.G., Tatchell, A.R. (2012), **Vogel's Textbook of Practical Organic Chemistry**, 5<sup>th</sup> Edition, Pearson.
4. Ahluwalia, V.K., Dhingra, S. (2004), **Comprehensive Practical Organic Chemistry: Qualitative Analysis**, University Press.
5. Ahluwalia, V.K., Aggarwal, R. (2004), **Comprehensive Practical Organic Chemistry: Preparation and Quantitative Analysis**, University Press.
6. Pasricha, S., Chaudhary, A. (2021), **Practical Organic Chemistry: Volume–I**, I K International Publishing house Pvt. Ltd, New Delhi.
7. Pasricha, S., Chaudhary, A. (2021), **Practical Organic Chemistry: Volume–II**, I K International Publishing house Pvt. Ltd, New Delhi.

### **Suggestive Readings**

1. Mukherji, S.M., Singh, S.P. (2017), **Reaction Mechanism in Organic Chemistry**, Trinity Press.
2. Singh, J., Awasthi, S. K., Singh, Jaya, **Fundamentals of Organic Chemistry-III**, Pragati Prakashan (2023)
3. Carey, F.A., Sundberg, R. J. (2008), **Advanced Organic Chemistry: Part B: Reaction and Synthesis**, Springer.
4. Bruice, P.Y. (2015), **Organic Chemistry**, 3<sup>rd</sup> Edition, Pearson.
5. Patrick, G. (2003), **BIOS Instant Notes in Organic Chemistry**, Viva Books.

**Note:** Examination scheme and mode shall be as prescribed by the Examination Branch, University of Delhi, from time to time.