

DISCIPLINE-SPECIFIC ELECTIVE COURSE - 17 (DSE-17)

Reactive Intermediates of Organic Chemistry

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		
Reactive Intermediates of Organic Chemistry (DSE-17)	04	02	--	02	—	--

Learning Objectives:

To learn and understand the involvement of intermediates, their role in reaction mechanisms, to predict their behaviour, and to apply this knowledge to organic synthesis. Also, to learn and understand the orbital interactions (Woodward-Hoffmann rules) in concerted reactions.

Learning Outcomes

At the completion of this course, the students should be able to:

- Understand the structure-reactivity pattern of reactive intermediates involved in organic reactions.
- Write the mechanism of organic reactions involving reactive intermediates and apply these reactions in organic synthesis

SYLLABUS OF DSE 17

Unit 1: Carbocations and Carbanions: :

(Hours: 11)

Difference between classical and non-classical carbocations. Introduction of neighboring group participation (NGP), ion-pairs, molecular rearrangements in acyclic, monocyclic, and bicyclic systems, stability and reactivity of bridgehead carbocations.

Carbanions: Generation, structure and stability, ambident ions and their general reactions; HSAB principle and its applications.

Unit 2: Carbenes

(Hours: 7)

: Structure of carbenes, generation of carbenes, addition and insertion reactions, rearrangement reactions of carbenes such as Wolff rearrangement, generation and reactions of ylid by carbenoid decomposition. Examples of inter/intramolecular insertions.

Unit 3: Nitrenes and Ylide

(Hours: 7)

Structure of nitrene, generation and reactions of nitrene and related electron-deficient nitrogen intermediates, Curtius, Hoffmann, Schmidt, Beckmann rearrangement reactions.

Ylides: Chemistry of Phosphorus and Sulfur ylids – Wittig and related reactions, Peterson olefination.

Unit 4: Radicals:

(Hours: 5)

Generation of radical intermediates and their addition to: i) on alkenes, alkynes (inter & intramolecular) for C-C bond formation and Baldwin's rules. ii) fragmentation and rearrangements. Name reactions involving radical intermediates, such as Barton deoxygenation and decarboxylation, McMurry coupling.

Practical Component:

Separation, purification, and identification of binary mixtures of organic compounds (neutral and acidic; neutral and basic) using chemical methods and preparation of a suitable crystalline derivative for both the components. (Examples: (i) Benzoic acid/Any dicarboxylic acid and Naphthalene (ii) *p*-toluidine/*p*-anisidine and Naphthalene)

1. Two-step synthesis

2.1 Synthesis of triacetoxybenzene

Step 1: Synthesis of *p*-benzoquinone from hydroquinone using KBrO₃ and

Step 2: Synthesis of Triacetoxybenzene from *p*-benzoquinone.

2.2 Synthesis of *p*-acetamido benzene sulphonamide

Step 1: Synthesis of *p*-Acetamido benzene sulfonyl chloride from acetanilide and

Step 2: Synthesis of *p*-Acetamido benzene sulphonamide from *p*-Acetamido benzene sulfonyl chloride.

2.3 Synthesis of benzopinacolone

Step 1: Synthesis of benzopinacol from benzophenone

Step 2: Synthesis of benzopinacolone from benzopinacol via pinacol-pinacolone rearrangement.

Recommended Reference and Textbooks:

1. A. Carey and R. A. Sundberg, Advanced Organic Chemistry, Part B: Reactions and Synthesis, 5th edition, Springer, New York, **2007**.
2. Carruthers and I. Coldham, Modern Methods of Organic Synthesis, First South Asian Edition 2005, Cambridge University Press.
3. March and M. B. Smith, March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 6th Edition, Wiley, **2007**.

For Practicals

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, Fifth 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
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