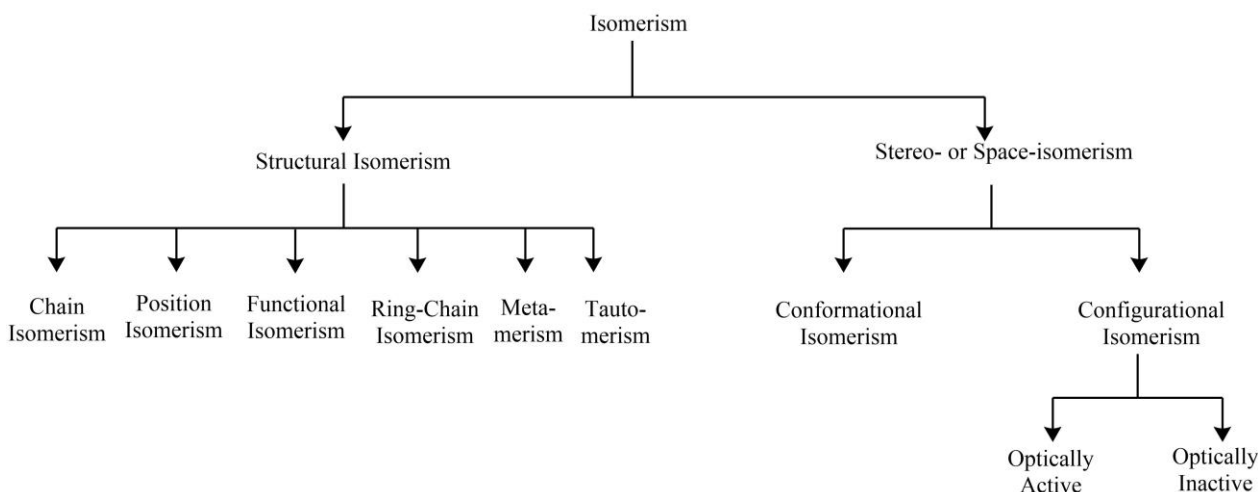


❖ Geometrical Isomerism in Alkenes and Oximes

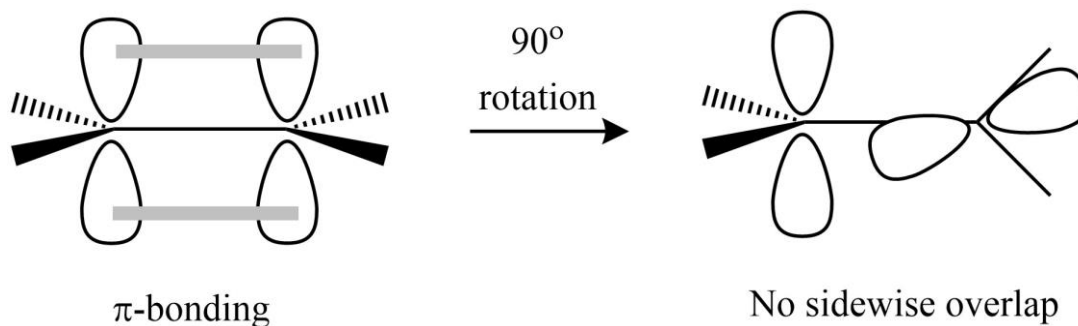
Before we study the geometrical isomerism in alkenes and oximes, we need to recall the general flow chart for different kinds of isomerisms first.



Since stereoisomerism can either be conformational or configurational, the latter possibility is of more importance in the case of oximes and alkenes as the rotation about the double bond is restricted. In this section, we will discuss the geometrical or configurational isomers of alkenes and oximes one by one.

➤ Geometrical Isomerism due to Double Bond

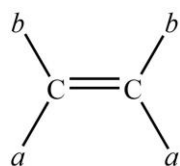
The carbon atom in alkenes is an sp^2 -hybridized one, and therefore, it has a half-filled atomic orbital perpendicular to the molecular plane. After using all its three hybrid orbitals for σ -bonding, the half-filled p_z orbital can be used for side-wise overlap to form a π -bond. Nevertheless, if we rotate one of the half-filled p_z by an angle of 90° , it will not be able to do so anymore.



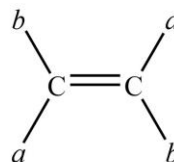
Hence, we can conclude that groups attached to sp^2 -hybridized carbon cannot be exchanged simply by rotating about the double bond as it is restricted by the orbital picture. This eliminates the possibility of conformational isomerism, and therefore, we are only left with the case of the configurational one.

➤ **Condition for Geometrical Isomerism arising from Double Bond**

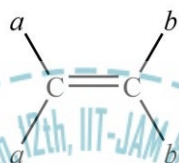
The presence of a double bond does not ensure the existence of geometrical isomers but some other conditions must also be satisfied. The primary condition is that two carbons of the double bond must have different kinds of substituents not only to carbons but to each other also.



cis-isomer



trans-isomer



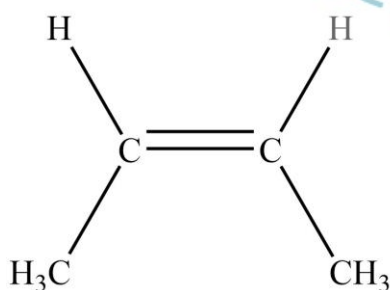
No geometrical isomerism possible

In other words, we can also say that no geometrical isomerism will be observed if one or both carbons carry the same kind of substituents.

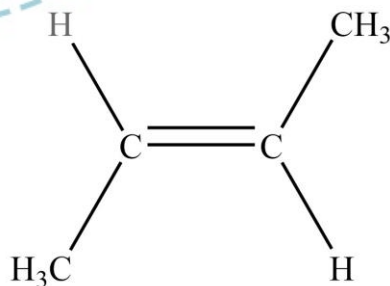
➤ **Geometrical Isomerism in Alkenes**

The geometrical isomers of alkenes are primarily labeled as cis-trans or Z-E types, depending upon the nature of the groups on each side of the double bond.

1. Geometrical isomerism in disubstituted alkenes (cis-trans nomenclature): If the alkene under consideration is a disubstituted one, we can label it as cis or trans isomer, depending upon their mutual orientation.



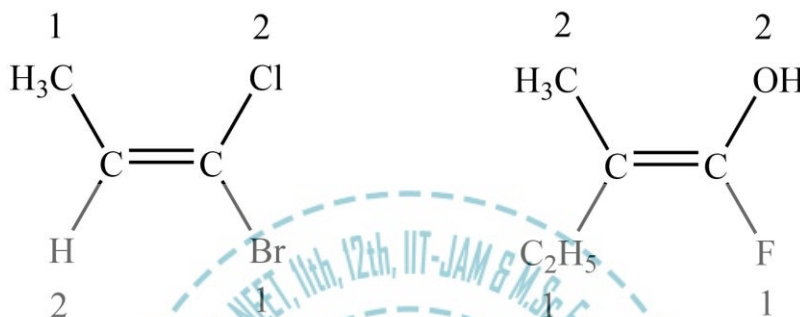
cis-isomer



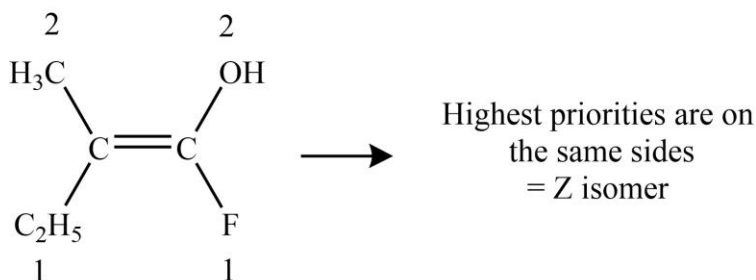
trans-isomer

2. Geometrical isomerism tri- or tetra-substituted alkenes (Z-E nomenclature): If the alkene under consideration is a tri- or tetra-substituted one, we cannot label it as cis or trans isomer, and therefore, we need to follow a special system for such compounds, called Z-E nomenclature. This system of nomenclature is also based upon the Chan-Ingold-Prelog system of priority assignment. The main postulates of the Z-E system of nomenclature are given below.

i) Priorities are assigned to different groups individually at both ends as per the sequence rule from the Chan-Ingold-Prelog system.



ii) Once the priorities are assigned, check if groups with higher priorities are on the same or opposite side of the double bond. If they are on the same side, the system is 'Z'; and if they are on the opposite side, the compound should be labeled as 'E' isomer.



3. Geometrical isomerism in compounds with two or more double bonds: If the alkene under consideration has two or more double bonds, the number of geometrical isomers depends not only upon the number of double bonds only but also upon whether the ends are symmetrical or not. This can be classified into two categories as discussed below.

i) When ends are unsymmetrical: If the ends of the alkenes are unsymmetrical, the total number of geometrical isomers (whether the number is odd or even) is given by the following equation.

$$N_{\text{isomer}} = 2^n \quad (7)$$

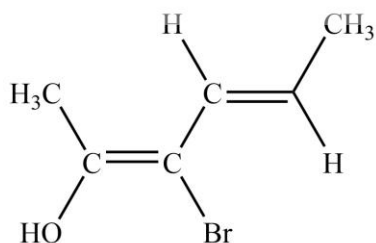
Where n represents the number of double bonds.

ii) When ends are symmetrical: If the ends of the alkenes are symmetrical, the total number of geometrical isomers (whether the number is odd or even) is given by the following equation.

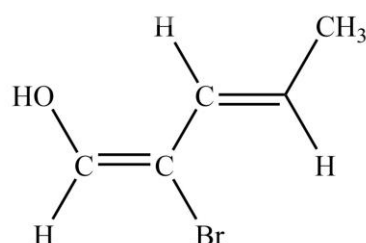
$$N_{\text{isomer}} = 2^{n-1} + 2^{(n/2-1)} \quad \text{if } n = \text{even} \quad (8)$$

$$N_{\text{isomer}} = 2^{n-1} + 2^{(n/2-1/2)} \quad \text{if } n = \text{odd} \quad (9)$$

Where n represents the number of double bonds.



(2Z,4E)-3-bromohexa-2,4-dien-2-ol

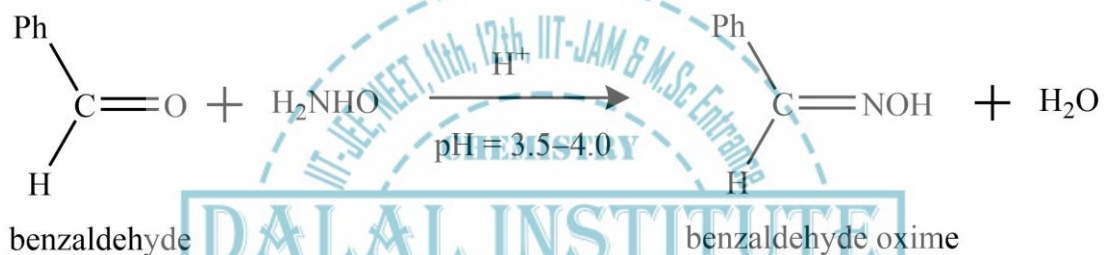
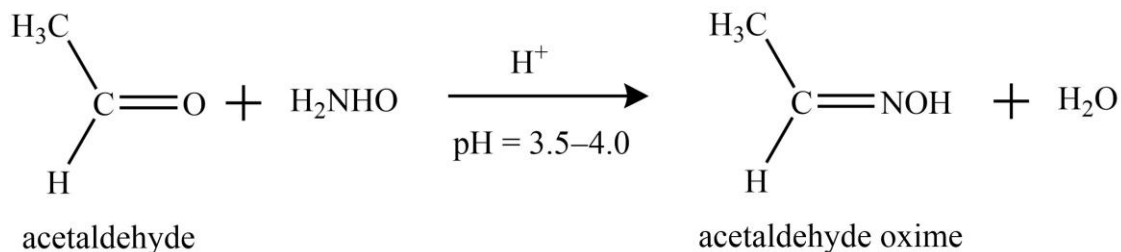


(1E,3E)-2-bromopenta-1,3-dien-1-ol

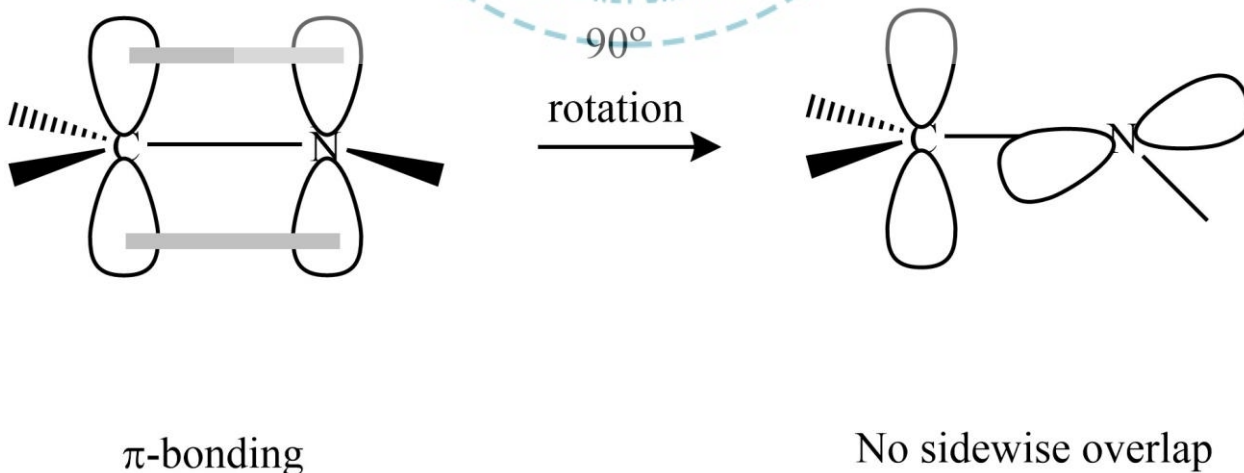
It is also obvious from the structures given above that besides tri- and tetra-substituted alkenes, the E-Z system of nomenclature also finds its application in compounds with many double bonds.

➤ **Geometrical Isomerism in Oximes**

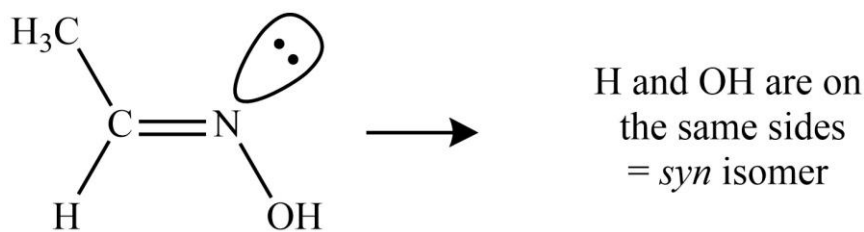
Oximes are compounds that have a carbon-nitrogen double bond, and can easily be prepared by treating hydroxylamine with ketones or aldehydes in somewhat acidic solutions.



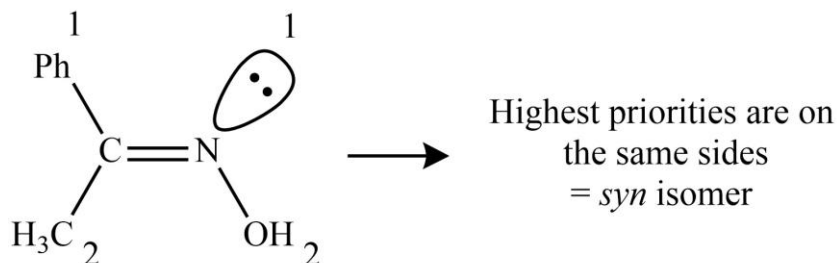
The carbon atom in oxime is an sp^2 -hybridized one, and therefore, it has a half-filled atomic orbital perpendicular to the molecular plane. After using all its three hybrid orbitals for σ -bonding, the half-filled p_z orbital can be used for side-wise overlap to form a π -bond. Nevertheless, if we rotate one of the half-filled p_z by an angle of 90° , it will not be able to do so anymore because the nitrogen atom is also sp^2 -hybridized with lone pair residing in one of the hybrid orbitals.



Now, if the H and OH are on the same side of the double bond, the compound will be called as *syn*; whereas if H and OH are on the opposite side of the double bond, the compound should be labeled as *anti*.



The nomenclature rule using H and OH is only applicable to aldoximes and cannot be applied to ketoximes because there is no H present. In such cases, we need to use priorities assignment using the Chan-Ingold-Prelog system with lone pair having the highest priority.



LEGAL NOTICE

This document is an excerpt from the book entitled “A Textbook of Organic Chemistry – Volume 1 by Mandeep Dalal”, and is the intellectual property of the Author/Publisher. The content of this document is protected by international copyright law and is valid only for the personal preview of the user who has originally downloaded it from the publisher’s website (www.dalalinstitute.com). Any act of copying (including plagiarizing its language) or sharing this document will result in severe civil and criminal prosecution to the maximum extent possible under law.



This is a low resolution version only for preview purpose. If you want to read the full book, please consider buying.

Buy the complete book with TOC navigation, high resolution images and no watermark.

Home

CLASSES

CSIR UGC – NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, IIT-JEE, NEET, 11th and 12th

Want to study chemistry for CSIR UGC – NET JRF + IIT-GATE; IIT-JAM + M.Sc Entrance; IIT-JEE + NEET + 11th +12th; and all other postgraduate, undergraduate & senior-secondary level examinations where chemistry is a paper?
[READ MORE](#)

BOOKS

Publications

Are you interested in books (Print and Ebook) published by Dalal Institute?
[READ MORE](#)

VIDEOS

Video Lectures

Want video lectures in chemistry for CSIR UGC – NET JRF + IIT-GATE; IIT-JAM + M.Sc Entrance; IIT-JEE + NEET + 11th +12th; and all other postgraduate, undergraduate & senior-secondary level examinations where chemistry is a paper?
[READ MORE](#)

Postgraduate Level

Senior-Secondary Level

Undergraduate Level

CSIR UGC – NET JRF & IIT-GATE

First Chemistry Batch
(1st January – 31st May)

Second Chemistry Batch
(1st July – 30th November)

11TH, 12TH, NEET & IIT-JEE

First Chemistry Batch
(1st April – 31st August)

Second Chemistry Batch
(1st October – 28th February)

M.SC ENTRANCE & IIT-JAM

First Chemistry Batch
(1st February – 30th June)

Second Chemistry Batch
(1st August – 31st December)

Regular Program

Online Course

Result

Regular Program

Online Course

Result

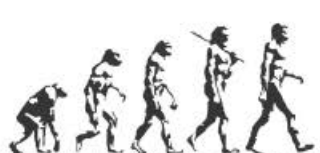
Regular Program

Online Course

Result

Join the revolution by becoming a part of our community and get all of the member benefits like downloading any PDF document for your personal preview.

[Sign Up](#)



JOIN THE REVOLUTION FROM BEAST TO

BUDDHA

D DALAL INSTITUTE

.....Chemical Science Demystified.....

Main Market, Sector 14, Rohtak, Haryana 124001, India
(+91-9802825820, info@dalalinstitute.com)
www.dalalinstitute.com

..... India's Best Coaching Center for Academic and Competitive Chemistry Exams
(CSIR UGC – NET JRF + IIT-GATE; IIT-JAM + M.Sc Entrance; IIT-JEE + NEET + 11th +12th; and all other postgraduate, undergraduate & senior-secondary level examinations where chemistry is a paper)

International
Edition



A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

DALAL INSTITUTE

Table of Contents

CHAPTER 1	11
Nature of Bonding in Organic Molecules	11
❖ Delocalized Chemical Bonding	11
❖ Conjugation	14
❖ Cross Conjugation	16
❖ Resonance	18
❖ Hyperconjugation	27
❖ Tautomerism	31
❖ Aromaticity in Benzenoid and Nonbenzenoid Compounds	33
❖ Alternant and Non-Alternant Hydrocarbons	35
❖ Huckel's Rule: Energy Level of π -Molecular Orbitals	37
❖ Annulenes	44
❖ Antiaromaticity	46
❖ Homoaromaticity	48
❖ PMO Approach	50
❖ Bonds Weaker Than Covalent	58
❖ Addition Compounds: Crown Ether Complexes and Cryptands, Inclusion Compounds, Cyclodextrins	65
❖ Catenanes and Rotaxanes	75
❖ Problems	79
❖ Bibliography	80
CHAPTER 2	81
Stereochemistry	81
❖ Chirality	81
❖ Elements of Symmetry	86
❖ Molecules with More Than One Chiral Centre: Diastereomerism	90
❖ Determination of Relative and Absolute Configuration (Octant Rule Excluded) with Special Reference to Lactic Acid, Alanine & Mandelic Acid	92
❖ Methods of Resolution	102
❖ Optical Purity	104
❖ Prochirality	105
❖ Enantiotopic and Diastereotopic Atoms, Groups and Faces	107
❖ Asymmetric Synthesis: Cram's Rule and Its Modifications, Prelog's Rule	113
❖ Conformational Analysis of Cycloalkanes (Upto Six Membered Rings)	116
❖ Decalins	122
❖ Conformations of Sugars	126
❖ Optical Activity in Absence of Chiral Carbon (Biphenyls, Allenes and Spiranes)	132
❖ Chirality Due to Helical Shape	137
❖ Geometrical Isomerism in Alkenes and Oximes	140
❖ Methods of Determining the Configuration	146

❖ Problems.....	151
❖ Bibliography.....	152
CHAPTER 3.....	153
Reaction Mechanism: Structure and Reactivity	153
❖ Types of Mechanisms.....	153
❖ Types of Reactions	156
❖ Thermodynamic and Kinetic Requirements.....	159
❖ Kinetic and Thermodynamic Control	161
❖ Hammond's Postulate.....	163
❖ Curtin-Hammett Principle	164
❖ Potential Energy Diagrams: Transition States and Intermediates	166
❖ Methods of Determining Mechanisms.....	168
❖ Isotope Effects	172
❖ Hard and Soft Acids and Bases.....	174
❖ Generation, Structure, Stability and Reactivity of Carbocations, Carbanions, Free Radicals, Carbenes and Nitrenes.....	176
❖ Effect of Structure on Reactivity	200
❖ The Hammett Equation and Linear Free Energy Relationship.....	203
❖ Substituent and Reaction Constants.....	209
❖ Taft Equation.....	215
❖ Problems.....	219
❖ Bibliography.....	220
CHAPTER 4.....	221
Carbohydrates	221
❖ Types of Naturally Occurring Sugars	221
❖ Deoxy Sugars	227
❖ Amino Sugars.....	229
❖ Branch Chain Sugars	230
❖ General Methods of Determination of Structure and Ring Size of Sugars with Particular Reference to Maltose, Lactose, Sucrose, Starch and Cellulose.....	231
❖ Problems.....	239
❖ Bibliography.....	240
CHAPTER 5.....	241
Natural and Synthetic Dyes	241
❖ Various Classes of Synthetic Dyes Including Heterocyclic Dyes	241
❖ Interaction Between Dyes and Fibers	245
❖ Structure Elucidation of Indigo and Alizarin	247
❖ Problems.....	252
❖ Bibliography.....	253
CHAPTER 6.....	254
Aliphatic Nucleophilic Substitution	254
❖ The S_N2 , S_N1 , Mixed S_N1 and S_N2 , S_Ni , S_N1' , S_N2' , S_Ni' and SET Mechanisms.....	254

❖ The Neighbouring Group Mechanisms.....	263
❖ Neighbouring Group Participation by π and σ Bonds	265
❖ Anchimeric Assistance	269
❖ Classical and Nonclassical Carbocations	272
❖ Phenonium Ions	283
❖ Common Carbocation Rearrangements.....	284
❖ Applications of NMR Spectroscopy in the Detection of Carbocations	286
❖ Reactivity – Effects of Substrate Structure, Attacking Nucleophile, Leaving Group and Reaction Medium	288
❖ Ambident Nucleophiles and Regioselectivity	294
❖ Phase Transfer Catalysis.....	297
❖ Problems.....	300
❖ Bibliography	301
CHAPTER 7	302
Aliphatic Electrophilic Substitution	302
❖ Bimolecular Mechanisms – SE_2 and SE_i	302
❖ The SE_1 Mechanism	305
❖ Electrophilic Substitution Accompanied by Double Bond Shifts	307
❖ Effect of Substrates, Leaving Group and the Solvent Polarity on the Reactivity	308
❖ Problems.....	310
❖ Bibliography	311
CHAPTER 8	312
Aromatic Electrophilic Substitution	312
❖ The Arenium Ion Mechanism	312
❖ Orientation and Reactivity	314
❖ Energy Profile Diagrams	316
❖ The Ortho/Para Ratio.....	317
❖ <i>ipso</i> -Attack	319
❖ Orientation in Other Ring Systems	320
❖ Quantitative Treatment of Reactivity in Substrates and Electrophiles	321
❖ Diazonium Coupling.....	325
❖ Vilsmeier Reaction	326
❖ Gattermann-Koch Reaction	327
❖ Problems.....	329
❖ Bibliography	330
CHAPTER 9	331
Aromatic Nucleophilic Substitution	331
❖ The $ArSN_1$, $ArSN_2$, Benzyne and S_RN_1 Mechanisms.....	331
❖ Reactivity – Effect of Substrate Structure, Leaving Group and Attacking Nucleophile.....	336
❖ The von Richter, Sommelet-Hauser, and Smiles Rearrangements	339
❖ Problems.....	343
❖ Bibliography	344

CHAPTER 10	345
Elimination Reactions	345
❖ The E ₂ , E ₁ and E ₁ CB Mechanisms	345
❖ Orientation of the Double Bond.....	348
❖ Reactivity – Effects of Substrate Structures, Attacking Base, the Leaving Group and The Medium	352
❖ Mechanism and Orientation in Pyrolytic Elimination.....	355
❖ Problems.....	358
❖ Bibliography.....	359
CHAPTER 11	360
Addition to Carbon-Carbon Multiple Bonds	360
❖ Mechanistic and Stereochemical Aspects of Addition Reactions Involving Electrophiles, Nucleophiles and Free Radicals.....	360
❖ Regio- and Chemoselectivity: Orientation and Reactivity	370
❖ Addition to Cyclopropane Ring	374
❖ Hydrogenation of Double and Triple Bonds	375
❖ Hydrogenation of Aromatic Rings.....	377
❖ Hydroboration	378
❖ Michael Reaction.....	379
❖ Sharpless Asymmetric Epoxidation	380
❖ Problems.....	382
❖ Bibliography	383
CHAPTER 12	384
Addition to Carbon-Hetero Multiple Bonds	384
❖ Mechanism of Metal Hydride Reduction of Saturated and Unsaturated Carbonyl Compounds, Acids, Esters and Nitriles	384
❖ Addition of Grignard Reagents, Organozinc and Organolithium Reagents to Carbonyl and Unsaturated Carbonyl Compounds.....	400
❖ Wittig Reaction.....	406
❖ Mechanism of Condensation Reactions Involving Enolates: Aldol, Knoevenagel, Claisen, Mannich, Benzoin, Perkin and Stobbe Reactions	411
❖ Hydrolysis of Esters and Amides.....	433
❖ Ammonolysis of Esters.....	437
❖ Problems.....	439
❖ Bibliography.....	440
INDEX	441



Mandeep Dalal

(M.Sc, Ph.D, CSIR UGC – NET JRF, IIT-GATE)

Founder & Educator, Dalal Institute

E-Mail: dr.mandeep.dalal@gmail.com

www.mandeepdalal.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder of "Dalal Institute" (India's best coaching centre for academic and competitive chemistry exams), the organization that is committed to revolutionize the field of school-level and higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK), and Springer (Netherlands).

Other Books by the Author

A TEXTBOOK OF INORGANIC CHEMISTRY – VOLUME I, II, III, IV

A TEXTBOOK OF PHYSICAL CHEMISTRY – VOLUME I, II, III, IV

A TEXTBOOK OF ORGANIC CHEMISTRY – VOLUME I, II, III, IV

ISBN: 978-81-952427-3-3



9 788195 242733 >

MRP: Rs 800.00

**D DALAL
INSTITUTE**

..... Chemical Science Demystified

Main Market, Sector 14, Rohtak, Haryana 124001, India

(info@dalalinstitute.com, +91-9802825820)

www.dalalinstitute.com