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 sp²-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 pz orbital can be used for side-wise overlap to form a π-bond. Nevertheless, if we rotate one of the half-filled pz by an angle of 90°, it will not be able to do so anymore.

Hence, we can conclude that groups attached to sp²-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.

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-trans isomers of disubstituted alkenes](image)
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.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{Cl} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{Br} \\
2 & \quad 1
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{OH} \\
\text{C} & \quad \text{C} \\
\text{C}_2\text{H}_5 & \quad \text{F} \\
1 & \quad 1
\end{align*}
\]

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.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{H} \\
& \quad \text{Br} \\
2 & \quad 1
\end{align*}
\]

\[
\begin{align*}
& \quad \text{C} \\
\text{C}_2\text{H}_5 & \quad \text{F} \\
1 & \quad 1
\end{align*}
\]

Highest priorities are on the opposite sides
\(= E \) isomer

Highest priorities are on the same sides
\(= Z \) 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.

\[ N_{\text{isomer}} = 2^n \]  \hspace{1cm} (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.

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

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

Where \( n \) represents the number of double bonds.

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.

\[ \text{H}_3\text{C} - \text{C} = \text{O} + \text{H}_2\text{NHO} \xrightarrow{\text{H}^+ \text{ pH = 3.5–4.0}} \text{H}_3\text{C} - \text{C} = \text{NOH} + \text{H}_2\text{O} \]

acetaldehyde  
acetaldehyde oxime

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 \( \sigma \)-bonding, the half-filled \( p_z \) orbital can be used for side-wise overlap to form a \( \pi \)-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.

\( \pi \)-bonding  
No sidewise overlap
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.
Want to study chemistry for CSIR UGC - NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, IIT-JEE, NEET, 11th and 12th?

Are you interested in books (Print and Ebook) published by Dalal Institute?

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?

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
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
❖ Hückel’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, Cycloextrins ...... 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
CHAPTER 3 ............................................................................................................................................... 153
Reaction Mechanism: Structure and Reactivity .................................................................................. 153
❖ Problems ........................................................................................................................................... 151
❖ Bibliography ..................................................................................................................................... 152
❖ 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 SN$_2$, SN$_1$, Mixed SN$_1$ and SN$_2$, SN$_i$, SN$_{1'}$, SN$_2'$, SN$_{1''}$ and SET Mechanisms .......... 254
The Neighbouring Group Mechanisms ......................................................................................... 263
Neighbouring Group Participation by π and σ Bonds ................................................................. 2 65
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 – SE₂ and SE₁ ....................................................................................... 302
The SE₁ 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
ipso-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 ArSN₁, ArSN₂, Benzyne and SrN₁ 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
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