

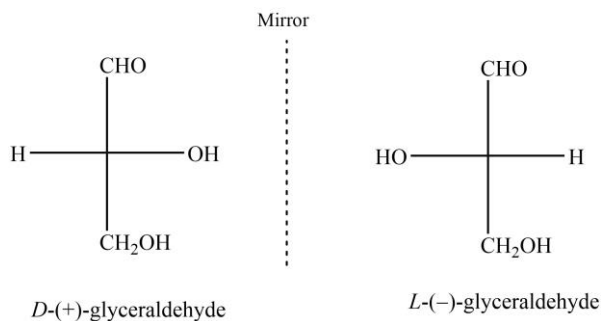
## ❖ Determination of Relative and Absolute Configuration (Octant Rule Excluded) with Special Reference to Lactic Acid, Alanine & Mandelic Acid

The three-dimensional character of organic molecules can be labeled absolutely or relative to some reference compound. In this section, we will study the relative and absolute configuration of various organic molecules with special reference to lactic acid, alanine & mandelic acid.

### ➤ Relative Configuration

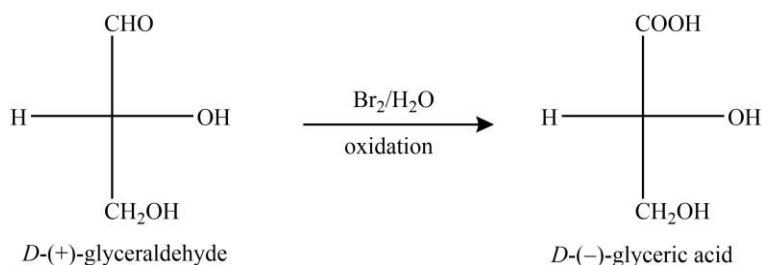
The relative configuration of an organic stereoisomer may simply be defined as the correlation between two enantiomers even if the absolute configuration is unknown.

The elucidation of the absolute configuration of a chiral molecule was not possible before 1951 due to the absence of any such method. Therefore, the assignment of various groups in space was carried out relative to the groups of a standard reference compound.



One of the most popular reference compounds for the determination of stereochemical notation of chiral organic molecules is glyceraldehyde.

**General route to assign D-L nomenclature:** All the compounds that can be obtained or transformed to *D*-(+)-glyceraldehyde are said to belong to *D*-series, whereas all the compounds that can be obtained or transformed to *L*-(-)-glyceraldehyde are said to belong to *L*-series. These predictions find their base in the fact that if no bond breaking-formation occurs at the chiral center, the configuration is retained. For instance, consider the case of (-)-glyceric acid.

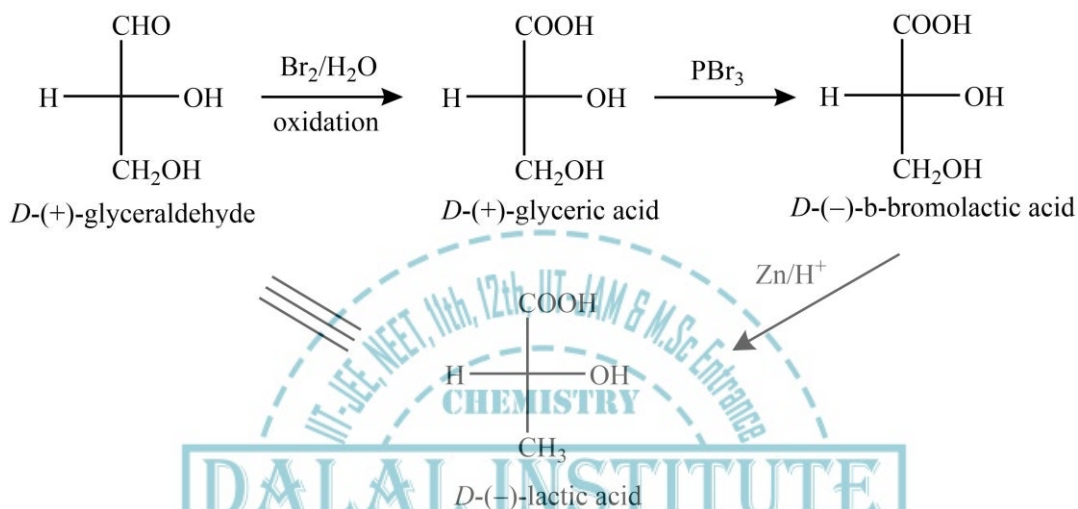


Since it can be obtained from *D*-(+)-glyceraldehyde, its name should be *D*-(-)-glyceric acid even though it is laevorotatory.

**Determination of Relative Configuration Lactic Acid, Alanine & Mandelic Acid:** The configuration of lactic acid, alanine & mandelic acid relative to glyceraldehyde (i.e., D-L configurations) can be obtained using the following chemical routes.

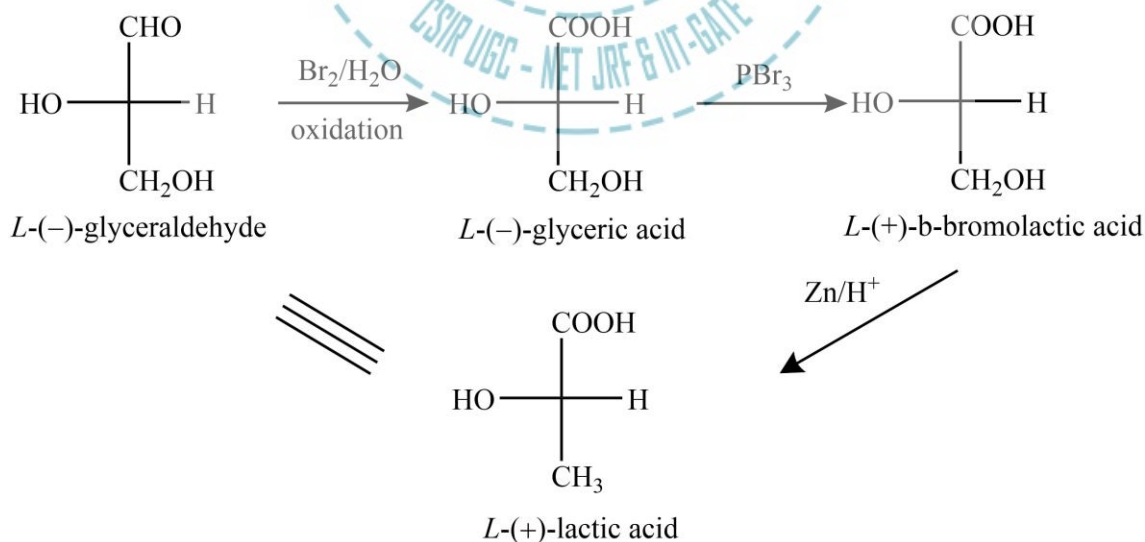
i) *Determination of relative configuration of lactic acid:*

As we know that lactic acid is optically active, and therefore, is bound to exist as enantiomeric pair. The configuration of one enantiomer relative to the glyceraldehyde can be obtained as given below.



It is obvious that, unlike D-(+)-glyceraldehyde, the D configuration of lactic acid is found to be levorotatory.

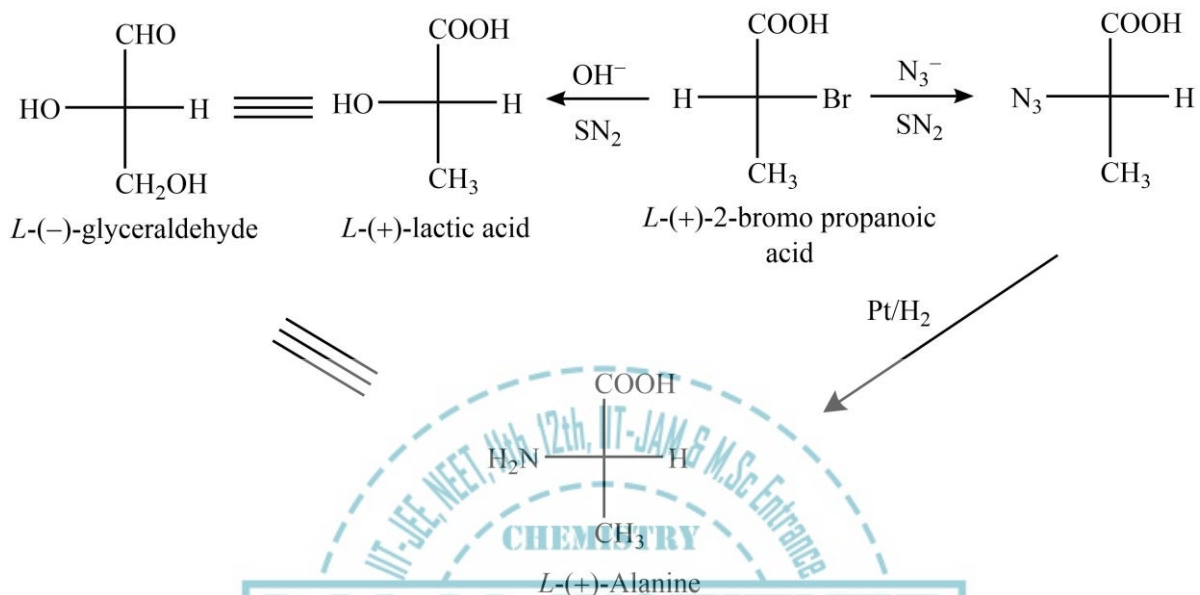
Since lactic acid is optically active, the configuration of mirror image isomer relative to the glyceraldehyde can be obtained as given below.



It is obvious that, unlike L-(-)-glyceraldehyde, the L configuration of lactic acid is found to be dextrorotatory.

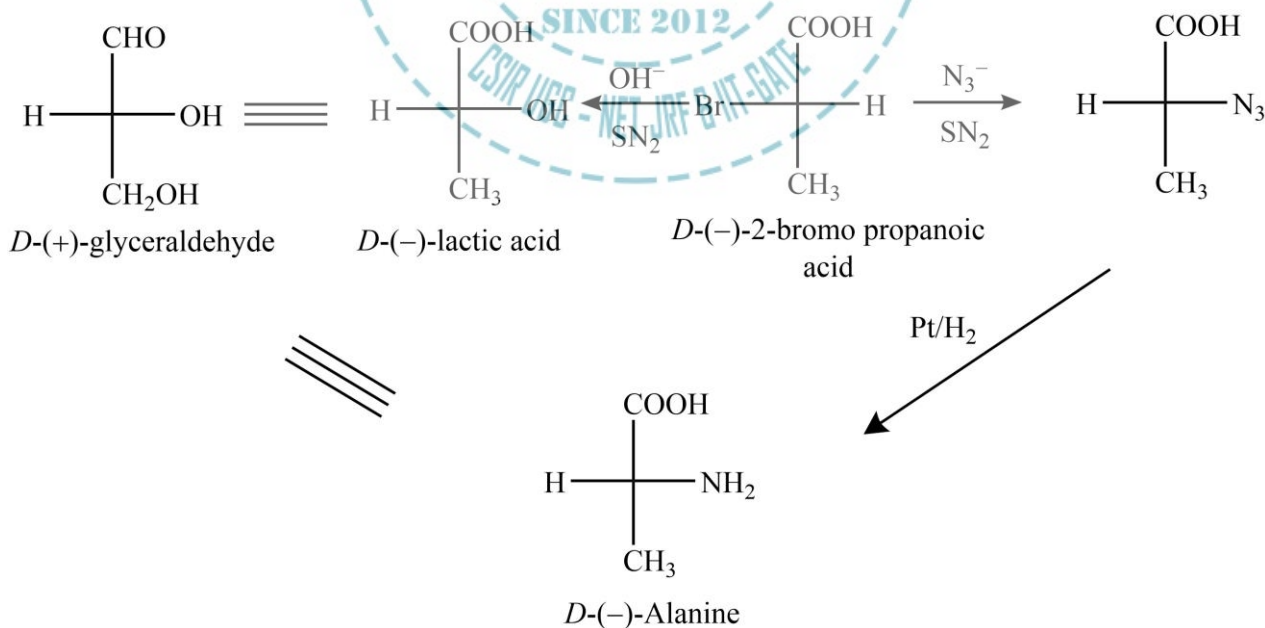
ii) Determination of relative configuration of alanine:

As we know that alanine is optically active, and therefore, is bound to exist as enantiomeric pair. The configuration of one enantiomer relative to the glyceraldehyde can be obtained as given below.



It is obvious that, unlike *L*-(-)-glyceraldehyde, the *L* configuration of alanine is found to be dextrorotatory.

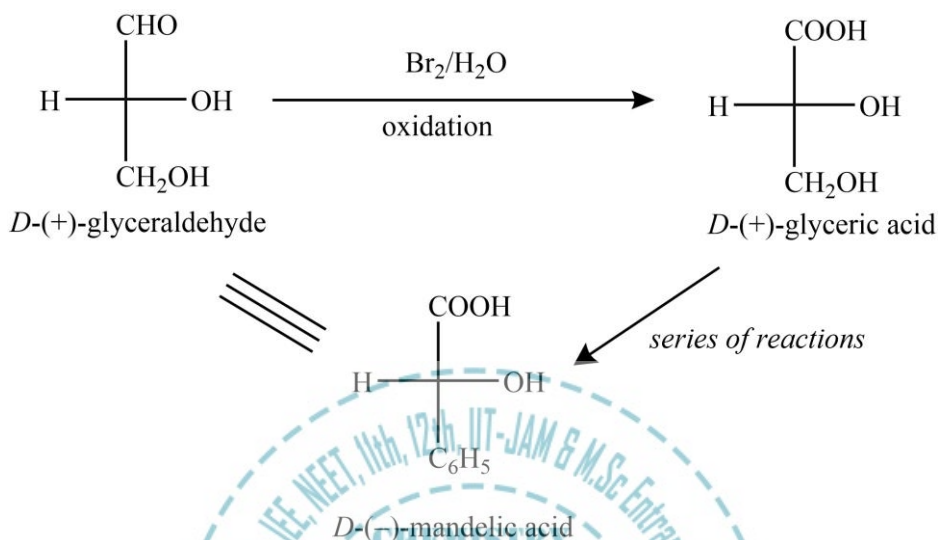
Since alanine is optically active, the configuration of mirror image isomer relative to the glyceraldehyde can be obtained as given below.



It is obvious that, unlike *D*-(+)-glyceraldehyde, the *D* configuration of alanine is found to be levorotatory.

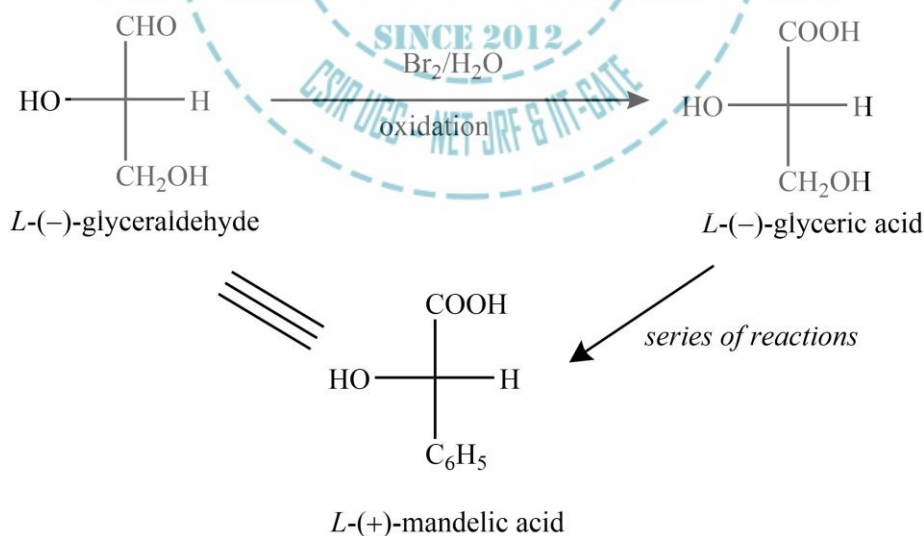
## iii) Determination of relative configuration of mandelic acid:

As we know that alanine is optically active, and therefore, is bound to exist as enantiomeric pair. The configuration of one enantiomer relative to the mandelic acid can be obtained as given below.



It is obvious that, unlike D-(+)-glyceraldehyde, the D configuration of mandelic acid is found to be levorotatory.

Since mandelic acid is optically active, the configuration of mirror-image isomer relative to the glyceraldehyde can be obtained as given below.



It is obvious that, unlike L-(-)-glyceraldehyde, the L configuration of mandelic acid is found to be dextrorotatory.

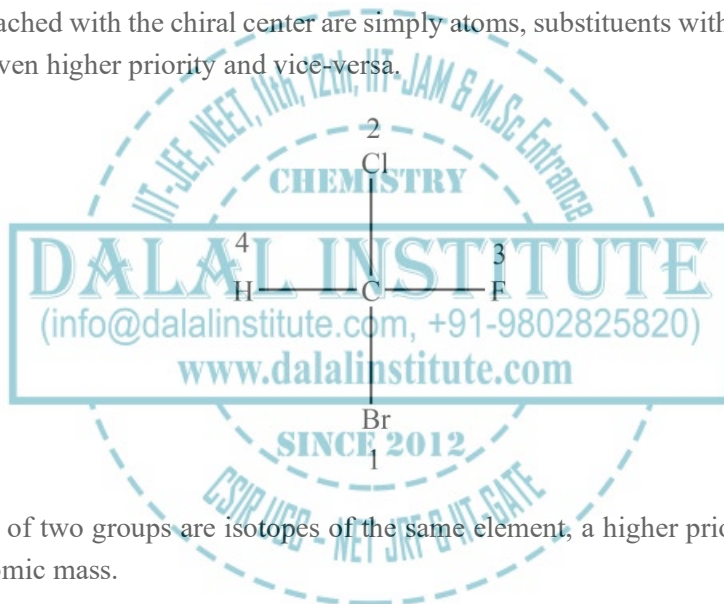
➤ **Absolute Configuration**

The absolute configuration of a particular stereoisomer of an organic molecule may simply be defined as the actual arrangement of atoms or groups in space.

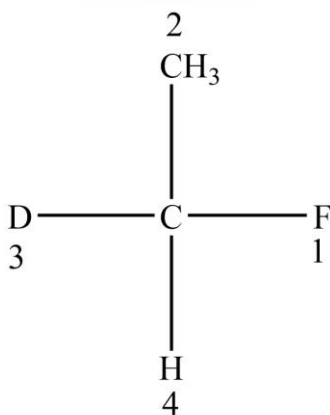
Since the D-L system of stereoisomeric nomenclature was relative and difficult to apply, a more simplistic and robust approach was needed. The problem was solved by R. S. Chan, C. K. Ingold and V. Prelog by developing a nomenclature method that was free from limitations posed by the relative approach. This nomenclature technique is generally called as Chan-Ingold-Prelog or R-S system. The whole procedure includes two steps; the first is the priority assignment of different groups and the second step involves the assignment of absolute configuration.

**Rules for priority assignment of different groups:** A priority sequence of (1), (2), (3), and (4) is assigned to all the four groups attached to the chiral center using the following set of rules.

i) If the substituents attached with the chiral center are simply atoms, substituents with a higher atomic number of bonded atoms are given higher priority and vice-versa.



ii) If the bonded atoms of two groups are isotopes of the same element, a higher priority will be given to the group with a higher atomic mass.

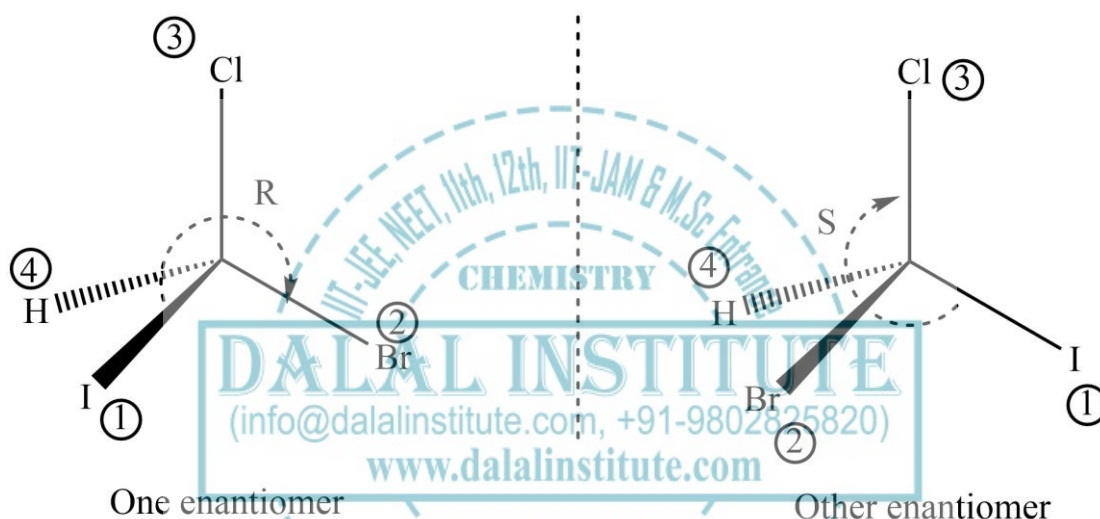




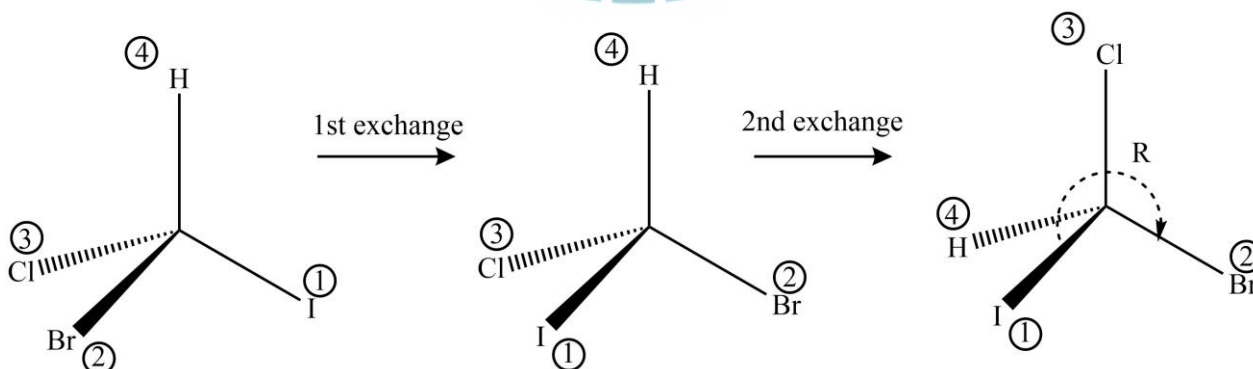
**Assignment of absolute configuration:** Since two of the most popular depiction of three-dimensional molecules on two-dimensional paper are Flying-Wedge and Fischer projection, we will study the determination of absolute configuration for both.

i) *Assignment of absolute configuration in Flying-Wedge representation:*

After assigning priorities to different groups the molecule is oriented in space such that the group of lowest priority goes away from the observer. Now if the tracking of decreasing priority of the remaining three groups comes gives rise to clockwise flight, the molecules should be labeled as R. However, if the tracking of decreasing priority of the remaining three groups comes gives rise to anticlockwise flight, the molecules should be labeled as S.



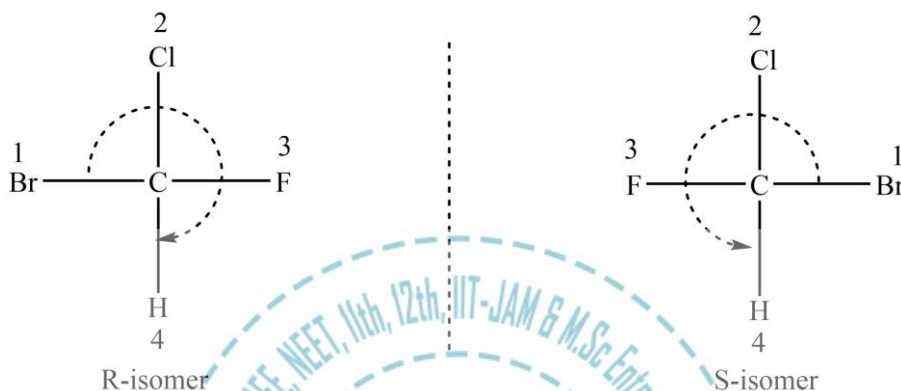
Furthermore, if the group with the lowest priority is toward the observer or in the plane of the paper, carry out an even number of exchanges to through the lowest-priority-group away from the observer before the R-S labeling.



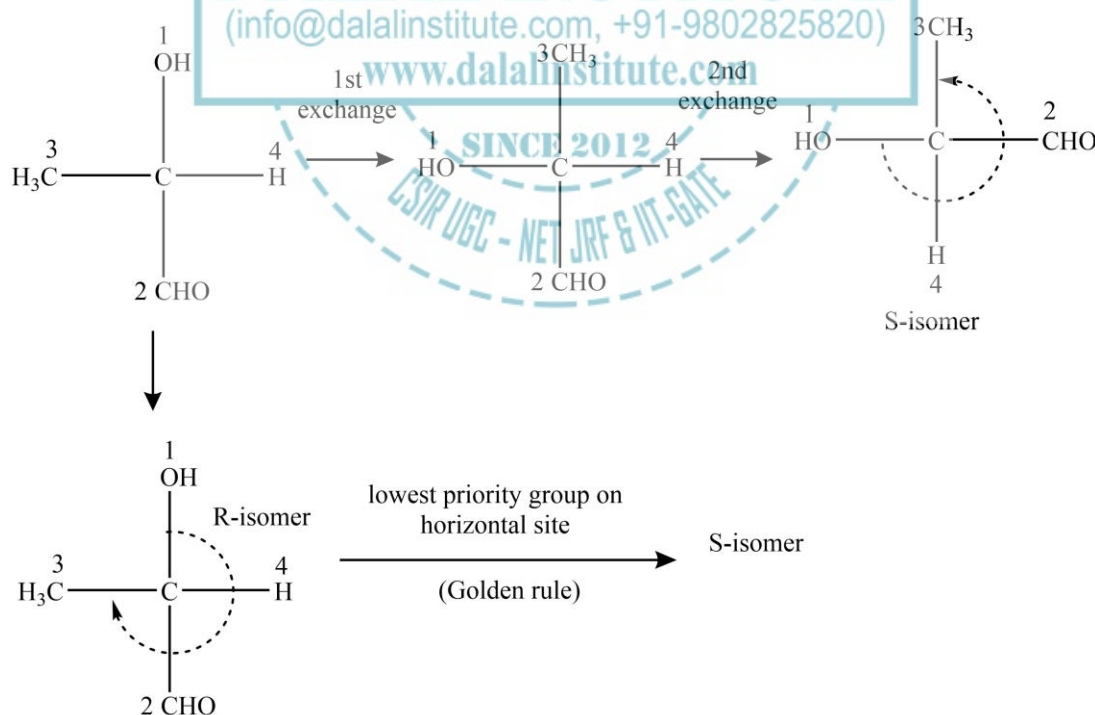
It is also worthy to note that the actual stereochemical notation can also be found by reverting the answer directly if the group with the lowest priority is toward the observer.

ii) Assignment of absolute configuration in Fischer representation:

After assigning priorities to different groups the Fischer projection of the molecule is transformed to an identical one by an even number of exchanges so that the group of lowest priority is at the vertical position. Now if the tracking of decreasing priority of the remaining three groups comes gives rise to clockwise flight, the molecules should be labeled as R. However, if the tracking of decreasing priority of the remaining three groups comes gives rise to anticlockwise flight, the molecules should be labeled as S.



Furthermore, if the group with the lowest priority is already located at the vertical position, nothing is needed but priority tracking only.



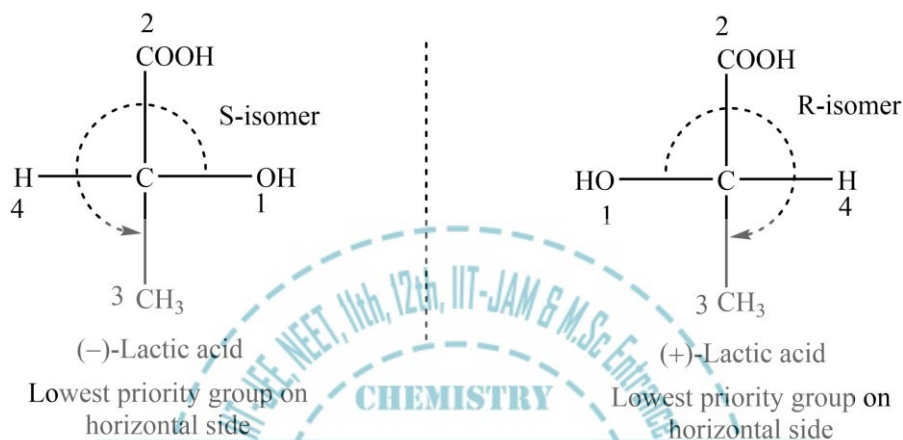
It is worthy to note that the actual stereochemical notation can also be found by reverting the answer directly if the group with the lowest priority is at the horizontal position, which is also called as the golden rule.



**Determination of Absolute Configuration Lactic Acid, Alanine & Mandelic Acid:** The absolute configuration of lactic acid, alanine & mandelic acid (i.e., R-S configurations) can be obtained using the following chemical routes.

*i) Determination of absolute configuration of Lactic Acid:*

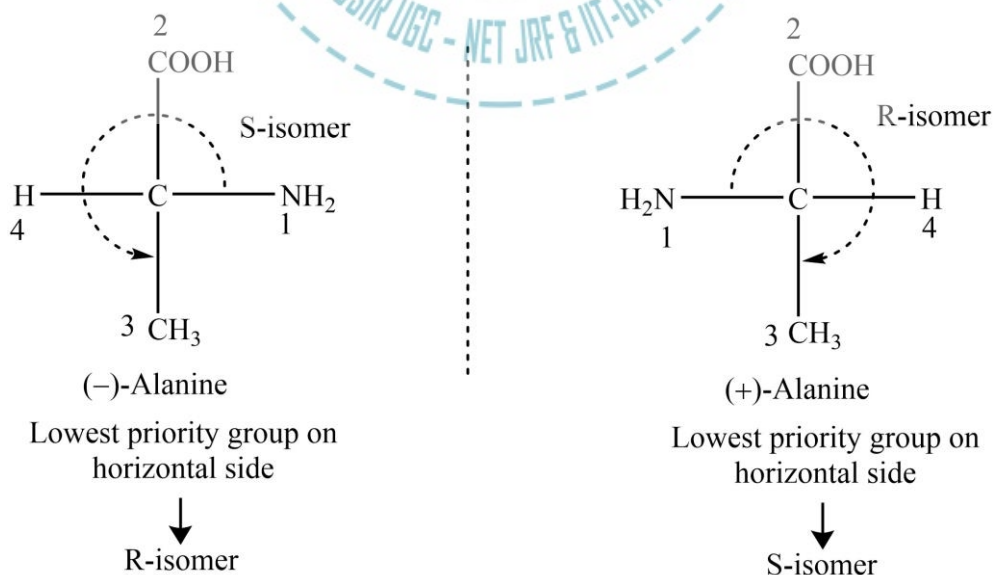
As we know that lactic acid is optically active, and therefore, is bound to exist as enantiomeric pair. The absolute configuration of both enantiomers can be obtained as given below.



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

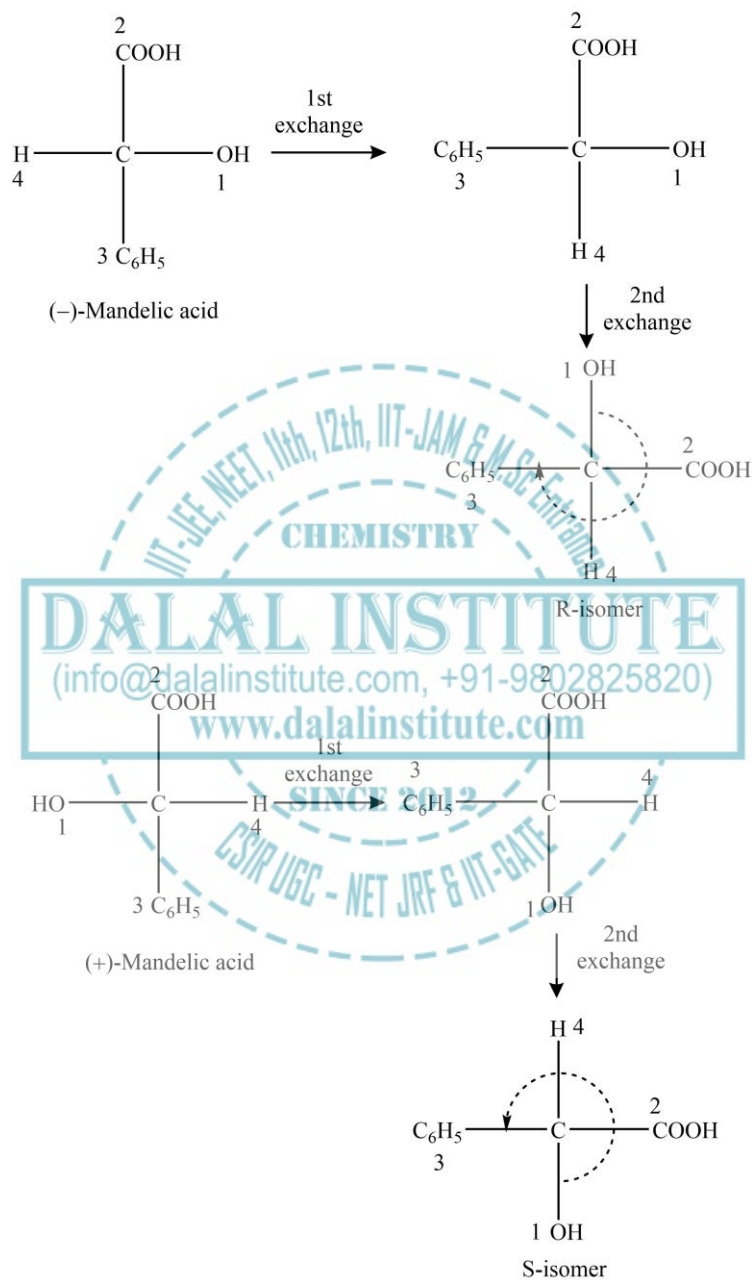
*ii) Determination of absolute configuration of alanine:*

As we know that alanine is optically active, and therefore, is bound to exist as enantiomeric pair. The absolute configuration of both enantiomers can be obtained as given below.



## ii) Determination of absolute configuration of Mandelic acid:

As we know that mandelic acid is optically active, and therefore, is bound to exist as enantiomeric pair. The absolute configuration of both enantiomers can be obtained as given below.



It is also worthy to note that *R*- and *S*-configuration are not bound to be dextro- or levorotatory in particular; in other words, *R*-configuration can be dextro-, as well as levorotatory. If *R* is dextro-, *S*-configuration will be levorotatory, and if *R* is levorotatory, *S*-configuration will be dextrorotatory.

## 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](http://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

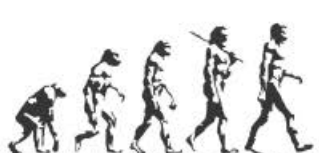
Regular Program

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](mailto:info@dalalinstitute.com))  
[www.dalalinstitute.com](http://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

<b>CHAPTER 1</b> .....	<b>11</b>
<b>Nature of Bonding in Organic Molecules</b> .....	<b>11</b>
❖ 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 $\pi$ -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
<b>CHAPTER 2</b> .....	<b>81</b>
<b>Stereochemistry</b> .....	<b>81</b>
❖ 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
<b>CHAPTER 3.....</b>	<b>153</b>
<b>Reaction Mechanism: Structure and Reactivity .....</b>	<b>153</b>
❖ 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
<b>CHAPTER 4.....</b>	<b>221</b>
<b>Carbohydrates .....</b>	<b>221</b>
❖ 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
<b>CHAPTER 5.....</b>	<b>241</b>
<b>Natural and Synthetic Dyes .....</b>	<b>241</b>
❖ 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
<b>CHAPTER 6.....</b>	<b>254</b>
<b>Aliphatic Nucleophilic Substitution .....</b>	<b>254</b>
❖ 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 $\pi$ and $\sigma$ 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
<b>CHAPTER 7 .....</b>	<b>302</b>
<b>Aliphatic Electrophilic Substitution .....</b>	<b>302</b>
❖ 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
<b>CHAPTER 8 .....</b>	<b>312</b>
<b>Aromatic Electrophilic Substitution .....</b>	<b>312</b>
❖ 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
<b>CHAPTER 9 .....</b>	<b>331</b>
<b>Aromatic Nucleophilic Substitution .....</b>	<b>331</b>
❖ 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



<b>CHAPTER 10 .....</b>	<b>345</b>
<b>Elimination Reactions .....</b>	<b>345</b>
❖ The E <sub>2</sub> , E <sub>1</sub> and E <sub>1</sub> 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
<b>CHAPTER 11 .....</b>	<b>360</b>
<b>Addition to Carbon-Carbon Multiple Bonds .....</b>	<b>360</b>
❖ 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
<b>CHAPTER 12 .....</b>	<b>384</b>
<b>Addition to Carbon-Hetero Multiple Bonds.....</b>	<b>384</b>
❖ 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
<b>INDEX.....</b>	<b>441</b>



*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**