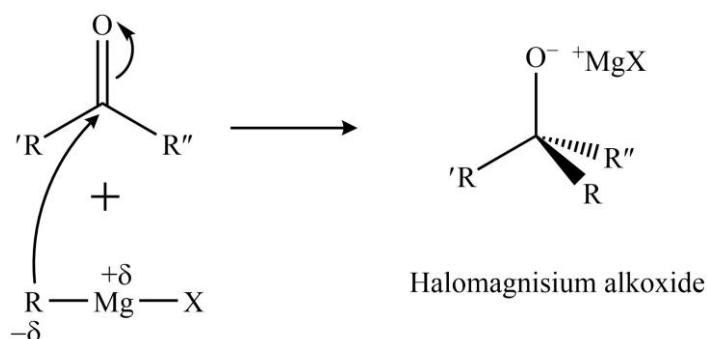


## ❖ Addition of Grignard Reagents, Organozinc and Organolithium Reagents to Carbonyl and Unsaturated Carbonyl Compounds

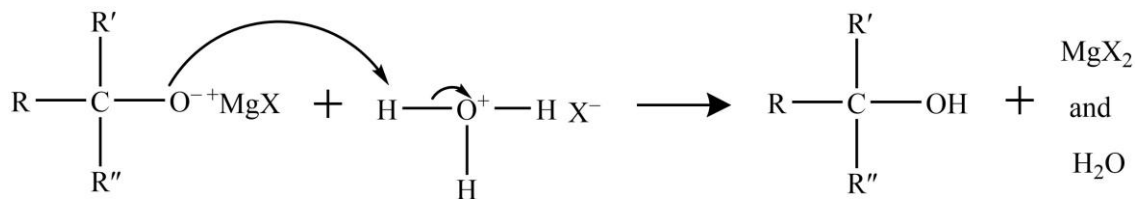
As far as the addition to carbon-heteroatom multiple bonds is concerned, three organometallic reagents are much more important than the others; organomagnesium (Grignard reagents), organozinc, and organolithium compounds. In this section, we will discuss the addition of these three types of reagents to carbonyl and unsaturated carbonyl compounds.

### ➤ Addition of Grignard Reagents to Carbonyl and Unsaturated Carbonyl Compounds

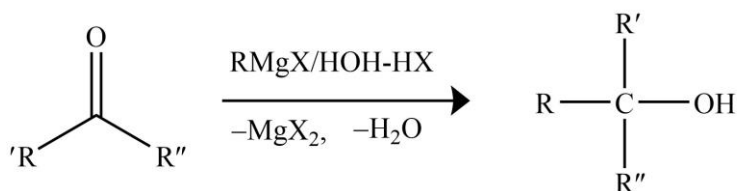
The typical addition mode of organomagnesium compounds (Grignard reagent) to common carbonyl compounds like ketone and aldehydes is given below.



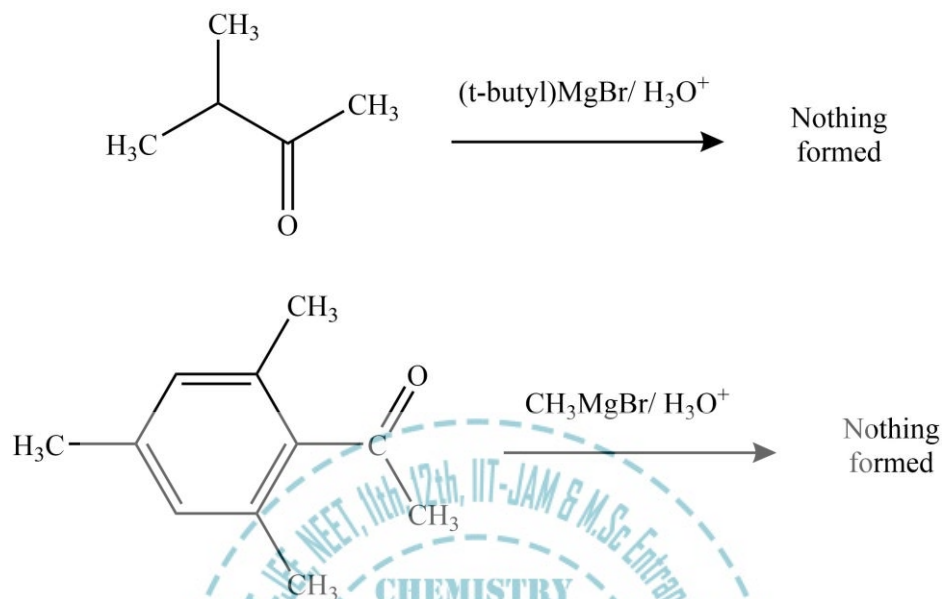
The halomagnesium alkoxide thus formed can react with  $\text{H}_2\text{O}$  (when an  $\text{HX}$  type mineral acid is available) to result in alcohols; which in turn, could be susceptible to dehydration (acid-catalyzed) if it is tertiary-type. To stop the alcohol's dehydration, we need to add some ammonium chloride ( $\text{NH}_4\text{Cl}$ ) to the water so that because its acidic character can be employed to transform  $\text{ROMgX}$  to  $\text{ROH}$ .



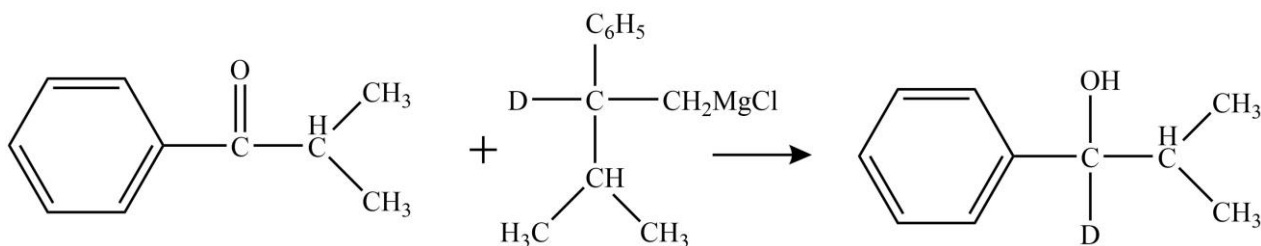
or



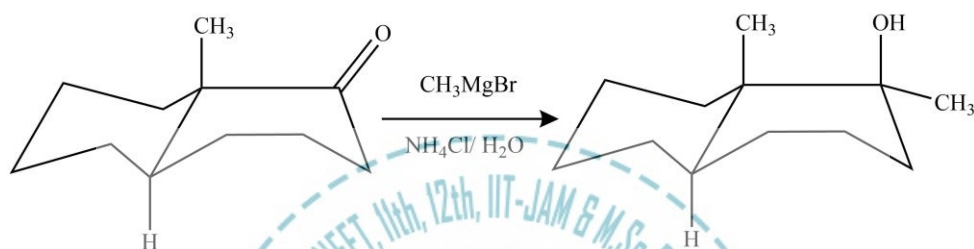
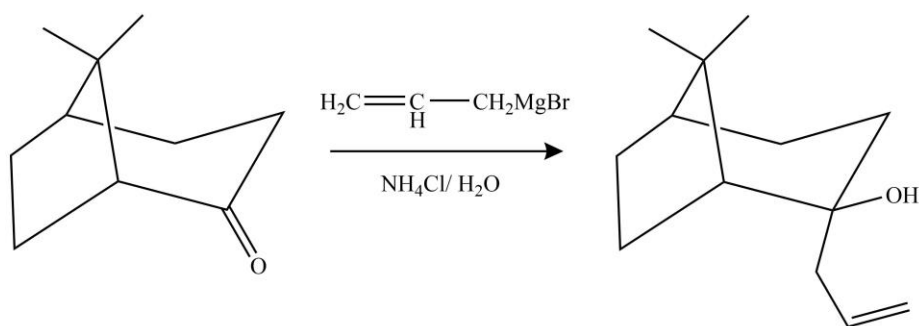
It is also worthy to note that bulky groups in the keto group, or in the reagent itself, greatly affect the nucleophilic addition in a negative way, or gets completely prohibited in some cases.



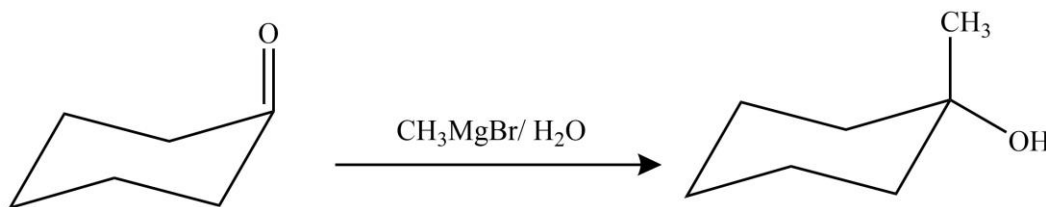
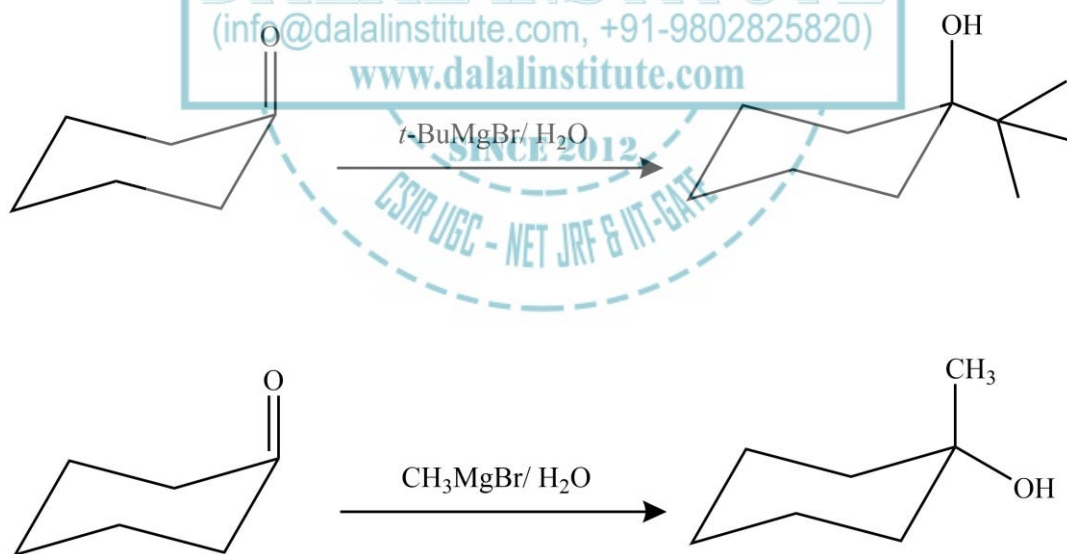
However, if a  $\beta$ -hydrogen is present in the bulky group of Grignard reagent, the transfer of hydride ion can result in the reduction of even highly hindered ketones. Moreover, if this is carried out via chiral Grignard reagent, the resulting product will also become optically active proving that the transfer of hydride ion does take place via the generation of cyclic transition state having six members.



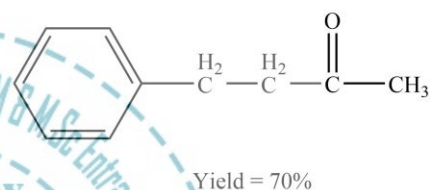
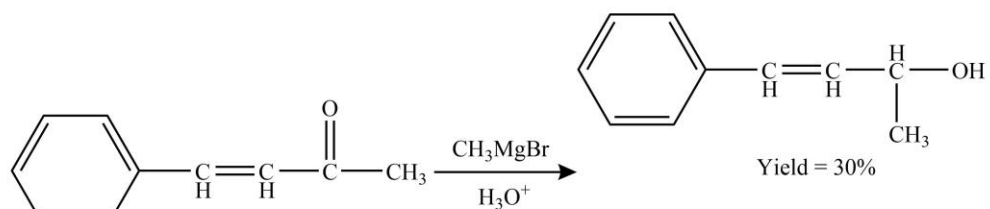
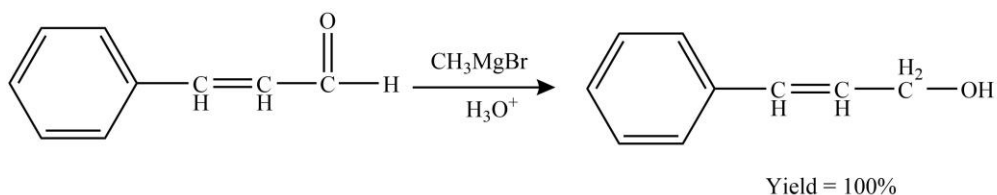
Also, if the Grignard addition takes place in cyclic ketones, the nucleophilic attack will happen from the carbonyl's face with less steric hindrance.



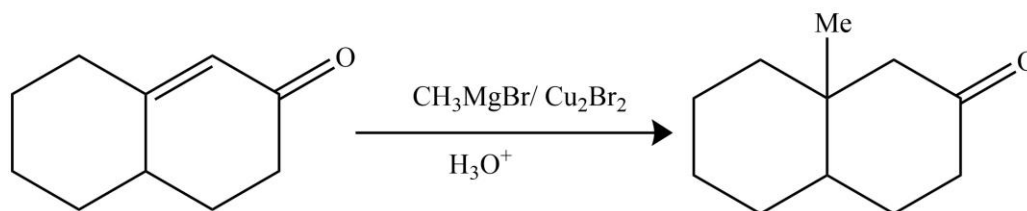
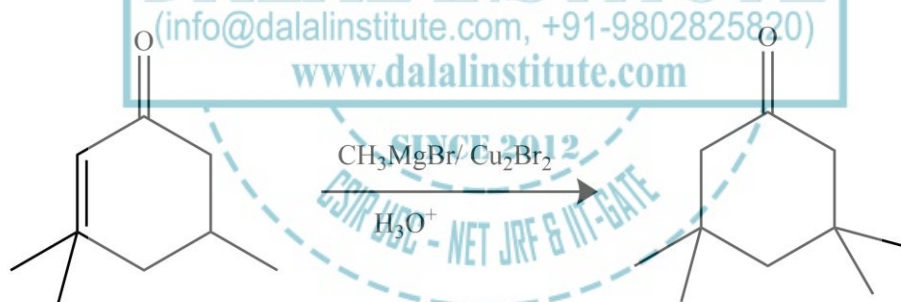
Since the organomagnesium reagent moves towards the substrate from a less hindered end, the final products' nature is also a function of the Grignard reagent used as it will push the hydroxy group to the axial site. On the other hand, a less bulky R (in comparison to OH) will make the hydroxy group occupy an equatorial site.



On a final note, if the aldehyde or the ketone used is  $\alpha$ -,  $\beta$ -unsaturated, the nucleophilic addition of Grignard reagents becomes much faster and effective than normal carbonyl compounds, yielding 1, 4- and 1, 2-addition products simultaneously. Moreover, these  $\alpha$ -,  $\beta$ -unsaturated ketone and aldehydes give 1, 4- and 1, 2- adducts as the major products, respectively.



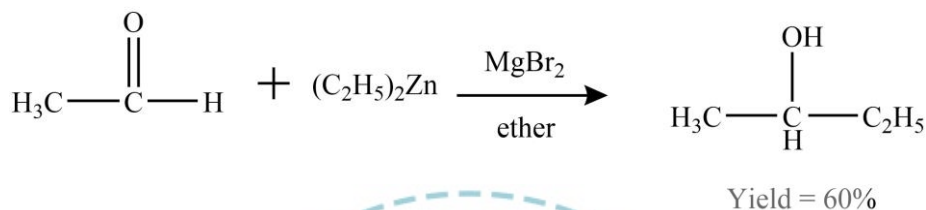
Nevertheless, it should also be noted that only 1, 4-adduct will be obtained if the addition over ketone is carried out in the presence of  $\text{Cu}_2\text{Br}_2$ .



Since the Grignard reagents are very strong bases, they are not suitable to act as nucleophiles with substrate containing acidic hydrogens. In other words, Grignard reagents will act as a base and will abstract the acidic hydrogen instead of participating as a nucleophile to attack the carbonyl group.

➤ **Addition of Organozinc Reagents to Carbonyl and Unsaturated Carbonyl Compounds**

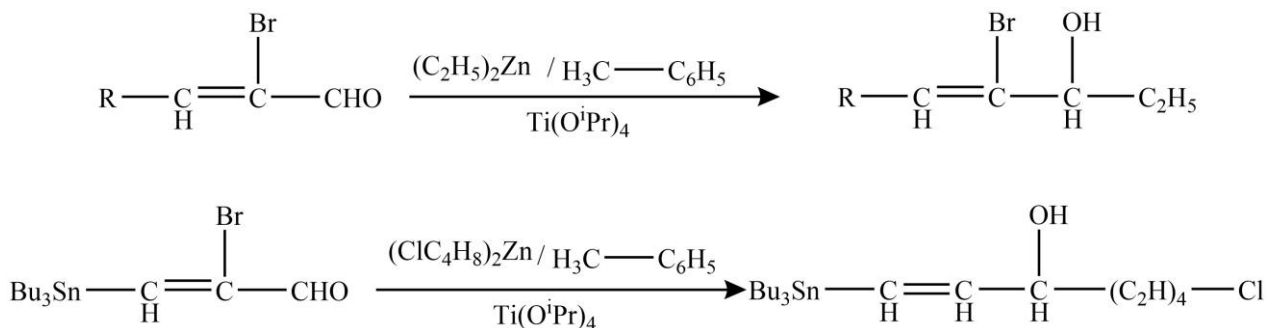
The rate of reaction for carbonyl compounds with dialkylzinc reagents is quite slow. It has also been observed that the rate for higher dialkylzinc is even lesser than lower dialkylzinc reagents. For instance, the reaction of diethylzinc with acetaldehyde takes hours for completion whereas the higher homologs may even take weeks. Nevertheless, allylzinc reagents show greater reactivity towards nucleophilic addition than normal dialkylzinc systems. Furthermore, the metal halide Lewis acids have been shown to enhance the rate of addition via dialkylzinc reagents.



The heteroatom's presence at the  $\alpha$ -site (relative to CO group) has also been found to be supportive of nucleophilic addition organozinc reagents.

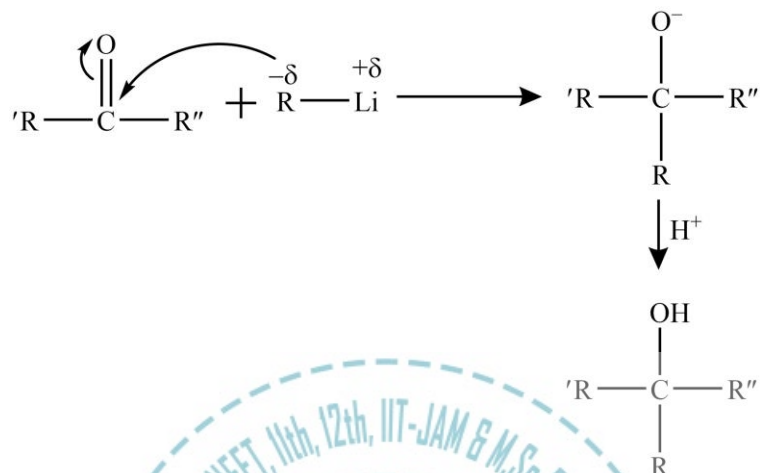


On a final note, it has also been proved that many titanium catalysts are supportive of the reactivity of organozinc reagents, specially  $\text{TiCl}_4$  and  $\text{Ti}(\text{O}^i\text{Pr})_4$ .



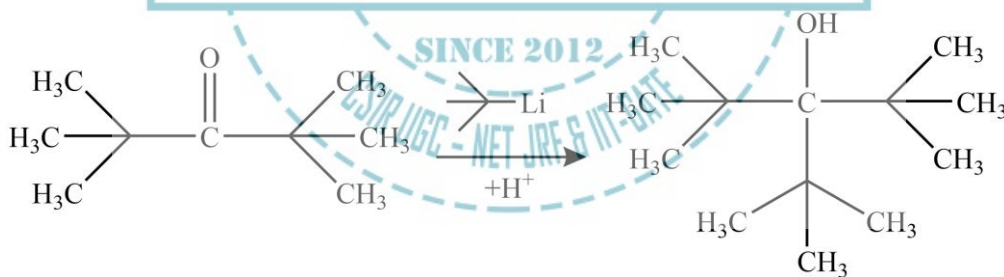
➤ **Addition of Organolithium Reagents to Carbonyl and Unsaturated Carbonyl Compounds**

Organolithium reagents react with organic carbonyl derivatives to generate lithium alkoxide, which in turn gives rise to alcohols upon hydrolysis.

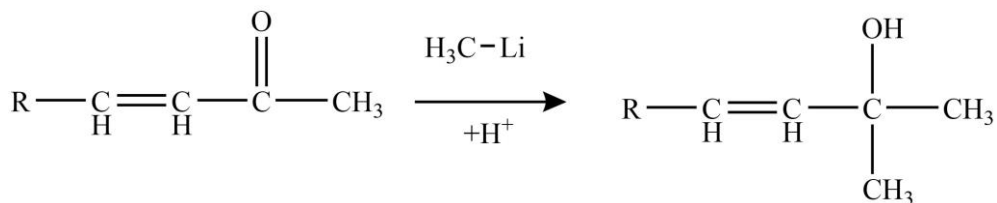


Sometimes a bioproduct via the  $\alpha$ -deprotonation can also be obtained because besides being a nucleophilic attacker, organolithium is a powerful base too.

Furthermore, it is also worthy to note that organolithium reagents are better than their organomagnesium counterparts; and therefore, some highly hindered carbonyls (who were unable to react at all with Grignard reagents) can also be used as a substrate to produce quite stable products.



On a final note, the conjugated addition doesn't happen in the case of organolithium, leaving 1, 2-adducts as the only products.





## 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

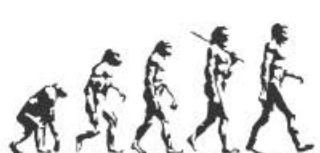
Regular Program

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](mailto:dr.mandeep.dalal@gmail.com)*

*[www.mandeepdalal.com](http://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](mailto:info@dalalinstitute.com), +91-9802825820)**

**[www.dalalinstitute.com](http://www.dalalinstitute.com)**