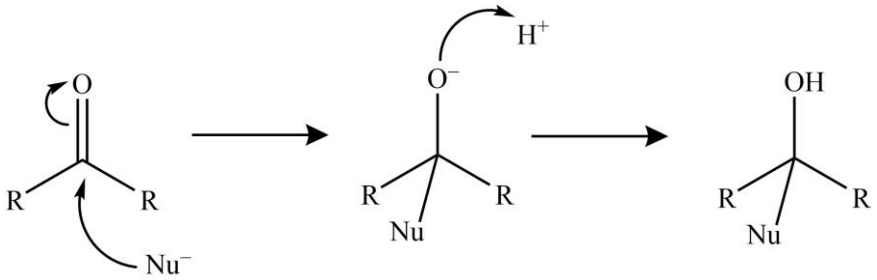
CHAPTER 12

Addition to Carbon-Hetero Multiple Bonds

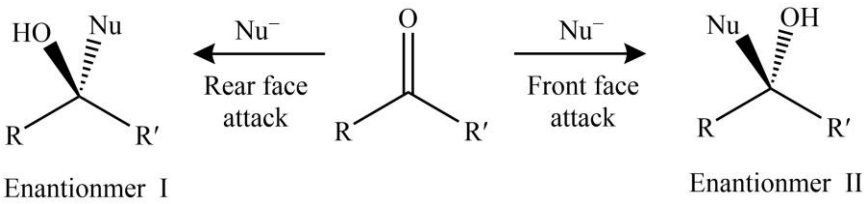
❖ Mechanism of Metal Hydride Reduction of Saturated and Unsaturated Carbonyl Compounds, Acids, Esters and Nitriles

Unlike the nucleophilic addition to carbon-carbon multiple bonds, the nucleophilic addition to carbon-heteroatom multiple bonds is much simpler to study as there is no regiochemical preference (i.e., the orientation of unsymmetrical addition) in most of the cases. For instance, consider >C=O, −C≡N, and −C=N types of bonds which are extremely polar (great difference in electronegativity of participating atoms); so the carbon atoms bear a partial positive charge which makes the molecule an electrophile and the carbon atom as the electrophilic center; and therefore, the electrophilic species of the attacking reagent always goes to the oxygen or nitrogen whereas the nucleophilic part of the reagent attacks at the carbon.



The reaction given above is also called a 1, 2-type nucleophilic addition, and a racemic mixture will be obtained if the alkyl substituents are different.

Furthermore, it is obvious that the first step is just the same as the first step of nucleophilic displacement at a carbonyl's C atom; nevertheless, the latter case rarely takes place because R groups (H and carbon groups like alkyl aryl, etc.) are extremely poor leaving groups supporting the former case (i.e., addition). The acyl substitution dominates in the case of carboxylic acid derivatives (like amides or acid chlorides) because of the presence of 'relatively' good leaving groups like NH_2, OR, Cl, etc.



Hence, we can conclude that the nature of 'R' groups dictates whether the nucleophilic attack at carbon-heteroatom multiple bonds will give rise to the addition or substitution.

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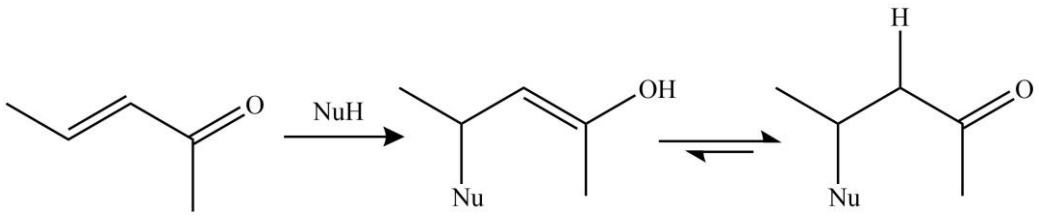
Until now we have discussed the basic ideas of addition to simple (i.e., non-conjugated) carbon-heteroatom multiple bonds; however, some systems do have unsaturation at least at α- and β-carbon. The nucleophilic addition in such cases is called conjugate addition and is different from ordinary nucleophilic additions to carbon-hetero bonds (i.e., 1, 2-nucleophilic additions) due to far separated attacking sites (i.e., 1, 4-nucleophilic additions). It is also important to recall the fact that normal alkenes neither show 1, 2- nor 1, 4-reactivity (possible only via activation by special substituents) due to lack of polarity.



The mechanism of conjugate addition can be understood by taking the example of an α, β-unsaturated carbonyl compound like cyclohexenone, where it can be showed that the β-position is an electrophilic site that can react with a nucleophile (from resonance structures). After the nucleophilic attack, the negative charge of the nucleophilic part of the attacking reagent is now distributed via resonance in α-carbon carbanion and alkoxide anion. Finally, the protonation results in a saturated carbonyl compound via keto-enol tautomerism (the equilibrium lies toward the keto form because it is more stable than the enol form due to a stronger C=O bond than C=C bond). Also, another electrophile will replace the proton if the reaction further proceeds via vicinal difunctionalization.

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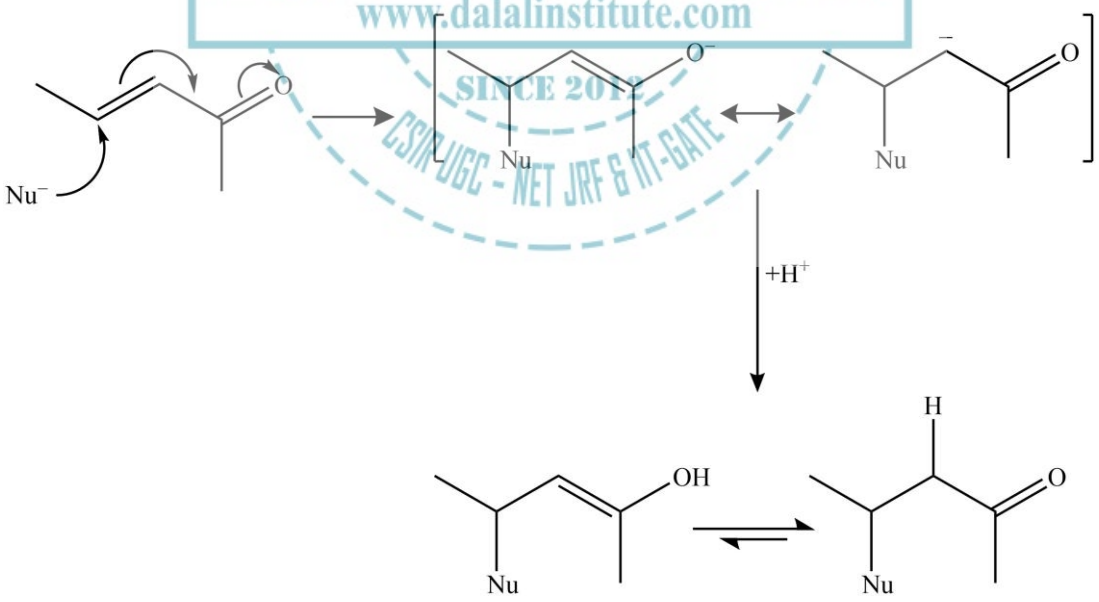

In this section, we will study the mechanism of a special type of addition to the carbon-heteroatom multiple bonds where the reduction of saturated and unsaturated carbonyl compounds (aldehydes, ketones, and acyl halides), acids, esters, and nitriles is carried out using metal hydrides.

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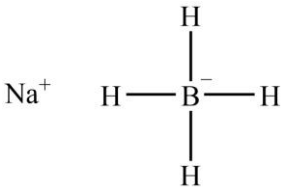
➢ ***Metal Hydride Reduction of Saturated Carbonyl Compounds***

Many metal hydrides can be used to reduce the saturated carbonyl compounds like aldehydes, ketones, and acid halides.

1. Reduction by Sodium Borohydride: The sodium borohydride ($NaBH_4$) is one of the most common sources of the hydride nucleophile. The hydride anion is produced in the course of reaction because of the polar nature of the metal-hydrogen bond.

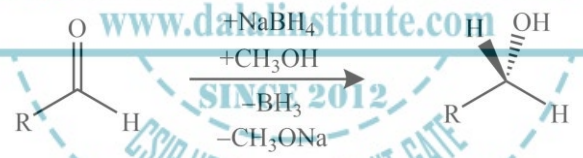


Sodium Borohydride

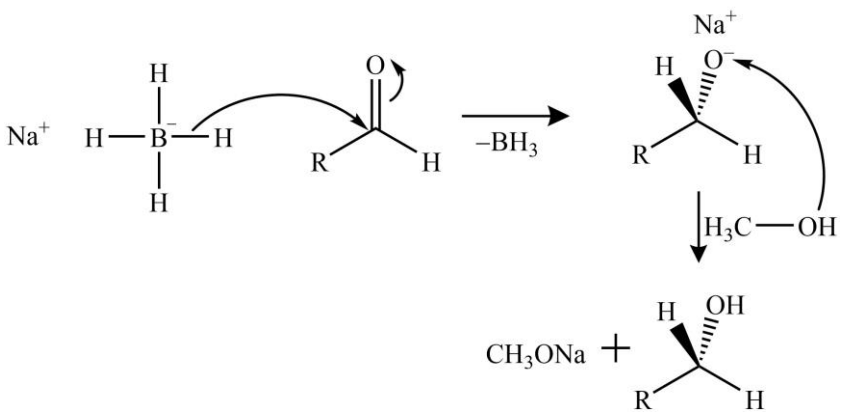
The hydride anion's addition to carbonyl compound results in an alkoxide anion which in turn gives rise to a reduced product.

i) Reduction of aldehydes by $NaBH_4$:

The hydride anion's addition to aldehyde results in an alkoxide anion, which in turn, gives rise to primary (1°) alcohols on protonation.



The mechanism for the aldehydic reduction by metal hydride involves the nucleophilic addition of the hydride ion to the carbonyl carbon. In many cases, the Na^+ ion activates the carbonyl group by attaching itself to the oxygen atom, which in turn, will raise the electrophilic character of the C=O group.



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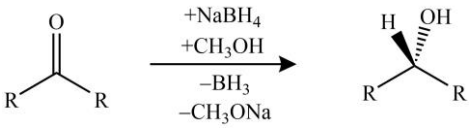
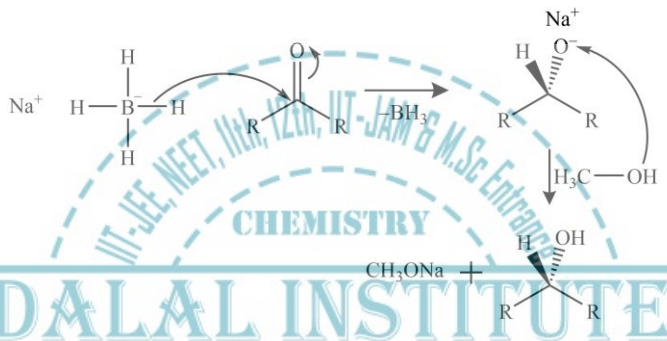
ii) Reduction of ketones by $NaBH_4$:

The hydride anion's addition to ketone results in an alkoxide anion which in turn gives rise to secondary (2°) alcohols on protonation.



The mechanism for the ketone reduction by metal hydride involves the nucleophilic addition of the hydride ion to the carbonyl carbon. In many cases, the Na^+ activates the carbonyl group by attaching itself to the oxygen atom, which in turn, will raise the electrophilic character of the C=O group.



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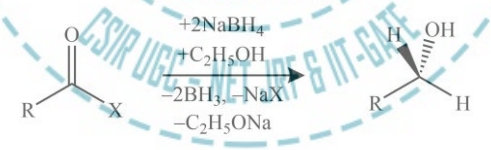
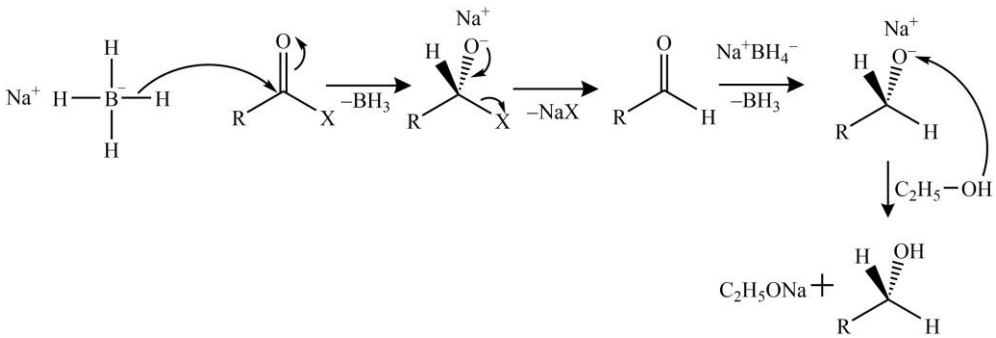
iii) Reduction of acyl halides by $NaBH_4$:

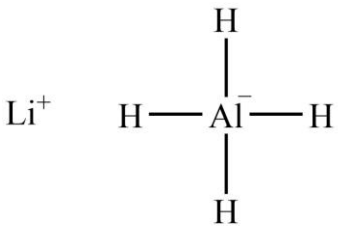
Two subsequent additions of hydride anions to acyl halides result in a sodium alkoxide anion which in turn gives rise to primary (1°) alcohols on protonation.



The mechanism for the acyl halides' reduction by metal hydrides involves the nucleophilic addition of the hydride ion to the carbonyl carbon. In many cases, the Na^+ activates the carbonyl group by attaching itself to the oxygen atom, which in turn, will raise the electrophilic character of the C=O group.



2. Reduction by Lithium aluminium hydride: The lithium aluminium hydride ($LiAlH_4$) is one of the most common sources of the hydride nucleophile. The hydride anion is produced in the course of reaction because of the polar nature of the metal-hydrogen bond.

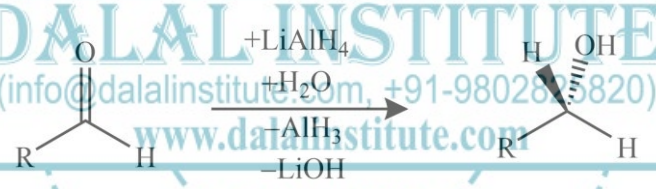


Lithium aluminium hydride

The hydride anion's addition to carbonyl compound results in a lithium alkoxide anion which in turn gives rise to a reduced product.

i) Reduction of aldehydes by $LiAlH_4$:

The hydride anion's addition to aldehyde results in an alkoxide anion which in turn gives rise to primary (1°) alcohols on protonation.



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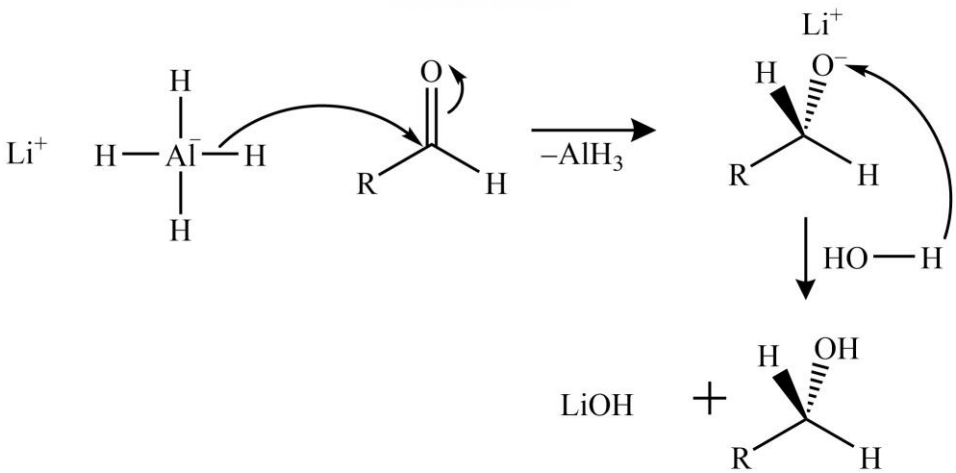
The mechanism for the aldehydic reduction by metal hydride involves the nucleophilic addition of the hydride ion to the carbonyl carbon. In many cases, the Li^+ activates the carbonyl group by attaching itself to the oxygen atom, which in turn, will raise the electrophilic character of the C=O group.



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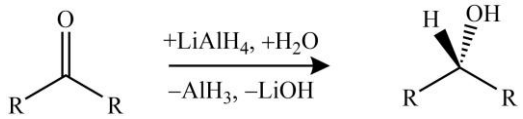
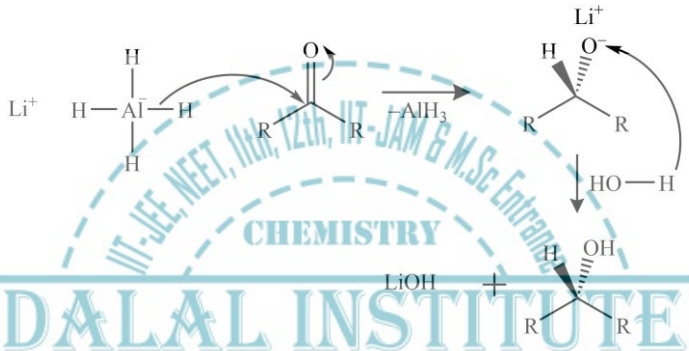
ii) Reduction of ketones by $LiAlH_4$:

The hydride anion's addition to ketone results in an alkoxide anion which in turn gives rise to secondary (2°) alcohols on protonation.



The mechanism for the ketone reduction by metal hydride involves the nucleophilic addition of the hydride ion to the carbonyl carbon. In many cases, the Li^+ activates the carbonyl group by attaching itself to the oxygen atom, which in turn, will raise the electrophilic character of the C=O group.



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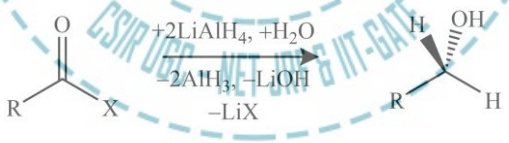
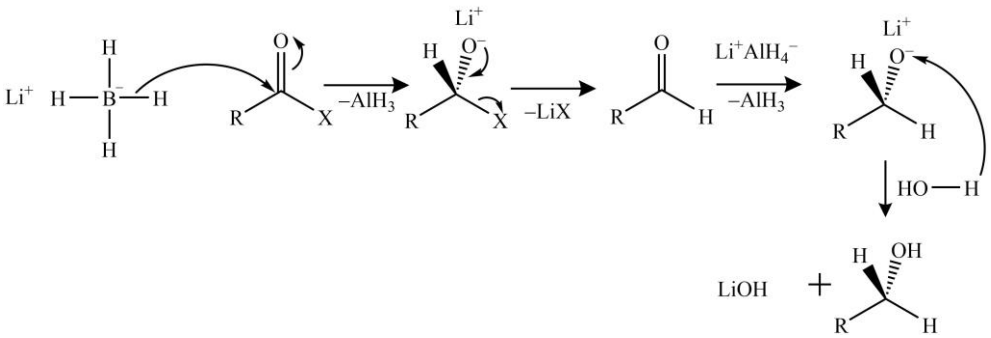
iii) Reduction of acyl halides by $LiAlH_4$:

Two subsequent additions of hydride anions to acyl halides results in an alkoxide anion which in turn gives rise to primary (1°) alcohols on protonation.



The mechanism for the acyl halides' reduction by metal hydride involves the nucleophilic addition of the hydride ion to the carbonyl carbon. In many cases, the Li^+ activates the carbonyl group by attaching itself to the oxygen atom, which in turn, will raise the electrophilic character of the C=O group.



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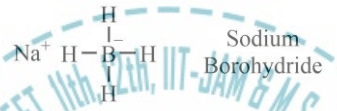
➢ ***Metal Hydride Reduction of Unsaturated Carbonyl Compounds***

Many metal hydrides can be used to reduce the unsaturated carbonyl compounds like α, β-unsaturated aldehydes, ketones, and acid halides.

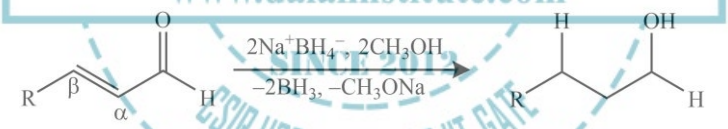
1. Reduction by Sodium Borohydride: It is well-known fact that isolated C=C bond cannot be reduced either by $LiAlH_4$ or by $NaBH_4$. However, if this C=C is in conjugation with C=O (i.e., conjugated aldehyde, ketones, or acid chlorides), the substrate can act as an electrophile via at the β-carbon or via the carbon of the carbonyl group. Now since the β-carbon is a "soft" electrophilic site, it will prefer to react with "soft" nucleophile like $NaBH_4$; whereas the carbonyl's carbon is a relatively "hard" electrophilic site, it will prefer to react with "hard" nucleophile like $LiAlH_4$ (HSAB Principle). Nevertheless, after the reduction of the C=C bond, the saturated aldehyde will also get reduced to the alcohol by $NaBH_4$ in the next step. Conversely, $LiAlH_4$ will show a 1, 2-addition, leaving an isolated C=C double bond unaltered.



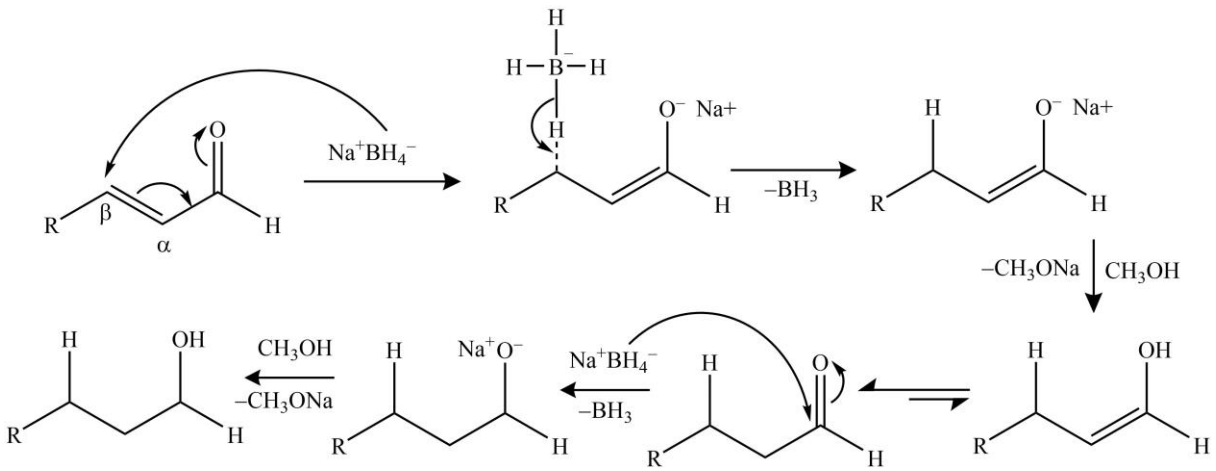
The hydride anion's addition to unsaturated carbonyl compound results in an alkoxide anion which in turn gives rise to a reduced product.

i) Reduction of α, β-unsaturated aldehydes by $NaBH_4$:

The hydride anion's addition to the α, β-unsaturated aldehyde results in an alkoxide anion which in turn gives rise to primary (1°) alcohols on protonation.



The mechanism for the aldehydic reduction by metal hydride that involves the 1, 4-nucleophilic addition of the hydride ion followed by a 1-2-addition to the carbonyl carbon is given below.



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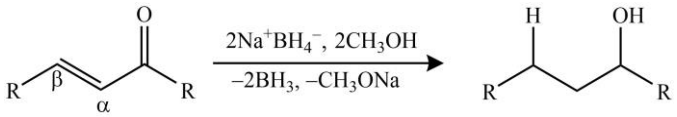
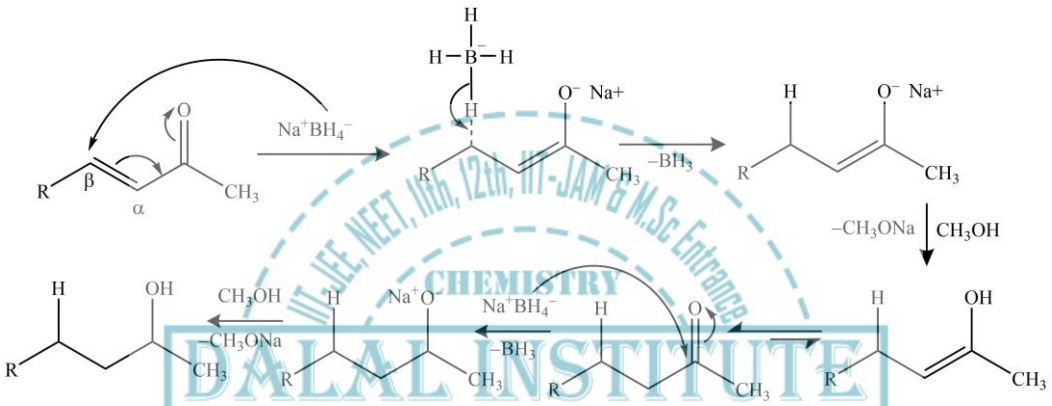
ii) Reduction of α, β-unsaturated ketones by $NaBH_4$:

The hydride anion's addition to α, β-unsaturated ketone results in an alkoxide anion which in turn gives rise to secondary (2°) alcohols on protonation.



The mechanism for the ketone reduction by metal hydride that involves the 1, 4-nucleophilic addition of the hydride ion, followed by a 1, 2-addition to the carbonyl carbon is given below.



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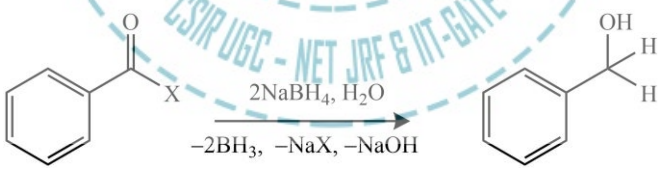
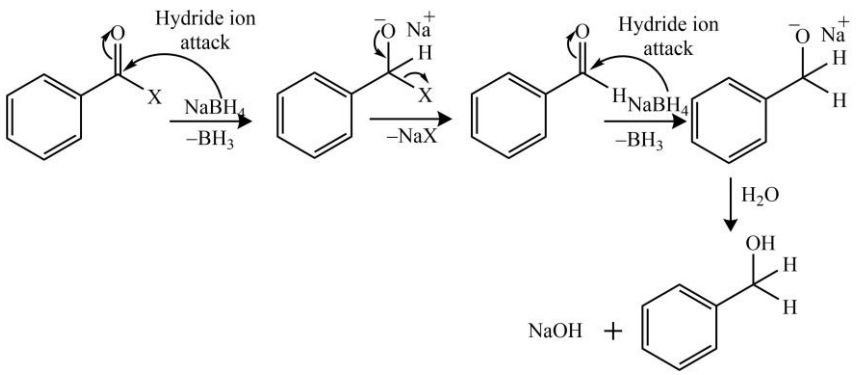
iii) Reduction of α, β-unsaturated acyl halides by $NaBH_4$:

Although it seems like an easy task, there are no reports of $NaBH_4$-catalyzed 1, 4-addition to acyl halides (with reasonable yield). Nevertheless, 1, 2-adducts for benzoyl chloride have been obtained.



The mechanism for the transformation of benzoyl chloride to benzyl alcohol via $NaBH_4$ is given below.



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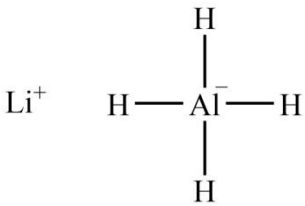
2. Reduction by Lithium aluminium hydride: Since the carbonyl's carbon is a relatively "hard" electrophilic site, it will prefer to react with "hard" nucleophile like $LiAlH_4$ (HSAB Principle). Hence, unlike $NaBH_4$, $LiAlH_4$ will show a 1, 2-addition, leaving an isolated double bond unaltered.



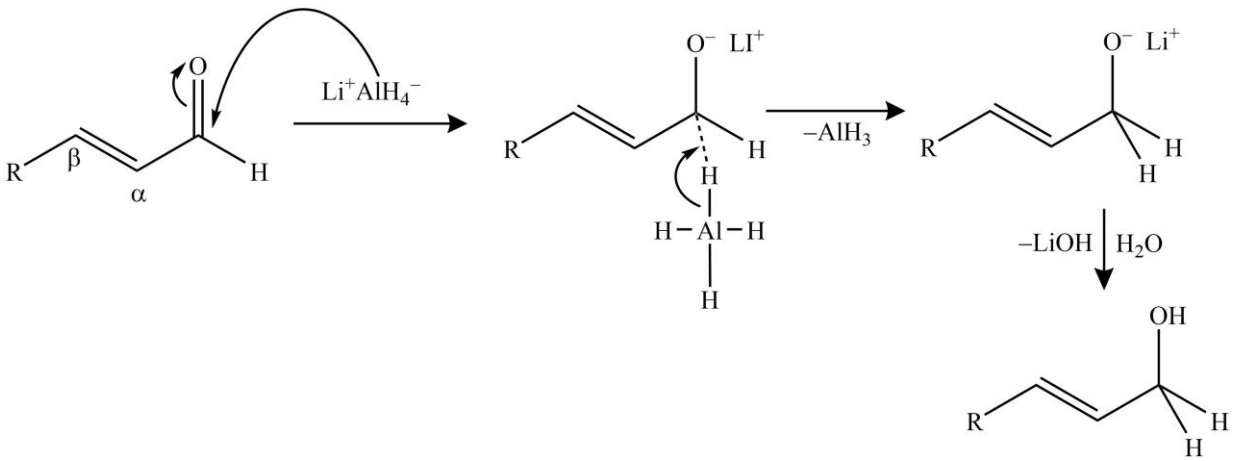
Lithium aluminium hydride

The hydride anion's addition to carbonyl compound results in a lithium alkoxide anion which in turn gives rise to a reduced product.

i) Reduction of α, β-unsaturated aldehydes by $LiAlH_4$:

The hydride anion's addition to α, β-unsaturated aldehyde results in an alkoxide anion which in turn gives rise to primary (1°) alcohols on protonation.

The mechanism for the α, β-unsaturated aldehydic reduction by metal hydride involves 1, 2-nucleophilic addition of the hydride ion to the carbonyl carbon as shown below. Furthermore, it is also worthy to note that conjugate addition in product might also be obtained alongside with very small yield.



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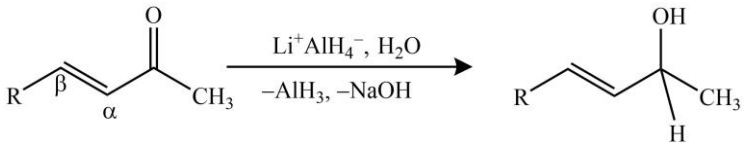
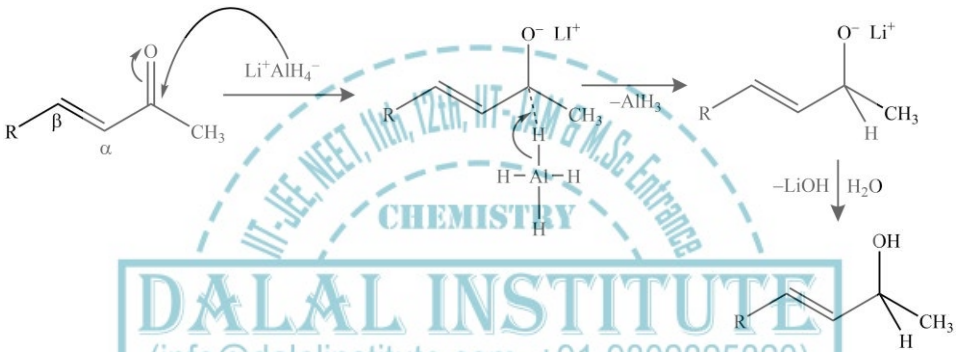
ii) Reduction of α, β-unsaturated ketones by $LiAlH_4$:

The hydride anion's addition to ketone results in an alkoxide anion which in turn gives rise to secondary (2°) alcohols on protonation.



The mechanism for the α, β-unsaturated ketonic reduction by metal hydride involves 1, 2-nucleophilic addition of the hydride ion to the carbonyl carbon as shown below. Furthermore, it is also worthy to note that conjugate addition in product might also be obtained alongside with very small yield.



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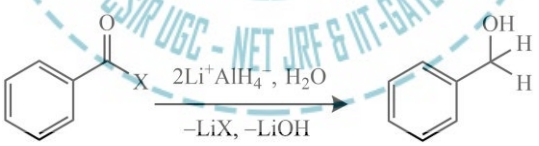
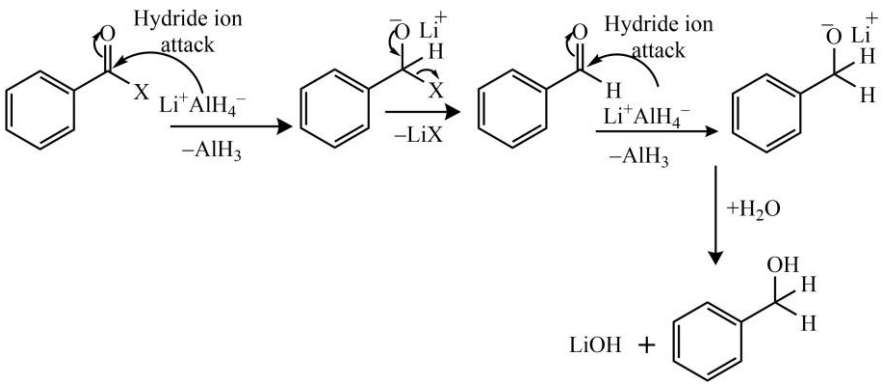
iii) Reduction of α, β-unsaturated acyl halides by $LiAlH_4$:

The hydride anion's addition to ketone or aldehyde results in an alkoxide anion which in turn gives rise to primary (1°) alcohols on protonation.



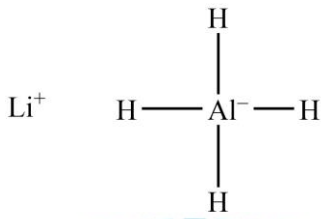
The mechanism for the transformation of benzoyl chloride to benzyl alcohol via $LiAlH_4$ is given below.



➢ ***Metal Hydride Reduction of Acids***

Many metal hydrides can be used to reduce the saturated and unsaturated carbonyl compounds like carboxylic acid.

1. Reduction by lithium aluminium hydride: The lithium aluminium hydride ($LiAlH_4$) is one of the most common sources of the hydride nucleophile. The hydride anion is produced in the course of reaction because of the polar nature of the metal-hydrogen bond.

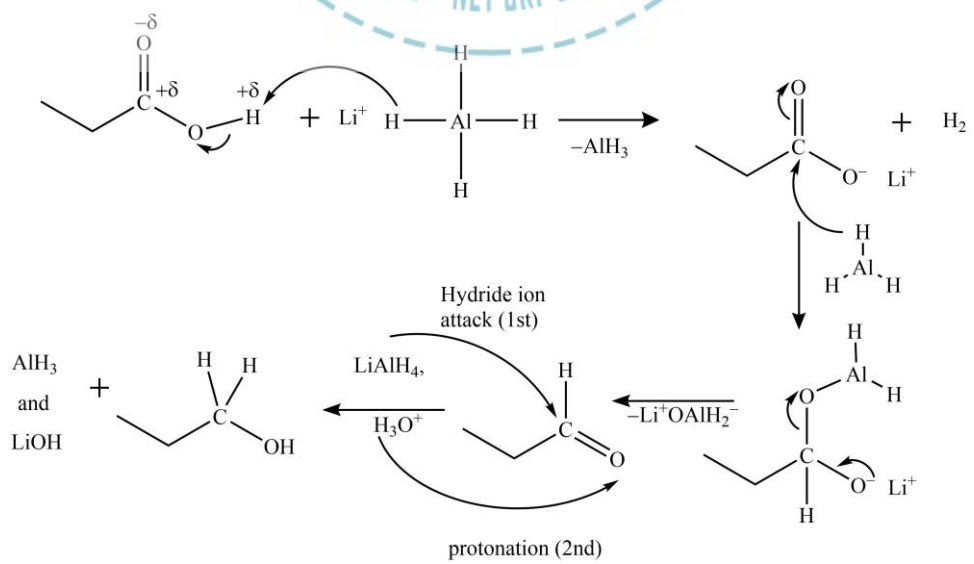


Lithium aluminium hydride

The hydride anion's addition to carbonyl compound results in an alkoxide anion which in turn gives rise to a reduced product.

The hydride anion's attack on carboxylic acid results in a carboxylate anion, which in turn, is attacked by AlH_3 to yield aldehyde. This aldehyde then gives rise to primary (1°) alcohols after 1, 2-addition.

The mechanism for the carboxylic acid's reduction by metal hydride (by LiAlH4 in this case) to give primary alcohols is given below.



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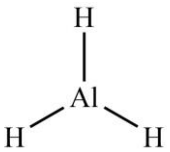
2. Reduction by aluminium hydride: The aluminum hydride, i.e., AlH_3, is one of the most common types of electrophilic addition for the reduction of carboxylic acid because simple borohydride cannot reduce carboxylic acids.



Aluminium hydride

In some cases, the reactivity of aluminium hydride is like lithium aluminium hydride; whereas sometimes it acts as borane (BH_3).

The hydride anion's addition to carboxylic acid results in a complex series of transition states which in turn gives rise to primary (1°) alcohols on protonation.

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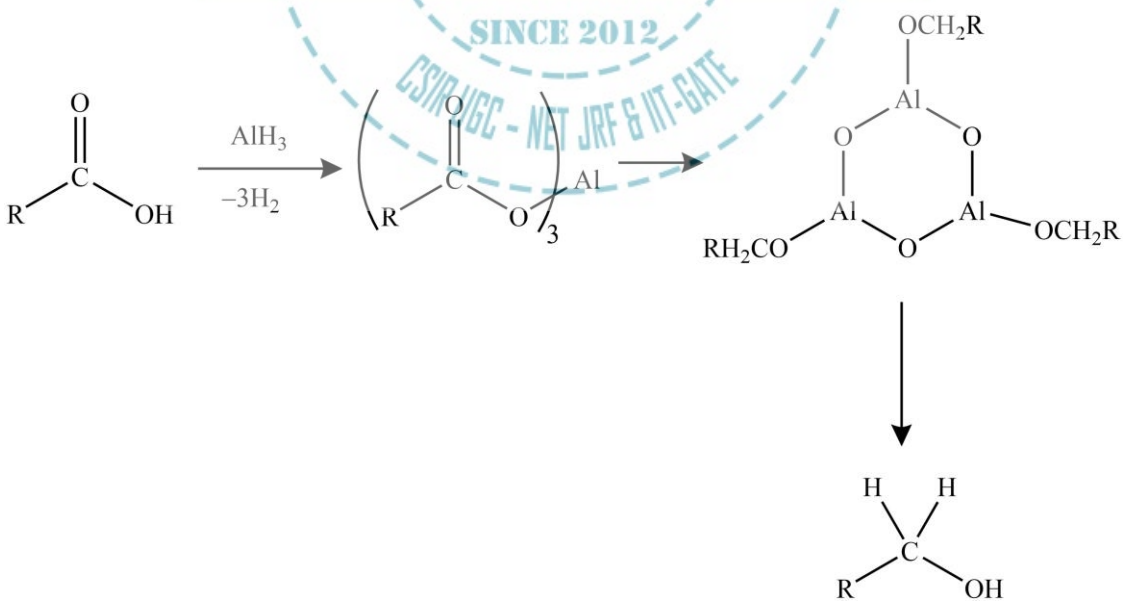
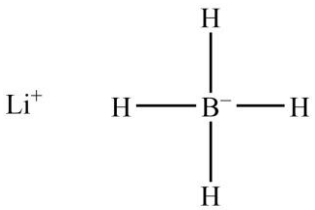
The mechanism responsible for the reduction of carboxylic acids by aluminium hydride involves the following steps.



➢ ***Metal Hydride Reduction of Esters***

Metal hydrides like lithium borohydride and lithium aluminium hydride can be used to reduce the carbonyl compounds like esters.

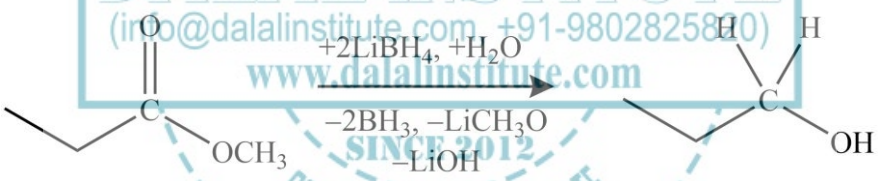
1. Reduction by lithium Borohydride: The lithium borohydride ($LiBH_4$) is one of the most common sources of the hydride nucleophile. The hydride anion is produced during reaction because of the polar nature of the metal-hydrogen bond.



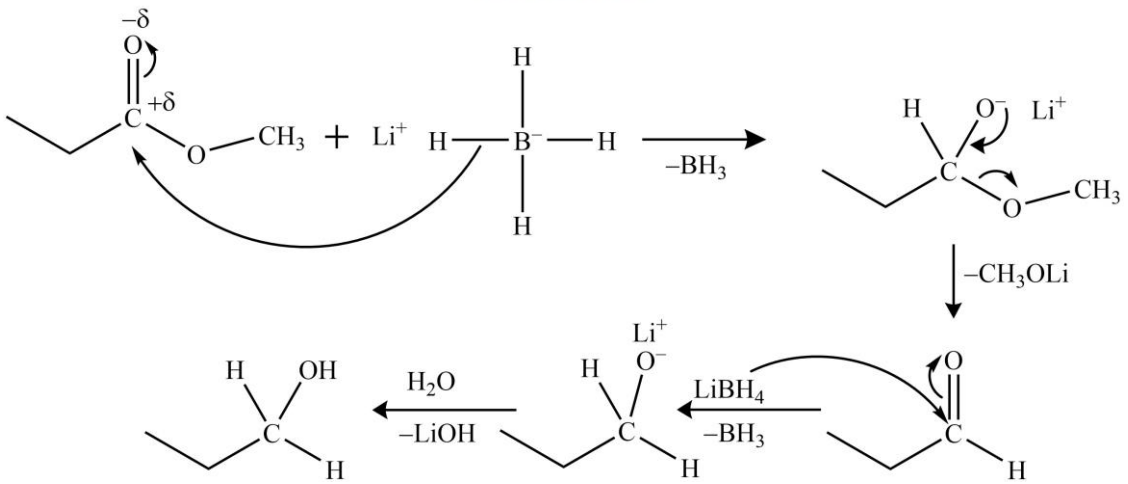
Lithium borohydride

The hydride anion's addition to carbonyl compound results in an alkoxide anion which in turn gives rise to the reduced product.

Two subsequent hydride anions' additions to ester result in an alkoxide anion which in turn gives rise to primary (1°) alcohols on protonation.



The mechanism for the ester reduction by metal hydride ($LiBH_4$ in this case) that involves the nucleophilic addition of the hydride ion to the carbonyl carbon is given below.



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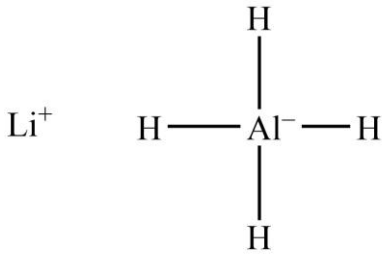
2. Reduction by Lithium aluminium hydride: The lithium aluminium hydride ($LiAlH_4$) is one of the most common sources of the hydride nucleophile. The hydride anion is produced during reaction because of the polar nature of the metal-hydrogen bond.



Lithium aluminium hydride

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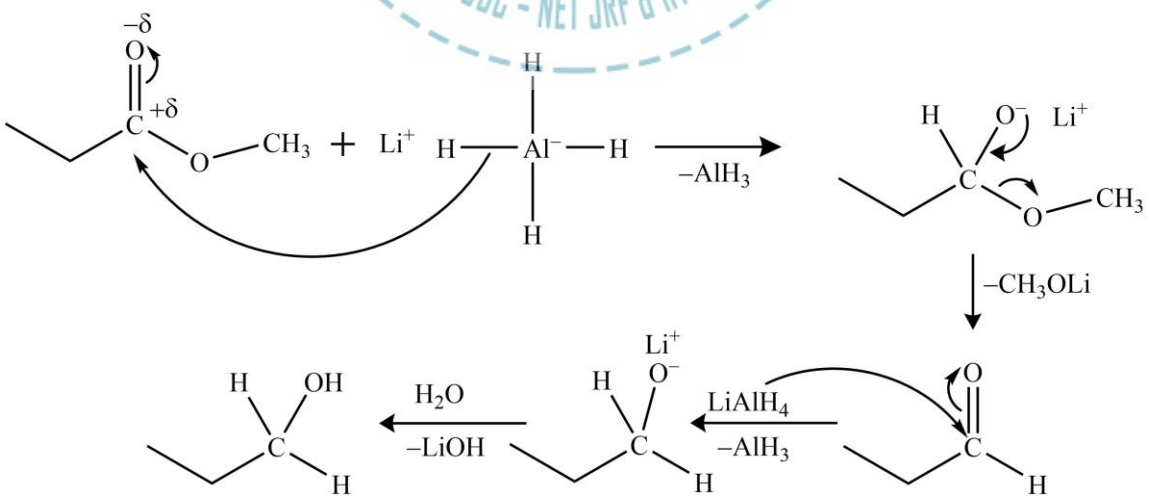
The mechanism for the ester reduction by metal hydride ($LiAlH_4$ in this case) that involves the nucleophilic addition of the hydride ion to the carbonyl carbon is given below.



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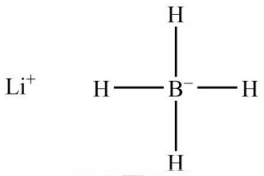
➢ ***Metal Hydride Reduction of Nitriles***

The nitriles' reduction may simply be defined as the chemical transformation in which a nitrile is reduced to either an aldehyde or an amine by the use of a suitable reagent. Many metal hydrides can be used to reduce the nitrile compounds to amines but $LiBH_4$ and $LiAlH_4$ are most common.

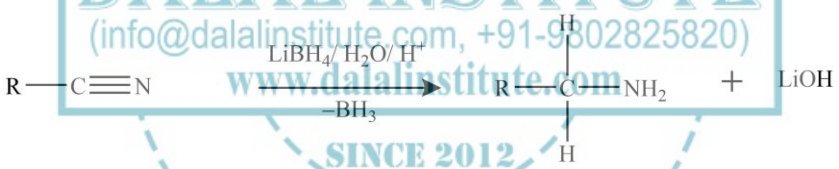
1. Reduction by lithium borohydride: The lithium borohydride ($LiBH_4$) is one of the most common sources of the hydride nucleophile. The hydride anion is produced during the reaction because of the polar nature of the metal-hydrogen bond.



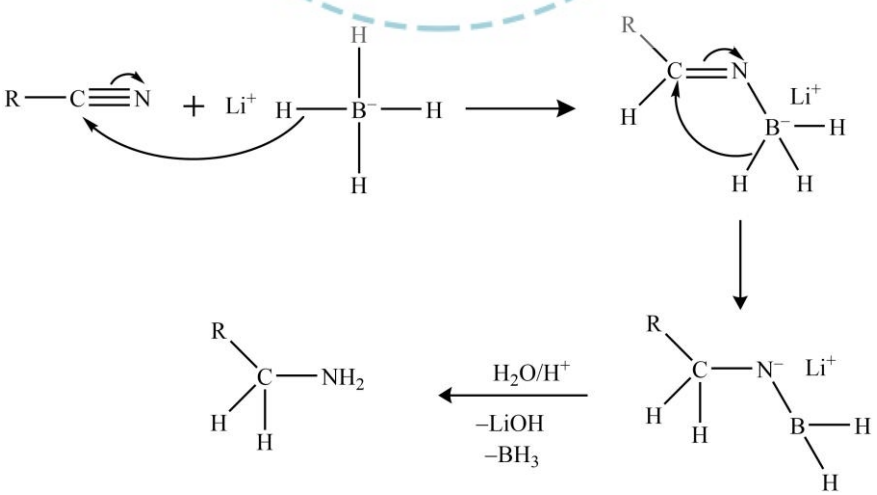
Lithium borohydride

The hydride anion's addition to nitrile compounds results in an anion which in turn gives rise to a reduced product.

Two subsequent additions of hydride anions to the carbon-nitrogen bond result in a lithium salt which in turn gives rise to primary (1°) amines on protonation.



The mechanism for the nitriles' reduction by metal hydride ($LiBH_4$ in this case) that involves the nucleophilic addition of the hydride ion to the carbon-nitrogen bond is given below.



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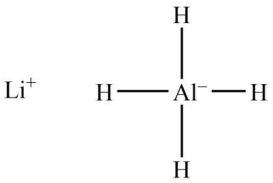
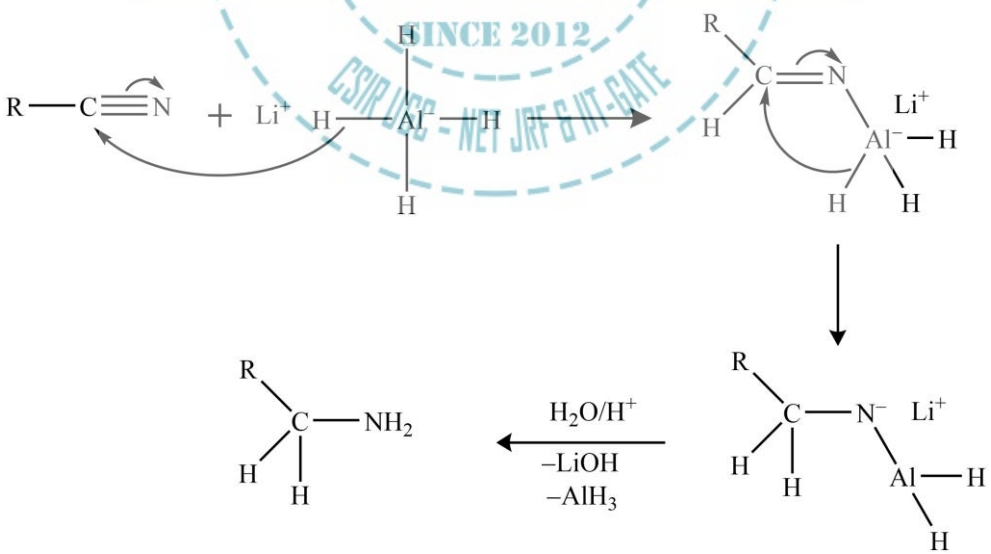


Lithium aluminium hydride

The hydride anion's addition to nitrile compounds results in an anion which in turn gives rise to a reduced product.

Two subsequent additions of hydride anions to the carbon-nitrogen bond result in a lithium salt which in turn gives rise to primary (1°) amines on protonation.

The mechanism for the nitriles' reduction by metal hydride ($LiAlH_4$ in this case) that involves the nucleophilic addition of the hydride ion to the carbon-nitrogen bond is given below.



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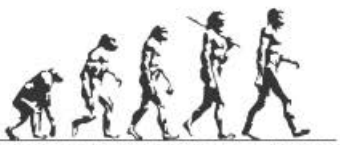

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Table of Contents

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 3 7
- 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 SN_2, SN_1, Mixed SN_1 and SN_2, SN_i, SN_1', SN_2', SN_i' 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 − SE_2 and SE_i 3 02
- 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
- *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 $ArSN_1$, $ArSN_2$, 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_1CB 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).

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