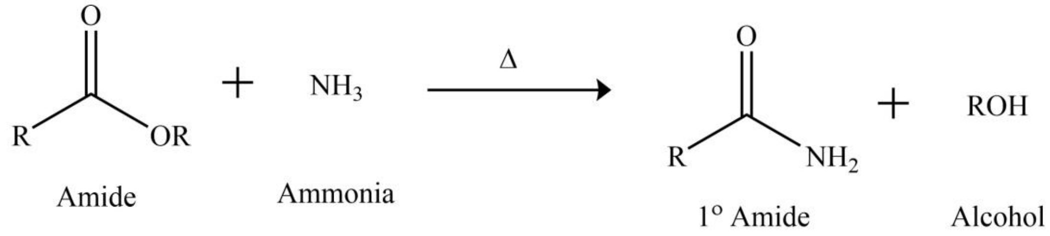
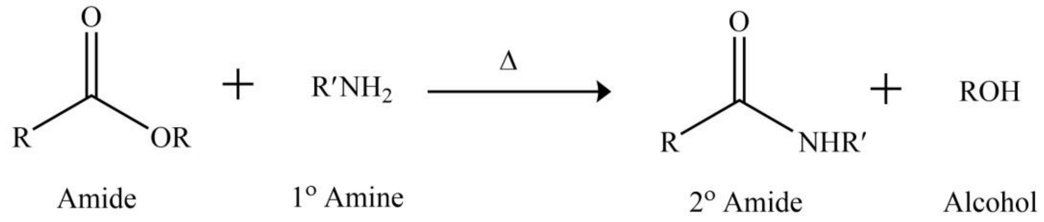
❖ Ammonolysis of Esters

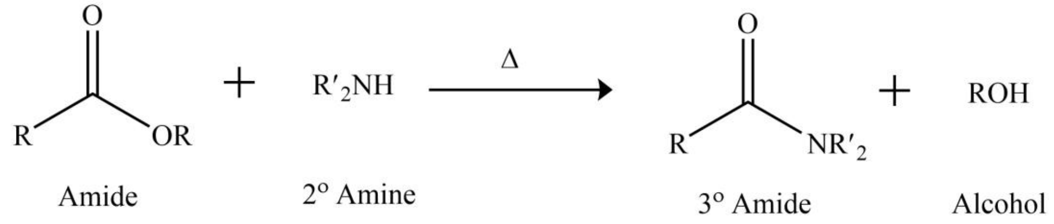
Before we study the ammonolysis of esters, we need to distinguish the term ‘ammonolysis’ from the term ‘aminolysis’ first. The precise definition of ‘ammonolysis’ includes the chemical reactions in which a compound is split into two parts by its reaction with ammonia; however, in broader terms, admins can also be used. On the other hand, the precise definition of ‘aminolysis’ includes the chemical reactions in which a compound is split into two parts by its reaction with amine; nevertheless, in broader terms, ammonia can also be used. Hence, we can conclude that the terms ‘ammonolysis’ and ‘aminolysis’ are pretty much similar not only w.r.t names but also in their approach; and therefore, are used in an exchangeable manner in different textbooks.

➢ *Definition and Examples Reactions of Ammonolysis of Esters*

Now we come to the ‘ammonolysis’ of esters, which popularly means that the esters can be converted into primary, secondary, and tertiary amides (along with alcohols) by treating them with ammonia, primary amines, and secondary amines respectively.







Since the RO^- is a very poor leaving group, the conventional nucleophilic addition-elimination pathway will not be useful as far the practicality is concerned. Hence, unlike the reaction of acyl chlorides with amines, the corresponding nucleophilic addition-elimination in case esters requires much stronger conditions.

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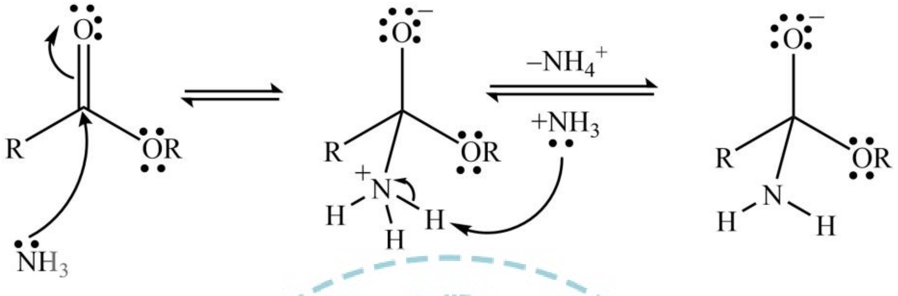
➢ ***Mechanism of Ammonolysis of Esters***

Before we discuss the mechanism of ammonolysis of esters, we understand different outcomes first. Initially, an ammonia molecule (or amine) attacks the carbonyl via nucleophilic addition; whilst a large amount of ammonia still present in the reaction solution, followed by the formation of an anionic tetrahedral intermediate due to deprotonation.



At this point, C=O double bond can only be restored only if either the alkoxy (RO^-) or the amide (NH_2^-) group is detached. Now although both are very poor leaving groups; the pKa values of alcohol and ammonia suggested that alkoxy groups (RO^-) are much weaker bases than ammonia's conjugate base (i.e., NH_2^-), and therefore, is a better leaving group. Consequently, the reassortment of the C=O bond will happen via loss of alkoxy group giving rise to an amide product.

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However, it is also worthy to note that the relative betterment of alkoxy as a leaving group doesn't make it a good leave group on the absolute scale; and therefore, the ammonolysis of esters isn't a very effective route for the amides' synthesis, indicating acyl chlorides as more suitable substrates.

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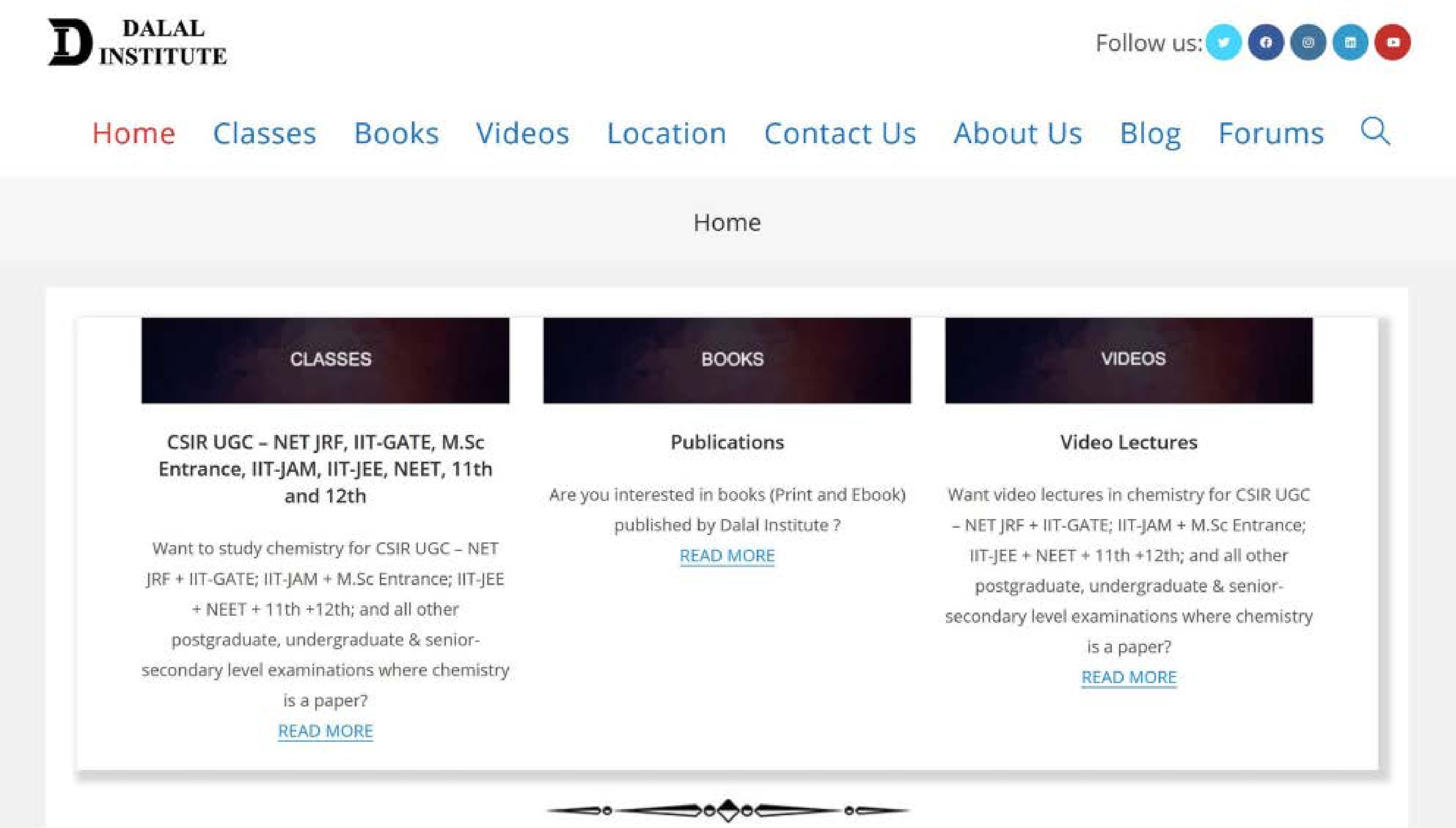

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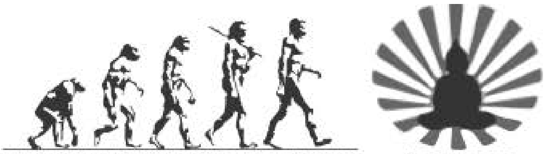

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Volume I

MANDEEP DALAL

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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$_R$N$_1$ 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**

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