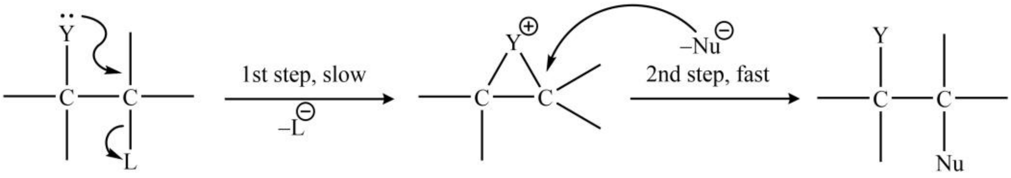
❖ Anchimeric Assistance

The anchimeric assistance may simply be defined as the increase in reaction-rate due to the presence of a neighboring group β- to the leaving group.

It is a well-known fact that many nucleophilic substitution reactions give rise to the same configuration (i.e., retention) instead of inversion or racemization due to neighboring group participation. Also, the rate of reaction for such reactions is very high because the group or atom at β-position to the leaving group is readily available for the nucleophilic attack in the first step (rate-determining step). The schematic representation of the whole process is shown below.



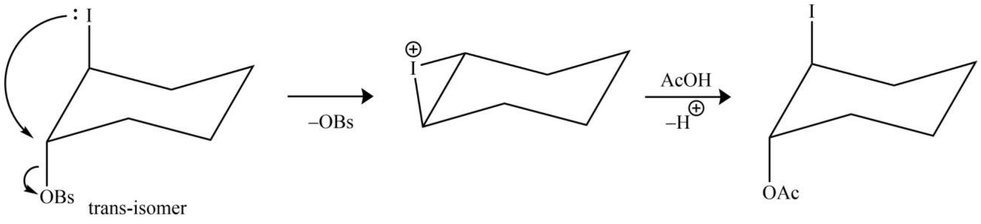
Since the first step is the rate-determining step, the reaction kinetics of the neighboring group mechanism is of the first order, which can be formulated as:

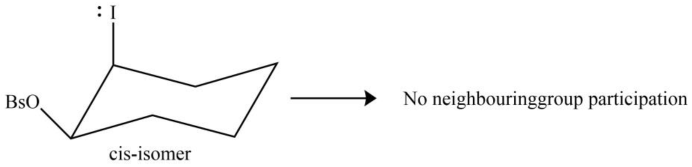
$$Rate = k[RX]$$

Where k is the rate constant and symbol $[RX]$ represents the molar concentration of the substrate.

➢ *Anchimeric Assistance by Heteroatom with Lone Pair*

The typical example of this type of anchimeric assistance that arises via neighboring group mechanisms is the reaction involving the acetolysis of trans-2-iodocyclohexyl brosylate in which the rate is 1.75×10^{6} times greater than what is in acetolysis of cis-isomer.

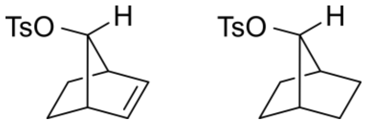




Also, it is obvious from the above route that the configuration would have changed if the reaction had taken place via the normal SN_2 route.

➢ *Anchimeric Assistance by Alkene*

The typical example of this type of anchimeric assistance that arises via neighboring group mechanism is the reaction involving the solvolysis of unsaturated tosylate in which the rate is 10^{11} times greater than what is in solvolysis of saturated tosylate.



The carbocationic intermediate will be stabilized by resonance where the positive charge is spread over several atoms. In the diagram below this is shown.

This effect is observed even if the alkene is more remote from the reacting center the alkene can still act in this way.

➢ *Anchimeric Assistance by Aromatic Ring*

The typical example of this type of anchimeric assistance that arises via neighboring group mechanism is the reaction tosylate with acetic acid in solvolysis in which the rate is much greater than what is in solvolysis via aliphatic counterpart.

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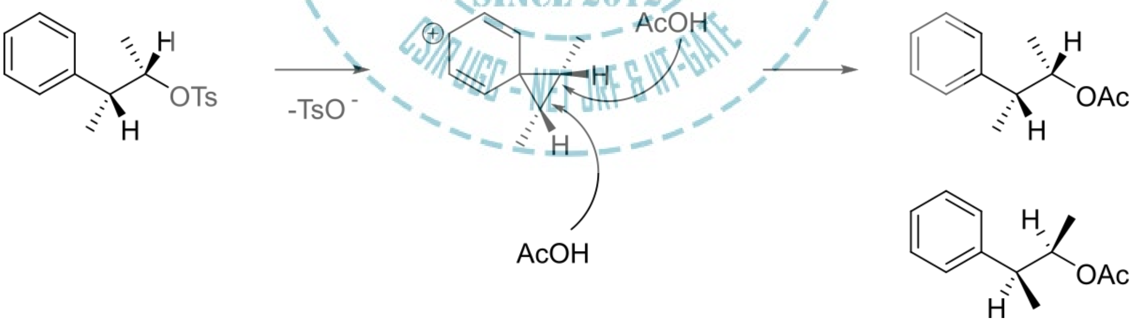
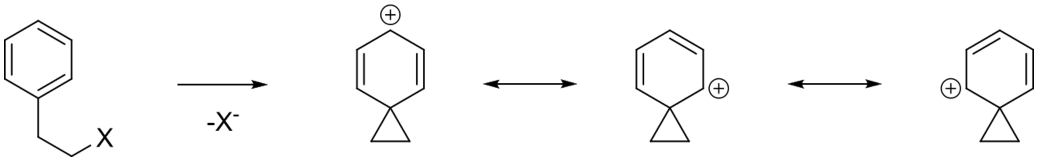


It is obvious from the above routes that the configuration would have changed if the reaction had taken place via the normal SN_2 route. An aromatic ring assists in the formation of a carbocationic intermediate called a phenonium ion by delocalizing the positive charge.



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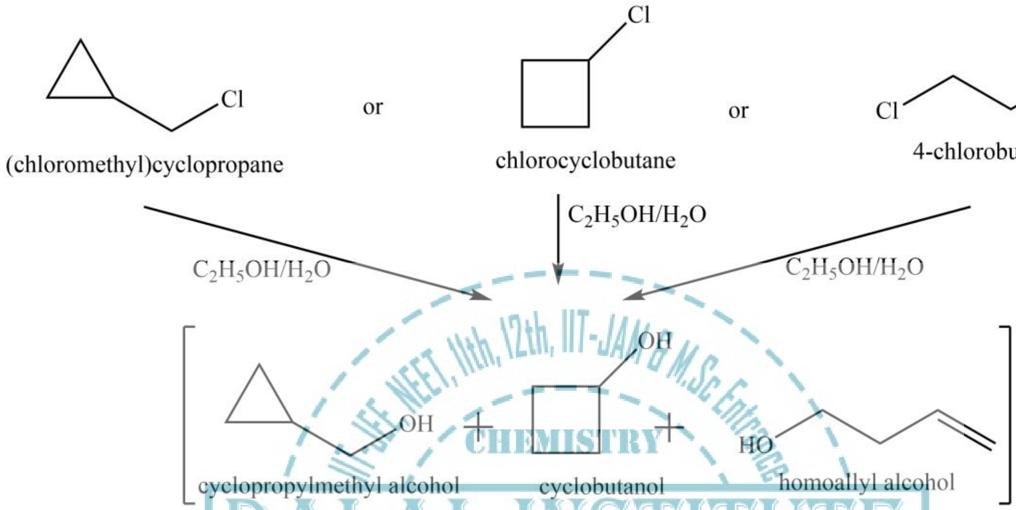
➢ *Anchimeric Assistance by Cyclopropylmethyl System*

The typical example of this type of anchimeric assistance that arises via neighboring group mechanism is the reaction of cyclopropylmethyl chloride with dilute ethyl alcohol in which the rate is much greater than what is expected in the normal SN_2 route. Similar results were obtained if we use cyclobutyl chloride or homoallyl chloride instead of cyclopropylmethyl chloride.



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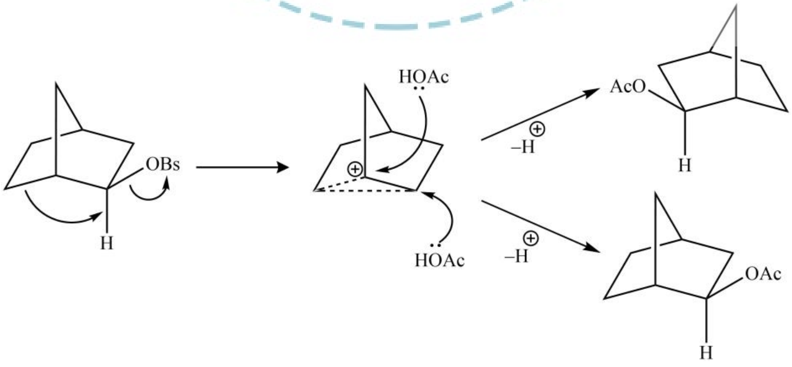
All this suggests that the carbocationic intermediate present in all three reactions must be the same, which in turn, is responsible for the same resulting products.

➢ *Anchimeric Assistance by Aliphatic Bonds*

The typical example of this type of anchimeric assistance that arises via neighboring group mechanism is the reaction of the acetolysis of exo-2-norbonyl brosylate yielding an racemic mixture of exo-acetates in which the rate is much greater than what is for endo-2-norbonyl brosylate.



Therefore, we conclude that the enhanced rate can be due to the anchimeric assistance by the aliphatic carbon-carbon single bond.

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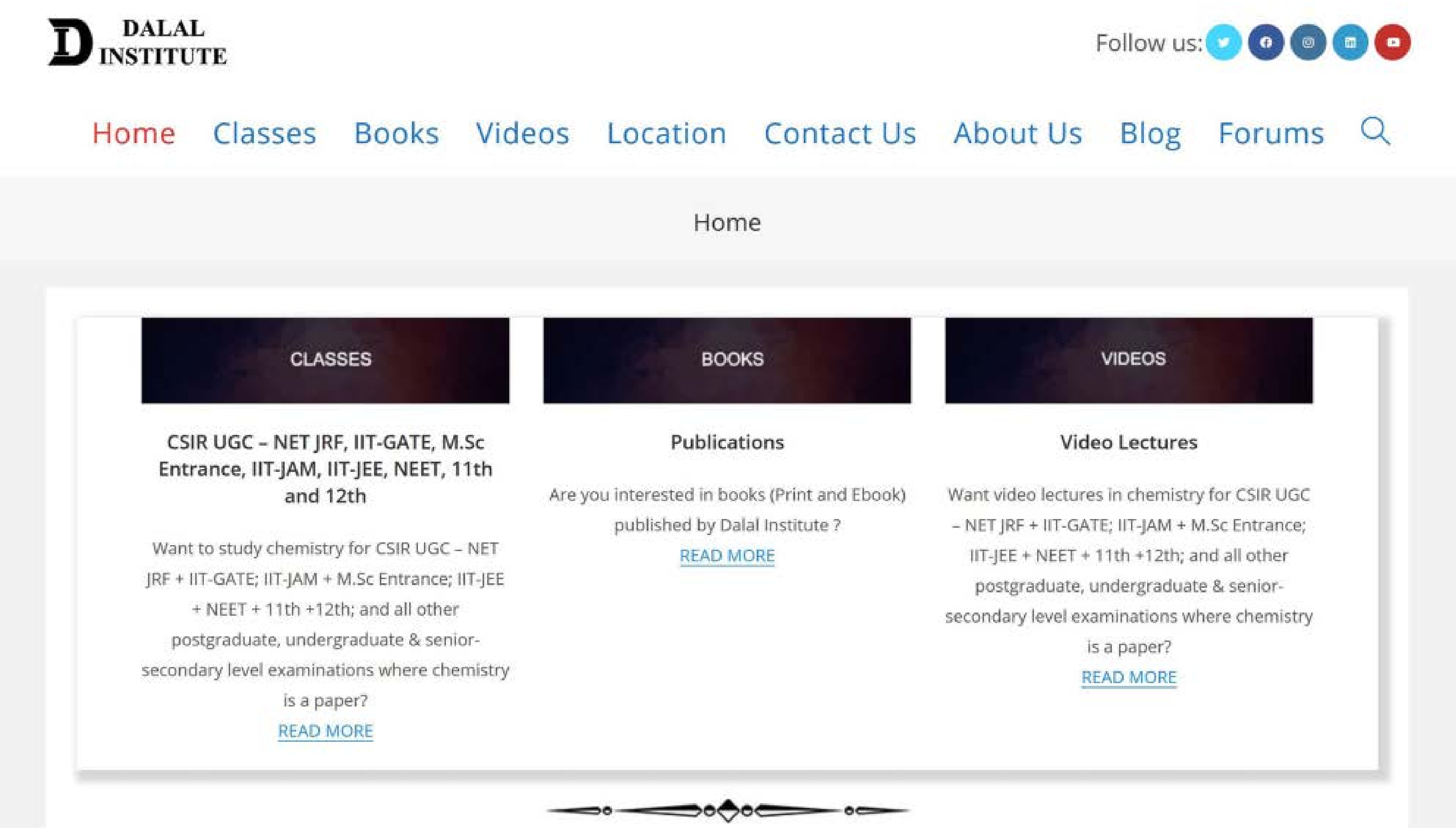

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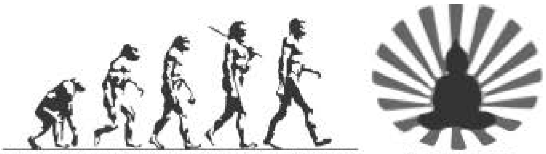

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Table of Contents

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$_R$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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