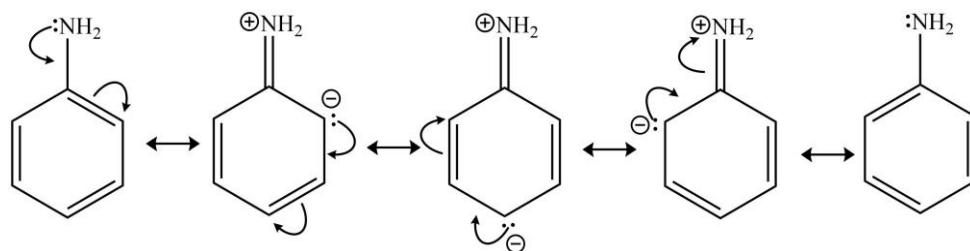
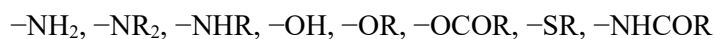


## ❖ Orientation and Reactivity

The orientation and reactivity in monosubstituted benzene for electrophilic substitution reaction can be divided into four major types as discussed below.

### ➤ Ring Activator with *o*-, *p*-Directing Influence

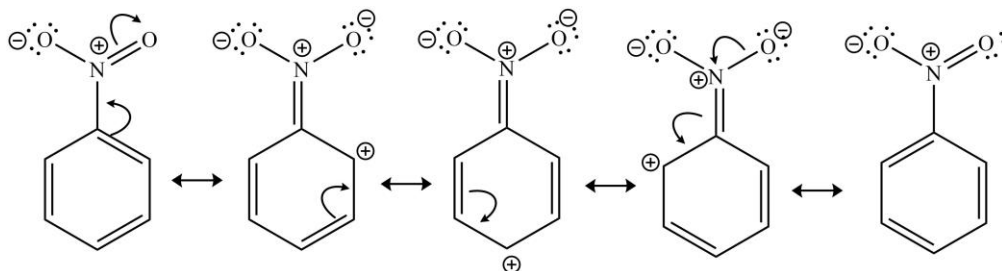
The substituents like  $-XY$ , where X has lone pairs of electrons and no conjugated double bond in extended part (Y), increase the electron density at the ring; and therefore, are strongly activating. Furthermore, these types of groups donate those lone pair of electrons to the  $\pi$ -system, creating a negative charge density at para and ortho sites; and therefore, become ortho/para-directing via resonance. Nevertheless, one might ask that what if these groups are electron-withdrawing via inductive effect. The answer would be the same (i.e., ring activated) because the electron donation via mesomeric effect is much dominant than the inductive effect in these types of groups. Some typical examples of this type of group are given below with  $NH_2$  as reference.



In other words, we can conclude that these groups make these positions more susceptible to an electron-deficient electrophile.

### ➤ Ring Deactivator with *m*-Directing Influence

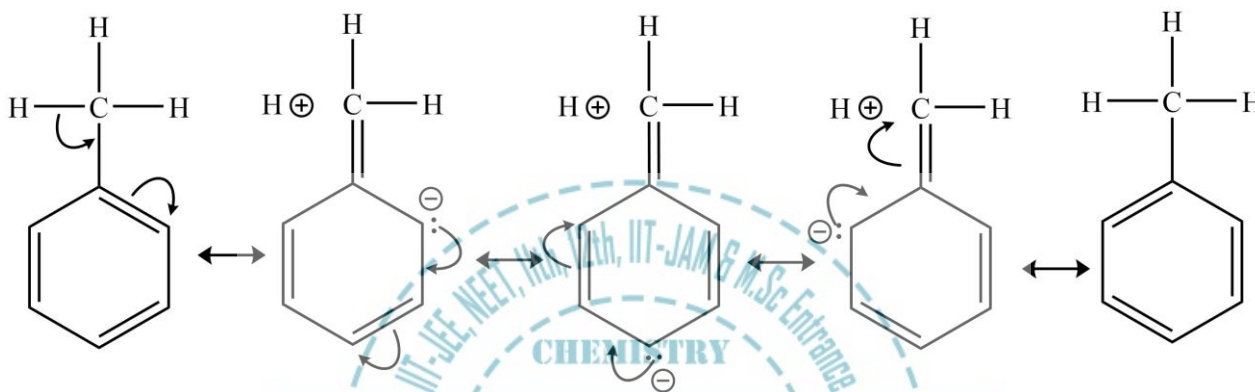
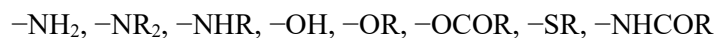
The substituents like  $-X=O$ , where there is a conjugated double bond (w.r.t ring), decrease the electron density at the ring; and therefore, are strongly deactivating. Furthermore, these types of groups accept those electrons from the  $\pi$ -system, creating a positive charge density at para and ortho sites; and therefore, become meta-directing via resonance. Some typical examples of this type of group are given below.



In other words, we can conclude that these groups make *m*-positions more susceptible towards an electron-deficient electrophile.

➤ **Ring Activator with *o*-, *p*-Directing Influence**

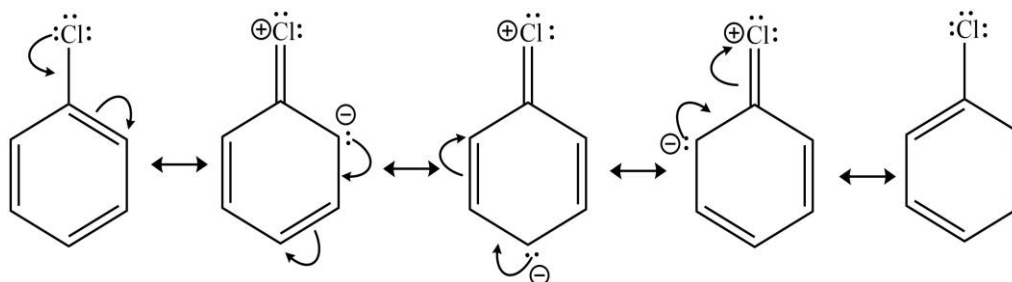
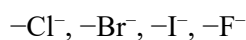
Alkyl groups as substituents increase the electron density at the ring via hyperconjugation; and therefore, are strongly activating. In other words, these groups make *o*- and *p*-positions more susceptible towards an electron-deficient electrophile. Furthermore, these groups are also electron releasing via inductive effect making them highly ring-activating species. Some typical examples of this type of substituents are given below with  $\text{CH}_3$  as reference.



In other words, these groups make *o*- and *p*-positions more susceptible towards an electron-deficient electrophile.

➤ **Ring Deactivator with *o*-, *p*-Directing Influence**

Although the halogens as substituents also have lone pairs of electrons, they decrease the electron density at the ring; and therefore, are strongly deactivating. This is because these types of groups donate those lone pair of electrons to the  $\pi$ -system via resonance (creating a negative charge density at *para* and *ortho* sites), but also withdraw electron density via inductive effect which is more dominant. Some typical examples of these types of groups are given below with  $\text{CH}_3$  as the reference.



In other words, these groups make these positions (*o*- and *p*- to the attached halogen) more susceptible towards the electron-deficient electrophile.

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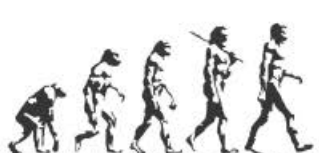
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# A TEXTBOOK OF ORGANIC CHEMISTRY

**Volume I**

**MANDEEP DALAL**



*First Edition*

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# 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>



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