



Contents

Preface

v

PART – I

1. Use of Water as a Solvent for Organic Reaction	1.1
1. Introduction	1.1
2. Reactions in Aqueous Phase	1.3
2.1 Pericyclic reactions	1.3
3. Conclusion	1.83
2. Organic Reactions in Super Critical Water or in Near Water (NCW) Region	2.1
1. Introduction	2.1
2. Organic Reactions in SC – H ₂ O	2.1
3. Organic Reactions in Near-critical Water (NCW) Region	2.4
3.1 Conversion of aryl halides into phenols	2.4
3.2 Claisen rearrangement	2.4
3.3 Pinacol-pinacolone rearrangement	2.4
3.4 Hydration of alkenes: synthesis of carvacrol from carvone	2.4
3.5 Diels-alder cycloaddition reaction	2.5
3.6 Fischer indole synthesis	2.5
3.7 Hydrolysis of esters and amides	2.6
3.8 Decarboxylation	2.6
3.9 Autocatalysis	2.7
4. Miscellaneous Reactions	2.8
5. Conclusion	2.9
3. Microwave Assisted Organic Reactions in Water	3.1
1. Introduction	3.1
2. Synthesis of Heterocycles	3.1

3. N-Alkylation of Nitrogen Heterocycles	3.2
4. Biginelli Reaction	3.3
5. 1, 3-Dioxanes	3.3
6. Heterocyclic Hydrazones	3.4
7. Aza-Michael Reaction	3.4
8. Trost's γ -Addition	3.5
9. Synthesis of Azides, Thiocyanates and Sulfones	3.6
10. Coupling Reactions	3.6
10.1 Suzuki reaction	3.6
10.2 Heck reaction	3.8
10.3 Sonogashira reaction	3.8
10.4 Hiyama reaction	3.9
11. Synthesis of Spiro 2, 5-Diketopiperazines	3.9
12. Synthesis of Diazepines	3.10
13. Synthesis of Trizines and Tetrazoles	3.10
14. Aminocarbonylation Reaction	3.10
15. Kröhnke Reaction	3.11
16. Deprotection of Acetals and Ketals	3.11
17. Nucleophilic Substitution of 6-Chloropurine	3.12
18. Stille Reaction	3.12
19. Cyanation Reactions	3.13
20. Synthesis of Ketones from Amines	3.13
21. Chemoselective Hydrogenation of α , α -Unsaturated Carbonyl Compounds	3.14
22. Hydrophosphinylations of Propargyl Alcohols and Ethynyl Steroids	3.15
23. N-Acylation	3.16
24. N-Alkylation	3.16
25. N-Arylation	3.17
26. Williamson's Ether Syntheses	3.17
27. Syntheses of Heterocycles	3.18
27.1 Five-membered N-heterocycles	3.18
27.2 Six-membered O-heterocycles	3.20
27.3 Six-membered N-heterocycles	3.21
27.4 Six-membered N, S-heterocycles	3.23
28. Mannich Reaction	3.24
29. Nucleophilic Aromatic Substitutions	3.25
30. Epoxide Ring-opening Reaction	3.27
31. Diels-Alder Cycloadditions	3.27

32. Miscellaneous Applications	3.30
32.1 Hofmann elimination	3.30
32.2 Synthesis of deferiprone	3.30
32.3 Hydrolysis of benzyl chloride	3.30
32.4 Hydrolysis of benzamide	3.30
32.5 Hydrolysis of N-phenyl benzamide	3.31
32.6 Hydrolysis of methyl benzoate to benzoic acid (saponification)	3.31
32.7 Oxidation of toluene	3.32
32.8 Coupling of amines with halides	3.32
32.9 N-Heterocyclisations	3.32
33. Conclusion	3.32
4. Organic Synthesis using Biocatalysts	4.1
1. Introduction	4.1
2. Biochemical (Microbial) Oxidations	4.3
3. Biochemical (Microbial) Reductions	4.9
4. Enzymes Catalysed Hydrolytic Processes	4.14
4.1 Enantioselective hydrolysis of meso diesters	4.14
4.2 Hydrolysis of N-acylamino acids	4.15
4.3 Miscellaneous applications of enzymes	4.16
5. Conclusion	4.18
PART – II	
5. Organic Synthesis in Super Critical Carbon Dioxide	5.1
1. Historical Development	5.1
2. Use of Super Critical Carbon Dioxide (Sc CO ₂) for Extracting Natural Products	5.2
3. Use of Super Critical Carbon Dioxide (Sc CO ₂) for Dry Cleaning	5.4
4. Use of Supercritical Carbon Dioxide (SC CO ₂) as Solvent for Organic Reactions	5.6
4.1 Asymmetric catalyst using super critical carbon dioxide	5.6
4.2 Supercritical polymerisations	5.7
4.3 Free Radical bromination	5.7
4.4 Hydrocarbon functionalization	5.7
4.5 Diels-Alder reaction	5.9
4.6 Kolbe-Schmitt synthesis	5.12
4.7 Bromination: displacement of a chlorinated aromatics	5.13
4.8 Freidel-Crafts reaction	5.13
4.10 Hydrogenation in SC – CO ₂	5.14
4.11 Hydroformylation in SC – CO ₂	5.18

4.12	Oxidations in SC – CO ₂	5.19
4.13	Radical reactions in SC – CO ₂	5.22
4.14	Acid-catalysed reactions	5.23
4.15	Coupling reactions	5.24
4.16	Stereochemical control in reactions using SC – CO ₂	5.27
4.17	Photochemical reactions in SC – CO ₂	5.30
4.18	Formation of silica nanoparticles using SC – CO ₂ and water in oil microemulsions	5.30
4.19	Miscellaneous applications	5.31
5.	Conclusion	5.37
6.	Organic Synthesis using Carbon Dioxide	6.1
1.	Introduction	6.1
2.	Synthetic Application of Carbon Dioxide	6.1
2.1	Synthesis of dimethyl carbonate	6.1
2.2	Synthetic of cyclic carbonates	6.2
2.3	Alternating polymensation of oxiranes and CO ₂	6.3
2.4	Synthesis of urea and urethane derivatives	6.3
2.5	Synthesis of carboxylic acids	6.6
2.6	Synthesis of esters	6.9
2.7	Synthesis of lactones	6.10
2.8	Hydroformylation	6.11
2.9	Homologation	6.11
2.10	Use of carbonic acid as acid catalyzed hydrolysis of ketals, acetals and epoxides	6.11
3.	Conclusion	6.12
PART – III		
7.	Organic Synthesis using Ionic Liquids	7.1
1.	Introduction	7.1
2.	Types of Ionic Liquids	7.2
3.	Preparation of Ionic Liquids	7.2
3.1	2,2,2-Trifluoro-N-(trifluoromethylsulphonyl) acetamide salts ¹³ (TSAC)	7.4
3.2	Monoalkylammonium nitrate salts ⁶	7.4
3.3	Tetraalkylammonium tetraalkylborides ⁶	7.4
3.4	Dialkylimidazolium and alkylpyridinium cation based Ionic liquids ¹³	7.4
3.5	Gold Nanoparticles based on imidazolium cation ionic liquids ¹³	7.4
3.6	Ionic liquids with functionalised alkyl chains ¹³	7.5

3.7	Chiral ionic liquids ¹³	7.5
3.8	Halogeno and alkylhalogenoaluminate ionic liquids (binary ionic liquids)	7.6
3.9	Microwave assisted solvent free preparation of ionic liquids	7.6
3.10	Ionic liquids with fluorine-containing anions	7.7
3.11	Typical preparation routes for ionic liquids	7.7
4.	Selection of a Suitable Ionic Liquid for a Particular Reaction	7.7
4.1	Formation of N-heterocyclic carbenes	7.8
4.2	The Baylis-Hillman reaction in ionic liquids	7.9
4.3	The Knoevenagel condensation	7.12
4.4	Claisen-Schmidt condensation	7.12
4.5	The Horner-Wadsworth-Emmons reaction in ionic liquids	7.13
5.	Synthetic Applications	7.14
5.1	Alkylation	7.14
5.2	Allylation	7.15
5.3	Hydroformylation	7.15
5.4	Alkoxy-carbonylation	7.16
5.5	Oxidations	7.16
5.6	Hydrogenations	7.19
5.7	Carbon-carbon bond forming reactions	7.21
6.	Task-specific Ionic Liquids (TSILs)	7.28
6.1	Brønsted acidic ionic liquids	7.28
6.2	Brønsted-basic ionic liquids	7.31
7.	Other Application of ionic liquids	7.32
7.1	Conversion of epoxies to halohydrins	7.32
7.2	Conversion of oxiranes (epoxides) into thiiranes	7.33
7.3	Thiocyanation of alkyl halides	7.33
7.4	Synthesis of cyclic carbonates	7.33
7.5	Biginelli reaction	7.34
7.6	Synthesis of 3-acetyl-5-[(z)-arylmethylidene] 1, 3-thiazolidine-2, 4-diones	7.34
7.7	Synthesis of symmetric urea derivatives	7.34
7.8	Synthesis of homoallylic amines	7.35
7.9	Conjugate addition of thiols to α , β -unsaturated ketones	7.35
7.10	Nucleophilic displacement reactions	7.35
7.11	Bromination of alkynes	7.35
7.12	Alkene metathesis	7.36
7.13	Electrophilic nitration of aromatics	7.37
7.14	Carbon-oxygen bond formation	7.37

7.15	Synthesis of 1-acetylnaphtholene	7.37
7.16	Synthesis of tonalid and traseolide	7.38
7.17	Selective hydrogenation of aromatic compounds	7.38
7.18	Alkylation of indole and 2-naphthol	7.39
7.19	Methylene insertion reactions	7.39
7.20	Synthesis of pravadoline	7.40
7.21	Synthesis of cyclotrimeratylene (CTV) and tris-(O-allyl) CTV	7.40
7.22	Cycloaddition of carbon dioxide to propylene oxide catalysed by ionic liquids	7.41
7.23	Epoxidation of electrophilic alkenes in ionic liquids	7.41
7.24	Oxidation of benzylic alcohols to carbonyl compounds with KMnO_4 in ionic liquids	7.42
8.	Biotransformations in Ionic Liquids	7.42
8.1	Synthesis of Z-aspartame	7.43
8.2	Conversion of 1, 3-dicyanobenzene to 3-cyanobenzamide and 3-cyanobenzoic acid	7.43
8.3	Transesterification reactions	7.43
8.4	Ammoniolysis of carboxylic acids	7.45
8.5	Synthesis of epoxides	7.45
8.6	Transesterification of chiral substrates	7.45
8.7	Synthesis of geranyl acetate	7.46
8.8	Transesterification of glucose and L-ascorbic acid	7.47
8.9	Enantioselective hydrolysis of a prochiral malonic ester	7.47
8.10	Kinetic resolution of N-acetyl- α -amino acid esters	7.48
8.11	Enantioselective hydrolysis of methyl phenyl glycinate and naproxen methyl ester and 2-(4-chlorophenoxy) propionic ester	7.48
8.12	Enantioselective esterification of ibuprofen and 2-substituted propanoic acids	7.49
8.13	Enantioselective aminolysis of methyl mandelate	7.50
9.	Application of Ionic Liquids as Solvents for Polymerization Processes	7.50
10.	Conclusion	7.52

PART – IV

8.	Polyethylene Glycol and its Solutions as Green Reaction Medium of Future	8.1
1.	Introduction	8.1
2.	Characteristics of PEG	8.1
3.	Use of PEG in Organic Reactions	8.2
3.1	Substitution reactions	8.2
3.2	Oxidation reactions	8.4
3.3	Reduction reactions	8.4

4. Peg as Phase-Transfer Catalyst (PTC)	8.6
4.1 Williamson ether synthesis	8.6
4.2 Substitution reactions using PEGs as PTC	8.6
4.3 Oxidation reactions using PEG as PTC	8.8
4.4 Reductions using PEG as PTC	8.9
5. L-Proline Catalysed Asymmetric Aldol Reactions	8.10
6. L-Proline Catalysed Asymmetric Transfer Aldol Reaction	8.11
7. Asymmetric Dihydroxylation of Olefins	8.12
8. Regioselective Heck Reaction	8.14
9. Baylis-Hillman Reaction	8.15
10. Synthesis of 2-Thiazol-4-Ones via PEG-Supported 1-Aminocarbonyl 1, 2-Diaza-1, 3-Butadiene	8.16
11. Catalytic Transfer Hydrogenation Reactions (CTH) to PEG-bound Substrates	8.18
12. Suzuki Cross-Coupling Reaction in PEG	8.20
13. Synthesis of Azo Compounds Using PEG	8.21
14. Oxidation of Cyclohexene to Adipic Acid in Polyethylene Glycol Based Aqueous Biphasic System Using Sodium Tungstate and Hydrogen Peroxide	8.23
15. Enzymatic Reactions	8.24
16. Synthesis of 2-Amino-2-Chromenes	8.24
17. Decarboxylation of Cinnamic Acid	8.25
18. Conclusion	8.26

PART – V

9. Organic Synthesis using Fluorous Phase Techniques	9.1
1. Introduction	9.1
2. Characteristics of Perfluorous Liquids	9.2
3. Phase Switching	9.3
4. Perfluorinated Catalysts	9.4
5. Some Application of Fluorous Phase Techniques	9.5
6. Conclusion	9.9
<i>Index</i>	<i>I.1</i>