Contents

1. Permanganate 1
1.1. Introduction 1
1.2. General Procedure for Oxidation of Primary Alcohols to Carboxylic Acids with Potassium Permanganate 5
1.3. Functional Group and Protecting Group Sensitivity to Potassium Permanganate 7
1.4. Side Reactions 9
1.5. References 10

2. Jones and Other CrO_3-Based Oxidations 13
2.1. Introduction 13
Mechanism 13
Inverse Addition 15
Solvent 16
Acidity 17
Zhao's Catalytic CrO_3 Oxidation 18
2.2. General Procedure for Oxidation of Primary Alcohols to Carboxylic Acids with Jones Reagent 19
2.3. Functional Group and Protecting Group Sensitivity to Jones Oxidation 21
2.4. Side Reactions 25
2.5. References 28

3. Pyridinium Dichromate (PDC) in Dimethylformamide. The Method of Corey and Schmidt 33
3.1. Introduction 33
3.2. General Procedure for Oxidation of Aliphatic Primary Alcohols to Carboxylic Acids with Pyridinium Dichromate in Dimethylformamide. Method of Corey and Schmidt 34
3.3. Functional Group and Protecting Group Sensitivity to PDC in DMF 36
3.4. Side Reactions 38
3.5. References 39

4. Heyns Oxidation 43
4.1. Introduction 43
Solvent 45
pH 46
Oxygen 48
Platinum 48
Poisons 49
Selectivity 50
Application 52
4.2. General Procedure for Heyns Oxidation of Primary Alcohols to Carboxylic Acids 52
4.3. Functional Group and Protecting Group Sensitivity to Heyns Oxidation 55
4.4. Side Reactions 56
4.5. References 58

5. Ruthenium Tetroxide and Other Ruthenium Compounds 61
5.1. Introduction 61
Procedure of Pappo and Becker 61
Sharpless' Modification 62
Mechanism 63
Solvent 63
Buffering 65
RuO_4 Source 65
Secondary Oxidant 66
Ruthenate and Perruthenate Oxidations 66
Application 68
5.2. General Procedure for Oxidation of Primary Alcohols to Carboxylic Acids with Catalytic RuO_4 68
5.3. Functional Group and Protecting Group Sensitivity to Oxidation with Catalytic RuO_4 70
5.4. Side Reactions 74
5.5. References 76

6. TEMPO-Mediated Oxidations 79
6.1. Introduction 79
Mechanism 81
Stoichiometric Oxidants 83
Amino 1-Oxyl Radicals 83
6.2. Anelli's Oxidation 83
Solvent 85
Catalyst 86
Phase-Transfer Catalyst 87

pH 87
Selectivity 88
6.2.1. General Procedure for Oxidation of Primary Alcohols to Carboxylic Acids by Anelli's Oxidation 90
6.3. Zhao's Modification of Anelli's Oxidation 93
6.3.1. General Procedure for Oxidation of Primary Alcohols to Carboxylic Acids by Zhao's Modification of Anelli's Oxidation 94
6.4. Oxidation of Epp and Widlanski 96
Mechanism 96
Selectivity 97
6.4.1. General Procedure for Oxidation of Primary Alcohols to Carboxylic Acids by the Protocol of Epp and Widlanski 98
6.5. Functional Group and Protecting Group Sensitivity to TEMPO-Mediated Oxidations 99
6.6. Side Reactions 100
6.7. References 101

7. Oxidation of Alcohols to Carboxylic Acids via Isolated Aldehydes 105
7.1. Introduction 105
7.2. References 109

Index 111