

Table of Contents

I. Introduction	1
1. The Oxidation States of Chromium	1
2. The Chemistry of Chromium(VI)	1
3. Chromium(VI) as Oxidant in Organic Chemistry	5
References of Chapter I	6
II. Oxidation of Carbon-Hydrogen Bonds	8
A. Oxidation of Alkanes	8
1. Oxidation of Alkanes With Chromic Acid in Acetic Acid	8
2. Oxidation of Alkanes With Chromic Acid in Aqueous Sulphuric Acid	16
3. Oxidation of Alkanes With Chromyl Chloride	18
4. Mechanism of Oxidation of Alkanes	19
B. Oxidation of Arylalkanes (Benzylic Oxidation)	23
1. Oxidation of Arylalkanes With Chromic Acid in an Acidic medium	23
2. Oxidation of Arylalkanes With Aqueous Sodium Dichromate	29
3. Oxidation of Arylalkanes With Chromyl Chloride (Etard Reaction)	33
4. Mechanism of Benzylic Oxidation	37
C. Allylic Oxidation	41
1. Allylic Oxidation of Olefins With Chromium(VI) in Acetic Acid and Acetic Anhydride	41
2. Allylic Oxidation With Chromium Trioxide-Heterocyclic Bases Addition Compounds	45
3. Allylic Oxidation With Tert-butyl-chromate	50
4. Mechanism of Allylic Oxidation	53
References of Chapter II	55
III. Oxidation of Carbon-Carbon Double Bonds	59
A. Oxidation of Alkenes	59
1. Oxidation of Alkenes With Chromium Trioxide in Acetic Anhydride or Acetic Acid	59

2. Oxidation of Alkenes With Chromic Acid in Aqueous Sulphuric Acid	71
3. Mechanism of Alkene Oxidation With Chromic Acid	77
4. Oxidation of Alkenes With Chromyl Chloride	80
5. Mechanism of Alkene Oxidation With Chromyl Chloride	86
6. Oxidation of Alkenes With Silver Chromate-Iodine	88
B. Oxidation of Enol-Derivatives	90
1. Oxidation of Enol-Ethers With Pyridinium Chlorochromate	90
2. Oxidation of O-Silylated Enolates With Chromyl Chloride	92
C. Ring Oxidation of Aromatic Compounds	92
1. Oxidation of Polynuclear Arenes With Chromium(VI) Under Acidic Conditions	93
2. Oxidation of Phenols and Aromatic Amines With Chromium(VI) Under Acidic Conditions	96
3. Oxidation of Phenols With Chromyl Chloride	106
4. Oxidation of Hydroquinone Silyl Ethers With Pyridinium Chlorochromate	107
5. Oxidation of Ortho-Allylphenols With Tetraalkylammonium Dichromate	109
6. Oxidation of Some Aromatic Heterocyclic Compounds With Chromium(VI)	109
References of Chapter III	114

IV. Oxidation of Alcohols 118

A. Oxidation of Alcohols by Chromium(VI) Under Acidic Conditions	118
1. Oxidation of Alcohols With Chromic Acid in Aqueous Sulphuric Acid	119
2. Oxidation of Alcohols With Chromic Acid in Acetic Acid or Aqueous Acetic Acid	124
3. Oxidation of Alcohols With Chromic Acid in Aqueous Sulfuric Acid and Acetone (Jones' Reagent).	132
4. Oxidation of Alcohols With Chromic Acid in Dimethylformamide or Dimethylsulphoxide Containing Sulphuric Acid	145
5. Oxidation of Alcohols With Chromic Acid in Two-phase systems	145
B. Oxidation of Alcohols With Compounds of Chromium(VI) and Heterocyclic Bases	150
1. Oxidation of Alcohols With Chromium Trioxide-(Pyridine) ₂ Complex	151
2. Oxidation of Alcohols With Pyridinium Dichromate	161
3. Oxidation of Alcohols With Pyridinium Chlorochromate (PCC)	167
4. Oxidation of Alcohols With Pyridinium Fluorochromate	178

5. Oxidation of Alcohols With Chromium Trioxide-3,5-Dimethylpyrazole Complex	180
6. Oxidation of Alcohols With 2,2'-Bipyridinium Chlorochromate	182
7. Oxidation of Benzylic and Allylic Alcohols With 4-(Dimethylamino)pyridinium Chlorochromate (DMAP · HCrO ₃ Cl)	182
8. Oxidation of Alcohols With Chromium(V) Reagents	185
C. Oxidation of Alcohols With Chromium(VI) Under Neutral Conditions	187
1. Oxidation of Alcohols With Di-tert-butylchromate (TBC)	187
2. Oxidation of Alcohols With Chromium Trioxide in Hexamethylphosphoramide	189
3. Oxidation of Alcohols With Tetraalkylammonium Chromates in Apolar Solvents	193
D. Oxidation of Alcohols With Supported Chromium(VI) Reagents	195
1. Oxidation of Alcohols With Chromium(VI) Reagents Supported on Organic Polymers	196
2. Oxidation of Alcohols With Chromium(VI) Reagents Adsorbed or Dispersed on Inorganic Support	200
E. Mechanism of Oxidation of Alcohols	204
F. Effect of the Structure and Stereochemistry of Secondary Alcohols on the Rate of Oxidation	208
References of Chapter IV	211

V. Oxidation of Aldehydes and Ketones 217

A. Oxidation of Aldehydes	217
1. Oxidation of Aldehydes With Chromic Acid Under Acidic Conditions	217
2. Oxidation of Aldehydes With Pyridinium Chlorochromate and Pyridinium Dichromate	218
3. Oxidation of Aldehydes With Chromium(V) Reagents	221
4. Mechanism of Aldehyde Oxidation	224
B. Oxidation of Ketones	225
1. Oxidation of Ketones With Chromic Acid Under Acidic Conditions	225
2. Mechanism of Ketone Oxidation	227
References of Chapter V	227

VI. Oxidation of Carbon-Metal Bonds 229

A. Oxidation of Organoboron Compounds	229
1. Oxidation of Organoboranes With Chromic Acid Under Acidic Conditions	230
2. Oxidation of Organoboranes With Pyridinium Chlorochromate	230

3. Oxidation of Trialkylborates With Pyridinium Chlorochromate	233
4. Oxidation of 1,1- and 1,2-diorganoboranes With Chromium Trioxide-(Pyridine) ₂	235
B. Oxidation of Organotin Compounds	
1. Oxidation of Organotin Compounds With Chromium Trioxide-(Pyridine) ₂ and Pyridinium Chlorochromate	236
References of Chapter VI	237
VII. Oxidation of Halides, Ethers, Acetals, Sulphides, and Some Nitrogen Containing Compounds	238
A. Oxidation of Alkyl Halides	238
B. Oxidation of Ethers	240
C. Oxidation of Acetals	243
D. Oxidation of Sulphides	244
E. Oxidation of Alkyl Aryl Amines	246
F. Oxidation of Oximes	246
G. Oxidation of Hydroxylamine	248
References of Chapter VII	249
VIII. Some Remarks on Selectivity and Synthetic Use of Chromium (VI) Oxidation	250
A. Oxidation of Carbon-Hydrogen Bond	250
1. Alkanes	250
2. Arylalkanes	250
3. Allylic Oxidation	252
B. Oxidation of Carbon-Carbon Double Bonds	253
1. Oxidation of Alkenes	253
2. Oxidation of Enol Derivatives	253
C. Ring Oxidation of Aromatic Compounds	254
D. Oxidation of Alcohols	254
E. Oxidation of Aldehydes and Ketones	257
F. Oxidation of Carbon-Metal Bonds	257
Subject Index	259