

Mark M. Green, Harold A. Wittcoff

Organic Chemistry Principles and Industrial Practice



 WILEY-VCH

Contents

Preface XV

What the Experts Say about this Book XIX

- 1 **How Petroleum is converted into Useful Materials:
Carbocations and Free Radicals are the Keys** 1
- 1.1 The Conflicting Uses for Petroleum: The Chemical Industry
and the Internal Combustion Engine 1
- 1.2 How do we achieve these Two Objectives? By Using two different Kinds of
Cracking: One depends on Free Radicals and the Other on Carbocations 2
- 1.3 What is in Petroleum? 3
- 1.4 The Historical Development of Steam Cracking 4
- 1.5 What was Available before Thermal and Steam Cracking? 6
- 1.6 Acetylene was Widely Available before Steam Cracking
and Exceptionally Useful but Everyone wanted to replace
this Dangerous Industrial Intermediate. Happily,
Double Bonds replaced Triple Bonds 6
- 1.7 Petroleum yields Ethylene and lays the Groundwork for a New Kind
of Chemical Industry 8
- 1.8 But What about that Thirsty Internal Combustion Engine?
The Development of Catalytic Cracking 8
- 1.9 Discovery of the Proper Catalyst for Catalytic Cracking:
From Natural Synthetic Zeolites 10
- 1.10 Let's compare the Mechanisms of Steam and Catalytic Cracking:
Free Radicals versus Carbocations 12
- 1.11 How are Free Radicals formed in Steam Crackers, and What do they do? 12
- 1.12 Now let's look at Catalytic Cracking and the Essential Role of Carbocations
and their Ability to rearrange the Structure of Organic Molecules 15
- 1.13 What's going on inside those Zeolite Pores? 16
- 1.14 Why do Steam Cracking and Catalytic Cracking produce such Different Results.
Or, in Other Words, Why do Carbocations and Free Radicals
behave so Differently? 19
- 1.15 Summary 20
- Study Guide Problems for Chapter 1 21

- 2 Polyethylene, Polypropylene and the Principles of Stereochemistry 23**
- 2.1 The Thermodynamics of Addition Polymerization: the Competition between Enthalpy and Entropy 23
- 2.2 Polyethylene is formed via a Free Radical Polymerization that involves the Classic Steps of all Chain Reactions: Initiation, Propagation, and Termination 24
- 2.3 Attempted Free Radical Polymerization of Propylene. It fails because of Resonance Stabilization of Allylic Radicals 27
- 2.4 So How is Polypropylene made? Organometallic Chemistry can do what Free Radical Chemistry cannot. And the Big Surprise is the Role of Stereochemistry and Specifically Chirality. This is Something No One suspected 29
- 2.5 There are More Kinds of Polyethylene than the One produced by the Free Radical Chain Mechanism 29
- 2.6 What have we learned from the Organometallic Method for Polymerizing Ethylene that leads to the Possibility of Polymerizing Propylene? 32
- 2.7 Do the Methyl Groups on Every Third Carbon on Each Individual Polypropylene Chain all have to be on the Same Side of the Chain? 34
- 2.8 What do the Opposite "Faces" of Propylene have to do with the Formation of Isotactic Polypropylene by the Ziegler–Natta Catalyst? 35
- 2.9 From the Ziegler–Natta Catalyst to Single-site Catalysts: Creating a Catalyst with a Precisely Known Structure that can Polymerize Propylene to an Isotactic Polypropylene 36
- 2.10 How does this Small Molecule Analog of the Ziegler-Natta Catalyst polymerize Propylene? 38
- 2.11 An Interesting Story concerning Industrial Conflict 40
- 2.12 Summary 41
- Study Guide Problems for Chapter 2 42
- 3 The Central Role of Electrophilic Aromatic Substitution 45**
- 3.1 Materials derived from Ethylene, Propylene and Benzene are All Around Us 45
- 3.2 The Carbon Atoms in Ethylene, Propylene and Benzene find their Way into Polystyrene, Polycarbonate, and Epoxy Resin 46
- 3.3 Industrial Synthesis of the Building Blocks of Polystyrene, Polycarbonate, and Epoxy Resin 47
- 3.4 How Isopropylbenzene is Industrially produced and the Struggle to reduce the Di- and Triisopropylbenzene Byproducts 49
- 3.5 How Ethylbenzene is produced Industrially 52
- 3.6 Zeolites and Ethylbenzene 52
- 3.7 How does the Zeolite Catalyst repress the Formation of Di- and Triethylbenzene? 54
- 3.8 So Why are Zeolites not used for the Formation of Cumene? 54
- 3.9 What Role does Cumene play in the Production of Epoxy Resin and Polycarbonate? 56

- 3.10 How Phenol and Acetone react together to form an Isomeric Mixture of the Intermediate $\text{HOC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{OH}$, which then goes on to form Isomers of Bisphenol A 56
- 3.11 We continue Our Backward Path. How are Phenol and Acetone formed from Cumene? 59
- 3.12 A Remarkable Rearrangement 60
- 3.13 Summary 62
- Study Guide Problems for Chapter 3 64

- 4 From Nucleophilic Chemistry to Crosslinking, with a Side Trip to Glycerol, in the Synthesis of Commercially Important Plastics 67**
- 4.1 The Structure and Use of Epoxy Resins 67
- 4.2 Epoxy Coatings and their Curing (Crosslinking) and Pot Life 68
- 4.3 The Molecular Source of the Toughness of Epoxy Resin 71
- 4.4 With Epichlorohydrin and Bisphenol A We are only One Step, a Nucleophilic Step, from Epoxy Resin. It all depends on the Reactivity of the Epoxide Ring 71
- 4.5 Just as for Formation of Epoxy Resin, Curing of Epoxy Resin also involves Nucleophilic Chemistry and the Reactivity of the Epoxide Ring 74
- 4.6 How Epichlorohydrin is synthesized from Allyl Chloride by a Classic Double Bond Addition Reaction followed by Formation of an Epoxide 76
- 4.7 How is Allyl Chloride produced industrially from Propylene? 77
- 4.8 A Less Temperature-dependent Way to make Epichlorohydrin 79
- 4.9 A Final Note about Epoxy Resins 80
- 4.10 What did the Original Shell Method for producing Epichlorohydrin have to do with Glycerol? The Answer is Alkyd Resins and this will teach Us More about Crosslinking and also introduce Nucleophilic Acyl Chemistry 80
- 4.11 The Earliest Production of Glycerol arose from Production of Soap 86
- 4.12 What Commercial Uses exist for Glycerol? 87
- 4.13 The Role of Glycerol in Dynamite, and the Nobel Prize 88
- 4.14 Glycerol plays a Role in the Production of Polyurethanes: Nucleophilic Chemistry and Crosslinking 89
- 4.15 Polyurethanes are a Product of the Chemical Reactivity of Isocyanates 90
- 4.16 A Route to Chemically Crosslinked Polyurethanes 92
- 4.17 Polyether Polyols are widely used for forming Crosslinked Polyurethanes. There are many Variations on this Theme 93
- 4.18 What About the Foamed Structure of the Polyurethane? Addition of a Small Amount of Water is a Common Answer 94
- 4.19 Let's return again to Bisphenol A and learn about an Entirely Different Kind of Plastic, Polycarbonate, which is Very Different from Epoxy, Alkyd Resins and Polyurethanes 95
- 4.20 How Polycarbonates are synthesized and the Unwelcome Role of Phosgene 96
- 4.21 Is there a Future in the Chemical Industry for a Chemical as Dangerous as Phosgene? 99
- 4.22 A few Remarks about the Double Meaning of Chloride as a Leaving Group 99

4.23	Summary	101
	Study Guide Problems for Chapter 4	103
5	The Nylon Story	107
5.1	What was the World of Polymers like When Carothers entered the Picture?	107
5.2	What did Carothers do at DuPont?	109
5.3	Carothers' Work at DuPont had Enormous Consequences for both DuPont and the Chemical Industry?	111
5.4	The Similarities and Distinctions of the Various Polyamides that make up the Family of Nylons	112
5.5	The Industrial Route to Adipic Acid and Hexamethylene Diamine: the Precursors of Nylon 6,6. Benzene is the Source	116
5.6	Hexamethylene Diamine from 1,3-Butadiene. Improving a Route to a New Kind of Rubber led to a Better Way to synthesize Hexamethylene Diamine: Industry and the Principle of Thermodynamic versus Kinetic Control of Reaction Products	119
5.7	The Role of Acrylonitrile in the Production of Nylons	122
5.8	From the Dicarboxylic Acid and the Diamine to Nylon?	125
5.9	Nylons made from a Single Monomer: Nylon 6	127
5.10	Another Nylon made from a Single Monomer: Nylon 11	129
5.11	Summary	132
	Study Guide Problems for Chapter 5	134
6	Competition for the Best Industrial Synthesis of Methyl Methacrylate	137
6.1	Economic and Environmental Factors are Driving Forces for Industrial Innovation	137
6.2	Plexiglas TM	137
6.3	The Classical Route to Methyl Methacrylate involves the Essential Role of Cyanohydrins, which can be Easily Converted to Unsaturated Carboxylic Acids	139
6.4	Problems in the Classical Approach to Synthesis of Methyl Methacrylate	142
6.5	What New Possibilities exist for Replacing the Old Process? Can the Ammonium Bisulfate Disposal Problem be Solved?	143
6.6	The Mitsubishi Gas Chemical Company Approach to improving the Synthesis of Methyl Methacrylate	144
6.7	The Double Bond still has to be Introduced to form the Final Methyl Methacrylate Product	146
6.8	Can Things still be Improved Further?	146
6.9	From Isobutene to Methyl Methacrylate: Mitsubishi Rayon versus Asahi	147
6.10	How Environmental Reasons stopped the Use of Tetraethyllead as an Octane Improver in Gasoline leading to its Replacement with Methyl Tertiary Butyl Ether (MTBE). But MTBE is synthesized from Isobutene, which <i>could have</i> blocked the Supply of Isobutene for Production of Methyl Methacrylate. But Environmental Concerns about MTBE have caused it to lose Favor as an Octane Improver in Gasoline therefore releasing Isobutene for Production	

- of Methyl Methacrylate. A Story of the Ups and Downs
of the Chemical Industry – What a Ride! 148
- 6.11 A Competitive Process for the Synthesis of Methyl Methacrylate
based on Ethylene 150
- 6.12 A Competitive Process for Synthesis of Methyl Methacrylate based
on Propylene 151
- 6.13 A Possible Commercial Synthesis of Methyl Methacrylate starting from Methyl
Acetylene 152
- 6.14 Summary 153
- Study Guide Problems for Chapter 6 155
- 7 Natural Rubber and Other Elastomers 157**
- 7.1 Introduction to Rubber 157
- 7.2 Why are Some Materials Rubbery? 158
- 7.3 The Conformational Basis of Elasticity 158
- 7.4 How does the Structure of Natural Rubber fit into the Theoretical
Picture of Elasticity drawn above? 160
- 7.5 Let's take a Short Diversion from Elastomers 162
- 7.6 Elastomers require Essentially Complete Recoverability from the Stretched State.
The Story of Vulcanization and How Sulfur supplies this Characteristic to Hevea
Rubber 163
- 7.7 What happens When Sulfur and Natural Rubber are mixed and heated? 164
- 7.8 Hypalon: an Elastomer that can be Crosslinked without the Presence of Double
Bonds 167
- 7.9 Many Synthetic Elastomers are produced by the Chemical Industry.
In Every Case the Physical Principles are Identical to those at Work in Natural
Rubber and the Essential Characteristic of an Elastomer must be present,
that is, a Crosslinked Flexible Polymer Chain 170
- 7.10 What Kinds of Polymer Properties will preclude Elastomeric Behavior?
What Kinds of Polymers could be called Anti-elastic? 177
- 7.11 Physical Interactions among Polymer Chains can be used to form Elastomers
with Unique Properties. How the Polymeric Glassy State can act as a Physical
Crosslink 177
- 7.12 Variations on the Block Theme produce Thermoplastic Polyurethane Elastomers
including Spandex (LycraTM), the Elastic Fiber.
Here, the Crosslinks involve a Kind of Physical Interaction, which is Different
from Glass Formation 183
- 7.13 Spandex: A Possible Synthesis 185
- 7.14 Ionomers: Yet Another Approach to Reversible Crosslinking 188
- 7.15 Summary 190
- Study Guide Problems for Chapter 7 191
- 8 Ethylene and Propylene: Two Very Different Kinds of Chemistry 195**
- 8.1 Ethylene and Propylene 195
- 8.2 The Industrial Importance of Ethylene and Propylene 195

8.3	Ethylene Oxide and Propylene Oxide are Very Large Volume Industrial Intermediates derived from Ethylene and Propylene but must be Industrially Synthesized in Entirely Different Ways	197
8.4	The Production of Propylene Oxide without using Chlorine	198
8.5	Why did Dow maintain the Hypochlorous Route to Propylene Oxide?	201
8.6	Before We continue to investigate the Difference in the Industrial Chemistry of Ethylene and Propylene, let's take a Diversion from the Main Theme of the Chapter. Why are Ethylene Oxide and Propylene Oxide so Important to the Chemical Industry? We find out by adding Water	201
8.7	Any Process that could produce Ethylene Glycol without Oligomeric Products would be Highly Desirable	204
8.8	We've seen the problems arising from the allylic hydrogens in propylene. Does the Reactivity of these Hydrogens bestow any Advantages?	204
8.9	The Importance of Polyacrylic Acid and its Esters	204
8.10	The Importance of Acrylonitrile and Polyacrylonitrile	206
8.11	How was Acrylonitrile produced in the "Old Days" before the "Propylene Approach" took over?	209
8.12	How was Acrylic Acid produced in the "Old Days" before the "Propylene Approach" took over?	209
8.13	An Early Example of Transition Metal Catalysis led to a Direct Route from Acetylene to Acrylic Acid	211
8.14	The Oxidation of Propylene to Acrylic Acid and to Acrylonitrile shuts down all Previous Processes. The Catalyst is the Key, but the Allylic Hydrogens are Essential	212
8.15	Summary	217
	Study Guide Problems for Chapter 8	218
9	The Demise of Acetaldehyde: A Story of How the Chemical Industry Evolves	221
9.1	An Interesting Example of Shutdown Economics	221
9.2	An Aspect of the Evolution of the Chemical Industry that begins with World War I	223
9.3	The Aldol Condensation leads to n-Butanol	224
9.4	Reactivity Principles associated with the Aldol Condensation	226
9.5	Pentaerythritol and other Polyhydric Alcohols synthesized via Aldol Condensations	229
9.6	A Prominent "Plasticizer" is synthesized via an Aldol Condensation	232
9.7	The Grandfather Molecule of the Aldol Condensation is Acetaldehyde. How was and is Acetaldehyde produced?	234
9.8	A Palladium-based Process, the Wacker Reaction, shuts down all Older Industrial Methods to Acetaldehyde	236
9.9	Hydroformylation – Another Triumph for Transition Metals	238
9.10	How is the Other Product, Acetic Acid, which formerly was made from Acetaldehyde, now produced?	243
9.11	Summary	244
	Study Guide Problems for Chapter 9	246

10	Doing Well by Doing Good	249
10.1	Many Companies in the Chemical Industry have been Amazed to Learn that Replacement of Dangerous and/or Toxic Chemicals Leads not only to Safety, but also to Greater Profit	249
10.2	What's the Problem with Acetylene? First, it is Explosive	249
10.3	What Else is Wrong with Acetylene?	251
10.4	What is the Precise Chemical Nature of these Carbide Salts?	252
10.5	Is Acetylene derived from Calcium Carbide of Commercial Importance?	254
10.6	Large-scale Production of Acetylene	255
10.7	How was Acetylene Used to Produce Industrial Intermediates?	258
10.8	Replacing Acetylene with Ethylene and Zinc with Palladium for the Production of Vinyl Acetate	260
10.9	What is Valuable about Vinyl Acetate?	262
10.10	Replacing Acetylene with Ethylene for the Production of Vinyl Chloride	265
10.11	The Production of 1,4-Butynediol shows an Entirely Different Face of Acetylene Reactivity	268
10.12	Phosgene and Chlorine – the Poison Gases of World War I. Can their Replacement for Industrial Processes by Safer Chemicals also be an Example of “Doing Well by Doing Good?”	273
10.13	Is there a Way to Eliminate Phosgene in the Industrial Synthesis of Polycarbonate?	274
10.14	Let's look at Another Competition, the Production of Methyl Methacrylate, in Terms of Cash and Finance Costs	281
10.15	Reducing the Use of Chlorine in Industrial Processes	282
10.16	HCN is a Dangerous Chemical Hastening its Replacement in the Synthesis of Methyl Methacrylate, as we have seen. But its Exquisite Reactivity has Fostered its Use in Other Processes and Particularly in a Potential Process for Getting rid of Ammonium Sulfate as a Byproduct in the Synthesis of Nylon 6	283
10.17	Routes to Caprolactam that Avoid Production of Ammonium Sulfate	284
10.18	Summary	287
	Study Guide Problems for Chapter 10	289

An Epilogue – The Future 293

Index 297