

# Contents

<b>1</b>	<b>Early Times of Photochemistry . . . . .</b>	<b>1</b>
1.1	Introduction . . . . .	1
1.2	Light and Chemistry . . . . .	3
1.3	Historic Notes . . . . .	4
	References . . . . .	7
<b>2</b>	<b>The Framework of Photochemistry: The Laws . . . . .</b>	<b>9</b>
2.1	The Relation with Light Wavelength . . . . .	10
2.2	Relation with Light Intensity . . . . .	16
2.3	Early Attempts to Rationalize Photochemical Reactions . . . . .	18
2.4	Relation with Light Quanta . . . . .	22
2.5	Measured Quantum Yield . . . . .	25
2.6	Mechanism . . . . .	33
2.7	Kinetics . . . . .	34
2.8	The “Laws” of Photochemistry . . . . .	35
	References . . . . .	37
<b>3</b>	<b>The Framework of Photochemistry: State Diagram . . . . .</b>	<b>41</b>
3.1	Absorption/Emission . . . . .	41
3.2	The Triplet State: Emission . . . . .	42
3.3	The Triplet State: Reactions . . . . .	52
3.4	Paradigms of Photochemistry . . . . .	56
3.5	Generalized Use of the State Diagram . . . . .	57
3.6	Moving Along the States . . . . .	58
	References . . . . .	60
<b>4</b>	<b>Some Paradigmatic Topics . . . . .</b>	<b>63</b>
4.1	Photochemistry for Synthesis . . . . .	63
4.1.1	Some Exemplary Cases of Early Reported Photoreactions: Santonin, Anthracene, 2+2 Cycloaddition . . . . .	65
4.1.2	The Synthetic Potential of Photochemistry . . . . .	74

4.1.3	A “Green” Synthetic Method . . . . .	78
4.2	Born to Measure . . . . .	79
4.2.1	<i>o</i> -Nitrobenzaldehyde and the Equivalence Law . . . . .	79
4.2.2	Mechanism: Early Studies . . . . .	81
4.2.3	Mechanism: Modern Studies . . . . .	83
4.2.4	<i>o</i> -Nitrobenzaldehyde as an Actinometer . . . . .	85
4.3	Oxygenation Reactions and Singlet Oxygen . . . . .	87
4.3.1	Photosensitized Oxygenations in Biologic Systems . . . . .	87
4.3.2	Oxygenation Reactions . . . . .	88
4.3.3	Mechanism . . . . .	90
4.4	Inorganic Photochemistry . . . . .	95
4.4.1	Early Work . . . . .	95
4.4.2	Photochemistry and Photophysics of Transition Metal Complexes . . . . .	97
4.4.3	Transition Metal Complexes as Sensitizers . . . . .	99
4.5	Energy from the Sun . . . . .	101
4.5.1	Ciamician in 1912 . . . . .	101
4.5.2	Bodenstein in 1915 . . . . .	103
4.5.3	The Beginning of Photocatalysis . . . . .	105
4.6	Cursory Elements of Photobiology . . . . .	106
4.6.1	Photosynthesis . . . . .	107
4.6.2	Vision . . . . .	114
4.6.3	Vitamin D . . . . .	116
4.6.4	Medicinal Applications of Photochemistry . . . . .	117
	References . . . . .	121
5	<b>The Role of Photochemistry in Chemistry . . . . .</b>	131
5.1	Photochemistry in Chemistry Meetings . . . . .	131
5.2	The Role of Photochemistry, 1912–2013 . . . . .	133
5.3	Publications in Photochemistry . . . . .	134
	References . . . . .	136
6	<b>Photochemistry, a Powerful Science . . . . .</b>	139
6.1	Harry Potter Meets Photochemistry . . . . .	139
6.2	This Is How It Happens: Time-Resolved Spectroscopy in Photochemistry . . . . .	142
6.2.1	Flash Photolysis with Lamps . . . . .	143
6.2.2	Laser Flash Photolysis and Pump-Probe Spectroscopy . . . . .	148
6.2.3	Two-Color Flash Photolysis . . . . .	153
6.2.4	Local Interactions . . . . .	154
6.2.5	Flash Photolysis with Different Detection . . . . .	157
6.3	This Is How It Happens: Blocking the Intermediates . . . . .	158
6.4	Anything You Can Do, Photochemistry Can Do Better: Generating Intermediates . . . . .	164
6.4.1	Carbocations . . . . .	165
6.4.2	Carbenes . . . . .	168

6.4.3	Nitrenes . . . . .	169
6.4.4	Aromatic Biradicals: Didehydrobenzenes and Didehydrotoluenes . . . . .	172
6.5	Anything You Can Do Photochemistry Can Do Better: Making (Strained) Molecules . . . . .	175
	References . . . . .	179
7	<b>Of Excited States Again . . . . .</b>	183
7.1	Expanding the State Diagram . . . . .	183
7.2	Upconversion . . . . .	187
7.3	Multiphotonic Processes . . . . .	190
7.4	Quantum Yield of Excited States Larger than One . . . . .	191
7.5	Ultrafast Processes . . . . .	193
7.6	Reactions via Upper States . . . . .	194
7.7	The Future of Photochemistry . . . . .	199
	References . . . . .	201
8	<b>Photochemical and Photocatalyzed Synthesis . . . . .</b>	205
8.1	Application in Synthesis: Synthetic Sequences . . . . .	205
8.1.1	Photochemical Steps in Synthetic Planning . . . . .	206
8.1.2	Old and New Strategies in Synthesis . . . . .	209
8.1.3	Synthesis via Chiral Auxiliary . . . . .	211
8.2	Asymmetric (Photochemical) Synthesis . . . . .	212
8.2.1	Absolute Asymmetric Synthesis . . . . .	212
8.2.2	Chirality Transfer . . . . .	213
8.3	Catalysis . . . . .	214
8.3.1	Organocatalysis . . . . .	214
8.3.2	Catalysis: Only the Complexed Reagent Is Activated . . . . .	215
8.3.3	Catalysis: Atropisomerism . . . . .	216
8.3.4	Catalysis: <i>Only</i> the Complexed Form Is Reactive . . . . .	217
8.3.5	By Using a Strong Chiral Complex in a Way to Limit Reversibility, Even When Hindered . . . . .	218
8.3.6	Polyfunctional Catalysis . . . . .	219
8.3.7	By Resorting to an Intrinsically Fast Reaction, Such as Proton Transfer . . . . .	220
8.3.8	Catalysis: Chiral Memory . . . . .	221
8.3.9	One-Pot Catalytic Procedure . . . . .	222
	References . . . . .	222
9	<b>Medicinal and Diagnostic Applications . . . . .</b>	227
9.1	Where and When . . . . .	227
9.1.1	Photochemical Drug Release . . . . .	227
9.1.2	Applications with UV Light . . . . .	228
9.1.3	Application with Near IR . . . . .	229
9.1.4	Nanoparticles . . . . .	230
9.1.5	Transition Metal Complexes . . . . .	232

9.2	Photochemical Internalization . . . . .	233
9.3	Upconversion for the Photoactivation of Drugs . . . . .	233
9.4	Diagnostic Applications: Two-Photon Fluorescence . . . . .	235
9.5	Diagnostic Applications. Aggregation-Enhanced Fluorescence . . . . .	239
9.6	Antimicrobics . . . . .	241
	References . . . . .	242
<b>10</b>	<b>Solar Energy Conversion . . . . .</b>	<b>245</b>
10.1	Non-photosynthetic Strategies . . . . .	246
10.2	Artificial Photosynthesis . . . . .	247
10.3	Dye-Sensitized Solar Cells . . . . .	253
10.4	Comparing Different Approaches . . . . .	254
10.5	Singlet Fission . . . . .	256
10.6	Hydrogen as an Energy Carrier . . . . .	257
10.7	Socioeconomic Issues . . . . .	258
	References . . . . .	259
<b>11</b>	<b>Actuators . . . . .</b>	<b>263</b>
11.1	Photochromism . . . . .	263
11.1.1	Fluorescent Switches . . . . .	263
11.1.2	Electrical Functions of Photochromic Molecules . . . . .	268
11.2	Two Color/One Color . . . . .	269
11.3	Photomechanical Actuators . . . . .	272
11.3.1	Molecular Motors from Molecular Movements . . . . .	272
11.3.2	Macroscopic Effects . . . . .	273
11.3.3	Mechanical Work from Crystal Deformations Caused by Molecular Transformations . . . . .	277
11.4	Self-Assembling . . . . .	279
	References . . . . .	281
<b>12</b>	<b>Photochemistry and Green Synthesis . . . . .</b>	<b>285</b>
12.1	Photochemistry for Bioresources . . . . .	285
12.2	Preparative Photochemistry . . . . .	286
12.2.1	Assessing the Green Potential . . . . .	286
12.3	What to Be Afraid of and What Not to Be Afraid of in Photochemical Reactions . . . . .	288
12.4	Method of Irradiation . . . . .	291
12.5	Scaling Up a Photochemical Reaction . . . . .	292
12.6	Destructive Green Photochemistry . . . . .	295
	References . . . . .	296
<b>Index . . . . .</b>		<b>299</b>