

Outline

<i>Preface</i>	<i>i</i>
Chapter 1. Introduction	1
1.1. Photochemistry of Organic Molecules	3
1.2. Photochemistry of Carbonyl Compounds	7
1.2.1. Hydrogen Abstraction	8
1.2.1.1. Intermolecular Hydrogen Abstraction	8
1.2.1.2. Intramolecular Hydrogen Abstraction	9
1.2.2. [2+2] Photocycloadditions	10
1.2.2.1. Cyclobutane Formation	10
1.2.2.2. Oxetane Formation	12
1.3. Nucleic Acid Damage and Skin Cancer Induced by UV light.	13
1.3.1. Solar Light Duality: Beneficial and Harmful	15
1.3.2. Photoinduced DNA Lesions	17
1.3.2.1. Direct DNA Damage	18
1.3.2.1.1. Cyclobutane Pyrimidine Dimers	18
1.3.2.1.2. Pyrimidine (6-4) Pyrimidone Adducts and Dewar Valence Isomers	22
1.3.2.1.3. Other Photoproducts	24
1.3.2.2. Indirect DNA Damage: Photosensitisation	25
1.3.2.2.1. Cyclobutane Pyrimidine Dimers	27

1.3.2.2.2. Photosensitisers _____	30
1.4. Photophysics _____	34
1.4.1. Transient Absorption Spectroscopy _____	34
1.4.2. Upper Triplet Excited States: Two Photon Photochemistry _____	38
1.5. References _____	41
<i>Chapter 2. General Objectives _____</i>	<i>55</i>
<i>Chapter 3. Transient UV-VIS Absorption Spectroscopic Characterisation of 2'-Methoxyacetophenone as a DNA Photosensitiser _____</i>	<i>59</i>
3.1. Introduction _____	61
3.2. Results and Discussion _____	62
3.3. Conclusions _____	69
3.4. Experimental Section _____	70
3.4.1. Synthesis and Characterisation _____	70
3.4.2. Irradiation Procedures _____	73
3.4.3. Laser Flash Photolysis _____	73
3.5. References _____	74
<i>Chapter 4. Triplet Energy Transfer versus Excited State Cyclisation as the Controlling Step in Photosensitised Bipyrimidine Dimerisation _____</i>	<i>77</i>
4.1. Introduction _____	79
4.2. Results and Discussion _____	81
4.3. Conclusions _____	92
4.4. Experimental Section _____	93
4.4.1. Synthesis and Characterisation _____	93
4.4.1.1. Compounds 2 a-c _____	93
4.4.1.2. Compounds 3 and 3' _____	94
4.4.1.3. Compounds 4 a,b _____	98

4.4.1.4. Compounds 5	103
4.4.1.5. Compounds 6	110
4.4.2. Irradiation Procedures	118
4.4.2.1. Photosensitised Irradiation with Acetone in H ₂ O	118
4.4.2.2. Analytical 2'-Methoxyacetophenone Photosensitised Irradiation	133
4.4.2.3. Preparative 2'-Methoxyacetophenone Photosensitised Irradiation	133
4.4.3. Absorption spectra	133
4.4.4. Phosphorescence spectroscopy	134
4.4.5. Phosphorescence spectroscopy	134
4.5. Annex	135
4.6. References	144

Chapter 5. Photosensitised Biphotonic Chemistry of Pyrimidine Derivatives

147

5.1. Introduction	149
5.2. Results and Discussion	153
5.3. Conclusions	158
5.4. Experimental Section	158
5.4.1. Synthesis and Characterisation	158
5.4.2. Irradiation Procedures and Spectral Measurements	164
5.4.2.1. High Energy Photosensitised Irradiations	164
5.4.2.2. Control experiment: Irradiation in the absence of photosensitiser	164
5.4.2.3. Steady-State Monochromatic Irradiations.	165
5.4.2.4. Securing equivalent photon fluxes in the laser and Xe-lamp irradiation	165
5.4.3. Spectral Measurements	166
5.5. References	167

Chapter 6.	<i>Instrumentation</i>	171
6.1.	General Instrumentation	173
6.1.1.	Nuclear Magnetic Resonance (NMR)	173
6.1.2.	Chromatography	173
6.1.2.1.	Thin-Layer Liquid Chromatography (TLC) and Liquid Chromatography (LC)	173
6.1.2.2.	Ultra Performance Liquid Chromatography Tandem Mass Spectrometer (UPLC-MS/MS)	173
6.2.	Photochemical Instrumentation	174
6.2.1.	UV-VIS Absorption Spectroscopy	174
6.2.2.	Steady-State Photolysis	174
6.2.3.	Laser Flash Photolysis Spectroscopy (LFP)	175
6.2.4.	Phosphorescence Emission Measurements	175
Chapter 7.	<i>General Conclusions</i>	178
Chapter 8.	<i>Summary-Resumen-Resum</i>	185
8.1.	Summary	187
8.2.	Resumen	189
8.3.	Resum	191
Chapter 9.	<i>Scientific Contribution</i>	193
9.1.	Contribution to Congresses	195
9.2.	Publications	195