

PLACE IN RETURN BOX

to remove this checkout from your record. TO AVOID FINES return on or before date due.

DATE DUE	DATE DUE	DATE DUE
		1/98 c/CIRC/DateDue.p65-p.14

INTRAMOLECULAR TRIPLET ENERGY TRANSFER IN FLEXIBLE MOLECULES

by

Petr Klán

A DISSERTATION

Submitted to Michigan State University In partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry 1998

ABSTRACT

INTRAMOLECULAR TRIPLET ENERGY TRANSFER IN FLEXIBLE MOLECULES by

.

Petr Klán

Intramolecular triplet energy transfer rate constants in various flexible bichromophoric systems D-(CH₂)_x-O-A (D = benzoyl, 4-methylbenzoyl; A = 2-naphthyl, 4-, 3-, 2-biphenyl; x = 3-14) have been determined by steady-state quenching and quantum yield measurements. The magnitude of the rate constants in 4-atom tether molecules is comparable to those with a rigid spacer between chromophores, so that a through-bond mechanism is presumed. As the tether becomes longer, through-space interaction dominates and is, in long molecules, the only mechanism responsible for transfer. Rates in long molecules were found remarkably high - lower only by one order of magnitude than in those with 4-atom tethers. It is explained by the existence of a small fraction of conformers having both chromophores in close proximity. Energy transfer in all systems reported here was exothermic. 2-Naphthyl acceptor was replaced by a biphenyl group and the transfer rate constants were found to be lower by a factor of approximately two, which is in agreement with earlier bimolecular measurements. When 4-methylbenzoyl group having π,π^* excited state was used instead of n,π^* excited benzoyl, the rate increase was small but consistent for all tether lengths. An unexpected sudden increase in rate for medium chain-length molecules is explained by a larger number of favorable conformers and further in biphenyl derivatives by a rotation along the terminal O-C bond between the tether and the aromatic ring. As was expected, inclusion of one oxygen atom in the polymethylene chain for polyethyleneoxide caused better flexibility and so higher transfer rates. To Jana, Katerina, and Barbara

ACKNOWLEDGMENTS

I am grateful to Dr. Peter J. Wagner for opening the door to the magical world of photochemistry for me. I wish to thank him for his guidance, support, and especially the freedom to work and explore science in his laboratory.

I am grateful to the National Science Foundation and Michigan State University for financial support in the form of research and teaching assistantships. I would like to thank the Chemistry Department and the Biochemistry Department for the use of their facilities.

It was pleasure to work with all my friends in the Wagner research group. I thank them for their help, encouragement, and entertaining discussions. I wish to thank to Dr. Ali Zand for comments on the thesis.

I am indebted to my wife Jana and my daughters Katerina and Barbara who came across the ocean to support me in my study and work. I thank them for their love and patience.

TABLE OF CONTENTS

LIST OF FIGURES	viii
LIST OF TABLES	. x
LIST OF SCHEMES	/iii
LIST OF ABBREVIATIONS	ix
1. INTRODUCTION	1
1.1 Objectives	1
1.2 Energy Transfer: Basic Principles	2
1.3 Bimolecular Energy Transfer	
1.3.1 Bimolecular Energy Transfer: Thermodynamic and Steric Effects	4
1.3.2 Bimolecular Energy Transfer: Electronic Effects	7
1.4 Intramolecular Processes	9
1.4.1 Rigid Molecules: Through-bond Interaction	9
1.4.2 Flexible Molecules: Through-space Interaction	14
1.5 Cyclization and Conformation of Flexible Molecules	24
1.6 Monitoring System: Calculation of the Transfer Rate Constants	32
1.7 Goals of Research	36
2. RESULTS	38
2.1 General Information	38
2.1.1 Bichromophores	38
2.1.2 Synthesis of Bichromophores	39
2.2 Stern-Volmer and Quantum Yield Measurements	41
2.3 Calculations	45
3. DISCUSSION	47
3.1 Thermodynamics	47
3.2 Energy Transfer Rate Constants	49
3.3 Flexibility of the Tether	54
3.4 Electronic Factors	60
3.5 Isomeric Differences	63
3.6 Summary	71
4. EXPERIMENTAL	72
4.1 Instrumentation	72
4.2 Preparation of Bichromophores	73
4.2.1 Synthesis of ω-Aryloxyalkyl Aryl Ketones	73
4.2.2 Synthesis of 4-(2-Aryloxyethyloxy)-1-phenylbutan-1-ones	116

4.2.3 Synthesis of Arylethyl Ethers	121
4.3 Ultraviolet and Phosphorescence Spectroscopy	122
4.4 Photochemical Procedures and Experiments	128
4.4.1 Purification of Solvents	128
4.4.2 Purification of Standards, Internal Standard, Actinometer, and Quencher	129
4.4.3 Glassware	130
4.4.4 Sample Preparation, Degassing, and Irradiation Procedures	130
4.4.5 Quenching Studies	131
4.4.6 Photoproduct Identification	132
4.4.7 Analysis of Photoproducts	133
4.4.8 Bimolecular Quenching	135
4.4.9 Quantum Yields Measurements	187
5. REFERENCES	214

LIST OF FIGURES

Figure 1. Frontier orbital representation of electron exchange in triplet energy transfer 3
Figure 2. Ouroboros from the book Chrysopoeia by an early alchemist Cleopatra during the Alexandrian Period in Egypt
Figure 3. Two types of exciplexes: n-type and π -type
Figure 4. Possible interactions for n,π^* acetone donor with acceptors possessing low lying n,π^* and π,π^* states: the first step of the electron exchange
Figure 5. Plot of the rate constants of the all-equatorial (ee) and equatorial-axial (ea) compounds 9 - 12 against the number of σ -bonds separating donor and acceptor12
Figure 6. Dependence of the frequency for intramolecular electron exchange on the number of atoms separating the phthalimide groups by a methylene chain, in HMPA.
Figure 7. End-to-end cyclization probability W(O) of the molecules 23 as a function of chain length. Curves labeled <i>syn</i> and <i>anti</i> describe the particular conformations of the ester group in 23
Figure 8. Distribution of the end-to-end distance r of 1-naphthalene-(CH ₂) _n -1- naphthalene. The numbers in the figure represents the number of CH ₂ groups n in the molecule
Figure 9. Unnormalized histogram of end-to-end distance for <i>n</i> -alkane chains from the Monte Carlo program. A total of 5x10 ⁵ samples were taken for each of the three chain lengths: (A) 8 carbon atoms, (B) 12 carbon atoms, (C) 18 carbon atoms 31
Figure 10. AM1 minimized structure of Bz-3-O-2Np showing the distance between the carbonyl oxygen and the closest carbon of the naphthyl group
Figure 11. AM1 minimized structure of Bz-7-O-2Np showing the distance between the carbonyl oxygen and the closest carbon of the naphthyl group
Figure 12. Rate constants for triplet energy transfer as a function of the number of atoms connecting donor and acceptor
Figure 13. Five characteristic conformations of D-9-OA: the simplified model
Figure 14. Rate constants for triplet energy transfer, k _{ET} , and for electron transfer, P, as a function of the number of atoms connecting the donor and the acceptor
Figure 15. An example of the difference between n- π and π - π interactions

Figure 16. Rate constants for triplet energy transfer, k _{ET} , as a function of the number of atoms connecting the donor and the acceptor
Figure 17. Rotation along the O-C terminal bond showing a "reactive volume": Bz-6- O4Bp (F), Bz-6-ONp (G), and Bz-6-O2Bp (H)
Figure 18. Representative example of the minimized geometry by MM2 calculation and the formal structure of Bz-6-O4Bp
Figure 19. Representative example of the minimized geometry by MM2 calculation and the formal structure of Bz-6-O2Bp
Figure 20. Phosphorescence emission spectra of acetophenone (AP), 4- methylacetophenone (MeAP), 2-ethoxynaphthalene (2EtONp), 4-ethoxybiphenyl (4EtOBp), 3-ethoxybiphenyl (3EtOBp), and 2-ethoxybiphenyl (2EtOBp) chromophores in 2-methyltetrahydrofuran at 77K

LIST OF TABLES

Table 1. Photokinetics of Model ω-Phenoxy Ketones in Cyclohexane 42
Table 2. Photokinetics of Naphthyloxy Ketones in Cyclohexane 43
Table 3. Photokinetics of Biphenyloxy Ketones with in Cyclohexane 44
Table 4. Triplet levels E_T of the donor and the acceptor chromophores
Table 5. Intramolecular Energy Transfer Rates in Naphthyloxy Bichromophores Obtained from Stern-Volmer and Quantum Yield Measurements
Table 6. Intramolecular Energy Transfer Rates in Biphenyloxy Ketones Obtained from Stern-Volmer and Quantum Yield Measurements.
Table 7. Molar Absorptivities of Bz-n-OPh, MeBz-n-OPh, and Bz-3-O-2-OPh 123
Table 8. Molar Absorptivities of Bz-n-O4Bp, Bz-n-O3Bp, and Bz-n-O2Bp 124
Table 9. Molar Absorptivities of Bz-n-ONp
Table 10. Molar Absorptivities of MeBz-n-ONp, MeBz-n-O4Bp, Bz-3-O-2-O4Bp, and actinometers
Table 11. Phosphorescence Emission Data
Table 12. Calibration constants
Table 13. HPLC Condition Sets. 134
Table 14. Stern-Volmer Quenching of the Acetophenone Formation in Bz-3-OPh with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.136
Table 15. Stern-Volmer Quenching of the Acetophenone Formation in Bz-4-OPh with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.137
Table 16. Stern-Volmer Quenching of the Acetophenone Formation in Bz-5-OPh with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.
Table 17. Stern-Volmer Quenching of the Acetophenone Formation in Bz-7-OPh with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.139
Table 18. Stern-Volmer Quenching of the Acetophenone Formation in Bz-10-OPh with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

Table 19. Stern-Volmer Quenching of the Acetophenone Formation in Bz-11-OPh with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.
Table 20. Stern-Volmer Quenching of the Acetophenone Formation in Bz-3-O-2-OPh with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane
Table 21. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in MeBz-3-OPh with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane
Table 22. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in MeBz-4-OPh with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane
Table 23. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in MeBz-5-OPh with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane
Table 24. Stern-Volmer Quenching of the Acetophenone Formation in Bz-3-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane
Table 25. Stern-Volmer Quenching of the Acetophenone Formation in Bz-4-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane. 147
Table 26. Stern-Volmer Quenching of the Acetophenone Formation in Bz-5-ONp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.148
Table 27. Stern-Volmer Quenching of the Acetophenone Formation in Bz-6-ONp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.149
Table 28. Stern-Volmer Quenching of the Acetophenone Formation in Bz-7-ONp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.150
Table 29. Stern-Volmer Quenching of the Acetophenone Formation in Bz-9-ONp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.
Table 30. Stern-Volmer Quenching of the Acetophenone Formation in Bz-10-ONp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.152
Table 31. Stern-Volmer Quenching of the Acetophenone Formation in Bz-11-ONp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane
Table 32. Stern-Volmer Quenching of the Acetophenone Formation in Bz-14-ONp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.
Table 33. Stern-Volmer Quenching of the Acetophenone Formation in Bz-3-O4Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.
Table 34. Stern-Volmer Quenching of the Acetophenone Formation in Bz-4-O4Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.156

Table 35. Stern-Volmer Quenching of the Acetophenone Formation in Bz-5-O4Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane. 157
Table 36. Stern-Volmer Quenching of the Acetophenone Formation in Bz-6-O4Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.158
Table 37. Stern-Volmer Quenching of the Acetophenone Formation in Bz-7-O4Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.159
Table 38. Stern-Volmer Quenching of the Acetophenone Formation in Bz-9-O4Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.160
Table 39. Stern-Volmer Quenching of the Acetophenone Formation in Bz-10-O4Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.161
Table 40. Stern-Volmer Quenching of the Acetophenone Formation in Bz-11-O4Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.162
Table 41. Stern-Volmer Quenching of the Acetophenone Formation in Bz-14-O4Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Benzene.163
Table 42. Stern-Volmer Quenching of the Acetophenone Formation in Bz-3-O2Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.164
Table 43. Stern-Volmer Quenching of the Acetophenone Formation in Bz-4-O2Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.165
Table 44. Stern-Volmer Quenching of the Acetophenone Formation in Bz-5-O2Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.166
Table 45. Stern-Volmer Quenching of the Acetophenone Formation in Bz-6-O2Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.167
Table 46. Stern-Volmer Quenching of the Acetophenone Formation in Bz-7-O2Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.168
Table 47. Stern-Volmer Quenching of the Acetophenone Formation in Bz-9-O2Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.169
Table 48. Stern-Volmer Quenching of the Acetophenone Formation in Bz-10-O2Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.170
Table 49. Stern-Volmer Quenching of the Acetophenone Formation in Bz-11-O2Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.
Table 50. Stern-Volmer Quenching of the Acetophenone Formation in Bz-14-O2Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.172

Table 51. Stern-Volmer Quenching of the Acetophenone Formation in Bz-3-O3Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.173
Table 52. Stern-Volmer Quenching of the Acetophenone Formation in Bz-6-O3Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane
Table 53. Stern-Volmer Quenching of the Acetophenone Formation in Bz-7-O3Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.175
Table 54. Stern-Volmer Quenching of the Acetophenone Formation in Bz-9-O3Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.176
Table 55. Stern-Volmer Quenching of the Acetophenone Formation in Bz-10-O3Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.177
Table 56. Stern-Volmer Quenching of the Acetophenone Formation in Bz-14-O3Bp with2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.178
Table 57. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in MeBz-3-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane
Table 58. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in MeBz-4-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane
Table 59. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in MeBz-5-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane181
Table 60. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in MeBz-6-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane
Table 61. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in MeBz-7-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane
Table 62. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in MeBz-11-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane
Table 63. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in MeBz-3-O4Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane
Table 64. Stern-Volmer Quenching of the Acetophenone Formation in Bz-3-O-2-O4Bpwith 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane
Table 65. Quantum Yields of the Acetophenone Formation in Bz-3-OPh withValerophenone as an Actinometer at 366 nm in Cyclohexane
Table 66. Quantum Yields of the Acetophenone Formation in Bz-4-OPh withValerophenone as an Actinometer at 366 nm in Cyclohexane

Table 67. Quantum Yields of the Acetophenone Formation in Bz-5-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 68. Quantum Yields of the Acetophenone Formation in Bz-7-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 69. Quantum Yields of the Acetophenone Formation in Bz-10-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 70. Quantum Yields of the Acetophenone Formation in Bz-11-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 71. Quantum Yields of the Acetophenone Formation in Bz-3-O-2-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 72. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-3-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 73. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-4-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 74. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-5-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 75. Quantum Yields of the Acetophenone Formation in Bz-3-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 76. Quantum Yields of the Acetophenone Formation in Bz-4-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 77. Quantum Yields of the Acetophenone Formation in Bz-5-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 78. Quantum Yields of the Acetophenone Formation in Bz-6-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 79. Quantum Yields of the Acetophenone Formation in Bz-7-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 80. Quantum Yields of the Acetophenone Formation in Bz-9-ONp with Valerophenone as an Actinometer at 366 nm in Cyclobexane
Table 81. Quantum Yields of the Acetophenone Formation in Bz-10-ONp with Valerophenone as an Actinometer at 366 nm in Cyclobevane
Table 82. Quantum Yields of the Acetophenone Formation in Bz-11-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane

Table 83. Quantum Yields of the Acetophenone Formation in Bz-14-ONp withValerophenone as an Actinometer at 366 nm in Cyclohexane
Table 84. Quantum Yields of the Acetophenone Formation in Bz-3-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 85. Quantum Yields of the Acetophenone Formation in Bz-4-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 86. Quantum Yields of the Acetophenone Formation in Bz-5-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 87. Quantum Yields of the Acetophenone Formation in Bz-6-O4Bp withValerophenone as an Actinometer at 366 nm in Cyclohexane
Table 88. Quantum Yields of the Acetophenone Formation in Bz-7-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 89. Quantum Yields of the Acetophenone Formation in Bz-9-O4Bp withValerophenone as an Actinometer at 366 nm in Cyclohexane
Table 90. Quantum Yields of the Acetophenone Formation in Bz-10-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 91. Quantum Yields of the Acetophenone Formation in Bz-11-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 92. Quantum Yields of the Acetophenone Formation in Bz-14-O4Bp with Valerophenone as an Actinometer at 366 nm in Benzene
Table 93. Quantum Yields of the Acetophenone Formation in Bz-3-O2Bp withValerophenone as an Actinometer at 366 nm in Cyclohexane
Table 94. Quantum Yields of the Acetophenone Formation in Bz-4-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 95. Quantum Yields of the Acetophenone Formation in Bz-5-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 96. Quantum Yields of the Acetophenone Formation in Bz-6-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 97. Quantum Yields of the Acetophenone Formation in Bz-7-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 98. Quantum Yields of the Acetophenone Formation in Bz-9-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane

Table 99. Quantum Yields of the Acetophenone Formation in Bz-10-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 100. Quantum Yields of the Acetophenone Formation in Bz-11-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 101. Quantum Yields of the Acetophenone Formation in Bz-14-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 102. Quantum Yields of the Acetophenone Formation in Bz-3-O3Bp withValerophenone as an Actinometer at 366 nm in Cyclohexane
Table 103. Quantum Yields of the Acetophenone Formation in Bz-6-O3Bp withValerophenone as an Actinometer at 366 nm in Cyclohexane
Table 104. Quantum Yields of the Acetophenone Formation in Bz-7-O3Bp withValerophenone as an Actinometer at 366 nm in Cyclohexane
Table 105. Quantum Yields of the Acetophenone Formation in Bz-9-O3Bp withValerophenone as an Actinometer at 366 nm in Cyclohexane
Table 106. Quantum Yields of the Acetophenone Formation in Bz-10-O3Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 107. Quantum Yields of the Acetophenone Formation in Bz-14-O3Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 108. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-3-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 109. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-4-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 110. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-5-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 111. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-6-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 112. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-7-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 113. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-11-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane
Table 114. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-3-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane

LIST OF SCHEMES

Scheme 1
Scheme 2. Norrish Type II Reaction
Scheme 3
Scheme 4
Scheme 5
Scheme 6
Scheme 7. Photokinetics of a Bichromophoric System
Scheme 8
Scheme 9
Scheme 10
Scheme 11. Synthesis of ω-Iodoalkyl Aryl Ketones73
Scheme 12. Synthesis of ω -Aryloxyalkanoaryl Ketones (R = H, Me)
Scheme 13. Synthesis of ω -Iodoalkanoaryl Ketones (R = H, Me)
Scheme 14. Synthesis of ω-Aryloxyalkanophenyl Ketones
Scheme 15. Synthesis of 4-(2-Aryloxyethyloxy)-1-phenylbutan-1-ones

LIST OF ABBREVIATIONS

- ITET Intramolecular triplet energy transfer
- ISC Intersystem crossing
- MO Molecular orbital
- SOC Spin orbit coupling
- RIS Rotational isomeric state

1. INTRODUCTION

1.1 Objectives

The subject of this dissertation is the intramolecular triplet energy transfer (ITET) between two chromophores connected by a flexible tether. In this project, I chose to study how interchromophore distance, character of chromophores, and changes in the tether affect energy transfer rate constants. It was achieved by systematically increasing the length of the polymethylene tether, altering the electronic nature and structure of the chromophores, and changing the structure of the tether. The energy transfer rate constants were obtained in photokinetic measurements in which the chemical yields of photocleavage products were monitored. In our bichromophoric systems, the photocleavage reaction competes with intramolecular energy transfer and this fact was used in the rate constant calculations; the cleavage reaction serving as a "system clock".

Intramolecular triplet energy transfer was studied on some rigid or flexible systems in the past but there was no systematic work on flexible bichromophores. Such research, however, started in our research group and I wished to build upon the results of my predecessors. Photochemistry has proved to be an excellent research tool for this study. Experiments were not very difficult to accomplish; the Stern-Volmer quenching technique used for lifetime measurements is well-known for its reliability; and the new results could be compared with those obtained in previously reported experiments.

Energy transfer is a universal process in nature and its understanding certainly represents required fundamental knowledge. Our research might help to understand it better. The introduction chapter contains information on what was known about triplet energy transfer previously and describes the monitoring system used for energy transfer rate constant calculations.

1.2 Energy Transfer: Basic Principles

Intramolecular triplet energy transfer is a specific example of energy transfer. It is necessary to define the type of interaction involved and to show general principles.

Electronically excited molecules may react chemically with other molecules in their vicinity or they may transfer energy to them. If an excited donor D^* , either singlet or triplet, transfers electronic energy to an acceptor molecule A with the simultaneous return to its ground state, the process is referred to as *electronic energy transfer*¹:

$$D^* + A \rightarrow D + A^*$$

Energy transfer can occur either by a radiative, through absorption of the emitted radiation or by a nonradiative pathway. There are two well established, different mechanisms for nonradiative energy transfer: the Coulomb and the exchange mechanism.¹

It is generally accepted that energy transfer from an excited triplet to the ground state of another moiety proceeds via *exchange* or *Dexter* mechanism.^{2,3} The energy transfer rate constant may be written as

$$k_{ET}$$
 (exchange) ~ $e^{-2R_{DA}/L}J$ (Equation 1)

where R_{DA} is the distance between the donor and the acceptor, L is a constant related to an effective average orbital radius of the donor and the acceptor, and J is the spectral overlap. Exchange mechanism requires an overlap of the orbitals - the partners being in a close proximity. As depicted in Figure 1, energy transfer by exchange mechanism can be symbolized as a double electron transfer involving both the HOMO's and LUMO's of the donor and the acceptor. For efficient triplet energy transfer the donor must absorb substantially the incident light, its intersystem crossing efficiency must be high, and its triplet energy must be higher than that of the acceptor.⁴



Figure 1. Frontier orbital representation of electron exchange in triplet energy transfer.⁴

If the donor and the acceptor are parts of the same molecule, the electron exchange process is called *intramolecular energy transfer*, which can occur by either a through-bond or a through-space mechanism, or by a combination of both. In systems where the through-bond mechanism was observed, chromophores were separated only by several bonds from each other.⁵ On the other hand, close proximity of both chromophores, when molecular structure allows, is necessary for a through-space mechanism.

Energy transfer in a molecule with the donor and the acceptor connected by a flexible tether has a nice parallel in an old Greek, Gnostic, and medieval symbol *Ouroboros* (Figure 2). The serpent biting its own tail, that had several meanings in many

ancient cultures, brought a mystical heritage into medieval alchemy⁶ as well as into modern photochemistry.⁷



Figure 2. Ouroboros from the book Chrysopoeia by an early alchemist Cleopatra during the Alexandrian Period in Egypt.⁸

1.3 Bimolecular Energy Transfer

There are many similarities between bimolecular and intramolecular energy transfer. The bimolecular interaction was studied extensively in the past and many findings are relevant to our intramolecular studies.

1.3.1 Bimolecular Energy Transfer: Thermodynamic and Steric Effects

According to Equation 1, triplet energy transfer by the exchange mechanism is a short-range phenomenon and the rate constant decreases exponentially with the donor - acceptor separation R_{DA} . Since it requires a close proximity of both partners, the exchange mechanism is also called the *overlap mechanism*. Triplet energy transfer is a

spin-allowed process according to the Wigner-Witmer spin-selection rules, where the total spin must not change during a reaction.⁹

The first example of triplet energy transfer was provided by the classic experiment of Terenin and Ermolaev,¹⁰ in which they demonstrated that the phosphorescence of naphthalene in a rigid solution at 77K could be excited by 366 nm light. Naphthalene itself did not absorb at this wavelength but benzophenone added to the solution did and provided energy transfer to naphthalene. A crude model derived from Dexter's formula (Equation 1) that describes the distance dependence of energy transfer by exchange mechanism as a function of distance (Equation 2) was reported.¹¹

$$\log k_{\text{ET}} (\text{exchange}) = 13 - (2R_{\text{DA}}/2.3)$$
 (Equation 2)

As a result, energy transfer rate $k_{ET} = 4.5 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$, for example, corresponds to distance, $R_{DA} = 5$ Å, between chromophores.

Bimolecular as well as intramolecular energy transfer rate constants depend on overall reaction thermodynamics. When the triplet level of the donor lies about 3 kcal mol⁻¹ or more higher than that of the acceptor, the bimolecular transfer is exothermic and nearly diffusion controlled.⁴ Scaiano, Wagner, and coworkers¹² found that bimolecular energy transfer rate constant between benzoyl donor ($E_T \sim 72$ kcal/mol)¹³ and 1-methylnaphtalene acceptor ($E_T \sim 61$ kcal/mol)¹⁴ in benzene was 8.4×10^9 M⁻¹s⁻¹. When both triplet energies are same, k_{ET} is smaller by about a factor of 100. Bimolecular rate constants for self-quenching by ground state ketone were found to be in the 10^6 - 10^8 M⁻¹s⁻¹ range.¹⁵

Steric effects were shown to be significant in some cases. The introduction of *gem*-dimethyl groups into diene used as a quencher reduces the rate constant of fluorescence quenching of diazabicyclooctene (1).¹⁶



On the other hand steric effects in bimolecular triplet energy transfer in quenching of α, α -dimethylvalerophenone (2) by 2,5-dimethyl-2,4-hexadiene and 2-chloronaphthalene were reported as unimportant, primarily because the interaction distance between the donor and the acceptor in solution is on order of 4 Å, long enough to preclude large steric effects.¹⁷



Scaiano, Wagner, and coworkers¹² measured rate constants for quenching of various triplet aryl ketones by conjugated dienes and some aromatics in order to study steric effects on energy transfer. They found that steric effects that limit closeness of approach are relatively unimportant in triplet energy transfer, primarily because diffusion control masks small steric decreases in in-cage energy transfer rates (Scheme 1). However, large stereoelectronic effects were found when π -system of donor or acceptor were twisted such that the orbital overlap necessary for electron exchange was minimized. Arrhenius plots for the ketone quenching by dienes revealed that the

differences in rates involved mainly entropy effects, E_a values were found to be similar for all chromophore pairs.¹²

$$D^* + A \xrightarrow{k_{\text{diff}}} \left[D^* \dots A \right] \xrightarrow{k_{\text{ET}}} \left[D \dots A^* \right] \longrightarrow D + A^*$$

$$k_{\text{-diff}}$$

Scheme 1.

1.3.2 Bimolecular Energy Transfer: Electronic Effects

Electronic effects - delocalization of excitation energy, as well as orientation of the overlapping orbitals can affect energy transfer.

It has been suggested that as much as 50% of the total spin density in the lowest triplet state (n,π^*) of benzophenone resides on the aromatic rings.¹⁸ The spin density distribution on the carbonyl group was found to be highest for the non-bonding orbital on oxygen.¹⁹ In the study of self-quenching deactivation of 4,4'-disubstituted benzophenone triplets via exciplex formation, a dual reaction pathway was observed.²⁰ It was concluded that the self-quenching of benzophenones having para electron-donating subtituent proceeded via exciplex 3 (n-type exciplex) between the half-filled n orbital of the carbonyl and the π system of the aromatic ring. A different exciplex 4 (π -type exciplex) was facilitated in benzophenones with para electron-withdrawing substituents between the half-filled π^* system of the donor and the unfilled π^* system of the acceptor (Figure 3).



Figure 3. Two types of exciplexes: n-type and π -type.

The quenching of acetone phosphorescence by a series of aryl alkyl ketones possessing lower triplet energies than acetone was reported.²¹ The quenching constants



Figure 4. Possible interactions for n,π^* acetone donor with acceptors possessing low lying n,π^* and π,π^* states: the first step of the electron exchange.

were found to be lower for ketones with n,π^* configuration than those with π,π^* . That difference was explained by assuming a different interaction between the partners (Figure 4). Concerted and stepwise mechanisms of electron exchange were discussed in terms of different geometries of $n - \pi$ and $\pi - \pi$ orbital overlap. The latter was assumed

8

to be more efficient because of a parallel geometry, same character of orbitals, and a lower steric hindrance.

On the other hand, a study of charge transfer in the photoreduction of various phenyl ketones²² showed the n,π^* and π,π^* triplets to be of similar reactivity.

1.4 Intramolecular Energy Transfer

1.4.1 Rigid Molecules: Through-bond Interaction

In molecules where substituents are attached to the ends of a rigid or a very short tether, through-bond interaction may be the only significant mechanism for any physical process between them, since the geometry of the molecule prevents their close proximity through space. Studies of such rigid systems bring a deeper understanding of geometric and electronic demands for such a process. Molecular rigidity, however, can be controlled by solvent viscosity and temperature as well.

In 1963, Hammond and coworkers²³ reported evidence for intramolecular triplet energy transfer (ITET) in 4-(1-naphthylmethyl)benzophenone (5). Irradiation of 5 at 366 nm, where only benzophenone absorbs, led to a characteristic phosphorescence emission of the only naphthyl moiety. This observation suggested that the phosphorescence can result from ITET between the chromophores. ITET was believed to proceed at rate of higher than 10^9 s⁻¹ with 100% efficiency.



Filipescu and coworkers²⁴ reported an exothermic ITET between nonconjugated chromophores with fixed orientation. An efficient transfer was found between tetralin-1,4-dione and fluorene chromophores held together by a rigid spacer (6).



Keller²⁵ reported that triplet excitation energy was completely transferred between anthrone and naphthalene chromophores separated by a spiro linkage in compounds **7** and **8**. The study presented an interesting opportunity to study an influence of chromophore orientation on ITET. In solutions with 10^{-4} - 10^{-5} M concentration, selective excitation of the anthrone chromophore populated excited singlet state which intersystem crossed to the triplet, underwent exothermic energy transfer and the naphthalene chromophore produced phosphorescence. The most intriguing aspect of this work is the occurrence of energy transfer in the perpendicular orientation, which precludes the orbital overlap needed for transfer. Keller reasoned that only a small deviation from orthogonality would be necessary to achieve energy transfer by dipoledipole mechanism. It was discussed that the exchange energy transfer, a probable source of energy transfer in these systems, might not be very dependent upon orientation of the chromophores.



Zimmerman and McKelvey²⁶ studied ITET from benzoyl to naphthyl group in a bichromophoric system with a rigid bicyclo[2.2.2]octane spacer. Their experiments and findings were very similar to those of Hammond's.²³

Intramolecular energy transfer as well as electron and hole transfer in rigid systems were studied by Closs and coworkers.²⁷ Their search was aimed at finding quantitative similarities and differences in these processes.

ITET was studied on compounds in which a 2-naphthyl group is connected via a rigid spacer with a 4-benzoylphenyl group, where the spacer was either a cyclohexane 9: (C-1,3) and 10: (C-1,4), or a decalin ring 11: (D-2,7) and 12: (D-2,6). The triplet energy transfer rates were measured in benzene at room temperature by flash photolysis exciting

the benzophenone chromophore and monitoring the decay of the T_1 - T_n absorption of the benzophenone or the buildup of the naphthalene T_1 - T_n absorption. ITET decreased



by nearly three orders of magnitude as the interchromophore distance increased in going from a cyclohexane to a decalin spacer (Figure 5: ee refers to all-equatorial, and ea to equatorial-axial substituents). It was also shown that triplet energy transfer can be regarded as a simultaneous two electron transfer and thus triplet energy transfer rates may be used to obtain information on electronic coupling in electron transfer and hole transfer.



Figure 5. Plot of the rate constants of the all-equatorial (ee) and equatorial-axial (ea) compounds 9 - 12 against the number of σ -bonds separating donor and acceptor; from ref. 27c.

For compounds 9 - 12 with 2-naphthyl and 4-benzoylphenyl groups in equatorialaxial position, ITET rates were slower (Figure 5). In line with ab initio MO calculations, isomers with axial substituents have transfer rates slower than all-equatorial isomers because the orbital overlap is poor for bonds held almost perpendicular to each other.²⁸ The nature of the electronic coupling in donor/acceptor systems with cyclohexane-type spacers were investigated using a superexchange pathway method based on ab initio MO theory with natural bond orbitals.²⁹ It was found that paths involving hops which skip over bonds make largest contribution to the total coupling. The dominant pathway in every case is through C-C antibonds. Koga, Sameshima, and Morokuma³⁰ showed how MO overlap is dependent on the rotation along the bonds between a chromophore and the cyclohexane or decalin spacers. The dependency was found to be small but real, and the study also showed that the electronic coupling in triplet energy transfer is proportional to the product of those of electron transfer and hole transfer.

Sigman and Closs studied free energy and structure dependence on ITET.³¹ A series of compounds containing 4-benzophenone or 4-acetophenone donors and various acceptors (9,9-dimethylfluorenyl, 9-spirofluorenyl, 4-biphenyl, 2-naphthyl, and 2-benzoquinonyl) connected by a 1,4-cyclohexane spacer in equatorial-axial or equatorial-equatorial position were studied by a nanosecond flash photolysis. The measured ITET rates showed an inverted parabolic, i.e. Marcus³², dependence on the free enthalpy of reaction.

1.4.2 Flexible Molecules: Through-space Interaction

As was shown in paragraph 1.4.1, ITET is proportional to the number of bonds when through-bond mechanism is applied. In through-space mechanism, however, a close proximity (overlap of orbitals) of both chromophores, allowed by a favorable geometry of the flexible tether, is necessary. Intramolecular quenching of the excited chromophore by the unexcited chromophore can significantly change the course of photochemical reactions. Thus, in addition to luminescence studies, triplet-sensitized cistrans geometrical isomerization³³ and Norrish Type II reaction^{34,35} of excited ketones were used in monitoring of intramolecular energy transfer.



Scheme 2. Norrish Type II Reaction

Triplet-sensitized cis-trans isomerization is a photochemical interconversion of cis and trans isomers containing an olefinic link thanks to the biradical character of the excited double bond. Norrish type II reaction (Scheme 2), a common reaction of aliphatic or aromatic ketones, is intramolecular hydrogen abstraction from the γ -position. In

addition to regenerating the reactant, the resulting biradical can cleave to give an olefin and an enol, or form a cycloalkanol.

Intramolecular energy transfer of both singlet and triplet excitation in compounds 13 (n = 1-3) was reported in some detail by Lamola and coworkers.³⁶ They found by luminescence studies that singlet excitation transfer from the lowest singlet state of the naphthalene group to form the lowest n,π^* singlet state of the benzophenone chromophore occurred with high but not total efficiency. Triplet energy transfer was believed to proceed at a rate of >10⁹ s⁻¹ with 100% efficiency.



One of the most significant studies on the effect of interchromophore distance on ITET was done by Cowan and Baum³⁷ in 1971. By a systematic increasing of the tether length in the benzoyl-styryl bichromophoric system 14 the energy transfer rate decreased. Selective excitation of the carbonyl group led to transfer of triplet energy to the styryl chromophore, resulting in a trans—cis styryl isomerization. The rate constants for ITET in benzene solution of 14, evaluated from triplet quenching data, were: 7.2×10^{10} , 1.0×10^{10} , and 3.3×10^9 s⁻¹ for series n = 2, 3, and 4, respectively.



14: n = 2, 3, 4

.

P
Ito and coworkers³⁸ studied intramolecular energy transfer in the bichromophoric compounds 15. The results from steady state quenching experiments indicated that energy transfer was fastest in the longest derivative (15: n = 3). It was concluded that energy transfer via the electron exchange is optimal when 15 has a sandwich conformation. Weak phosphorescence of the bichromophoric system was attributed to energy transfer from benzophenone to the most sterically hindered triisopropylbenzophenone group. Thus, it was reported that excitation preferentially resides at the most sterically hindered chromophore based on an entropy factor. Relatively small decrease in internal rotation entropy upon electronic excitation of the hindered group was considered to be more significant factor than E_T difference between chromophores. These findings can be compared to bimolecular studies¹² in which entropic effects on k_{ET} were found to be more important then E_a values (Paragraph 1.3.1). Their arguments remain, however, unconvincing.



Energy transfer migration in macromolecular systems is a subject of current interest, which reflects its role in photodegradation, photostabilization, photocuring, and photooxidation. Scaiano and Selwyn³⁹ studied properties of polymers and copolymers of p-methoxyacrylophenone by flash photolysis. Efficient triplet energy transfer migration

with a hopping frequency 4.3×10^{11} s⁻¹ in chloroform at -60°C was calculated. This high number (the actual in-cage rate constants were found to be $(5-10) \times 10^{10}$ s⁻¹),⁴⁰ however, may suggest that intermolecular quenching is more efficient than they assumed or energy hops across the coiled polymer play an important role.

Winnik and coworkers⁴¹ have examined end-to-end cyclization in the intramolecular phosphorescence quenching reaction of ω -alkenyl esters of benzophenone-4-carboxylic acid (16). Since the corresponding bimolecular quenching rate constants are 10^2 to 10^3 times smaller than k_{diff}, the intramolecular reaction is preceded by a conformational equilibrium. Chain shorter than 8 atoms between chromophores cannot achieve conformations where the π electrons of the double bond overlap with the half-filled n orbital on the benzophenone carbonyl oxygen. A sharp maximum of intramolecular quenching for the 12-atom-tether derivative and following decrease is explained by the entropic factors associated with achieving a reactive configuration; for chains n > 8, the activation energy is independent of chain length.



In the experiments of Shimada and Szwarc, electron exchange frequency values P were obtained by ESR for the molecules containing either two 1-naphthyl or two phthalimide groups connected to polymethylene chain.⁴² The dependence of P upon the number of the atoms between the two phthalimide groups is shown in Figure 6. The

authors concluded that the value of P reflect conformational changes of the investigated chains. Substitution of oxygen for the methylene group in the chain increased P by a factor of about 3, provided that the number of tether atoms was 8 or higher.



Figure 6. Dependence of the frequency for intramolecular electron exchange on the number of atoms separating the phthalimide groups by a methylene chain, in HMPA at the temperature indicated. (\bullet) PI-(CH₂)_n-PT; (O) PI-(CH₂CH₂O)_mCH₂CH₂PT where PI is the N-phthalimide group. From ref. 42.

Intramolecular fluorescence quenching in $1,\omega$ -bis(dimethylamino)alkanes was shown by Halpern and coworkers.⁴³ In this reaction, one of the amino groups absorbed light and fluoresced with a quantum yield that was diminished by an intramolecular interaction. Intramolecular fluorescence quenching rate constants showed a minimum for 8 methylene groups between the substituents with a sudden increase and leveling off for 12 - 20 methylenes. The authors concluded that the molecular geometry in the transition state for intramolecular quenching resemble that of a cycloalkane. Zachariasse⁴⁴ examined intramolecular excimer formation in the molecules pyrene- $(CH_2)_n$ -pyrene. The dependence of excimer to monomer emission intensity ratio on chain length showed a characteristic maximum for 3, a minimum for 7-8, and a sudden increase and leveling off for 10-16 atoms between substituents, similar to what was observed in other examples.

Wagner and Nakahira⁴⁵ studied steady-state photochemistry of 6-(4'methoxyphenyl)-1-phenylhexane-1,6-dione (17). By monitoring Norrish Type II reaction products from both ends, they found that triplet state lifetimes of both chromophores were nearly identical. Since the lifetimes of these chromophores, when in separate molecules, are quite different, they concluded that an energy transfer equilibrium exists between the lowest triplet states of both chromophores (${}^{3}n,\pi^{*}$ of the benzoyl group and ${}^{3}\pi,\pi^{*}$ of the methoxybenzoyl group).



The photochemistry of three α -benzoyl- ω -azidoalkanes PhCO(CH₂)_nN₃ was studied by quenching experiments and triplet energy transfer rates were determined by monitoring Norrish Type II products.⁵⁵ Rates 3.7x10⁸, 0.29x10⁸, and <0.03x10⁸ s⁻¹, for n

= 3, 4, and 5, respectively, were found. The authors suggested that almost 50% of the quenching interaction may involve some process other than energy transfer.



Wagner and coworkers⁴⁶ studied the effect of reversible intramolecular energy transfer on the photochemistry of diketones (18: Ar = Ph, 2-methylphenyl). Scheme 3 shows an example of photochemical behavior of 18 (n = 4, Ar = Ph). The acetophenone chromophore has triplet energy ~ 72 kcal/mol while the benzophenone chromophore ~ 69 kcal/mol. 18A underwent Norrish Type II photoelimination but its efficiency was lowered by exothermic energy transfer to 18B. In benzene, 18B was photostable and slowly transferred energy uphill to 18A. As in other short flexible bichromophoric systems, through-space ITET competed with through-bond mechanism.





Irreversible triplet energy transfer was studied on diketones 19 (n = 3-7) in which extremely rapid enolization of the excited *o*-methylbenzophenone chromophore shortened the triplet lifetime such that uphill energy transfer to benzoyl chromophore could not compete.⁴⁶ The transfer rate constants dropped from 4-atom tether to 5-atom tether molecule and then reached a constant value for all longer derivatives. Throughspace energy transfer was assumed to dominate for those longer molecules in which a certain number of conformations allow a close proximity of the chromophores.



Wagner and El-Taliawi⁴⁷ published a study of ITET in flexible cinnamyl esters of ω -benzoylcarboxylic acids (20). Irradiation of 20 at 366 nm, where the styrene barely

absorbs, produced efficient cis-trans isomerization. They extended the results of Cowan and Baum³⁷ by increasing the number of atoms between chromophores. It was shown by a comparison to Closs' rigid molecules, in which k_{ET} values drop 1 order of magnitude with each additional bond between chromophores,⁵ that the higher ITET rate constants in more flexible, longer molecules are caused by through-space interaction. In the molecules with a short tether, however, through-bond interaction, similar to the ITET in rigid systems, was suggested. ITET rate constants for 20 were: $4x10^9$, $2x10^9$, $1x10^9$, and $5 \times 10^8 \text{ s}^{-1}$ for n = 1, 2, 3, and 4, respectively.



Qiao⁴⁸ studied ITET in ω -(4-biphenoxy)alkanophenones (21). The molecules were irradiated at 313 nm in benzene and Norrish Type II photoelimination was followed. As in the Wagner and El-Taliawi work,⁴⁷ ITET rate constants dropped approximately a factor of 2 for each additional bond between chromophores.



A series of spectroscopic measurements on flexible polymethylene biradicals in liquid solution was reported by Closs, Forbes, and coworkers.⁴⁹ In order to get information about the chain-length dependence of the intramolecular exchange interaction J, time-resolved electron paramagnetic resonance spectroscopy was used. The cyclic ketones 22 (n = 8-26) were irradiated by a 308 nm laser flash pulses and the triplet biradicals 23 were formed in the photoinduced Norrish Type I reaction (Scheme 4). Through-bond contributions were found to dominate for the shortest acyl-alkyl biradicals, while the through-space (solvent) mechanism was the major contribution to Jin the long-chain molecules. In the short acyl-alkyl biradicals, J decreased distinctly with every additional atom in the chain and leveled off when the chain became longer (n > 13). Such dependence, however, was not observed for alkyl-alkyl biradicals (formed as byproducts in the same photocleavage), where the difference in J for short and long chains was negligible. Interesting results about how a double bond or a phenyl ring in the chain could change flexibility, and so the exchange interaction in the alkyl-alkyl biradicals, were also reported.⁵⁰



Scheme 4.

1.5 Cyclization and Conformation of Flexible Molecules

The concepts of cyclization and chain flexibility have been linked since earliest days of concern about conformation in chemistry. In this work, intramolecular energy transfer in flexible molecules is dependent on conformations of the tether. This section summarize basic information about cyclization dynamics and kinetics in chemistry as well as in photochemistry.

There are many known examples of chemical reactions or physical processes occurring between substituents attached at the ends of a flexible chain molecule.⁵¹ While the stereochemical demands for ring formation can be much higher than simple proximity of the reactants in the ends of the flexible chain,⁵² a physical process such as Coulomb energy transfer occurs whenever the terminal donor and acceptor approach to within 6 to 10 Å and even over distances of 50 Å.⁵³ Many of the factors that influence the cyclization of hydrocarbon chains can be seen in a comparison of normal alkanes and appropriate cycloalkanes. This comparison is normally carried out by examining the internal energies or heats of formation (ΔE_f^o or ΔH_f^o) and entropies of formation (ΔS_f^o) of these pairs of compounds and estimating the changes in energy and entropy which occur upon cyclization.⁵¹

Intramolecular reactions can have their bimolecular counterparts. Scheme 5 shows the parallel between diffusion together of two molecules and rotation together of two functional groups in the same molecule.⁷ The major difference between them is that conformational equilibrium constants of intramolecular reaction are much more sensitive

to structure than are diffusion constants. Rotation control represents the intramolecular equivalent of diffusion-controlled reaction and should be expected whenever the reaction between A and B is known to be diffusion-controlled. In slow reactions, the intramolecular rate constant is dependent on the conformational equilibrium constant.





It was shown by Wagner that kinetics of *photochemical* intramolecular processes are more complex than chemical processes.⁷ In Scheme 6, where F and U represent conformations of the molecule, favorable and unfavorable, respectively, for a given intramolecular interaction, three kinetic situations can be described. The star superscript means an excited state, and k_d and k_d' are rate constants of decay.

$$F \xrightarrow{hv} F^* \xrightarrow{k_r} \text{product}$$

$$k_{UF} \| k_{FU} \quad k_{UF^*} \| k_{FU^*}$$

$$U \xrightarrow{hv} U^*$$

Scheme 6.

For relatively slow excited-state reactions, *conformational equilibrium* is established: k_{FU*} and k_{UF*} are much faster than k_r and k_d . Thus, the observed rates include excited-state conformational equilibrium constants: $k_{obs} = k_r k_{UF*} / (k_{FU*} + k_{UF*})$ $= \chi_{F*}k_r$. The quantum yields is expressed as $\Phi = \chi_{F*}k_r / (\chi_{F*}k_r + \chi_{F*}k_d + \chi_{U*}k_{d'})$.

For fast reactions and/or slow conformational change, the reaction is limited by the ground-state population of favorable conformations: $k_{obs} = k_r$ for k_{FU*} , $k_{UF*} \ll k_r$, k_d ; $\Phi = \chi_{F*}k_r / (k_r + k_d)$. From the two kinetically distinct excited states (F* and U*), only F* leads to the reaction and the situation is called *ground state control*.⁵⁴ Its bimolecular counterpart is called "*static quenching*".

If conformational change and decay are competitive, it is said that *rotation*controlled reaction occurs: $k_{obs}(U) = k_{UF*}$ for $k_{UF*} \sim k_d$ and $k_{FU*} \ll k_r$.

Wagner⁵⁵ pointed out that the actual rate of an intramolecular process, k_p , is a sum over all favorable conformations which allow the reaction. The contribution of each individual conformation to the total process depends both on the fractional population of

that conformer (χ_{fi}) and on the rate of the process associated with that particular geometry (k_{pi}) (Equation 3) for χ_f (total) = 1 - χ_u (total), where χ_u are all unfavorable conformations.

$$k_{p} = \sum_{i} \chi_{fi} k_{pi}$$
 (Equation 3)

In one of the most thorough studies of ring closure, Mandolini and Illuminati carried out detailed kinetic studies of intramolecular nucleophilic substitution reactions.⁵⁶ Arrhenius parameters were obtained for lactone formation from $Br(CH_2)_n$. ${}_2CO_2$ ⁻. Activation energy E_a was found to be large for n = 3 and decreased substantially for n = 4-6, which does not quite follow a pattern of the strain energy of small rings. Large values of energy E_a were found for 8- and 9-member ring formation. Entropy of activation $\Delta S^{\#}$ was large for n = 3-6 and then dropped and oscillated with E_a in a compensatory manner, so that reactions with particularly unfavorable activation energies had less negative entropies $\Delta S^{\#}$.

Mathematical models play an important role in understanding chain conformation and chain dynamics. There are many kinds of models which have been applied and they range from simple models to very realistic models, in which structural aspects of the polymer are taken explicitly into account.^{51,57} In discrete models, individual polymer chains are confined to discrete points in space. Average properties associated with the polymer are calculated by summing over all possible conformations according to

$$\langle P \rangle = \frac{\sum_{j}^{\Sigma} P_{j} \exp(-E_{j}/RT)}{\sum_{j}^{\Sigma} \exp(-E_{j}/RT)}$$

(Equation 4)

where P_j is the magnitude of the property P associated with the j-th chain in the sample, and E_j is the energy associated with the chain. The denominator in Equation 4 represents the conformational partition function.

One of the common realistic models of hydrocarbon chain involves carbons confined to the vertices of the diamond lattice.^{58,59,60} This model is simple enough to be tractable for long chains, yet sophisticated enough to allow a wide variety of properties of hydrocarbon chains to be calculated. Many of these features are contained within the 3-fold rotational isomeric state model (RIS model).⁶¹ According to the model, a hydrocarbon chain is viewed as a molecule with fixed bond lengths and bond angles. The rotational potential about each bond is accommodated into the model as a series of discrete rotational states associated with the energy minima of the rotation (usually the trans and two gauche states).

A number of approaches have been taken to develop general theories of cyclization probability and cyclization dynamics.⁵¹ Fraser and Winnik⁵⁹ showed a Monte Carlo simulation on a diamond lattice (RIS model) that was used to estimate the intramolecular cyclization probability of a bulky benzophenone connected to amine by a polymethylene chain (**24**: *a* is a spherical reactive volume with diameter 3.1 Å).



This probability determined the chain length dependence of relative rate constants in exciplex formation between photoexcited amine and chromophore when the intrinsic rate for this reaction is very low and therefore this cyclization is conformationally controlled. Figure 7 shows end-to-end probability and the odd-even oscillation are artifacts associated with the parity of lattice sites which designate the reactive volume. This oscillation is a typical feature of RIS simulations.



Figure 7. End-to-end cyclization probability W(O) of the molecules 24 as a function of chain length. Curves labeled *syn* and *anti* describe the particular conformations of the ester group in 24. From ref. 59.

Shimada and coworkers^{62,63,64} have published an important series of papers reporting on the kinetics of intramolecular electron exchange in the molecules containing either two 1-naphthyl or two phthalimide groups connected to methylene chains. A simulation of the cyclization dynamics in these systems based on RIS model was reported. An exact enumeration or Monte Carlo calculations were used to calculate the distribution of end-to-end distances. Their results are shown in Figure 8.



Figure 8. Distribution of the end-to-end distance r of 1-naphthalene- $(CH_2)_n$ -1-naphthalene. The numbers in the figure represents the number of CH_2 groups n in the molecule. From ref. 62.

A distribution of end-to-end chain distances was shown by Closs and coworkers in the recent study of spin and reaction dynamics in flexible polymethylene biradicals (Figure 9).⁶⁵ That procedure put the chain into a diamond lattice and constructed the conformations by assigning each four-carbon fragment in the chain one of the three dihedral angles: trans coplanar, plus gauche, and minus gauche.



Figure 9. Unnormalized histogram of end-to-end distance for *n*-alkane chains from the Monte Carlo program. A total of 5×10^5 samples were taken for each of the three chain lengths: (A) 8 carbon atoms, (B) 12 carbon atoms, (C) 18 carbon atoms. From ref. 65.

<u>1.6 Monit</u>	
The	
• 1	
ensited sta	
were condu	
centainly b	
baitophil	
energy	
photoe	
intran	
birad	
exchu	
the L	
o dej	
center	
40%) (
which H	
^{cause} of	
abstracria	
^{or the} of y	
^{hydro} gen	

1.6 Monitoring System: Calculation of the Rate Constants

The energy transfer study can be accomplished in one of two ways: spectroscopically or photochemically. Measurements of growth or disappearance of an excited state signal by means of fluorescence, phosphorescence, or UV spectroscopy were conducted in many studies described in this chapter. Such measurements would certainly be feasible in our systems; but the photochemical approach we used seems to be ideal for several reasons discussed below.

The Norrish type II reaction^{35, 66} has proved to be an extraordinary tool for energy transfer studies^{45,46,47,55} and it was used in this work as well. The Norrish type II photoelimination and cyclization of phenyl alkyl ketones proceeds exclusively via intramolecular γ -hydrogen abstraction by an excited carbonyl group, producing a 1,4biradical as a primary photoproduct.⁶⁷ It is well known that the reaction comes exclusively from the triplet excited state of the ketone. Depending on conformation of the biradical, the further reactions are possible. When the p orbitals of the radical centers can overlap, cyclobutanol is formed (usually 5-10%). When the p orbitals of the radical centers are parallel to the β -bond, the bond will cleave to give an enol and an alkene (25-40%) or the starting ketone by disproportionation (50-70%).⁷ Carbonyl compounds which have n,π^* triplet state as the lowest excited state abstract hydrogen efficiently. The cause of this chemical reactivity is the singly occupied n orbital on oxygen. Hydrogen abstraction can also occur from a π,π^* state but with a much lower rate. Inductive effects of the of γ and δ substituents influence the rate of hydrogen abstraction as well.³⁴ The hydrogen abstraction reaction competes with energy transfer to an acceptor

chromopho: clock" to cu ÷ .) เป็นแบบไปอุท following by intersystem formation. ----nutavora intramo donor form

•

Ph-

chromophore. The kinetics of the Norrish type II reaction was adopted as the "system clock" to calculate energy transfer rate constants.

Scheme 7 shows a detailed kinetic analysis of the photochemistry of flexible bichromophoric systems. The ketone donor is excited by irradiation into its singlet state following by intersystem crossing into triplet state. It is known that the quantum yield of intersystem crossing in aromatic ketones is nearly one.⁴ The efficiency of triplet formation is barely lowered by competing processes from the singlet: fluorescence and internal conversion. Those processes are same for both favorable (coiled) as well as unfavorable (uncoiled) conformations. Coiled conformation allow through-space intramolecular energy transfer from an excited donor to a ground state acceptor. If the donor excitation is not quenched by the energy transfer, γ -hydrogen abstraction occurs to form a biradical.



Rate constar	
k _{et} -	
к н -	
ш Т	
14-	
Scheme 7.]	
. ۳	
where	
late c	

probal

indirec

general

where ¢

presence

of the exc

Sin

yield for the

Rate constant	ts:	
k _{ET} -	intramolecular energy transfer	A - acceptor
k _H -	γ-hydrogen abstraction	TS - through-space
k. _H -	reverse hydrogen abstraction	
k _{cyc} -	cyclobutanol formation (Norrish type II reaction)	
k ₁₁ -	β -cleavage reaction (Norrish type II reaction)	

Scheme 7. Photokinetics of a Bichromophoric System

Two measurements of phenyl ketone photochemistry provide insight into understanding their behavior: the *quantum yield* and the *excited triplet lifetime*.

The quantum yield for the type II reaction can be expressed as:⁶⁸

$$\Phi_{II} = \Phi_{ISC} k_{H} \tau P_{II} \qquad (Equation 5)$$

where Φ_{ISC} is the quantum yield of intersystem crossing from singlet to triplet, k_H is the rate constant for biradical formation, τ is the lifetime of the triplet state, and P_{II} is the probability that the biradical will collapse to give products. Triplet lifetime (τ) is an indirect measurement extracted from a steady state kinetics quenching experiment which generates a Stern-Volmer plot.⁶⁹ The Stern-Volmer expression is $\phi_0/\phi = 1 + k_q\tau_0[Q]$, where ϕ_0 is the quantum yield in the absence of quencher, ϕ is the quantum yield in the presence of quencher, k_q is the bimolecular rate constant for quenching, τ_0 is the life time of the excited state being quenched, [Q] is the concentration of quencher.

Since $\Phi_{ISC} = 1$; $1/\tau = k_H + k_{ET}$;⁷⁰ and provided that $k_H \ge 10^7 \text{ s}^{-1}$, the quantum yield for the type II reaction (from Equation 5) can be expressed as $\Phi_{II} = P_{II}$ when energy

transfer doct transfer com Thu e transfer the tr so th varie studio

10⁸-10⁹

transfer does no compete with γ -hydrogen abstraction ($k_{ET} = 0$). In case that energy transfer competes with k_{H} , Φ_{II} can be written as:

$$\Phi_{II} = k_H \tau P_{II} = k_H P_{II} / (k_H + k_{ET})$$
 (Equation 6)

Thus, there are seven reasons why the Norrish type II reaction is an excellent tool for measurements of energy transfer rate constants in bichromophores:

1. Triplet excited ketone, providing both hydrogen abstraction and energy transfer, guarantees that only triplet energy transfer is monitored ($\Phi_{ISC} = 1$).

2. Hydrogen abstraction and energy transfer are essentially the only reactions of the triplet ketone.

3. The rates of the abstraction and the transfer are of the same order in this work, so the "system clock" provides reliable data. The rate of hydrogen abstraction could be varied by changing the substituents on the benzoyl group.

4. Stern-Volmer quenching measurements are accompanied by quantum yield studies which can verify their results.

5. Stern-Volmer technique is known to be of a high precision.

6. Quenching rate constants k_q are known for large number of ketones.

7. Laser spectroscopy is difficult in the range of our lifetime measurements $(1/t \sim 10^8 - 10^9 \text{ s}^{-1})$.

et and the second s	
dominates	
complex in:	
of the word	
course	
intram	
in ter	
excit	
rate o	
and	
naph	
accer	
alterat	
large in	
molecui	

1.7 Goals of Research

It was suggested that through-bond mechanism of intramolecular triplet energy transfer is predominant in short flexible molecules while through-space mechanism dominates in flexible medium-length-tether molecules.⁴⁷ In order to obtain a more complex insight into how ITET is influenced by all chain lengths, a comprehensive study of the molecules with short, medium, and long tethers (4- to 15-atom tethers) has been undertaken.

As mentioned earlier, character of chromophores may significantly affect the course of the energy transfer between them.¹ Only bimolecular energy transfer^{4,15} and intramolecular energy transfer in rigid molecules²⁷ have been investigated systematically in terms of electronic effects in the past. An influence of chromophore triplet energy E_{T} , excitation type, excitation delocalization, and its ability for the orbital overlap on ITET rate constants has been studied in molecules with different tether lengths. Acetophenone and 4-methylacetophenone chromophores have been used as the donors, and 2-naphthyloxy and 4-/3-/2-biphenyloxy chromophores have been examined as the acceptors.

Regioselective character of chromophore approach has been studied by an alteration of the tether length along with a modification of the chromophore character.

It has been known for a long time that a change of the tether character may have a large impact on various intramolecular cyclizations and physical processes in flexible molecules. 50,56,63 The polymethylene chain, -(CH₂)_n-, in a flexible molecule was replaced

by a more

constants h

by a more flexible polyethylene oxide, $-(CH_2CH_2O)_m$ -, and the differences in ITET rate constants have been investigated.

2.1.1 Bichr

TL.

Scheme

2. RESULTS

2.1 General Information

2.1.1 Bichromophores

The compounds in Scheme 8 and 9 were prepared and used for this dissertation.

Scheme 8.





Compound	R	А	n = x
Bz-n-OPh	Н	phenyl	3-5, 7, 10, 11
Bz-n-ONp	Н	2-naphthyl	3-7, 9-11, 14
Bz-n-O4Bp	н	4-biphenyl	3-7, 9-11, 14
Bz-n-O3Bp	н	3-biphenyl	3, 6, 7, 9, 10, 14
Bz-n-O2Bp	н	2-biphenyl	3-7, 9-11, 14
MeBz-n-OPh	CH ₃	phenyl	3-5
MeBz-n-ONp	CH ₃	2-naphthyl	3-7, 12
MeBz-n-O4Bp	CH ₃	4-biphenyl	3

Bz = benzoyl.

2.1.2 S

Scheme 9.

pheny three

prep.

ω-chl

Nal ii

reactic

follow

Here syr

Grignard

Scheme 9.



D-3-O-2-OA

Compound	A
Bz-3-O-2-OPh	phenyl
Bz-3-O-2-O4Bp	4-biphenyl
Bz = benzoyl	

2.1.2 Synthesis of Bichromophores

 ω -Aryloxyalkanoaryl ketones D-(CH₂)_x-O-A (D = benzoyl, 4-methylbenzoyl; A = phenyl, 2-naphthyl, 2-, 3-, 4-biphenyl, x = 3-11, 14) (Scheme 8 and 9) were prepared by three different synthetic routes. Full synthetic procedures are described in Chapter 4.

 ω -Aryloxyalkanoaryl ketones D-(CH₂)_x-O-A (x = 3, 4) (Scheme 8 and 9) were prepared by a standard Grignard reaction of the appropriate arylmagnesium bromide with ω -chloroalkanenitrile, followed by a nucleophilic substitution of chlorine by iodine using NaI in acetone. The iodo ketone D-(CH₂)_x-I was converted into the bichromophore by reaction of its ethylene glycol ketal with the appropriate sodium phenolate, A-ONa, followed by a deprotection reaction.

 ω -Aryloxyalkanoaryl ketones D-(CH₂)_x-O-A (x = 5-7, 11, 14) (Scheme 8 and 9) were synthesized in the first step by a standard addition of the appropriate aryl bromide Grignard with a cyclic ketone. The cycloalkyl hypochlorite was prepared from the

resulting cy resulting in • • concentration prepared fr those in the Th The pro was de by rea CN v Pheny 04B 4-bip into 2 purifiec resulting cycloalkyl alcohol and then was subjected to photochemical ring opening⁷¹ resulting in ω -chloro acyclic ketone D-(CH₂)_x-Cl in CCl₄. The yield in this step was found to be very sensitive to stirring and dilution. Thus, mechanical stirring and a low concentration of the starting material worked best. The final bichromophore was prepared from the chloride in a series of nucleophilic substitution reactions similar to those in the first procedure.

The synthesis of ω -aryloxyalkanoaryl ketones D-(CH₂)_x-O-A (x = 9-11) (Scheme 8 and 9) started by protecting the ω -bromoalkanol Br-(CH₂)_x-OH with 2,3-dihydropyran. The protected bromoalcohol reacted with the appropriate sodium phenolate. The alcohol was deprotected and converted to A-O-(CH₂)_x-Cl using SOCl₂ and then to A-O-(CH₂)_x-I by reaction with NaI in acetone. The corresponding ω -aryloxyalkyl nitrile A-O-(CH₂)_x-Cl using SOCl₂ and then the nitrile with the phenyl Grignard Ar-MgBr provided the final bichromophores.

Dr. J. Qiao synthesized some ketones studied in this work: Bz-n-OPh and Bz-n-O4Bp (n = 3-5).

 γ -(2-Aryloxyethyloxy)butyrophenones D-3-O-2-OA (D = benzoyl; A = phenyl or 4-biphenyl) were synthesized in four steps, starting with a conversion of 2-chloroethanol into 2-aryloxyethanol, followed by reaction of its sodium salt with γ -iodobutyrophenone.

All bichromophores were recrystallized from hexane/ethyl acetate mixtures and purified by flash chromatography when necessary. Their purity was 99%+ in all cases,

 $e \times cept$ for compounds with the 3-biphenyl group as the acceptor which contained 2-3% of their 4-biphenyl isomers.

2.2 Photokinetic Measurements

Cyclohexane or benzene 0.001 M solutions of a bichromophore with different **Concentrations** of the quencher (2,5-dimethyl-2,4-hexadiene) were irradiated at 366 nm where only donors absorb. Valerophenone 0.001 M solutions were irradiated **simultaneously** as actinometer ($\Phi_{II} = 0.3$)⁷² for quantum yield measurements.⁷³ Triplet **lifetimes** (τ) were determined by Stern-Volmer steady-state quenching techniques⁶⁹ that **gave** straight lines whose slopes were equal to $k_q\tau$. All Stern-Volmer plots were linear **with** correlation coefficients 0.97-0.99. The type II photoproduct yields (acetophenone or **4**-methylacetophenone) were determined by HPLC; conversions were always kept under **1 5**%. The olefinic coproduct from the photocleavage was not analyzed. Minor HPLC **Peaks**, observed in some ketones, were assumed to be cyclobutanol coproducts but were **not** analyzed.

Tables 1 - 3 list Norrish type II quantum yield, $k_q \tau$ and $1/\tau$ values for all systems. Quantum yields were corrected for optical density at 366 nm in cyclohexane or benzene. Some bichromophores used in this work were not very soluble in cyclohexane and therefore it was difficult to obtain precise optical density and molar absorptivity values in
this solvent. For many long molecules, 0.001 M concentration was nearly a saturated solution and their molar absorptivity values in cyclohexane were interpolated from their values in benzene. Typical values of molar absorptivities ε_{366} were as low as 3-5 Lmol⁻¹cm⁻¹. Reciprocal lifetimes $1/\tau$ were calculated from $k_q\tau$ and the known bimolecular rate constants (k_q) $8x10^9$ M⁻¹s⁻¹ for cyclohexane^{72,74} and $6x10^9$ M⁻¹s⁻¹ for benzene.⁷⁴

D-n-OA	Φ _{II}	$k_q \tau, M^{-1}$	$1/\tau$, $10^8 {\rm s}^{-1}$
Bz-3-OPh	0.45±0.00	30.7±0.4	2.6
Bz-4-OPh	0.44±0.01	232.4±16.0	0.34
Bz-5-OPh	0.35±0.01	89.5±0.3	0.89
Bz-7-OPh	0.29±0.00	62.4±2.3	1.3
Bz-10-OPh	0.26±0.01	57.3±1.2	1.4
Bz-11-OPh	0.26±0.01	58.2±0.4	1.4
MeBz-3-OPh	0.61±0.02	153.4±2.7	0.50
MeBz-4-OPh	0.56±0.02	1090.6±87.3	0.07
MeBz-5-OPh	0.43±0.02	412.4±1.5	0.19
Bz-3-O-2-OPh	0.44±0.01	24.7±1.6	3.2

Table 1. Photokinetics of Model ω -Phenoxy Ketones in Cyclohexane^a

"Measured at room temperature; the deviation values are reproducibility from two measurements.

D-n-OA	Φιι	$k_q \tau$, M^{-1}	$1/\tau$, 10^8 s^{-1}
Bz-3-ONp	0.13±0.00	4.2±0.1	19.0
Bz-4-ONp	0.04±0.00	16.3±0.5	4.9
Bz-5-ONp	0.16±0.00	19.5±0.1	4.1
Bz-6-ONp	0.16±0.00	22.2±0.7	3.6
Bz-7-ONp	0.17±0.00	23.2±0.0	3.4
Bz-9-ONp	0.11±0.02	15.0±1.4	5.3
Bz-10-ONp	0.13±0.01	13.6±1.1	5.9
Bz-11-ONp	0.18±0.00	24.7±0.2	3.2
Bz-14-ONp	0.15±0.00	30.8±3.0	2.6
MeBz-3-ONp	0.03±0.00	3.4±0.0	23.5
MeBz-4-ONp	0.01±0.00	15.7±0.2	5.1
MeBz-5-ONp	0.03±0.00	20.3±0.0	3.9
MeBz-6-ONp	0.04±0.00	23.7±0.6	3.4
MeBz-7-ONp	0.05±0.00	25.8±1.1	3.1
MeBz-11-ONp	0.06±0.00	28.8±1.6	2.8

Table 2. Photokinetics of Naphthyloxy Ketones in Cyclohexane^a

"Measured at room temperature; the deviation values are reproducibility from two measurements.

D-n-OA	Φ_{II}	$k_q \tau, M^{-1}$	$1/\tau$, 10^8 s^{-1}
Bz-3-O4Bp	0.17±0.02	7.7±0.6	10.4
Bz-4-O4Bp	0.05±0.00	20.7±0.3	3.9
Bz-5-O4Bp	0.13±0.00	27.3±0.9	2.9
Bz-6-O4Bp	0.14±0.00	30.4±0.2	2.6
Bz-7-O4Bp	0.17±0.01	32.5±0.1	2.5
Bz-9-O4Bp	0.13±0.00	20.5±0.2	3.9
Bz-10-O4Bp	0.07±0.01	23.3±0.4	3.4
Bz-11-O4Bp	0.21±0.01	33.4±0.7	2.4
Bz-14-O4Bp	0.24 ± 0.00^{b}	28.4±0.2 ^b	2.1
Bz-3-O3Bp	0.20±0.00	10.1±0.1	7.9
Bz-6-O3Bp	0.17±0.01	32.8±0.2	2.4
Bz-7-O3Bp	0.18±0.01	27.5±0.0	2.9
Bz-9-O3Bp	0.15 ^c	36.1 ^{<i>c</i>}	2.2
Bz-10-O3Bp	0.18±0.01	28.6±0.1	2.8
Bz-14-O3Bp	0.17±0.00	35.7±0.5	2.2
Bz-3-O2Bp	0.23±0.01	11.9±0.1	6.7
Bz-4-O2Bp	0.05±0.00	36.7±0.0	2.2
Bz-5-O2Bp	0.17±0.00	32.5±0.3	2.5
Bz-6-O2Bp	0.13±0.00	25.7±0.6	3.1
Bz-7-O2Bp	0.13±0.00	21.6±0.4	3.7
Bz-9-O2Bp	0.13±0.01	29.8±0.6	2.7
Bz-10-O2Bp	0.13±0.00	23.9±0.9	3.3
Bz-11-O2Bp	0.19±0.01	35.7±2.0	2.2
Bz-14-O2Bp	0.20±0.01	39.2±0.6	2.0
MeBz-3-O4Bp	0.04±0.00	8.9±0.1	9.0
Bz-3-O-2-O4Bp	0.17±0.00	10.5±0.9	7.6

Table 3. Photokinetics of Biphenyloxy Ketones with in Cyclohexane^a

^aMeasured at room temperature; the deviation values are reproducibility from two measurements. ^bIn benzene. ^cSingle measurement.

2.3 Calculations

In order to gain a better understanding of our experimental results, molecular mechanics (MM2) and semi empirical (AM1) calculations were conducted. CS Chem3D Pro(tm), version 3.5.1, has been used in all calculations. The AM1 protocol was used from the CS MOPAC Std(tm), version 3.5.1.

Minimizations (semi empirical AM1 calculations) were performed to get information about the distance between the donor and acceptor chromophores in a fully stretched molecule. Such conformation provides the largest distance possible (Figures 10 and 11).



Figure 10. AM1 minimized structure of Bz-3-O-2Np showing the distance between the carbonyl oxygen and the closest carbon of the naphthyl group.



Figure 11. AM1 minimized structure of Bz-7-O-2Np showing the distance between the carbonyl oxygen and the closest carbon of the naphthyl group.

t 3 kŋ

he

3. DISCUSSION

This chapter discusses the significance of the experimental results and presents the conclusions of our study. Scheme 10 is an example of both energy transfer and the Norrish type II reaction in a representative bichromophore system in this work.





3.1 Thermodynamics

Intramolecular as well as intermolecular triplet-triplet energy transfer rates are known to be dependent on interchromophore energy gap (ΔE) (Chapter 1). The ΔE can be measured in two ways: (a) from the phosphorescence spectra of independent

chromophores or (b) by energy transfer measurements. The two do not always correlate,^{75,76} because rate constants are dependent also on other factors. Frerking concluded that ΔE values derived from phosphorescence spectra in his diketone study were generally higher than those derived from energy transfer rate constants.⁷⁵

Thus, the energy gap ΔE can be express by the equation:

$$\Delta E = E_{T}(\text{donor}) - E_{T}(\text{acceptor}) \qquad (Equation 7)$$

where E_T (donor) is triplet energy of the donor and E_T (acceptor) is triplet energy of the acceptor.

Energy transfer in all molecules reported in this work is exothermic and practically irreversible.⁴ In order to achieve a specific excitation of the donor, cyclohexane or benzene solutions of ketones were irradiated at 366 nm where the acceptors, 2-naphthyloxy and biphenyloxy chromophores ($\varepsilon_{366} \ge 0.1 \text{ Lmol}^{-1}\text{m}^{-1}$), barely absorb. Triplet levels E_T of the donor and the acceptor chromophores are listed in Table 4.

Table 4. Triplet levels E_T of the donor and the acceptor chromophores

Chromophore	E _T (kcal/mol)
benzoyl	72 ⁷⁷
4-methylbenzoyl	73 ⁷⁸
2-naphthyloxy	62 ⁷⁹
4-biphenyloxy	68 ⁸⁰
3-biphenyloxy	69 ⁸⁰
2-biphenyloxy	69 ⁸⁰

3.2 Energy Transfer Rate Constants

Norrish type II reaction was used as a tool for energy transfer studies in this work (Chapter 1). Two measurements of Norrish Type II photochemistry provide understanding its behavior: (a) the excited triplet lifetime, τ ; and (b) the quantum yield of the reaction, Φ .

Energy transfer rate constants (k_{ET}) were calculated from triplet lifetimes determined by Stern-Volmer quenching and from quantum yield measurements (Tables 5, 6). Determination of γ -hydrogen abstraction rates (k_{H}) in bichromophores from those data is crucial for k_{ET} calculations because its rate competes only with energy transfer (Scheme 10). Two different calculations were applied in which k_{H} were obtained from: (a) 1/t of model phenoxy ketones or (b) quantum yields. They are fully discussed below.

Quantum yields and triplet lifetimes of six model phenoxy ketones (Bz-n-OPh for n = 6, 9, 14; MeBz-n-OPh for n = 6, 7, 11) were interpolated from the values obtained in the photokinetic measurements of the other model phenoxy ketones (Table 1).

D-n-OA	$k_{\rm ET}^{a}$, 10 ⁸ s ⁻¹	$k_{\rm ET}^{b}$, 10 ⁸ s ⁻¹
Bz-3-ONp	16.3	13.5
Bz-4-ONp	4.5	4.5
Bz-5-ONp	3.1	2.2
Bz-6-ONp	2.5	1.9
Bz-7-ONp	2.0	1.4
Bz-9-ONp	3.8	3.2
Bz-10-ONp	4.4	3.0
Bz-11-ONp	1.7	1.0
Bz-14-ONp	1.1	1.1
MeBz-3-ONp	22.9	22.3
MeBz-4-ONp	5.0	5.0
MeBz-5-ONp	3.6	3.6
MeBz-6-ONp	3.1	3.1
MeBz-7-ONp	2.8	2.7
MeBz-11-ONp	2.5	2.3

.

Table 5. Intramolecular Energy Transfer Rates in Naphthyloxy BichromophoresObtained from Stern-Volmer and Quantum Yield Measurements.

^aRates k_H obtained from $1/\tau$ of model phenoxy ketones. ^bRates k_H obtained from quantum yields.

D-n-OA	$k_{\rm ET}^{a}$, 10 ⁸ s ⁻¹	$k_{\rm ET}^{b}$, 10 ⁸ s ⁻¹
Bz-3-O4Bp	7.8	6.5
Bz-4-O4Bp	3.5	3.5
Bz-5-O4Bp	2.0	1.8
Bz-6-O4Bp	1.6	1.5
Bz-7-O4Bp	1.2	1.0
Bz-9-O4Bp	2.5	2.1
Bz-10-O4Bp	2.0	2.5
Bz-11-O4Bp	1.0	0.5
Bz-14-O4Bp	0.7 ^c	0.2 ^c
Bz-3-O3Bp	5.3	4.4
Bz-6-O3Bp	1.4	1.2
Bz-7-O3Bp	1.6	1.1
Bz-9-O3Bp	0.8	1.0
Bz-10-O3Bp	1.4	0.9
Bz-14-O3Bp	0.8	0.8
Bz-3-O2Bp	4.1	3.3
Bz-4-O2Bp	1.8	2.0
Bz-5-O2Bp	1.5	1.3
Bz-6-O2Bp	2.1	1.9
Bz-7-O2Bp	2.4	2.0
Bz-9-O2Bp	1.3	1.4
Bz-10-O2Bp	1.9	1.7
Bz-11-O2Bp	0.8	0.6
Bz-14-O2Bp	0.6	0.5
MeBz-3-O4Bp	8.5	8.4
Bz-3-O-2-O4Bp	4.4	4.7

Table 6. Intramolecular Energy Transfer Rates in Biphenyloxy Ketones Obtained from Stern-Volmer and Quantum Yield Measurements.

^{*a*}Rates k_H obtained from $1/\tau$ of model phenoxy ketones. ^{*b*}Rates k_H obtained from quantum yields. ^{*c*}In benzene.

(a) k_H obtained from $1/\tau$ of model phenoxy ketones

 γ -Hydrogen abstraction is presumed to be the only reaction observed in the model phenoxy ketones. Those compounds provide information about the quantum efficiencies and the rate constants for the photoelimination reaction in the absence of triplet energy transfer because transfer to the phenoxy group (E_T ~ 81 kcal/mol)⁸¹ is highly endothermic and charge transfer quenching by anisole is slow.⁸²

When k_H in the model compound is assumed to be equivalent to that in the corresponding bichromophore, intramolecular energy transfer rate constants k_{ET} can be calculated according to Equation 8,

$$k_{ET} = 1/\tau - k_H - k_2 [K]$$
 (Equation 8)

where τ is the triplet lifetime of the bichromophore, $k_{\rm H}$ is 1/ τ of the corresponding model ketone, k_2 is the calculated bimolecular quenching (8x10⁶ M⁻¹s⁻¹ for 2-naphthyloxy ketones; 3x10⁶ M⁻¹s⁻¹ for biphenyloxy ketones),¹⁵ and [K] is the bichromophore concentration. Bimolecular quenching rates were about 2 orders of magnitude lower than those of intramolecular because ketone concentrations were 0.001 M. It does not contribute significantly to decay and could be neglected in our calculations. Intramolecular energy transfer rates for all bichromophores are listed in Tables 5 and 6.

(b) k_H calculated from quantum yields

The values k_H and P_{II} depend on the aromatic acceptor in D-n-OA, especially in those with 3- and 4-methylene tethers. It is known that Norrish type II intramolecular abstraction of γ -hydrogen atom is strongly dependent on inductive effects of γ and δ substituents.^{34,68} Thus, the rate constants k_H may be different in model compounds and in bichromophores.

The quantum yield of Norrish type II reaction can be expressed as

$$\Phi_{II} = \Phi_{ISC} k_H \tau P_{II} \qquad (Equation 9)^{68}$$

where Φ_{ISC} is the quantum yield of intersystem crossing from singlet to triplet, k_{H} is the rate constant for biradical formation, τ is the lifetime of the triplet state, and P_{II} is the probability that the biradical will collapse to give products. Since Φ_{ISC} is equal to one³⁴ and $1/\tau = k_{H} + k_{ET}$,⁷⁰ provided that there are no other reactions of the excited ketone, energy transfer rates can be calculated from k_{H} derived from the quantum yields.⁶⁸ The value $1/\tau$ really equals ($k_{H} + k_{ET} + k_{x}$), where k_{x} is the rate constant for any other reaction. The quantum yields in Tables 1-3 then provide direct information about k_{H} in the bichromophoric systems.

The quantum yield in the absence of energy transfer in model phenoxy ketones can be expressed as $\Phi_{II}^{o} = P_{II}$ (Chapter 1.4). Since the quantum yield in bichromophore is $\Phi_{II} = k_H \tau P_{II}$ (Equation 9), $k_H = 1/\tau \cdot \Phi_{II} / \Phi_{II}^{o}$. The rate constants for hydrogen abstraction (k_H) and consequently energy transfer rate constants (k_{ET}) were calculated from Equation 10.

$$k_{ET} = 1/\tau - \Phi_{II}/\Phi_{II}^{\circ}.1/\tau$$
 (Equation 10)

Energy transfer rate constants calculated from quantum yields and reciprocal lifetimes of bichromophores according to Equation 10 are listed in Tables 5 and 6. The accuracy of the quantum yield measurements is assumed to be not as high. Stern-Volmer

calculations are statistically more precise because each measurement consists of 20 independent HPLC measurements while quantum yield experiments only of 4.

Benzophenone triplets are quenched by anisole *via* exciplex⁸³ with bimolecular rate constant 3×10^6 M⁻¹s⁻¹, two orders of magnitude slower than average intramolecular rate constant in our systems. Charge transfer quenching of acetophenone by anisole is known to be slow too.⁸² However, intramolecular quenching in short model phenoxy ketones (Bz-3-OPh, MeBz-3-OPh) could be more significant and cause lower quantum yields and consequently lower calculated rate constants. This assumption has to be proved by further research.

3.3 Flexibility of the Tether

Figure 12 compares intramolecular energy transfer constants for three bichromophoric systems Bz-n-ONp, Bz-n-O4Bp, and MeBz-n-ONp with those of Closs' rigid molecules²⁷ in which the benzophenone donor and the naphthalene acceptor are attached to a rigid spacer (cyclohexane or decalin ring) in all-equatorial positions. Closs showed that in such isomers with two *anti* dihedral angles, through-bond energy transfer rate constants are higher about one order of magnitude than in those with substituents in equatorial-axial positions (i.e. *anti-gauche*).

The rate constant in Bz-3-ONp is nearly identical to that of the Closs' rigid benzophenone-naphthalene system (Figure 12) as well as Cowan's flexible benzoylstyryl bichromophore³⁷ in which chromophores are separated by four atoms. We conclude that through-bond interaction predominates in all flexible 4-atom tether molecules. In systems with 5-atom tether, overall energy transfer rate constants are higher by about a factor of 5 than in that of a rigid bichromophoric molecule. Molecular flexibility apparently produces some conformations in which the two chromophores are close enough that through-space contribution becomes competitive with through-bond interaction. Such coiled conformations contain predominantly *gauche* rotation states which lower through-bond transfer but raise through-space interaction. For longer molecules, Figure 12 and especially the insert suggest that more than 99% of the total energy transfer occurs through space. Thus, the rate constants in longer flexible systems no longer fall an order of magnitude per additional bond, as they do for molecules with rigid spacers.

Rates in flexible molecules are still remarkably high in long derivatives - only one order of magnitude lower than those in molecules with 4-atom tethers. Long distance through-bond triplet energy transfer was found to be 25 s⁻¹ in rigid steroid molecule in which the benzophenone donor is separated by 10 atoms from the naphthalene acceptor.⁸⁴ This rate constant is 7 orders of magnitude smaller than that of the corresponding flexible derivative Bz-9-ONp ($k_{ET} = 3.8 \times 10^8 \text{ s}^{-1}$).



Figure 12. Rate constants for triplet energy transfer as a function of the number of atoms connecting donor and acceptor: \bullet Bz-n-ONp; \bigcirc MeBz-n-ONp; \blacksquare Bz-n-OBp; \triangle 4-PhCOPh-"rigid spacer"-2Np from ref. 27. Bz-n-ONp and the rigid molecule rate constants (from refs. 27, 84) are shown in the insert.

Energy transfer rate constants in Figure 12 level off to some extent in molecules with seven or more atoms between chromophores. We conclude that conformational factors produce a nearly constant percentage of geometries with the two chromophores close enough for through-space energy transfer. Similar plateaus have been observed in studies on electron transfer in bichromophoric radical anions,⁸⁵ spin-orbit exchange interaction in biradicals,⁸⁶ and many cyclization reactions.⁵¹ Monte Carlo calculations of Closs, Forbes, and coworkers⁸⁷ as well as exact enumeration calculations of Sisido and

Shimada⁸⁸ proved that even for very long molecules, which have 10 to 25-atom tethers, there is still a certain fraction of conformations allowing a close proximity of both ends. This fraction is certainly very small. A crude comparison of our plateau intramolecular energy transfer rate constants ($k_{ET} \sim 10^8 \text{ s}^{-1}$) with those of bimolecular *in-cage* transfer constants ($k_{ET} \sim 5-10 \times 10^{10} \text{ s}^{-1}$)^{89,90} or the rate of diffusion-controlled exothermic triplet transfer when donor and acceptor were 3-4 Å apart ($k_{ET} \sim 10^{12} \text{ s}^{-1}$)⁹¹ suggests that the fraction should be smaller than 1%.

Intramolecular triplet energy transfer occurs over longer distances than do intramolecular bond formations. Plot in Figure 12 lacking the characteristic rate constant profile of cyclization reactions^{51,92} reflects such difference. Exothermic bimolecular energy transfer between corresponding chromophores used in this work is nearly diffusion controlled. Analogous intramolecular processes can be controlled by bond rotation kinetics and/or by ground state conformational equilibria.⁷ Since excitation of the carbonyl chromophore should not alter conformational equilibria, most of the energy transfer occurs in conformers already sufficiently coiled before excitation. Each conformation has its own probability of undergoing energy transfer that depends mainly on the distance between chromophores and their orientations. Thus, the observed rate constant of an intramolecular process is a weighted average over all favorable conformations.⁹³

All conformers whose chromophores are 6 Å or less apart should contribute to the total transfer. When the chromophores are within 3-4 Å, energy transfer is practically instant ($k_{ET} \sim 10^{11}$ - 10^{12} s⁻¹)^{89,90,91} and provides the intramolecular equivalent of static

quenching. When the interchromophore distance is 5-6 Å $(k_{ET} \sim 10^8 \cdot 10^9 \text{ s}^{-1})^{94}$ some unfavorable conformers may rotate into such static quenching geometries within donor lifetime. Energy transfer in those cases competes with hydrogen abstraction $(k_{ET} \sim 10^8 \text{ s}^{-1})$.

The intramolecular energy transfer rate constant in the bichromophore Bz-3-O-2-O4Bp is higher by about a factor of three than that of the analogous Bz-6-O4Bp, having also 7-atom tether (Table 6). As was depicted in other examples,^{85,95} the exchange of a methylene group for oxygen increases flexibility of the chain thanks to a reduction of the gauche torsional strain.

Figure 13 depicts five characteristic model situations in which energy transfer rate constants depend on interchromophore distance or ability of the system to bring them close within the lifetime of the donor. The D-A distance 3 Å in the conformation A suggests that the energy transfer is instant ($\geq 10^{11}$ s⁻¹). Rotation along one C-C bond in B will bring the acceptor as close to the donor as in A. Such conformer may have a sufficient time to rotate into a favorable geometry within the lifetime of the benzoyl donor (Tables 2, 3) provided that the rotation rate constant is at least 10^9 s⁻¹. The D-A distance 6 Å in C corresponds to energy transfer rate constant 10^8 s⁻¹. In both systems B and C, energy transfer competes with Norrish type II hydrogen abstraction. In the totally stretched conformation D, the donor and the acceptor are about 14 Å apart what prevents energy transfer. The special case E shows a typical low energy "W" conformation^{92.96} in which donor and acceptor are not in close proximity and/or their orientations are not favorable. However, through-space (solvent) energy hop from the chromophore to a

chain atom (eventually from chain to chain) might contribute to the total energy transfer. The transfer rate constant is assumed to be high because the total transfer path is about 4.5 Å. The calculations of electronic coupling in the rigid systems using ab initio MO theory revealed that paths involving hops which skip over bonds make largest contribution to the total through-bond coupling.⁹⁷ Energy and electron transfer hops in proteins are currently at the center of interest.⁹⁸



Figure 13. Five characteristic conformations of D-9-OA: the simplified model.

3.4 Electronic Factors

An unexpected jump in energy transfer rates for Bz-x-O-2Np and Bz-x-O-4Bp with 10- and 11-atom tethers in Figure 12 indicates a larger number of conformations which allow through-space intramolecular energy transfer. Both systems exhibit the same profile for the dependence of k_{ET} on tether length.



Figure 14. Rate constants for triplet energy transfer, k_{ET} , and for electron transfer, P, as a function of the number of atoms connecting the donor and the acceptor: \bigoplus Bz-n-ONp; \bigoplus phthalimide-(CH₂)_{n+1}-phthalimide from ref. 85.

Since the structure of the 2-naphthyl group resembles that of 4-biphenyl, as will be discussed later in this dissertation, electronic effects seem to be the only factors causing differences in behavior of these two bichromophores. Szwarc and coworkers⁸⁵ investigated electron exchange between two phthalimide groups connected by a polymethylene chain. Their results are in good agreement with our observations as shown in Figure 14.

Intramolecular energy transfer rates in Figure 12 are consistently lower for the 4biphenyl chromophore compared to the naphthyl group approximately by a factor of two. It is known that the lowest energy conformation of the biphenyl ground state in solution is twisted while in the T_1 state the two rings are coplanar.⁹⁹ The conformational change in biphenyl slows energy or electron transfer because of unfavorable Franck-Condon factors as was shown in some bimolecular^{15,99a} and intramolecular energy transfer¹⁰⁰ studies. This effect is independent of whether through-bond or through space interaction predominates.

Benzoyl donor has an n,π^* lowest triplet excited state while 4-methylbenzoyl has a π,π^* .³⁴ A π,π^* excitation is more delocalized and π - π overlap of the chromophores should be geometrically more efficient than n- π overlap because of a parallel geometry, same character of orbitals, and less steric hindrance.¹⁰¹ The rate constants in Figure 12 are higher by a factor of only 1.2 to 1.5 for all tether lengths when a 4-methylbenzoyl group (MeBz-n-ONp) rather than a benzoyl group (Bz-n-ONp) is the donor. The difference is very small but consistent and a shift from through-bond to through-space mechanism obviously does not play any role in this case. The rate constant for MeBz-3O4Bp (Table 6) is a bit higher than that of Bz-3-O4Bp too. Thus, a better excitation delocalization and possibly a better orbital overlap seem to have a little effect on energy transfer. Figure 15 suggests that not only delocalization but also a change of chromophore orientation in the course of the transfer should be detectable. When only π,π^* excitations are involved, electron exchange is linked to π -type orbitals only. For n,π^* excited benzoyl, however, one electron jumps from π^* orbital of the donor into π^* orbital of the acceptor while the other has to jump from π orbital of the acceptor into n orbital the donor. Such exchange involves a change of orbital orientation during the process. Aromatic systems are parallel in π - π interaction but the interaction between π and n orbitals is best when the systems are perpendicular.⁸³ Those are, of course, extreme situations and it is logical that even geometries being far from ideal orientation might allow electron transfer.¹⁰² Nevertheless, the difference between benzoyl and 4methylbenzoyl donors was found to be very small.



Figure 15. An example of the difference between $n-\pi$ and $\pi-\pi$ interactions.

3.5 Isomeric Differences

When we compare molecules having the benzoyl donor connected to 4-, 3-, or 2substituted biphenyloxy groups (Figure 16), there are three characteristic regions in the graph to be discussed.

All derivatives with 4 to 6-atom tether display parallel reactivity. It is known that the barrier to rotation in 2-biphenyl substituted group is significantly higher than in those of 3-biphenyl and 4-biphenyl substituted groups thanks to steric reasons.¹⁰³ Alkyloxy

63

group that is attached to *ortho* position of biphenyl interacts with *ortho* hydrogens of the other ring when both rings are coplanar. Thus, conformational change from twisted ground state into coplanar triplet in 2-biphenyl group is more energetically difficult than in other biphenyls and Franck-Condon factors slow energy transfer even more. On the other side, the *ortho* but especially *para* electron-donating alkyloxy groups stabilize the planar rotation transition state by increasing the electron density at the carbon in the pivot bond. This stabilization is a consequence of the resonance effect in the ground state that decreases the rotational energy barrier.¹⁰³ An alkyloxy substituent in *meta* position has apparently no electronic influence by resonance. We conclude that 2-biphenyloxy acceptor lowers energy transfer rates because of steric reasons and that 4-biphenyloxy ketones have higher rate constants thanks to buttressing resonance effect, totally absent in 3-biphenyl derivatives.

The behavior of the longest derivatives (11 to 15-atom tether) is comparable to those of the short tethers. Kinetics of energy transfer in these molecules evidently resembles energy transfer in the corresponding bimolecular reactions. Diffusion is replaced by molecular mechanics of very flexible system. This is another example of the phenomenon that all effects influencing triplet energy transfer rates have comparable impact regardless which mechanism, either through-bond or through-space, is involved.



Figure 16. Rate constants for triplet energy transfer, k_{ET} , as a function of the number of atoms connecting the donor and the acceptor: \blacksquare Bz-n-O4Bp; ∇ Bz-n-O3Bp; \square Bz-n-O2Bp.

More complex situation was observed in the medium-tether molecules. In the region of 7 to 10-atom tethers, all molecules show a rate constant jump which occurs at different tether length depending on the acceptor. According to Figure 16, the jump began in bichromophores: Bz-6-O2Bp (7-atom tether) and Bz-9-O4Bp (10-atom tether). Bz-n-O3Bp has a similar rate constant profile as Bz-n-O2Bp. On the other hand, the rate constants in Bz-9-O3Bp and Bz-9-O2Bp dropps by a factor of two compared to Bz-9-O4Bp. O4Bp.

Energy transfer rate differences in short as well as long bichromophores with a biphenyloxy acceptor have been explained in terms of electronic and steric reasons. In medium tether molecules, a rotation along a single bond in the chain could rationalize their complex behavior. Figure 17 analyses a hypothetical example of one fixed conformation in which C-O rotation is the only change of geometry. Three different acceptors are compared in terms of a "reactive volume" originating from the rotation. Such "reactive volume" has a meaning of energy transfer possibility. Orientation of chromophores is crucial and not every rotamer is favorable for energy transfer.

The position of the phenyl ring attached to oxygen in biphenyl as well as naphthyl acceptors is not influenced by the rotation and is identical for all of them. The more distant phenyl in the 4-biphenyl and 2-naphthyl chromophores (**F**, **G**; Figure 17) is obviously too far from the carbonyl donor; its position remains constant during the rotation and so it has negligible contribution to energy transfer. Rotation of the 3biphenyl and especially 2-biphenyl (**H**; Figure 17) groups can, however, cause that the more distant ring approaches the donor close enough to provide efficient energy transfer.

Let us assume that orientation of all phenyl rings in biphenyl and naphthyl chromophores has the same statistical distribution. In this crude model, in which we would like to analyze individual transfer contribution of each phenyl ring in the acceptor, we assume that whenever one ring has favorable orientation, the other has too. Thus, this approximation considers orientation effect relatively unimportant. On the other hand, distance between the more distant phenyl and the donor strongly depends on the structure of the acceptor. The second phenyl in 4-biphenyl chromophore is totally ineffective. In 2-

biphenyl, however, 50% of all favorable geometries of the phenoxy ring place the more distant phenyl into favorable orientation and distance. It is clearly shown in Figure 17 that the more distant phenyl is significantly closer to the carbonyl donor (2.5 Å) than the phenoxy ring. This means that energy transfer should be significantly higher for 2biphenyloxy bichromophore (\mathbf{F}) than in that of 4-biphenyloxy derivative (\mathbf{H}). Energy transfer rates in Bz-6-O4Bp and Bz-7-O4Bp were found to be higher than in those of Bz-6-O2Bp and Bz-7-O-2Bp by factors of 1.3 and 2, respectively (Table 6, Figure 16). The C-O rotation evidently would not affect transfer when through-bond mechanism is involved or when the tether is long enough that molecular dynamics masks such small structural differences. This conformational analysis based on only one example is very crude. But it is apparent that study of rotation along C-O bond in different geometries and rotation along some other bonds could bring similar conclusions. Such systematic study would require a detailed statistical investigation. The donor chromophore is discussed as a group without specific orientation demands in this paragraph. This is another approximation that has to be taken into consideration.



Figure 17. Rotation along the O-C terminal bond showing a "reactive volume": Bz-6-O4Bp (F), Bz-6-ONp (G), and Bz-6-O2Bp (H).

Intramolecular energy transfer rates for Bz-x-O4Bp (x = 6,7) are smaller than in those of Bz-x-O2Bp by approximately a factor of two (Table 6). Figures 18 and 19 show an example of two minimized geometries for two bichromophores - Bz-6-O4Bp and Bz-6-O2Bp - that illustrates another rationalizing in search for differences between 4biphenyl derivatives on one side and 2- or 3-biphenyl derivatives on the other. The structure in Figure 18 demonstrates a situation when the phenoxy ring in 4-biphenyl is about 5 Å from the carbonyl oxygen but it is difficult to find a low energy conformation in which the other ring would approach the donor as close. In Bz-6-O2Bp (Figure 19) where the tether is even more stretched than the other one, the conformation allows the more distant ring to be in a close proximity to the carbonyl oxygen. Those geometries are, of course, two among thousands possible and only very detailed statistical analysis can provide definitive solution for this problem. The present reasoning provides, however, another good explanation of this unusual and novel observations.



Figure 18. Representative example of the minimized geometry by MM2 calculation and the formal structure of Bz-6-O4Bp.



Figure 19. Representative example of the minimized geometry by MM2 calculation and the formal structure of Bz-6-O2Bp.

3.6 Summary

This study presents a consistent picture of the intramolecular triplet energy transfer in flexible molecules with all tether lengths. Various factors have been changed in order to get information about how energetics, sterics, and dynamics influence the course of the transfer. Much has been learned in this work regarding the difference between through-bond and through space mechanisms. A remarkable finding, that even as long as 15-atom-tether bichromophoric molecules still provide relatively fast energy transfer, was presented. Further calculations are necessary for a more complete understanding of how a change of the chromophore character and the molecular dynamics affect energy transfer.

4. EXPERIMENTAL

4.1 Instrumentation

¹H and ¹³C NMR spectra were obtained on either a 300 MHz Varian Gemini or a 300 MHz Varian VXR-300 instrument.

IR spectra were recorded on a Nicolet IR/42 Fourier Transform IR spectrometer. Samples were prepared using a pressed KBr disc technique.

UV spectra were recorded on a Shimadzu UV-160 spectrometer with matched 1.0 cm quartz cells.

High resolution mass spectra were obtained on a Joel JMS-HX110 double focusing mass spectrometer in the MSU Mass Spectroscopic Facility. The electron impact and direct probe methods were used.

HPLC analyses were performed on either a Rainin HPXL apparatus equipped with a Dynamax UV-D absorbance detector or a Dynamax SD-200 system equipped with a Dynamax Diode Array Detector PDA-1 using a normal phase Rainin Microsorb Si80-125-CS silica gel column and a 100 μ L loop.

Gas chromatography analyses were performed on a Varian 3400 machine with a flame ionization detector with a Hewlett-Packard 3395 integrating recorder.

Phosphorescence spectra were recorded on a Perkin-Elmer MPF-44A fluorescence spectrophotometer with a Hewlett-Packard 3393A integrating recorder. Spectra were recorded at 77K in a 2-methyltetrahydrofuran or ethanol glass in a 4 mm Pyrex NMR sample tube.

Melting points were obtained on a Thomas Hoover capillary melting point apparatus. Melting points are not corrected.

4.2 Preparation of Bichromophores

4.2.1 Synthesis of ω -Aryloxyalkyl Aryl Ketones

A. Synthesis of ω -Iodoalkyl Aryl Ketones from Cycloalkanones

ω-Iodoalkyl aryl ketones Ar-CO- $(CH_2)_x$ -I (Ar = phenyl, 4-methylphenyl; x = 4-7,

11, 14) were prepared in three steps following the route given below:



Scheme 11. Synthesis of ω-Iodoalkyl Aryl Ketones

1-Phenylcyclopentanol

In a 250 mL three necked round bottom flask equipped with a condenser and purged with argon a solution of the cyclopentanone (10.0 g, 0.1 mol) in diethyl ether (20 mL) was added dropwise to a solution of phenylmagnesium bromide, prepared from phenyl bromide (16.5 g, 0.105 mol) and magnesium (2.7 g, 0.110 mol), in diethyl ether (60 mL) at 5°C. After all the ketone had been added, the mixture was stirred at 25°C for 1 hr., and then 10% hydrochloric acid solution was added dropwise to the mixture until all of the solid disappeared. The diethyl ether layer was separated and washed with saturated sodium hydrogen carbonate solution, distilled water and dried over MgSO₄. Diethyl ether was evaporated to yield the crude product (70%). The product was used without further purification in the next step.

1-Phenylcyclopentanol: ¹H NMR (CDCl₃): δ (ppm) 1.5-1.8 (m, 8H), 7.2-7.6 (m, 5H).

Note: Due to poor solubilities of products with seven and more carbons in the ring it was necessary to use more diethyl ether in this synthesis until the cycloalkanone was all dissolved.

5-Chloro-1-phenylpentan-1-one¹⁰⁴

A mixture of the 1-phenylcyclopentanol (12.8 g, 0.08 mol), Clorox bleach (350 mL), and acetic acid (35 mL) in carbon tetrachloride (350 mL) was vigorously stirred at 0°C for 8 hours. Carbon tetrachloride layer was separated and aqueous layer was extracted with carbon tetrachloride (3x 100 mL). The combined yellow carbon tetrachloride layers were washed with saturated sodium hydrogen carbonate solution, distilled water, and dried over MgSO₄.

MgSO₄ was filtered off and carbon tetrachloride (400 mL) was added. The solution was then refluxed and stirred with mechanical stirrer under argon for about 12 hrs., initiated with incandescent lamp light. After the reaction was completed (the product formation was monitored by either TLC or NMR) carbon tetrachloride was evaporated and the crude product (85%) was purified by distillation.

Notes: Due to poor solubilities of products with 8 and more carbons in the ring it was necessary to use more carbon tetrachloride during the extraction procedure. Those compounds were purified by crystallization.

5-Chloro-1-phenylpentan-1-one: ¹H NMR (CDCl₃): δ (ppm) 1.8-1.9 (m, 4H), 3.0 (t, 2H), 3.6 (t, 2H), 7.4-7.9 (m, 5H).

5-Iodo-1-phenylpentan-1-one

A mixture of the 5-chloro-1-phenylpentan-1-one (13.8 g, 0.07 mol) and sodium iodide (52.5 g, 0.35 mol) in dry acetone (600 mL) was refluxed for 24 hrs. in dark. The

solvent was evaporated and distilled water (300 mL) was added. The product was extracted with diethyl ether (200 mL, 2x 50 mL), the combined ether layer was washed with saturated sodium thiosulfate solution and distilled water, and dried over MgSO₄. The solvent was evaporated and the product was recrystallized from hexane/ethyl acetate mixture (9:1). The yield was 95% and its purity was checked by TLC.

5-Iodo-1-phenylpentan-1-one: ¹H NMR (CDCl₃): δ (ppm) 1.8-2.0 (m, 4H), 3.0 (t, 2H), 3.3 (t, 2H), 7.4-7.9 (m, 5H).

B. Synthesis of ω-Aryloxyalkyl Aryl Ketones

 ω -Aryloxyalkyl aryl ketones Ar-CO-(CH₂)_x-OAr' (Ar = phenyl, 4-methylphenyl; Ar' = phenyl, 2-naphthyl, 2/3/4-biphenyl, x = 4-7, 14) were prepared in three steps following the route given below:



Scheme 12. Synthesis of ω -Aryloxyalkanoaryl ketones (R = H, Me)
Ethylene glycol ketal of 5-iodo-1-phenylpentan-1-one

The mixture of the 5-iodo-1-phenylpentan-1-one (19.3 g, 0.067 mol), *p*-toluenesulfonic acid (0.03 g), and ethyleneglycol (14.6 g, 0.23 mol) in benzene (60 mL) was refluxed for 24 hrs. using a modified Dean-Stark trap and molecular sieve (4Å). The reaction was completed when the solvent over the sieve was clear. The solution was then washed with saturated sodium hydrogen carbonate solution, distilled water, and dried over MgSO₄. The solvent was evaporated and the product (80% yield) was used in the next step without further purification.

Ethylene glycol ketal of 5-iodo-1-phenylpentan-1-one: ¹**H NMR** (CDCl₃): δ (ppm) 1.4-1.9 (m, 6H), 3.2 (t, 2H), 3.8 (t, 2H), 4.0 (t, 2H), 7.4-8.0 (m, 5H).

Ethylene glycol ketal of 5-phenoxy-1-phenylpentan-1-one

A solution of ethylene glycol ketal of the 5-iodo-1-phenylpentan-1-one (17.6 g, 0.053 mol) and sodium phenolate, prepared from a phenol (50 g, 0.053 mol) and sodium (1.3 g, 0.058 mol) in absolute methanol, in dimethylformamide (200 mL) was stirred at 50°C for 30 hrs. Distilled water was added (200 mL) and the product was extracted with diethyl ether (3x 100 mL). The combined ether layer was washed with saturated sodium chloride solution, distilled water, and dried over MgSO₄. The solvent was evaporated and the crude product (85%) was used in the next step without further purification.

77

Ethylene glycol ketal of 5-phenoxy-1-phenylpentan-1-one: ¹**H NMR** (CDCl₃): δ (ppm) 1.3-1.9 (m, 6H), 3.7 (t, 2H), 3.8-4.1 (m, 4H), 6.9-8.0 (m, 5H).

5-Phenoxy-1-phenylpentan-1-one

A solution of ethylene glycol ketal of the 5-phenoxy-1-phenylpentan-1-one (13.5 g, 0.047 mol) and a catalytic amount of 10% hydrochloric acid in acetone (300 mL) was stirred at 40°C for 24 hrs. Distilled water (300 mL) was added and the product was extracted with diethyl ether (3x 100 mL). The combined ether layer was washed with saturated sodium hydrogen carbonate solution, distilled water, and dried over MgSO₄. The solvent was evaporated and the crude product (75-80%) was purified by flash chromatography and recrystallized from hexane/ethyl acetate mixture (8:2).

5-Phenoxy-1-phenylpentan-1-one (Bz-4-OPh)

¹**H NMR** (CDCl₃, 300 MHz): δ (ppm) 1.75-2.03 (m, 4H), 3.07 (t, J = 6.9 Hz, 2H), 4.01 (t, J = 6.0 Hz, 2H), 6.89 (d, J = 7.8 Hz, 2H), 6.93 (t, J = 7.4 Hz, 1H), 7.24-7.31 (m, 2H), 7.43-7.50 (m, 2H), 7.56 (t, J = 7.2, 1H), 7.97 (d, J = 7.4 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 20.93, 28.82, 38.10, 67.40, 114.46, 120.58, 128.04, 128.59, 129.42, 132.99, 136.96, 158.94, 200.02.

FTIR (KBr): 3069, 2944, 2876, 1686, 1601, 1499, 1258, 1032, 735 cm⁻¹.

HRMS: 254.1307 calculated for $C_{17}H_{18}O_2$, found 254.1319.

UV-VIS: ε_{366} (cyclohexane) = 4.5 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 4.0 Lmol⁻¹cm⁻¹.

Melting Point: $69.5-70.5^{\circ}$ C (lit. 69.0° C¹⁰⁵); white crystals.

The following compounds were prepared according to the representative procedure above.

6-Phenoxy-1-phenylhexan-1-one (**Bz-5-OPh**)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.50-1.65 (q, J = 6.6 Hz, 2H), 1.77-1.90 (m, 4H), 3.01 (t, J = 7.2 Hz, 2H), 3.97 (t, J = 6.4 Hz, 2H), 6.89 (d, J = 7.7 Hz, 2H), 6.93 (t, J = 7.4 Hz, 1H), 7.23-7.31 (m, 2H), 7.42-7.50 (m, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.96 (t, J = 7.0 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.01, 25.87, 29.19, 38.45, 67.54, 114.46,
120.51, 128.03, 128.57, 129.41, 132.95, 137.00, 159.01, 200.00.

FTIR (KBr): 3069, 2942, 2870, 1678, 1599, 1498, 1475, 1244, 1197, 752 cm⁻¹.

HRMS: 268.1463 calculated for $C_{18}H_{20}O_2$, found 268.1460.

UV-VIS: ε_{366} (cyclohexane) = 4.8 Lmol⁻¹cm⁻¹.

Melting Point: $52.0-53.0^{\circ}$ C (lit. $53.5-54.5^{\circ}$ C¹⁰⁶); white crystals.

8-Phenoxy-1-phenyloctan-1-one (Bz-7-OPh)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.35-1.57 (m, 6H), 1.68-1.88 (m, 4H), 2.97 (t, J = 7.4 Hz, 2H), 3.95 (t, J = 6.5 Hz, 2H), 6.89 (d, J = 7.7 Hz, 2H), 6.92 (t, J = 7.3 Hz, 1H), 7.24-7.32 (m, 2H), 7.41-7.50 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.96 (d, J = 7.1 Hz, 2H). ¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.25, 25.95, 29.24 (large peak), 29.28, 38.57, 67.76, 114.46, 120.45, 128.05, 128.56, 129.40, 132.90, 137.05, 159.07, 200.50. FTIR (KBr): 3068, 2936, 2865, 1686, 1601, 1498, 1493, 1240, 1039, 748 cm⁻¹. HRMS: 296.1776 calculated for C₂₀H₂₄O₂, found 296.1772. UV-VIS: ε₃₆₆ (cyclohexane) = 5.0 Lmol⁻¹cm⁻¹; ε₃₆₆ (benzene) = 4.4 Lmol⁻¹cm⁻¹. Melting Point: 44.5-45.0°C; white crystals.

12-Phenoxy-1-phenyldodecan-1-one (Bz-11-O-Ph):

The final product was recrystallized three times from hexane/ethyl acetate mixture (7:3).

¹H NMR (CDCl₃, 300 MHz): δ (ppm) 1.25-1.50 (m, 14H), 1.67-1.85 (m, 4H), 2.96 (t, J = 7.1 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 6.90 (d, J = 7.7 Hz, 2H), 6.92 (t, J = 7.4 Hz, 1H), 7.21-7.32 (m, 2H), 7.42-7.50 (m, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.96 (d, J = 7.1 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.38, 26.07, 29.30, 29.39 (large peak),
29.44, 29.48, 29.55, 38.64, 67.86, 114.48, 120.43, 128.07, 128.55, 129.51, 132.86,
137.09, 159.12, 200.63.

FTIR (KBr): 2912, 2849, 1682, 1475, 1250, 1028, 750, 691 cm⁻¹.

HRMS: 352.2402 calculated for C₂₄H₃₂O₂, found 352.2413.

UV-VIS: ϵ_{366} (benzene) = 4.5 Lmol⁻¹cm⁻¹.

Melting Point: 42.5-43.5°C; white crystals.

6-Phenoxy-1-(p-methylphenyl)hexan-1-one (MeBz-5-OPh)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.50-1.64 (q, J = 7.2 Hz, 2H), 1.70-1.90 (m, 4H), 2.39 (s, 3H), 2.96 (t, J = 7.2 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 6.83-6.95 (m, 3H), 7.21-7.30 (m, 4H), 7.85 (d, J = 8.1 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 21.61, 24.11, 25.87, 29.18, 38.33, 67.54,
114.43, 120.49, 128.15, 129.23, 129.38, 134.44, 143.68, 158.99, 199.93.

FTIR (KBr): 2945, 2872, 1674, 1603, 1498, 1476, 1304, 1248, 1182, 1010, 754, 690 cm⁻¹.

HRMS: 282.1620 calculated for C₁₉H₂₂O₂, found 283.1694 (+FAB, MH⁺).

UV-VIS: ε_{366} (cyclohexane) = 4.9 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 4.0 Lmol⁻¹cm⁻¹.

Melting Point: 49.0-50.0°C; white crystals.

6-(2-Naphthyloxy)-1-phenylhexan-1-one (Bz-5-ONp)

¹**H NMR** (CDCl₃, 300 MHz): δ (ppm) 1.55-1.70 (q, J = 7.1 Hz, 2H), 1.78-1.99 (m, 4H), 3.03 (t, J = 7.4 Hz, 2H), 4.09 (t, J = 6.3 Hz, 2H), 7.10-7.17 (m, 2H), 7.28-7.36 (m, 1H), 7.38-7.49 (m, 3H), 7.56 (t, J = 7.1 Hz, 1H), 7.69-7.79 (m, 3H), 7.97 (d, J = 7.0 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.02, 25.93, 29.15, 38.46, 67.69, 106.53, 118.97, 123.48, 126.29, 126.70, 127.62, 128.04, 128.58, 128.88, 129.32, 132.96, 134.58, 137.00, 156.99, 200.25.

FTIR (KBr): 2932, 1684, 1628, 1601, 1390, 1258, 1217, 1183, 1047, 839, 754, 690 cm⁻¹.

HRMS: 318.1620 calculated for $C_{22}H_{22}O_2$, found 318.1618.

UV-VIS: ε_{366} (cyclohexane) = 5.0 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 4.2 Lmol⁻¹cm⁻¹. Melting Point: 57.0-58.0°C; white crystals.

7-(2-Naphthyloxy)-1-phenylheptan-1-one (**Bz-6-ONp**)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.45-1.65 (m, 4H), 1.75-1.97 (m, 4H), 3.00 (t, J = 7.4 Hz, 2H), 4.08 (t, J = 6.5 Hz, 2H), 7.11-7.18 (m, 2H), 7.29-7.37 (m, 1H), 7.39-7.50 (m, 3H), 7.56 (t, J = 7.1 Hz, 1H), 7.69-7.79 (m, 3H). 7.97 (d, J = 7.0 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.28, 26.07, 29.16 (large peak), 38.51,
67.87, 106.57, 119.05, 123.51, 126.33, 126.73, 127.67, 128.09, 128.61, 128.91, 129.35,
132.97, 134.65, 137.13, 157.10, 200.45.

FTIR (KBr): 2938, 2867, 1684, 1630, 1599, 1468, 1446, 1390, 1262, 1221, 1036, 837, 739, 689 cm⁻¹.

HRMS: 332.1776 calculated for C₂₃H₂₄O₂, found 332.1779.

UV-VIS: ε_{366} (cyclohexane) = 5.1 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 4.3 Lmol⁻¹cm⁻¹.

Melting Point: 84.0-85.0°C; white crystals.

8-(2-Naphthyloxy)-1-phenyloctan-1-one (Bz-7-ONp)

¹**H NMR** (CDCl₃, 300 MHz): δ (ppm) 1.38-1.60 (m, 6H), 1.70-1.92 (m, 4H), 2.98 (t, J = 7.23 Hz, 2H), 4.07 (t, J = 6.5 Hz, 2H), 7.15-7.19 (m, 2H), 7.24-7.28 (m, 1H), 7.39-7.50 (m, 3H), 7.56 (t, J = 7.4 Hz, 1H), 7.69-7.78 (m, 3H), 7.96 (d, J = 7.0 Hz, 2H). ¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.25, 26.00, 29.20, 29.25, 29.29, 38.56,
67.91, 106.51, 119.02, 123.47, 126.28, 126.68, 127.62, 128.06, 128.57, 128.87, 129.30,
132.90, 134.60, 137.06, 157.07, 200.50.

FTIR (KBr): 2934, 2865, 1687, 1633, 1599, 1512, 1468, 1348, 1264, 1223, 1127, 1036, 857, 806, 742, 688 cm⁻¹.

HRMS: 346.1933 calculated for C₂₄H₂₆O₂, found 346.1931.

UV-VIS: ε_{366} (cyclohexane) = 5.0 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 4.4 Lmol⁻¹cm⁻¹. Melting Point: 44.0-45.0°C; white crystals.

12-(2-Naphthyloxy)-1-phenyldodecan-1-one (Bz-11-ONp)

The final product was recrystallized from hexane/ethyl acetate mixture (7:3).

¹**H NMR** (CDCl₃, 300 MHz): δ (ppm) 1.25-1.57 (m, 14H), 1.68-1.90 (m, 4H), 2.96 (t, J = 7.1 Hz, 2H), 4.07 (t, J = 6.6 Hz, 2H), 7.12-7.19 (m, 2H), 7.28-7.35 (m, 1H), 7.39-7.49 (m, 3H), 7.55 (t, J = 6.9 Hz, 1H), 7.69-7.78 (m, 3H), 7.96 (d, J = 7.0 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.36, 26.10, 29.24, 29.36, 29.39, 29.47
(large peak), 29.54 (large peak), 38.62, 67.98, 106.49, 119.02, 123.42, 126.25, 126.67, 127.61, 128.04, 128.53, 128.84, 129.27, 132.85, 134.60, 137.07, 157.06, 200.60.

FTIR (KBr): 2914, 2869, 1682, 1631, 1514, 1346, 1261, 1226, 1126, 856, 806, 742, 688 cm⁻¹.

HRMS: 402.2559 calculated for $C_{28}H_{34}O_2$, found 402.2552.

UV-VIS: ε_{366} (benzene) = 4.5 Lmol⁻¹cm⁻¹.

Melting Point: 64.0-65.0°C; white crystals.

15-(2-Naphthyloxy)-1-phenylpentadecan-1-one (Bz-14-ONp)

The final product was recrystallized from hexane/ethyl acetate mixture (7:3).

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.25-1.54 (m, 20H), 1.66-1.92 (m, 4H), 2.94 (t, J = 7.2 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 7.10-7.17 (m, 2H), 7.27-7.35 (m, 1H), 7.37-7.48 (m, 3H), 7.50-7.57 (m, 1H), 7.68-7.78 (m, 3H), 7.95 (d, J = 6.9 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.34, 26.09, 29.23, 29.35, 29.46 (large peak), 29.55 (large peak), 29.59 (large peak), 38.62, 67.98, 106.49, 119.02, 123.40, 126.24, 126.65, 127.60, 128.04, 128.52, 128.82, 129.26, 132.83, 134.59, 137.07, 157.09, 200.60.

FTIR (KBr): 2917, 2849, 1684, 1628, 1601, 1464, 1262, 1221, 1026, 841, 740, 689 cm⁻¹.

HRMS: 444.3028 calculated for $C_{31}H_{40}O_2$, found 444.3022.

UV-VIS: ε_{366} (benzene) = 4.6 Lmol⁻¹cm⁻¹.

Melting Point: 97.5-99.0°C; white crystals.

6-(4-Biphenyloxy)-1-phenylhexan-1-one (Bz-5-O4Bp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.50-1.69 (q, J = 7.1 Hz, 2H), 1.75-1.90 (m, 4H), 3.01 (t, J = 6.9 Hz, 2H), 4.00 (t, J = 6.3 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 7.22-7.59 (m, 10H), 7.96 (d, J = 7.5 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 23.96, 25.85, 29.15, 38.43, 67.73, 114.71, 126.57, 126.67, 128.01, 128.07, 128.56, 128.66, 132.94, 133.95, 136.95, 140.80, 158.57, 200.23.

FTIR (KBr): 3034, 2936, 2862, 1674, 1606, 1524, 1489, 1471, 1292, 1255, 1199, 1176, 974, 833, 761, 686 cm⁻¹.

HRMS: 344.1776 calculated for C₂₄H₂₄O₂, found 344.1776.

UV-VIS: ε_{366} (cyclohexane) = 4.9 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 4.3 Lmol⁻¹cm⁻¹.

Melting Point: 70.0-71.5°C; white crystals.

7-(4-Biphenyloxy)-1-phenylheptan-1-one (Bz-6-O4Bp)

¹H NMR (CDCl₃, 300 MHz): δ (ppm) 1.40-1.62 (m, 4H), 1.71-1.89 (m, 4H), 2.98 (t, J = 7.2 Hz, 2H), 3.99 (t, J = 6.3 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 7.22-7.60 (m, 10H), 7.96 (d, J = 7.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.17, 25.93, 29.04, 29.10, 38.42, 67.85, 114.69, 126.55, 126.65, 127.99, 128.09, 128.62, 128.65, 132.87, 133.50, 136.97, 140.81, 158.61, 200.34.

FTIR (KBr): 2932, 2867, 1682, 1608, 1524, 1489, 1448, 1276, 1258, 1201, 1041, 831, 758, 689 cm⁻¹.

HRMS: 358.1933 calculated for $C_{25}H_{26}O_2$, found 358.1930.

UV-VIS: ε_{366} (cyclohexane) = 4.9 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 4.4 Lmol⁻¹cm⁻¹.

Melting Point: 124.0-125.0°C; white crystals.

8-(4-Biphenyloxy)-1-phenyloctan-1-one (Bz-7-O4Bp)

¹H NMR (CDCl₃, 300 MHz): δ (ppm) 1.36-1.59 (m, 6H), 1.70-1.88 (m, 4H), 2.97 (t, J = 7.2 Hz, 2H), 3.99 (t, J = 6.3 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 7.23-7.58 (m, 10H), 7.96 (d, J = 7.5 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.21, 25.89, 29.20 (large peak), 29.23, 38.50, 67.93, 114.70, 126.55, 126.66, 128.02, 128.05, 128.53, 128.66, 132.86, 133.47, 136.99, 140.82, 158.63, 200.47.

FTIR (KBr): 2924, 2849, 1680, 1607, 1523, 1489, 1449, 1252, 1163, 1076, 841, 762, 687 cm⁻¹.

HRMS: 372.2090 calculated for C₂₆H₂₈O₂, found 372.2075.

UV-VIS: ε_{366} (cyclohexane) = 4.9 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 4.5 Lmol⁻¹cm⁻¹.

Melting Point: 72.5-73.0°C; white crystals.

12-(4-Biphenyloxy)-1-phenyldodecan-1-one (Bz-11-O4Bp)

The final product was recrystallized three times from hexane/ethyl acetate mixture (7:3).

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.20-1.57 (m, 14H), 1.70-1.90 (m, 4H), 2.99 (t, J = 7.4 Hz, 2H), 4.02 (t, J = 6.5 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 7.25-7.62 (m, 10H), 7.98 (d, J = 7.5 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.36, 26.05, 29.29, 29.37, 29.47 (large peak), 29.54 (large peak), 29.72, 38.62, 68.05, 114.74, 126.57, 126.69, 128.04, 128.08, 128.21, 128.54, 128.68, 132.85, 133.49, 137.07, 140.88, 158.70, 200.61.

FTIR (KBr): 2912, 2849, 1680, 1606, 1489, 1446, 1286, 1253, 1201, 1024, 839, 758, 689 cm⁻¹.

HRMS: 428.2715 calculated for $C_{30}H_{36}O_2$, found 428.2716.

UV-VIS: ϵ_{366} (benzene) = 4.6 Lmol⁻¹cm⁻¹.

Melting Point: 80.5-81.0°C; white crystals.

15-(4-Biphenyloxy)-1-phenylpentadecan-1-one (Bz-14-O4Bp)

The final product was recrystallized three times from hexane/ethyl acetate mixture (6:4).

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.20-1.53 (m, 20H), 1.65-1.84 (m, 4H), 2.98 (t, J = 7.2 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 7.23-7.60 (m, 10H), 7.98 (d, J = 7.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.37, 26.05, 29.29, 29.38 (large peak),
29.50, 29.57, 29.60 (large peak), 38.62, 68.06, 114.72, 126.56, 126.68, 128.03, 128.08,
128.52, 128.67, 132.84, 133.48, 137.06, 140.86, 158.69, 200.62.

FTIR (KBr): 2916, 2849, 1684, 1608, 1494, 1257, 1201, 1030, 831, 758, 688 cm⁻¹.

HRMS: 470.3185 calculated for $C_{33}H_{42}O_2$, found 470.3181.

UV-VIS: ϵ_{366} (benzene) = 4.5 Lmol⁻¹cm⁻¹.

Melting Point: 120.5-121.0°C; white crystals.

6-(2-Biphenyloxy)-1-phenylhexan-1-one (Bz-5-O2Bp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.40-1.52 (q, J = 7.1 Hz, 2H), 1.67-1.81 (m, 4H), 2.91 (t, J = 6.9 Hz, 2H), 3.96 (t, J = 6.3 Hz, 2H), 6.94-7.04 (m, 2H), 7.23-7.58 (m, 10H), 7.93 (d, J = 8.1 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 23.83, 25.81, 29.00, 38.41, 68.14, 112.56, 120.80, 126.70, 127.76, 128.01, 128.56 (large peak), 129.59, 130.81, 130.91, 132.92, 136.96, 138.57, 155.90, 200.23.

FTIR (KBr): 3059, 2940, 1684, 1597, 1504, 1483, 1433, 1261, 1231, 1122, 1008, 752, 698 cm⁻¹.

HRMS: 344.1776 calculated for $C_{24}H_{24}O_2$, found 345.1856 (+FAB, MH⁺).

UV-VIS: ε_{366} (cyclohexane) = 4.8 Lmol⁻¹cm⁻¹.

Colorless liquid.

7-(2-Biphenyloxy)-1-phenylheptan-1-one (**Bz-6-O2Bp**)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.25-1.50 (m, 4H), 1.62-1.80 (m, 4H), 2.91 (t, J = 7.5 Hz, 2H), 3.95 (t, J = 6.3 Hz, 2H), 6.94-7.04 (m, 2H), 7.22-7.58 (m, 10H), 7.93 (d, J = 8.7 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.16, 25.94, 28.91, 28.97, 38.41, 68.28,
112.50, 120.74, 126.69, 127.75, 128.02, 128.52 (large peak), 129.57, 130.81, 130.91,
132.88, 137.02, 138.58, 155.94, 200.31.

FTIR (KBr): 2941, 1686, 1595, 1505, 1474, 1435, 1265, 1235, 1194, 1122, 1034, 966, 750, 702 cm⁻¹.

HRMS: 358.1933 calculated for C₂₅H₂₆O₂, found 358.1922.

UV-VIS: ε_{366} (cyclohexane) = 4.8 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 4.3 Lmol⁻¹cm⁻¹. Melting Point: 50.5-51.0°C; white crystals.

8-(2-Biphenyloxy)-1-phenyloctan-1-one (Bz-7-O2Bp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.23-1.50 (m, 6H), 1.62-1.80 (m, 4H), 2.94 (t, J = 7.5 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 6.95-7.05 (m, 2H), 7.24-7.59 (m, 10H), 7.96 (d, J = 7.9 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.14, 25.87, 29.03 (large peak), 29.18, 38.47, 68.29, 112.46, 120.67, 126.65, 127.72, 127.97, 128.49 (large peak), 129.54, 130.77, 130.84, 132.81, 136.99, 138.55, 155.92, 200.39.

FTIR (KBr): 2934, 1686, 1597, 1483, 1435, 1261, 1122, 754, 698 cm⁻¹.

HRMS: 372.2089 calculated for $C_{26}H_{28}O_2$, found 373.2167 (+FAB, MH⁺).

UV-VIS: ε_{366} (cyclohexane) = 4.8 Lmol⁻¹cm⁻¹.

Colorless liquid.

12-(2-Biphenyloxy)-1-phenyldodecan-1-one (Bz-11-O2Bp)

The final product was recrystallized from hexane/ethyl acetate mixture (7:3).

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.18-1.46 (m, 14H), 1.60-1.84 (m, 4H), 2.96 (t, J = 7.5 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 6.94-7.04 (m, 2H), 7.24-7.58 (m, 10H), 7.96 (d, J = 7.2 Hz, 2H). ¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.35, 26.03, 29.13, 29.22, 29.36, 29.46
(large peak), 29.51, 38.61, 68.36, 112.44, 120.67, 126.68, 127.75, 128.03, 128.51 (large peak), 129.57, 130.80 (large peak), 132.84, 137.06, 138.59, 155.99, 200.57.

FTIR (KBr): 2921, 1696, 1595, 1473, 1437, 1265, 1232, 1205, 1120, 1010, 750, 702 cm⁻¹.

HRMS: 428.2715 calculated for C₃₀H₃₆O₂, found 428.2711.

UV-VIS: ϵ_{366} (benzene) = 4.5 Lmol⁻¹cm⁻¹.

Melting Point: 41.0-42.0°C; white crystals.

15-(2-Biphenyloxy)-1-phenylpentadecan-1-one (Bz-14-O2Bp)

The final product was recrystallized from hexane/ethyl acetate mixture (6:4).

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.19-1.42 (m, 20H), 1.62-1.80 (m, 4H), 2.94 (t, J = 7.2 Hz, 2H), 3.93 (t, J = 6.6 Hz, 2H), 6.93-7.03 (m, 2H), 7.24-7.57 (m, 10H), 7.94 (d, J = 7.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.37, 26.04, 29.14, 29.24, 29.38, 29.54
(large peak), 29.63 (large peak), 38.63, 68.38, 112.45, 120.67, 126.68, 127.77, 128.03, 128.40, 128.53, 129.58, 130.81 (large peak), 132.83, 138.75, 139.08, 156.00, 200.60.

FTIR (KBr): 2920, 2851, 1684, 1599, 1469, 1433, 1264, 1238, 1124, 748, 729, 690 cm⁻¹.

HRMS: 470.3185 calculated for $C_{33}H_{42}O_2$, found 470.3194.

UV-VIS: ε_{366} (benzene) = 4.6 Lmol⁻¹cm⁻¹.

Melting Point: 47.0-48.5°C; white crystals.

7-(3-Biphenyloxy)-1-phenylheptan-1-one (Bz-6-O3Bp)

¹**H NMR** (CDCl₃, 300 MHz): δ (ppm)) 1.40-1.62 (m, 4H), 1.70-1.90 (m, 4H), 2.98 (t, J = 7.2 Hz, 2H), 4.02 (t, J = 6.3 Hz, 2H), 6.88 (d, J = 8.1 Hz, 1H), 7.10-7.62 (m, 11H), 7.96 (d, J = 8.1 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.18, 25.94, 29.05, 29.15, 38.42, 67.81,
113.17, 113.46, 119.46, 127.13, 127.32, 127.99, 128.52, 128.65, 129.67, 132.86, 136.99,
141.08, 142.64, 159.41, 200.33.

FTIR (KBr): 2939, 1682, 1597, 1485, 1300, 1219, 758, 723, 691 cm⁻¹.

HRMS: 358.1933 calculated for $C_{25}H_{26}O_2$, found 358.1926.

UV-VIS (cyclohexane): $\varepsilon_{366} = 4.9 \text{ Lmol}^{-1} \text{ cm}^{-1}$.

Melting Point: 45.0-46.0°C; white crystals.

8-(3-Biphenyloxy)-1-phenyloctan-1-one (Bz-7-O3Bp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.35-1.58 (m, 6H), 1.68-1.88 (m, 4H), 2.96 (t, J = 7.5 Hz, 2H), 4.00 (t, J = 6.3 Hz, 2H), 6.87 (d, J = 8.1 Hz, 1H), 7.10-7.61 (m, 11H), 7.95 (d, J = 6.9 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.22, 25.92, 29.16, 29.21, 29.24, 38.52,
67.90, 113.20, 113.47, 119.44, 127.15, 127.31, 128.01, 128.53, 128.66, 129.66, 132.85,
137.02, 141.11, 142.65, 159.44, 200.44.

FTIR (KBr): 2936, 1688, 1601, 1473, 1302, 1213, 1033, 966, 756, 690 cm⁻¹.

HRMS: 372.2090 calculated for $C_{26}H_{28}O_2$, found 373.2166.

UV-VIS (cyclohexane): $\varepsilon_{366} = 4.8 \text{ Lmol}^{-1} \text{ cm}^{-1}$.

Melting Point: 39.0-40.0°C; white crystals.

15-(3-Biphenyloxy)-1-phenylpentadecan-1-one (Bz-14-O3Bp)

The final product was recrystallized from hexane/ethyl acetate mixture (7:3).

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.18-1.45 (m, 20H), 1.65-1.85 (m, 4H), 2.94 (t, J = 7.5 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 6.87 (d, J = 8.4 Hz, 1H), 7.10-7.60 (m, 11H), 7.94 (d, J = 7.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.37, 26.07, 29.27 (large peak), 29.32,
29.39 (large peak), 29.50, 29.62 (large peak), 38.62, 68.03, 113.22, 113.50, 119.43,
126.67, 127.16, 127.32, 128.03, 128.52, 128.67, 129.66, 132.67, 137.08, 142.67, 159.48,
200.61.

FTIR (KBr): 2915, 2851, 1686, 1595, 1468, 1217, 760, 691 cm⁻¹.

HRMS: 470.3185 calculated for $C_{33}H_{42}O_2$, found 470.3171.

UV-VIS (benzene): $\epsilon_{366} = 4.6 \text{ Lmol}^{-1} \text{ cm}^{-1}$.

Melting Point: 62.0-63.0°C; white crystals.

6-(2-Naphthyloxy)-1-(p-methylphenyl)hexan-1-one (MeBz-5-ONp)

¹H NMR (CDCl₃, 300 MHz): δ (ppm) 1.57-1.66 (q, J = 7.2 Hz, 2H), 1.78-1.96 (m, 4H), 2.40 (s, 3H), 2.99 (t, J = 7.2 Hz, 2H), 4.08 (t, J = 6.5 Hz, 2H), 7.10-7.16 (m, 2H), 7.22-7.46 (m, 4H), 7.66-7.78 (m, 3H), 7.86 (d, J = 8.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 21.59, 24.11, 25.91, 29.12, 38.31, 67.67, 106.51, 118.94, 123.44, 126.25, 126.67, 127.58, 128.13, 128.85, 129.22, 129.28, 134.50, 134.56, 143.65, 156.97, 199.89.

FTIR (KBr): 2948, 1674, 1629, 1599, 1468, 1388, 1259, 1182, 1005, 833, 812, 744 cm⁻¹.

HRMS: 332.1776 calculated for $C_{23}H_{24}O_2$, found 332.1796.

UV-VIS: ε_{366} (cyclohexane) = 4.8 Lmol⁻¹cm⁻¹.

Melting Point: 77.0-78.0°C; white crystals.

7-(2-Naphthyloxy)-1-(p-methylphenyl)heptan-1-one (MeBz-6-ONp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.42-1.62 (m, 4H), 1.72-1.93 (m, 4H), 2.41 (s, 3H), 2.97 (t, J = 7.2 Hz, 2H), 4.08 (t, J = 6.5 Hz, 2H), 7.10-7.16 (m, 2H), 7.22-7.46 (m, 4H), 7.68-7.75 (m, 3H), 7.87 (d, J = 8.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 21.62, 24.36, 26.02, 29.13, 38.36, 67.83, 105.51, 119.00, 123.45, 126.27, 126.68, 127.24, 127.62, 128.18, 128.42, 128.86, 129.24, 129.30, 134.60 (large peak), 143.65, 157.05, 200.10.

FTIR (KBr): 3057, 2939, 2867, 1680, 1628, 1599, 1466, 1390, 1262, 1219, 1184, 1037, 839, 793, 741 cm⁻¹.

HRMS: 346.1933 calculated for $C_{24}H_{26}O_2$, found 346.1942.

UV-VIS: ε_{366} (cyclohexane) = 4.9 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 4.3 Lmol⁻¹cm⁻¹.

Melting Point: 88.5-90.0°C; white crystals.

8-(2-Naphthyloxy)-1-(p-methylphenyl)octan-1-one (MeBz-7-ONp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm)) 1.40-1.58 (m, 6H), 1.70-1.90 (m, 4H), 2.41 (s, 3H), 2.95 (t, J = 7.2 Hz, 2H), 4.07 (t, J = 6.6 Hz, 2H), 7.11-7.17 (m, 2H), 7.22-7.46 (m, 4H), 7.69-7.78 (m, 3H), 7.87 (d, J = 8.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 21.61, 24.36, 25.98, 29.18, 29.64, 29.30, 38.44, 67.89, 106.47, 119.01, 123.43, 126.26, 126.67, 127.61, 128.17, 128.82, 129.22, 129.28, 134.59 (large peak), 143.62, 157.05, 200.22.

FTIR (KBr): 3056, 2930, 2855, 1674, 1630, 1601, 1466, 1388, 1259, 1217, 1182, 1118, 831, 806, 744 cm⁻¹.

HRMS: 360.2089 calculated for C₂₅H₂₈O₂, found 360.2099.

UV-VIS: ε_{366} (benzene) = 4.4 Lmol⁻¹cm⁻¹.

Melting Point: 48.5-49.0°C; white crystals.

12-(2-Naphthyloxy)-1-(p-methylphenyl)dodecan-1-one (MeBz-11-ONp)

¹**H NMR** (CDCl₃, 300 MHz): δ (ppm)) 1.25-1.55 (m, 14H), 1.65-1.90 (m, 4H), 2.40 (s, 3H), 2.93 (t, J = 7.4 Hz, 2H), 4.07 (t, J = 6.6 Hz, 2H), 7.10-7.17 (m, 2H), 7.22-7.46 (m, 4H), 7.69-7.78 (m, 3H), 7.86 (d, J = 8.3 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 21.60, 24.48, 26.09, 29.24, 29.38, 29.47
(large peak), 29.54 (large peak), 38.52, 67.98, 106.49, 119.02, 123.41, 126.24, 126.66, 127.60, 128.17, 128.83, 129.20 (large peak), 129.26, 134.60, 143.56, 157.08, 200.30.

FTIR (KBr): 2914, 2849, 1678, 1599, 1466, 1263, 1226, 1180, 854, 808, 779, 743 cm⁻¹.

HRMS: 416.2715 calculated for $C_{29}H_{36}O_2$, found 416.2703.

UV-VIS: ε_{366} (benzene) = 4.5 Lmol⁻¹cm⁻¹.

Melting Point: 70.0-71.0°C; white crystals.

C. Synthesis of ω -Iodoalkyl Aryl Ketones from ω -Chloroalkyl Nitriles

 ω -Iodoalkyl aryl ketones Ar-CO-(CH₂)_x-I (Ar = phenyl, 4-methylphenyl; x = 3, 4) were prepared in two steps following the route given below:



Scheme 13. Synthesis of ω -Iodoalkanoaryl Ketones (R = H, Me)

4-Chloro-1-phenylbutan-1-one

In a 250 mL three necked round bottom flask equipped with a condenser and purged with argon a solution of the 3-chlorobutyronitrile (8.0 g, 0.1 mol) in diethyl ether (10 mL) was added dropwise to a solution of phenylmagnesium bromide prepared from phenyl bromide (16.5 g, 0.105 mol) and magnesium (2.7 g, 0.11 mol) in diethyl ether (60 mL) at 5°C. After all the nitrile had been added, the mixture was stirred at 25°C for 2 hrs. and it was poured into a mixture of distilled water and ice (about 50 mL). The mixture was slowly neutralized by 10% hydrochloric acid solution and heated and stirred at 35°C for 2 hrs. The product was extracted with diethyl ether (3x 50 mL), and the combined ether layer was washed with saturated sodium hydrogen carbonate solution, distilled water, and dried over MgSO₄. The solvent was evaporated to yield the crude product (75%) which was used in the next step without further purification.

4-*Chloro-1-phenylbutan-1-one*: ¹H NMR (CDCl₃): δ (ppm) 2.2 (tt, 2H), 3.1 (t, 2H), 3.7 (t, 2H), 7.4-7.9 (m, 5H).

4-Iodo-1-phenylbutan-1-one

The mixture of the 4-chloro-1-phenylbutan-1-one (12.8 g, 0.07 mol) and sodium iodide (52.5 g, 0.35 mol) in dry acetone (600 mL) was refluxed for 24 hrs. in dark. The solvent was evaporated and distilled water (300 mL) was added. The product was extracted with diethyl ether (200 mL, 2x 50 mL), the combined ether layer was washed with saturated sodium thiosulfate solution and distilled water, and dried over MgSO₄.

The solvent was evaporated and the product was recrystallized from hexane/ethyl acetate mixture (9:1). The yield was 90%.

4-Iodo-1-phenylbutan-1-one: ¹H NMR (CDCl₃): δ (ppm) 2.2 (tt, 2H), 3.1 (t, 2H), 3.3 (t, 2H), 7.4-7.9 (m, 5H).

D. Synthesis of ω-Aryloxyalkyl Aryl Ketones

 ω -Aryloxyalkyl aryl ketones Ar-CO-(CH₂)_x-OAr' (Ar = phenyl, 4-methylphenyl; Ar' = phenyl, 2-naphthyl, 2/3/4-biphenyl, x = 3-4) were prepared in three steps according to the Scheme 13.

Ethylene glycol ketal of 4-iodo-1-phenylbutan-1-one

The mixture of the 4-iodo-1-phenylbutan-1-one (18.4g, 0.067 mol), ptoluenesulfonic acid (0.03 g), and ethyleneglycol (14.6 g, 0.23 mol) in benzene (60 mL) was refluxed for 24 hrs. using a modified Dean-Stark trap and molecular sieve (4Å). The reaction was completed when the solvent over the sieve was clear. The solution was then washed with saturated sodium hydrogen carbonate solution, distilled water, and dried over MgSO₄. The solvent was evaporated and the product (80% yield) was used in the next step without further purification.

Ethylene glycol ketal of 4-iodo-1-phenylbutan-1-one: ¹**H NMR** (CDCl₃): δ (ppm) 1.6-1.9 (m, 4H), 3.2 (t, 2H), 3.8 (t, 2H), 4.0 (t, 2H), 7.4-8.0 (m, 5H).

Ethylene glycol ketal of 4-phenoxy-1-phenylbutan-1-one

A solution of ethylene glycol ketal of the 4-iodo-1-phenylbutan-1-one (16.9 g, 0.053 mol) and sodium phenolate, prepared from a phenol (50 g, 0.053 mol) and sodium (1.3 g, 0.058 mol) in absolute methanol, in dimethylformamide (200 mL) was stirred at 50°C for 30 hrs. Distilled water was added (200 mL) and the product was extracted with diethyl ether (3x 100 mL). The combined ether layer was washed with saturated sodium chloride solution, distilled water, and dried over MgSO₄. The solvent was evaporated and the crude product (85%) was used in the next step without further purification. *Ethylene glycol ketal of 4-phenoxy-1-phenylbutan-1-one*: ¹H NMR (CDCl₃): δ (ppm) 1.3-1.9 (m, 4H), 3.7 (t, 2H), 3.8-4.1 (m, 4H), 6.9-8.0 (m, 5H).

4-Phenoxy-1-phenylbutan-1-one

A solution of ethylene glycol ketal of the 4-phenoxy-1-phenylbutan-1-one (12.8 g, 0.047 mol) and a catalytic amount of 10% hydrochloric acid in acetone (300 mL) was stirred at 40°C for 24 hrs. Distilled water (300 mL) was added and the product was extracted with diethyl ether (3x 100 mL). The combined ether layer was washed with saturated sodium hydrogen carbonate solution, distilled water, and dried over MgSO₄. The solvent was evaporated and the crude product (75-80%) was purified by flash chromatography and recrystallized from hexane/ethyl acetate mixture (8:2).

4-Phenoxy-1-phenylbutan-1-one (**Bz-3-OPh**)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 2.25 (tt, J = 6.5, 7.1 Hz, 2H), 3.22 (t, J = 7.1 Hz, 2H), 4.08 (t, J = 6.5 Hz, 2H), 6.91 (d, J = 7.8 Hz, 2H), 6.94 (t, J = 7.4 Hz, 1H), 7.23-7.31 (m, 2H) 7.43-7.49 (m, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.99 (d, J = 7.0 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 23.79, 34.95, 66.77, 114.45, 120.67, 128.03, 128.59, 129.44, 133.07, 136.90, 158.83, 199.61.

FTIR (KBr): 3069, 3042, 2911, 1688, 1601, 1497, 1279, 1036, 743 cm⁻¹.

HRMS: 240.1150 calculated for $C_{16}H_{16}O_2$, found 240.1149.

UV-VIS: ε_{366} (cyclohexane) = 3.1 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 2.5 Lmol⁻¹cm⁻¹.

Melting Point: $62.5-63.0^{\circ}$ C (lit. 63.0° C¹⁰⁵); white crystals.

The following compounds were prepared according to the representative procedure above.

4-Phenoxy-1-(p-methylphenyl)butan-1-one (MeBz-3-OPh)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 2.17 (tt, J = 6.0, 7.2 Hz, 2H), 2.34 (s, 3H), 3.11 (t, J = 7.2 Hz, 2H), 4.00 (t, J = 6.0 Hz, 2H), 6.80-6.90 (m, 3H), 7.15-7.25 (m, 4H), 7.85 (d, J = 8.1 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 21.59, 23.81, 34.78, 66.79, 114.39, 120.60,
128.10, 129.22, 129.39, 134.39, 143.77, 158.80, 199.21.

FTIR (KBr): 2943, 2803, 1674, 1606, 1585, 1486, 1366, 1248, 1172, 1036, 817, 748, 688 cm⁻¹.

HRMS: 254.1307 calculated for C₁₇H₁₈O₂, found 254.1297.

UV-VIS: ε_{366} (cyclohexane) = 2.9 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 2.3 Lmol⁻¹cm⁻¹. Melting Point: 58.3-59.0°C; white crystals.

5-Phenoxy-1-(p-methylphenyl)pentan-1-one (MeBz-4-OPh)

¹**H NMR** (CDCl₃, 300 MHz): δ (ppm) 1.80-1.98 (m, 4H), 2.38 (s, 3H), 3.00 (t, J = 6.6 Hz, 2H), 3.97 (t, J = 6.0 Hz, 2H), 6.82-6.95 (m, 3H), 7.20-7.32 (m, 4H), 7.84 (d, J = 7.8 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 20.97, 21.59, 28.80, 37.94, 67.41, 114.41,
120.51, 128.11, 129.20, 129.37, 134.44, 143.68, 158.90, 199.64.

FTIR (KBr): 2957, 1678, 1601, 1500, 1464, 1292, 1251, 1178, 1049, 979, 791, 758 cm⁻¹.

HRMS: 268.1463 calculated for $C_{18}H_{20}O_2$, found 268.1459.

UV-VIS: ε_{366} (cyclohexane) = 4.1 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 3.7 Lmol⁻¹cm⁻¹.

Melting Point: 83.0-83.5°C; white crystals.

4-(2-Naphthyloxy)-1-phenylbutan-1-one (Bz-3-ONp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 2.31 (tt, J = 6.0, 7.1 Hz, 2H), 3.25 (t, J = 7.1 Hz), 4.19 (t, J = 6.0 Hz, 2H), 7.11-7.16 (m, 2H), 7.29-7.36 (m, 1H), 7.39-7.50 (m, 3H), 7.56 (t, J = 7.0 Hz, 1H), 7.68-7.78 (m, 3H), 8.00 (d, J = 7.0 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 23.77, 35.00, 66.94, 106.63, 118.84, 123.57, 126.33, 126.73, 127.61, 128.04, 128.60, 128.93, 129.37, 133.09, 134.55, 136.90, 156.80, 199.60.

FTIR (KBr): 3056, 1682, 1630, 1595, 1464, 1275, 1228, 1026, 852, 742 cm⁻¹.

HRMS: 290.1307 calculated for $C_{20}H_{18}O_2$, found 290.1305.

UV-VIS: ε_{366} (cyclohexane) = 3.0 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 2.4 Lmol⁻¹cm⁻¹.

Melting Point: 64.5-65.5°C; white crystals.

5-(2-Naphthyloxy)-1-phenylpentan-1-one (Bz-4-ONp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.88-2.07 (m, 4H), 3.09 (t, J = 6.9 Hz, 2H), 4.13 (t, J = 5.8 Hz, 2H), 7.07-7.15 (m, 2H), 7.27-7.35 (m, 1H), 7.37-7.50 (m, 3H), 7.56 (t, J = 7.2 Hz, 1H), 7.67-7.78 (m, 3H), 7.97 (d, J = 7.0 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 21.00, 28.80, 38.13, 67.60, 106.56, 118.99,
123.55, 126.35, 126.74, 127.66, 128.08, 128.63, 128.93, 129.37, 133.04, 134.60, 136.99,
156.95, 200.03.

FTIR (KBr): 2928, 1686, 1630, 1599, 1464, 1258, 1219, 1186, 976, 843, 735 cm⁻¹.

HRMS: 304.1463 calculated for C₂₁H₂₀O₂, found 304.1471.

UV-VIS: ε_{366} (cyclohexane) = 5.0 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 4.0 Lmol⁻¹cm⁻¹.

Melting Point: 94.5-95.0°C; white crystals.

4-(4-Biphenyloxy)-1-phenylbutan-1-one (Bz-3-O4Bp)

¹H NMR (CDCl₃, 300 MHz): δ (ppm) 2.27 (tt, J = 6.0, 6.9 Hz, 2H), 3.22 (t, J = 6.9 Hz, 2H), 4.11 (t, J = 6.0 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 7.24-7.60 (m, 10H), 7.98 (d, J = 7.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 23.73, 34.88, 66.93, 114.69, 126.60, 126.66, 127.99, 128.09, 128.56, 128.67, 133.05, 133.71, 136.83, 140.73, 158.37, 199.54.

FTIR (KBr): 3031, 2942, 1692, 1604, 1522, 1471, 1246, 1201, 1041, 763, 694 cm⁻¹.

HRMS: 316.1463 calculated for $C_{22}H_{20}O_2$, found 316.1465.

UV-VIS: ε_{366} (cyclohexane) = 3.0 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 2.4 Lmol⁻¹cm⁻¹.

Melting Point: 87.0-88.0°C; white crystals.

5-(4-Biphenyloxy)-1-phenylpentan-1-one (Bz-4-O4Bp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.85-2.03 (m, 4H), 3.07 (t, J = 6.9 Hz, 2H), 4.04 (t, J = 5.7 Hz, 2H), 6.95 (d, J = 9.0 Hz, 2H), 7.23-7.59 (m, 10H), 7.97 (d, J = 7.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 20.84, 28.74, 38.00, 67.58, 114.65, 126.53, 126.63, 127.96, 128.04, 128.52, 128.63, 132.92, 133.56, 136.87, 140.74, 158.45, 199.91.

FTIR (KBr): 2951, 2874, 1684, 1608, 1489, 1289, 1259, 1201, 1180, 1029, 831, 758, 689 cm⁻¹.

HRMS: 330.1620 calculated for $C_{23}H_{22}O_2$, found 330.1621.

UV-VIS: ε_{366} (cyclohexane) = 4.8 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 4.2 Lmol⁻¹cm⁻¹.

Melting Point: 132.0-132.8°C; white crystals.

4-(2-Biphenyloxy)-1-phenylbutan-1-one (Bz-3-O2Bp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 2.19 (tt, J = 5.7, 7.2 Hz, 2H), 3.07 (t, J = 7.2 Hz, 2H), 4.11 (t, J = 5.7 Hz, 2H), 7.02-7.12 (m, 2H), 7.32-7.64 (m, 10H), 7.90 (d, J = 7.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 23.74, 34.65, 67.28, 112.61, 120.91, 126.65, 127.71, 127.88, 128.38, 128.53, 129.47, 130.67, 130.91, 132.84, 136.63, 138.52, 155.56, 199.54.

FTIR (KBr): 3059, 2934, 1686, 1597, 1597, 1504, 1483, 1435, 1262, 1123, 1055, 1003, 754, 700 cm⁻¹.

HRMS: 316.1463 calculated for C₂₂H₂₀O₂, found 316.1467.

UV-VIS: ε_{366} (cyclohexane) = 2.9 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 2.5 Lmol⁻¹cm⁻¹.

Colorless liquid.

5-(2-Biphenyloxy)-1-phenylpentan-1-one (Bz-4-O2Bp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.75-1.93 (m, 4H), 2.93 (t, J = 6.9 Hz, 2H), 4.00 (t, J = 5.4 Hz, 2H), 6.94-7.05 (m, 2H), 7.24-7.57 (m, 10H), 7.86 (d, J = 8.1 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 21.08, 28.72, 38.09, 68.20, 112.45, 120.89,
126.75, 127.81, 128.01, 128.54 (large peak), 129.56, 130.88, 132.91, 136.87, 138.54,
153.37, 155.84, 200.05.

FTIR (KBr): 2946, 1684, 1597, 1483, 1433, 1264, 1199, 1128, 958, 775, 734 cm⁻¹.

HRMS: 330.1620 calculated for $C_{23}H_{22}O_2$, found 330.1632.

UV-VIS: ε_{366} (cyclohexane) = 4.7 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 3.6 Lmol⁻¹cm⁻¹.

Melting Point: 67.0-68.0°C; white crystals.

4-(3-Biphenyloxy)-1-phenylbutan-1-one (Bz-3-O3Bp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 2.28 (tt, J = 6.0, 6.9 Hz, 2H), 3.23 (t, J = 6.9 Hz, 2H), 4.14 (t, J = 6.0 Hz, 2H), 6.89 (d, J = 8.1 Hz, 1H), 7.12-7.62 (m, 11H), 8.00 (d, J = 7.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 23.78, 34.87, 66.91, 113.15, 113.43, 119.61, 127.11, 127.34, 127.98, 128.54, 128.66, 129.70, 133.02, 136.85, 140.98, 142.68, 159.19, 199.48.

FTIR (KBr): 2974, 1687, 1583, 1568, 1468, 1309, 1215, 1016, 870, 758, 688 cm⁻¹.

HRMS: 316.1463 calculated for $C_{22}H_{20}O_2$, found 316.1463.

UV-VIS (cyclohexane): $\varepsilon_{366} = 2.8 \text{ Lmol}^{-1} \text{ cm}^{-1}$.

Melting Point: 91.0-92.5°C; white crystals.

4-(2-Naphthyloxy)-1-(p-methylphenyl)butan-1-one (MeBz-3-ONp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 2.29 (tt, J = 6.1, 7.0 Hz, 2H), 2.39 (s, 3H), 3.21 (t, J = 7.0 Hz, 2H), 4.17 (t, J = 6.1 Hz, 2H), 7.11-7.16 (m, 2H), 7.22-7.46 (m, 4H), 7.68-7.78 (m, 3H), 7.90 (d, J = 8.3 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 21.63, 23.83, 34.87, 67.00, 106.62, 118.85, 123.54, 126.32, 126.73, 127.60, 128.15, 128.91, 129.27, 129.33, 134.43, 134.54, 143.84, 156.81, 199.26.

FTIR (KBr): 2965, 1684, 1630, 1601, 1466, 1367, 1257, 1180, 1120, 1016, 835, 821, 746 cm⁻¹.

HRMS: 304.1463 calculated for $C_{21}H_{20}O_2$, found 304.1461.

UV-VIS: ε_{366} (cyclohexane) = 2.7 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 2.4 Lmol⁻¹cm⁻¹.

Melting Point: 80.0-81.0°C; white crystals.

5-(2-Naphthyloxy)-1-(p-methylphenyl)pentan-1-one (MeBz-4-ONp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.90-2.05 (m, 4H), 2.41 (s, 3H), 3.06 (t, J = 6.9 Hz, 2H), 4.13 (t, J = 5.9 Hz, 2H), 7.10-7.16 (m, 2H), 7.23-7.47 (m, 4H), 7.69-7.78 (m, 3H), 7.88 (d, J = 8.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 21.03, 21.62, 28.77, 37.97, 67.56, 106.49, 118.95, 123.48, 126.28, 126.69, 127.60, 128.16, 128.87, 129.25, 129.30, 134.69, 134.54, 143.73, 156.91, 199.67.

FTIR (KBr): 2957, 2930, 1678, 1601, 1464, 1388, 1257, 1215, 1180, 970, 839, 806, 746 cm⁻¹.

HRMS: 318.1620 calculated for $C_{22}H_{22}O_2$, found 318.1604.

UV-VIS: ε_{366} (cyclohexane) = 4.8 Lmol⁻¹cm⁻¹.

Melting Point: 125.0-126.5°C; white crystals.

4-(4-Biphenyloxy)-1-(p-methylphenyl)butan-1-one (MeBz-3-O4Bp)

¹**H NMR** (CDCl₃, 300 MHz): δ (ppm) 2.25 (tt, J = 6.0, 7.1 Hz, 2H), 2.40 (s, 3H), 3.19 (t, J = 7.1 Hz, 2H), 4.10 (t, J = 6.0 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 7.22-7.58 (m, 9H), 7.89 (d, J = 8.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 21.63, 23.84, 34.78, 67.04, 114.73, 126.62,
126.69, 128.14 (large peak), 128.69, 129.26, 133.71, 134.42, 140.80, 143.83, 158.43,
199.22.

FTIR (KBr): 2948, 2872, 1682, 1606, 1489, 1288, 1251, 1199, 1047, 839, 758, 687 cm⁻¹.

HRMS: 330.1620 calculated for C₂₃H₂₂O₂, found 330.1619.

UV-VIS: ε_{366} (cyclohexane) = 2.8 Lmol⁻¹cm⁻¹.

Melting Point: 97.0-98.0°C; white crystals.

E. Synthesis of ω -Aryloxyalkyl Phenyl Ketones from ω -Bromoalkanols

 ω -Aryloxyalkanoaryl ketones Ph-CO-(CH₂)_x-OAr (Ar = phenyl, 2-naphthyl,

2/3/4-biphenyl, x = 9, 10) were prepared in three steps following the route given below:



Scheme 14. Synthesis of ω-Aryloxyalkanophenyl ketones

THP-ether of 10-bromodecanol

Concentrated hydrochloric acid (0.1 mL) was added to a mixture of 2,3dihydropyran (2.18 g, 0.026 mol) and the 10-bromodecanol (3.1 g, 0.013 mol). Reaction commenced immediately on shaking and was moderated by cooling in a ice-water bath. The mixture was stirred for another 30 minutes at this temperature and then at room temperature for 12 hrs. The mixture was diluted with diethyl ether (50 mL) and washed with sodium hydrogen carbonate solution. The etheral layer was dried over MgSO₄. The solvent was evaporated and the crude product (90%) was used in the next step without further purification.

THP-ether of 10-bromodecanol: ¹**H NMR** (CDCl₃): δ (ppm) 1.2-2.0 (m, 22H), 3.3 (t, 3H), 3.8 (t, 2H), 4.1 (t, 3H), 4.7 (t, 1H).

10-Phenoxydecanol

A solution of THP-ether of 10-bromodecanol (3.9 g, 0.012 mol) and a corresponding sodium phenolate, prepared from a phenol (1.1 g, 0.012 mol) and sodium (0.3 g, 0.013 mol) in absolute methanol, in dimethylformamide (60 mL) was stirred at 50°C for 30 hrs. Distilled water was added (60 mL) and the product was extracted with diethyl ether (3x 50 mL). The combined ether layer was washed with saturated sodium chloride solution, distilled water, and dried over MgSO₄. The solvent was evaporated and the product was dissolved in methanol (50 mL) and concentrated hydrochloric acid (10 mL), and the mixture was heated under reflux for 2 hrs. After cooling, the solution, diluted with diethyl ether (60 mL). The etheral layer was washed with distilled water and dried over MgSO₄. The solvent was evaporate solution, diluted with diethyl ether (60 mL). The etheral layer was washed with distilled water and the next step without further purification.

9-Phenoxydecanol: ¹H NMR (CDCl₃): δ (ppm) 1.0-1.9 (m, 16H), 3.7 (t, 2H), 4.1 (t, 2H),
6.9-8.0 (m, 5H).

10-Phenoxydecyl chloride

The 10-phenoxydecanol (2.5 g, 0.01 mol) was dissolved in dimethylformamide (30 mL) and thionyl chloride (1.4 g, 0.012 mol) was added dropwise while stirring at 0°C. The mixture was then stirred at 50°C for 12 hrs. Distilled water was added (30 mL) and the product was extracted with diethyl ether (3x 25 mL). The combined ether layer was washed with saturated sodium chloride solution, distilled water, and dried over MgSO₄. The solvent was evaporated and the crude product (90%) was used in the next step without further purification.

10-Phenoxydecyl chloride: ¹H NMR (CDCl₃): δ (ppm) 1.0-1.9 (m, 16H), 3.5 (t, 2H), 4.0 (t, 2H), 6.9-7.7 (m, 5H).

10-Phenoxydecyl iodide

The mixture of the 10-phenoxydecyl chloride (2.4 g, 0.009 mol) and sodium iodide (5.0 g, 0.035 mol) in dry acetone (80 mL) was refluxed for 24 hrs. in dark. The solvent was evaporated and distilled water (80 mL) was added. The product was extracted with diethyl ether (50 mL, 2x 30 mL), the combined ether layer was washed with saturated sodium thiosulfate solution and distilled water, and dried over MgSO₄.

The solvent was evaporated and the product (90%) was either recrystallized from hexane/ethyl acetate mixture (8:2).

10-Phenoxydecyl iodide: ¹**H NMR** (CDCl₃): δ (ppm) 1.0-1.9 (m, 16H), 3.2 (t, 2H), 3.9 (t, 2H), 6.9-7.7 (m, 5H).

11-Phenoxyundecanonitrile

A solution of the 10-phenoxydecyl iodide (2.9 g, 0.008 mol) and sodium cyanide (0.44 g, 0.009 mol) in dimethylformamide (40 mL) was stirred at 50°C for 12 hrs. Distilled water was added (40 mL) and the product was extracted with diethyl ether (3x40 mL). The combined ether layer was washed with saturated sodium chloride solution and distilled water, and was dried over MgSO₄. The solvent was evaporated and the crude product (85%) was purified by crystallization from hexane/ethyl acetate mixture (7:3).

Note: The product has to be pure in order to get high yield in the next step.

11-Phenoxyundecanonitrile: ¹H NMR (CDCl₃): δ (ppm) 1.0-1.9 (m, 16H), 2.3 (t, 2H),
3.9 (t, 2H), 6.9-7.7 (m, 5H).

11-Phenoxy-1-phenylundecan-1-one

In a 100 mL three necked round bottom flask equipped with a condenser and purged with argon a solution of the 11-phenoxyundecanonitrile (1.8 g, 0.007 mol) in diethyl ether (10 mL) was added dropwise to a solution of phenylmagnesium bromide, prepared from phenyl bromide (1.1 g, 0.007 mol) and magnesium (0.19 g, 0.008 mol), in

diethyl ether (30 mL) at 5°C. After all the nitrile had been added, the mixture was stirred at 35°C for 4 hrs. and poured into a mixture of distilled water and ice (about 50 mL). The mixture was slowly neutralized by 10% hydrochloric acid solution and stirred at 35°C for 2 hrs. The product was extracted with diethyl ether (3x 40 mL), the combined ether layer was washed with saturated sodium bicarbonate solution, distilled water, and dried over MgSO₄. The solvent was evaporated and the crude product (75%) was purified by flash chromatography and recrystallized from hexane/ethyl acetate mixture (9:1).

11-Phenoxy-1-phenylundecan-1-one (Bz-10-OPh)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.25-1.50 (m, 12H), 1.65-1.85 (m, 4H), 2.96 (t, J = 7.2 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 6.90 (d, J = 7.7 Hz, 2H), 6.92, (t, J = 7.3 Hz, 1H), 7.21-7.26 (m, 2H), 7.40-7.52 (m, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.99 (d, J = 7.1 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.36, 26.05, 29.29, 29.37 (large peak),
29.40, 29.46, 29.52, 38.62, 67.84, 114.47, 120.42, 128.05, 128.54, 129.39, 132.86,
137.08, 159.10, 200.61.

FTIR (KBr): 3067, 2916, 2851, 1686, 1601, 1499, 1251, 1044, 750, 690 cm⁻¹.

HRMS: 338.2246 calculated for $C_{23}H_{30}O_2$, found 338.2253.

UV-VIS: ε_{366} (benzene) = 4.5 Lmol⁻¹cm⁻¹.

Melting Point: 83.0-83.5°C; white crystals.

The following compounds were prepared according to the representative procedure above.

10-(2-Naphthyloxy)-1-phenyldecan-1-one (Bz-9-ONp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.30-1.59 (m, 10H), 1.65-1.90 (m, 4H), 2.95 (t, J = 7.2 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 7.10-7.17 (m, 2H), 7.27-7.34 (m, 1H), 7.39-7.50 (m, 3H, b, j), 7.54 (t, J = 7.2 Hz, 1H), 7.69-7.78 (m, 3H), 7.95 (d, J = 7.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.31, 26.06, 29.20, 29.32 (large peak),
29.39 (large peak), 38.58, 67.92, 106.47, 118.99, 123.41, 126.22, 126.65, 127.59,
128.02, 128.52, 128.80, 129.25, 132.83, 134.57, 137.07, 157.05, 200.53.

FTIR (KBr): 2914, 2849, 1682, 1631, 1597, 1512, 1468, 1448, 1352, 1213, 1126, 1028, 1001, 856, 804, 740, 689 cm⁻¹.

HRMS: 374.2246 calculated for $C_{26}H_{30}O_2$, found 374.2248.

UV-VIS: ε_{366} (cyclohexane) = 5.0 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 4.5 Lmol⁻¹cm⁻¹.

Melting Point: 59.5-60.0°C; white crystals.

11-(2-Naphthyloxy)-1-phenylundecan-1-one (Bz-10-ONp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.25-1.60 (m, 12H), 1.65-1.90 (m, 4H), 2.94 (t, J = 7.5 Hz, 2H), 4.05 (t, J = 6.6 Hz, 2H), 7.10-7.16 (m, 2H), 7.27-7.34 (m, 1H), 7.38-7.49 (m, 3H), 7.50-7.57 (m, 1H), 7.68-7.76 (m, 3H), 7.94 (d, J = 7.2 Hz, 2H).
¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.33, 26.02, 29.21, 29.36 (large peak),
29.30, 29.40, 29.43, 29.49, 38.59, 67.97, 106.48, 118.99, 123.40, 126.24, 126.65,
127.59, 128.01, 128.52, 128.82, 129.56, 132.84, 134.57, 137.05, 157.06, 200.57.

FTIR (KBr): 2918, 2835, 1684, 1466, 1281, 1221, 837, 736, 690 cm⁻¹.

HRMS: 388.2402 calculated for C₂₇H₃₂O₂, found 388.2409.

UV-VIS: ε_{366} (benzene) = 4.6 Lmol⁻¹cm⁻¹.

Melting Point: 91.0-92.0°C; white crystals.

10-(4-Biphenyloxy)-1-phenyldecan-1-one (Bz-9-O4Bp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.32-1.52 (m, 10H), 1.65-1.85 (m, 4H), 2.97 (t, J = 7.5 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 7.22-7.58 (m, 10H), 7.95 (d, J = 7.0 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.36, 26.06, 29.30, 29.36 (large peak),
29.43 (large peak), 38.63, 68.07, 114.78, 126.60, 126.72, 128.08, 128.12, 128.57,
128.71, 132.90, 133.54, 137.10, 140.90, 158.73, 200.62.

FTIR (KBr): 2924, 2847, 1680, 1606, 1524, 1489, 1469, 1286, 1258, 1202, 1003, 839, 758 cm⁻¹.

HRMS: 400.2402 calculated for C₂₈H₃₂O₂, found 400.2396.

UV-VIS: ϵ_{366} (benzene) = 4.6 Lmol⁻¹cm⁻¹.

Melting Point: 73.5-74.0°C; white crystals.

11-(4-Biphenyloxy)-1-phenylundecan-1-one (Bz-10-O4Bp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.25-1.55 (m, 12H), 1.62-1.88 (m, 4H), 2.95 (t, J = 7.5 Hz, 2H), 3.98 (t, J = 6.6 Hz, 2H), 6.95 (d, J = 9.0 Hz, 2H), 7.22-7.58 (m, 10H), 7.95 (d, J = 7.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.31, 26.01, 29.25, 29.34 (large peak),
29.40, 29.44 (large peak), 29.49, 38.59, 68.00, 114.72, 126.55, 126.66, 128.02, 128.05,
128.51, 128.66, 132.84, 133.46, 137.62, 140.83, 158.66, 200.56.

FTIR (KBr): 2915, 2849, 1682, 1608, 1526, 1489, 1288, 1271, 1046, 987, 831, 688 cm⁻¹.

HRMS: 414.2559 calculated for $C_{29}H_{34}O_2$, found 414.2547.

UV-VIS: ε_{366} (benzene) = 4.5 Lmol⁻¹cm⁻¹.

Melting Point: 125.0-126.0°C; white crystals.

10-(2-Biphenyloxy)-1-phenyldecan-1-one (Bz-9-O2Bp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.22-1.48 (m, 10H), 1.66-1.82 (m, 4H), 2.97 (t, J = 7.2 Hz, 2H), 3.96 (t, J = 6.6 Hz, 2H), 6.96-7.05 (m, 2H), 7.26-7.58 (m, 10H), 7.97 (d, J = 7.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.28, 25.97, 29.08, 29.15, 29.30, 29.63, 29.69, 38.53, 68.28, 112.39, 120.65, 126.61, 127.72, 127.98, 128.48 (large peak), 129.54, 130.77 (large peak), 132.80, 136.99, 138.55, 155.95, 200.47.

FTIR (KBr): 2928, 2855, 1688, 1597, 1483, 1435, 1262, 1122, 752, 698 cm⁻¹. **HRMS**: 400.2402 calculated for C₂₈H₃₂O₂, found 400.2402. **UV-VIS**: ε_{366} (cyclohexane) = 4.9 Lmol⁻¹cm⁻¹; ε_{366} (benzene) = 4.5 Lmol⁻¹cm⁻¹. Colorless liquid.

11-(2-Biphenyloxy)-1-phenylundecan-1-one (**Bz-10-O2Bp**)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.20-1.43 (m, 12H), 1.65-1.80 (m, 4H), 2.95 (t, J = 7.5 Hz, 2H), 3.94 (t, J = 6.3 Hz, 2H), 6.94-7.04 (m, 2H), 7.24-7.58 (m, 10H), 7.95 (d, J = 7.8 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.35, 26.02, 29.12, 29.19, 29.35 (large peak), 29.44, 29.47, 38.60, 68.36, 112.46, 120.67, 126.67, 127.74, 128.01, 128.48, 128.52, 129.58, 130.81, 130.85, 132.83, 137.06, 138.60, 156.00, 200.56.

FTIR (KBr): 2921, 1692, 1595, 1476, 1435, 1263, 1232, 1122, 756, 696 cm⁻¹.

HRMS: 414.2559 calculated for C₂₉H₃₄O₂, found 414.2541.

UV-VIS: ε_{366} (benzene) = 4.6 Lmol⁻¹cm⁻¹.

Melting Point: 45.0-46.0°C; white crystals.

10-(3-Biphenyloxy)-1-phenyldecan-1-one (**Bz-9-O3Bp**)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 1.22-1.55 (m, 10H), 1.68-1.90 (m, 4H), 2.95 (t, J = 7.5 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 6.87 (d, J = 8.1 Hz, 1H), 7.10-7.62 (m, 11H), 7.96 (d, J = 6.6 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.23, 25.92, 29.19, 29.22, 29.24 (large peak), 29.26, 38.48, 67.89, 113.21, 113.47, 119.43, 127.11, 127.30, 128.02, 128.53, 128.70, 129.65, 132.85, 137.01, 141.11, 142.62, 159.42, 200.39.

FTIR (KBr): 2924, 2847, 1680, 1606, 1489, 1287, 1258, 839, 758, 689 cm⁻¹.

HRMS: 400.2402 calculated for $C_{28}H_{32}O_2$, found 400.2400.

UV-VIS (cyclohexane): $\varepsilon_{366} = 4.9 \text{ Lmol}^{-1} \text{ cm}^{-1}$.

Melting Point: 55.0-56.0°C; white crystals.

11-(3-Biphenyloxy)-1-phenylundecan-1-one (Bz-10-O3Bp)

¹**H NMR** (CDCl₃, 300 MHz): δ (ppm) 1.22-1.50 (m, 12H), 1.65-1.85 (m, 4H), 2.95 (t, J = 6.9 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 6.88 (d, J = 8.1 Hz, 1H), 7.10-7.60 (m, 11H), 7.94 (d, J = 7.2 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.36, 26.04, 29.31, 29.35 (large peak),
29.41, 29.44, 29.50, 38.61, 68.02, 113.23, 113.50, 119.43, 127.17, 127.33, 128.04,
128.52, 128.68, 129.68, 132.83, 137.08, 141.15, 142.67, 159.48, 200.58.

FTIR (KBr): 3057, 2915, 2851, 1687, 1601, 1471, 1302, 1211, 756, 690 cm⁻¹.

HRMS: 414.2559 calculated for $C_{29}H_{34}O_2$, found 414.2550.

UV-VIS (benzene): $\epsilon_{366} = 4.5 \text{ Lmol}^{-1} \text{ cm}^{-1}$.

Melting Point: 56.0-57.0°C; white crystals.

4.2.2 Synthesis of 4-(2-aryloxyethyl)oxy-1-phenylbutan-1-ones

 $4-(2-Aryloxyethyl)oxy-1-phenylbutan-1-ones Ph-CO-(CH_2)_3-O-(CH_2)_2-O-Ar (Ar = phenyl, 4-biphenyl) were prepared in four steps following the route given below:$



3. acetone, H_2O , H_3O^+ , heat

Scheme 15. Synthesis of 4-(2-aryloxyethyl)oxy-1-phenylbutan-1-ones

THP-ether of 2-iodoethanol

Concentrated hydrochloric acid (1 mL) was added to a mixture of 2,3dihydropyran (21.3g, 0.25 mol) and 2-chloroethanol (14 g, 0.17 mol). Reaction commenced immediately on shaking and was moderated by cooling in a ice-water bath. The mixture was stirred for additional 30 minutes at this temperature and then at room temperature for 12 hrs. The mixture was diluted with diethyl ether (200 mL) and washed with sodium hydrogen carbonate solution. The etheral solution was dried over MgSO₄. The solvent was evaporated, the crude product was dissolved in acetone (250 mL), and sodium iodide (50 g, 0.33 mol) was added. The mixture was refluxed for 24 hrs. Distilled water (250 mL) was added and the product was extracted with diethylether. The combined organic layer was washed with saturated sodium thiosulfate solution and distilled water, and dried over MgSO₄. The solvent was evaporated and the crude product was used without any further purification (60%).

THP-ether of 2-iodoethanol: ¹H NMR (CDCl₃): δ (ppm)): 1.2-2.0 (m, 6H), 3.1-4.1 (m, 6H), 4.7 (t, 1H).

2-Phenoxyethanol

A solution of THP-ether of 2-iodoethanol (3.1 g, 0.012 mol) and sodium phenolate, prepared from a phenol (1.1 g, 0.012 mol) and sodium (0.3 g, 0.013 mol) in absolute methanol, in dimethylformamide (60 mL) was stirred at 50°C for 30 hrs. Distilled water was added (60 mL) and the product was extracted with diethyl ether (3x 50 mL). The combined ether layer was washed with saturated sodium chloride solution, distilled water, and dried over MgSO₄. The solvent was evaporated and the product was dissolved in methanol (50 mL) and concentrated hydrochloric acid (10 mL), and the mixture was refluxed for 2 hrs. After cooling, the solution was neutralized by the addition of an excess of sodium hydrogen carbonate solution and diluted with diethyl ether (50 mL). The organic layer was washed with distilled water, dried over MgSO₄, and the solvent was evaporated. The crude product (75%) was used in the next step without further purification.

2-Phenoxyethanol: ¹H NMR (CDCl₃): δ (ppm) 2.1 (t, 1H), 3.9 (t, 2H), 4.1 (t, 2H), 6.8-7.5 (m, 5H).

4-(2-Phenoxyethyl)oxy-1-phenylbutan-1-one

2-Phenoxyethanol (1.2 g, 0.009 mol) from the previous step was dissolved in dry tetrahydrofuran and NaH (0.24 g, 0.01 mol) was added while stirring. Ethylene glycol ketal of 4-iodo-1-phenylbutan-1-one (2.5 g, 0.009 mol) (Procedure **4.2.3**) was added dropwise to the mixture with temperature kept under 30°C. The mixture was stirred at 50°C for 48 hrs. The mixture was washed with saturated sodium chloride solution and distilled water, and dried over MgSO₄. Tetrahydrofuran was evaporated and acetone (30 mL) and 10% hydrochloric acid were added. The mixture was stirred at 40°C for 24 hrs., cooled, and distilled water (30 mL) was added. The product was extracted with diethyl ether (3x 25 mL). The combined ether layer was washed with saturated sodium bicarbonate solution, distilled water, and dried over MgSO₄. The solvent was evaporated and the crude product (70%) was purified by flash chromatography and recrystallized from hexane/ethyl acetate (8:2).

4-(2-Phenoxyethyloxy)-1-phenylbutan-1-one (Bz-3-O-2-OPh)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 2.05 (tt, J = 6.3, 8.2 Hz, 2H), 3.07 (t, J = 8.2 Hz, 2H), 3.62 (t, J = 6.3 Hz, 2H), 3.78 (t, J = 5.1 Hz, 2H), 4.09 (t, J = 6.3 Hz, 2H), 6.86-6.96 (m, 3H), 7.21-7.29 (m, 2H), 7.39-7.56 (m, 3H), 7.95 (d, J = 7.8 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.16, 35.01, 67.24, 69.22, 70.41, 114.59, 120.81, 128.04, 128.52, 129.39, 132.94, 136.99, 158.77, 200.03.

FTIR (KBr): 2957, 2878, 1686, 1599, 1450, 1361, 1254, 1120, 1045, 893, 758, 691 cm⁻¹.

HRMS: 284.1413 calculated for C₁₈H₂₀O₂, found 284.1412.

UV-VIS: ε_{366} (cyclohexane) = 3.9 Lmol⁻¹cm⁻¹.

Melting Point: 53.0-54.0°C; white crystals.

The following compound was prepared according to the representative procedure above.

4-(4-Biphenyloxyethyloxy)-1-phenylbutan-1-one (Bz-3-O-2-O4Bp)

¹**H** NMR (CDCl₃, 300 MHz): δ (ppm) 2.06 (tt, J = 6.0, 6.9 Hz, 2H), 3.10 (t, J = 6.9 Hz, 2H), 3.64 (t, J = 6.0 Hz, 2H), 3.80 (t, J = 4.5 Hz, 2H), 4.14 (t, J = 4.8 Hz, 2H), 6.93-7.00 (d, J = 8.7 Hz, 2H), 7.25-7.56 (m, 10H), 7.95 (d, J = 6.9 Hz, 2H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 24.12, 34.96, 67.43, 69.20, 70.39, 114.86, 126.62, 126.67, 127.99, 128.05, 128.50, 128.67, 132.92, 133.85, 136.97, 140.72, 158.34, 199.99.

FTIR (KBr): 2932, 2874, 1684, 1608, 1489, 1448, 1288, 1249, 1134, 1047, 831, 758, 688 cm⁻¹.

HRMS: 360.1725 calculated for $C_{24}H_{24}O_2$, found 361.1802 (+FAB, MH⁺).

UV-VIS: ε_{366} (cyclohexane) = 3.8 Lmol⁻¹cm⁻¹.

Melting Point: 81.5-82.0°C; white crystals.

4.2.3 Synthesis of Arylethyl Ethers

Arylethyl ethers Ar-O-Et (Ar = phenyl, 2-naphthyl, 2/3/4-biphenyl) were prepared in a single step according to the following procedure.

2-Ethoxynaphthalene

A solution of ethyl iodide (3.1 g, 0.02 mol) and sodium phenolate, prepared from a phenol (1.9 g, 0.02 mol) and sodium (0.5 g, 0.022 mol) in absolute methanol, in dimethylformamide (100 mL) was stirred at 50° C for 30 hrs. Distilled water was added (50 mL) and the product was extracted with diethyl ether (3x 50 mL). The combined ether layer was washed with saturated sodium chloride solution, distilled water, and dried over MgSO₄. The solvent was evaporated and the crude product (85%) was purified by recrystallization from hexane/ethyl acetate (7:3).

2-Ethoxynaphthalene

¹**H** NMR (CDCl₃): δ (ppm) 1.49 (t, J = 7.2 Hz, 3H), 4.15 (q, J = 6.9 Hz, 2H), 7.13 - 7.79 (m, 7H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 14.80, 63.38, 106.41, 118.96, 123.46, 126.26, 126.67, 127.60, 128.83, 129.31, 134.55, 156.86.

FTIR (**KBr**): 2988, 2876, 1628, 1599, 1466, 1388, 1257, 1184, 1109, 1041, 750 cm⁻¹.

Melting Point: 37.0-38.0°C; white crystals.

The following compound was prepared according to the representative procedure above.

4-Ethoxybiphenyl

¹**H** NMR (CDCl₃): δ (ppm) 1.44 (t, J = 6.6 Hz, 3H), 4.07 (q, J = 7.2 Hz, 2H), 6.95 - 7.57 (m, 9H).

¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 14.87, 63.46, 114.68, 126.59, 126.68, 128.09, 128.69, 133.53, 140.81, 158.46.

FTIR (KBr): 2965, 1605, 1522, 1396, 1271, 1201, 1051, 837, 763, 690 cm⁻¹.

Melting Point: 73.0-74.0°C; white crystals.

4.3 Ultraviolet and Phosphorescence Spectroscopy

Ultraviolet (UV) spectra of the ketones were taken in cyclohexane and benzene for the purpose of measuring their molar absorptivity, ε , at 366 nm. These data are listed in Tables 7-9. This information was particularly important for quantum yield experiments where the quantum yields were corrected for optical density of both the ketone and the actinometer. Also, molar absorptivities were used for indirect calculation of the calibration factor for HPLC measurements. Some ketones used in this work were weakly soluble in cyclohexane and therefore it was difficult to obtain molar absorptivities in this solvent. Typical maximum ketone concentrations in cyclohexane were 10^{-2} M. Since the molar absorptivities at 366 nm were found to be very low, 3-5 Lmol⁻¹m⁻¹, the effect of instrumental noise is expected to be high.¹⁰⁷ Maximum concentrations of some longer ketones with 7 to 14-atom tethers were only $3-5x10^{-3}$ M, so molar absorptivity measurements were below the level of reliability. Absorptivities ε_{366} of those compounds were taken in benzene in order to have a comparison for a solvent where all ketones are relatively soluble. Their ε_{366} values in cyclohexane were then interpolated from ε_{366} in benzene. Absorptivities of long bichromophores (x = 7-14) in benzene were found to be essentially constant.

Bichromophore	ε ₃₆₆ , Lmol ⁻¹ m ⁻¹	ε ₃₆₆ , Lmol ⁻¹ m ⁻¹
	(cyclohexane)	(benzene)
Bz-3-OPh	3.1	2.5
Bz-4-OPh	4.5	4.0
Bz-5-OPh	4.8	
Bz-7-OPh	5.0	4.4
Bz-10-OPh		4.5
Bz-11-OPh		4.5
MeBz-3-OPh	2.9	2.3
MeBz-4-OPh	4.1	3.7
MeBz-5-OPh	4.9	4.0
Bz-3-O-2-OPh	3.9	

Table 7. Molar Absorptivities of Bz-n-OPh, MeBz-n-OPh, and Bz-3-O-2-OPh

Bichromophore	ε ₃₆₆ , Lmol ⁻¹ m ⁻¹	ε ₃₆₆ , Lmol ⁻¹ m ⁻¹
	(cyclohexane)	(benzene)
Bz-3-O4Bp	3.0	2.4
Bz-4-O4Bp	4.8	4.2
Bz-5-O4Bp	4.9	4.3
Bz-6-O4Bp	4.9	4.4
Bz-7-O4Bp	4.9	4.5
Bz-9-O4Bp		4.6
Bz-10-O4Bp		4.5
Bz-11-O4Bp		4.6
Bz-14-O4Bp		4.5
Bz-3-O2Bp	2.9	2.5
Bz-4-O2Bp	4.7	3.6
Bz-5-O2Bp	4.8	
Bz-6-O2Bp	4.8	4.3
Bz-7-O2Bp	4.8	
Bz-9-O2Bp	4.9	4.5
Bz-10-O2Bp		4.6
Bz-11-O2Bp		4.5
Bz-14-O2Bp		4.6
Bz-3-O3Bp	2.8	
Bz-6-O3Bp	4.9	
Bz-7-O3Bp	4.8	
Bz-9-O3Bp	4.9	4.4
Bz-10-O3Bp		4.5
Bz-14-O3Bp		4.6

Table 8. Molar Absorptivities of Bz-n-O4Bp, Bz-n-O3Bp, and Bz-n-O2Bp

Bichromophore	ε_{366} , Lmol ⁻¹ m ⁻¹ (cyclobexane)	ε_{366} , Lmol ⁻¹ m ⁻¹ (benzene)
	(c)cronexane)	
Bz-3-ONp	3.0	2.4
Bz-4-ONp	5.0	4.0
Bz-5-ONp	5.0	4.2
Bz-6-ONp	5.1	4.3
Bz-7-ONp	5.0	4.4
Bz-9-ONp	5.0	4.5
Bz-10-ONp		4.6
Bz-11-ONp		4.5
Bz-14-ONp		4.6

Table 9. Molar Absorptivities of Bz-n-ONp

Table 10. Molar Absorptivities of MeBz-n-ONp, MeBz-n-O4Bp, Bz-3-O-2-O4Bp, and actinometers

Bichromophore	ε ₃₆₆ , Lmol ⁻¹ m ⁻¹ (cyclohexane)	ε ₃₆₆ , Lmol ⁻¹ m ⁻¹ (benzene)
MeBz-3-ONp	2.7	2.4
MeBz-4-ONp	4.8	
MeBz-5-ONp	4.8	
MeBz-6-ONp	4.9	4.3
MeBz-7-ONp		4.4
MeBz-11-ONp		4.5
MeBz-3-O4Bp	2.8	
Bz-3-O-2-O-4Bp	3.8	
valerophenone	4.8	4.0
4-methylvalerophenone	4.7	3.8

Chromophore	0,0 b	and ^a	0,0 bar	nd (lit.)
	(nm)	(kcal)	(nm)	(kcal)
Acetophenone	387	73.9		74.1 ¹⁰⁸
4-Methylacetophenone	394	72.6	392 ¹⁰⁹	72.9
2-Ethoxynaphthalene	460	62.2	462 ¹¹⁰	61.9
4-Ethoxybiphenyl	444	64.4		66.0 ¹¹¹
3-Ethoxybiphenyl	433	66.0		67.0 ¹¹¹
2-Ethoxybiphenyl	438	65.3		67.0 ¹¹¹
Valerophenone	390	73.3	393 ¹¹²	72.7
Bz-5-OPh	387	73.9		
Bz-11-OPh	386	74.0		

Table 11. Phosphorescence Emission Data

^a0.001M solutions in 2-methyltetrahydrofuran at 77K. Excitation wavelength used for all measurements was 300 nm or 330 nm.

Phosphorescence emission spectra were measured at 77K in a 2methyltetrahydrofuran glass in a 4 mm Pyrex sample tube. Those data and literature values are summarized in Table 11. The spectra showing emission of all chromophores used in this work are shown in Figure 20. The spectra of the model phenoxy ketones did not differ significantly from those of the chromophore molecules (Table 11).



Figure 20. Phosphorescence emission spectra of acetophenone (AP), 4methylacetophenone (MeAP), 2-ethoxynaphthalene (2EtONp), 4-ethoxybiphenyl (4EtOBp), 3-ethoxybiphenyl (3EtOBp), and 2-ethoxybiphenyl (2EtOBp) chromophores in 2-methyltetrahydrofuran at 77K.

4.4 Photochemical Procedures and Experiments

4.4.1 Purification of Solvents

Cyclohexane

Reagent-grade cyclohexane (Aldrich) (3.5 L) was stirred with concentrated sulfuric acid (0.5 L) for 2 days. The cyclohexane layer was separated and was washed with 100 mL portions of concentrated sulfuric acid several times until the acid layer remained colorless. The cyclohexane was then washed with deionized water and saturated hydrogen carbonate solution. The cyclohexane layer was separated, dried over magnesium sulfate, and filtered. The solvent was refluxed over calcium hydride (100 g) for 48 hours, and distilled through a 0.3 meter column. A high reflux ratio was maintained, and the initial 10% was discarded. The middle portion (ca. 80%, b.p.: 81°C) was collected and used in photochemical experiments.

Benzene

Reagent-grade benzene (Aldrich) (3.5 L) was stirred with concentrated sulfuric acid (0.5 L) for 2 days. The benzene layer was separated and was washed with 100 mL portions of concentrated sulfuric acid several times until the acid layer remained colorless. The benzene was then washed with deionized water and saturated hydrogen carbonate solution. The benzene layer was separated, dried over magnesium sulfate, and filtered. Phosphorus pentoxide (100 g) was added, the solution was refluxed for 48 hours, and distilled through a 1 meter column packed with glass helices. A high reflux ratio was maintained and the initial 10% was discarded. The middle portion (ca. 80%, b.p.: 80°C) was collected and used in photochemical experiments.

4.4.2 Purification of Standards, Internal Standard, Actinometer, and Quencher

Acetophenone (AP)

Acetophenone (Aldrich) was purified by fractional distillation and used without further purification.

4-Methylacetophenone (MeAP)

4-Methylacetophenone (Aldrich) was purified by fractional distillation and used without further purification.

Methyl Benzoate (MeBe)

Methyl benzoate (Aldrich) was purified by fractional distillation and used without further purification.

Valerophenone (VP)

Valerophenone (Aldrich) was purified by fractional distillation.

2,5-Dimethyl-2,4-hexadiene (DMHD)

Special care was taken to insure that only pure, sublimed quencher 2,5-dimethyl-2,4-hexadiene (Chemical Samples Co.) was used. Even nicely crystalline material present at the frozen liquid surface contained some amount of impurities which could adversely affect the results of a quenching experiment.

4.4.3 Glassware

All photolysis glassware (syringes, volumetric flasks, pipettes, etc.) were rinsed with acetone and deionized water and boiled in a solution of Alconox laboratory detergent in deionized water for 24 hrs. They were then rinsed with deionized water and boiled in deionized water for 24 hrs. This cycle was repeated 3 times. After a final rinse with deionized water, the glassware was oven dried at 140°C overnight and cooled to room temperature before use.

Ampoules used for irradiation were made from 13x100 mm Pyrex culture tubes by flame heating them approximately 2 cm from the top with an oxygen - natural gas torch and drawing them to a uniform 15 cm length.

4.4.4 Sample Preparation, Degassing, and Irradiation Procedures

All solutions were prepared by directly weighing the desired material into volumetric flasks or by dilution of stock solutions. Samples were prepared: 2.8-mL aliquots were placed *via* syringes in 13x100 Pyrex tubes that were then degassed in three freeze-pump-thaw cycles using liquid nitrogen before being sealed with an oxygen - natural gas torch while still under vacuum. Samples were irradiated in a "merry-go-

round" apparatus¹¹³ immersed in a water bath. All measurements were conducted at 366 nm excitation. The 366 nm band was isolated from a medium pressure 450 W Hanovia mercury arc lamp by filtration with Corning 7-83 filters.

4.4.5 Quenching Studies

Bichromophore 0.001M solutions in cyclohexane or benzene with different concentrations of the quencher (2,5-dimethyl-2,4-hexadiene) were used. Valerophenone solutions were irradiated simultaneously as actinometer for quantum yield measurements.¹¹⁴ Triplet lifetimes were determined by Stern-Volmer quenching techniques. The slope $k_q \tau_0$ in the plot ϕ_0/ϕ versus [Q] was calculated using a method of least squares with the intercept in $\phi_0/\phi = 1$ for [Q] = 0 by definition.

For each Stern-Volmer measurement, four solutions of the bichromophore with different concentrations of the quencher and one solution without the quencher were prepared. Two tubes of each solution were used in the irradiation. Two bichromophore solutions and two actinometer solutions were prepared for quantum yield measurements and two tubes of each were irradiated. The Stern-Volmer and quantum yield measurements were then repeated with new solutions.

The 0.001 M valerophenone solutions were used for irradiations of less than 5 hours. For long irradiations, an appropriate number of consecutive valerophenone samples, changed every 5 hours, was used. The total acetophenone yield was then calculated as a sum over all partial measurements.

4.4.6 Photoproduct Identification

The only photoproducts common for all photoreactions in this work are *acetophenone* and *4-methylacetophenone*. Their direct identification was based on ¹H NMR, ¹³C NMR, and HPLC comparison with the standards.

NMR identification

The 0.1 M solution in the NMR tube of the bichromophore and model phenoxy ketone (Bz-3-OPh, Bz-5-OPh, Bz-5-O4Bp, MeBz-5-ONp) were irradiated at 366 nm until the conversion of the photoproduct was about 50%. ¹H NMR spectra were taken and photoproduct peaks (AP, MeAP, olefinic double bond) were compared with NMR spectra of the standards. The 0.1 M solution of Bz-5-O4Bp was irradiated at 313 nm and the photoproduct AP was isolated by flash chromatography (hexane/ethyl acetate mixture 9:1). ¹H NMR and ¹³C NMR spectra were compared with those of the standard.

HPLC identification

For every set of measurements, a solution of the standard and the bichromophore, the irradiated sample, and the mixture of both, were compared and the peaks corresponding to the photoproduct identified. HPLC conditions were developed so as to ensure that the peaks of the photoproduct and the internal standard (methyl benzoate) did not contain any impurities. All chemicals used in irradiations were analyzed before each experiment for their purity by HPLC.

4.4.7 Analysis of Photoproducts

The photoproduct yields (acetophenone or 4-methylacetophenone) were determined by HPLC and the reaction conversion was kept under 15%. Larger amount of photoproduct can absorb incoming light and it would increase experimental error. The photoproducts were monitored at 250 or 265 nm in the HPLC detector because the photoproduct molar absorptivity is relatively high in this region. HPLC conditions were developed in order to get the photoproduct and standard peaks as far from the much larger bichromophore and quencher peaks as possible.

Each sample was measured twice. In case that the two values differed by more than 5%, the measurement was repeated.

The concentration of the photoproduct, [P], was obtained using Equation 11,

$[P] = C \times [MeBe] \times A_P / A_{MeBe} \qquad (Equation 11)$

where [P] is the concentration of the photoproduct (AP, MeAP), C is the calibration constant for the photoproduct, [MeBe] is the concentration of the standard methyl benzoate (MeBe); A_P is the integrated area for the photoproduct: A_{AP} for acetophenone; A_{MeAP} for 4-methylacetophenone; and A_{IS} is the integrated area for the internal standard.

Table 12. Calibration constants

Photoproduct	wavelength	С
AP	250	0.144
AP	265	1.280
MeAP	250	0.036
MeAP	265	0.440

The calibration constant C was obtained from the calibration curve. The values of C for 250 and 265 nm are shown in Table 12.

The correlation coefficients were calculated in KaleidaGraph 3.0 software using a standard linear regression calculation.

HPLC condition sets used in Stern-Volmer and quantum yield studies are summarized in Table 13.

HPLC condition set	Hexane/AcOEt % ratio	Detection wavelength (nm)
1	97/3	250
2	93/7	250
3	97/3	265
4	93/7	265
5	98/2	265
6	95/5	265
7	95/5	250
8	98/2	250
9	$97/3 \Rightarrow 80/20^a$	250
10	$99/1 \Rightarrow 90/10^a$	250

Table 13. HPLC Condition Sets.

^{*a*}20 min concentration gradient.

4.4.8 Bimolecular Quenching

The bimolecular self-quenching rate constants were obtained for the donor and acceptor chromophore molecules. The 2-ethoxynaphthene or 4-ethoxybiphenyl solutions with the mixture of valerophenone of the same concentration (0.1 - 0.001 M) in cyclohexane were irradiated under the same condition as quenching experiments described above. The dependence of bimolecular quenching on concentration was found to be linear. For 0.001 M concentration, the quenching was found to be $8x10^6 \text{ M}^{-1}\text{s}^{-1}$ and $3x10^6 \text{ M}^{-1}\text{s}^{-1}$ for 2-ethoxynaphthene and 4-ethoxybiphenyl, respectively.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
0.350	3.22	0.0000	1.00
0.309	2.85	0.0055	1.13
0.260	2.40	0.0111	1.34
0.236	2.17	0.0167	148
0.202	1.86	0.0222	1.73
0.202	1.00	0.0222	1.75

Run I

 $k_{q}\tau = 31.10$

[Ketone] = 1.0200×10^{-3} M. [MeBe] = 6.3841×10^{-4} M. Irradiation for 2.5 h. HPLC condition set 1. Correlation coefficient = 0.995.

Run	2
-----	---

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,/Φ
0.304	4.64	0.0000	1.00
0.264	4.02	0.0055	1.15
0.240	3.66	0.0111	1.26
0.210*	3.21	0.0166	145
0.173*	2.64	0.0222	1.76

 $k_q \tau = 30.31$

[Ketone] = 1.0154×10^{-3} M. [MeBe] = 1.0606×10^{-3} M. Irradiation for 3.0 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.980.

Table 15. Stern-Volmer Quenching of the Acetophenone Formation in Bz-4-OPh with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.659	6.07	0.0000	1.00
0.324*	2.99	0.0055	2.03
0.208	1.92	0.0111	3.16
0.145	1.33	0.0166	4.56
0.110*	1.01	00222	6.00
		· · · · · · · · · · · · · · · · · · ·	

Run 1

[Ketone] = 0.9948×10^{-3} M. [MeBe] = 6.3841×10^{-4} M. Irradiation for 3.0 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.997.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.483	7.37	0.0000	1.00
0.234	3.57	0.0047	2.07
0.145	2.21	0.0093	3.34
0.104	1.59	0.0140	4.63
0.087*	1.33	0.0186	5.54

$k_q \tau$	=	248.4	

 $k_q \tau = 216.4$

[Ketone] = 0.9909×10^{-3} M. [MeBe] = 1.0606×10^{-3} M. Irradiation for 4.0 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.998.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.679	6.25	0.0000	1.00
0.436*	4.02	0.0055	1.56
0.354	3.26	0.0111	1.92
0.272*	2.51	0.0166	2.49
0.226	2.08	0.0222	3.00
			······································

Table 16. Stern-Volmer Quenching of the Acetophenone Formation in Bz-5-OPh with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

[Ketone] =	1.00	77×10^{-3}	М.	[MeBe]	=	6.3841x10 ⁻⁴	М.	Irradiation	for	3.0	h.	HPLC
condition set	2.*/	Average	of 1	tube. Co	orre	elation coeffic	cient	= 0.998.				

 $k_{g}\tau = 89.2$

Run	2
*****	~

Run 1

AAP/AMeBe	[AP], 10 ⁻⁵ M	[Q], M	Φ,/Φ
0.540	8.25	0.0000	1.00
0.384	5.86	0.0047	1.41
0.304*	4.64	0.0093	1.78
0.245*	3.74	0.0140	2.21
0.197*	3.00	0.0187	2.75
<u></u>			••••••••••••••••••••••••••••••••••••••
		k	$L_q \tau = 89.8$

[Ketone] = 1.0211×10^{-3} M. [MeBe] = 1.0606×10^{-3} M. Irradiation for 4.0 h. HPLC condition set 2. *Average of 1 tube. Correlation coefficient = 0.997.

Table 17. Stern-Volmer Quenching of the Acetophenone Formation in Bz-7-OPh with	h
2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.	

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ ₀ /Φ
0.656	8.88	0.0000	1.00
0.399	5.40	0.0106	1.64
0.276	3.73	0.0213	2.38
0.217*	2.94	0.0319	3.02
0.173*	2.34	0.0425	3.79

[Ketone] = 1.0291×10^{-3} M. [MeBe] = 9.4014×10^{-4} M. Irradiation for 3.4 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.990.

Run 1

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.333	5.65	0.0000	1.00
0.239*	4.07	0.0065	1.39
0.185	3.15	0.0130	1.79
0.154*	2.61	0.0195	2.16
0.130*	2.20	0.0260	2.56
	······································		

 $k_q \tau = 60.1$

[Ketone] = 1.0257×10^{-3} M. [MeBe] = 1.1825×10^{-3} M. Irradiation for 3.0 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

Table 18. S	tern-Volmer (Quenching of	the Aceto	phenone	Formation	in Bz-	10-OPh	with
2,5-Dimethy	yl-2,4-hexadie	ne at 366 nm	in Cycloh	exane.				

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
0.535	7.24	0.0000	1.00
0.312	4.23	0.0106	1.71
0.249	3.37	0.0213	2.15
0.198	2.68	0.0319	2.70
0.155*	2.10	0.0425	3.44
		k	$a\tau = 56.1$

,5-Dimentyi-2,4-nexadiene at 500 nm m C

[Ketone] = 9.8679×10^{-4} M. [MeBe] = 9.4014×10^{-4} M. Irradiation for 3.4 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.996.

Run 1

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ ₀ /Φ
0.320	4.61	0.0000	1.00
0.203	2.92	0.0106	1.58
0.137*	1.97	0.0213	2.33
0.117*	1.68	0.0319	2.73
0.090	1.30	0.0426	3.55
			·

 $k_q \tau = 58.4$

[Ketone] = 1.0045×10^{-3} M. [MeBe] = 1.0107×10^{-3} M. Irradiation for 3.0 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.996.

able 1	9. Stern-Volmer Quenching of the Acetop	henone Formation in Bz-11-O	Ph wi
2, 5-D im	ethyl-2,4-hexadiene at 366 nm in Cyclohex	cane.	

AAP/AMeBe	[AP], 10 ⁻⁵ M	[Q], M	Φ₀⁄Φ
0.326	4.69	0.0000	1.00
0.209*	3.01	0.0106	1.56
0.155*	2.23	0.0213	2.10
0.115*	1.65	0.0319	2.85
0.092*	1.33	0.0426	3.54

/ith Τ 2

[Ketone] = 1.0128×10^{-3} M. [MeBe] = 1.0107×10^{-3} M. Irradiation for 3.0 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.998.

Run I

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,/Φ
0.462	6.65	0.0000	1.00
0.361	5.19	0.0047	1.28
0.302*	4.35	0.0094	1.53
0.256*	3.68	0.0142	1.81
0.217*	3.12	0.0189	2.13

[Ketone] = 9.6455×10^{-4} M. [MeBe] = 1.0107×10^{-3} M. Irradiation for 3.0 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

Table 20. Stern-Volmer Quenching of the Acetophenone Formation in Bz-3-O-2-OPh with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.653	9.13	0.0000	1.00
0.560	7.82	0.0068	1.17
0.482	6.73	0.0135	1.36
0.425*	5.94	0.0203	1.54
0.382	5.33	0.0270	1.71
		k	$z_q \tau = 26.3$

Run 1

[Ketone] = 1.0165×10^{-3} M. [MeBe] = 0.9725×10^{-3} M. Irradiation for 4 h. HPLC condition set 1. ^{*}Average of 1 tube. Correlation coefficient = 0.999.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.744	9.43	0.0000	1.00
0.625	7.91	0.0074	1.19
0.559*	7.09	0.0149	1.33
0.510	6.46	0.0224	1.46
0.429	5.44	0.0298	1.73

 $k_q \tau = 23.1$

[Ketone] = 0.9741×10^{-3} M. [MeBe] = 0.8814×10^{-3} M. Irradiation for 5 h. HPLC condition set 1. ^{*}Average of 1 tube. Correlation coefficient = 0.990.

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁴ M	[Q], M	Φ₀⁄Φ
0.494	1.83	0.0000	1.00
0.187	0.69	0.0106	2.64
0.114	0.42	0.0212	4.33
0.079*	0.29	0.0318	6.28
0.067*	0.25	0.0424	7.38

Table 21. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in MeBz-3-OPh with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

 $k_{q}\tau = 156.0$

 $k_{q}\tau = 150.7$

[Ketone] = 9.9877×10^{-4} M. [MeBe] = 1.0283×10^{-3} M. Irradiation for 10.0 h. HPLC condition set 8. *Average of 1 tube. Correlation coefficient = 0.999.

Run 1

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
2.448	11.19	0.0000	1.00
1.236	5.65	0.0067	1.98
0.815	3.73	0.0134	3.00
0.613	2.80	0.0201	3.99
0.484	2.21	0.0267	5.06

[Ketone] = 9.9877×10^{-4} M. [MeBe] = 1.2703×10^{-3} M. Irradiation for 4.5 h. HPLC condition set 8. Correlation coefficient = 0.999.

Table 22. Stern-Volmer Quenching of the 4-Methylacetophenone Formation	in
MeBz-4-OPh with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.	

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁵ M	[Q], M	Φ ₀ /Φ
3.538	16.18	0.0000	1.00
0.469	2.14	0.0067	7.55
0.228	1.04	0.0134	15.51
0.158*	0.72	0.0201	22.45
0.101*	0.46	0.0267	35.06

[Ketone] = 1.0919×10^{-3} M. [MeBe] = 1.2704×10^{-3} M. Irradiation for 4.5 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.991.

Run 1

8.62	0.0000	1.00
		1.00
1.40	0.0053	6.14
0.75	0.0107	11.55
0.57	0.0160	15.12
0.36	0.0213	23.98
	1.40 0.75 0.57 0.36	1.40 0.0053 0.75 0.0107 0.57 0.0160 0.36 0.0213

$k_q \tau =$	1003.3
--------------	--------

[Ketone] = 0.9987×10^{-3} M. [MeBe] = 0.8803×10^{-3} M. Irradiation for 3.0 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.990.

Table 23. Stern-Volmer Que	nching of the 4-Methy	ylacetophenone l	Formation in
MeBz-5-OPh with 2,5-Dimet	hyl-2,4-hexadiene at :	366 nm in Cyclo	ohexane.

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁵ M	[Q], M	Φ₀⁄Φ
3.067	9.71	0.0000	1.00
1.202	3.81	0.0053	2.55
0.679*	2.15	0.0107	4.52
0.422*	1.34	0.0160	7.28
0.287*	0.91	0.0213	10.69

$[Ketone] = 0.9987 \times 10^{-3}$	³ M.	[MeBe]	= 0.8802x	10 ⁻³ M.	Irradiation	for	3.0	h.	HPLC
condition set 1. *Average	e of 1	tube. Co	orrelation co	efficien	t = 0.988.				

Run 1

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁵ M	[Q], M	Φ₀⁄Φ
2.650	11.26	0.0000	1.00
0.768	3.26	0.0065	3.45
0.420*	1.79	0.0130	6.30
0.317*	1.35	0.0195	8.35
0.216*	0.92	0.0260	12.28

 $k_q \tau = 410.9$

[Ketone] = 0.9420×10^{-3} M. [MeBe] = 1.1825×10^{-3} M. Irradiation for 3.0 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.995.

Table 24.	Stern-Volmer Quenching of the Acetophenone Formation	in
Bz-3-ON	p with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohex	ane.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁴ M	[Q], M	Φ₀/Φ
0.903	1.29	0.0000	1.00
0.874	1.26	0.0099	1.03
0.844	1.22	0.0198	1.07
0.805	1.16	0.0296	1.12
0.774*	1.11	0.0395	1.17
	·····	·····	
		1	$\kappa_{q}\tau = 4.0$

[Ketone] = 1.0447×10^{-3} M. [MeBe] = 1.0104×10^{-3} M. Irradiation for 14.5 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.995.

Run	2
	-

Run 1

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.647	9.31	0.0000	1.00
0.619	8.92	0.0100	1.04
0.606	8.72	0.0201	1.07
0.565	8.14	0.0301	1.14
0.552	7.95	0.0401	1.17

[Ketone] = 1.0309×10^{-3} M. [MeBe] = 1.0168×10^{-3} M. Irradiation for 13.0 h. HPLC condition set 1. Correlation coefficient = 0.987.

 $k_q \tau = 4.3$

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.702	8.99	0.0000	1.00
0.589	7.55	0.0103	1.19
0.518	6.64	0.0207	1.35
0.475	6.09	0.0310	1.48
0.429	5.50	0.0414	1.63

Table 25. Stern-Volmer Quenching of the Acetophenone Formation in Bz-4-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

 $k_{\rm q}\tau = 15.7$

 $k_{q}\tau = 16.8$

[Ketone] = 0.9623×10^{-3} M. [MeBe] = 0.8917×10^{-3} M. Irradiation for 11.0 h. HPLC condition set 1. Correlation coefficient = 0.997.

Run 1

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ _σ /Φ
0.620	8.58	0.0000	1.00
0.540	7.47	0.0107	1.15
0.448	6.19	0.0214	1.39
0.404	5.59	0.0322	1.54
0.360	4.98	0.0429	1.72

[Ketone] = 0.9594×10^{-3} M. [MeBe] = 0.9635×10^{-3} M. Irradiation for 12.0 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.998.

n 1			
A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φৢ⁄Φ
0.497	6.80	0.0000	1.00
0.399	5.46	0.0114	1.25
0.341*	4.66	0.0228	1.46
0.301	4.11	0.0342	1.65

3.59

Table 26. Stern-Volmer Quenching of the Acetophenone Formation in Bz-5-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

$k_q \tau = 19.6$	
-------------------	--

1.90

[Ketone] = 0.9171×10^{-3} M. [MeBe] = 0.9548×10^{-3} M. Irradiation for 3.2 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

0.0456

Run	2
-----	---

0.262*

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.360	4.93	0.0000	1.00
0.330	4.52	0.0046	1.09
0.307	4.20	0.0092	1.17
0.287	3.93	0.0138	1.26
0.264*	3.61	0.0184	1.37

 $k_q \tau = 19.4$

[Ketone] = 0.9454×10^{-3} M. [MeBe] = 0.9548×10^{-3} M. Irradiation for 4.0 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.998.
Table 27. Stern-Volmer Quenching of the Acetophenone Formation in Bz-6-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,/Φ
0.402	5.15	0.0000	1.00
0.317	4.07	0.0103	1.27
0.268	3.44	0.0207	1.50
0.237	3.04	0.0310	1.69
0.206	2.65	0.0414	1.95
			·····
		k	$t_q \tau = 22.9$

[Ketone] = 0.9091×10^{-3} M. [MeBe] = 0.8917×10^{-3} M. Irradiation for 2.0 h. HPLC condition set 1. Correlation coefficient = 0.999.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,/Φ	
0.526	8.71	0.0000	1.00	
0.418	6.93	0.0104	1.26	
0.362	5.99	0.0207	1.45	
0.319	5.28	0.0311	1.65	
0.279*	4.62	0.0414	1.89	

[Ketone] = 0.9130×10^{-3} M. [MeBe] = 1.1576×10^{-3} M. Irradiation for 3.2 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ _σ /Φ
0.610	10.20	0.0000	1.00
0.497	8.30	0.0104	1.23
0.413	6.89	0.0207	1.48
0.356	5.94	0.0311	1.72
0.312*	5.21	0.0415	1.96

Table 28. Stern-Volmer Quenching of the Acetophenone Formation in Bz-7-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

 $k_q \tau = 23.1$

[Ketone] = 0.9479×10^{-3} M. [MeBe] = 1.1576×10^{-3} M. Irradiation for 3.2 h. HPLC condition set 2. *Average of 1 tube. Correlation coefficient = 0.999.

Run 1

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.371	6.20	0.0000	1.00
0.299	4.99	0.0114	1.24
0.234*	3.91	0.0228	1.58
0208*	3.47	0.0342	1.78
0.181*	3.03	0.0456	2.05
		·····	
			$x_{\alpha}\tau = 23.2$

[Ketone] = 0.8630×10^{-3} M. [MeBe] = 1.1576×10^{-3} M. Irradiation for 3.2 h. HPLC condition set 2. *Average of 1 tube. Correlation coefficient = 0.999.

Table 29. Stern-Volmer Quenching of the Acetophenone Formation in Bz-9-ONp with

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
0.499	6.54	0.0000	1.00
0.434	5.69	0.0084	1.15
0.385	5.04	0.0167	1.30
0.359*	4.70	0.0251	1.39
0.321	4.20	0.0334	1.56

2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

[Ketone] = 2.0347×10^{-3} M. [MeBe] = 0.9166×10^{-3} M. Irradiation for 6 h. HPLC condition set 7. *Average of 1 tube. Correlation coefficient = 0.997.

Run	2
-----	---

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ	
0.333*	4.51	0.0000	1.00	
0.294*	3.98	0.0073	1.13	
0.283*	3.83	0.0146	1.18	
0.254	3.43	0.0219	1.31	
0.241*	3.26	0.0292	1.39	

 $k_q \tau = 13.6$

[Ketone] = 1.0307×10^{-3} M. [MeBe] = 0.9489×10^{-3} M. Irradiation for 6 h. HPLC condition set 7. *Average of 1 tube. Correlation coefficient = 0.990.

AAP/AMeBe	[AP], 10 ⁻⁵ M	[Q], M	Φ _σ /Φ
0.319*	4.17	0.0000	1.00
0.285	3.73	0.0059	1.12
0.271*	3.55	0.0118	1.18
0.255*	3.35	0.0177	1.25
0.236	3.10	0.236	1.35
			······································

Table 30. Stern-Volmer Quenching of the Acetophenone Formation in Bz-10-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

[Ketone] = 1.0	244×10^{-3} M.	[MeBe] =	0.9166×10^{-3}	М.	Irradiation	for	6 h	. HPLC
condition set 2.	[*] Average of 1	tube. Correl	lation coeffici	ent =	= 0.993.			

 $k_a \tau = 14.7$

Run 1

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,/Φ
0.375*	5.07	0.0000	1.00
0.340*	4.60	0.0073	1.10
0.322*	4.37	0.0146	1.16
0.302*	4.08	0.0219	1.24
0.270*	3.65	0.0292	1.39
		1	$x_{\alpha}\tau = 12.4$

[Ketone] = 1.0141×10^{-3} M. [MeBe] = 0.9490×10^{-3} M. Irradiation for 6 h. HPLC condition set 7. *Average of 1 tube. Correlation coefficient = 0.987.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
0.400	6.34	0.0000	1.00
0.329	5.22	0.0089	1.22
0.279*	4.42	0.0178	1.44
0.242*	3.83	0.0267	1.65
0.211*	3.34	0.0356	1.90

Table 31. Stern-Volmer Quenching of the Acetophenone Formation in Bz-11-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

$k_q \tau$	=	24.9	
			-

[Ketone] = 1.0764×10^{-3} M. [MeBe] = 1.0959×10^{-3} M. Irradiation for 4.0 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

Run	2

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,/Φ
0.360	4.92	0.0000	1.00
0.313*	4.28	0.0049	1.15
0.296	4.05	0.0098	1.22
0.264	3.61	0.0147	1.36
0.243*	3.32	0.0196	1.48
L			

 $k_q \tau = 24.5$

[Ketone] = 1.0242×10^{-3} M. [MeBe] = 0.9548×10^{-3} M. Irradiation for 4.0 h. HPLC condition set 2. *Average of 1 tube. Correlation coefficient = 0.995.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀⁄Φ
0.355	5.11	0.0000	1.00
0.283*	4.07	0.0066	1.26
0.237	3.41	0.0132	1.50
0.215*	3.09	0.0199	1.65
0.190	2.73	0.0265	1.87

2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

[Ketone] = 0.9986×10^{-3} M. [MeBe] = 1.0077×10^{-3} M. Irradiation for 6 h. HPLC condition set 8. *Average of 1 tube. Correlation coefficient = 0.996.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.339	4.88	0.0000	1.00
0.270	3.89	0.0083	1.25
0.235	3.39	0.0167	1.44
0.204	2.95	0.0250	1.66
0.174	2.50	0.0333	1.95
			· · · · · · · · · · · · · · · · · · ·
		1	$\kappa_{q}\tau = 27.7$

 $[Ketone] = 0.9986 \times 10^{-3} M.$ $[MeBe] = 1.0018 \times 10^{-3} M.$ Irradiation for 4 h. HPLC condition set 7. *Average of 1 tube. Correlation coefficient = 0.996.

Table 33. Stern-Volmer Quenching of the Acetophenone Formation in Bz-3-O4Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁴ M	[Q], M	Φ,/Φ
0.693	1.06	0.0000	1.00
0.647	0.99	0.0091	1.07
0.597*	0.91	0.0181	1.16
0.565	0.86	0.0272	1.23
0.533	0.81	0.0362	1.30

Run	1
-----	---

[Ketone] = 1.0312×10^{-3} M. [MeBe] = 1.0606×10^{-3} M. Irradiation for 13 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

	Run	2
--	-----	---

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,/Φ
0.410	6.15	0.0000	1.00
0.378	5.66	0.0105	1.09
0.358*	5.36	0.0210	1.15
0.336*	5.04	0.0316	1.22
0.318*	4.77	0.0421	1.29
. <u></u>			

[Ketone] = 1.0177×10^{-3} M. [MeBe] = 1.0386×10^{-3} M. Irradiation for 14 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

 $k_q \tau = 7.0$

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.163	2.39	0.0000	1.00
0.133	1.96	0.0123	1.22
0.110*	1.61	0.0246	1.48
0.094*	1.38	0.0369	1.73
0.080	1.18	0.0491	2.03

Table 34. Stern-Volmer Quenching of the Acetophenone Formation in Bz-4-O4Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

$k_q \tau$	=	20.4	
------------	---	------	--

[Ketone] = 1.0049×10^{-3} M. [MeBe] = 1.0224×10^{-3} M. Irradiation for 6 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

Run	2
-----	---

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.053	0.79	0.0000	1.00
0.045	0.67	0.0105	1.19
0.037	0.55	0.0210	1.44
0.032*	0.48	0.0316	1.67
0.028	0.42	0.0421	1.88
	·····		

 $k_q \tau = 20.9$

[Ketone] = 0.9988×10^{-3} M. [MeBe] = 1.0386×10^{-3} M. Irradiation for 6 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.238	3.49	0.0000	1.00
0.194	2.85	0.0089	1.22
0.163	2.40	0.0178	1.46
0.139	2.04	0.0267	1.71
0.123	1.80	0.0357	1.93
		k	$x_q \tau = 26.3$

[Ketone] =	0.9842×10^{-3}	Μ.	[MeBe] =	1.0224×10^{-3}	Μ.	Irradiation	for	3	h.	HPLC
condition se	t 1. Correlation	n co	efficient = ().999.						

Run	2
-----	---

[AP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
3.63	0.0000	1.00
2.84	0.0105	1.28
2.26	0.0210	1.60
1.92	0.0316	1.89
1.66	0.0421	2.19
	[AP], 10 ⁻⁵ M 3.63 2.84 2.26 1.92 1.66	[AP], 10 ⁻⁵ M [Q], M 3.63 0.0000 2.84 0.0105 2.26 0.0210 1.92 0.0316 1.66 0.0421

$k_q \tau$	=	28.2
------------	---	------

[Ketone] = 0.9987×10^{-3} M. [MeBe] = 1.0386×10^{-3} M. Irradiation for 6 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

Table 36. Stern-Volmer Quenching of the Acetophenone Formation in B: 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.	z-6-O4Bp with
Run 1	

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ _σ /Φ
0.480	7.05	0.0000	1.00
0.351	5.15	0.0123	1.37
0.294*	4.32	0.0246	1.63
0.229*	3.36	0.0369	2.10
0.188*	2.76	0.0491	2.55
			at = 30.2

[Ketone] = 1.0099×10^{-3} M. [MeBe] = 1.0224×10^{-3} M. Irradiation for 6 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.995.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.322	4.63	0.0000	1.00
0.245	3.52	0.0098	1.32
0.191*	2.75	0.0196	1.69
0.170*	2.45	0.0294	1.89
0.149	2.15	0.0392	2.16
L <u>ean</u>			

 $\mathbf{k_q}\tau = 30.6$

[Ketone] = 0.9890×10^{-3} M. [MeBe] = 1.0039×10^{-3} M. Irradiation for 5 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.995.

Table 37. Stern-Volmer Quenching of the Acetophenone Formation in Bz-7-O4Bp with	h
2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.	

0.298 0.237	4.38	0.0000	1.00
0.237			
	3.47	0.0089	1.26
0.188	2.77	0.0178	1.58
0.158	2.31	0.0267	1.89
0.139*	2.03	0.0357	2.15

[Ketone] = 1.0014×10^{-3} M. [MeBe] = 1.0224×10^{-3} M. Irradiation for 3 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,/Φ
0.368	5.30	0.0000	1.00
0.289	4.17	0.0098	1.27
0.229	3.30	0.0196	1.61
0.189*	2.72	0.0294	1.95
0.160*	2.31	0.0392	2.30

 $k_q \tau = 32.3$

[Ketone] = 1.0293×10^{-3} M. [MeBe] = 1.0039×10^{-3} M. Irradiation for 5 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

1				
A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ	
0.330	7.23	0.0000	1.00	
0.274*	5.99	0.0095	1.21	
0.240	5.25	0.0190	1.38	

0.0285

0.0380

1.56

1.82

 $k_q \tau = 20.8$

4.63

9.97

A

Table 38. Stern-Volmer Quenching of the Acetophenone Formation in Bz-9-O4Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

[Ketone] = 0.9	9987x10 ⁻³ N	M. []	MeBe] =	1.5219×10^{-3}	М.	Irradiation	for	5	h.	HPLC
condition set 1.	[*] Average o	f 1 tu	be. Correl	ation coeffici	ent =	= 0. 99 7.				

D	^
Run	
ILMIT	-

0.211

0.181*

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,/Φ
0.372	8.15	0.0000	1.00
0.310*	6.79	0.0096	1.20
0.266*	5.83	0.0191	1.40
0.238*	5.20	0.0287	1.57
0.208*	4.56	0.0382	1.79

[Ketone] = 0.9987×10^{-3} M. [MeBe] = 1.5219×10^{-3} M. Irradiation for 5 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

Table 39. Stern-Volmer Quenching of the Acetophenone Formation in Bz-10-O4Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

[AP], 10 ⁻⁵ M	[Q], M	Φ₀⁄Φ
3.47	0.0000	1.00
2.83	0.0123	1.22
2.29	0.0246	1.51
1.81	0.0369	1.92
1.59	0.0491	2.18
	[AP], 10 ⁻⁵ M 3.47 2.83 2.29 1.81 1.59	[AP], 10 ⁻⁵ M [Q], M 3.47 0.0000 2.83 0.0123 2.29 0.0246 1.81 0.0369 1.59 0.0491

 $[Ketone] = 0.9921 \times 10^{-3} M.$ $[MeBe] = 1.0224 \times 10^{-3} M.$ Irradiation for 6 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.995.

Run	2
	_

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
0.153	2.38	0.0000	1.00
0.124	1.94	0.0093	1.23
0.105*	1.63	0.0186	1.46
0.094	1.46	0.0279	1.62
0.083	1.30	0.0372	1.83

[Ketone] = 1.0404×10^{-3} M. [MeBe] = 1.0782×10^{-3} M. Irradiation for 6 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.998.

Table 40. Stern-Volmer Quenching of the Acetophenone Formation in Bz-11-O4Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

AAP/AMeBe	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.626	9.74	0.0000	1.00
0.472	7.35	0.0093	1.33
0.393	6.12	0.0186	1.59
0.319	4.97	0.0279	1.96
0.275	4.28	0.0372	2.28
	e an inne an aire an aire an an aire an an aire an an an aire an		
		k	$x_q \tau = 34.1$

Run 1

[Ketone] =	1.0391x10 ⁻³	Μ.	[MeBe] =	1.0782×10^{-3}	Μ.	Irradiation	for	6	h.	HPLC
condition se	t 1. Correlatio	n co	efficient = 0	.999.						

Run	2

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.433	6.61	0.0000	1.00
0.327*	5.00	0.0091	1.32
0.271	4.14	0.0181	1.60
0.230*	3.51	0.0272	1.88
0.199*	3.04	0.0363	2.17

 $\mathbf{k}_{\mathbf{q}}\tau = 32.6$

[Ketone] = 0.9690×10^{-3} M. [MeBe] = 1.0606×10^{-3} M. Irradiation for 6 h. HPLC condition set 1. ^{*}Average of 1 tube. Correlation coefficient = 0.999.

Table 41. Stern-Volmer Quenching of the Acetophenone Formation in Bz-14-O4Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Benzene.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,/Φ
0.558	8.04	0.0000	1.00
0.473	6.81	0.0055	1.18
0.434	6.25	0.0109	1.29
0.383	5.51	0.0164	1.46
0.344*	4.95	0.0219	1.62

[Ketone] = 1.0249×10^{-3} M. [MeBe] = 1.0018×10^{-3} M. Irradiation for 6 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.997.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,/Φ
0.670	9.64	0.0000	1.00
0.579	8.34	0.0047	1.16
0.534*	7.69	0.0093	1.25
0.496	7.14	0.0140	1.35
0.425*	6.12	0.0187	1.57
L		·····	

[Ketone] = 1.0198×10^{-3} M. [MeBe] = 1.0018×10^{-3} M. Irradiation for 6 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.987.

 $k_{a}\tau = 28.6$

Table 42. Stern-Volmer Quenching of the Acetophenone Formation in Bz-3-O2Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
1.014	14.60	0.0000	1.00
0.904	13.02	0.0098	1.12
0.799	11.50	0.0197	1.27
0.743	10.69	0.0295	1.37
0.702*	10.10	0.0394	1.44

[Ketone] = 1.0170×10^{-3} M. [MeBe] = 1.0027×10^{-3} M. Irradiation for 14 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.994.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,/Φ
0.572*	8.23	0.0000	1.00
0.504	7.26	0.0095	1.13
0.463*	6.67	0.1909	1.23
0.428	6.17	0.0286	1.33
0.396*	5.70	0.0382	1.44

 $k_q \tau = 11.8$

[Ketone] = 0.9987×10^{-3} M. [MeBe] = 1.0028×10^{-3} M. Irradiation for 10 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.998.

[AP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
1.30	0.0000	1.00
1.08	0.0075	1.20
0.84	0.0149	1.55
0.70	0.0223	1.87
0.62	0.0298	2.07
	[AP], 10 ⁻⁵ M 1.30 1.08 0.84 0.70 0.62	[AP], 10 ⁻⁵ M [Q], M 1.30 0.0000 1.08 0.0075 0.84 0.0149 0.70 0.0223 0.62 0.0298

[Ketone] = 1.04	11×10^{-3} M.	[MeBe] =	0.8813×10^{-3}	М.	Irradiation	for	5	h.	HPLC
condition set 1. * A	Average of 1	tube. Correl	lation coeffici	ent =	= 0.995.				

Run 1

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ _o /Φ
0.128	1.62	0.0000	1.00
0.106	1.35	0.0071	1.21
0.084	1.06	0.0143	1.53
0.073*	0.92	0.0214	1.76
0.062*	0.78	0.0286	2 07

[Ketone] = 1.0411×10^{-3} M. [MeBe] = 0.8814×10^{-3} M. Irradiation for 6 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.998.

Table 44. Stern-Volmer Quenching of the Acetophenone Formation in Bz-5-O2Bp	with
2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.	

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀⁄Φ
0.390	5.61	0.0000	1.00
0.311	4.48	0.0077	1.25
0.264	3.80	0.0154	1.47
0.222*	3.20	0.0231	1.75
0.196	2.82	0.0308	1.99

[Ketone] =	1.0043×10^{-3}	М.	[MeBe] =	1.0007×10^{-3}	М.	Irradiation	for	5	h.	HPLC
condition set	1. [*] Average	of 1	tube. Corre	lation coeffici	ient =	= 0.999.				

Run	2

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.342	4.92	0.0000	1.00
0.251	3.62	0.0093	1.36
0.214	3.08	0.0185	1.60
0.179	2.58	0.0278	1.91
0.154*	2.22	0.0371	2.22

[Ketone] = 1.0099×10^{-3} M. [MeBe] = 1.0095×10^{-3} M. Irradiation for 5 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

AAP/AMeBe	[AP], 10 ⁻⁵ M	[Q], M	Φ ₀ /Φ
0.272	3.92	0.0000	1.00
0.250	3.60	0.0076	1.09
0.197	2.84	0.0152	1.38
0.173	2.49	0.0227	1.57
0.152	2.19	0.0303	1.79

Table 45. Stern-Volmer Quenching of the Acetophenone Formation in Bz-6-O2Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

[Ketone] =	1.0098x10 ⁻³	Μ.	[MeBe] =	1.0018x10 ⁻³	М.	Irradiation	for	6 h	. HPLC
condition set	t 8. Correlatio	on co	efficient = 0	.992.					

 $k_{q}\tau = 25.1$

Run 1

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.308*	4.44	0.0000	1.00
0.269*	3.87	0.0066	1.15
0.220*	3.17	0.0131	1.40
0.197*	2.84	0.0197	1.56
0.189*	2.72	0.0262	1.63

[Ketone] = 0.9987×10^{-3} M. [MeBe] = 0.9960×10^{-3} M. Irradiation for 7 h. HPLC condition set 8. *Average of 1 tube. Correlation coefficient = 0.984.

Table 46. Stern-Volmer Quenching of the Acetophenone Formation in Bz-7-O2Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

AAP/AMeBe	[AP], 10 ⁻⁵ M	[Q], M	Φ₀⁄Φ
0.510	7.35	0.0000	1.00
0.438	6.30	0.0091	1.17
0.370*	5.32	0.0181	1.38
0.344	4.96	0.0272	1.48
0.276*	3.98	0.0362	1.85

Run 1

$[Ketone] = 0.9933 \times 10^{-3}$	' M .	[MeBe]	=	1.0107x10 ⁻³	М.	Irradiation	for	6 h	. HPLC
condition set 1. *Average	e of 1	tube. Cor	rel	ation coeffici	ient :	= 0.982.			

Run	2
	_

0.283	3.92	0.0000	1.00
0.237*	3.27	0.0086	1.20
0.215*	2.97	0.0172	1.32
0.175*	2.41	0.0257	1.62
0.163	2.26	0.0343	1.74

[Ketone] = 0.9896×10^{-3} M. [MeBe] = 0.9636×10^{-3} M. Irradiation for 6 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.990.

Table 47. Stern-Volmer (Quenching of the A	cetophenone F	formation in	Bz-9-O2Bp v	₩it
2,5-Dimethyl-2,4-hexadie	ene at 366 nm in Cyc	clohexane.			

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
0.361	4.57	0.0000	1.00
0.300	3.80	0.0071	1.20
0.252	3.19	0.0143	1.43
0.214	2.72	0.0214	1.68
0.195 [*]	2.47	0.0286	1.85

h

[Ketone] = 1	$.0136 \times 10^{-3}$	М.	[MeBe]	= 0.8	814×10^{-3}	М.	Irradiation	for	6	h.	HPLC
condition set 1	. *Average	of 1	tube. Cor	relatio	n coeffici	ient =	= 0.999.				

Run	2
	_

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.397	5.26	0.0000	1.00
0.314	4.16	0.0076	1.26
0.278	3.68	0.0153	1.43
0.229*	3.03	0.0229	1.73
0.215	2.85	0.0306	1.84
<u></u>			
		k	$x_{\alpha}\tau = 29.2$

[Ketone] = 1.0037×10^{-3} M. [MeBe] = 0.9166×10^{-3} M. Irradiation for 6 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.992.

- ā

Table 48. Stern-Volmer Quenching of the Acetophenone Formation in Bz-10-O2Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
0.380	5.14	0.0000	1.00
0.329	4.45	0.0061	1.16
0.296*	4.00	0.0123	1.28
0267*	3.62	0.0184	1.42
0.243*	3.30	0.0245	1.56

Run I

[Ketone] = 1.0131×10^{-3} M. [MeBe] = 0.9490×10^{-3} M. Irradiation for 7 h. HPLC condition set 7. *Average of 1 tube. Correlation coefficient = 0.999.

Run	2

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
0.402	5.79	0.0000	1.00
0.329	4.74	0.0070	1.22
0.296*	4.26	0.0139	1.36
0.269*	3.87	0.0209	1.50
0.239*	3.44	0.0278	1.68
<u></u>			

[Ketone] = 1.0035×10^{-3} M. [MeBe] = 1.0077×10^{-3} M. Irradiation for 7 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.996.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ ₀ /Φ
0.471	6.37	0.0000	1.00
0.380	5.14	0.0064	1.24
0.316	4.28	0.0127	1.49
0.284	3.84	0.0191	1.66
0.261	3.54	0.0255	1.80

Table 49. Stern-Volmer Quenching of the Acetophenone Formation in Bz-11-O2Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

$k_q \tau = 33.5$	
-------------------	--

[Ketone] = 1.0220×10^{-3} M. [MeBe] = 0.9490×10^{-3} M. Irradiation for 7 h. HPLC condition set 1. Correlation coefficient = 0.993.

Nun L	Run	2
-------	-----	---

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.536	7.72	0.0000	1.00
0.413	5.95	0.0070	1.30
0.346*	4.98	0.0139	1.55
0.304	4.37	0.0209	1.76
0.261*	3.76	0.0278	2.05

 $k_q \tau = 37.8$

[Ketone] = 1.0080×10^{-3} M. [MeBe] = 1.0077×10^{-3} M. Irradiation for 7 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

1 /			
A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ _σ /Φ
0.422	6.07	0.0000	1.00
0.340*	4.90	0.0060	1.24

Table 50. Stern-Volmer Quenching of the Acetophenone Formation in Bz-14-O2Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

		k	$_{1}\tau = 38.6$
0.216*	3.11	0.0240	1.95
0.251	3.61	0.0180	1.68
0.295	4.25	0.0120	1.43
0.340*	4.90	0.0060	1.24
0.422	6.07	0.0000	1.00

[Ketone] = 0.9999×10^{-3} M. [MeBe] = 1.0077×10^{-3} M. Irradiation for 6 h. HPLC condition set 8. *Average of 1 tube. Correlation coefficient = 0.998.

D	2
кип	2

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀⁄Φ
0.484	6.97	0.0000	1.00
0.346	4.98	0.0083	1.40
0.277*	3.99	00167	1.75
0.236*	3.40	0.0250	2.05
0.218*	3.14	0.0333	2.22

 $k_q \tau = 39.8$

 $[Ketone] = 1.0113 \times 10^{-3} M.$ $[MeBe] = 1.0018 \times 10^{-3} M.$ Irradiation for 6 h. HPLC condition set 8. *Average of 1 tube. Correlation coefficient = 0.990.

0.802 0.726 [*]	11.55	0.0000	1.00
0.726*	10.45		
	10.45	0.0098	1.11
0.677	9.75	0.0197	1.18
0.612*	8.82	0.0295	1.31
0.569*	8.19	0.0394	1.41

Table 51. Stern-Volmer Quenching of the Acetophenone Formation in Bz-3-O3Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

[Ketone] = 1.0138×10^{-3} M. [MeBe] = 1.0027×10^{-3} M. Irradiation for 14 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.998.

Run	2
	_

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀⁄Φ
0.498	7.17	0.0000	1.00
0.476	6.85	0.0095	1.05
0.424	6.11	0.0191	1.18
0.386	5.55	0.0286	1.29
0.357*	5.14	0.0382	1.40

 $k_q \tau = 10.0$

 $k_q \tau = 10.3$

[Ketone] = 0.9987×10^{-3} M. [MeBe] = 1.0028×10^{-3} M. Irradiation for 10 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.992.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀⁄Φ
0.337	4.85	0.0000	1.00
0.269	3.87	0.0076	1.25
0.217	3.12	0.0152	1.55
0.196	2.83	0.0227	1.71
0.170*	2.45	0.0303	1.98
<u>.</u>			T = 32.6

Table 52. Stern-Volmer Quenching of the Acetophenone Formation in Bz-6-O3Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

[Ketone] = 0.9	987x10 ⁻³ M.	[MeBe] =	1.0018x10 ⁻³	М.	Irradiation	for	6 ł	n.	HPLC
condition set 8.	[*] Average of 1	tube. Correl	ation coeffici	ent =	= 0.997.				

Run	2
	-

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ ₀ /Φ
0.411	5.91	0.0000	1.00
0.340	4.90	0.0066	1.21
0.290	4.18	0.0131	1.42
0.239	3.45	0.0197	1.72
0.225*	3.23	0.0262	1.83

[Ketone] = 0.9931×10^{-3} M. [MeBe] = 0.9960×10^{-3} M. Irradiation for 7 h. HPLC condition set 8. *Average of 1 tube. Correlation coefficient = 0.993.

 $k_q \tau = 33.1$

174

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀⁄Φ
0.646	9.31	0.0000	1.00
0.505	7.28	0.0091	1.28
0.404*	5.81	0.0181	1.60
0.369*	5.32	0.0272	1.75
0.333*	4.80	0.0362	1.94

Table 53. Stern-Volmer Quenching of the Acetophenone Formation in Bz-7-O3Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

[Ketone] =	0.9933x	10 ⁻³ M.	[MeBe]	= 1.00	07×10^{-3}	Μ.	Irradiation	for	6 h.	HPLC
condition se	t 1. [*] Aver	age of 1	tube. Con	rrelation	coeffici	ent =	= 0.989.			

Run	2
Nun	4

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀⁄Φ
0.406	5.61	0.0000	1.00
0.322	4.44	0.0086	1.26
0.275	3.80	0.0172	1.48
0.241*	3.34	0.0257	1.68
0.208*	2.88	0.0343	1.95

 $k_q \tau = 27.4$

[Ketone] = 1.0041×10^{-3} M. [MeBe] = 0.9636×10^{-3} M. Irradiation for 6 h. HPLC condition set 1. *Average of 1 tube. Correlation coefficient = 0.999.

[AP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
3.89	0.0000	1.00
3.21	0.0065	1.21
2.60	0.0129	1.50
2.42	0.0194	1.61
1.96	0.0258	1.99
	[AP], 10 ⁻³ M 3.89 3.21 2.60 2.42 1.96	[AP], 10 ⁻⁵ M [Q], M 3.89 0.0000 3.21 0.0065 2.60 0.0129 2.42 0.0194 1.96 0.0258

Table 54. Stern-Volmer Quenching of the Acetophenone Formation in Bz-9-O3Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

[Ketone] = 1.0087×10^{-3} M. [MeBe] = 0.9960×10^{-3} M. Irradiation for 6 h. HPLC condition set 10. *Average of 1 tube. Correlation coefficient = 0.989.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
0.336	4.84	0.0000	1.00
0.293	4.23	0.0065	1.15
0.250	3.61	0.0129	1.34
0.211*	3.04	0.0194	1.59
0.193*	2.78	0.0258	1.74

Table 55. Stern-Volmer Quenching of the Acetophenone Formation in Bz-10-O3Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

[Ketone] = 0.99	87x10 ⁻³ M.	[MeBe] =	0.9960x10 ⁻³	М.	Irradiation	for	6 h	. HPLC
condition set 10.	Average of 1	l tube. Corre	elation coeffic	cient	= 0.996.			

 $k_q \tau = 28.7$

 $k_q \tau = 28.5$

Run 1

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ ₀ /Φ
0.313	4.51	0.0000	1.00
0.262	3.78	0.0065	1.19
0.224*	3.23	0.0130	1.40
0.201	2.90	0.0194	1.56
0.182*	2.62	0.0259	1.72
L		······································	

[Ketone] = 1.0035×10^{-3} M. [MeBe] = 0.9960×10^{-3} M. Irradiation for 6 h. HPLC condition set 10. *Average of 1 tube. Correlation coefficient = 0.999.

Table 56. Stern-Volmer Quenching of the Acetophenone Formation in Bz-14-O3Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,⁄Φ
0.303	4.37	0.0000	1.00
0.238	3.42	0.0065	1.28
0.204	2.93	0.0130	1.49
0.183*	2.64	0.0194	1.66
0.155 [*]	2.23	0.0259	1.96
	······································		
		k	$a_{q}\tau = 36.3$

Run 1

[Ketone] = 0.99	985×10^{-3} M.	[MeBe] =	0.9960×10^{-3}	Μ.	Irradiation	for	6 h.	HPLC
condition set 8. *	Average of 1	tube. Corre	lation coeffici	ent =	= 0.996.			

ה	1
Kun	1
T / D / D	~

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ,/Φ
0.310	4.46	0.0000	1.00
0.263	3.78	0.0062	1.18
0.217	3.12	0.0123	1.43
0.194	2.79	0.0185	1.60
0.162*	2.33	0.0246	1.92
		1	$x_q \tau = 35.2$

[Ketone] = 1.0028×10^{-3} M. [MeBe] = 1.0042×10^{-3} M. Irradiation for 6 h. HPLC condition set 8. *Average of 1 tube. Correlation coefficient = 0.994.

Table 57. Stern-Volmer Quenc	hing of the 4-Methylacetop	henone Formation in
MeBz-3-ONp with 2,5-Dimethy	yl-2,4-hexadiene at 366 nm	in Cyclohexane.

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁴ M	[Q], M	Φ₀⁄Φ
0.312	1.37	0.0000	1.00
0.302	1.33	0.0099	1.03
0.292*	1.28	0.0198	1.07
0.285	1.25	0.0296	1.10
0.275*	1.21	0.0352	1.14

[Ketone] = 1.03	347x10 ⁻³ M.	[MeBe]	$= 1.0104 \times 10^{-3}$	М.	Irradiation	for	48	h.	HPLC
condition set 1.	Average of	tube. Co	rrelation coeffic	cient	= 0.999.				

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
0.192	8.44	0.0000	1.00
0.186	8.18	0.0100	1.03
0.181	7.97	0.0200	1.06
0.174	7.64	0.0301	1.10
0.169*	7.45	0.0401	1.13

[Ketone] = 1.0201×10^{-3} M. [MeBe] = 1.0168×10^{-3} M. Irradiation for 44 h. HPLC condition set 2. *Average of 1 tube. Correlation coefficient = 0.997.

Table 58. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in MeBz-4-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

[MeAP], 10 ⁻⁴ M	[Q], M	Φ₀⁄Φ
1.44	0.0000	1.00
1.31	0.0092	1.09
1.12	0.0185	1.29
1.01	0.0277	1.42
0.90	0.0369	1.59
	[MeAP], 10 ⁻⁴ M 1.44 1.31 1.12 1.01 0.90	[MeAP], 10 ⁴ M [Q], M 1.44 0.0000 1.31 0.0092 1.12 0.0185 1.01 0.0277 0.90 0.0369

$[Ketone] = 0.9611 \times 10^{-3}$, М .	[MeBe]	=	1.1311×10^{-3}	М.	Irradiation	for	88	h.	HPLC
condition set 3. *Average	e of 1	tube. Co	rre	lation coeffic	eient	= 0.996.				

Run	2
	_

Run 1

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁴ M	[Q], M	Φ₀⁄Φ
0.280	1.18	0.0000	1.00
0.232*	0.98	0.1014	1.20
0.212	0.89	0.0203	1.32
0.188*	0.80	0.0304	1.49
0.171*	0.72	0.0406	1.63

 $k_q \tau = 15.9$

 $[Ketone] = 1.0578 \times 10^{-3} \text{ M}.$ $[MeBe] = 0.9635 \times 10^{-3} \text{ M}.$ Irradiation for 68 h. HPLC condition set 6. *Average of 1 tube. Correlation coefficient = 0.997.

Table 59. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in Cyclohexane. Μ

AMeAP AMeBe	[MeAP], 10 ⁻⁴ M	[Q], M	Φ₀/Φ
0.328	1.54	0.0000	1.00
0.268	1.26	0.0097	1.22
0.236	1.11	0.0194	1.39
0.236	0.99	0.0291	1.56
0.181	0.85	0.0388	1.81

leBz-5-ONn with	2 5-Dimethyl-2	4-hexadiene	at	366	nm	in
	2,5 Dimotry 1 2	, i nexualene		500		

$[Ketone] = 1.0469 \times 10^{-3}$	M. [MeBe]	=	1.0654×10^{-3}	Μ.	Irradiation	for	65.5	h.	HPLC
condition set 6. Correlat	ion coefficien	nt =	0.997.						

Run	2
1/11/1	~

Run I

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁴ M	[Q], M	Φ₀/Φ
0.417	1.89	0.0000	1.00
0.346	1.57	0.0109	1.20
0.314	1.42	0.0217	1.33
0.245	1.11	0.0326	1.70
0.219	0.99	0.0435	1.90
		·	
			$k_q \tau = 20.2$

[Ketone] = 1.2562×10^{-3} M. [MeBe] = 1.0283×10^{-3} M. Irradiation for 41 h. HPLC condition set 6. Correlation coefficient = 0.988.

Table 60. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁴ M	[Q], M	Φ ₀ /Φ
0.350	1.90	0.0000	1.00
0.270	1.46	0.0099	1.30
0.237	1.28	0.0199	1.48
0.196	1.06	0.0298	1.79
0.184	1.00	0.0397	1.90
		······	

MeBz-6-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

[Ketone] =	1.0189x10 ⁻³	М.	[MeBe]	=	1.2281×10^{-3}	М.	Irradiation	for	42	h.	HPLC
condition set	t 6. Correlatio	on co	befficient	=	0.991.						

 $k_q \tau = 24.3$

Run	2
	_

Run 1

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁴ M	[Q], M	Φ₀⁄Φ
0.448	1.39	0.0000	1.00
0.369	1.14	0.0096	1.21
0.322	0.98	0.0191	1.39
0280	0.87	0.0287	1.60
0.229	0.71	0.0383	1.96

[Ketone] = 1.0160×10^{-3} M. [MeBe] = 0.9607×10^{-3} M. Irradiation for 45 h. HPLC condition set 4. Correlation coefficient = 0.990.

Table 61. Stern-Volmer Quenching of the 4-Methylacetophenone Formation inMeBz-7-ONp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁴ M	[Q], M	Φ,/Φ
0.635	1.97	0.0000	1.00
0.489	1.52	0.0096	1.30
0.418	1.30	0.0191	1.52
0.378	1.17	0.0287	1.68
0.330	1.02	0.0383	1.93
		k	$a\tau = 24.7$

пип і

[Ketone] = 0.9931×10^{-3} M. [MeBe] = 0.9607×10^{-3} M. Irradiation for 45 h. HPLC condition set 6. Correlation coefficient = 0.995.

Run	2
T (1004 0	~

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁴ M	[Q], M	Φ,/Φ
0.675	1.99	0.0000	1.00
0.528	1.55	0.0097	1.28
0.453	1.33	0.0195	1.49
0.371	1.09	0.0292	1.82
0.332	0.98	0.0390	2.04
L			

[Ketone] = 0.9709×10^{-3} M. [MeBe] = 0.9078×10^{-3} M. Irradiation for 27 h. HPLC condition set 6. Correlation coefficient = 0.998.

 $\mathbf{k_q}\tau = 26.9$

Table 62. Stern-Volmer (Quenching of the 4-Methy	lacetophenone	Formation in
MeBz-11-ONp with 2,5-E	Dimethyl-2,4-hexadiene at	366 nm in Cyc	lohexane.

[MeAP], 10 ⁻⁴ M	[Q], M	Φ₀⁄Φ
1.40	0.0000	1.00
1.09	0.0097	1.28
0.88	0.0195	1.59
0.74	0.0292	1.88
0.64	0.0390	2.19
	······	
	1.40 1.09 0.88 0.74 0.64	I.40 0.0000 1.09 0.0097 0.88 0.0195 0.74 0.0292 0.64 0.0390

[Ketone] = 0.9	554x10 ⁻³ M.	[MeBe]	$= 0.9078 \times 10^{-3}$	M.	Irradiation	for	17	h.	HPLC
condition set 3.	*Average of 1	tube. Cor	relation coeffic	cient	= 0.999.				

Run	2

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁴ M	[Q], M	Φ,/Φ
0.521	2.21	0.0000	1.00
0.419	1.78	0.0101	1.25
0.333*	1.41	0.0203	1.57
0.285	1.21	0.0304	1.83
0.248*	1.05	0.0406	2.10
· · · · · · · · · · · · · · · · · · ·			
			$k_{g}\tau = 27.2$

[Ketone] = 0.9525×10^{-3} M. [MeBe] = 0.9635×10^{-3} M. Irradiation for 20 h. HPLC condition set 6. *Average of 1 tube. Correlation coefficient = 0.999.
Table 63. Stern-Volmer Quenching of the 4-Methylacetophenone Formation in
MeBz-3-O4Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁴ M	[Q], M	Φ,⁄Φ
0.293	1.29	0.0000	1.00
0.272	1.20	0.0099	1.08
0.245	1.08	0.0198	1.19
0.230*	1.01	0.0296	1.27
0.220	0.97	0.0395	1.33
	······································		

$[Ketone] = 0.9850 \times 10^{-1}$	³ M.	[MeBe] =	= 1.0104x10 ⁻³	М.	Irradiation	for	44	h.	HPLC
condition set 5. *Averag	e of 1	tube. Corr	elation coeffic	cient	= 0.994.				

 $k_q \tau = 8.8$

Run 1

A _{MeAP} /A _{MeBe}	[MeAP], 10 ⁻⁵ M	[Q], M	Φ₀⁄Φ
0.199	8.77	0.0000	1.00
0.184	8.10	0.0100	1.08
0.172	7.57	0.0200	1.16
0.158	6.97	0.0301	1.26
0.144	6.33	0.0401	1.39

[Ketone] = 1.0275×10^{-3} M. [MeBe] = 1.0104×10^{-3} M. Irradiation for 47 h. HPLC condition set 4. *Average of 1 tube. Correlation coefficient = 0.994.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ₀/Φ
0.307	4.43	0.0000	1.00
0.279	4.01	0.0077	1.10
0.267*	3.84	0.0154	1.15
0.255*	3.67	0.0231	1.21
0.237	3.42	0.0308	1.30

-74

Table 64. Stern-Volmer Quenching of the Acetophenone Formation in Bz-3-O-2-O4Bp with 2,5-Dimethyl-2,4-hexadiene at 366 nm in Cyclohexane.

Run 1

Run 2

Г

0.237	3.42	0.0308	1.30
			$\kappa_q \tau = 9.6$

[Ketone] = 0.9988×10^{-3} M. [MeBe] = 1.0106×10^{-3} M. Irradiation for 5 h. HPLC

CADI 10-5 M ...

condition set 9. *Average of 1 tube. Correlation coefficient = 0.991.

A _{AP} /A _{MeBe}	[AP], 10 ⁻⁵ M	[Q], M	Φ _o /Φ
0.284	4.08	0.0000	1.00
0.252	3.63	0.0093	1.13
0.228	3.28	0.0185	1.25
0.217*	3.13	0.0278	1.31
0.201*	2.89	0.0371	1.41
		f	
		k	$x_q \tau = 11.5$

 $[Ketone] = 1.0155 \times 10^{-3} M.$ $[MeBe] = 1.0194 \times 10^{-3} M.$ Irradiation for 5 h. HPLC condition set 9. *Average of 1 tube. Correlation coefficient = 0.995.

4.4.9 Quantum Yields Measurements

The quantum yields for product formation were measured by irradiating 0.001M ketone solutions parallel to 0.001M solutions of valerophenone actinometer in sealed, degassed tubes. In those measurements, the same procedures were used as described in the previous paragraphs.

Quantum yields were calculated from the equation

$$\Phi = [P] / I_o \qquad (Equation 12)$$

where [P] is the concentration of photoproduct and I_o is the intensity of light absorbed by the sample. The value of I_o was determined by parallel irradiation of the actinometer (Φ = 0.3).⁷³ The intensity of light, I_o , can be then calculated by

$$I_0 = [P] / 0.3$$
 (Equation 13)

For irradiations at 366 nm, due to the low molar absorptivity coefficients of the actinometer and bichromophores, not all light was absorbed by the samples and corrections were made to compensate for light absorption differences. These corrections were made with the following equation:

$$I_{corr} = I_o \cdot (1-10^{-A})_{bichromophore} / (1-10^{-A})_{actinometer}$$
 (Equation 14)

where I_{corr} is the corrected intensity of light and A is optical density. All quantum yields were corrected.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	1.521	10.55	1.589	11.02	0.44
2	1.259	9.77	1.306	10.14	0.45

Table 65. Quantum Yields of the Acetophenone Formation in Bz-3-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

73

Run 1: [Ketone] = 0.9995×10^{-3} M. [MeBe] = 4.8182×10^{-4} M. [Valerophenone] = 1.0232×10^{-3} M. Irradiation for 4 h. HPLC condition set 8.

Run 2: [Ketone] = 0.9995×10^{-3} M. [MeBe] = 5.3911×10^{-4} M. [Valerophenone] = 0.9961×10^{-3} M. Irradiation for 4 h. HPLC condition set 8.

Table 66. Quantum Yields of the Acetophenone Formation in Bz-4-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	2.106	14.61	1.589	11.02	0.42
2	1.849	14.35	1.306	10.14	0.45

Average Quantum Yield = 0.44

Run 1: [Ketone] = 1.0034×10^{-3} M. [MeBe] = 4.8182×10^{-4} M. [Valerophenone] = 1.0232×10^{-3} M. Irradiation for 4 h. HPLC condition set 8.

Run 2: [Ketone] = 0.9837×10^{-3} M. [MeBe] = 5.3911×10^{-4} M. [Valerophenone] = 0.9961×10^{-3} M. Irradiation for 4 h. HPLC condition set 8.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	1.814	12.59	1.589	11.02	0.34
2	1.581	12.27	1.306	10.14	0.36

Table 67. Quantum Yields of the Acetophenone Formation in Bz-5-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 1.0069×10^{-3} M. [MeBe] = 4.8182×10^{-4} M. [Valerophenone] = 1.0232×10^{-3} M. Irradiation for 4 h. HPLC condition set 8.

Run 2: [Ketone] = 1.0069×10^{-3} M. [MeBe] = 5.3911×10^{-4} M. [Valerophenone] = 0.9961×10^{-3} M. Irradiation for 4 h. HPLC condition set 8.

Table 68. Quantum Yields of the Acetophenone Formation in Bz-7-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	1.581	10.97	1.589	11.02	0.29
2	1.308	10.15	1.306	10.14	0.29

Average Quantum Yield = 0.29

Run 1: [Ketone] = 0.9960×10^{-3} M. [MeBe] = 4.8182×10^{-4} M. [Valerophenone] = 1.0232×10^{-3} M. Irradiation for 4 h. HPLC condition set 8.

Run 2: [Ketone] = 10129×10^{-3} M. [MeBe] = 5.3911×10^{-4} M. [Valerophenone] = 0.9961×10^{-3} M. Irradiation for 4 h. HPLC condition set 8.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AF} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	1.494	10.37	1.589	11.02	0.27
2	1.148	8.91	1.306	10.14	0.25

Table 69. Quantum Yields of the Acetophenone Formation in Bz-10-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 1.0200×10^{-3} M. [MeBe] = 4.8182×10^{-4} M. [Valerophenone] = 1.0232×10^{-3} M. Irradiation for 4 h. HPLC condition set 8.

Run 2: [Ketone] = 10052×10^{-3} M. [MeBe] = 5.3911×10^{-4} M. [Valerophenone] = 0.9961×10^{-3} M. Irradiation for 4 h. HPLC condition set 8.

Table 70. Quantum Yields of the Acetophenone Formation in Bz-11-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	1.489	10.33	1.589	11.02	0.27
2	1.162	9.02	1.306	10.14	0.26

Average Quantum Yield = 0.26

Run 1: [Ketone] = 0.9960×10^{-3} M. [MeBe] = 4.8182×10^{-4} M. [Valerophenone] = 1.0232×10^{-3} M. Irradiation for 4 h. HPLC condition set 8.

Run 2: [Ketone] = 1.0129×10^{-3} M. [MeBe] = 5.3911×10^{-4} M. [Valerophenone] = 0.9961×10^{-3} M. Irradiation for 4 h. HPLC condition set 8.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AF} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.653	9.15	0.531	7.44	0.45
2	0.744	9.44	0.650	8.25	0.42

Table 71. Quantum Yields of the Acetophenone Formation in Bz-3-O-2-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 1.0165×10^{-3} M. [MeBe] = 0.9725×10^{-3} M. [Valerophenone] = 0.9937×10^{-3} M. Irradiation for 4 h. HPLC condition set 1.

Run 2: [Ketone] = 0.9741×10^{-3} M. [MeBe] = 0.8814×10^{-3} M. [Valerophenone] = 1.0048×10^{-3} M. Irradiation for 5 h. HPLC condition set 1.

Table 72. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-3-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{MeAP} /A _{MeBe} (Ketone)	[MeAP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	2.490	7.95	0.477	6.09	0.65
2	2.185	7.35	0.439	6.39	0.57

Average Quantum Yield = 0.61

Run 1: [Ketone] = 1.0224×10^{-3} M. [MeBe] = 0.8873×10^{-3} M. [Valerophenone] = 1.0060×10^{-3} M. Irradiation for 3 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0811×10^{-3} M. [MeBe] = 1.0107×10^{-3} M. [Valerophenone] = 1.0109×10^{-3} M. Irradiation for 3 h. HPLC condition set 1.

Run	A _{MeAP} /A _{MeBe} (Ketone)	[MeAP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	2.958	9.45	0.477	6.09	0.55
2	3.042	10.43	0.439	6.39	0.57

Table 73. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-4-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 0.9987×10^{-3} M. [MeBe] = 0.8873×10^{-3} M. [Valerophenone] = 1.0060×10^{-3} M. Irradiation for 3 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0609×10^{-3} M. [MeBe] = 1.0107×10^{-3} M. [Valerophenone] = 1.0109×10^{-3} M. Irradiation for 3 h. HPLC condition set 1.

Table 74. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-5-OPh with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{MeAP} /A _{MeBe} (Ketone)	[MeAP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	3.067	9.80	0.477	6.09	0.47
2	2.547 [*]	8.58	0.439	6.39	0.40

Average Quantum Yield = 0.43

Run 1: [Ketone] = 0.99869×10^{-3} M. [MeBe] = 0.8873×10^{-3} M. [Valerophenone] = 1.0060×10^{-3} M. Irradiation for 3 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0801×10^{-3} M. [MeBe] = 1.0107×10^{-3} M. [Valerophenone] = 1.0109×10^{-3} M. Irradiation for 3 h. HPLC condition set 1. *Average of 2 tubes.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.420	4.01	1.526	14.58	0.13
2	0.366	3.50	1.410	13.47	0.12

Table 75. Quantum Yields of the Acetophenone Formation in Bz-3-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 1.0340×10^{-3} M. [MeBe] = 0.6636×10^{-3} M. [Valerophenone] = 1.0232×10^{-3} M. Irradiation for 4 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0000×10^{-3} M. [MeBe] = 0.6636×10^{-3} M. [Valerophenone] = 0.9612×10^{-3} M. Irradiation for 4 h. HPLC condition set 1.

Table 76. Quantum Yields of the Acetophenone Formation in Bz-4-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AF} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.012	1.67	0.101	14.05	0.03
2	0.076	1.06	0.585	8.16	0.04

Average Quantum Yield = 0.04

Run 1: [Ketone] = 0.9856×10^{-3} M. [MeBe] = 1.0870×10^{-3} M. [Valerophenone] = 0.9986×10^{-3} M. Irradiation for 4 h. HPLC condition set 6.

Run 2: [Ketone] = 1.0185×10^{-3} M. [MeBe] = 1.0900×10^{-3} M. [Valerophenone] = 1.0084×10^{-3} M. Irradiation for 4 h. HPLC condition set 7.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.053	7.37	0.101	14.05	0.15
2	0.321	4.48	0.585	8.16	0.16

Table 77. Quantum Yields of the Acetophenone Formation in Bz-5-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 1.0050×10^{-3} M. [MeBe] = 1.0870×10^{-3} M. [Valerophenone] = 0.9986×10^{-3} M. Irradiation for 4 h. HPLC condition set 6.

Run 2: [Ketone] = 1.0365×10^{-3} M. [MeBe] = 1.0900×10^{-3} M. [Valerophenone] = 1.0084×10^{-3} M. Irradiation for 4 h. HPLC condition set 7.

Table 78. Quantum Yields of the Acetophenone Formation in Bz-6-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.056	7.79	0.101	14.05	0.16
2	0.317	4.42	0.585	8.16	0.15

Average Quantum Yield = 0.16

Run 1: [Ketone] = 0.9927×10^{-3} M. [MeBe] = 1.0870×10^{-3} M. [Valerophenone] = 0.9986×10^{-3} M. Irradiation for 4 h. HPLC condition set 6.

Run 2: [Ketone] = 0.9927×10^{-3} M. [MeBe] = 1.0900×10^{-3} M. [Valerophenone] = 1.0084×10^{-3} M. Irradiation for 4 h. HPLC condition set 7.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ^{.5} M	A _{AF} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.058	8.07	0.101	14.05	0.17
2	0.334*	4.66	0.585	8.16	0.17

Table 79. Quantum Yields of the Acetophenone Formation in Bz-7-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 0.9814×10^{-3} M. [MeBe] = 1.0870×10^{-3} M. [Valerophenone] = 0.9986×10^{-3} M. Irradiation for 4 h. HPLC condition set 6.

Run 2: [Ketone] = 1.0103×10^{-3} M. [MeBe] = 1.0900×10^{-3} M. [Valerophenone] = 1.0084×10^{-3} M. Irradiation for 4 h. HPLC condition set 7. *Average of 2 tubes.

Table 80. Quantum Yields of the Acetophenone Formation in Bz-9-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.250	3.30	0.785	10.36	0.09
2	0.333	4.55	0.760	10.39	0.13

Average Quantum Yield = 0.11

Run 1: [Ketone] = 2.0347×10^{-3} M. [MeBe] = 0.9166×10^{-3} M. [Valerophenone] = 1.0048×10^{-3} M. Irradiation for 6 h. HPLC condition set 7.

Run 2: [Ketone] = 1.0307×10^{-3} M. [MeBe] = 0.9490×10^{-3} M. [Valerophenone] = 0.9961×10^{-3} M. Irradiation for 6 h. HPLC condition set 7.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.319	4.21	0.785	10.36	0.12
2	0.375*	5.12	0.760	10.39	0.14

Table 81. Quantum Yields of the Acetophenone Formation in Bz-10-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 1.0244×10^{-3} M. [MeBe] = 0.9166×10^{-3} M. [Valerophenone] = 1.0048×10^{-3} M. Irradiation for 6 h. HPLC condition set 7.

Run 2: [Ketone] = 1.0142×10^{-3} M. [MeBe] = 0.9490×10^{-3} M. [Valerophenone] = 0.9961×10^{-3} M. Irradiation for 6 h. HPLC condition set 7. *Average of 2 tubes.

Table 82. Quantum Yields of the Acetophenone Formation in Bz-11-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.060	8.35	0.101	14.05	0.17
2	0.371	5.82	0.585	9.18	0.18

Average Quantum Yield = 0.18

Run 1: [Ketone] = 1.0192×10^{-3} M. [MeBe] = 1.0870×10^{-3} M. [Valerophenone] = 0.9986×10^{-3} M. Irradiation for 4 h. HPLC condition set 6.

Run 2: [Ketone] = 1.0193×10^{-3} M. [MeBe] = 1.0900×10^{-3} M. [Valerophenone] = 1.0084×10^{-3} M. Irradiation for 4 h. HPLC condition set 7.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.355	5.15	0.647	9.39	0.16
2	0.339	4.89	0.675	9.74	0.15

Table 83. Quantum Yields of the Acetophenone Formation in Bz-14-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 0.9986×10^{-3} M. [MeBe] = 1.0077×10^{-3} M. [Valerophenone] = 1.0109×10^{-3} M. Irradiation for 6 h. HPLC condition set 8.

Run 2: [Ketone] = 0.9986×10^{-3} M. [MeBe] = 1.0018×10^{-3} M. [Valerophenone] = 0.9996×10^{-3} M. Irradiation for 6h. HPLC condition set 8.

Table 84. Quantum Yields of the Acetophenone Formation in Bz-3-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.367	5.92	0.945	15.25	0.19
2	0.336	5.14	1.072	16.40	0.15

Average Quantum Yield = 0.17

Run 1: [Ketone] = 1.0122×10^{-3} M. [MeBe] = 1.1208×10^{-3} M. [Valerophenone] = 1.0553×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0121×10^{-3} M. [MeBe] = 1.0621×10^{-3} M. [Valerophenone] = 1.0171×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.158	2.55	0.945	15.25	0.05
2	0.179	2.74	1.072	16.40	0.05

Table 85. Quantum Yields of the Acetophenone Formation in Bz-4-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 1.0298×10^{-3} M. [MeBe] = 1.1208×10^{-3} M. [Valerophenone] = 1.0553×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run 2: [Ketone] = 0.9995×10^{-3} M. [MeBe] = 1.0621×10^{-3} M. [Valerophenone] = 1.0171×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Table 86. Quantum Yields of the Acetophenone Formation in Bz-5-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.394	6.36	0.945	15.25	0.12
2	0.471	7.20	1.072	16.40	0.13

Average Quantum Yield = 0.13

Run 1: [Ketone] = 1.0169×10^{-3} M. [MeBe] = 1.1208×10^{-3} M. [Valerophenone] = 1.0553×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run 2: [Ketone] = 0.9879×10^{-3} M. [MeBe] = 1.0621×10^{-3} M. [Valerophenone] = 1.0171×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.423	6.83	0.945	15.25	0.13
2	0.531	8.12	1.072	16.40	0.15

Table 87. Quantum Yields of the Acetophenone Formation in Bz-6-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 1.0330×10^{-3} M. [MeBe] = 1.1208×10^{-3} M. [Valerophenone] = 1.0553×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0051×10^{-3} M. [MeBe] = 1.0621×10^{-3} M. [Valerophenone] = 1.0171×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Table 88. Quantum Yields of the Acetophenone Formation in Bz-7-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.574	9.26	0.945	15.25	0.18
2	0.597	9.13	1.072	16.40	0.16

Average Quantum Yield = 0.17

Run 1: [Ketone] = 1.0209×10^{-3} M. [MeBe] = 1.1208×10^{-3} M. [Valerophenone] = 1.0553×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0209×10^{-3} M. [MeBe] = 1.0621×10^{-3} M. [Valerophenone] = 1.0171×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.158*	2.41	0.359	5.48	0.13
2	0.154*	2.35	0.359	5.48	0.13

Table 89. Quantum Yields of the Acetophenone Formation in Bz-9-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 0.9987×10^{-3} M. [MeBe] = 1.0606×10^{-3} M. [Valerophenone] = 1.0171×10^{-3} M. Irradiation for 3 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0236×10^{-3} M. [MeBe] = 1.0606×10^{-3} M. [Valerophenone] = 1.0171×10^{-3} M. Irradiation for 3 h. HPLC condition set 1. *Average of 2 tubes

Table 90. Quantum Yields of the Acetophenone Formation in Bz-10-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.247	3.99	0.945	15.25	0.08
2	0.230	3.52	1.072	16.40	0.06

Average Quantum Yield = 0.07

Run 1: [Ketone] = 1.0139×10^{-3} M. [MeBe] = 1.1208×10^{-3} M. [Valerophenone] = 1.0553×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0139×10^{-3} M. [MeBe] = 1.0621×10^{-3} M. [Valerophenone] = 1.0171×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.756	12.20	0.945	15.25	0.24
2	0.447	6.43	0.751	10.80	0.18

Table 91. Quantum Yields of the Acetophenone Formation in Bz-11-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 1.0040×10^{-3} M. [MeBe] = 1.1208×10^{-3} M. [Valerophenone] = 1.0553×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0274×10^{-3} M. [MeBe] = 0.9989×10^{-3} M. [Valerophenone] = 1.0023×10^{-3} M. Irradiation for 4 h. HPLC condition set 1.

Table 92. Quantum Yields of the Acetophenone Formation in Bz-14-O4Bp with Valerophenone as an Actinometer at 366 nm in Benzene.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.558	8.05	0.674	9.72	0.24
2	0.550	7.93	0.674	9.72	0.24

Average Quantum Yield = 0.24

Run 1: [Ketone] = 1.0249×10^{-3} M. [MeBe] = 1.0018×10^{-3} M. [Valerophenone] = 1.0281×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0003×10^{-3} M. [MeBe] = 1.0018×10^{-3} M. [Valerophenone] = 1.0281×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	1.014	18.44	2.094	38.07	0.24
2	0.572	10.07	1.318	23.21	0.22

Table 93. Quantum Yields of the Acetophenone Formation in Bz-3-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Average Quantum Yield = 0.23

Run 1: [Ketone] = 1.0170×10^{-3} M. [MeBe] = 1.2627×10^{-3} M. [Valerophenone] = 0.9819x10⁻³ M. Irradiation for 14 h. HPLC condition set 1.

Run 2: [Ketone] = 0.9987×10^{-3} M. [MeBe] = 1.2228×10^{-3} M. [Valerophenone] = 0.9888x10⁻³ M. Irradiation for 10 h. HPLC condition set 1.

[AP] from valerophenone is a sum over consecutive measurements.

Table 94. Quantum Yields of the Acetophenone Formation in Bz-4-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.103	1.31	0.650	8.25	0.05
2	0.128	1.62	0.820	10.41	0.05

Average Quantum Yield = 0.05

Run 1: [Ketone] = 1.0411×10^{-3} M. [MeBe] = 0.8814×10^{-3} M. [Valerophenone] = 1.0048x10⁻³ M. Irradiation for 5 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0412×10^{-3} M. [MeBe] = 0.8814×10^{-3} M. [Valerophenone] = 1.0048x10⁻³ M. Irradiation for 6 h. HPLC condition set 1.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	θ
1	0.390	5.68	0.661	9.62	0.18
2	0.342	5.02	0.633	9.29	0.16

Table 95. Quantum Yields of the Acetophenone Formation in Bz-5-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Average Quantum Yield = 0.17

Run 1: [Ketone] = 1.0043×10^{-3} M. [MeBe] = 1.0107×10^{-3} M. [Valerophenone] = 0.9887×10^{-3} M. Irradiation for 5 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0099×10^{-3} M. [MeBe] = 1.0195×10^{-3} M. [Valerophenone] = 1.0109×10^{-3} M. Irradiation for 5 h. HPLC condition set 1.

Table 96. Quantum Yields of the Acetophenone Formation in Bz-6-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.272	3.92	0.624	9.00	0.13
2	0.308	4.42	0.679	9.74	0.14

Average Quantum Yield = 0.13

Run 1: [Ketone] = 1.0099×10^{-3} M. [MeBe] = 1.0018×10^{-3} M. [Valerophenone] = 1.0183×10^{-3} M. Irradiation for 6 h. HPLC condition set 8.

Run 2: [Ketone] = 0.9987×10^{-3} M. [MeBe] = 0.9960×10^{-3} M. [Valerophenone] = 1.0035×10^{-3} M. Irradiation for 7 h. HPLC condition set 8.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.510	7.42	1.153	16.78	0.13
2	0.284	3.83	0.647	8.72	0.13

Table 97. Quantum Yields of the Acetophenone Formation in Bz-7-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 0.9933×10^{-3} M. [MeBe] = 1.0107×10^{-3} M. [Valerophenone] = 1.0183×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run 2: [Ketone] = 0.9826×10^{-3} M. [MeBe] = 0.9364×10^{-3} M. [Valerophenone] = 1.0060×10^{-3} M. Irradiation for 4 h. HPLC condition set 1.

Table 98. Quantum Yields of the Acetophenone Formation in Bz-9-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.361	4.58	0.820	10.41	0.13
2	0.397	5.24	0.914	12.06	0.13

Average Quantum Yield = 0.13

Run 1: [Ketone] = 1.0136×10^{-3} M. [MeBe] = 0.8814×10^{-3} M. [Valerophenone] = 1.0048×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0037×10^{-3} M. [MeBe] = 0.9166×10^{-3} M. [Valerophenone] = 1.0047×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.345	4.71	0.763	10.43	0.13
2	0.344	4.99	0.814	11.81	0.12

Table 99. Quantum Yields of the Acetophenone Formation in Bz-10-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 1.0131×10^{-3} M. [MeBe] = 0.9490×10^{-3} M. [Valerophenone] = 0.9961×10^{-3} M. Irradiation for 7 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0035×10^{-3} M. [MeBe] = 1.0077×10^{-3} M. [Valerophenone] = 1.0109×10^{-3} M. Irradiation for 7 h. HPLC condition set 1.

Table 100. Quantum Yields of the Acetophenone Formation in Bz-11-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.471	6.44	0.763	10.43	0.18
2	0.536	7.78	0.814	11.81	0.19

Average Quantum Yield = 0.19

Run 1: [Ketone] = 1.0220×10^{-3} M. [MeBe] = 0.9490×10^{-3} M. [Valerophenone] = 0.9961×10^{-3} M. Irradiation for 7 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0080×10^{-3} M. [MeBe] = 1.0077×10^{-3} M. [Valerophenone] = 1.0109×10^{-3} M. Irradiation for 7 h. HPLC condition set 1.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.422	6.12	0.647	9.39	0.19
2	0.484	6.98	0.675	9.74	0.21

Table 101. Quantum Yields of the Acetophenone Formation in Bz-14-O2Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 0.9999×10^{-3} M. [MeBe] = 1.0077×10^{-3} M. [Valerophenone] = 1.0109×10^{-3} M. Irradiation for 6 h. HPLC condition set 8.

Run 2: [Ketone] = 1.0113×10^{-3} M. [MeBe] = 1.0018×10^{-3} M. [Valerophenone] = 0.9996×10^{-3} M. Irradiation for 6h. HPLC condition set 8.

Table 102. Quantum Yields of the Acetophenone Formation in Bz-3-O3Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.802	14.58	2.094	38.07	0.20
2	0.498	8.77	1.318	23.21	0.19

Average Quantum Yield = 0.20

Run 1: [Ketone] = 1.0138×10^{-3} M. [MeBe] = 1.2627×10^{-3} M. [Valerophenone] = 0.9819×10^{-3} M. Irradiation for 14 h. HPLC condition set 1.

Run 2: [Ketone] = 0.9987×10^{-3} M. [MeBe] = 1.2228×10^{-3} M. [Valerophenone] = 0.9888×10^{-3} M. Irradiation for 10 h. HPLC condition set 1.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.337	4.86	0.624	9.00	0.16
2	0.411	5.89	0.679	9.74	0.18

Table 103. Quantum Yields of the Acetophenone Formation in Bz-6-O3Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 0.9987×10^{-3} M. [MeBe] = 1.0018×10^{-3} M. [Valerophenone] = 1.0183×10^{-3} M. Irradiation for 6 h. HPLC condition set 8.

Run 2: [Ketone] = 0.9931×10^{-3} M. [MeBe] = 0.9960×10^{-3} M. [Valerophenone] = 1.0035×10^{-3} M. Irradiation for 7 h. HPLC condition set 8.

Table 104. Quantum Yields of the Acetophenone Formation in Bz-7-O3Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.642	9.34	1.153	16.78	0.17
2	0.406	5.47	0.647	8.72	0.19

Average Quantum Yield = 0.18

Run 1: [Ketone] = 0.9933×10^{-3} M. [MeBe] = 1.0107×10^{-3} M. [Valerophenone] = 1.0183×10^{-3} M. Irradiation for 6 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0041×10^{-3} M. [MeBe] = 0.9364×10^{-3} M. [Valerophenone] = 1.0060×10^{-3} M. Irradiation for 4 h. HPLC condition set 1.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.270	3.87	0.526	7.54	0.15

Table 105. Quantum Yields of the Acetophenone Formation in Bz-9-O3Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 1.0087×10^{-3} M. [MeBe] = 0.9960×10^{-3} M. [Valerophenone] = 1.0035×10^{-3} M. Irradiation for 6 h. HPLC condition set 10. Single measurement.

Table 106. Quantum Yields of the Acetophenone Formation in Bz-10-O3Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.336	4.82	0.526	7.54	0.19
2	0.313	4.49	0.536	7.69	0.17

Average Quantum Yield = 0.18

Run 1: [Ketone] = 0.9987×10^{-3} M. [MeBe] = 0.9960×10^{-3} M. [Valerophenone] = 1.0035×10^{-3} M. Irradiation for 6 h. HPLC condition set 10.

Run 2: [Ketone] = 1.0035×10^{-3} M. [MeBe] = 0.9960×10^{-3} M. [Valerophenone] = 1.0035×10^{-3} M. Irradiation for 6 h. HPLC condition set 10.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.303	4.35	0.536	7.69	0.17
2	0.310	4.42	0.502	7.48	0.18

Table 107. Quantum Yields of the Acetophenone Formation in Bz-14-O3Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 0.9985×10^{-3} M. [MeBe] = 0.9960×10^{-3} M. [Valerophenone] = 1.0035×10^{-3} M. Irradiation for 6 h. HPLC condition set 10.

Run 2: [Ketone] = 1.0028×10^{-3} M. [MeBe] = 1.0342×10^{-3} M. [Valerophenone] = 0.9986×10^{-3} M. Irradiation for 6 h. HPLC condition set 8.

Table 108. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-3-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{MeAP} /A _{MeBe} (Ketone)	[MeAP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.040	1.70	0.224	27.63	0.03
2	0.041	1.95	0.212	29.26	0.04

Average Quantum Yield = 0.03

Run 1: [Ketone] = 0.9837×10^{-3} M. [MeBe] = 0.9636×10^{-3} M. [Valerophenone] = 1.0232×10^{-3} M. Irradiation for 48 h. HPLC condition set 3.

Run 2: [Ketone] = 0.9961×10^{-3} M. [MeBe] = 1.0782×10^{-3} M. [Valerophenone] = 1.0193×10^{-3} M. Irradiation for 48 h. HPLC condition set 3.

Run	A _{MeAP} /A _{MeBe} (Ketone)	[MeAP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.107	4.92	1.164	148.99	0.01
2	0.060	2.76	0.522	69.78	0.01

Table 109. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-4-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Average Quantum Yield = 0.01

Run 1: [Ketone] = 0.9893×10^{-3} M. [MeBe] = 1.0459×10^{-3} M. [Valerophenone] = 1.0158×10^{-3} M. Irradiation for 41 h. HPLC condition set 3.

Run 2: [Ketone] = 1.0058×10^{-3} M. [MeBe] = 1.0444×10^{-3} M. [4-methylvalerophenone] = 1.0065×10^{-3} M. Irradiation for 24 h. HPLC condition set 3.

[AP] from valerophenone is a sum over consecutive measurements.

Table 110. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-5-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{MeAP} /A _{MeBe} (Ketone)	[MeAP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.328	15.09	1.164	148.99	0.03
2	0.197	9.05	0.522	69.78	0.04

Average Quantum Yield = 0.03

Run 1: [Ketone] = 0.9777×10^{-3} M. [MeBe] = 1.0459×10^{-3} M. [Valerophenone] = 1.0158×10^{-3} M. Irradiation for 41 h. HPLC condition set 3.

Run 2: [Ketone] = 1.0236×10^{-3} M. [MeBe] = 1.0444×10^{-3} M. [4-methylvalerophenone] = 1.0065×10^{-3} M. Irradiation for 24 h. HPLC condition set 3.

Run	A _{MeAP} /A _{MeBe} (Ketone)	[MeAP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.400	18.41	1.164	148.99	0.04
2	0.238	10.94	0.522	69.78	0.05

Table 111. Ouantum Yields of the 4-Methylacetophenone Formation in MeBz-6-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 1.0103×10^{-3} M. [MeBe] = 1.0459×10^{-3} M. [Valerophenone] = 1.0158x10⁻³ M. Irradiation for 41 h. HPLC condition set 3.

Run 2: [Ketone] = 1.0110×10^{-3} M. [MeBe] = 1.0444×10^{-3} M. [4-methylvalerophenone] = 1.0065x10⁻³ M. Irradiation for 24 h. HPLC condition set 3. [AP] from valerophenone is a sum over consecutive measurements.

Table 112. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-7-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{MeAP} /A _{MeBe} (Ketone)	[MeAP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.530	24.39	1.164	148.99	0.05
2	0.276	12.68	0.522	69.78	0.05

Average Quantum Yield = 0.05

Run 1: [Ketone] = 1.0126×10^{-3} M. [MeBe] = 1.0459×10^{-3} M. [Valerophenone] = 1.0158x10⁻³ M. Irradiation for 41 h. HPLC condition set 3.

Run 2: [Ketone] = 1.0272×10^{-3} M. [MeBe] = 1.0444×10^{-3} M. [4-methylvalerophenone] = 1.0065x10⁻³ M. Irradiation for 24 h. HPLC condition set 3.

Run	A _{MeAP} /A _{MeBe} (Ketone)	[MeAP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.575	26.46	1.164	148.99	0.05
2	0.302	13.88	0.522	69.78	0.06

Table 113. Quantum Yields of the 4-Methylacetophenone Formation in
 MeBz-11-ONp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 1.0082×10^{-3} M. [MeBe] = 1.0459×10^{-3} M. [Valerophenone] = 1.0158x10⁻³ M. Irradiation for 41 h. HPLC condition set 3.

Run 2: [Ketone] = 0.9849×10^{-3} M. [MeBe] = 1.0444×10^{-3} M. [4-methylvalerophenone] = 1.0065x10⁻³ M. Irradiation for 24 h. HPLC condition set 3.

[AP] from valerophenone is a sum over consecutive measurements.

Table 114. Quantum Yields of the 4-Methylacetophenone Formation in MeBz-3-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run	A _{MeAP} /A _{MeBe} (Ketone)	[MeAP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.049	2.08	0.224	27.63	0.04
2	0.244	0.76	0.947	11.86	0.03

Average Quantum Yield = 0.04

Run 1: [Ketone] = 0.9844×10^{-3} M. [MeBe] = 0.9636×10^{-3} M. [Valerophenone] = 1.0232x10⁻³ M. Irradiation for 48 h. HPLC condition set 3.

[AP] from valerophenone is a sum over consecutive measurements. Run 2: [Ketone] = 0.9876×10^{-3} M. [MeBe] = 0.8696×10^{-3} M. [Valerophenone] = 1.0224x10⁻³ M. Irradiation for 45 h. HPLC condition set 1.

Run	A _{AP} /A _{MeBe} (Ketone)	[AP], 10 ⁻⁵ M	A _{AP} /A _{MeBe} (Valerophenone)	[AP], 10 ⁻⁵ M	Φ
1	0.307	4.47	0.661	9.62	0.18
2	0.284	4.17	0.633	9.29	0.17

Table 115. Quantum Yields of the Acetophenone Formation in Bz-3-O-2-O4Bp with Valerophenone as an Actinometer at 366 nm in Cyclohexane.

Run 1: [Ketone] = 0.9988×10^{-3} M. [MeBe] = 1.0107×10^{-3} M. [Valerophenone] = 0.9887×10^{-3} M. Irradiation for 5 h. HPLC condition set 1.

Run 2: [Ketone] = 1.0155×10^{-3} M. [MeBe] = 1.0195×10^{-3} M. [Valerophenone] = 1.0109×10^{-3} M. Irradiation for 5 h. HPLC condition set 1.

5. REFERENCES

1. Birks, J. B. "Photophysics of Aromatic Molecules"; John Wiley; New York, 1970, Ch. 11.

2. Dexter, D. L. J. Chem. Phys. 1953, 21, 836.

3. Yardley, J. T. "Introduction to Molecular Energy Transfer"; Academic Press; New York, 1980.

4. Lamola, A. A. "Electronic Energy Transfer in Solution: Theory and Applications," in *Techniques of Organic Chemistry* 14; Weisberger, A., Ed.; Wiley; New York, 1969.

5. Closs, G. L.; Piotrowiak, P.; MacInnis, J. M; Fleming, G. R. J. Am. Chem. Soc. 1988, 110, 2652.

6. Read, J. "From Alchemy to Chemistry", Dover; New York, 1995.

7. Wagner, P. J. Acc. Chem. Res. 1983, 16, 461.

8. Internet source of the illustration: http://www.dragon.org/chris/ouroboros.html.

9. Wigner, E.; Wittmer, E. E. Z. Phys. 1928, 51, 859.

10. Terenin, A. N.; Ermolaev, V. L. Dokl. AN SSSR 1952, 85, 547.

11. Ermolaev, V. L. Sov. Physics, Doklady 1967, 6, 600.

12. Sciano, J. C.; Leigh, W. J.; Meador, M. A.; Wagner, P. J. J. Am. Chem. Soc. 1985, 107, 5806.

13. Kearns, D. R.; Case, W. A. J. Am. Chem. Soc. 1966, 88, 5087.

- 14. Lewis, G. N.; Kasha, M. J. Am. Chem. Soc. 1944, 66, 2100.
- 15. a) Singer, L. A.; Brown, R. E.; Davis, G. A. J. Am. Chem. Soc. 1973, 95, 8639.
 b) Wolf, M. W.; Brown, R. E.; Singer, L. A. J. Am. Chem. Soc. 1977, 99, 526.

16. Day, A. C.; Wright, T. R. Tetrahedron Lett. 1969, 14, 1067.

17. Wagner, P. J.; McGrath J. M.; Zepp, R. G. J. Am. Chem. Soc. 1972, 94, 6883.

18. Mucha, J. A.; Pratt, D. W. J. Chem. Phys. 1977, 66, 5339.

19. Hochstrasser, R. M.; Scott, G. W.; Zewail, A. H. Mol. Phys. 1978, 36, 475.

20. Wolf, M. W.; Brown, R. E.; Singer, L. A. J. Am. Chem. Soc. 1977, 99, 526.

21. Mirbach, M. F.; Ramamurthy, V.; Mirbach, M. J.; Turro, N. J.; Wagner, P. J. *Nouv. J. Chim.* **1980**, *4*, 471.

22. Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. J. Am. Chem. Soc. 1986, 108, 7727.

23. Leermakers, P. A.; Byers, G. W., Lamola, A. A.; Hammond, G. S. J. Am. Chem. Soc. 1963, 85, 2670.

24. Filipescu, N.; DeMember, J. R.; Minn, F. L. J. Am. Chem. Soc. 1969, 91, 4169.

25. a) Keller, R. A. J. Am. Chem. Soc. 1968, 90, 1940.
b) Keller, R. A.; Dolby, L. J. J. Am. Chem. Soc. 1969, 91, 1293.

26. Zimmerman, H. E.; McKelvey, R. D. J. Am. Chem. Soc. 1971, 93, 3638.

27. a) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. J. Am. Chem. Soc. 1983, 105, 670.
b) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. J. Am. Chem. Soc. 1984, 106, 3047.
c) Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Fleming, G. R. J. Am. Chem. Soc.
1988, 110, 2652.
d) Closs, G. L.; Miller, J. R. Science 1988, 240, 440.
e) Johnson, M. D.; Miller, J. R.; Green, N. S.; Closs, G. L. J. Phys. Chem. 1989, 93, 1173.
f) Closs, G. L.; Johnson, M. D.; Miller, J. R.; Piotrowiak, P. J. Am. Chem. Soc. 1989, 111, 3751.

g) Liang, N.; Miller, J. R.; Closs, G. L. J. Am. Chem. Soc. 1989, 111, 8740.

28. a) Chattoraj, M.; Bal, B.; Closs, G. L.; Levy, D. H. J. Phys. Chem. 1991, 95, 9666.
b) Chattoraj, M.; Paulson, B.; Shi, Y.; Closs, G. L.; Levy, D. H. J. Phys. Chem. 1993, 97, 13046.

29. Curtiss, L. A.; Naleway, C. A.; Miller, J. R. J. Phys. Chem. 1995, 99, 1182.

30. Koga, N.; Sameshima, K.; Morokuma, K. J. Phys. Chem. 1993, 97, 13117.

31. Sigman, M. E.; Closs, G. L. J. Phys. Chem. 1991, 95, 5012.

32. Marcus, R. A. Annu. Rev. Phys. Chem. 1964, 15, 155.

33. Saltiel, J.; Sun, Y.-P. "Cis-trans Isomerization of C=C Double Bonds," in *Photochromism, Molecules and Systems*; Durr, H., Boulas-Laurent, H., Eds.; Elsevier; Amsterdam 1990.

34. Wagner, P. J.; Park, B.-S. "Photoinduced Hydrogen Atom Abstraction by Carbonyl Compounds," Org. Photochem.; Padwa, A., Ed.; **1991**, 11, 111.

35. Norrish, R. G. W. Trans. Faraday Soc. 1939, 33, 1521.

36. Lamola, A. A.; Leemakers, P. A.; Byers, G. W.; Hammond, G. S. J. Am. Chem. Soc. 1965, 87, 2322.

37. Cowan, D. O.; Baum, A. A. J. Am. Chem. Soc. 1971, 93, 1153.

38. Ito, Y.; Kawatsuki, N.; Giri, B. P.; Yoshida, M.; Matsuura, T. J. Org. Chem. 1985, 50, 2893.

39. Scaiano, J. C.; Selwyn, J. C. Macromolecules 1981, 14, 1723.

40. a) Anderson, R. W.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. J. Chem. Phys.
1974, 61, 2500.
b) Wagner, P.J.; Kochevar I. J. Am. Chem. Soc. 1968, 90, 2232.

41. a) Winnik, M. A.; Hsiao, C. K. Chem. Phys. Lett. 1975, 33, 518.
b) Mar, A.; Fraser, S.; Winnik, M. A. J. Am. Chem. Soc. 1981, 103, 4941.

42. Shimada, K.; Shimozato, Y.; Szwarc, M. J. Am. Chem. Soc. 1975, 97, 5834.

43. Halpern, A. A.; Legenze, M. W.; Ramachandran, J. J. Am. Chem. Soc. 1979, 101, 5736.

44. Zachariasse, K.; Kuhnle, W. Z. Phys. Chem. (Frankfurt am Main) 1976, 101, 267.

45. Wagner, P. J.; Nakahira, T. J. Am. Chem. Soc. 1973, 95, 8474.

46. a) Wagner, P. J.; Giri, B. P.; Frerking, H. W. Jr.; DeFrancesco, J. J. Am. Chem. Soc.
1992, 114, 8326.
b) Wagner, P. J.; Frerking, H. W. Jr. Can. J. Chem. 1995, 73, 2047.

47. Wagner, P. J.; El-Taliawi, G. M. J. Am. Chem. Soc. 1992, 114, 8325.

48. Qiao, J. Unpublished results.

49. a) Forbes, M. D. E.; Closs, G. L.; Calle, P.; Gautam, P. J. Phys. Chem. 1993, 97, 3384.

b) Forbes, M. D. E.; Schulz, G. R. J. Am. Chem. Soc. 1994, 116, 10174.
c) Avdievich, N. I.; Forbes, M. D. E. J. Phys. Chem. 1995, 99, 9660.
d) Closs, G. L.; Forbes, M. D. E.; Piotrowiak, P. J. Am. Chem. Soc. 1992, 114, 3285.

- 50. a) Forbes, M. D. E.; Bhagat, K. J. Am. Chem. Soc. 1994, 115, 3382.
 b) Forbes, M. D. E. J. Phys. Chem. 1993, 97, 3390.
 c) Forbes, M. D. E. J. Phys. Chem. 1993, 97, 3396.
 d) Avdievich, N. I. J. Phys. Chem. 1996, 100, 1993.
- 51. Winnik, M. A. Chem. Rev. 1981, 81, 491.
- 52. Illuminati, G.; Mandolini, L. Acc. Chem. Res. 1981, 14, 95.
- 53. Stryer, L.; Haughland, R. P. Proc. Natl. Acad. Sci. 1967, 58, 720.
- 54. Baldwin, J. E.; Krueger, S. M. J. Am. Chem. Soc. 1969, 91, 6444.
- 55. Wagner, P. J.; Scheve, B. J. J. Am. Chem. Soc. 1979, 101, 378.
- 56. Illuminati, G.; Mandolini, L. Acc. Chem. Res. 1981, 14, 95.
- 57. Sisido, M. Macromolecules 1971, 4, 737.
- 58. Nairn, J. A.; Braun, C. L. J. Chem. Phys. 1981, 74, 2441.
- 59. Fraser, S. J.; Winnik, M. A. J. Chem. Phys. 1981, 75, 4683.
- 60. Fraser, S. J.; Saunders, D. S.; Winnik, M. A. Eur. Polym. J. 1983, 19, 991.

61. Flory, P. J. "Statistical Mechanics of Chain Molecules"; Wiley-Interscience; New York, 1969.

- 62. Sisido, M.; Shimada, K. J. Am. Chem. Soc. 1977, 99, 7785.
- 63. Shimada, K.; Shimozato, Y.; Szwarc, M. J. Am. Chem. Soc. 1975, 97, 5834.
- 64. a) Shimada, K.; Szwarc, M. J. Am. Chem. Soc. 1975, 97, 3313.
 b) Shimada, K.; Szwarc, M. J. Am. Chem. Soc. 1975, 97, 3321.
- 65. Closs, G. L.; Forbes, M. D. E.; Piotrowiak, P. J. Am. Chem. Soc. 1992, 114, 3285.
- 66. Wagner, P. J. Acc. Chem. Res. 1971, 4, 168.
- 67. Wagner, P. J.; Kelso, P. A.; Zepp, R. G. J. Am. Chem. Soc. 1972, 94, 7480.

68. Wagner, P. J.; Kemppainen, A. E. J. Am. Chem. Soc. 1968, 90, 5896.

69. Stern, O.; Volmer, M. Physik Z. 1919, 20, 183.

70. Wagner, P. J.; Jelinek, T.; Kemppainen, A. E. J. Am. Chem. Soc. 1972, 94, 7512.

71. Greene, F. D.; Savitz, M. L.; Osterholtz, F. D.; Lau, H. H.; Smith, W. N.; Zanet, P. M. J. Org. Chem. 1963, 28, 55.

72. Wagner, P.J.; Kochevar I. J. Am. Chem. Soc. 1968, 90, 2232.

73. Wagner, P. J.; Kochevar, I. E.; Kemppainen, A. E. J. Am. Chem. Soc. 1972, 94, 7489.

74. Scaiano, J. C.; Leigh, W. J.; Meador, M. A.; Wagner, P. J. J. Am. Chem. Soc. 1985, 107, 5806.

75. Frerking, H. W. Ph.D. Dissertation, Michigan State University, 1978.

76. Wagner, P. J.; Thomas, M. J.; Harris, E. J. Am. Chem. Soc. 1976, 98, 7675.

77. Kearns, D. R.; Case, W. A. J. Am. Chem. Soc. 1966, 88, 5087.

78. Gallivan, J. B. Can. J. Chem. 1972, 50, 3601.

79. Marchetti, A. P.; Kearns, D. R. J. Am. Chem. Soc. 1967, 89, 768.

80. Estimated from $E_T = 64$ kcal/mol for 4-hydroxybiphenyl: Taylor, H. V.; Allred, A. L.; Hoffman, B. M. J. Am. Chem. Soc. **1973**, 95, 3215.

81. "Handbook of Photochemistry"; Murov, S. L.; Carmichael, I.; Hug, G. L., Eds.; Marcel Dekker, Inc.: New York, 1993.

82. Kochevar, I.; Wagner, P. J. J. Am. Chem. Soc. 1972, 94, 3859.

83. Wolf, M. W.; Brown, R. E.; Singer, L. A. J. Am. Chem. Soc. 1977, 99, 526.

84. a) Keller, R. A.; Dolby, L. J. J. Am. Chem. Soc. 1969, 91, 1293.
b) Breen, D. E.; Keller, R. A. J. Am. Chem. Soc. 1968, 90, 1935.

85. Shimada, K.; Shimozato, Y.; Szwarc, M. J. Am. Chem. Soc. 1975, 97, 5834, and references therain.

86. a) Forbes, M. D. E.; Closs, G. L.; Calle, P.; Gautam, P. J. Phys. Chem. 1993, 97, 3384.

b) Forbes, M. D. E.; Schulz, G. R. J. Am. Chem. Soc. 1994, 116, 10174.

c) Avdievich, N. I.; Forbes, M. D. E. J. Phys. Chem. 1995, 99, 9660.

- 87. a) Closs, G. L.; Forbes, M. D. E.; Piotrowiak, P. J. Am. Chem. Soc. 1992, 114, 3285.
 b) Avdievich, N. I.; Forbes, M. D. E. J. Phys. Chem. 1995, 99, 9660.
- 88. Sisido, M.; Shimada, K. J. Am. Chem. Soc. 1977, 99, 7785.
- 89. Wagner, P.J.; Kochevar I. J. Am. Chem. Soc. 1968, 90, 2232.
- 90. Anderson, R. W.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. J. Chem. Phys. 1974, 61, 2500.

91. Saltiel, J.; Shannon, P. T.; Zafiriou, O. C.; Uriarte, A. K. J. Am. Chem. Soc. 1980, 102, 6799.

77

- 92. Illuminati, G.; Mandolini, L. Acc. Chem. Res. 1981, 14, 95.
- 93. Wagner, P. J.; Scheve, B. J. J. Am. Chem. Soc. 1979, 101, 378.
- 94. a) Terenin, A.; Ermolayev, V. Trans. Faraday Soc. 1956, 52, 1042.
 b) Ermolaev, V. L. Sov. Physics, Doklady 1967, 6, 600.

95. Mark, J. E.; Flory, P. J. J. Am. Chem. Soc. 1966, 88, 3702.

96. a) Goodman, J. M.; Hoffmann, H. M. R.; Vinter, J. G. Tetrahedron Lett. 1995, 36, 7757.

b) Vinter, J. G.; Hoffmann, H. M. R. J. Am. Chem. Soc. 1974, 96, 5466.

97. a) Chattoraj, M.; Bal, B.; Closs, G. L.; Levy, D. H. J. Phys. Chem. 1991, 95, 9666.
b) Chattoraj, M.; Paulson, B.; Shi, Y.; Closs, G. L.; Levy, D. H. J. Phys. Chem. 1993, 97, 13046.

98. Mutz, M. W.; MccLendon, G. L; Wishart, J. F.; Gaillard, E. R.; Corin, A. F. Proc. Natl. Acad. Sci. USA, 1996, 93, 9521.

99. a) Wagner, P. J. J. Am. Chem. Soc. 1967, 89, 2820.
b) Takei, Y.; Yamaguchi, T.; Osamura, Y.; Fuke, K.; Kaya, K. J. Phys. Chem. 1988, 92, 577.

c) Hutchison Jr., C. A.; Kemple, M. D. J. Chem. Phys. 1979, 71, 866.

100. a) Sigman, M. E.; Closs, G. L. J. Phys. Chem. 1991, 95, 5012.
b) Miller, J. R.; Paulson, B. P.; Bal, R.; Closs, G. L. J. Phys. Chem. 1995, 99, 6923.

101. Mirbach, M. F.; Ramamurthy, V.; Mirbach, M. J.; Turro, N. J.; Wagner, P. J. Nouv. J. Chim. **1980**, *4*, 471.

102. Harcourt, R. D.; Ghiggino, K. P.; Scholes, G. D.; Speiser, S. J. Chem. Phys. 1996, 105, 1897.

103. a) Katritzky, A. R.; Topsom, R. D. Chem. Rev. 1977, 77, 639.
b) Topsom, R. D. Acc. Chem. Res. 1983, 16, 292.
c) Wolf, C.; König, W. A.; Roussel, C. Liebigs Ann. Chem. 1995, 781.
d) Wolf, C.; Hochmuth, D. H.; König, W. A.; Roussel, C. Liebigs Ann. Chem. 1996, 357.

104. Greene, F. D.; Savitz, M. L.; Osterholtz, F. D.; Lau, H. H.; Smith, W. N.; Zanet, P. M. J. Org. Chem. 1963, 28, 55.

105. Axiotis, G. P.; Gauthier, R.; Chastrette, M. J. Organometal. Chem. 1979, 166, 87.

106. Wu, T.-C.; Xiong, H.; Riecke, R. D. J. Org. Chem. 1990, 55, 5045.

107. Rothman, L. D.; Crouch, S. R.; Ingle Jr., J. D. Anal. Chem. 1975, 47, 1226.

108. Ghoshal, S. K. Bull. Chem. Soc. Jpn. 1981, 54, 3556.

109. Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenbery, R. J. Am. Chem. Soc. 1967, 89, 5466.

110. Marchetti, A. P.; Kearns, D. R. J. Am. Chem. Soc. 1967, 89, 768.

111. Estimated from $E_T = 64$ kcal/mol for 4-hydroxybiphenyl: Taylor, H. V.; Allred, A. L.; Hoffman, B. M. J. Am. Chem. Soc. **1973**, 95, 3215.

112. DeFranesco, J. V.; Ph.D. Dissertation; Michigan State University; 1992.

113. Moses, F. G.; Liu, R. S. H.; Monroe, B. M. Mol. Photochem. 1969, 1, 245.

114. Wagner, P. J.; Kochevar, I. E.; Kemppainen, A. E. J. Am. Chem. Soc. 1972, 94, 7489.
