SYNTHESIS AND PHOTOCHEMISTRY OF 3,5-DIALKYL-3,5-DIHYDRO-3,5-DIPHENYL-4H-PYRAZOL-4-ONES

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ABSTRACT

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Oxyallyls have been proposed as reactive intermediates in a number of classical organic reactions. Nevertheless, the nature of the electronic ground state of oxyallyls (singlet or triplet state) remains unclear. In this connection, the photochemistry of trans-3,5-dihydro-3,5-dimethyl-3,5-diphenyl-4H-pyrazol-4-one (trans-1a) as a source of 2,4-diphenyl-3-pentanone-2,4-diyl (1,3-dimethyl-1,3-diphenyloxyallyl, DMDPOXA) was studied in both steady state and transient experiments.

According to the photophysical data, trans-1a has the lowest excited triplet state. One pathway of its decomposition is the expulsion of nitrogen forming the triplet DMDPOXA (T-DMDPOXA). T-DMDPOXA was observed in the femtosecond TR UV-VIS spectra of trans-1a and its lifetime estimated. Subsequent ISC in the T-DMDPOXA leads to the singlet DMDPOXA with the zwitterionic nature (S-DMDPOXA). The zwitterionic S-DMDPOXA was observed in the femtosecond TR UV-VIS spectra of trans-1a in carbon tetrachloride-methanol. The lifetime of the zwitterionic oxyallyl (S-DMDPOXA) was estimated for the first time.

Disrotatory ring closure of the S-DMDPOXA leads to cis and trans-2,3-dimethyl-2,3-diphenylcyclopropanone (cis and trans-14). The formation of cis and trans-14, phenyldiazoethane (13) and phenylmethylketene (7) was confirmed by the nanosecond TRIR spectroscopy during the photodecomposition of trans-1a. Disrotatory ring opening of cis and trans-14 with subsequent controtary electrocyclic ring closure forms 8. The hydrogen in 8 leads to 9, which then forms cis and trans-1,3-dimethyl-1-phenyl-2-indanone (cis and trans-10) by the keto-enol tautomerisation.

The products of the retro-1,3-dipolar cycloaddition of the excited triplet state of trans-1a (another pathway of decomposition): 7 and 13 were observed in the nanosecond TRIR spectra. Similar fragmentation was observed for trans-4,5-dihydro-3,5-dimethyl-3,5-diphenyl-3H-pyrazol-4-ol (trans-2a) forming 13 in the TRIR spectra.
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To my wife, my parents and my Moscow family
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER 1. INTRODUCTION</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Non-Kekulé molecules</td>
<td>1</td>
</tr>
<tr>
<td>Oxyallyls</td>
<td>2</td>
</tr>
<tr>
<td>Experimental attempts to observe oxyallyls</td>
<td>4</td>
</tr>
<tr>
<td>Project goals</td>
<td>7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER 2. STEREOSELECTIVE SYNTHESIS OF CIS AND TRANS-3,5-DIALKYL-3,5-DIHYDRO-3,5-DIPHENYL-4H-PYRAZOL-4-ONE</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>12</td>
</tr>
<tr>
<td>Synthesis of 3,5-dialkyl-3,5-dihydro-3,5-diphenyl-4H-pyrazol-4-ones</td>
<td>13</td>
</tr>
<tr>
<td>Absorption properties of cis and trans-3,5-dialkyl-3,5-dihydro-3,5-diphenyl-4H-pyrazol-4-ones</td>
<td>16</td>
</tr>
<tr>
<td>Discussion</td>
<td>17</td>
</tr>
<tr>
<td>Synthetic procedures</td>
<td>18</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER 3. PHOTOCHEMISTRY OF TRANS-3,5-DIHYDRO-3,5-DIMETHYL-3,5-DIPHENYL-4H-PYRAZOL-4-ONE</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photochemistry of 4,5-dihydro-3,5-dimethyl-(cis and trans-3,5-diphenyl)-3H-pyrazol-4-ol (cis and trans-2a)</td>
<td>33</td>
</tr>
</tbody>
</table>
Absorption and emission properties of cis and trans-2a .................. 33

Direct irradiation and triplet sensitization of cis and trans-2a
(spin correlation effect) ............................................................... 37

Spectroscopy and photophysical properties of trans-3,5-dihydro-3,5-dimethyl-
-3,5-diphenyl-4H-pyrazol-4-one (trans-1a) ....................................... 44

Absorption properties of cis and trans-1a ........................................ 44

Emission properties of trans–1a .................................................... 47

Direct irradiation and triplet sensitization of trans-1a ....................... 51

UV-VIS spectroscopy in the steady state photolysis of trans-1a.
Observation of long-lived 8 in the UV-VIS spectra .......................... 53

IR spectroscopy during the steady state photolysis of trans-1a.
Observation of 8 in the infrared spectra ......................................... 55

$^1$H NMR spectroscopy in the steady state photolysis of trans-1a.
Observation of 8 in the $^1$H NMR spectra .................................... 58

Isolation of cis and trans-10 ....................................................... 61

Isolation of cis and trans-6 ....................................................... 61

Quantum yield of photodecomposition of trans-3,5-dihydro-3,5-dimethyl-
-3,5-diphenyl-4H-pyrazol-4-one (trans-1a) and 4,5-dihydro-3,5-dimethyl-
-(trans-3,5-diphenyl)-3H-pyrazol-4-ol (trans-2a) ............................. 62
CHAPTER 4. TIME-RESOLVED IR AND UV-VIS STUDIES OF TRANS-1A

Introduction........................................................................................................67

Results..................................................................................................................67

Nanosecond time-resolved FTIR studies.........................................................67

Nanosecond time-resolved UV-VIS studies.....................................................74

Nanosecond time-resolved UV-VIS studies at 77 K......................................76

Femtosecond time-resolved UV-VIS studies..................................................79

Discussion...........................................................................................................85

Conclusions.........................................................................................................90

EXPERIMENTAL SECTION.................................................................................92

General..............................................................................................................92

Materials............................................................................................................92

Nanosecond infrared time-resolved (TRIR) experiments..............................93

Nanosecond UV-VIS time-resolved (TR UV) experiments...........................93
Femtosecond UV-VIS time-resolved (TR UV) experiments…………………93

Time-resolved emission experiments…………………………………….94

Matrix IR experiments…………………………………………………...94

DFT calculations…………………………………………………………94

REFERENCES……………………………………………………………………….95

APPENDIX A. SUPPORTING INFORMATION FOR CHAPTER 2………………105

APPENDIX B. SUPPORTING INFORMATION FOR CHAPTER 3………………131

APPENDIX C. SUPPORTING INFORMATION FOR CHAPTER 4………………149
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1. Absorption spectrum of <em>trans-1c</em> in acetonitrile at 298 K</td>
<td>16</td>
</tr>
<tr>
<td>2.2. Absorption spectrum of <em>cis-1b</em> in acetonitrile at 298 K</td>
<td>17</td>
</tr>
<tr>
<td>3.1. UV-VIS spectrum of <em>cis-2a</em> in acetonitrile at 298 K</td>
<td>33</td>
</tr>
<tr>
<td>3.2. UV-VIS spectrum of <em>trans-2a</em> in acetonitrile at 298 K</td>
<td>34</td>
</tr>
<tr>
<td>3.3. UV-VIS spectrum of <em>trans-2a</em> in acetonitrile at 298 K (red). 77 K emission spectrum of <em>trans-2a</em> in 4:1 ethanol/methanol after a 337 nm laser pulse (blue)</td>
<td>34</td>
</tr>
<tr>
<td>3.4. Kinetic trace of 450 nm of time-resolved emission from excited state of <em>trans-2a</em> in 4:1 ethanol/methanol at 77 K after a 337 nm laser pulse</td>
<td>35</td>
</tr>
<tr>
<td>3.5. Time-resolved emission spectral evolution of <em>trans-2a</em> in 4:1 ethanol/methanol at 77 K after a 337 nm laser pulse</td>
<td>36</td>
</tr>
<tr>
<td>3.6. 77 K emission spectra of <em>trans-2a</em> in 4:1 ethanol/methanol measured 60 ns (■) and 1100 ns (■) after a 337 nm laser pulse. 77 K emission spectrum of <em>trans-2a</em> in 4:1 ethanol/methanol with 337 nm excitation (■)</td>
<td>36</td>
</tr>
<tr>
<td>3.7. Time evolution of UV-VIS spectra of <em>trans-2a</em> in carbon tetrachloride acquired after a 350 nm irradiation (0- 5 min.)</td>
<td>44</td>
</tr>
<tr>
<td>3.8. Absorption spectrum (red) and emission spectrum (blue) of <em>cis-1a</em> in acetonitrile at 298 K</td>
<td>45</td>
</tr>
<tr>
<td>3.9. Absorption spectrum (red) and emission spectrum (blue) of <em>trans-1a</em> in acetonitrile at 298 K</td>
<td>46</td>
</tr>
</tbody>
</table>
3.10. Absorption spectrum of *trans-1a* in acetonitrile at 298 K (red). Emission spectrum of *trans-1a* in acetonitrile at 298 K (green). 77 K emission spectrum of *trans-1a* in 4:1 ethanol/methanol with 360 nm excitation (blue)........................................48

3.11. Kinetic trace of 520 nm of time-resolved emission from *trans-1a* in 4:1 ethanol/methanol at 77 K after a 360 nm laser pulse.................................................................49

3.12. 77 K time-resolved emission spectral evolution of *trans-1a* in 4:1 ethanol/methanol after a 360 nm laser pulse (60 J/pulse).................................................................50

3.13. 77 K emission spectra of *trans-1a* in 4:1 ethanol/methanol measured 10 ns (■) and 100 ns (●) after a 360 nm laser pulse (60 J/pulse). 77 K emission spectrum of *trans-1a* in EPA with 360 nm excitation (▼)........................................50

3.14. Time evolution of UV-VIS spectra of *trans-1a* in carbon tetrachloride acquired after a 350 nm irradiation (0-5 min.).................................................................53

3.15. UV-VIS spectra of *trans-10* and *trans-1a*........................................................................................................54

3.16. Time evolution of UV-VIS spectra of *trans-1a* in methanol acquired after a 350 nm irradiation (0-50 min.).................................................................55

3.17. Time evolution of infrared spectra of *trans-1a* in carbon tetrachloride acquired after a 350 nm irradiation (0-60 min.).................................................................56

3.18. Time evolution of infrared spectra of *trans-1a* in acetonitrile acquired after a 350 nm irradiation (0-150 min.).................................................................56

3.19. Time evolution of infrared spectra of *trans-1a* in acetonitrile acquired after a 254 nm irradiation (0 - 35 min.).................................................................58

3.20. Ketonization of enol *11* forming cis and *trans-12*.................................................................60
4.1. Time-resolved FTIR difference spectra of \textit{trans-1a} in argon- and oxygen-saturated carbon tetrachloride acquired 2 \textit{\textmu}s after a 355 nm laser pulse………………..69

4.2. Kinetic traces of 1814 cm$^{-1}$, 2038 cm$^{-1}$ and 2102 cm$^{-1}$ of TRIR absorptions in compound \textit{trans-1a}…………………………………………………………………………69

4.3. Time-resolved FRIR difference spectra of \textit{trans-2a} in argon-saturated carbon tetrachloride taken 2 \textit{\textmu}s after a 355 nm laser pulse……………………………………………………72

4.4. Kinetic trace of 2041 cm$^{-1}$ of TRIR absorption in compound \textit{trans-2a}………………………………72

4.5. Transient UV-VIS spectra of \textit{trans-1a} acquired in argon-saturated carbon tetrachloride after a 355 nm laser pulse………………………………………………………75

4.6. Kinetic trace of 290 nm of transient UV-VIS absorption in compound \textit{trans-1a}…………..76

4.7. Transient UV-VIS spectra of excited triplet state of \textit{trans-1a} acquired after a 355 nm laser pulse………………………………………………………………………………77

4.8. Kinetic trace of 380 nm of transient UV-VIS absorption in compound \textit{trans-1a}……………..78

4.9. Kinetic trace of 520 nm of transient UV-VIS absorption in compound \textit{trans-1a}…………..78

4.10. Transient UV-VIS spectral evolution of \textit{trans-1a} in argon-saturated carbon tetrachloride after a 340 nm laser pulse…………………………………………………………79

4.11. Kinetic trace of 400 nm of transient UV-VIS absorption in the compound \textit{trans-1a} after a 340 nm laser pulse…………………………………………………………80

4.12. Transient UV-VIS spectral evolution of \textit{trans-1a} in argon-saturated acetonitrile after a 267 nm laser pulse (0 - 50 ps)…………………………………………………………..80
4.13. Transient UV-VIS spectral evolution of \textit{trans-1a} in argon-saturated acetonitrile
after a 267 nm laser pulse (50-1000 ps)………………………………………………………81

4.14. Kinetic trace of 400 nm of transient UV-VIS absorption in the compound
\textit{trans-1a} after a 267 nm laser pulse………………………………………………………81

4.15. Transient UV-VIS spectra of \textit{trans-1a} in carbon tetrachloride (red) and
in carbon tetrachloride:methanol (15:1 v/v)(blue) both acquired 60 ps after
a 340 nm laser pulse………………………………………………………………………………82

4.16. Transient UV-VIS spectral evolution of \textit{trans-1a} in carbon
tetrachloride: methanol (15:1 v/v) after a 340 nm laser pulse (0.5 - 510 ps)………………83

4.17. Kinetic trace of 652 nm of transient UV-VIS spectra in compound \textit{trans-1a}
in carbon tetrachloride:methanol (15:1 v/v) after a 340 nm laser pulse…………………...83

4.18. Photodecomposition of neat dispiro[5.1.5.1] tetradecane-7,14-dione……………….…….84

4.19. Lifetimes of excited triplet states of azo compounds in rigid glasses at 77 K
and in solution at 298 K………………………………………………………………………………85

B1. \textsuperscript{1}H NMR spectrum of \textit{trans-2a} in deuterated acetonitrile at 300 MHz
before irradiation at 350 nm (0.5 - 2.0 ppm region)………………………………………...131

B2. \textsuperscript{1}H NMR spectrum of \textit{trans-2a} in deuterated acetonitrile at 300 MHz
after irradiation for 10 minutes at 350 nm (0.5 - 2.0 ppm region)………………………131

B3. \textsuperscript{1}H NMR spectrum of \textit{trans-2a} in deuterated acetonitrile at 300 MHz
before irradiation at 350 nm (2.6 - 4.5 ppm region)………………………………………...132

B4. \textsuperscript{1}H NMR spectrum of \textit{trans-2a} in deuterated acetonitrile at 300 MHz
after irradiation for 10 minutes at 350 nm (2.6 - 4.5 ppm region)……………………………………132

B5. $^1$H NMR spectrum of cis-2a in deuterated acetonitrile at 300 MHz
before irradiation at 350 nm (1.0 - 2.1 ppm region)………………………………………………133

B6. $^1$H NMR spectrum of cis-2a in deuterated acetonitrile at 300 MHz
after irradiation for 5 minutes at 350 nm (1.0 - 2.0 ppm region)…………………………………133

B7. $^1$H NMR spectrum of cis-2a in deuterated acetonitrile at 300 MHz
before irradiation at 350 nm (3.4 - 4.5 ppm region)……………………………………………….134

B8. $^1$H NMR spectrum of cis-2a in deuterated acetonitrile at 300 MHz
irradiation for 5 minutes at 350 nm (3.4 - 4.5 ppm region)………………………………………134

B9. $^1$H NMR spectrum of trans-2a in deuterated acetonitrile at 300 MHz before
irradiation at 370 nm (1.0 - 2.0 ppm region)……………………………………………………..135

B10. $^1$H NMR spectrum of trans-2a in deuterated acetonitrile at 300 MHz
after irradiation for 14 hours at 370 nm (1.4 - 3.0 ppm region)……………………………………135

B11. $^1$H NMR spectrum of trans-2a in deuterated acetonitrile at 300 MHz
before irradiation at 350 nm (3.0 - 4.5 ppm region)………………………………………………136

B12. $^1$H NMR spectrum of trans-2a in deuterated acetonitrile at 300 MHz
after irradiation for 14 hours at 350 nm (3.0 - 4.6 ppm region)……………………………………136

B13. $^1$H NMR spectrum of cis-2a in deuterated acetonitrile at 300 MHz
before irradiation at 370 nm (1.4 - 3.0 ppm region)………………………………………………137

B14. $^1$H NMR spectrum of cis-2a in deuterated acetonitrile at 300 MHz
after irradiation for 4 hours at 370 nm (1.4 - 3.0 ppm region)……………………………………137
B15. $^1$H NMR spectrum of cis-$2a$ in deuterated acetonitrile at 300 MHz before irradiation
   at 370 nm (3.0 - 4.6 ppm region)……………………………………………………………..138

B16. $^1$H NMR spectrum of cis-$2a$ in deuterated acetonitrile at 300 MHz
   before irradiation at 370 nm (3.0 - 4.6 ppm region)……………………………………137

B17. $^1$H NMR spectrum of trans-$1a$ in deuterated acetonitrile at 300 MHz
   after irradiation at 350 nm for 3 hours…………………………………………………..139

B18. $^1$H NMR spectrum of trans-$1a$ in deuterated acetonitrile at 300 MHz
   after irradiation at 350 nm for 3 hours in the presence of DMBP (molar ratio 1:1)………139

B19. Time evolution of UV-VIS spectra of trans-$1a$ in acetonitrile acquired
   after a 254 nm irradiation (0-40 sec.)……………………………………………………140

B20. Time evolution of UV-VIS spectra of trans-$1a$ in acetonitrile acquired
   after a 350 nm irradiation (0-20 min.)……………………………………………………140

B21. Extinction coefficients of 5-methylene-1,3-cyclohexane (MCH)
   at various wavelengths……………………………………………………………………...141

B22. Infrared spectrum of solution of phenylethylketene in carbon tetrachloride……… 141

B23. $^1$H NMR spectrum of trans-$1a$ in deuterated acetonitrile at 300 MHz
   after irradiation at 254 nm for 10 minutes………………………………………………142

B24. $^1$H NMR spectrum in deuterated acetonitrile of trans-$1a$ at 300 MHz
   after irradiation at 254 nm for 10 minutes (10 minutes later)…………………………….143

B25. $^1$H NMR spectrum of trans-$1a$ in deuterated methanol at 300 MHz
   after irradiation at 350 nm for 1 hour………………………………………………………144
B26. $^1$H NMR spectrum of trans-1a in deuterated methanol at 300 MHz after irradiation at 350 nm for 1 hour (96 hours later)………………………………………………144

C1. Transient absorption spectrum of triplet propane-1,3-diyl diradical in heptane (266 nm excitation, 12 mJ/pulse; $\lambda_{\text{max}} = 320$ nm)…………………………………149

C2. Substituent effects on the lifetime of triplet 1-(4-acetylphenyl)-2-(4-substituted phenyl) propan-1,3-diyls…………………………………………………………149

C3. Transient UV-VIS spectra of trans-1a acquired in argon-saturated carbon tetrachloride after a 355 nm laser pulse………………………………………………150

C4. Kinetic trace of 290 nm of transient UV-VIS absorption in compound trans-1a………………150

C5. DR-anti,anti singlet UB3LYP/6-31G(d) C$_2$ Geometry………………………………………………151

C6. DR-anti,anti triplet UB3LYP/6-31G(d) C$_2$ Geometry…………………………………………………………152

C7. DR-anti,syn singlet UB3LYP/6-31G(d) C$_2$ Geometry……………………………………………………153

C8. DR-anti,syn triplet UB3LYP/6-31G(d) C$_2$ Geometry……………………………………………………154

C9. DR-syn,syn singlet UB3LYP/6-31G(d) C$_2$ Geometry…………………………………………………………155

C10. DR-syn,syn triplet UB3LYP/6-31G(d) C$_2$ Geometry……………………………………………………156
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1. Direct irradiation and triplet sensitization of <em>cis</em> and <em>trans</em>-2a at 350 nm</td>
<td>41</td>
</tr>
<tr>
<td>4.1. Experimental and calculated carbonyl frequencies of products in the photodecomposition of <em>trans</em>-1a</td>
<td>73</td>
</tr>
</tbody>
</table>
## LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1. Singlet and triplet states of oxyallyl.</td>
<td>3</td>
</tr>
<tr>
<td>1.2. Racemization of cis and trans-di-tert-butylcyclopropanones.</td>
<td>4</td>
</tr>
<tr>
<td>1.3. Photoinduced formation of cis-bicyclo[3.3.0]oxyallyl.</td>
<td>5</td>
</tr>
<tr>
<td>1.4. Irradiation of quadricyclanone with formation of 3-oxobicyclo[3.2.0] hept-6-ene-2,4-diyl.</td>
<td>6</td>
</tr>
<tr>
<td>1.5. Bicyclo[1.1.0]butan-2-ones.</td>
<td>7</td>
</tr>
<tr>
<td>1.6. Proposed photochemical generation of 1,3-dialkyl-1,3-diphenyl-2-propanone-1,3-diyl (DADPOXA).</td>
<td>8</td>
</tr>
<tr>
<td>1.7. Generation of 1,3-diphenyl-2-propanone-1,3-diyl [DADPOXA (R=H)].</td>
<td>9</td>
</tr>
<tr>
<td>1.8. Photodecomposition of 2,4-diakyl-2,4-diphenylcyclobutane-1,3-dione and proposed decomposition of 3,5-dialkyl-3,5-dihydro-3,5-diphenyl-4H-pyrazol-4-one.</td>
<td>10</td>
</tr>
<tr>
<td>1.9. Photodecomposition of 2,2,4,4-tetramethylcyclobutane-1,3-dione and 3,3,5,5-tertamethyl-3,5-dihydro-4H-pyrazol-4-one.</td>
<td>11</td>
</tr>
<tr>
<td>2.1. Retrosynthetic analysis of cis-1a, cis-1b and cis-1c.</td>
<td>12</td>
</tr>
<tr>
<td>2.2. Synthesis of cis-1b and cis-1a.</td>
<td>14</td>
</tr>
<tr>
<td>2.3. Synthesis of trans-1c.</td>
<td>15</td>
</tr>
</tbody>
</table>
3.1. Direct irradiation and triplet sensitization of trans-THP .........................................................38

3.2. Photodecomposition of trans-3,5-diphenyl-1-pyrazoline .........................................................39

3.3. Direct irradiation and triplet sensitization of cis and trans-2a .................................................40

3.4. Fragmentation of trans-2a during direct irradiation .................................................................43

3.5. Photodecomposition of trans-1a .............................................................................................52

3.6. Irradiation of trans-1a in deuterated methanol at 350 nm .......................................................59

3.7. Energy diagram of trans-1a ......................................................................................................63

3.8. Scheme of photodecomposition of trans-1a in the direct irradiation and
triplet sensitization .........................................................................................................................65

4.1. Photodecomposition of trans-1a .............................................................................................68

4.2. Photodecomposition of trans-2a .............................................................................................71

4.3. Singlet and triplet states of 2,4-diphenyl-2-pentanone-1,3-diyl
(S-DMDPOXA and T-DMDPOXA, respectively) .................................................................88

4.4. Photodecomposition of trans-3,5-diphenyl-1-pyrazoline .......................................................89
<table>
<thead>
<tr>
<th>Chart</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1. []-Conjugated non-Kekulé molecules</td>
<td>1</td>
</tr>
</tbody>
</table>
CHAPTER 1. INTRODUCTION

Non-Kekulé molecules

Non-Kekulé molecules have been of interest for theoretical and experimental organic chemists for over 100 years (Chart 1.1).\(^1\) Schlenck and Brauns synthesized the first non-Kekulé molecule (tetraphenyl derivative of \(m\)-benzoquinodimethane) in 1915. These compounds are comprised of molecules with even numbers of electrons but no classical closed shell structure (classical Kekulé structures) can be written for them. While theoretical chemists can predict the nature of the ground state (singlet or triplet) of these molecules and the energy difference between the ground state and the first excited state using computational methods, experimental chemists must confirm these predictions. Depending on the nature of the lowest spin ground state and the energy difference between the ground state and the first excited state, non-Kekulé molecules show different physical and chemical properties. These molecules can be used as functional materials with interesting magnetic, optical and electronic properties.

\textbf{Chart 1.1}. \(\pi\)-Conjugated non-Kekulé molecules.

\begin{center}
\begin{tabular}{c c c}
\textbf{m-Benzozquinodimethane (MBQDM)} & \textbf{Trimethyleneethane (TMM)} & \textbf{Tetramethyleneethane (TME)} \\
\textbf{Schlenck and Brauns} & \textbf{Dowd 1966} & \textbf{Dowd 1970} \\
1915 & & \\
\end{tabular}
\end{center}

\begin{center}
\begin{tabular}{c c c}
\textbf{2,4-Dimethylene cyclobutane-1,3-diyli (DMCBD)} & \textbf{Oxallyl (OXA)} & \textbf{Dialkylidiphenyloxallyl (DMDPOXA)} \\
\textbf{Dougherty 1985} & & \textbf{Dowd and Paik 1986} \\
& & \\
\end{tabular}
\end{center}
Oxyallyls

Trimethylenemethane (TMM) is one of the best studied and computed non-Kekulé molecules (Chart 1.1).\(^1\) The substitution of O for one of the CH\(_2\) groups in TMM leads to the non-Kekulé molecule called “oxyallyl”. Oxyallyls have been proposed as reactive intermediates in a number of classical organic reactions: \(^2\)-\(^4\)

1) **Favorskii rearrangement (Wallach degradation):** Reaction of \(\text{-}\)-chloroketones with sodium hydroxide to form esters or carboxylic acids. This reaction was used in the synthesis of \((\text{+})\)-iridomycin.\(^{2b}\)

2) **[3+2]- and [4+3]-cycloaddition of oxyallyls:** Reaction of \(\text{-}\text{-}\text{-}\)-dibromoketones with diiron nonacarbonyl \(\text{Fe}_2(\text{CO})_9\) to produce an iron stabilized oxyallyl zwitterion, which reacts with alkenes or dienes to produce cyclic ketones (Noyori annulation). Noyori annulation was used in the synthesis of tropane alkaloids\(^{3c}\) and phorbol.\(^{3d}\) Also, other ways to generate oxyallyls were used in the [4+3]-cycloaddition reactions of oxyallyls with dienes to afford biologically active compounds: \((\text{+})\)-dactylo,\(^{3e}\) \((-\text{-})\)-colchicine,\(^{3f}\) taxol derivatives.\(^{3h}\)

3) **Nazarov cyclization:** The protic- or Lewis acid catalyzed cyclization of divinyl ketones via pentadienylic cations (zwitterionic oxyallyls). Stereospecific electrocyclic Nazarov cyclization found application in the synthesis of various natural products and biologically active compounds, for example, Hardings’ synthesis of \((\pm)\)-trichodiene,\(^{4a}\) Miesch’s synthesis of \((\pm)\)-silphinene\(^{4b}\) and Cheng’s synthesis of inverto-yuehchukene.\(^{4c}\)

4) **Photochemical rearrangement of cyclohexadienones:** Irradiation of 4,4\(\text{-}\)-substituted 2,5-cyclohexadien-1-ones led to zwitterionic oxyallyl with subsequent formation of bicyclo[3.1.0]hexan-3-en-2-ones.

Oxyallyls have also been proposed as intermediate species in the rearrangement of vinyl allene oxides (\(\tau_{1/2} = 20\) s at 298 K and pH=7.4)\(^{6c}\) to cyclopent-2-ene-ones in the biosynthesis of prostaglandins.\(^6\) The theoretical studies show that rearrangement of several vinyl allene oxides to cyclopent-2-ene-1-ones proceeds stepwise via biradical/zwitterionic oxyallyls.\(^{6d}\)

Understanding the nature and the reactivity of oxyallyls means finding an explanation for the mechanisms of classic organic reactions, predicting new synthetic reactions and transformations and finding out the mechanism of metabolism of lipids in plants and corals. However, the nature of the electronic ground state of oxyallyls (singlet or triplet state) and their
reactivity (diradical or zwitterion) remain unclear. There is only one report about the direct spectroscopic observation of oxyallyls.\textsuperscript{7}

Two singlet states ($^1A_1$ and $^1B_2$) and the triplet state ($^3B_2$) are the lowest electronic states of oxyallyl (Scheme 1.1).\textsuperscript{1c} It has been proposed that the $^1A_1$ state should be lower in energy as compared with the $^3B_2$ state, since it has a higher degree of C=O $\pi$-bonding. However, some calculations predict that the $^1A_1$ and $^3B_2$ states of oxyallyl are isoenergetic.\textsuperscript{8}

\textit{Scheme 1.1}. Singlet and triplet states of oxyallyl.

The $^1B_2$ state should be less stable than $^1A_1$ and $^3B_2$ states, because the $^1B_2$ state has no C=O $\pi$-bonding. The $^1A_1$ state can have either a diradical or zwitterionic nature. Borden\textsuperscript{9} calculated the solvent effect on the ring opening of cyclopropanone and concluded that the $^1A_1$ state is better described as a diradical rather than zwitterion. These data were in agreement with experimental results.\textsuperscript{10} However, substitution on the $\pi$-carbons of oxyallyl with alkyl groups lowers the energy of the $^1A_1$ state in comparison with the $^3B_2$ state.\textsuperscript{1c,1d} The ground state of $\alpha,\alpha'$-substituted oxyallyls ($^1A_1$) has zwitterionic character with reduced double bond character in the carbonyl group. As a result, the calculated carbonyl frequency of tetramethyl substituted oxyallyl (1670 cm$^{-1}$) is lower than the calculated carbonyl frequency of the parent oxyallyl (1730 cm$^{-1}$).\textsuperscript{1d} Similarly, Hess\textsuperscript{11} calculated the frequencies for several non-benzenoid oxyallyls and found that their ground states are singlet states ($^1A_1$) with zwitterion character rather than diradical character.
Experimental attempts to observe oxyallyls

Green\textsuperscript{10} found that trans-2,3-di-\textit{tert}-butylcyclopropanone undergoes thermal racemization (Scheme 1.2). Efforts to trap intermediate oxyallyl in the stereomutation of trans-2,3-di-\textit{tert}-butylcyclopropanone were not successful. Sorensen and Sun\textsuperscript{12} reported that cis-2,3-di-\textit{tert}-butylcyclopropanone thermally rearranges to trans-2,3-di-\textit{tert}-butylcyclopropanone.

\textit{Scheme 1.2.} Racemization of cis- and trans-di-\textit{tert}-butylcyclopropanones.

Oxyallyls were also proposed as intermediates in the rearrangement of the highly unstable allene oxides. 1,3-Di-\textit{tert}-butylallene oxide undergoes thermal conversion to trans-2,3-di-\textit{tert}-butylcyclopropanone.\textsuperscript{13} Likewise, the photochemically generated fluorenylideneallene oxide rearranges to produce the corresponding cyclopropanone.\textsuperscript{14} It was found that the rate of fluorenylideneallene oxide conversion depends on the polarity of the medium. Therefore, it was proposed that the corresponding oxyallyl has zwitterionic character. All these experimental data strongly suggest oxyallyls as intermediates.

One way to stabilize an oxyallyl relative to cyclopropanone is to hinder its ring closure using bulky alkyl groups at the a-carbons. In this case, the cyclopropanones formed are expected to be highly strained and their energy will be higher than the energy of corresponding oxyallyls. Consequently, several sterically congested cis-2,3-dialkycyclopropanones\textsuperscript{15} were synthesized.
However, the equilibrium concentration of oxyallyls in these experiments was so low that no direct spectroscopic observation of oxyallyls was possible.

Another possible way to stabilize an oxyallyl is to confine it within a four- or five-membered ring.\textsuperscript{16} Irradiation of cycloocta-2,7-dienone leads to \textit{cis}-bicyclo[3.3.0]oxyallyl (oxyallyl confined with a five-membered ring) (Scheme 1.3). The oxyallyl was trapped with methanol, ethyl vinyl ether, alkenes and furan.\textsuperscript{17} These trapping experiments prove that the oxyallyl intermediate is formed during the irradiation of cycloocta-2,7-dienone. Calculations predict that the \textit{1}A\textsubscript{1} and \textit{3}B\textsubscript{2} states of this oxyallyl are the degenerate states. The energy of the \textit{3}B\textsubscript{2} state is only 0.8 kcal/mole lower than that of the \textit{1}A\textsubscript{1} state. However, trapping experiments suggest that this oxyallyl has a zwitterionic nature. The authors believe that this oxyallyl is a polarized singlet diradical (\textit{1}A\textsubscript{1}) rather than a zwitterion.

\textit{Scheme 1.3.} Photoinduced formation of \textit{cis}-bicyclo[3.3.0]oxyallyl.\textsuperscript{16}

In another study of an oxyallyl confined to a five-membered ring, irradiation of tetracyclo[3.2.0.0\textsubscript{2},7.04,6]heptanone (quadricyclanone) gave 3-oxobicyclo[3.2.0]hept-6-ene-2,4-diyd (Scheme 1.4). This oxyallyl was trapped with methanol, ethyl vinyl ether and furan.\textsuperscript{7a} It was
assumed that the ground state of this oxyallyl is a singlet state (EPR silent) having a diradical nature rather than zwitterionic.

**Scheme 1.4.** Irradiation of quadricyclanone with formation of 3-oxobicyclo[3.2.0]hept-6-ene-2,4-diyd.

Recently, in a study of oxyallyl confined to a four-membered ring, single crystal X-ray diffraction studies were performed with 1,3-substituted bicyclo[1.1.0]butan-2-ones (Scheme 1.5). These experiments showed that these compounds have interesting bonding features: an extremely long C1-C3 bond and short C1-C2 and C2-C3 bonds. These features were attributed to the oxyallyl-cyclopropanone manifold.\(^\text{18}\)
Thus, the available theoretical and experimental data suggest that the ground states of oxyallyls are singlet states ($^1A_1$) of diradical or zwitterionic nature. No experimental observations of triplet states of oxyallyls ($^3B_2$) were reported.

**Project goals**

Oxyallyl is too short-lived to be observed in steady state experiments. Our objective in this work was to extend the lifetime of oxyallyl through structural modifications and to study the nature and reactivity of this modified oxyallyl using transient spectroscopies.

The first step was to stabilize the radical sites of oxyallyl using aromatic rings and alkyl groups, instead of confining the radical sites or substituting bulky groups at $\alpha$-carbons of oxyallyl. These modifications were meant to be able to extend the lifetime of oxyallyl (Chart 1.1). It was expected that the steric hindrance between the aromatic rings and the alkyl groups in the resulting 1,3-dialkyl-1,3-diphenyl-2-propanone-1,3-diyl (DADPOXA) would hinder the ring closure.

The next step was to synthesize a precursor, which upon laser flash photolysis would produce the DADPOXA (Scheme 1.6). The generated DADPOXA could be observed using transient IR or UV-VIS spectroscopies. Depending on the nature of the excited state of the precursor, decomposition of its excited singlet state would lead to the singlet state of the DADPOXA ($^1A_1$) with the diradical nature (OXA-DR) or the zwitterionic nature (OXA-ZW), while decomposition of its excited triplet state would produce the triplet state of DADPOXA ($^3B_2$). Thus, the $^3B_2$ state of DADPOXA would undergo intersystem crossing (ISC) producing...
the $^1A_1$ state of DADPOXA. The ground state of DADPOXA should probably be a singlet state ($^1A_1$) of zwitterionic nature (OXA-ZW) rather than a diradical nature (OXA-DR). However, the $^1A_1$ and the $^3B_2$ states of DADPOXA might also be isoenergetic states.

**Scheme 1.6.** Proposed photochemical generation of 1,3-dialkyl-1,3-diphenyl-2-propanone-1,3-diyl (DADPOXA).

Several possible precursors of DADPOXA were investigated. 1,3-Diphenyl-2-propanone-1,3-diyl [DADPOXA (R=H)] was proposed as a reactive intermediate in the reaction of 1,3-dibromo-1,3-diphenyl-2-propanone with Fe$_2$(CO)$_9$ producing 1-phenyl-2-indanone (Scheme 1.7).\textsuperscript{3b} The DADPOXA (R=H) was trapped with furan, indicating that the ground state of this oxyallyl is a singlet state of zwitterionic nature. However, DADPOXA (R=H) cannot be produced photochemically from 1,3-dibromo-1,3-diphenyl-2-propanone because its photodebromination is a stepwise process.\textsuperscript{19} That is why 1,3-dialkyl-1,3-dibromo-1,3-diphenyl-2-propanones could not be used as photochemical precursors for DADPOXA.
Scheme 1.7. Generation of 1,3-diphenyl-2-propanone-1,3-diyl [DADPOXA (R=H)].

Other possible precursors of DADPOXA are 2,4-dialkyl-2,4-diphenylcyclobutane-1,3-diones (Scheme 1.8). Photodecomposition of 2,4-diethyl-2,4-diphenylcyclobutane-1,3-dione (R = Et) led to a mixture of cis and trans-1,3-diethyl-1-phenyl-2-indanones (R = Et).²⁰ It was proposed that photodecomposition of the starting compound by Norrish type I [α]-cleavage with subsequent expulsion of carbon monoxide leads to a 3,5-diphenyl-4-heptanone-3,5-diyl [DADPOXA (R = Et)]. The DADPOXA (R=Et) forms cis and trans-1,3-diethyl-1-phenyl-2-indanones (R = Et).
However, undesired fragmentation of the starting compound to give phenylethylketene substantially decreased the yield of DADPOXA (R = Et) and this fragmentation reaction needed to be eliminated. Photodecomposition of the similar 2,2,4,4-tetramethylcyclobutane-1,3-dione led to 2,4-dimethyl-2-pentanone-2,4-diyl (tetramethyl oxyallyl) with subsequent ring closure to form 2,2,3,3-tetramethylcyclopropanone and dimethylketene (30 % fragmentation) (Scheme 1.9). Subsequently the decarbonylation of 2,2,3,3-tetramethylcyclopropanone gave 2,3-dimethyl-2-butene. However, photodecomposition of bichromic 3,3,5,5-tetramethyl-4H-pyrazol-4-one (λ > 300 nm or 185 nm) produced 2,2,3,3-tetramethylcyclopropanone as a major product. 22 2,2,3,3-Tetramethylcyclopropanone rearranged to produce 2,3-dimethyl-2-butene (300 nm irradiation) or 2,4-dimethylpent-1-en-3-one (185 nm irradiation). Therefore, the
photodecomposition of bichromic 3,3,5,5-tetramethyl-3,5-dihydro-4H-pyrazol-4-one leads to a more predominant expulsion of nitrogen rather than carbon monoxide producing mostly tetramethyl oxyallyl with a small amount of fragmentation products.

**Scheme 1.9.** Photodecomposition of 2,2,4,4-tetramethylcyclobutane-1,3-dione and 3,3,5,5-tertamethyl-3,5-dihydro-4H-pyrazol-4-one.

The photodecomposition of the similar bichromic 3,5-dialkyl-3,5-dihydro-3,5-diphenyl-4H-pyrazol-4-ones should also lead to a more predominant formation of the desired DADPOXA (Scheme 1.8). The photochemistry of these compounds has not been studied and cis and trans-3,5-dihydro-3,5-dimethyl-3,5-diphenyl-4H-pyrazol-4-ones\(^{23}\) (R = CH\(_3\)) are the only known cis and trans-3,5-dialkyl-3,5-diaryl-3,5-dihydro-4H-pyrazol-4-ones. Thus, the challenge is to develop the synthesis and to study the photochemistry of cis and trans-3,5-dialkyl-3,5-dihydro-3,5-diphenyl-4H-pyrazol-4-ones in order to observe and to characterize different DADPOXA using transient spectroscopies.
CHAPTER 2. STEREOSELECTIVE SYNTHESIS OF CIS AND TRANS-3,5-DIALKYL-3,5-DIHYDRO-3,5-DIPHENYL-4H-PYRAZOL-4-ONES.

Introduction

Cis and trans-3,5-dihydro-3,5-dimethyl-3,5-diphenyl-4H-pyrazol-4-ones\(^{23}\) (cis- and trans-1a, respectively) are the only known cis and trans-3,5-dialkyl-3,5-diaryl-3,5-dihydro-4H-pyrazol-4-ones (1) and potential precursors for allenes\(^{24}\), functionalized cyclopropanones\(^{25}\) and cyclopropyldienes\(^{26}\) (Scheme 2.1).

Scheme 2.1. Retrosynthetic analysis of cis-1a, cis-1b and cis-1c.

\[
\begin{array}{c}
\text{cis-1} \quad \xrightarrow{\text{Oxidation}} \quad \text{2} \quad \xrightarrow{\text{Alkyl addition}} \quad \text{3} \\
\text{cis-1} \quad \xrightarrow{\text{Aldol / dehydration reaction}} \quad \text{5} \quad \xrightarrow{\text{Ring closure}} \quad \text{trans-4}
\end{array}
\]

a: Ar = Ar' = Ph, R = R' = Me
b: Ar = Ar' = Ph, R = Et, R' = Me,
c: Ar = Ar' = Ph, R = R' = Et

Retrosynthetic analysis of cis or trans-1a suggests a challenging stereospecific synthesis of other derivatives of 1. Consider, for example, the synthesis of 3-ethyl-3,5-dihydro-(cis- or trans-3,5-diphenyl)-5-methyl-4H-pyrazol-4-one (cis or trans-1b, respectively) and trans-3,5-diethyl-3,5-dihydro-3,5-diphenyl-4H-pyrazol-4-one (cis or trans-1c, respectively). The key step in the
synthesis of cis-1b and cis-1c should be synthesis of 1,3-diphenyl-2-penten-1-one (5b, []-ethylchalcone) using crossed aldol/dehydration reaction of acetophenone and propiophenone. Other steps should be similar to that used for the synthesis of cis-1a. Reaction of triethylaluminum with (4S,5S)- and (4R,5R)-5-ethyl-4,5-dihydro-1-[(4-methylphenyl)sulfonyl]-3,5-diphenyl-1H-pyrazol-4-ol [(4S,5S)- and (4R,5R)-3b], instead of trimethylaluminum, should lead to stereoselective addition of ethyl group producing 3,5-diethyl-4,5-dihydro-(cis-3,5-diphenyl)-3H-pyrazol-4-ol (cis-2c), the oxidation of which would afford cis-1c. It would be a challenge to study photochemistry of 1a, 1b and 1c.

**Synthesis of 3,5-dialkyl-3,5-dihydro-3,5-diphenyl-4H-pyrazol-4-ones**

While []-alkylchalcones (5) are well known organic synthons for the preparation of biologically active heterocyclic compounds, only []-methylchalcones (5a) are easily available by self-condensation of acetophenones in the presence of Lewis acids. Further the known methods of synthesis of []-alkylchalcones with differing substituents at the []-position and/or at the aromatic rings are complicated. Though crossed aldol/dehydration is a simple and classical way to synthesize these []-alkylchalcones, self-condensation of the reacting ketones, especially when both reactants have enolizable hydrogens and close pKₐ (e. g. acetophenone and propiophenone) is a problem. Regardless, one-pot Mukaiyama30 crossed aldol condensation of trimethylsilylenol ethers of acetophenone with various ketones afforded crossed aldol products, which were in situ dehydrated using trifluoroacetic acid. In this manner, we report Mukaiyama-related crossed aldol condensation between acetophenone and propiophenone, which was successfully accomplished using titanium (IV) chloride/tributyl amine providing selectively 3-hydroxy-1,3-diphenyl-1-pentanone with 86% yield. We found that reaction of 3-hydroxy-1,3-diphenyl-1-pentanone in situ with methanesulfonyl chloride/triethylamine gave 5b(Scheme 2.2).
Scheme 2.2. Synthesis of cis-1b and cis-1a.

\[
\begin{align*}
\text{a: } R &= R' = \text{Me} \\
\text{b: } R &= \text{Et}, R' = \text{Me}
\end{align*}
\]

Conditions: (a) 1. TiCl\(_4\), Bu\(_3\)N, CH\(_2\)Cl\(_2\), -78\(^0\)C; 2. MsCl, Et\(_3\)N, -78\(^0\)C → rt; (b) 30% H\(_2\)O\(_2\), 8% NaOH, CH\(_3\)OH, rt; (c) 1. p-toluenesulfonyl hydrazine, isobutyric acid, CH\(_2\)Cl\(_2\), 70\(^0\)C; 2. HCl (g), 0\(^0\)C; d) Al(CH\(_3\))\(_3\), toluene, 75\(^0\)C; (e) CrO\(_3\), H\(_2\)SO\(_4\), H\(_2\)O, acetone, 0\(^0\)C.

Unfortunately purification of 5b led to the non-conjugated (E,Z)-1,3-phenyl-3-penten-1-one. Treatment of crude 5b with hydrogen peroxide in the alkaline methanol similar to the process used with 1,3-diphenyl-2-buten-1-one (5a)\(^{32}\) gave a mixture of cis and trans-[3-ethyl-3-phenyloxiranyl]phenyl-methanone (cis and trans-4b) in 22% yield over two steps. When one pot synthesis of 5b was used for self-aldol/dehydration reaction of acetophenone, it afforded 5a in 50% yield. The \(^1\)H NMR spectra of 5a and 5b contain an allylic hydrogen at 7.15 ppm, which is characteristic for (E)-[\(\square\)]-alkylchalcones.\(^{29c}\) The main side reaction during crossed-aldol/dehydration reactions is titanium-induced polymerization of 5a and 5b.

The synthesis of (4S,5S) and (4R,5R)-3b was presumed to be similar to the stereoselective synthesis\(^{21}\) of (4S,5S) and (4R,5R)-4,5-dihydro-5-methyl-1-[(4-methylphenyl)sulfonyl]-3,5-diphenyl-1H-pyrazol-4-ol [(4S,5S) and (4R,5R)-3a]. We optimized this synthesis getting (4S,5S) and (4R,5R)-3a in higher yield (51%) and in less time by heating.
trans-4a with p-toluenesulfonyl hydrazine at 70°C followed by treatment with dry hydrogen chloride. Reaction of cis-4a with p-toluenesulfonyl hydrazine under the same conditions more slowly gave (4S,5R) and (4R,5S)-4,5-dihydro-5-methyl-1-[(4-methylphenyl)sulfonyl]-3,5-diphenyl-1H-pyrazol-4-ol [(4S,5R) and (4R,5S)-3a] stereoselectively in 50% yield. Due to this improved procedure the reaction of trans-4b with p-toluenesulfonyl hydrazine gave (4S,5S) and (4R,5R)-3b in 61% yield. Reaction of (4S,5S) and (4R,5R)-3b with trimethylaluminum afforded cis-2b stereoselectively for three days in a reaction similar to that reported for 3a. Ultimately Jones oxidation of cis-2b gave cis-1b (4% overall yield).

The reaction of (4S,5S) and (4R,5R)-3b with triethylaluminum should lead to cis-2c stereoselectively with subsequent oxidation affording cis-1c. However, reaction of (4S,5S) and (4R,5R)-3b with triethylaluminum at 70°C for a week gave 70% conversion to the addition product. Subsequent Jones oxidation of this addition product gave mostly trans-1c along with 3,5-dihydro-(trans-3,5-diphenyl)-5-ethyl-3-vinyl-4H-pyrazol-4-one (trans-1d)(16% ¹H NMR) (Scheme 2.3).

**Scheme 2.3.** Synthesis of trans-1c.
Most likely, trans-\textbf{1d} formed from the same intermediate (6) as trans-\textbf{1c}. The lower reactivity of (4S,5S) and (4R,5R)-\textbf{3b} with triethylaluminum in comparison with trimethylaluminum can be explained by steric hindrance in \textit{6} for facial delivery of the ethyl group.

\textit{Absorption properties of cis and trans-3,5-dialkyl-3,5-dihydro-3,5-diphenyl-4H-pyrazol-4-ones}

Additional derivatives of \textbf{1}, \textit{cis-1b} and \textit{trans-1c} have similar absorption properties to that of \textit{cis} and \textit{trans-1a}. The extinction coefficient of \textit{cis-1b} at 357 nm (\(\varepsilon = 269\)) is close to the extinction coefficient of \textit{cis-1a} at 354 nm (\(\varepsilon = 248\)) (Figure 2.1). Also \textit{trans-1c} has almost the same extinction coefficient at 361 nm (\(\varepsilon = 154\)) as does \textit{trans-1a} at 356 nm (\(\varepsilon = 147\)) (Figure 2.2).

\textbf{Figure 2.1.} Absorption spectrum of \textit{trans-1c} in acetonitrile at 298 K.

An increase in the size of the substituent in \textit{cis}-azo compounds increases the wavelength maximum of the absorption.\textsuperscript{33-35} A similar effect was observed for \textbf{1} in that an increase in the length of an alkyl substituent at C-3 and C-5 position of \textbf{1} also leads to a shift of the absorption maximum into the red region. For example, the absorption maximum for \textit{trans-1c} (\(\lambda_{\text{max}} = 361\)
nm) is a little red shifted in comparison with *trans*-1a (\(\lambda_{\text{max}} = 356\) nm). Also absorption maximum of *cis*-1b (\(\lambda_{\text{max}} = 357\) nm) is somewhat red shifted in comparison with *cis*-1a (\(\lambda_{\text{max}} = 354\) nm).

![Absorption spectrum of *cis*-1b in acetonitrile at 298 K.](image)

**Figure 2.2.** Absorption spectrum of *cis*-1b in acetonitrile at 298 K.

**Discussion**

*Trans* and *cis*-1a were synthesized stereoselectively in five steps using a modified Pirkle\textsuperscript{23} procedure. A novel one-pot crossed aldol/dehydration reaction was developed affording 5a and 5b in 40 - 50% yield. This procedure can be used for the synthesis of other \(\alpha\)-alkylchalcones. Also the new derivative of 1, *cis*-1b was synthesized stereoselectively in five steps starting from 5b.\textsuperscript{36} However, the reaction of (4\(S\),5\(S\)) and (4\(R\),5\(R\))-3b with triethylaluminum with subsequent oxidation of formed addition product gave, instead of the expected *cis*-1c, *trans*-1c. Since yields of *cis*-1b and *trans*-1c were low, we decided to study only the photochemistry of *cis* and *trans*-1a. Photodecomposition of *cis* or *trans*-1a should produce a 2,4-diphenyl-3-pentanone-2,4-diyl (DMDPOXA), which can be observed using transient spectroscopies.
**Synthetic procedures**

*One-pot crossed aldol/dehydration synthesis of 1,3-diphenyl-2-buten-1-one (5a)*

To a solution of acetophenone (10.4 g, 87 mmol) in CH$_2$Cl$_2$ (110 ml) at –78°C under an argon atmosphere was added dropwise a 1M solution of TiCl$_4$ in CH$_2$Cl$_2$ (100 ml, 100 mmol) followed by Bu$_3$N (22.3 g, 121 mmol). The red mixture was stirred for 1 hour at this temperature. Then, acetophenone (11.1 g, 93 mmol) was added dropwise and resulting solution was stirred at –78°C for 2 h. According to TLC (hexane-EtOAc 9:1) aldol (R$_f$ = 0.14) was formed. After adding MsCl (22.2 g, 194 mmol) and Et$_3$N (9.9 g, 98 mmol) dropwise, the mixture was allowed to warm to r. t. and was stirred for 3 h. According to TLC (hexane-EtOAc 9:1) 5a was formed (R$_f$ = 0.40). Then, the mixture was worked up with a mixture of ice (1400 g) and CH$_2$Cl$_2$ (400 mL). The organic layer was separated off and the aqueous layer was extracted with CH$_2$Cl$_2$ (600 mL). The combined organic layers were washed with 0.15 M NaHCO$_3$ soln (3 x 200 mL), dried (Na$_2$SO$_4$), and evaporated under reduced pressure. Acetophenone and Bu$_3$N were distilled off under reduced pressure (p = 0.1 Torr) and the residue was purified by flash column chromatography (silica gel, firstly with hexane, then hexane-CH$_2$Cl$_2$ 1:1) to afford 9.5 g of 5a as brown oil (49%).

5a: $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.97 (dd, $J$ = 7, 1.5 Hz, 2H), 7.38 - 7.55 (m, 8H), 7.16 (q, $J$=1.2 Hz, 1H), 2.59 (d, $J$ = 1.2 Hz, 3H).
$^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 18.9, 122.1, 126.5, 128.3, 128.5, 128.6, 129.1, 132.5, 139.4, 142.8, 155.0, 191.8.

IR (neat): 3059, 1655, 1574, 1446, 1274, 1212, 950, 752, 699 cm$^{-1}$.

5a was also synthesized using procedure in ref. [6c].

**Synthesis**$^{32b}$ of cis and trans-[3-methyl-3-phenyloxiranyl]phenylmethanone (cis and trans-4a)

Cis and trans-4a was synthesized using a procedure in ref. [32b].

![Synthesis of 4a](image)

**Trans-4a**: mp 87 - 90$^\circ$C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.90 (d, $J$ = 7 Hz, 2H), 7.3 - 7.7 (m, 8H), 4.16 (s, 1H), 1.64 (s, 3H); 17.0, 62.8, 66.9, 125.2, 128.3, 128.8, 128.9, 134.0, 135.7, 140.5, 193.0.

IR (neat): 3061, 2978, 1683, 1598, 1449, 1382, 1227, 748, 693, 659 cm$^{-1}$.

**Cis-4a**: mp 150-156$^\circ$C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.83 (d, $J$ = 7 Hz, 2H), 7.48 - 7.6 (m, 1H), 7.35 - 7.45 (m, 2H), 7.25 - 7.35 (m, 2H), 7.10 - 7.22 (m, 3H), 4.34 (s, 1H), 1.93 (s, 3H).

$^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 24.4, 64.5, 66.2, 126.2, 127.8, 128.0, 128.8, 133.4, 135.6, 136.7, 192.5.

IR (neat): 3064, 2963, 1681, 1598, 1446, 1227, 761, 688, 653 cm$^{-1}$. 
One-pot crossed aldol/dehydration synthesis of 1,3-diphenyl-2-penten-1-one (5b)

To a stirred solution of acetophenone (10 g, 83 mmol) in CH₂Cl₂ (110 ml) at -78°C under an argon atmosphere was added dropwise 1M solution of TiCl₄ in CH₂Cl₂ (100 mL, 100 mmol) followed by Bu₃N (21.9 g, 119 mmol). The red mixture was stirred for 1.5 h at this temperature (formation of titanium enolate of acetophenone). Then, propiophenone (12.5 g, 93 mmol) was added dropwise and resulting solution was stirred at -78°C for 2.5 h. The complete formation of aldol was checked using TLC (hexane-EtOAc 9:1). After adding MsCl (21 g, 183 mmol) and Et₃N (9.4 g, 93 mmol) dropwise, the mixture was allowed to warm to r. t. and was stirred for 3 h. Then, the mixture was worked up with a mixture of CH₂Cl₂ (200 mL), ice (1000 g) and H₂O (200 mL). The organic layer was separated off and the aqueous layer was extracted with CH₂Cl₂ (600 mL). The combined organic layers were washed with 0.15 M NaHCO₃ soln (3 ¥ 200 mL), dried (Na₂SO₄) and evaporated under reduced pressure. The residue was purified by flash column chromatography (silica gel, firstly with hexane, hexane-CH₂Cl₂ 1:1) to afford 22 g of crude 5b as brown oil (according to GC/MS and ¹H NMR data crude 5b is a mixture of 5b, propiophenone and none-conjugated (E,Z)-1,3-diphenyl-3-penten-1-one). It was not possible to completely purify 5b, therefore, crude 5b was used in the next step; the presence of impurities did not influence the epoxidation reaction.
Synthesis of cis and trans-[3-ethyl-3-phenyloxiranyl]phenyl-methanone
(cis and trans-4b)

To a stirred heterogeneous solution of crude 5b (4.00 g) in MeOH (50 mL) at 0°C was added dropwise 30% aq H2O2 (4.85 g, 43 mmol) and 8% NaOH (5.18 g, 10 mmol) (pH = 11). The crude product did not dissolve completely forming bright yellow heterogeneous liquid. The mixture was allowed to warm to r. t. and stirred for 2 d.

\[
\begin{align*}
\text{MeOH} & \quad \text{H}_2\text{O}_2 \quad \text{8\% NaOH} \quad \text{Na}_2\text{SO}_4 \\
5b & \quad \text{cis-4b} \quad \text{trans-4b}
\end{align*}
\]

Then, the mixture was poured into a mixture of ice (100 g) and H2O (100 mL). The resulting solution was extracted with CH2Cl2 (3 x 100 mL), and the organic layer was dried (Na2SO4) and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane-EtOAc 9:1) to afford 0.61 g of trans-4b (yellowish solid) and 0.4 g of cis-4b (white solid) (22% yield over two steps).

\text{Cis-4b}: \text{mp 117 - 119°C.}
\text{Rf = 0.23 (hexane-EtOAc 9:1).}
\text{H NMR (300 MHz, CDCl3):} \text{[l] = 7.82 (dd, } J = 7.4, 3.3 \text{ Hz, 2H), 7.53 (t, } J = 6.6 \text{ Hz, 1H), 7.41 (t, } J = 8.3 \text{ Hz, 2H), 7.24 - 7.29 (m, 2H), 7.15-7.2 (m, 3H), 4.36 (s, 1H), 2.35 - 2.49 (m, 1H), 1.92 - 2.05 (m, 1H), 1.01 (t, } J = 7.5 \text{ Hz, 3H).}
\text{13C NMR (75.5 MHz, CDCl3):} \text{[l] = 8.81, 30.5, 64.8, 68.2, 126.8, 127.8, 127.9, 128.1, 128.6, 133.4, 135.4, 135.7, 192.8.}
\text{MS (70 eV, EI):} \text{m/z (%)} = 252 (2) [M]^+, 223 (95), 117 (39), 105 (100), 91 (32), 77 (74).
\text{HRMS (EI):} \text{m/z calc for C}_{17}\text{H}_{16}\text{O}_2: 252.1150; \text{found: 252.1150.}

\text{Trans-4b}: \text{mp 59 - 61°C.}
R_f = 0.38 (hexane-EtOAc 9:1).

^1^H NMR (300 MHz, CDCl_3) □ = 8.00 (dd, J = 7.7, 3.3 Hz, 2H), 7.63 (t, J = 6.9 Hz, 1H), 7.35 - 7.55 (m, 7H), 4.15 (s, 1H), 2.09 - 2.19 (m, 1H), 1.58 - 1.69 (m, 1H), 0.91 (t, J = 7.5 Hz, 3H).

^1^3^C NMR (75.5 MHz, CDCl_3): □ = 9.4, 23.8, 67.1, 67.5, 125.9, 128.1, 128.3, 128.8, 128.9, 133.9, 135.7, 138.8, 193.1.

IR (neat): 3063, 2976, 2935, 2879, 1682, 1596, 1448, 1398, 1226, 940, 841, 747, 696, 662 cm⁻¹.

MS (70 eV, EI): m/z (%) = 252 (2) [M]^+ , 223 (95), 117(39), 105 (100), 91 (32), 77 (74).

HRMS (EI): m/z calcd for C_{17}H_{16}O_{2}: 252.1151; found: 252.1150.

**Synthesis of (4S,5S) and (4R,5R)-4,5-dihydro-5-methyl-1-[(4-methylphenyl)sulfonyl]-3,5-diphenyl-1H-pyrazol-4-ol**

[(4S,4S) and (4R, 5R)-3b]

To a stirred solution of trans-4b (0.7 g, 2.8 mmol) in CH_2Cl_2 (6 mL) at r. t. was added p-toluenesulfonyl hydrazine (0.721 g, 3.9 mmol) and isobutyric acid (4 mL).

\[ \text{trans-4b} \xrightarrow{1) \text{Ts-NH}_2\text{NH}_2, \text{isobutyric acid}} \xrightarrow{2) \text{HCl}} \text{[(4S,5S) and (4R, 5R)-3b]} \]

The resulting solution was heated to 65°C and kept for 15 min. in a closed vial. The formation of p-toluenesulfonyl hydrazone of trans-4b was checked using GC. This hydrazone underwent Eschenmoser type fragmentation on the GC column to produce phenylacetylene and propiophenone. Then, dry HCl was passed through the mixture at 0°C to form a lot of white precipitate. According to TLC (hexane-EtOAc 3:1) trans-4b had reacted completely. The mixture was worked up with a mixture of ice (30 g) and H_2O (20 mL). The resulting mixture was extracted with CH_2Cl_2 (60 mL). The organic layer was separated off and washed with 0.15 M NaHCO_3 soln., dried (Na_2SO_4) and evaporated under reduced pressure. The residue was
purified by column chromatography (silica gel, hexane-EtOAc 3:1) to afford 0.7 g of (4S, 5S) and (4R,5R)-3b (yield 60%) as white oil. It was dried overnight (p = 0.1 Torr) and became white powder.

(4S, 5S) and (4R,5R)-3b: mp 63 - 66°C.

1H NMR (300 MHz, CDCl3): \[= 7.9 (dd, J = 5.3, 3 Hz, 2H), 7.64 (dd, J = 6.8, 1.5 Hz, 2H), 7.39 (t, J = 3 Hz, 3H), 7.16 - 7.31 (m, 7H), 5.23 (d, J = 8.1 Hz, 1H), 2.68 - 2.81 (m, 1H), 2.44 - 2.56 (m, 1H), 2.40 (s, 3H), 1.55 (d, J = 8.1 Hz, 1H), 1.01 (t, J = 7.5 Hz, 3H).

13C NMR (75.5 MHz, CDCl3): \[ = 8.5, 21.5, 29.6, 78.9, 81.3, 127.2, 127.4, 127.8, 128.4, 128.5, 128.6, 129.1, 130.0, 130.1, 135.5, 137.0, 143.4, 152.6.

IR (neat): 3516, 1598, 1496, 1448, 1344, 1160, 1066, 763, 668 cm\(^{-1}\).

MS (70 eV, EI): m/z (%) = 420 (21) [M]\(^+\), 265 (75), 236 (26), 155 (11), 132 (49), 115 (23), 104 (100).

HRMS (EI): m/z calcld for C\(_{24}\)H\(_{24}\)N\(_2\)O\(_3\)S: 420.1508; found: 420.1506.

**Modified literature synthesis of (4S,5R) and (4R,5S)-4,5-dihydro-5-methyl-1-[(4-methylphenyl)sulfonyl]-3,5-diphenyl-1H-pyrazol-4-ol[(4S,5R) and (4R,5S)-3a]**

To a stirred solution of cis-4a (2.82 g, 12 mmol) in CH\(_2\)Cl\(_2\) (21 mL) at r. t. was added p-toluenesulfonyl hydrazine (2.83 g, 15 mmol) and isobutyric acid (13 mL). The resulting solution was stirred at r. t. for 30 min. Then, the mixture was heated to 70°C and kept at this temperature for 3 h in a closed vial. According to TLC (hexane-EtOAc 3:1), the starting compound (R\(_f\) = 0.46) had reacted to form p-toluenesulfonyl hydrazone of cis-4a (R\(_f\) = 0.18).

\[ \text{cis-4a} \rightarrow 1) \text{Ts-NH}_{2}\text{NH}_2 \quad \text{isobutyric acid} \quad 2) \text{H}_2\text{C} \rightarrow \text{(4S,5R)-3a} \text{ and (4R,5S)-3a} \]
The formation of \( p \)-toluenesulfonyl hydrazone of \( cис-4a \) was checked using GC. This hydrazone underwent Eschenmoser type fragmentation on the GC column to produce phenylacetylene and acetophenone. Then, dry HCl was passed through the mixture at 0\(^{0}\)C for 25 min to form \((4S,5R)\) and \((4R,5S)-3a\) \((R_f = 0.13, \text{hexane-EtOAc 3:1})\). The mixture was worked up with a mixture of H\(_2\)O (100 mL) and ice (100 g). Then, the resulting solution was extracted with CH\(_2\)Cl\(_2\) (3\(\times\)100 ml). The organic layer was washed with 0.15 M NaHCO\(_3\) soln., dried (Na\(_2\)SO\(_4\)) and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane-EtOAc 3:1) to afford \((4S,5R)\) and \((4R,5S)-3a\) as orange oil. The oil was dried overnight under reduced pressure \((p = 0.1 \text{ Torr})\) to form orange powder 0.7 g of \((4S,5R)\) and \((4R,5S)-3a\) (yield 51\% ).

\((4S,5R)\) and \((4R,5S)-3a\): mp 140 - 146\(^{0}\)C.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.84\) (dd, \(J = 5.7, 1.8 \text{ Hz}, 4\text{H}), 7.64\) (dd, \(J = 8, 1.8 \text{ Hz}, 2\text{H}), 7.37 - 7.43\) (m, 6H), 7.28 (dd, \(J = 12, 3.9 \text{ Hz}, 2\text{H}), 4.84\) (d, \(J = 7.2 \text{ Hz}, 1\text{H}), 2.42\) (s, 3H), 1.88 (s, 3H), 1.52 (d, \(J = 7.2 \text{ Hz}, 1\text{H}).

\(^{13}\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta = 21.6, 22.5, 75.9, 83.9, 127.2, 128.2, 128.5, 128.6, 129.3, 130.2, 136.3, 137.0, 143.0, 153.5.

IR (neat): 3469, 2973, 2867, 1597, 1495, 1447, 1342, 1165, 1055, 1028, 766, 689, 668 cm\(^{-1}\).

**Modified literature synthesis of \((4S,5S)\) and \((4R,5R)-4,5\text{-dihydro-5-methyl-1-\[(4-methylphenyl)sulfonyl]\text{-3,5-diphenyl-1H-pyrazol-4-ol}}\ ([\(4S,5S\) and \((4R,5R)-3a\])

To a stirred solution of \(транс-4a\) (0.13 g, 0.5 mmol) in CH\(_2\)Cl\(_2\) (1 mL) at r. t. was added 0.13 g \(p\)-toluenesulfonyl hydrazine (0.13 g, 0.7 mmol) and isobutyric acid (0.52 g).
The resulting solution was heated to 70°C and kept at this temperature for 20 minutes in a closed vial. According to TLC (hexane-EtOAc 3:1), the starting compound (R_f = 0.55) had reacted completely to form p-toluenesulfonfyl hydrazone of trans-4a (R_f = 0.3). The formation of this hydrazone was checked using GC. p-Toluenesulfonfyl hydrazone of trans-4a underwent Eschenmoser type fragmentation on the GC column to produce phenylacetylene and acetophenone. Then, dry HCl was passed through the mixture at 0°C to form a lot of white precipitate. According to TLC (hexane-EtOAc 3:1) p-toluenesulfonfyl hydrazone of trans-4a (R_f = 0.3) had reacted with dry HCl to form (4S,5S) and (4R,5R)-3a (R_f = 0.17). The mixture was worked up with H_2O (5 mL) and extracted with CH_2Cl_2 (15 mL). The organic layer was washed with 0.15 M NaHCO_3 soln., dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane-EtOAc 3:1) to afford 0.13 g of (4S,5S) and (4R,5R)-3a as orange oil (yield 59%).

(4S,5S) and (4R,5R)-3a: ¹H NMR (300 MHz, CDCl_3): δ = 7.85 (dd, J = 6.3 Hz, 3.6 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.39 - 7.41 (m, 3H), 7.22 - 7.30 (m, 6H), 7.19 (d, J = 8.1 Hz, 2H); 5.16 (d, J = 9.3 Hz, 1H); 2.39 (s, 3H); 2.34 (d, J = 9 Hz, 1H); 1.97 (s, 3H).

¹³C NMR (75.5 MHz, CDCl_3): δ = 17.3, 21.6, 75.4, 85.5, 125.3, 127.2, 127.8, 128.7, 129.2, 130.0, 130.2, 136.9, 142.4, 143.5, 153.2.

(4S,5S) and (4R,5R)-3a: ¹H NMR (300 MHz, CDCl_3): δ = 7.82 (dd, J = 7, 2 Hz, 2H), 7.65 (d, J = 8 Hz, 2H), 7.08 - 7.4 (m, 10H), 5.11 (d, J = 9 Hz, 1H), 2.38 (s, 3H), 2.34 (d, J = 9 Hz, 1H), 1.97 (s, 3H).

Synthesis of 4,5-dihydro-3,5-dimethyl-(trans-3,5-diphenyl)-3H-pyrazol-4-ol (trans-2a)

To a stirred solution of (4S,5R) and (4R,5S)-3a (2.34 g, 5.8 mmol) in toluene (34 g) under an argon atmosphere at 0°C was added dropwise 2M solution of Me₃Al in toluene (25.5 mL, 51 mmol).
The mixture was allowed to warm to r.t. and was then heated to 75°C and kept at this temperature for 3 d. According to TLC (hexane-EtOAc 3:1), the starting compound (R_f = 0.17) was consumed forming trans-2a (R_f = 0.19). The cerium system was used to develop trans-2a on the TLC plate. The mixture was allowed to cool to r.t. and was added dropwise to a mixture of CH_2Cl_2 (100 mL), H_2O (100 mL) and ice (100 g). Then, 6 M HCl (30 mL) was added dropwise to the mixture and the aqueous layer was extracted with CH_2Cl_2 (3 × 100 ml). The organic layer was dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane-EtOAc 9:1) to afford 0.61 g of trans-2a (yield 40%) as white solid.

Trans-2a: mp 130 - 131°C.

^1^H NMR (300 MHz, CDCl_3): δ = 7.48 (d, J = 7.2 Hz, 2H), 7.41 (d, J = 7.8 Hz, 2H), 7.29 - 7.44 (m, 6H), 4.14 (d, J = 4.8 Hz, 1H), 1.73 (s, 3H), 1.30 (s, 3H), 1.08 (d, J = 4.8 Hz, 1H).

^13^C NMR (75.5 MHz, CDCl_3): δ = 23.0, 24.3, 79.2, 96.7, 97.0, 124.9, 124.9, 126.7, 127.1, 127.2, 128.2, 128.6, 128.7, 129.0, 138.3, 145.2.

Synthesis of 4,5-dihydro-3,5-dimethyl-(cis-3,5-diphenyl)-3H-pyrazol-4-ol (cis-2a)

The synthesis of cis-2a from (4S,5S) and (4R,5R)-3a was similar to that of trans-2a.


Cis-2a: mp 152 - 153°C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.19 - 7.31 (m, 10H), 4.35 (d, $J = 6$ Hz, 1H), 2.05 (d, $J = 6$Hz, 1H), 1.71 (s, 3H).

$^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 21.4, 81.7, 94.6, 124.9, 127.2, 128.6, 144.5.

**Synthesis of 3-ethyl-(cis-3,5-diphenyl)-4,5-dihydro-5-methyl-3H-pyrrol-4-ol (cis-2b)**

To a stirred solution of (4$^S$,5$^S$) and (4$^R$,5$^R$)-3b (0.6 g, 1.4 mmol) in dry toluene (6 g) under an argon atmosphere at 0°C was added dropwise 2M Me$_3$Al in toluene (7.8 ml, 17 mmol). The mixture was allowed to warm to r. t. and was then heated to 75°C and kept at this temperature for 3 d.

According to TLC (hexane-EtOAc 3:1) the starting compound ($R_f= 0.17$) was consumed forming cis-2b. The cerium system was used to develop cis-2b on the TLC plate. The mixture was worked up with a mixture of CH$_2$Cl$_2$ (25 mL), ice (25 g) and H$_2$O (25 mL). Then, 6 M HCl (30 mL) was added dropwise to the mixture and the aqueous layer was extracted with CH$_2$Cl$_2$ (3-50 mL). Organic layer was dried (Na$_2$SO$_4$) and the solvent was evaporated under reduced
pressure. The residue was purified by column chromatography (silica gel, hexane-EtOAc 9:1) to afford 0.15 g of cis-2b (yield 38%) as yellowish solid.

\textit{Cis-2b}: mp 111-112°C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.26 - 7.40 (m, 10H), 4.13 (d, $J$ = 5.7 Hz, 1H), 1.94 - 2.01 (m, 1H), 1.63 (s, 3H), 1.34 - 1.41 (m, 1H), 1.06 (d, $J$ = 5.7 Hz, 1H), 0.84 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 8.8, 22.9, 32.6, 79.1, 95.8, 100.0, 125.0, 127.1, 127.2, 128.0, 128.7, 128.9, 136.8, 145.4.

IR (neat): 3441, 2976, 2926, 1600, 1493, 1445, 1379, 1052, 1027, 753, 693 cm$^{-1}$.

MS (70 eV, EI): m/z (%) = 252 (6) [M]+-N$_2$, 221 (26), 205 (7), 178 (7), 143 (25), 128 (22), 115 (37), 105 (83), 91 (100), 77 (51), 44 (100).

HRMS (Cl): m/z calcd for C$_{18}$H$_{20}$N$_2$O, 281.1654; found: 281.1659.

\textit{Synthesis of trans-3,5-diethyl-3,5-dihydro-3,5-phenyl-4H-pyrazol-4-one (trans-1c)}

To a stirred solution of (4$S$,5$S$) and (4$R$,5$R$)-3b (0.5 g, 1.2 mmol) in dry toluene (5 g) under an argon atmosphere at 0°C was added dropwise 1.9 M solution of Me$_3$Al in toluene (6.5 ml, 12 mmol). The mixture was allowed to warm to r. t. and was then heated to 75°C and kept at this temperature for a week. The mixture was added dropwise to a mixture of H$_2$O (100 mL), ice (100 g) and CH$_2$Cl$_2$ (100 mL).

![Diagram showing the synthesis of trans-2c and trans-2d](image)

Then, 6 M HCl (30 mL) was added dropwise to the mixture and the aqueous layer was extracted with CH$_2$Cl$_2$ (3×100 mL). The organic layer was dried (Na$_2$SO$_4$) and the solvent was evaporated under reduced pressure. The residue was purified by preparative TLC (silica gel; hexane-EtOAc 9:1) to afford 0.053 g of trans-2c (along with 17% of trans-2d according to $^1$H NMR spectrum).
and 0.151 g of starting compound (70% conversion). The cerium system was also used to develop trans-2c on the TLC plate.

To a stirred solution of trans-2c (0.05 g, 0.2 mmol) in acetone (1.9 ml) at 0°C was added dropwise Jones reagent for 2 h. According to TLC (silica gel, hexane-EtOAc 9:1) trans-2c (Rf = 0.52) had reacted completely to form trans-1c (Rf = 0.47). The mixture was quenched with i-PrOH (2 mL), and the green precipitate was filtered off and washed with acetone (5 mL). The solvent was evaporated and H2O (5 mL) was added to the residue.

The aqueous solution was extracted with CH2Cl2 (10 mL), and the organic layer was dried (Na2SO4) and evaporated under reduced pressure. The residue was purified by preparative TLC (silica gel, hexane-EtOAc 9:1) to afford 0.033 g of trans-1c (along with 16% trans-1d) as white solid (14% yield over the two last steps).

Trans-1c: mp 69 - 72°C.

1H NMR (300 MHz, CDCl3): □ = 7.29 - 7.39 (m, 8H), 7.60 - 7.69 (m, 2H), 2.10 - 2.22 (m, 1H), 1.84 - 1.96 (m, 1H), 0.67 (t, J = 7.5 Hz, 3H).

13C NMR (75.5 MHz, CDCl3): □ = 125.5, 126.2, 127.9, 128.1, 128.8, 130.2, 136.4, 90.3, 32.7, 8.6.

MS (70 eV, EI): m/z (%)= 264 (14) [M]+-N2, 235 (21), 207 (100), 178 (60), 129 (28), 91 (33).

UV-VIS (CH3CN): □max = 361 nm (□154).

HRMS (CI): m/z [M]++H calcd for C19H20N2O, 293.1654; found: 293.1649.

Trans-1d: 1H NMR (300 MHz, CDCl3): □ = 7.29 - 7.39 (m, 8H), 7.60 - 7.69 (m, 2H), 6.01 (q, J = 17.4, 10.5 Hz, 1H), 5.17 (d, J = 10.4 Hz, 1H), 4.96 (d, J = 17.4 Hz, 1H), 2.28 - 2.41 (m, 1H), 1.97 - 2.10 (m, 1H), 0.74 (t, J = 7.5 Hz, 3H).
$^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 125.5, 126.2, 127.9, 128.1, 128.8, 130.2, 136.4, 119.1, 91.0, 31.8, 8.8.

MS (70 eV, EI): m/z (%) = 262 (43) [M$^+$-N$_2$], 234 (63), 235 (100), 205 (35), 207 (11), 115 (43), 91 (32), 77 (20).

Synthesis of cis-3,5-dihydro-3,5-dimethyl-3,5-diphenyl-4H-pyrazol-4-one (cis-1a)

To a stirred solution of cis-2a (0.13 g, 0.5 mmol) in acetone (2.5 ml) at 0°C was added dropwise Jones reagent $^{84}$ (0.3 g) for 1 h.

According to TLC (hexane-EtOAc 9:1) the starting compound ($R_f$ = 0.17) was oxidized completely forming cis-1a. The cerium system was used to develop cis-2a on the TLC plate. Then, the mixture was worked up with isopropyl alcohol (2 ml). The green precipitate was filtered off and washed with acetone (5 ml). The solvent was evaporated and water (5 ml) was added to the residue. The aqueous solution was extracted with dichloromethane (10 ml). The organic layer was dried (Na$_2$SO$_4$) and evaporated under reduced pressure to afford 0.128 g of cis-1a (yield 99%).

Cis-1a: mp 72 - 74°C.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.26 (m, 10H), 1.85 (s, 6H).

$^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 24.1, 87.0, 125.3, 128.2, 128.8, 136.4, 215.0.

IR (neat): 3055, 2977, 2930, 1758, 1598, 1489, 1443, 1371, 1025, 934, 765, 696 cm$^{-1}$.

MS (70 eV, EI): m/z (%) = 236 (17) [M$^+$-N$_2$], 208 (20), 193 (100), 165 (8), 115 (11).

UV-VIS (CH$_3$CN): $\lambda_{max}$ = 354 nm ($\varepsilon$248).
Synthesis of trans-3,5-dihydro-3,5-dimethyl-3,5-phenyl-4H-pyrazol-4-one
(trans-1a)

The synthesis of trans-1a (yield 96%) from trans-2a was similar to that of cis-1a.

![Chemical structure of trans-2a and trans-1a](image)

Trans-1a: mp 132-133\(^0\)C.
R$_f$ = 0.45 (hexane-EtOAc 9:1).
$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.30 - 7.55 (m, 10H), 1.66 (s, 6H).
$^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 23.5, 86.7, 125.3, 128.4, 128.8, 129.0, 137.2, 214.7.
MS (70 eV, EI): m/z (%) = 236 (16) [M]$^-$N$_2$, 208 (16), 193 (100), 178 (69), 89 (17).
UV-VIS (CH$_3$CN): $\lambda_{max}$ = 356 nm (\(\epsilon\) 147).

Synthesis of cis-3-ethyl-3,5-dihydro-3,5-diphenyl-5-methyl-4H-pyrazol-4-one (cis-1b)

The synthesis of cis-1b (yield 96%) form cis-2b is similar to that of cis-1a.

![Chemical structure of cis-2b and cis-1b](image)

Cis-1b: mp 58 - 61\(^0\)C.
$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.54 (m, 4H), 7.33 - 7.44 (m, 6H), 2.15 - 2.35 (m, 1H), 1.9 - 2.1 (m, 1H), 1.55 (s, 3H), 0.74 (s, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 8.7, 24.4, 31.8, 86.7, 90.1, 125.4, 125.5, 128.1, 128.8, 128.9, 136.7, 137.0, 214.8.

IR (neat): 3054, 2984, 2918, 1763, 1597, 1490, 1443, 1073, 1027, 775, 696 cm$^{-1}$.

MS (70 eV, EI): m/z (%) = 250 (20) [M]+-N$_2$, 234 (63), 222 (24), 193 (100), 178 (57), 128 (14), 91 (33).

UV-VIS (CH$_3$CN): $\lambda_{max}$ = 357 nm ($\epsilon$ 269).

HRMS (Cl): m/z [M+H] calcd for C$_{18}$H$_{10}$N$_2$O, 279.1497; found: 279.1495.
CHAPTER 3. PHOTOCHEMISTRY OF TRANS-3,5-DIHYDRO-3,5-DIMETHYL-3,5-DIPHENYL-4H-PYRAZOL-4-ONE

Photochemistry of 4,5-dihydro-3,5-dimethyl-(cis and trans-3,5-diphenyl)-3H-pyrazol-4-ol (cis and trans-2a)

Absorption and emission properties of cis and trans-2a

4,5-Dihydro-3,5-dimethyl-(cis and trans-3,5-diphenyl)-3H-pyrazol-4-ol (cis and trans-2a) are quite similar to cis and trans-1a and possess only absorptions due to the azo chromophore. Therefore, cis and trans-2a were used as model compounds for cis and trans-1a. The absorption bands of cis and trans-2a with maxima at 337 nm (ε = 159 and ε = 160, respectively) in the UV-VIS spectra correspond to a $S_0 \rightarrow S_1(n,p^*)$ transition of the azo group (Figure 3.1 and Figure 3.2).

Figure 3.1. UV-VIS spectrum of cis-2a in acetonitrile at 298 K.
**Figure 3.2.** UV-VIS spectrum of trans-2a in acetonitrile at 298 K.

**Figure 3.3.** UV-VIS spectrum of trans-2a in acetonitrile at 298 K (red). 77 K emission spectrum of trans-2a in 4:1 ethanol/methanol after a 337 nm laser pulse (blue).
The photophysical properties of $trans$-$2a$ were studied. $Trans$-$2a$ showed a very weak emission at room temperature, because of the high quantum yield of photodecomposition of $trans$-$2a$ ($\Phi_D = 0.80$ in carbon tetrachloride). However, the photodecomposition rate of $trans$-$2a$ at 77 K becomes so low that the rate of the radiative decay of the excited singlet state can compete with it. As a result, a strong emission from $trans$-$2a$ was observed at 77 K in 4:1 ethanol/methanol and decayed mono-exponentially with a lifetime of 811 ns (Figure 3.3 and Figure 3.4).

![Figure 3.4. Kinetic trace of 450 nm of time-resolved emission from excited state of $trans$-$2a$ in 4:1 ethanol/methanol at 77 K after a 337 nm laser pulse.](image)

Evolution of the excited singlet state to the excited triplet state manifold and also decay of the excited triplet state can be followed by time-resolved emission experiments in rigid glasses at 77 K. A change in the time-resolved emission spectra can be observed during the conversion of the excited singlet state to the excited triplet state. The time-resolved emission spectra from excited states of $trans$-$2a$ measured after a 337 nm laser pulse (60 μJ/pulse) were the same (Figure 3.5) and coincident with the emission spectrum from $trans$-$2a$ in 4:1 ethanol/methanol at 77 K (Figure 3.6). Thus, the mono-exponential decay of the emission ($\approx 811$ ns) and the lack
of change in the time-resolved emission spectra show that only one excited state of $trans$-$2a$ emits at 77 K (excited singlet or excited triplet state).

**Figure 3.5.** Time-resolved emission spectral evolution of $trans$-$2a$ in 4:1 ethanol/methanol at 77 K after a 337 nm laser pulse.
Figure 3.6. 77 K emission spectra of trans-2a in 4:1 ethanol/methanol measured 60 ns (■) and 1100 ns (●) after a 337 nm laser pulse. 77 K emission spectrum of trans-2a in 4:1 ethanol/methanol with 337 nm excitation (▼).

The 0,0 band in the emission spectrum from trans-2a at 77 K could not be resolved using a conventional spectrophotometer. Thus, onsets were used to estimate the energy of the excited state in the emission spectra (Figure 3.3). The energy of the excited state of trans-2a is approximately 77 kcal/mole (onset at ~362 nm). This energy is close to the energy of the excited singlet state of azo compounds 37-39 (75 - 85 kcal/mole) and much higher than the energy of the excited triplet state of the azo compounds (55 - 65 kcal/mole).38,39 Also intersystem crossing (ISC) from the excited singlet state to the excited triplet state is usually relatively slow for azoalkanes.35,34,40 Thus, the emission from trans-2a at 77 K was tentatively assigned to the fluorescence. Fluorescence from 1-pyrazolines is a well-known phenomenon.41

Direct irradiation and triplet sensitization of cis and trans-2a

(spin correlation effect)

A study of stereochemistry in photochemical products during photodecompositions of cyclic azoalkanes was used to understand the nature of lowest excited state of cyclic azoalkanes (so called “spin correlation effect”).34,35 For example, direct irradiation of trans-3,6-diethyl-3,6-dimethyltetrahydropyridazine (trans-THP) produced mostly trans-1,2-diethyl-1,2-dimethylcyclobutane (10:1 ratio trans-CB : cis-CB)42 (Scheme 3.1). However, irradiation of trans-THP in the presence of thioxanthone as a triplet sensitizer gave a mixture of cis and trans-CB (1:1.4 ratio, respectively).42
Scheme 3.1. Direct irradiation and triplet sensitization of trans-THP. 

Direct irradiation of trans-THP produces the excited singlet state, and then subsequent loss of nitrogen leads to the singlet trans-3,6-dimethyloctane-3,6-diyl (trans-S-3,6-DR). The lifetime of this diradical is shorter than the rotation around the bond ($k_r = 10^6 - 10^8$ s$^{-1}$). Therefore, ring closure of the trans-S-3,6-DR proceeds with retention of stereochemistry forming mostly trans-CB (10:1 trans-CB: cis-CB). Triplet sensitization of trans-THP produces the excited triplet state, which decomposes to the triplet trans-3,6-dimethyloctane-3,6-diyl (trans-T-3,6-DR). The lifetime of the trans-T-3,6-DR ($k_{ISC} = 10^4 - 10^6$ s$^{-1}$) is longer than the rotation around the bond ($k_r = 10^6 - 10^8$ s$^{-1}$). That is why a mixture of cis and trans-T-3,6-DR is formed. The ISC by spin orbital coupling (SOC) in the cis and trans-T-3,6-DR with subsequent ring closure of the formed cis and trans-S-3,6-DR leads to the mixture of cis and trans-CB (1.4 : 1 ratio, respectively). Regardless of retention of stereochemistry observed upon direct
irradiation of \textit{trans-THP}, triplet sensitization of \textit{trans-THP} leads to the loss of stereochemistry in the photochemical products.

The stereochemistry of photodecomposition of \textit{trans}-3,5-diphenyl-1-pyrazoline was studied in order to understand the nature of its lowest excited state.\textsuperscript{45c} Irradiation of \textit{trans}-3,5-diphenyl-1-pyrazoline formed \textit{trans}-1,2-diphenyl cyclopropane (90 %) and \textit{cis}-1,2-diphenyl cyclopropanone (10 %) with 70 % yield (Scheme 3.2). It means that \textit{trans}-3,5-diphenyl-1-pyrazoline decomposes from the excited singlet state with retention of stereochemistry in the photochemical products. The products of fragmentation (up to 30%), styrene and phenylcarbene, were also observed during photodecomposition of \textit{trans}-3,5-diphenyl-1-pirazoline.\textsuperscript{45a,45b} Phenylcarbene was trapped with methanol and acetic acid. Mechanism of fragmentation of 1-pyrazolines will be discussed in detail later in Chapter 4.

\textit{Scheme 3.2. Photodecomposition of \textit{trans}-3,5-diphenyl-1-pyrazoline.}

A similar approach was used to study the nature of the lowest excited state of \textit{cis} and \textit{trans-2a}. The photodecomposition of \textit{cis} and \textit{trans-2a} led to the formation of \textit{cis} and \textit{trans}-2,3-dimethyl-2,3-diphenylcyclopropanol (\textit{cis} and \textit{trans-6}), respectively, which was followed by \textsuperscript{1}H NMR spectroscopy in both direct irradiation (350 nm) and triplet sensitization experiments (350 nm and 370 nm) (Scheme 3.3). 4,4\textsuperscript{¢}-Dimethoxybenzophenone (DMBP) was used as the triplet sensitizer ($E_T = 70$ kcal/mole\textsuperscript{46}) for the photodecomposition of \textit{cis} and \textit{trans-2a}. This sensitizer has an extinction coefficient at 350 nm ($\epsilon = 372$), that is much higher than that of either \textit{cis} or
**trans-2a** and a non-reactive excited triplet state with a *[* configuration. DMBP has previously been used as a triplet sensitizer for the decomposition of 2,3-diazabicyclo [2.2.1]hept-2-ene.47

**Scheme 3.3.** Direct irradiation and triplet sensitization of *cis* and *trans*-2a.

Direct irradiation of *trans*-2a in different deuterated solvents (CD$_3$CN, C$_6$D$_6$, CD$_3$CD) at 350 nm led to *trans*-6 with 77% yield (Table 3.1). Only traces of *cis*-6 were observed in the $^1$H NMR spectrum during this photodecomposition (Figure B1-Figure B4). Irradiation of *cis*-2a under the same conditions produced *cis*-6 (Figure B5-Figure B8). Thus, direct irradiation of *cis* and *trans*-2a leads to the excited singlet state with subsequent decomposition affording the singlet *cis* and *trans*-2,4-diphenyl-3-hydroxypentane-2,4-diy (cis-S-2,4-DR and trans-S-2,4-DR, respectively). The lifetime of these diradicals is considerably less than the time required for rotation around the bond. Therefore, ring closure of the cis-S-2,4-DR and trans-S-2,4-DR proceeds with the retention of stereochemistry forming *cis* and *trans*-6, respectively.
**Table 3.1.** Direct irradiation and triplet sensitization of *cis* and *trans-2a*.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>Irradiation</th>
<th>Solvent</th>
<th>Convn. (%)</th>
<th><em>Trans-6</em> (%)</th>
<th><em>Cis-6</em> (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><em>trans-2a</em></td>
<td>350 nm direct</td>
<td>CD$_3$CN</td>
<td>40</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C$_6$D$_6$</td>
<td>32</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CD$_3$OD</td>
<td>49</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td><em>cis-2a</em></td>
<td>350 nm direct</td>
<td>CD$_3$CN</td>
<td>70</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C$_6$D$_6$</td>
<td>68</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td><em>trans-2a</em></td>
<td>350 nm Sens. DMBP$^a$</td>
<td>CD$_3$CN</td>
<td>68</td>
<td>17</td>
<td>83</td>
</tr>
<tr>
<td>4</td>
<td><em>cis-2a</em></td>
<td>350 nm Sens. DMBP$^a$</td>
<td>CD$_3$CN</td>
<td>47</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td><em>trans-2a</em></td>
<td>370 nm Sens. DMBP$^a$</td>
<td>CD$_3$CN</td>
<td>57</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td><em>cis-2a</em></td>
<td>370 nm Sens. DMBP$^a$</td>
<td>CD$_3$CN</td>
<td>43</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

a) 4,4$^{\text{I}}$-Dimethoxybenzophenone (DMBP) was used as triplet sensitizer (1:1 *2a*:DMBP molar ratio)

b) Determined by $^1$H NMR spectroscopy; error ± 5 % of the stated value. The toluene was used as an internal standard

Triplet sensitization of *trans-2a* with DMBP (1:1 *trans-2a*: DMBP) in deuterated acetonitrile at 350 nm led to the mixture of *cis-6* (83 %) and *trans-6* (17 %) according to the $^1$H NMR spectrum. Surprisingly, Irradiation of *cis-2a* under the same conditions (triplet sensitization) produced only *cis-6*. The formation of 17 % of *trans-6* during triplet sensitization of *trans-2a* can be explained by partial absorption of light by *trans-2a* at 350 nm, that is why the triplet sensitization of *trans-2a* was done at 370 nm.

The DMBP-sensitized (370 nm, $\varepsilon = 68$) photodecomposition of *trans-2a* (no absorption at 370 nm) with 500-W Xenon lamp (a monochromator was used for wavelength selection) produced only *cis-6* (76 % yield) according to $^1$H NMR spectrum (Figure B9-Figure B12). It can
be explained as follows; triplet sensitization of \textit{trans}-2a forms the excited triplet state. The decomposition of the excited triplet state of \textit{trans}-2a produces the triplet \textit{trans}-2,4-diphenyl-3-hydroxypentane-2,4-diyl (\textit{trans-}\textbf{T-2,4-DR}). The lifetime of this diradical is longer than the time required for rotation around the bond. Therefore, the \textit{trans-}\textbf{T-2,4-DR} forms the thermodynamically more stable triplet \textit{cis}-2,4-diphenyl-3-hydroxypentane-2,4-diyl (\textit{cis-}\textbf{T-2,4-DR}). ISC by SOC in the \textit{cis-}\textbf{T-2,4-DR} leads to the short-lived \textit{cis-S-2,4-DR} and its ring closure forms \textit{cis-6}.

The DMBP-sensitized (370 nm) photodecomposition of \textit{cis-2a} (no absorption at 370 nm) produced only \textit{cis-6} (71 % yield) according to $^1$H NMR spectrum (Figure B13-Figure B16). It can be explained as follows; the triplet sensitization of \textit{cis-2a} leads to the excited triplet state of \textit{cis-2a}. Decomposition of this excited triplet state leads to the thermodynamically stable \textit{cis-}\textbf{T-2,4-DR}. The ISC in the \textit{cis-}\textbf{T-2,4-DR} by SOC forms the \textit{cis-S-2,4-DR} with subsequent ring closure affording only \textit{cis-6}. These results confirm that \textit{trans-2a} has singlet photochemistry and emission from the excited state of \textit{trans-2a} at 77 K corresponds to fluorescence (Figure 3.3).

Direct irradiation of \textit{trans-2a} in benzene at 350 nm for 1 hour produced mostly \textit{trans-6}. Similar to the situation with 3,5-diphenyl-1-pyrazoline, the photodecomposition of \textit{trans-2a} gave fragmentation products. It was proposed that the first step is the retro-1,3-dipolar cycloaddition of 3,5-diphenyl-1-pyrazoline\textsuperscript{45} producing phenyldiazomethane and styrene. The next step is the photodecomposition of labile phenyldiazomethane with the expulsion of nitrogen to afford phenylcarbene. The fragmentation products of \textit{trans-2a}: 2-phenylpropionaldehyde (around 10 %) and styrene were observed in the $^1$H NMR spectrum (Scheme 3.4). $^1$H and $^{13}$C NMR spectra of 2-phenylpropionaldehyde were compared with its authentic $^1$H and $^{13}$C NMR spectra.\textsuperscript{48}
Scheme 3.4. Fragmentation of trans-2a during direct irradiation.

The photodecomposition of cis and trans-2a can also be followed by UV-VIS spectroscopy. Irradiation of trans-2a in carbon tetrachloride at 350 nm leads to a decrease of the absorption band with a maximum at 337 nm (photodecomposition of trans-2a) and contaminant growth of an absorption band with a maximum at 290 nm (formation of trans-6) in the UV-VIS spectra (Figure 3.7).
Figure 3.7. Time evolution of UV-VIS spectra of trans-2a in carbon tetrachloride acquired after a 350 nm irradiation (0-5 min.).

Spectroscopy and photophysical properties of trans-3,5-dihydro-3,5-dimethyl-3,5-diphenyl-4H-pyrazol-4-one (trans-1a)

Absorption properties of cis and trans-1a

Cis and trans-3,5-dihydro-3,5-dimethyl-3,5-diphenyl-4H-pyrazol-4-one (cis and trans-1a) have almost the same $^1$H NMR, $^{13}$C NMR, MS and IR spectra. The hydrogens of the methyl groups of cis-1a are shifted somewhat to the low field in the $^1$H NMR spectrum as compared with the absorptions of similar hydrogens of trans-1a. Also a slight difference between cis and trans-1a can be observed in HPLC chromatogram (80:20 acetonitrile-water). The cis-isomer is a bit more polar than trans-isomer. Azo compounds show a weak n,π* band in the 300-400 nm region. Cis-isomers of azo compounds have extinction coefficients higher than those of the trans-isomers. UV-VIS spectroscopy is a much better tool to differentiate cis and trans-1a. The extinction coefficient of cis-1a at 354 nm (ε = 248) is twice that of the extinction coefficient
of trans-1a at 356 nm (ε = 147) (Figure 3.8 and Figure 3.9) The low extinction coefficients of cis and trans-1a (ε_max ~ 10³) and a hypsochromic shift of absorption maximum with increase of solvent polarity suggest that the lowest excited singlet states of cis and trans-1a have n,π* configuration. Cis and trans-1a showed weak emission at room temperature. The emission maximum from cis-1a (ε_max=505 nm) in acetonitrile following excitation at 320 nm is somewhat red shifted in comparison with the emission maximum from trans-1a (ε_max = 513 nm) (Figure 3.8 and Figure 3.9).

Figure 3.8. Absorption spectrum (red) and emission spectrum (blue) of cis-1a in acetonitrile at 298 K.
Figure 3.9. Absorption spectrum (red) and emission spectrum (blue) of trans-1a in acetonitrile at 298 K.

Cis and trans-1a are bichromic compounds in that they contain both azo and carbonyl groups. Two distinct absorption bands with maxima at 337 nm and 354 nm are better resolved in the UV-VIS spectrum of cis-1a in acetonitrile (Figure 3.8). The same absorption bands are not well resolved in the UV-VIS spectrum of trans-1a (Figure 3.9). Cis and trans-2a are quite similar to cis and trans-1a and they only possess an azo chromophore, which has an absorption maximum at 337 nm (ε = 159 and ε = 160, respectively) in the UV-VIS spectra (Figure 3.1 and Figure 3.2). Therefore, the similar band with a maximum at 337 nm in the absorption spectra of cis and trans-1a was assigned to the absorption from the azo group [S₀ → S₁(n,p*) transition].

The remaining absorption band with a maximum at 354 nm found in the UV-VIS spectra of cis and trans-1a was assigned to the carbonyl absorption [S₀ → S₁(n,p*) transition].

The two distinct absorption maxima observed in the UV-VIS spectra of cis-1a cannot correspond to the vibrational structure of cis-1a (Dν ≈ 588 cm⁻¹). The vibrational structure of azo compounds is well resolved in non-polar solvents⁴⁹ and no vibrational structure for cis-1a can be seen in the absorption or emission spectra in polar acetonitrile.
**Emission properties of trans-1a**

It is established that *cis* and *trans-1a* have two different absorbing groups. Thus, the following question arises: Which group determines the nature of the lowest excited state of *trans-1a*?

Turro\(^{50}\) gave the following definition of the nature of the lowest excited states of bichromic compounds:

“The lowest excited state of a molecule independently absorbing, but formally conjugated chromophores is determined by the chromophore moiety possessing the lowest excitation energy.”

*Cis* and *trans-1a* are a bichromic compounds and most likely the azo and carbonyl groups of *cis* and *trans-1a* are formally conjugated. Since the overlap of the azo and the carbonyl group was observed in the PE spectra for a compound that is similar to *cis* and *trans-1a*, 3,3,5,5-tetramethyl-3,5-dihydro-4H-pyrazol-4-one.\(^{51}\) Thus, the lowest excited state of *cis* and *trans-1a* should be determined by the azo group, which has lower excitation energy than the carbonyl group.

Irradiation of *cis* or *trans-1a* at 350 nm should lead to \(S_0 \rightarrow S_1\; (n \rightarrow \pi^*)\) transition of the carbonyl group. Subsequently rapid ISC from the \(S_1\; (n \rightarrow \pi^*)\) state produces the \(T_2\; (n \rightarrow \pi^*)\) state of the carbonyl group. The triplet energy of azoalkanes is lower than the triplet energy of ketones consequently ketones are often used as triplet sensitizers for azoalkanes.\(^{52}\) As a result internal triplet energy transfer from the \(T_2\; (n \rightarrow \pi^*)\) state of the carbonyl group to the \(T_1\; (n \rightarrow \pi^*)\) state of the azo group should be observed. The carbonyl moiety in *cis* and *trans-1a* is quite similar to 1,3-diphenyl-2-propanone. For example, the triplet energy of 1,3-diphenyl-2-propanone \([T_2\; (n \rightarrow \pi^*), 72.2\; \text{kcal/mole}]\)^\(^{53}\) is much higher than the triplet energy of azoalkanes \([T_1\; (n \rightarrow \pi^*), 55-65\; \text{kcal/mole}]\), so the excited state of *cis* and *trans-1a* should resemble the excited triplet state of an azo compound.

*Cis* and *trans-1a* most likely will have a similar photochemistry in the steady state photolysis. However, the photochemistry of these isomers can be different in the transient experiments. Therefore, the photochemistry and photophysical properties of one of the isomers, *trans-1a* were studied. Similar to *trans-2a*, *trans-1a* showed a very weak emission \((\phi \approx 10^{-4})\) at room temperature (Figure 3.9 and Figure 3.10). However, the quantum yield of
photodecomposition of *trans-1a* at room temperature ($\Phi_D = 0.09$ in methanol) is considerably less in comparison with the quantum yield of photodecomposition of *trans-2a* ($\Phi_D = 0.80$ in methanol). Nevertheless, the emission from *trans-1a* ($\Phi_e \approx 0.017$) was observed in 4:1 ethanol/methanol at 77 K and the excited state of *trans-1a* decayed mono-exponentially with a lifetime of 75 ns (Figure 3.10 and Figure 3.11). Thus, differences in the quantum yield of photodecomposition and differences in the lifetimes of the excited states at 77 K between *trans-1a* and *trans-2a* (881 ns for *trans-2a* versus 75 ns for *trans-1a*) support the notion that the introduction of the carbonyl group in *trans-1a* leads to the change in the nature of the lowest excited state. Most likely, the carbonyl group in *trans-1a* induces ISC from the excited singlet state to the non-reactive excited triplet state.

*Figure 3.10.* Absorption spectrum of *trans-1a* in acetonitrile at 298 K (red). Emission spectrum of *trans-1a* in acetonitrile at 298 K (green). 77 K emission spectrum of *trans-1a* in 4:1 ethanol/methanol with 360 nm excitation (blue).
Figure 3.11. Kinetic trace of 520 nm of time-resolved emission from trans-1a in 4:1 ethanol/methanol at 77 K after a 360 nm laser pulse.

Excited triplet states are difficult to observe at room temperature due to the quenching by oxygen and/or impurities. Nevertheless, they can be observed in rigid glasses at 77 K or in plastics at room temperature. For some years, the excited triplet states of azo compounds could not be observed even in rigid glasses at 77 K. It had been proposed that the excited triplet state of azoalkanes decayed by a very fast radiationless route to the ground state. Therefore, triplet sensitizers were used to populate the excited triplet state of azoalkanes. Recently, the excited triplet states of several fused derivatives of 2,3-diazobicyclo[2.2.1]hept-2-ene (DBH) were studied in rigid glasses at 77 K and in nanosecond transient UV-VIS experiments.

Similar to trans-2a, time-resolved emission spectra from the excited state of trans-1a were measured after a 360 nm laser flash (60 µJ/pulse)(Figure 3.12). These emission spectra were the same over different times and coincident with emission spectrum from trans-1a in a 4:1 ethanol/methanol glass at 77 K (Figure 3.13). Again, as was the case for trans-2a, the lack of change in the time-resolved emission spectra and the mono-exponentional decay of the emission show that only one excited state of trans-1a emits at 77 K (excited singlet or triplet state).
Figure 3.12. 77 K time-resolved emission spectral evolution of \textit{trans-1a} in 4:1 ethanol/methanol after a 360 nm laser pulse (60 mJ/pulse).

Figure 3.13. 77 K emission spectra of \textit{trans-1a} in 4:1 ethanol/methanol measured 10 ns (■) and 100 ns (●) after a 360 nm laser pulse (60 mJ/pulse). 77 K emission spectrum of \textit{trans-1a} in EPA with 360 nm excitation (▲).
Based on the emission spectrum of \textit{trans-1a} at 77 K, the estimated energy of the excited state is 66 kcal/mole (onset at \(\approx 415\) nm)(Figure 3.10). This energy is quite close to the energy of excited triplet states of azoalkanes\textsuperscript{38,39} (56-65 kcal/mole) and considerably less than the energy of excited singlet states of azoalkanes \textsuperscript{37,38,39} (76-85 kcal/mole). Thus, these data again confirmed that the emission from \textit{trans-1a} at 77 K corresponds to the phosphorescence. If one compares the emission spectra from \textit{trans-1a} at 298 K and 77 K, one sees that the emission spectrum at room temperature represents an overlap of the fluorescence and the phosphorescence spectra. Based on the emission spectrum from \textit{trans-1a} at room temperature, the energy of the excited singlet state of \textit{trans-1a} was estimated to be 76 kcal/mole (onset at \(\approx 380\) nm)(Figure 3.10). Therefore, \textit{trans-1a} has low singlet-triplet energy gap (\(\Delta E_{ST} \approx 76-66 \approx 10\) kcal/mole). It was also found that the emission spectra and lifetimes of the excited triplet state of \textit{trans-1a} in the EPA glass and in the rigid glass containing ethyl iodide (1:2:1 ethyl iodide/ethanol/isopentane) at 77 K were identical (no external heavy atom effect). Thus, the relatively high emission rate constant, the small singlet-triplet energy gap and the lack of heavy atom effect on the phosphorescence of \textit{trans-1a} suggest that excited triplet state of \textit{trans-1a} has n,\(\pi^*\) nature.\textsuperscript{37}

The emission spectrum from biacetyl at room temperature resembles the emission spectrum from \textit{trans-1a}. The emission spectrum from biacetyl results from an overlap of the fluorescence (0,0 band at 460 nm \(\approx 62\) kcal/mole) and the phosphorescence (0,0 band at 520 nm \(\approx 56\) kcal/mole) emissions.\textsuperscript{50} The phosphorescence lifetime of biacetyl at room temperature in hexane is rather long (\(\tau_p = 0.5\) ms). Therefore, the phosphorescence of biacetyl can be quenched with oxygen. However, the emission lifetime of \textit{trans-1a} at room temperature is very short and no quenching of phosphorescence of \textit{trans-1a} was observed in the emission spectra after the purging of oxygen.

\textit{Direct irradiation and triplet sensitization of trans-1a}

The energy of the carbon-nitrogen bond cleavage in \textit{trans-1a} should be close to the energy of the carbon-nitrogen bond cleavage in 3,5-diphenyl-1-pyrazoline\textsuperscript{35} (33 kcal/mole, 140 kJ/mole) and the energy of the carbon-carbon bond cleavage in \textit{trans-1a} should be close to the energy of the carbon-carbon bond cleavage in substituted ketones\textsuperscript{34} (RCO-CR', 72 kcal/mole,
300 kJ/mole). Therefore, the excited triplet state of \( \text{trans-1a} \) \((\approx 66 \text{ kcal/mole})\) should decompose by the cleavage of the carbon-nitrogen bond producing the triplet 2,4-diphenyl-3-pentanone-2,4-diyl (DMDPOXA).

Direct irradiation of \( \text{trans-1a} \) in acetonitrile at 350 nm led to a mixture of \( \text{cis} \) and \( \text{trans-1,3-dimethyl-1-phenyl-2-indanone} \) \((\text{cis and trans-10})\) with 57% yield (Scheme 3.5). Irradiation of \( \text{trans-1a} \) at 254 nm in acetonitrile or irradiation at 350 nm in different solvents (carbon tetrachloride, acetonitrile, methanol, benzene) always led to the same photochemical products \((\text{cis and trans-10})\). During photodecomposition of \( \text{trans-1a} \), a fragmentation of \( \text{trans-1a} \) was also observed affording phenylmethylketene (7) and styrene. As mentioned before similar fragmentation was observed for 3,5-diphenyl-1-pyrazoline\(^\text{45}\) and \( \text{trans-2a} \). The percent of this fragmentation during irradiation of \( \text{trans-1a} \) at 350 nm in methanol \((\approx 10\%)\) is comparable to the fragmentation of 3,5-diphenyl-1-pyrazoline during its irradiation in the ethanol \((10\%)\).\(^\text{45a}\) No trapping products of the singlet or triplet DMDPOXA were observed when \( \text{trans-1a} \) was irradiated in methanol, acrylonitrile and furan.

**Scheme 3.5.** Photodecomposition of \( \text{trans-1a} \).
DMBP was also used as the triplet sensitizer for the photodecomposition of \textit{trans-1a}. Irradiation of a 5-6x10^{-3} M solution of \textit{trans-1a} in deuterated acetonitrile in the presence of DMBP gave the same photochemical products: \textit{cis} and \textit{trans-10} (7:1) in the \textsuperscript{1}H NMR spectrum (Figure B18). Predominant formation of \textit{cis-10} cannot be attributed to the hydrogen abstraction by triplet excited state of DMBP, because it has a non-reactive triplet nature. Also no predominant formation of \textit{cis-10} was observed when a mixture of \textit{cis} and \textit{trans-10} was irradiated at 350 nm in the presence of DMBP.

\textit{UV-VIS spectroscopy in the steady state photolysis of trans-1a.}

\textit{Observation of long-lived 8 in the UV-VIS spectra}

The formation of an intermediate was observed in the UV-VIS spectra during the irradiation of \textit{trans-1a} at 350 nm in carbon tetrachloride (Figure 3.14). Similar UV-VIS spectra were observed during the photodecomposition of \textit{trans-1a} at 254 nm or 350 nm in acetonitrile (Figure B19 and Figure B20). This intermediate has a much higher extinction coefficient than \textit{trans-1a}. Also during irradiation of \textit{trans-1a}, the color of the solution turning bright yellow signals that a highly conjugated intermediate was formed.

\textbf{Figure 3.14.} Time evolution of UV-VIS spectra of \textit{trans-1a} in carbon tetrachloride acquired after a 350 nm irradiation (0- 5 min.).
This broad absorption in the UV-VIS spectra cannot be attributed to photochemical products (cis or trans-10), because cis and trans-10 do not absorb at wavelengths higher than 350 nm (Figure 3.15). Thus, this broad absorption in the UV-VIS spectra that overlaps with that of the starting compound and the change of solution color during the irradiation is a result of formation of highly conjugated cyclohexadiene intermediate (8)(Scheme 3.5). 5-Methylene-1,3-cyclohexane (MCH, $t_{1/2} = 31$ min. at 60$^0$C) has a structure similar to 8 and was characterized by UV-VIS and $^1$H-NMR spectroscopies$^{58}$ (Figure B21). 8 should have an extinction coefficient at 350 nm higher than the extinction coefficient of MCH at 350 nm ($e = 520$) because of the extended conjugation with the carbonyl group that explains the overlap of trans-1a in the UV-VIS spectra during irradiation.

Figure 3.15. UV-VIS spectra of trans-10 and trans-1a.

No formation of 8, as observed in the UV-VIS spectra, and no color change were observed during the irradiation of trans-1a at 350 nm in methanol (Figure 3.16). The UV-VIS spectra produced during the irradiation of trans-1a in methanol looked similar to the UV-VIS spectra of trans-10 (Figure 3.15). Most likely a hydrogen shift in 8, forming cis and trans-10, is faster in the more polar methanol than in the much less polar carbon tetrachloride. Therefore, 8
cannot be observed in the UV-VIS spectra during steady state photolysis of trans-1a in methanol.

![UV-VIS spectra of trans-1a in methanol](image)

**Figure 3.16.** Time evolution of UV-VIS spectra of trans-1a in methanol acquired after a 350 nm irradiation (0-50 min.).

**IR spectroscopy during the steady state photolysis of trans-1a. Observation of 8 in the infrared spectra**

Irradiation of 5-6x10^-2 M solution of trans-1a in carbon tetrachloride or acetonitrile at 350 nm led to a formation of three absorptions at 2103 cm\(^{-1}\), 1755 cm\(^{-1}\) and 1691 cm\(^{-1}\) in the infrared spectra (Figure 3.17 and Figure 3.18). The strong absorption at 2103 cm\(^{-1}\), which is characteristic for ketenes, was assigned to phenylmethylketene (7). 7 was synthesized following a Dehmlow procedure.\(^{58}\) However, 7 was highly unstable and polymerized rapidly in the presence of oxygen. Phenylethylketene, which was synthesized by the same Dehmlow procedure,\(^{58}\) was more stable than 7. Phenylethylketene in carbon tetrachloride has strong ketene absorption at 2099 cm\(^{-1}\) (Figure B22), which is close to the 2103 cm\(^{-1}\) band observed in the infrared spectra during the irradiation of trans-1a.
Figure 3.17. Time evolution of infrared spectra of trans-1a in carbon tetrachloride acquired after a 350 nm irradiation (0-60 min.).

Figure 3.18. Time evolution of infrared spectra of trans-1a in acetonitrile acquired after a 350 nm irradiation (0-150 min.).
The 1755 cm\(^{-1}\) band in the infrared spectra formed during the irradiation of \textit{trans-1a} was assigned to the vibrational frequency of carbonyl group of \textit{cis} and \textit{trans-10}. Isolated neat \textit{trans-10} has a carbonyl stretching frequency at 1749 cm\(^{-1}\), which is close to the 1755 cm\(^{-1}\) band. The 1755 cm\(^{-1}\) band overlaps with the 1764 cm\(^{-1}\) band (vibrational frequency of carbonyl group of \textit{trans-1a}) during photodecomposition.

The 1691 cm\(^{-1}\) band in the infrared spectra during the irradiation of \textit{trans-1a} was assigned to the carbonyl stretching frequency of \textit{8}. Unsaturated ketones exist in \textit{s-trans} and \textit{s-cis} conformations. For example, benzalacetone in carbon disulfide shows both \textit{s-cis} (1699 cm\(^{-1}\)) and \textit{s-trans} (1674 cm\(^{-1}\)) isomers at room temperature. \textit{8} has only a \textit{s-cis} conformation with a carbonyl stretching band at 1691 cm\(^{-1}\), which is close to the stretching of the carbonyl group of \textit{s-cis} conformation of benzalacetone (1699 cm\(^{-1}\)). Since \textit{8} cannot be isolated, B3LYP/6-31G(d) Gaussian 98 was also used to estimate the vibrational frequency of the conjugated carbonyl group in \textit{8}. Calculated carbonyl frequency of \textit{8} was around 1713 cm\(^{-1}\), which is in an agreement with the experimental value (1691 cm\(^{-1}\)).

Irradiation of 5-6 x10\(^{-2}\) M solution of \textit{trans-1a} in acetonitrile at 254 nm led to a much faster photodecomposition in comparison with irradiation at 350 nm (Figure 3.19). The same bands formed in the infrared spectra during irradiation of \textit{trans-1a} in acetonitrile at 254 nm and 350 nm. An increase of solvent polarity leads to the decrease of percent of fragmentation reaction (7) in the infrared spectra (Figure 3.17 and Figure 3.18). A similar effect was observed in the photodecomposition of 3,5-diphenyl-1-pyrazoline.\(^{45b}\)
Figure 3.19. Time evolution of infrared spectra of trans-1a in acetonitrile acquired after a 254 nm irradiation (0 - 35 min.).

$^1$H NMR spectroscopy in the steady state photolysis of trans-1a. Observation of 8 in $^1$H NMR spectra

Irradiation of trans-1a in deuterated acetonitrile at 350 nm led to a mixture of cis and trans-10 as seen in the $^1$H NMR spectrum (Figure B17). 8 could not be observed in the $^1$H NMR spectra during irradiation at 350 nm, because of a low quantum yield of photodecomposition of trans-1a. However, the photodecomposition of trans-1a at 254 nm is much faster than from irradiation at 350 nm and produces a much larger amount of 8 (1691 cm$^{-1}$ band) in the infrared spectra (Figure 3.19). Thus, a 254 nm excitation of trans-1a was used in order to observe 8. Irradiation of 3-4x10$^{-2}$ M solution of trans-1a in deuterated acetonitrile at 254 nm for 10 minutes gave a mixture of cis and trans-10 along with an intermediate (Figure B23). The structure of this intermediate was assigned to 8 based on the following characteristic peaks in the $^1$H NMR spectrum: 1.45 ppm (s, 3H), 1.78 ppm (d, 3H, $J = 4.2$ Hz), 4.17 ppm (broad s, 1H), 6.15 ppm (m, 1H), 6.25 ppm (dd, 1H, $J = 9.6$ Hz, 5.4 Hz), 6.30 ppm (dd, 1H, $J = 9.6$ Hz, 5.4 Hz), 6.75 ppm (dd, 1H, $J = 9.6$ Hz, 4.2 Hz). The signals of 8 disappeared in the $^1$H NMR spectrum after several
minutes in the dark with the contaminant growth of signals corresponding to cis and trans-10 (Figure B24). Disappearance of 8 resulted in the color change of irradiated solution from bright yellow to the slightly yellowish color. These results suggest that the 1,5-H thermal shift in 8 produces intermediate 1,3-dimethyl-2-hydroxy-3-phenyl indene (9) with the subsequent ketonization forming cis and trans-10 (Scheme 3.6). 9 was not observed in the 1H NMR spectra during 254 nm irradiation of trans-1a.

Scheme 3.6. Irradiation of trans-1a in deuterated methanol at 350 nm.

Irradiation of 5-6x10^{-2} M solution of trans-1a in deuterated methanol at 350 nm produces mostly the long-lived intermediate (τ ≈ 40 hours) along with cis and trans-1,3-dimethyl-3-deutero-1-phenyl-2-indanone (cis and trans-12) (Scheme 3.6) as seen in the 1H NMR spectrum (Figure B25). The signals of this intermediate in the 1H NMR spectrum decreased in the dark with the contaminant growth of cis and trans-12 (almost 1:1 molar ratio) (Figure B26). No intermediate 8 was observed in the 1H NMR spectrum. Based on the 1H NMR spectrum and the kinetic data, the structure of long-lived intermediate was assigned to 1,3-dimethyl-2-deuteroxy-2-phenyl indene (11). Long-lived 11 is formed by the exchange of protium in the enol 9 with deuterium. The observation of 11 again proves that the 1,5-H shift in 8 leads to the 9 with subsequent formation of cis and trans-10. The long lifetime of 11 can be explained by stability...
of this enol due to the delocalization of negative charge in the corresponding enolate by the phenyl group. For example, it was found that 2-indanone (pKₐ = 12.2) is much more acidic than acetone (pKₐ = 19.2), also the enol content in 2-indadone (pKₑ = 3.79) is 10⁴ higher than enol content in cyclopentanone (pKₑ = 7.94). The delocalization of negative charge generally slows down the rate of proton transfer to the carbon.

Different rates of ketonization of 2-methyl-1-en-1-ol (enol of 2-methylpropanal) were observed in CDCl₃ (τ ≈ 3 min) and in CD₃OD (τ = 52 hours). Similarly lifetime of enol 9 in CD₃CN is much shorter than the lifetime of enol 11 (τ = 40 hours) in CD₃OD. It was found that traces of impurities in CDCl₃ (Fluka, H₂O+D₂O < 0.01 %) make ketonization rate of 2-methyl-2-en-1-ol very fast. Most likely, traces of water, which are always present in CD₃CN, also facilitated the ketonization of 9.

Figure 3.20. Ketonization of enol 11 forming cis and trans-12.

The UV-VIS spectra of trans-1a during irradiation at 350 nm in deuterated methanol were similar to the UV-VIS spectra during the irradiation of trans-1a at 350 nm in methanol (Figure 3.16). Most likely, 11 has absorption properties similar to cis and trans-12.
Isolation of cis and trans-10

Trans-1a (0.200 g, 0.76 mmol) was dissolved in 10 ml acetonitrile. The resulting solution was degassed with argon for 15 minutes and irradiated for 12 hours at 350 nm. During irradiation, the color of the solution became bright yellow. The acetonitrile was then evaporated under reduced pressure, and the residue was purified by column chromatography on silica (98:2, hexane-ethyl acetate) affording 0.074 g yellowish oil (cis and trans-10, 57 % yield) and 0.072 g starting trans-1a.

trans-10: $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.37-7.39 (m, 2H), 7.18 - 7.25 (m, 6H), 3.57 (q, $J$ = 7.2 Hz, 1H), 1.74 (s, 3H), 1.43 (d, $J$ = 7.2 Hz, 3H).
$^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 14.1, 24.0, 45.0, 57.7, 123.8, 124.9, 126.6, 126.9, 127.9, 128.0, 128.5, 141.5, 142.1, 144.8, 220.0.
IR (neat): 3063, 2968, 2926, 2869, 1749, 1597, 1447, 1373, 1290, 1151, 1075, 1026, 964, 909, 731, 697 cm$^{-1}$.
HRMS (EI): m/z calcd for C$_{17}$H$_{16}$O, 236.1201; found: 236.1204.

cis-10: $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.37-7.39 (m, 2H), 7.18 - 7.25 (m, 6H), 3.59 (q, $J$ = 7.8 Hz, 1H), 1.74 (s, 3H), 1.36 (d, $J$ = 7.6 Hz, 3H).
$^{13}$C NMR (75.5 MHz, CDCl$_3$): $\delta$ = 17.6, 24.9, 46.3, 57.9, 124.1, 125.2, 126.6, 127.0, 127.2, 128.0, 128.4, 141.8, 142.9, 145.7, 220.0.

Isolation of cis and trans-6

5-6$	imes$10$^{-2}$ M solution of trans-2a in deuterated solvent (C$_6$D$_6$, CD$_3$CN and CD$_3$OD) was degassed with argon for 15 minutes and irradiated at 350 nm for 1 hour. The solvent was evaporated under reduced pressure to afford 0.010 g yellowish oil (77 % yield). According to the $^1$H NMR spectrum, around 10 % 2-phenylpropionaldehyde was observed in irradiated solution. The $^1$H NMR spectrum 2-phenylpropionaldehyde was in an agreement with authentic data [$^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 9.7 (d, $J$ = 1.5Hz, 1H), 7.4-7.2 (m, 5H), 3.6 (dq, $J$ = 1.5, 7.1 Hz),
1.4 (d, J = 7.1 Hz, 3H, CH₃); $^{13}$C NMR (75 MHz, CDCl₃): δ = 201.1, 137.8, 129.1, 128.4, 127.6, 53.0 and 14.6).

*trans*-6: $^1$H NMR (300 MHz, C₆D₆): δ = 7.35-7.63 (m, 10H) 1.74 (s, 3H), 1.43 (s, 3H), 1.19 (s, 3H), 1.90 (d, J = 3 Hz, 1H), 1.52 (d, J = 3 Hz, 1H).

$^{13}$C NMR (75.5 MHz, C₆D₆): δ = 20.3, 26.7, 33.4, 35.6, 63.2, 125.4, 130.91, 141.5, 144.6.

HRMS (EI): m/z calcd for C₁₇H₁₈O 238.1358; found: 238.1359.

5-6×10⁻² M solution of *cis*-2a in deuterated solvent (C₆D₆, CD₃CN and CD₃OD) was degassed with argon for 15 minutes and irradiated at 350 nm for 15 minutes. The solvent was evaporated under reduced pressure to afford 0.010 g yellowish oil (73 % yield).

*cis*-6: $^1$H NMR (300 MHz, C₆D₆) δ = 6.94-7.40 (m, 10H), 1.61 (s, 1H), 1.74 (s, 3H), 4.34 (d, J = 1.5 Hz, 1H), 1.36 (d, J = 7.6 Hz, 3H), 1.24 (d, J = 1.5 Hz, 1H).

$^{13}$C NMR (75.5 MHz, C₆D₆): δ = 15.7, 34.7, 59.3, 121.5, 125.3, 125.6, 127.2, 127.7, 127.9, 128.0, 128.3, 128.6, 128.8, 129.1, 144.3.

HRMS (EI): m/z calcd for C₁₇H₁₈O 238.1358; found: 238.1359.

*Quantum yield of photodecomposition of trans-3,5-dihydro-3,5-dimethyl-3,5-diphenyl-4H-pyrazol-4-one (trans-1a) and 4,5-dihydro-3,5-dimethyl-(trans-3,5-diphenyl)-3H-pyrazol-4-ol (trans-2a)*

The quantum yields were determined using benzophenone-benzohydrol actinometry (Φact = 0.68). The quantum yield of the photodecomposition of *trans*-1a in methanol at 350 nm was approximately 0.09. The following quantum yields of the photodecomposition of *trans*-2a were obtained after irradiation at 350 nm: 0.68 (acetonitrile), 0.57 (methanol) and 0.80 (carbon tetrachloride). Also a high quantum yield of the photodecomposition (0.98) was obtained after the irradiation of the similar 3,3,5,5-tetramethyl-3,5-dihydro-4H-pyrazol at 350 nm in hexane.
Discussion

The photophysical and photochemical properties of \textit{trans-1a} were studied for the first time. Photophysical data suggest that excitation of \textit{trans-1a} leads to the excited singlet state (Scheme 3.7). This is followed by ISC producing the excited triplet state of \textit{trans-1a}. The energy of the excited singlet state is quite high (~76 kcal/mole), making it hard for radiationless decay to the ground state to compete with ISC to the excited triplet state (~66 kcal/mole). Another proof of effective ISC in the excited singlet state of \textit{trans-1a} is the very weak fluorescence at room temperature (Φ ≥ 10^{-4}, Φ ≈ 0) and the small singlet-triplet energy gap (ΔE_{ST} ≈ ΔE_s - ΔE_T ≈ 10 kcal/mol). The excited triplet state of \textit{trans-1a} is non-reactive because its rate of radiationless decay (k_{QP} ≈ k_0P ≈ 1.3×10^{10} s^{-1}, τ_{QP} ≈ 78 ns at 77 K) to the ground state is much faster than the rate of radiative decay (k_0P ≈ 2.2×10^{5} s^{-1}, τ_P = τ_P/Φ_P = 75 ns / 0.017 = 4.5 μs at 77 K) and the rates of decomposition (k_D < 10^{-6} s^{-1}, τ_D > 0.8 ms at 77 K).

\textit{Scheme 3.7}. Energy diagram of \textit{trans-1a}.

Similar photophysical data were observed for 3,3,5,5-tetramethyl-3,5-dihydro-4\textit{H}-
-pyrazol-4-one. A sufficient rate of ISC from its excited singlet state to the excited triplet state was proposed based on the PE spectra (overlap of azo and carbonyl group) and low fluorescence quantum yield ($\Phi_F = 0.002$). The excited triplet state of 3,3,5,5-tetramethyl-3,5-dihydro-4H-pyrazol-4-one is also non-reactive ($\Phi_D = 0.012^{25a}$) and undergoes fast radiationless decay to the ground state (calculated $k_{QP} \approx 10^8$ s$^{-1}$). Thus, trans-1a has similar photophysical properties with much faster radiationless decay of the excited triplet state ($k_{QP} \approx 1.3 \times 10^{10}$ s$^{-1}$) to the ground state.

The irradiation of trans-1a in different solvents at 254 nm or irradiation at 350 nm produced cis and trans-10. Based on the products of steady state photolysis, the following scheme of the photodecomposition of trans-1a was proposed (Scheme 3.8). Irradiation of trans-1a at 350 nm or 254 nm leads to the excited singlet state. Fast ISC produces the non-reactive excited triplet state of trans-1a. Radiationless decay of the excited triplet state to the ground state is much faster than rates of its decomposition. The two pathways for the decomposition of the excited triplet state of trans-1a were proposed. One pathway is the expulsion of nitrogen forming the triplet 2,4-diphenyl-3-pentanone-2,4-diyl (T-DMDPOXA). Subsequent ISC by SOC in the T-DMDPOXA leads to the singlet 2,4-diphenyl-3-pentanone-2,4-diyl (S-DMDPOXA). Most likely, the S-DMDPOXA has zwitterionic nature.
Scheme 3.8. Scheme of photodecomposition of trans-1a in the direct irradiation and triplet sensitization.

Then, oxidopentadienyl cation (zwitterionic S-DMDPOXA) forms 8 by a controtary 4 \( \square \) electrocyclic ring closure. Similar oxidopentadienyl cation (Nazarov type-intermediate\(^{57}\)) was proposed as an intermediate in the rearrangement of allene oxide to cyclopent-2-en-1-one in the biosynthesis prostaglandins.\(^6\) Observation of 8 (closed form of S-DMDPOXA) assumed existence of S-DMDPOXA. The subsequent thermal 1,5-H shift in 8 leads to 9, which then forms cis and trans-10 by keto-enol tautomerisation. The formation of enol 11 (\( t = 40 \) hours) during irradiation of trans-1a at 350 nm in deuterated methanol confirms that cis and trans-10
forms by the thermal 1,5-H shift with the subsequent ketonization of enol 9. Another pathway of decomposition of the excited triplet state of trans-1a is the fragmentation forming 7 and styrene. The mechanism of this fragmentation reaction will be discussed in details in Chapter 4.

The major difference between the direct irradiation of trans-1a (Figure B17) and the triplet sensitization with DMBP (Figure B18) is predominant formation of cis-10 rather than trans-10 during the triplet sensitization of trans-1a. These results suggest that irradiation of trans-1a in the presence of DMBP leads to the excited triplet state of 8, which forms stereoselectively cis-10. Observation of the same photochemical products in the direct and triplet-sensitized experiments confirms that trans-1a has triplet photochemistry.

No trapping products of the T-DMDPOXA or S-DMDPOXA were observed when trans-1a was irradiated in methanol, acrylonitrile and furan. These results suggest that the rate of ISC in the T-DMDPOXA forming the S-DMDPOXA and the rate of intramolecular ring closure of S-DMDPOXA are faster than the rate of intermolecular adduct formation. Since T-DMDPOXA and S-DMDPOXA are short-lived intermediates their nature and reactivity could be studied by transient spectroscopies.
CHAPTER 4. TIME-RESOLVED FTIR AND UV-VIS STUDIES

OF TRANS-1a

Introduction

Time-resolved FTIR (TRIR)\(^{62}\) and time-resolved UV-VIS (TR UV)\(^{63}\) spectroscopies can be used as tools to determine the structure and to measure lifetimes of short-lived intermediates (excited states,\(^{64}\) radical,\(^{65}\) diradicals,\(^{66}\) carbenes\(^{67}\)) in solution. They are powerful and complimentary techniques for these studies. Bands in TRIR spectra are sharper and better to use to characterize structure than absorption bands in transient UV-VIS spectra, which are usually featureless and broad. However, since many short-lived intermediates do not possess fingerprint IR bands and, as a result, cannot be observed in the TRIR spectra, TR UV-VIS spectroscopy is the only tool of choice.

Results

Nanosecond time-resolved FTIR studies

As mentioned in Chapter 3, the two ways of decomposition of the excited triplet state of trans-1a were proposed (Scheme 4.1). One way (path A) is the expulsion of nitrogen to produce the triplet 2,4-diphenyl-2-pentanone-2,4-diyl (T-DMDPOXA) with subsequent formation of cis and trans-10. Another way of its decomposition (path B or path C) is the fragmentation reaction with two probable mechanisms. The first is a “one-step” mechanism, in which fragmentation of excited triplet state of trans-1a produces directly phenylmethylketene (7), phenylmethylcarbene and nitrogen (path C). Subsequent rearrangement of phenylmethylcarbene leads to styrene. The second is a “two-step” mechanism (path B) in which the first step is the retro-1,3-dipolar cycloaddition of excited triplet state of trans-1a forming 7 and phenyldiazoethane (13). The next step is the photodecomposition of labile 13 with the expulsion of nitrogen to afford phenylmethylcarbene. Similar fragmentation to that of trans-1a was observed for other 1-pyrazolines.\(^{69}\) For example, the retro-1,3-dipolar cycloaddition was proposed in the steady state.
photolysis of 3,5-diphenyl-1-pyrazoline.\textsuperscript{43} 7,13 and the T-DMDPOXA contain strong IR chromophores, therefore, it is a challenge to observe them in the TRIR spectra.

**Scheme 4.1.** Photodecomposition of trans-1a.

The TRIR spectrum of trans-1a in argon-saturated carbon tetrachloride was obtained with nanosecond time resolution (Figure 4.1). The three positive transients at 1814 cm\(^{-1}\), 2038 cm\(^{-1}\) and 2102 cm\(^{-1}\) were observed “instantaneously” (within the response time of the instrument - 30 ns) after the 355 nm laser pulse and remained unchanged throughout the rest of the experimental time window (500 ms) (Figure 4.2). No ground state bleaching in the TRIR spectra was observed in trans-1a.

As it was mentioned in Chapter 3, similar to the 2102 cm\(^{-1}\) transient in the TRIR spectra of trans-1a, the strong absorption at 2103 cm\(^{-1}\) was observed in the steady state infrared spectra of UV-irradiated trans-1a solutions and was assigned to the absorption of the ketene moiety of 7.
(Figure 3.11). Thus, the 2102 cm$^{-1}$ band in the transient FTIR spectra was unambiguously assigned to the ketene absorption of 7.

**Figure 4.1.** Time-resolved FTIR difference spectra of trans-1a in argon-saturated (blue) and oxygen-saturated (red) carbon tetrachloride acquired 2 ms after a 355 nm laser pulse.
**Figure 4.2.** Kinetic traces of 1814 cm\(^{-1}\), 2038 cm\(^{-1}\) and 2102 cm\(^{-1}\) of TRIR absorptions in compound \textit{trans-1a}.

Another proposed product of the 1,3-retro dipolar cycloaddition of excited triplet state is \textit{13}. The matrix-isolated \textit{13} has a very strong absorption of diazo group at 2050 cm\(^{-1}\) in the matrix infrared spectra\(^{68}\), which is similar to that of the absorption at 2038 cm\(^{-1}\) observed in the TRIR spectra of \textit{trans-1a}. The absorption of \textit{13} was not observed in the steady state IR spectra of UV-irradiated \textit{trans-1a} solutions, because even matrix-isolated \textit{13} at 5 K easily decomposes producing phenylmethylcarbene with subsequent rearrangement to styrene.\(^{68}\) Actually, styrene was one of the photochemical products during photodecomposition of \textit{trans-1a}. Therefore, the strong absorption at 2038 cm\(^{-1}\) in the TRIR spectra of \textit{trans-1a} was assigned to the diazo group absorption of \textit{13}.

We were challenged to use the nanosecond TRIR spectroscopy as a tool to monitor the retro-1,3-dipolar cycloaddition of additional 1-pyrazoline. For example, \textit{trans-2a} is similar to 3,5-diphenyl-1-pyrazoline and \textit{trans-1a}. The products of fragmentation of the excited singlet state of \textit{trans-2a} observed during steady state photolysis of \textit{trans-2a} were 2-phenylpropionaldehyde and styrene (Scheme 4.2). Therefore, if a fragmentation of excited singlet state of \textit{trans-2a} is a retro-1,3-dipolar cycloaddition, the transient absorption of \textit{13} should be also observed in the TRIR spectra.
Scheme 4.2. Photodecomposition of trans-2a.

The TRIR spectrum of trans-2a is shown in Figure 4.3. The formation of the transient absorption at 2041 cm\(^{-1}\) was observed “instantaneously” in the TRIR spectrum after the laser pulse and this transient remained unchanged until the end of acquisition time ca. 10 ms (Figure 4.4). Absorption at 2041 cm\(^{-1}\) in the TRIR spectra of trans-2a is exactly the same absorption at 2038 cm\(^{-1}\) in the TRIR spectra of trans-1a. Based on the similar photochemistry of trans-1a and trans-2a, similar absorptions in the TRIR spectra and agreement with the McMahon data\(^{68}\) (2050 cm\(^{-1}\) band of matrix-isolated 13), 2038 cm\(^{-1}\) (trans-1a) and 2041 cm\(^{-1}\) (trans-2a) transients were unambiguously assigned to the absorption of 13. Other photodecomposition products of the excited singlet state of trans-2a, trans-16 and enol of 2-phenyl propionaldehyde do not have strong absorptions in the infrared spectra, that is why they were not observed in the TRIR spectra. To the best of our knowledge, this is the first example of nanosecond TRIR spectroscopy being used to monitor the retro-1,3-dipolar cycloaddition of 1-pyrazolines.
**Figure 4.3.** Time-resolved FRIR difference spectra of *trans-2a* in argon-saturated carbon tetrachloride taken 2 ms after a 355 nm laser pulse.

**Figure 4.4.** Kinetic trace of 2041 cm\(^{-1}\) of TRIR absorption in compound *trans-2a*.

Another 1814 cm\(^{-1}\) in the TRIR spectra of *trans-1a* looks similar to the carbonyl absorption of cyclopropanones (1813-1843 cm\(^{-1}\)). The formation of 2,2,3,3-tetramethylcyclopropanone was also observed during photodecomposition of related 3,3,5,5-tetramethyl-3,5-dihydro-pyrazol-4-one. Calculated vibrational frequencies of carbonyl groups for
cis and trans-2,3-dimethyl-2,3-diphenylcyclopropanone (cis and trans-14, respectively) using B3LYP/31G(d) Gaussian 98 are 1841 cm⁻¹ and 1843 cm⁻¹ (Table 4.1), which are in an agreement with its experimental value (1814 cm⁻¹). Thus, the 1814 cm⁻¹ band in the TRIR spectra was assigned to the overlap of carbonyl stretching frequencies of cis and trans-14. In-pulse formation of cis and trans-14 suggest that a lifetime of T-DMDPOXA is less than 30 ns (response time of TRIR spectrometer). Observation of cis and trans-14 gives credence for the zwitterionic S-DMDPOXA, because the cis and trans-14 are closed forms of the zwitterionic S-DMDPOXA. To our knowledge cis and trans-14 has been never previously observed.

Table 4.1. Experimental and calculated carbonyl frequencies of products in the photodecomposition of trans-1a.

<table>
<thead>
<tr>
<th>Label</th>
<th>Structure</th>
<th>Observed frequency (cm⁻¹)</th>
<th>Calculated frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-14a</td>
<td><img src="image" alt="Structure" /></td>
<td>1814</td>
<td>1843 (238), 1841 (238)</td>
</tr>
<tr>
<td>cis-14a</td>
<td><img src="image" alt="Structure" /></td>
<td>-</td>
<td>1514 (287)</td>
</tr>
<tr>
<td>S-DMDPOXAb</td>
<td><img src="image" alt="Structure" /></td>
<td>-</td>
<td>1443 (11)</td>
</tr>
<tr>
<td>T-DMDPOXAb</td>
<td><img src="image" alt="Structure" /></td>
<td>-</td>
<td>1514 (287)</td>
</tr>
<tr>
<td>8a</td>
<td><img src="image" alt="Structure" /></td>
<td>1691</td>
<td>1713 (283)</td>
</tr>
<tr>
<td>trans-10a</td>
<td><img src="image" alt="Structure" /></td>
<td>1753</td>
<td>1765 (162)</td>
</tr>
</tbody>
</table>

a: B3LYP/6-31G(d) and b:UB3LYP/6-31G(d) Gaussian 98 scaled by 0.96. Calculated intensities are given in parentheses.

The absorption at 1814 cm⁻¹ in the TRIR spectra was not observed in the steady state infrared spectra of UV-irradiated trans-1a solutions. Instead of this band, the absorption at 1693 cm⁻¹
74

was observed which was assigned to the vibrational frequency of the carbonyl group of 8 (Figure 3.17). It is well known that cyclopropanones exist in the equilibrium with oxyallyls.\textsuperscript{13,15} Disrotatory ring opening of cis and trans-14 leads to the zwitterionic S-DMDPOXA (Scheme 4.1). Then, the electrocyclic ring closure of the S-DMDPOXA with subsequent rearrangement forms 8. According to the kinetic traces (Figure 4.2), the ring closure of the S-DMDPOXA to form a three-membered ring of cis and trans-14 (\( \leq 30 \) ns, \( k \geq 3 \times 10^7 \) s\(^{-1} \)) is kinetically more favored than the formation of five-membered ring of 8 (\( > 500 \) s, \( k < 2 \times 10^3 \) s\(^{-1} \)).

One of the ways to detect triplet diradicals is to trap them with oxygen to produce peroxides.\textsuperscript{70} The T-DMDPOXA being a triplet diradical can also be trapped with oxygen leading to the reduction of absorption intensity at 1814 cm\(^{-1}\) in the TRIR spectra. However, the lifetime and amplitude of the 1814 cm\(^{-1}\) transient were identical in the experiments with argon- or oxygen-saturated solutions of trans-1a (Figure 4.1). Based on this result the lifetime of the T-DMDPOXA can be estimated. The rate constant for bimolecular reaction of T-DMDPOXA with oxygen should be similar to the rate constant of triplet 1,3-diphenylcyclopentan-1,3-diyl (4.3\( \times 10^9 \) M\(^{-1}\)s\(^{-1} \)).\textsuperscript{70d} If the concentration of oxygen in carbon tetrachloride is about 12.4x10\(^{-3}\) M (298 K)\textsuperscript{71} and the rate constant of bimolecular reaction with oxygen is about 4.3x10\(^9\) M\(^{-1}\)s\(^{-1} \), the lifetime of T-DMDPOXA should be \( \leq 1 / (12.4x10^{-3} x 4.3x10^9) \leq 19 \) ns. This value is close to the lifetimes of similar triplet states of 1,3-diphenylpropane-1,3-diyls (5-16 ns)\textsuperscript{72} (Figure C2).

According to these data, the lifetime of T-DMDPOXA (estimated \( \leq 19 \) ns) is shorter than the response time of the TRIR instrument (30 ns). Therefore, femtosecond TRIR spectroscopy or femtosecond TR UV-VIS spectroscopies can be used to study the T-DMDPOXA. The use of femtosecond TR UV-VIS spectroscopy is reasonable because the T-DMDPOXA should have a high extinction coefficient due to the conjugation of radical sites with the aromatic rings. For this reason, the transients (\textit{7,13} and \textit{cis} and \textit{trans-14}) in the nanosecond TR UV-VIS spectra can be assigned based on the nanosecond TRIR spectra and the formation of these transients can be followed in the femtosecond TR UV-VIS spectra.

\textit{Nanosecond time-resolved UV-VIS studies}

The TR UV-VIS spectra of trans-1a in argon-saturated carbon tetrachloride solutions were acquired after a 355 nm laser pulse with nanosecond time resolution (Figure 4.5). An
intense band around 290 nm was observed for \textit{trans-1a} in the TR UV-VIS spectra. This transient formed “instantaneously” and decayed with a lifetime longer than 500 \(\mu\)s (Figure 4.6). The saturation of the solution with oxygen did not quench 290 nm transient. The kinetic data, absence of oxygen quenching and spectroscopic features of 290 nm transient, which are similar to the TRIR studies suggest that 290 nm transient is an overlap of 7, 13 and \textit{cis} and \textit{trans-14}. Most likely, 290 nm band is the overlap of transient absorptions of the aromatic rings of 7, 13 and \textit{cis} and \textit{trans-14}. No short-lived transients corresponding to the \textit{T-DMDPOXA} were found in the TR UV-VIS spectra.

\textbf{Figure 4.5.} Transient UV-VIS spectra of \textit{trans-1a} acquired in argon-saturated carbon tetrachloride after a 355 nm laser pulse.
Figure 4.6. Kinetic trace of 290 nm of transient UV-VIS absorption in compound trans-1a.

Nanosecond time-resolved UV-VIS studies at 77 K

The TR UV-VIS spectra from trans-1a in EPA at 77 K after a 355 nm laser pulse with nanosecond time resolution are shown in Figure 4.7. A broad positive band at 375–405 nm and a negative band with a maximum at ≈ 520 nm were observed in the 77 K TR UV-VIS spectra. The transient absorption signals formed within the response time of the instrument and decayed mono-exponentially with a lifetime of $t_1 = 78 \pm 2$ ns for 375-405 nm transient and bi-exponentially with lifetimes of $t_1 = 9.7 \pm 0.4$ ns; $t_2 = 72.9 \pm 3.9$ ns for 520 nm transient. The short component of 520 nm transient corresponds to the light scattering.
Figure 4.7. Transient UV-VIS spectra of excited triplet state of \textit{trans-1a} acquired after a 355 nm laser pulse.

The same transient with the maximum around 520 nm and the same lifetime (75.0±0.4 ns) was observed in the 77 K time-resolved emission spectra of \textit{trans-1a} in the EPA at 77 K (Figure 3.11 and Figure 3.12) and was assigned to the emission from the excited triplet state of \textit{trans-1a}. The similarity of spectroscopic characteristics and lifetimes of 520 nm transient (\(t_2=72.9±3.9 \text{ ns}\)) in the 77 K TR UV-VIS spectra with 520 nm transient in the time-resolved emission spectra allow us to assign this transient to the phosphorescence (Figure 4.9). Thus, because the lifetime of transient absorption at 520 nm equals to the lifetime of the transient absorption at 375-405 nm, the 375-405 nm transient can be assigned to the \(T_1-T_n\) absorption of excited triplet state of \textit{trans-1a} (Figure 4.8). This \(T_1-T_n\) absorption spectrum of excited triplet state of \textit{trans-1a} was obtained only in the 375-405 nm region, because the laser pulse and the emission from the excited triplet state of \textit{trans-1a} interfere with this spectrum at the shorter and at the longer wavelength of the 375-405 nm transient, respectively (Figure 4.7). It is a challenge to obtain the \(T_1-T_n\) absorption spectrum of \textit{trans-1a} and to compare it with the femtosecond TR UV-VIS spectra of \textit{trans-1a}.
Figure 4.8. Kinetic trace of 380 nm of transient UV-VIS absorption in compound trans-1a.

Figure 4.9. Kinetic trace of 520 nm of transient UV-VIS absorption in compound trans-1a.
**Femtosecond time-resolved UV-VIS studies**

The TR UV-VIS spectra of trans-1a in argon-saturated carbon tetrachloride were obtained with picosecond resolution. The transient broad absorption between 380 nm and 550 nm with a maximum around 380 nm was formed “instantaneously” and decayed with a lifetime of about 3 ns after 267 nm or 340 nm 100 fs laser pulse (Figure 4.10-Figure 4.14). The saturation of solution with oxygen did not lead to a quenching or to a decrease of intensity of the 380-550 nm transient. The lifetime of 380-550 nm transient (≈ 3 ns) explains why this transient was not observed in the nanosecond TR UV-VIS spectra (Figure 4.5 and Figure 4.6) and could not be trapped with oxygen, which means that this transient is a precursor for cis and trans-14. Thus, 380-550 nm transient was assigned to the T-DMDPOXA.

![Graph](image-url)

**Figure 4.10.** Transient UV-VIS spectral evolution of trans-1a in argon-saturated carbon tetrachloride after a 340 nm laser pulse.
**Figure 4.11.** Kinetic trace of 400 nm of transient UV-VIS absorption in the compound \textit{trans-1a} after a 340 nm laser pulse.

**Figure 4.12.** Transient UV-VIS spectral evolution of \textit{trans-1a} in argon-saturated acetonitrile after a 267 nm laser pulse (0 - 50 ps).
Figure 4.13. Transient UV-VIS spectral evolution of trans-1a in argon-saturated acetonitrile after a 267 nm laser pulse (50-1000 ps).

Figure 4.14. Kinetic trace of 400 nm of transient UV-VIS absorption in the compound trans-1a after a 267 nm laser pulse.

TR UV-VIS spectra of trans-1a in carbon tetrachloride: methanol (15 : 1 v/v) were acquired after a 340 nm laser pulse with picosecond time resolution. Surprisingly, transient
absorption at 380-550 nm (Figure 4.10 and Figure 4.11) disappeared and another band was observed in the TR UV-VIS spectra with a maximum at 652 nm (Figure 4.15-Figure 4.16). The 652 nm band formed “instantaneously” and decayed with a lifetime of about 650 ps (Figure 4.17).

![Figure 4.15. Transient UV-VIS spectra of trans-1a in carbon tetrachloride (red) and in carbon tetrachloride:methanol (15:1 v/v)(blue) both acquired 60 ps after a 340 nm laser pulse.](image)

*Trans-1a* has the same photochemistry in methanol and carbon tetrachloride, so the same excited triplet state of *trans-1a* is formed in both solvents. Therefore, the observation of the 652 nm transient and the disappearance of the band at 380-550 nm (**T-DMDPOXA**) in the femtosecond TR UV-VIS spectra upon the addition of methanol is a proof that the 380-550 nm band cannot correspond to the excited triplet state of *trans-1a*. No shift of absorption of the excited triplet state of *trans-1a* should be observed upon the addition of methanol.
Figure 4.16. Transient UV-VIS spectral evolution of *trans-1a* in carbon tetrachloride: methanol (15:1 v/v) after a 340 nm laser pulse (0.5 - 510 ps).

Figure 4.17. Kinetic trace of 652 nm of transient UV-VIS spectra in compound *trans-1a* in carbon tetrachloride:methanol (15:1 v/v) after a 340 nm laser pulse.

Similar to transient at 652 nm in the femtosecond TR UV-VIS spectra the absorption at 650 nm was observed at 77 K in rigid glass during irradiation of lumisantonin and was assigned
to zwitterionic oxyallyl formed. Another observation of oxyallyl with a zwitterionic nature was made by Garcia-Garibay.\textsuperscript{77} The irradiation of neat dispiro[5.1.5.1]tetradecane-7,14-dione led to the formation of broad absorption at 400-700 nm with a maximum around 580 nm (Figure 4.18). This absorption was also assigned to the zwitterion of the corresponding oxyallyl formed. Thus, the 652 nm transient in the femtosecond TR UV-VIS spectra was assigned to the zwitterionic S-DMDPOXA. The disappearance of 380-550 nm transient (T-DMDPOXA) in the TR UV-VIS spectra and formation of 652 nm transient can be explained as follows, the addition of polar protic methanol leads to the stabilization of zwitterion structure of the S-DMDPOXA over the diradical structure, it facilitates ISC in the T-DMDPOXA forming zwitterionic S-DMDPOXA.

\textbf{Figure 4.18.} Photodecomposition of neat dispiro[5.1.5.1] tetradecane-7,14-dione.\textsuperscript{77}
Discussion

The photochemistry of trans-1a was studied using nanosecond TRIR, nanosecond TR UV-VIS and femtosecond TR UV-VIS spectroscopes.

Based on the trapping experiments with oxygen in the nanosecond TRIR and nanosecond TR UV-VIS experiments, the lifetime of the T-DMDPOXA (≤ 19 ns) was shorter than time resolution of TRIR instrument (30 ns). Therefore, femtosecond TRIR or TR UV-VIS spectroscopies can be used to study the T-DMDPOXA. The vibrational frequencies of the carbonyl groups in the T-DMDPOXA and S-DMDPOXA were estimated using UB3LYP/31G (d) Gaussian 98 (Table 4.1). Calculations showed that the frequencies of the carbonyl stretching bands in the T-DMDPOXA and S-DMDPOXA should be observed at 1443 cm⁻¹ and 1514 cm⁻¹ in the femtosecond TRIR spectra, respectively. These computational data can be explained as follows; due to a conjugation of radical sites with the carbonyl group in the T-DMDPOXA the carbonyl group looses its double bond character, which resulted in the low vibrational frequency (1443 cm⁻¹) and the low amplitude of the carbonyl group as compared with the vibrational frequency (1843 cm⁻¹) and the amplitude of carbonyl stretching in cis and trans-14. Therefore, T-DMDPOXA might not be observed in the femtosecond TRIR spectra. Nevertheless, the lifetime of T-DMDPOXA can be obtained by “indirect” ways. The rate of decay of T-DMDPOXA equals to the rate of formation of cis and trans-14, which can be measured in the femtosecond TRIR experiments. The calculated low vibrational frequency of carbonyl group (1514 cm⁻¹) in the S-DMDPOXA as compared with cis and trans-14 can be explained by a contribution of the zwitterionic S-DMDPOXA with the reduced double bond character in the C-O bond. As it was mentioned in Chapter 1, the zwitterionic character in the oxyallyl became more predominant over the diradical character upon the α-substitution in the oxyallyl. Our calculation of the vibrational frequencies of carbonyl groups of T-DMDPOXA and S-DMDPOXA are in an agreement with Borden¹⁶b calculations of the similar cyclopentane-2-one-1,3-diyl. The vibrational frequencies of carbonyl group of a singlet cyclopentane-2-one-1,3-diyl (1736 cm⁻¹), triplet cyclopentane-2-one-1,3-diyl (1387 cm⁻¹) and corresponding cyclopropanone [ bicyclo[2.1.0]pentan-5-one (1830 cm⁻¹)] were calculated.¹⁶b Borden suggested that the lower
carbonyl frequency for triplet diradical in comparison with carbonyl frequencies of singlet diradical and cyclopropanone is due to the reduction of double bond character in the C-O bond.

We used the femtosecond TR UV-VIS spectroscopy to study the T-DMDPOXA. The transient absorption at 380-550 nm with maximum around 380 nm and lifetime of \( \approx 3 \) ns in the femtosecond TR UV-VIS spectra of trans-1a was assigned to the T-DMDPOXA. The \( T_1 - T_n \) absorption of trans-1a (375-405 nm transient) in the nanosecond 77 K TR UV-VIS spectra (Figure 4.7) look similar to the broad transient absorption at 380-550 nm in the femtosecond TR UV-VIS spectra (Figure 4.10). However, the transient at 380–550 nm cannot correspond to the \( T_1 - T_n \) absorption of trans-1a, because the large difference \((10^5-10^6)\) between the lifetimes of the excited triplet states of azo compounds in rigid glasses at 77 K and their lifetimes in the solutions at 298 K was observed\(^7\) (Figure 4.19). If the lifetime of the excited triplet state of trans-1a at 77 K is 75 ns, its lifetime in the solution at 298 K should be at least in the picosecond region (1-10 ps). Also it was found\(^7\) that the lifetime of the excited triplet state of similar azocumene at 298 K is around 9.5 ps (time of radiationless decay to the ground state), which is considerably faster than the time of its decomposition (600 ps).

<table>
<thead>
<tr>
<th>azoalkane</th>
<th>( \tau (298 \text{ K}) ) ns</th>
<th>( \tau (77 \text{ K}) ) ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>630 ± 20</td>
<td>24.3 ± 0.2</td>
</tr>
<tr>
<td>b</td>
<td>440 ± 10</td>
<td>58.7 ± 0.4</td>
</tr>
<tr>
<td>c</td>
<td>200 ± 10</td>
<td>43.4 ± 1.2</td>
</tr>
<tr>
<td>d</td>
<td>580 ± 20</td>
<td>25.6 ± 0.7</td>
</tr>
<tr>
<td>e</td>
<td>( n. d^a )</td>
<td>4.5 ± 0.3</td>
</tr>
<tr>
<td>f</td>
<td>( n. d^a )</td>
<td>10.1 ± 0.5</td>
</tr>
<tr>
<td>g</td>
<td>( n. d^a )</td>
<td>2.9 ± 0.2</td>
</tr>
</tbody>
</table>

\( ^a \) Not detected on nanosecond time scale.

**Figure 4.19.** Lifetimes of excited triplet states of azo compounds in rigid glasses at 77 K and in solution at 298 K.\(^57\)
The 380-550 nm transient with the lifetime of \(\approx 3\) ns cannot also correspond to the S-DMDPOXA, because similar to that singlet 1,3-diradicals\(^{74}\) have shorter lifetimes of about 0.12 ps. By the way, the absorption spectra and lifetimes of triplet states of 1,3-diphenylpropane-1,3-diyls (13-16 ns)\(^{72}\) are similar to the 380-550 nm transient. The absorption maximum of 380-550 nm transient is slightly red shifted (\(\approx 380\) nm) as compared with the absorption maxima of triplet states of 1,3-diphenylpropane-1,3-diyls (320-340 nm, Figure C1) probably due to a conjugation of radical sites of the T-DMDPOXA with the carbonyl group and aromatic rings. The shorter lifetime of 380-550 nm transient (~3 ns) as compared with lifetimes of triplet 1,3-diphenylpropane-1,3-diyls (\(\approx 5-16\) ns, Figure C2) can be explained by the zwitterionic nature of the S-DMDPOXA and the fast rate of ISC in the T-DMDPOXA. According to Salem and Rowland theory,\(^{70a,75}\) zwitterionic contribution to a singlet wavefunction enhances ISC in triplet diradicals. Calculations [B3LYP/31G(d) Gaussian 98] predict that T-DMDPOXA and S-DMDPOXA should be isoenergetic (Figure C5-Figure C8), which also explain observed short lifetime of the T-DMDPOXA. The 380-550 nm transient was not observed in the nanosecond TR UV-VIS, which means that this transient is the precursor for cis and trans-14 (closed forms of S-DMDPOXA). Thus, the 380-550 nm transient can be assigned to the T-DMDPOXA. This was the first time when absorption spectrum of triplet oxyallyl derivative was observed and its lifetime was measured.

In the femtosecond TR UV-VIS spectra of trans-1a in carbon tetrachloride-methanol (15:1 v/v), the appearance of absorption at 652 nm with the lifetime of \(\approx 0.65\) ns was observed. As it was mentioned before similar absorption at 650 nm was observed at 77 K in rigid glass during irradiation of lumisantonin\(^{76}\) and was assigned to zwitterionic oxyallyl formed. Another zwitterionic oxyallyl with a maximum around 580 nm was observed during irradiation of dispiro[5.1.5.1]tetradecane-7,14-dione (Figure 4.20).\(^{77}\) The disappearance of 380-550 nm transient (T-DMDPOXA) and formation of 652 nm transient suggest that the addition of polar protic methanol leads to the stabilization of the zwitterion structure of S-DMDPOXA facilitating ISC in the T-DMDPOXA affording the zwitterionic S-DMDPOXA (Scheme 4.3).
Scheme 4.3. Singlet and triplet states of 2,4-diphenyl-3-pentanone-1,3-diyl (S-DMDPOXA and T-DMDPOXA, respectively).

The zwitterionic S-DMDPOXA lives shorter (≈ 0.65 ns) than the T-DMDPOXA (≈ 3 ns) due to the singlet nature of the S-DMDPOXA. At the same time the zwitterionic S-DMDPOXA have longer lifetime than the singlet propane-1,3-diyls (≈ 1 ps), because conjugation of carbonyl group and aromatic rings in the zwitterionic S-DMDPOXA stabilize it. Also it was suggested that the substitution at α-carbons of oxyallyl should stabilize better the zwitterionic oxyallyl rather than diradical oxyallyl. The calculation of vibrational frequency of carbonyl group of the S-DMDPOXA (1514 cm\(^{-1}\)) showed zwitterionic contribution (Table 4.1). Therefore, the transient absorption at 652 nm can be assigned to the zwitterionic S-DMDPOXA. Even some reports about the spectroscopic properties of the zwitterionic oxyallyls are available, to the best of our knowledge we did the first estimation of the lifetime of the zwitterionic oxyallyl (S-DMDPOXA).

Short lifetimes of the T-DMDPOXA and S-DMDPOXA explain, why these intermediates cannot be trapped with oxygen, acrylonitrile, methanol and furan (Chapter 3). The rate of ISC in the T-DMDPOXA and rates of electrocyclic ring closure of the zwitterionic S-DMDPOXA is faster than competitive rates of adduct formation.
The 7 and 13 were products of the retro-1,3-dipolar cycloaddition of the excited triplet state of trans-1a. Similar fragmentation for trans-2a forming 13 was observed in the TRIR spectra. As it was mentioned before similar fragmentation with the formation of styrene and phenylcarbene was observed in the steady state photolysis of 3,5-diphenyl-1-pyrazoline (Scheme 4.4).45 Two mechanisms of its fragmentation were proposed. The first is a “one-step” mechanism, in which the fragmentation of 3,5-diphenyl-1-pyrazoline produces directly with the formation of phenylcarbene, styrene and nitrogen (path B). The second is a “two-step” mechanism (path C) in which a first step is a retro-1,3-dipolar cycloaddition of 3,5-diphenyl-1-pyrazoline to produce phenyldiazomethane and styrene. The next step is the decomposition of photochemically labile phenyldiazomethane, which leads to the expulsion of nitrogen to afford phenylcarbene. Even at 5.5 K, phenylcarbene was observed during the irradiation of neat 3,5-diphenyl-1-pyrazoline in the triplet ESR spectra.45a Because of the instability of phenyldiazomethane, it was hard to prove that the fragmentation of 3,5-diphenyl-1-pyrazoline proceeded by the retro-1,3-dipolar cycloaddition.

**Scheme 4.4.** Photodecomposition of trans-3,5-diphenyl-1-pyrazoline.
Buchwalter and Closs\textsuperscript{45a} made mention of this fragmentation reaction of 3,5-diphenyl-1-pyrazoline: “Present data cannot distinguish between a retro-1,3-dipolar addition and direct fragmentation.” Schneider and Bippi\textsuperscript{45b} also pointed out the fragmentation of 3,5-diphenyl-1-pyrazoline: “It was suggested previously that [3+2] cycloreversions may effectively compete with biradical processes in the decomposition of monocyclic 1-pyrazolines, although, to our best knowledge, a quantitative determination of the primary products of such reactions has been never achieved.” To the best of our knowledge, the nanosecond TRIR spectroscopy was used to monitor the retro-1,3-dipolar cycloaddition of 1-pyrazolines (\textit{trans-1a} and \textit{trans-2a}) for the first time.

**Conclusions**

\textit{Trans} and \textit{cis-1a} were synthesized in the five steps using modified Pirkle\textsuperscript{23} procedure. The novel one-pot crossed aldol/dehydration reaction was developed producing 5a and 5b in 40 - 50\% yield. This procedure can be used for the synthesis of other [-alkylchalones. The new derivatives of 3,5-dialkyl-3,5-dihydro-3,5-diphenyl-4\textit{H}-pyrazol-4-one (1), \textit{cis-1b} and \textit{trans-1c} were synthesized stereoselectively in five steps starting from 5b.\textsuperscript{36}

Since the yields of \textit{cis-1b} and \textit{trans-1c} were low, the photochemistry of \textit{trans-1a} was studied. The photophysical and photochemical properties of \textit{trans-1a} never have been studied before. According to the photophysical data \textit{trans-1a} has the lowest excited triplet state. Irradiation of \textit{trans-1a} at 350 nm or 254 nm leads to the excited singlet state. Fast ISC produces the non-reactive excited triplet state of \textit{trans-1a}. The radiationless decay of the excited triplet state to the ground state is much faster than the rates of its decomposition. The two pathways for the decomposition of the excited triplet state of \textit{trans-1a} were proposed. One pathway is the expulsion of nitrogen forming the \textbf{T-DMDPOXA}. The transient absorption at 380-550 nm with the lifetime of \(\approx 3\) ns in the femtosecond TR UV-VIS spectra of \textit{trans-1a} was assigned to the \textbf{T-DMDPOXA}. To our knowledge, it was the first time when the triplet oxyallyl diradical was observed and its lifetime was estimated. Subsequent ISC by SOC in the \textbf{T-DMDPOXA} leads to the \textbf{S-DMDPOXA} with the zwitterionic nature. In the femtosecond TR UV-VIS spectra of \textit{trans-1a} in carbon tetrachloride-methanol (15:1 v/v), the appearance of the absorption at 652 nm with the lifetime of \(\approx 0.65\) ns was assigned to the zwitterionic \textbf{S-DMDPOXA}. Even some reports about the spectroscopic properties of the zwitterionic oxyallyls are available; we did the first
estimation of the lifetime of zwitterionic oxyallyl (S-DMDPOXA). Disrotatory ring closure of the S-DMDPOXA leads to cis and trans-14. The formation of cis and trans-14, phenyldiazoethane (13) and phenylmethylketene (7) was proved by the nanosecond TRIR spectroscopy during the photodecomposition of trans-1a. The observation of cis and trans-14 (another closed forms of S-DMDPOXA) in the TRIR spectra again support the existence of the S-DMDPOXA. Then, the disrotatory ring opening of cis and trans-14 leads to oxidopentadienyl cation (resonance form of the zwitterionic S-DMDPOXA), which forms 8 by the controtary 4 \[ \text{electrocyclic ring closure} \]. The subsequent thermal 1,5-H shift in 8 lead to 9, which then forms cis and trans-10 by the keto-enol tautomerisation.

7 and 13 observed in the TRIR spectra were the products of the retro-1,3-dipolar cycloaddition of the excited triplet state of trans-1a. We observed similar fragmentation for trans-2a forming 13 in the TRIR spectra. The use of the TRIR spectroscopy proved that the fragmentation of trans-1a and trans-2a is the retro-1,3-dipolar cycloaddition. For the first time nanosecond TRIR spectroscopy was used to monitor the 1,3-retro dipolar cycloaddition of 1-pyrazolines.
EXPERIMENTAL SECTION

General

UV-VIS spectra were measured with Shimadzu UV-2401PC spectrometer. Steady state photoluminescence spectra were recorded on Jobin-Yvon Fluorolog-3 FL-11 spectrofluorimeter (450 W Xe lamp, R928 Hamamatsu single photon counting PMT detector). $^1\text{H}$ and $^{13}\text{C}$ NMR spectra were recorded on Bruker Advance 300 MHz system. GC-MS and DIP spectra were obtained on Shimadzu GC/MS-QP5050A spectrometer. Chemical shifts were recorded as $\delta$ values in parts per million (ppm). $^1\text{H}$ and $^{13}\text{C}$ NMR spectra were acquired in deuterochloroform (CDCl$_3$) at 20$^\circ$C. Melting points were determined using a Thomas Hoover capillary melting point apparatus. High-resolution mass spectra were done in the Mass Spectrometry Laboratory, University of Illinois at Urbana-Champaign, IL. HPLC measurements were performed on Hitachi LC-7000 series instrument equipped with Alltech Nucleosil C18 column. Analytical photolysis were performed by irradiation of $1\times10^{-2}$ M solutions of trans-1a in a 1 cm quartz cell, using a Rayonet Srinivasan-Griffin photochemical reactor with sets of sixteen lamps with $\lambda_{\text{max}}$ of emission at 254, 300 and 350 nm.

Materials

All reactions were carried out under an atmosphere of dry argon. Thin layer chromatography was performed using commercially prepared silica gel plates, polyester backed, 200 $\mu$m and visualization was effected with short wavelength UV light (254nm) and/or cerium solution [4.12 g -(NH$_4$)$_6$Mo$_4$O$_{24}$, 1.12g-Ce(SO$_4$)$_2$*H$_2$O, 10ml conc. H$_2$SO$_4$ and 100 ml H$_2$O]. Jones reagent$^{84}$ (0.67 g CrO$_3$, 1.6 g H$_2$O and 1.07 g conc. H$_2$SO$_4$) was used for oxidation. Flash chromatography was performed using silica gel 60 Å, 32-63 $\mu$m. Tributylamine and triethylamine were distilled over NaOH and were stored over NaOH. Acetophenone, propiophenone and methanesulfonyl chloride were distilled prior to use. Dichloromethane was distilled over CaH$_2$. Toluene was distilled over sodium prior to use.
Nanosecond infrared time-resolved (TRIR) experiments

The detailed description of time-resolved FTIR setup is available elsewhere. Briefly, the third harmonic of a Spectra Physics YAG:Nd³⁺ laser (354.7 nm) was used as an excitation source in all experiments. The laser was operated in pulsed mode with repetition rate 10 Hz and the energy varied from 1.5 to 5 mJ per pulse. The sample solutions were pumped through 1 mm thick CaF₂ flow cell with flow rate up to 150 ml per minute. All spectra recorded in 1500-2800 cm⁻¹ spectral window with resolution 8 cm⁻¹ every 20 ns. The raw data were processed and visualized with custom written LabView based software.

Nanosecond UV-VIS time-resolved (TR UV) experiments

The time-resolved UV-vis spectrometer has been describe elsewhere. Briefly, the third harmonic of a Continuum YAG:Nd³⁺ laser (354.7 nm) was used as an excitation source in all experiments. The laser was operated with repetition rate 5 Hz and the energy was kept between 0.5 and 3 mJ per pulse. Solutions were pumped through a quartz flow cell with three polished window with flow rate up to 150 ml per minute. Transient UV-VIS spectra were acquired every 10 nm in 330-820 nm spectral interval.

Femtosecond UV-VIS time-resolved (TR UV) experiments

The detailed description of home-built ultrafast UV-VIS setup is available elsewhere. Briefly, the frequency converted (340 nm) output from Spectra-Physics Hurricane femtosecond laser was used as an excitation source. The probe pulses were generated in CaF₂ crystal and overlapped with pump inside the sample flow cell. The solution was degassed with argon and pumped through 2 mm thick CaF₂ flow cell with flow rate up to 150 ml per minute. The absorption of the sample at excitation wavelength was 0.8-1.0 (2 mm cell) and was constantly checked to ensure the decomposition of the starting material less than 10 %.
**Time-resolved emission experiments**

Emission lifetimes were measured with nitrogen-pumped broadband dye laser (2-3 nm fwhm) from PTI (GL-3300 N₂ laser, GL-301 dye laser). PPO 365/380 (2,5-diphenyloxazole) laser dye was used to tune the unfocused excitation. Frozen glass emission samples at 77 K were prepared by inserting a 5 mm (internal diameter) NMR tube containing a 10⁻⁵ M solution (4:1 EtOH/MeOH, EPA or ethyl iodide was used to induce phosphorescence).

**Matrix IR experiments**

The detailed description of matrix IR experiments is available elsewhere. Briefly, matrix IR experiments were performed using an Iwatani Cryo Mini closed cycle helium cryostat. A CsI window was attached to the copper holder at the bottom of the cold head. Tow opposing ports of a vacuum shroud surrounding the cold head were fit with KBr with a quartz plate for UV irradiation and a deposition plate for admitting the sample and matrix gas. Irradiation was carried out with a Bunkoukeiki 150 W xenon lamp. Matrix IR experiments were done with cis and trans-1a.

**DFT Calculations**

DFT calculations were performed using Gaussian 98. The geometries were optimized using B3LYP level of theory with 6-31G(d) basis sets. The IR frequencies were calculated using the same basis set and were scaled up by a factor of 0.96.
REFERENCES


(77) http://www.chem.ucla.edu/dept/faculty/mgghome/intermediates_files/slide8.jpg.


C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, revision A 11.3; Gaussian, Inc.: Pittsburg, PA, 2002.


APPENDIX A: SUPPORTING INFORMATION FOR CHAPTER 2.
NMR (CDCl₃) δ 1.97 (s, 3H), 2.34 (d, 1H, J = 9 Hz), 2.38 (s, 3H), 5.11 (d, 1H, J = 9 Hz)

NMR (CDCl₃) δ 7.08-7.4 (m, 10H), 7.65 (d, 2H, J = 8 Hz), 7.82 (dd, 2H, J = 2-3.7 Hz)

Figure B1. $^1$H NMR spectrum of trans-2a in deuterated acetonitrile at 300 MHz before direct irradiation at 350 nm (0.5 - 2.0 ppm region).

Figure B2. $^1$H NMR spectrum of trans-2a in deuterated acetonitrile at 300 MHz after direct irradiation for 10 minutes at 350 nm (0.5 - 2.0 ppm region).
Figure B3. $^1$H NMR spectrum of *trans*-2a in deuterated acetonitrile at 300 MHz before direct irradiation at 350 nm (2.6 - 4.5 ppm region).

Figure B4. $^1$H NMR spectrum of *trans*-2a in deuterated acetonitrile at 300 MHz after direct irradiation for 10 minutes at 350 nm (2.6 - 4.5 ppm region).
Figure B7. $^1$H NMR spectrum of cis-2a in deuterated acetonitrile at 300 MHz before direct irradiation at 350 nm (3.4 - 4.5 ppm region).

Figure B8. $^1$H NMR spectrum of cis-2a in deuterated acetonitrile at 300 MHz after direct irradiation for 5 minutes at 350 nm (3.4 - 4.5 ppm region).
**Figure B9.** $^1$H NMR spectrum of \textit{trans-2a} in deuterated acetonitrile at 300 MHz before triplet sensitization at 370 nm (1.0 - 2.0 ppm region).

**Figure B10.** $^1$H NMR spectrum of \textit{trans-2a} in deuterated acetonitrile at 300 MHz after triplet sensitization for 14 hours at 370 nm (1.4 - 3.0 ppm region).
Figure B11. $^1$H NMR spectrum of *trans*-2a in deuterated acetonitrile at 300 MHz before triplet sensitization at 370 nm (3.0 - 4.5 ppm region).

Figure B12. $^1$H NMR spectrum of *trans*-2a in deuterated acetonitrile at 300 MHz after triplet sensitization for 14 hours at 370 nm (3.0 - 4.6 ppm region).
**Figure B13.** $^1$H NMR spectrum of \( \text{cis-2a} \) in deuterated acetonitrile at 300 MHz before triplet sensitization at 370 nm (1.4 - 3.0 ppm region).

**Figure B14.** $^1$H NMR spectrum of \( \text{cis-2a} \) in deuterated acetonitrile at 300 MHz after before triplet sensitization for 4 hours at 370 nm (1.4 - 3.0 ppm region).
Figure B15. $^1$H NMR spectrum of cis-2a in deuterated acetonitrile at 300 MHz before triplet sensitization at 370 nm (3.0 - 4.6 ppm region).

Figure B16. $^1$H NMR spectrum of cis-2a in deuterated acetonitrile at 300 MHz after triplet sensitization for 4 hours at 370 nm (3.0 - 4.6 ppm region).
Figure B17. $^1$H NMR spectrum of trans-1a in deuterated acetonitrile at 300 MHz after direct irradiation at 350 nm for 3 hours.

Figure B18. $^1$H NMR spectrum of trans-1a in deuterated acetonitrile at 300 MHz after triplet sensitization with DMBP (molar ratio 1:1) at 350 nm for 3 hours.
**Figure B19.** Time evolution of UV-VIS spectra of \textit{trans-1a} in acetonitrile acquired after a 254 nm irradiation (0-40 sec.).

**Figure B20.** Time evolution of UV-VIS spectra of \textit{trans-1a} in acetonitrile acquired after a 350 nm irradiation (0-20 min.).
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$^1$H NMR($C_6D_6$) $\delta$ (ppm) 3.1 (m, 2H), 4.8 (m, 2 m), 6.1 (m, 2H)

**Figure B21.** Extinction coefficients of 5-methylene-1,3-cyclohexane (MCH) at various wavelengths.

**Figure B22.** Infrared spectrum of solution of phenylethylketene in carbon tetrachloride.
Figure B23. $^1$H NMR spectrum of \textit{trans-1a} in deuterated acetonitrile at 300 MHz after irradiation at 254 nm for 10 minutes.
Figure B24. $^1$H NMR spectrum in deuterated acetonitrile of $trans$-1a at 300 MHz after irradiation at 254 nm for 10 minutes (10 minutes later).
Figure B25. $^1$H NMR spectrum of trans-1a in deuterated methanol at 300 MHz after irradiation at 350 nm for 1 hour.

Figure B26. $^1$H NMR spectrum of trans-1a in deuterated methanol at 300 MHz after irradiation at 350 nm for 1 hour (96 hours later)
cis- and trans-
APPENDIX C: SUPPORTING INFORMATION FOR CHAPTER 4.

**Figure C1.** Transient absorption spectrum of triplet 1,3-diaryl-propane-1,3-diyl diradical in heptane (266 nm excitation, 12 mJ/pulse; \( \lambda_{\text{max}} = 320 \) nm).

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**Figure C2.** Substituent effects on the lifetime of triplet 1-(4-acetylphenyl)-2-(4-substituted phenyl) propan-1,3-diyls.
**Figure C3.** Transient UV-VIS spectra of trans-1a acquired in argon-saturated carbon tetrachloride after a 355 nm laser pulse.

**Figure C4.** Kinetic trace of 290 nm of transient UV-VIS absorption in compound trans-1a.
**Figure C5.** DR-anti,anti singlet UB3LYP/6-31G(d) C$_2$ Geometry

Nuclear repulsion energy 1174.513378 Hartree
UB3LYP/6-31G(d) energy ($S^2_{\text{before}} = 0.9020$, $S^2_{\text{after}} = 0.2231$)
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Figure C6. DR-anti,anti triplet UB3LYP/6-31G(d) C\textsubscript{2} Geometry

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Figure C7. DR-anti,syn singlet UB3LYP/6-31G(d) C1 Geometry

Nuclear repulsion energy 1198.8218970134 Hartree
UB3LYP/6-31G(d) energy (S^2_{before} = 0.8666, S^2_{after} = 0.1877)
-732.604028621 Hartree

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**Figure C8.** DR-anti,syn

triplet UB3LYP/6-31G(d) C1 Geometry

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Nuclear repulsion energy 1198.3750810074 Hartree

UB3LYP/6-31G(d) energy \( S^2_{\text{before}} = 2.0502 \), \( S^2_{\text{after}} = 2.0016 \)

-732.603574601 Hartree
Figure C9. DR-syn,syn
singlet UB3LYP/6-31G(d) C1 Geometry

Nuclear repulsion energy: 1236.2229865552 Hartree
UB3LYP/6-31G(d) energy (\(S^2\) before = 0.8609, \(S^2\) after = 0.1750)
-732.601877522 Hartree

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Figure C10. DR-syn, syn
triplet UB3LYP/6-31G(d) C1 Geometry

Nuclear repulsion energy

1228.9775535102 Hartree

UB3LYP/6-31G(d) energy ($S^2_{\text{before}} = 2.0499$, $S^2_{\text{after}} = 2.0016$)

-732.601467289 Hartree

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