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1 **Photochemical reactivity of phenyl (methyl)tetrazolium ketone- Hydrogen atom transfer vs**  
2 **electron transfer**

3

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9

10 Abstract:

11 Phenyl (methyl)tetrazolium ketone (**1**) is a synthesis intermediate of tetrazolyloxime fungicides and  
12 can be also generated upon their irradiation. Its photolysis is highly solvent dependent which  
13 prompted us to investigate more deeply the reaction mechanism. Nanosecond laser flash photolysis  
14 of **1** yielded the triplet excited state ( $\lambda_{\text{max}} = 390/570$  nm) immediately after the pulse. This latter was  
15 converted into different secondary species that were identified using their specific reactivity as well  
16 as product studies. The ketyl radical ( $\lambda_{\text{max}} = 315/475$  nm) was generated in less than 0.02  $\mu\text{s}$  in a good  
17 H-donor solvent such as 2-propanol and in around 0.06  $\mu\text{s}$  in cyclohexane, a medium H-donor  
18 solvent. In 2-propanol, ketyl radicals decayed by a second order reaction to yield pinacol (yield 45%)  
19 while in cyclohexane, they decayed by a second order reaction in the bulk leading to pinacol (yield  
20 21%) and by recombination with the cyclohexyl radical in the cage in an apparent first order reaction  
21 to generate an adduct (yield 10%). In a polar and non H-atom donor solvent as acetonitrile, the  
22 zwitterionic diradical ( $\lambda_{\text{max}} = 460$  nm) was formed in 0.6  $\mu\text{s}$  with final formation of an atypic dimer.  
23 Thus two mechanisms of hydrogen atom transfer are observed. In polar acetonitrile solvent, a two-  
24 step-process occurs where the electron is transferred first and the proton follows. In non-polar 2-  
25 propanol and cyclohexane solvents, a one-step process takes place where the electron and the  
26 proton are simultaneously transferred.

27

28 Key words: Fungicide, laser flash photolysis, ketyl radical; zwitterionic diradical, hydrogen atom  
29 transfer, proton coupled electron transfer.

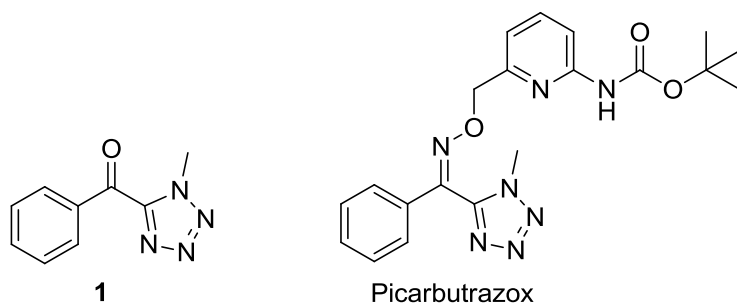
30

31 **Introduction**

32 Plant protection is a key issue in connection with food supply of the mankind. Due to resistance to  
33 existing pesticides and environmental requirements and legislation, an increasing number of  
34 chemical compounds are synthesized and tested in this regard. Chemical structures of such  
35 compounds become more and more complex. Concomitantly with these developments, the weak  
36 stability of highly active compounds becomes a decisive problem. In this context, photostability plays  
37 a key role. Often, new highly active compounds loss almost completely their activity when exposed  
38 to solar light in field. A deep understanding of the mechanisms of corresponding photochemical  
39 reactions is necessary for either suppress or at least reduce these processes or to conceive or design  
40 photostable molecules and finally diminish the "chemical impact" of plant protection in the  
41 environment.

42 Recently, we performed a detailed investigation on the photodegradation mechanism of  
43 tetrazolyloxime fungicides in order to increase their photostability.<sup>1</sup> In the course of these  
44 investigations, we observed the formation of the aromatic ketone **1** (Scheme 1) among other  
45 compounds. Compound **1** is also a synthesis intermediate of fungicides such as picarbutrazox  
46 (Scheme 1).<sup>2</sup>

47



49 Scheme 1. Chemical structure of **1** and picarbutrazox

50

51 We became interested in the photochemical transformations of ketone **1** because of the possibility  
52 of hydrogen atom transfer. In fact in such reactions, hydrogen is often transferred according to two  
53 mechanisms: Either the electron and the proton are transferred simultaneously (hydrogen atom  
54 transfer, HAT) to the electronically excited reaction partner or the electron is transferred first and the  
55 proton follows.<sup>3</sup> These two elementary steps are part of a larger ensemble of proton coupled  
56 electron transfer processes (PCET).<sup>4, 5</sup>

57

## 58 Experimental

### 59 General information

60 Ketone **1** was a gift from Bayer Crop Science. All other reagents were of the highest grade available  
61 and used as received. UV-vis spectra were recorded using a Varian Cary 3 spectrophotometer. <sup>1</sup>H and  
62 <sup>13</sup>C NMR spectra were measured in CDCl<sub>3</sub> with TMS as an internal standard by using a 600 MHz (<sup>1</sup>H  
63 resonance) a Bruker spectrometer. The identification of photoproducts was performed using High  
64 resolution mass spectrometry (HRMS) constituted of an Orbitrap Q-Exactive (Thermoscientific)  
65 coupled to an ultra-high performance liquid chromatography (UHPLC) instrument Ultimate 3000  
66 RSLC (Thermoscientific). Analyses were carried out in both negative and positive electrospray modes  
67 (ESI<sup>+</sup> and ESI<sup>-</sup>). UHPLC separations were performed using a Phenomenex reversed phase column C<sub>18</sub>  
68 grafted silica, (100 mm length, 2.1 mm i.d., 1.7 μm particle size). The binary solvent system used was  
69 composed of acetonitrile (MeCN) and water acidified with 0.5% v/v formic acid. The gradient  
70 program was 5% ACN for the 7 first min, followed by a linear gradient to 99% in 7.5min and kept  
71 constant until 20 min. The flow rate was set at 0.45 mL/min and injection volume was 5 μL.  
72 Identification of photoproducts was based on structural elucidation of mass spectra and the use of  
73 accurate mass determination obtained with the Orbitrap high resolution. HPLC-UV analyses were  
74 performed using a NEXERA XR HPLC-DAD apparatus using the same column and the same HPLC  
75 conditions as previously indicated.

76

### 77 Laser flash photolysis

78 Transient absorption experiments were carried out on a nano laser flash photolysis spectrometer  
79 from Applied Photophysics (LKS.60) using a frequency-quadrupled Nd:YAG laser (Quanta-Ray GCR-  
80 130-1, pulse duration 9 ns). The procedures used for transient absorption spectroscopy  
81 measurements have been described previously.<sup>10</sup> The spectral characteristics of **1** are given in Table  
82 SI-1 and Figure SI-1. The maximum of absorption is just below 270 nm and **1** was therefore excited at  
83 266 nm. Peroxodisulfate was used as a chemical actinometer.  
84

## 85 **Steady state irradiations**

86 For preparative purpose, irradiations were conducted in a tube placed in a Rayonet ( $\lambda = 300$  nm). For  
87 quantum yield measurements, solutions were irradiated in parallel beam using a high pressure  
88 mercury lamp equipped with an Oriel monochromator. The photon flux was measured using a  
89 radiometer QE65000 from Ocean optics. The percentage of **1** conversion was determined by HPLC-  
90 UV.  
91

## 92 **Identification of photoproducts**

93 Photoproduct **2**: Compound **1** (220.5 mg, 1.17 mmol) was dissolved in 30 mL of MeCN, poured in  
94 quartz tubes and degassed with argon during 10 min. The tubes were then placed in a Rayonet and  
95 irradiated at 300 nm for 40 min. The solvent was evaporated under reduced pressure and the crude  
96 was purified by silica column chromatography (petroleum ether/ethyl acetate: 80:20). Starting  
97 material was isolated in 58 % yield (150 mg, 0.68 mmol) and product **2** was obtained in 26 % yield  
98 (48.3 mg, 0.13 mmol) as a white solid ( $R_f$  (petroleum ether/ethyl acetate: 70/30) = 0.22, melting point  
99 range : [82.0°C-82.7°C]). NMR <sup>1</sup>H (600 MHz, CDCl<sub>3</sub>, ppm) :  $\delta$  = 3.74 (s, 3 H), 5.50 (s, 1 H), 5.52 (d,  $J$  =  
100 14.82 Hz, 1 H), 5.87 (d,  $J$  = 14.82 Hz, 1 H), 7.19 (m, 3 H), 7.26 (t,  $J$  = 6.68 Hz, 2 H), 7.54 (t,  $J$  = 7.82 Hz, 2  
101 H), 7.71 (t,  $J$  = 7.40 Hz, 1 H), 8.18 (d,  $J$  = 7.87 Hz, 2 H) ppm. NMR <sup>13</sup>C (150 MHz, CDCl<sub>3</sub>, ppm) :  $\delta$  =  
102 35.18, 57.12, 73.44, 125.36, 128.87, 129.27, 129.50, 131.45, 134.39, 135.60, 136.48, 151.17, 155.35,  
103 182.44 ppm (Figure SI-2). UHPLC-HRMS:  $m/z$  = 377.1463 in ES<sup>+</sup>.

104 Photoproduct **3** in 2-propanol (i-PrOH): Compound **1** (92 mg, 0.49 mmol) was dissolved in 60 mL of i-  
105 PrOH, poured in quartz tubes and degassed with argon during 10 min. The tubes are then placed in a  
106 Rayonet and irradiated at 300 nm for 4 h. The solvent was evaporated under reduced pressure and  
107 the crude was purified by silica column chromatography (petroleum ether/ethyl acetate: 95/5 to  
108 50/50). Product **3** was obtained in 46 % yield (85 mg, 0.22 mmol) as a white solid ( $R_f$  (petroleum  
109 ether/ethyl acetate: 80/20) = 0.76, brown stain on TLC with vanillin revelator, melting point range :  
110 [189.6°C-190.3°C]). NMR <sup>1</sup>H (600 MHz, CDCl<sub>3</sub>, ppm) :  $\delta$  = 3.89 (s, 3 H), 6.85 (d,  $J$  = 7.54 Hz, 4 H), 7.07  
111 (s, 2 H), 7.13 (t,  $J$  = 7.78 Hz, 4 H), 7.25 (t,  $J$  = 7.40 Hz, 2 H) ppm. NMR <sup>13</sup>C (150 MHz, CDCl<sub>3</sub>, ppm) :  $\delta$  =  
112 35.55, 79.07, 127.12, 127.45, 128.78, 134.29, 157.70 ppm (Figure SI-3). UHPLC-HRMS:  $m/z$  = 379.1618  
113 in ES<sup>+</sup> and 377.1485 in ES<sup>-</sup>.

114 Photoproduct **3** in n-heptane: Compound **1** (96 mg, 0.51 mmol) was dissolved in 110 mL of n-  
115 heptane, poured in quartz tubes and degassed with argon during 10 min. The tubes were then placed  
116 in a Rayonet and irradiated at 300 nm for 2 h 30. The solvent was evaporated under reduced  
117 pressure and the crude was purified by silica column chromatography (petroleum ether/ethyl  
118 acetate: 95/5 to 50/50). Product **3** was obtained in 15 % yield (29 mg, 0.08 mmol) as a white solid.

119 Photoproduct **4**: Compound **1** (220.2 mg, 1.17 mmol) was dissolved in 80 mL of cyclohexane, poured  
120 in quartz tubes and degassed with argon during 10 min. The tubes were then placed in a Rayonet and  
121 irradiated at 300 nm for 6 h. The solvent was evaporated under reduced pressure and the crude was  
122 purified by silica column chromatography (petroleum ether/ethyl acetate: 90:10). Stains on TLC

123 plates were revealed with vanilline. Product **3** was obtained as major product in 21 % yield (94 mg,  
124 0.25 mmol) as a white solid. Minor product **4** was obtained in 10 % yield (31 mg, 0.11 mmol) as a  
125 clear liquid ( $R_f$  (petroleum ether/ethyl acetate : 80/20) = 0.30, blue stain on TLC with vanillin  
126 revelator). NMR  $^1\text{H}$  (600 MHz,  $\text{CDCl}_3$ , ppm) :  $\delta$  = 0.99 (qd,  $J$  = 3.48, 12.42 Hz, 1 H), 1.13 (m, 2 H), 1.24  
127 (m, 2 H), 1.47 (qt,  $J$  = 3.48, 13.02 Hz, 1 H), 1.70 (m, 2 H), 1.82 (m, 1 H), 2.05 (d,  $J$  = 12.18 Hz, 1 H), 2.7  
128 (tt,  $J$  = 2.82, 12.12 Hz, 1 H), 2.85 (s, 1 H), 3.83 (s, 3 H), 7.30 (m, 5 H) ppm. NMR  $^{13}\text{C}$  (150 MHz,  $\text{CDCl}_3$ ,  
129 ppm) :  $\delta$  = 26.24, 26.29, 26.36, 27.73, 35.72, 46.82, 77.53, 125.43, 127.90, 128.58, 140.32, 157.57  
130 ppm (Figure SI-4). UHPLC-HRMS:  $m/z$  = 273.1703 in  $\text{ES}^+$ .

131

## 132 Results

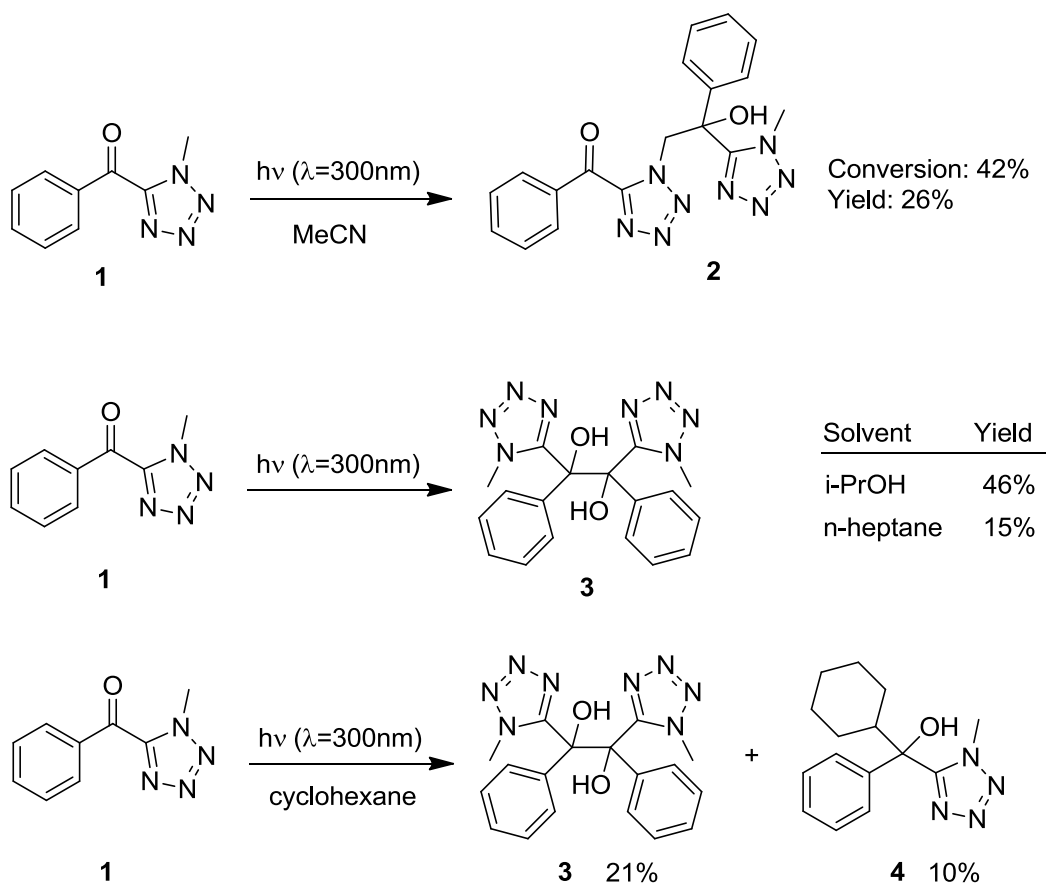
### 133 Product studies

134 When compound **1** was irradiated in acetonitrile at  $\lambda$ =300 nm, we observed the formation of  
135 compound **2**. The reaction was stopped at a conversion of 42% (Scheme 2). Further irradiation led to  
136 a very unselective transformation and the complex product mixture could not be characterized.  
137 Irradiation of compound **1** in *i*-PrOH, cyclohexane or *n*-heptane yielded compound **3**. In cyclohexane,  
138 compound **4** was also obtained in small amounts. Formation of compound **3** resembles the well-  
139 known photo-pinacolization<sup>6</sup> while the formation of compound **2** is unusual.

140 Compound **3** results from a reaction in which hydrogen atom transfer plays a central role. In such  
141 processes stable ketyl radicals are formed and dimerization leads to pinacol products such as **3**. It  
142 must be noted that the best yield of this product is observed when *i*-PrOH was used as an efficient H-  
143 atom donor and as a solvent. In the case of the poor hydrogen atom donor *n*-heptane, the formation  
144 of **3** is much less efficient. In cyclohexane that is a medium hydrogen atom donor, the yield is  
145 intermediate. Interestingly, the cyclohexyl radicals resulting from the oxidation of the solvent are  
146 able to combine with the ketyl radicals generated from ketone **1** to form compound **4**. The behavior  
147 of **1** in MeCN used as a polar solvent with poor hydrogen atom donation properties looks very atypic.  
148 The detection of **2** suggests the intermediary formation of a methyl radical and a ketyl radical  
149 localized on two different starting molecules. We hypothesized that photochemical electron transfer  
150 is involved in the formation of these radicals and of compound **2**.

151 In order to get a deeper insight into the reaction mechanism, a detailed physico-chemical  
152 investigation was performed.

153



154

155 Scheme 2. Photochemical transformations of the aromatic ketone **1**.

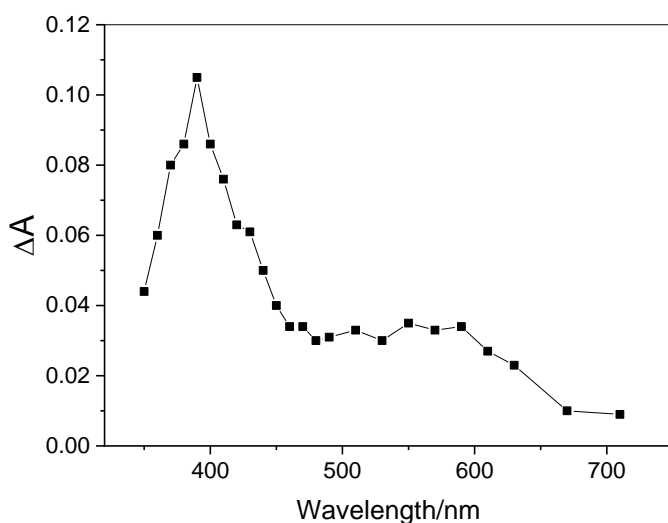
156

157 **Formation of the triplet excited state.**

158 The laser flash photolysis of **1** at 266 nm yielded the same transient species in MeCN, i-PrOH,  
 159 cyclohexane and n-heptane. It was observed immediately following the laser pulse and showed two  
 160 maxima at 390 and 570 nm (Figure 1). By plotting the absorbance measured at 380 nm at the end of  
 161 the pulse against the pulse energy, one got an  $\epsilon \times \Phi$  product of  $3300 \pm 500 \text{ M}^{-1} \text{ cm}^{-1}$  in cyclohexane and  
 162 n-heptane, where  $\epsilon$  is the molar absorption coefficient of the species at 380 nm and  $\Phi$ , the quantum  
 163 yield of the transient formation. The assignment of this transient to the triplet excited state,  $^3\mathbf{1}^*$ , was  
 164 made possible by studying its reactivity with oxygen and anthracene. In MeCN, the lifetime of the  
 165 transient was reduced by a half upon deoxygenation of the solution ( $0.34 \mu\text{s}$  in air-saturated solution  
 166 against  $0.6 \mu\text{s}$  in argon-saturated solution) demonstrating the scavenging effect of oxygen (Figure 2).  
 167 Moreover, the irradiation of **1** in the presence of anthracene led to an accelerated decay of the  
 168 transient at 380 nm and to the formation of the triplet excited state of anthracene well visible at 420  
 169 nm (Figure SI-5). This result brings evidence that an energy transfer took place between the transient  
 170 and ground state anthracene and confirms that the transient was  $^3\mathbf{1}^*$ . The quantum yield of  $^3\mathbf{1}^*$   
 171 formation was estimated to be equal to  $0.26 \pm 0.05$ .

172

173



174

175 Figure 1 : Transient absorption spectrum measured immediately after the pulse by excitation of **1** at  
 176 266 nm in aerated MeCN. (**1**)=  $6 \times 10^{-5}$  M,  $A_{266} = 0.77$

177

178 **Reactivity of the triplet.**

179 The decay of  ${}^3\mathbf{1}^*$  in deoxygenated medium obeyed an apparent first order kinetics, but was solvent-  
 180 dependent. As shown in Table 1, the apparent first-order decay rate constant varied in the order  
 181 MeCN ~ n-heptane < cyclohexane < i-PrOH, i.e. increased with the H-donor capacity of the solvent. In  
 182 pure i-PrOH, the decay of  ${}^3\mathbf{1}^*$  was too fast to be accurately measured. The rate constant of reaction of  
 183  ${}^3\mathbf{1}^*$  with i-PrOH was therefore measured in MeCN/i-PrOH mixtures. From the linear dependence of  
 184 the apparent first-order decay rate constant on i-PrOH concentration, a value of  $(4.3 \pm 0.4) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$   
 185 was obtained (Figure SI-6).

186

Transient	MeCN	n-heptane	cyclohexane	i-PrOH
Decay rate constant of ${}^3\mathbf{1}^*$	$(1.8 \pm 0.2) \times 10^6 \text{ s}^{-1}$	$(2.0 \pm 0.3) \times 10^6 \text{ s}^{-1}$	$(1.7 \times 10^7) \pm 0.3 \text{ s}^{-1}$	$> 5 \times 10^7 \text{ s}^{-1}$
Decay rate constant of secondary species	$1.7 \times 10^5 \text{ s}^{-1}$ $t_{1/2} = 4.1 \text{ } \mu\text{s}$	-	$2.5 \times 10^5 \text{ s}^{-1}$ (main process ~80%) $2k/\epsilon_{330} = 6.5 \times 10^5 \text{ cm}^{-1} \text{ s}^{-1}$ (minor process ~20%) $t_{1/2} \sim 3.5 \text{ } \mu\text{s}$	$2k/\epsilon_{330} = 2.7 \times 10^5 \text{ cm}^{-1} \text{ s}^{-1}$ $t_{1/2} \sim 40 \text{ } \mu\text{s}$
Quantum yield of <b>1</b> photolysis	$0.17 \pm 0.03$		$0.064 \pm 0.02$	0

187

188 Table 1 : Decay rate constants of the transients in deoxygenated solvents and quantum yields of **1**  
 189 photolysis air air-saturated medium. (**1**)=  $6 \times 10^{-5}$  M

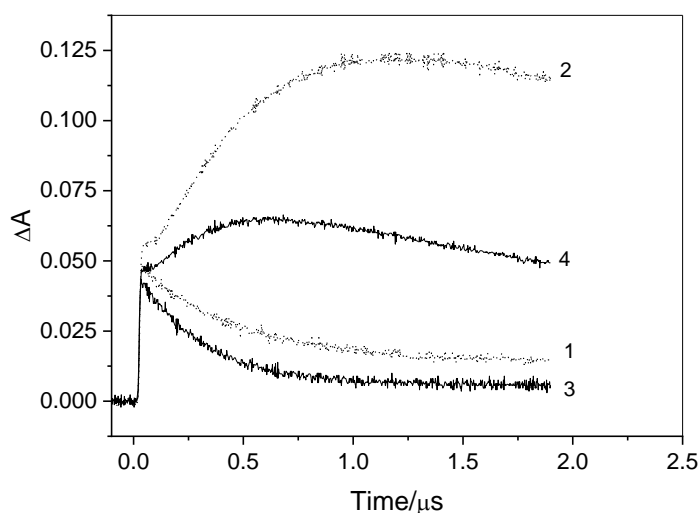
190 The reactivity of  ${}^3\mathbf{1}^*$  with **1** was also investigated using concentrations of **1** up to  $10^{-2}$  M. In this set of  
 191 experiments, the solutions were excited at 355 nm to reduce the absorption of solutions. The decay

192 rate constant of  ${}^3\mathbf{1}^*$  increased linearly with  $\mathbf{1}$  concentration. A bimolecular reaction rate constant of  
193  $(9.2\pm 0.9)\times 10^7 \text{ M}^{-1}\text{s}^{-1}$  was deduced from the linear plot.

194

#### 195 **Characterization of the secondary transients.**

196 Secondary species were detected after the decay of  ${}^3\mathbf{1}^*$  in i-PrOH, cyclohexane and MeCN. In MeCN,  
197 the growth of the secondary species was slow and kinetically correlated with the decay of  ${}^3\mathbf{1}^*$  (Figure  
198 2). Moreover, the addition of oxygen accelerated the secondary transient formation while reducing  
199 the intensity of the signal in accordance with a partial scavenging of  ${}^3\mathbf{1}^*$  by oxygen (Figure 2). This  
200 fully confirmed the mother-daughter relationship between the two species. In i-PrOH and  
201 cyclohexane, the formation of the secondary transient and the  ${}^3\mathbf{1}^*$  decay were both very fast in  
202 agreement with a relationship between the two species (Figure SI-7).



203

204

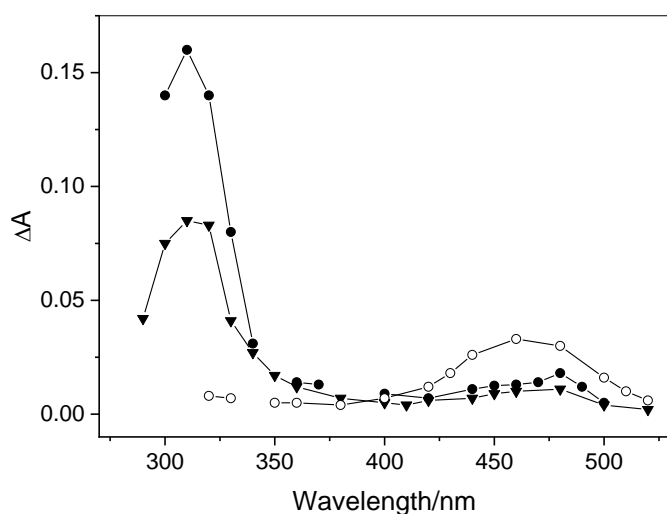
205 Figure 2: Decay of  ${}^3\mathbf{1}^*$  at 550 nm and growth of the secondary transient at 460 nm. Curves 1 and 2 in  
206 deoxygenated MeCN and curves 3 and 4 in air-saturated MeCN. ( $\mathbf{1}$ ) =  $6\times 10^{-5} \text{ M}$ ,  $A_{266} = 0.77$

207

208 In i-PrOH and cyclohexane, the secondary species absorption spectra were very similar. They  
209 presented two absorption bands with maxima located at 310-320 nm and 470-480 nm. For these two  
210 maxima, the intensity of the absorption is twice higher in i-PrOH than in cyclohexane reflecting a  
211 more efficient formation in the former solvent. The secondary transient formed in MeCN was  
212 different as it showed an absorption band with maximum at 460 nm and no visible other band within  
213 the wavelength range 310-350 nm (Figure 3).

214





215

216 Figure 3: Transient absorption spectra measured by excitation of **1** at 266 nm in argon-saturated i-  
 217 PrOH ( $\blacktriangledown$ ), cyclohexane ( $\bullet$ ), and acetonitrile ( $\circ$ ) after the disappearance of  ${}^3\mathbf{1}^*$ : 100 ns following the  
 218 pulse in i-PrOH, 350 ns in cyclohexane, and 2  $\mu$ s in MeCN. The other experimental conditions are the  
 219 same as those in Figure 1.

220

221 The lifetimes and reactivities of the secondary species are presented in Table 1. The secondary  
 222 species formed in i-PrOH and cyclohexane were not detected in air-saturated medium, probably due  
 223 to a fast quenching by oxygen. In deoxygenated i-PrOH, the secondary species decayed by a second  
 224 order kinetics with a rate constant equal to  $2k/\varepsilon=2.7\times 10^5\text{ cm}^{-1}\text{s}^{-1}$  at 330 nm (Figure SI-8). Based on  
 225 these kinetic data, on the formation of pinacol **2** and on the known photoreactivity of  
 226 benzophenones in i-PrOH, the secondary transient can be assigned to the ketyl radical **A** (Scheme 3).<sup>7</sup>

227 In deoxygenated cyclohexane, the decay of the ketyl radical was about 10-fold faster than in i-PrOH  
 228 (Table 1, Figure SI-9). The lower viscosity of cyclohexane compared to i-PrOH ( $0.98\times 10^{-3}\text{ Pa}\cdot\text{s}$  against  
 229  $2.37\times 10^{-3}\text{ Pa}\cdot\text{s}$  at 20°C) can only explain a part of this difference. Indeed,  $2k/\varepsilon$  in cyclohexane at 330  
 230 nm is expected to be equal to  $6.5\times 10^5\text{ cm}^{-1}\text{s}^{-1}$ , i.e. 2.4-fold bigger than in i-PrOH. The fast decay of the  
 231 ketyl radical in cyclohexane could also be due to a mixture of pseudo-first order and second order  
 232 kinetics. This is possible if we make the hypothesis that a part of the ketyl radicals **A** react with the  
 233 cyclohexyl radicals **B**, formed after the H atom abstraction, before escaping the cage. This  
 234 recombination would be the first order contribution of the decay. It is fully in agreement with the  
 235 detection of **4**. Once in the bulk, the ketyl radical would decay by a second order kinetics. Such a dual  
 236 kinetics was nicely described in the photolysis of benzophenone dissolved in soft rubber  
 237 poly(ethylene-co-butylene) films.<sup>8</sup> By fitting the ketyl radical decay taking  $2k/\varepsilon_{330} = 6.5\times 10^5\text{ cm}^{-1}\text{s}^{-1}$ ,  
 238 we obtained that about 80% of the reaction corresponds to the first order geminate recombination  
 239 in the cage and 20% to the bimolecular recombination in the bulk. When **1** was irradiated in i-PrOH,  
 240 no geminate recombination was observed. This is in accordance with the literature data that reports  
 241 the exclusive pinacols formation for benzophenones irradiated in i-PrOH.<sup>9</sup>

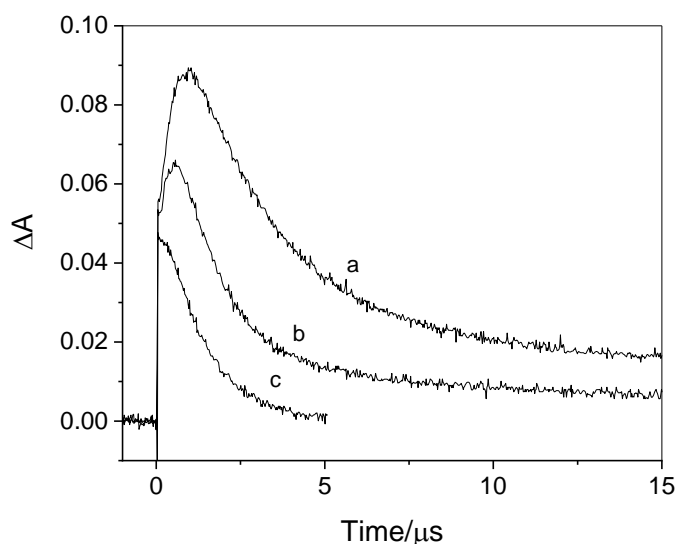
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243

244 The formation of **3** in n-heptane suggests that the ketyl radical **A** is also formed in this solvent.  
245 However, we could not observe it at 480 nm. It is probably formed in too small amounts to be  
246 detected.

247 The secondary species formed in MeCN is not the ketyl radical **A** for several reasons. First, its  
248 transient absorption spectrum was different from that of the ketyl radical. Moreover, it reacted with  
249 oxygen but with a moderate rate constant ( $2.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) (Figure SI-10). In deoxygenated medium, it  
250 decayed by a clean pseudo-first order kinetics with a rate constant of  $1.7 \times 10^5 \text{ s}^{-1}$ . The last peculiarity  
251 of the secondary transient formed in MeCN is its reactivity with water. A significant enhancement on  
252 its decay was measured upon the addition of water (4 and 30%, v/v) (Figure 4) while the ketyl radical  
253 was not affected by water in i-PrOH. This result suggests an ionic character for the species and we  
254 concluded that it is the zwitterionic diradical.

255



256

257 Figure 4 : Decay at 460 nm of the secondary species formed in MeCN in the absence of water (a), in  
258 the presence of 4% of water (b), in the presence of 30% of water (c). The other experimental  
259 conditions are the same as those in Figure 1.

260

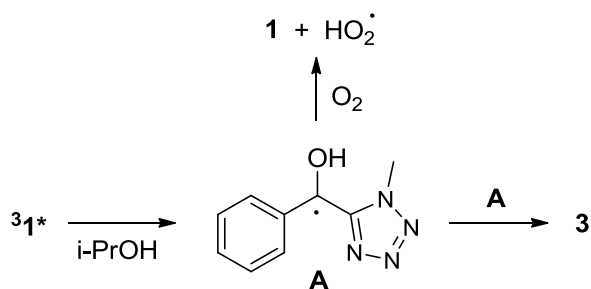
261

262 **Mechanisms.**

263 In i-PrOH, the formation of a ketyl radical by H-atom abstraction from i-PrOH is very usual (scheme  
264 3). This is consistent with the known photoreactivity of aromatic carbonyls in H-donor solvents.<sup>10</sup> In  
265 the presence of oxygen, the ketyl radical would give the H atom to oxygen<sup>11</sup> and regenerate **1**. This  
266 explains the absence of phototransformation of **1** in air-saturated medium (Table 1). In the absence  
267 of oxygen, the recombination of two ketyl radicals **A** would lead to pinacol **3**. This pinacolisation is  
268 fully in line with the observed second order decay kinetics observed by laser flash photolysis.

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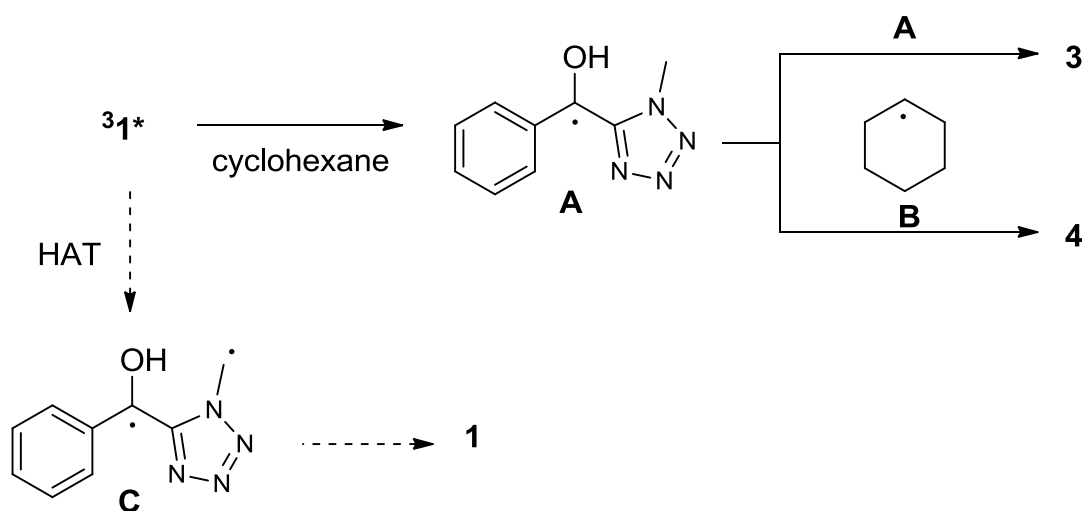
271

272 Scheme 3: Formation of pinacol **3** via the ketyl radical **A**

273

274 In cyclohexane, the formation of the ketyl radical **A** also takes place as indicated by the formation of  
 275 pinacol **3** (Scheme 4). The yield is however lower than in *i*-PrOH, 21% against 46%, in accordance with  
 276 the existence of competitive reactions, in particular the geminate recombination in the cage of  
 277 solvent. In such a reaction also compound **4** is formed by combination of a ketyl radical **A** with a  
 278 cyclohexyl radical **B**.

279



280

281 Scheme 4: Formation of pinacol **3** and of the adduct **4** via the ketyl radical **A**

282

283 In *n*-heptane, that is a poor H-atom donor solvent, the ketyl radical **A** could not be detected in the  
 284 laser flash photolysis experiments. Yet, photoproduct **3** was formed in the preparative product  
 285 studies. These experiments being conducted at a very high **1** concentration, **1** might have been the H-  
 286 donor, since we demonstrated that a non-negligible reaction between  $31^*$  and **1** can take place. The  
 287 high **1** concentration used in preparative reactions has probably affected the photoproducts yields. In  
 288 particular in cyclohexane where the ketyl radical **A** decays by a mixed first order and second order  
 289 kinetics, increasing **1** concentration is expected to increase the ketyl radical **A** concentration and to  
 290 favor pinacolisation. Due to the poor H-donor capacity of *n*-heptane, we initially considered as  
 291 possible to detect in this solvent the neutral diradical **C** formed through intramolecular H atom  
 292 transfer.<sup>12</sup> This hypothesis was not confirmed experimentally. Either the reaction does not take place,  
 293 or this species is too short lived to be detected as shown for other benzophenone derivatives.<sup>11</sup>

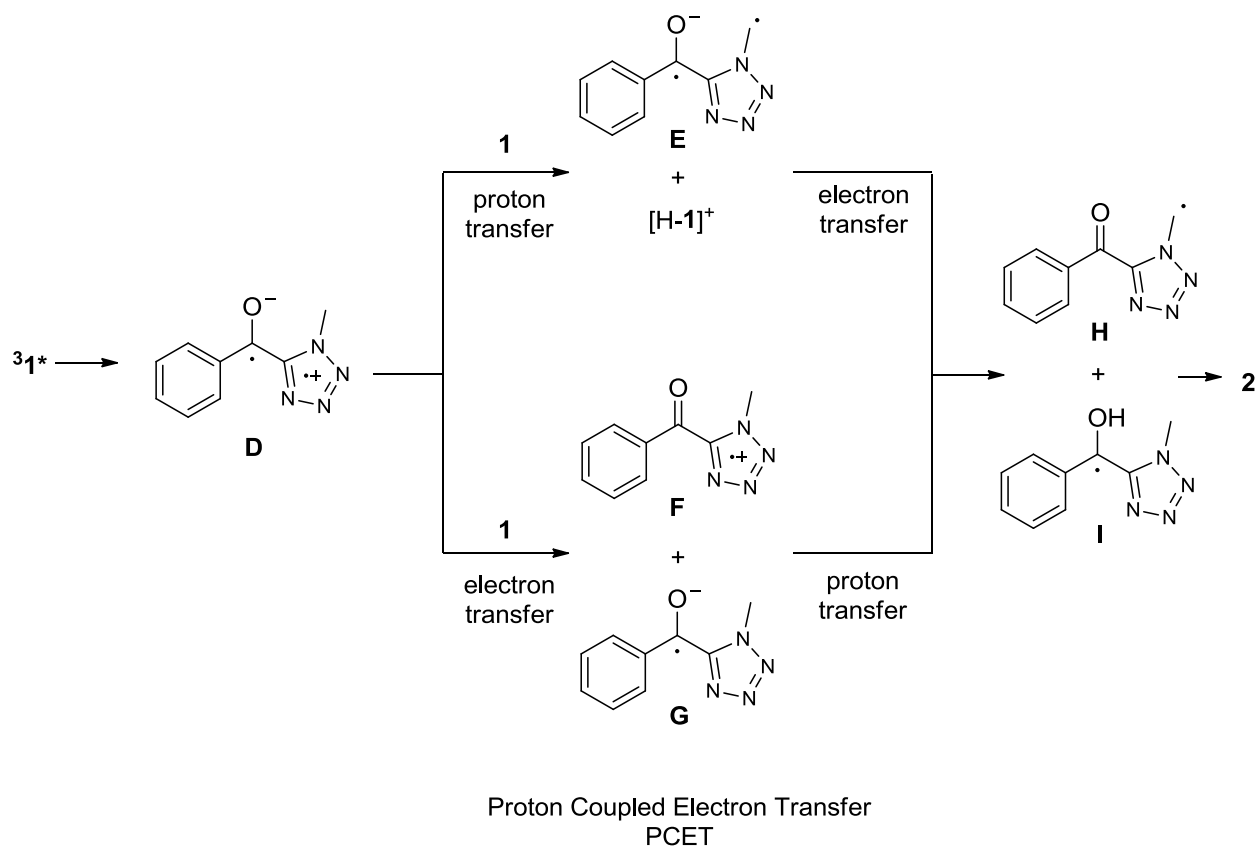
294

295 In MeCN that is more polar than the other solvents together with a poor H-donor molecule, a very  
296 different situation seems to take place. The experimental data are in line with the formation of an  
297 ionic intermediary structure that is likely the zwitterionic radical **D** formed by an intramolecular  
298 electron transfer (Scheme 5). This assignment is confirmed by the specific reactivity of the secondary  
299 species formed in MeCN compared that of ketyl radical **A**.

300 Under these conditions, we didn't detect a ketyl radical intermediate. As a consequence, we exclude  
301 an intermolecular hydrogen transfer from the solvent and suggest an intermolecular hydrogen  
302 transfer between the zwitterionic intermediate **D** and **1** at its ground state (Scheme 5). The  
303 zwitterionic intermediate **D** can be deprotonated leading to a diradical anion **E** and the protonated  
304 ketone  $[H-1]^+$ . An electron is then transferred and the neutral radicals **H** and **I** are formed. Radical  
305 combination leads to the unusual regioisomer of the coupling product **2**. Alternatively, an electron is  
306 transferred first leading to the intermediates **F** and **G**. Proton transfer leads again to the neutral  
307 intermediates **H** and **I**. Most probably, the transfer of both particles of the hydrogen atom is coupled  
308 (proton coupled electron transfer, PCET). As the intermolecular hydrogen transfer is favored in a  
309 polar solvent an increase of the polarity in the transition state of the PCET step is possible. In a  
310 corresponding intermolecular step (HAT), the neutral diradical intermediate **C** would be formed as  
311 depicted in Scheme 4, this is not the case. Furthermore, it must be pointed out that the one step  
312 hydrogen transfer needs a highly structured transition state with highly negative  $\Delta S^\ddagger$  values while for  
313 the electron transfer in a two-step hydrogen transfer this value is close to zero.<sup>13</sup> The herein  
314 described reaction compound **1** leading to the unusual coupling product **2** is therefore directly linked  
315 to the formation of the zwitterionic diradical **D**.

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321 Scheme 5: Formation of dimer **2** via the zwitterionic diradical **D** involving proton coupled electron  
322 transfer.

323

324 **Conclusion**

325 The photochemical reactivity of phenyl (methyl)tetrazolium ketone **1** has been studied in detail by  
326 means of preparative product studies and laser flash photolysis. When efficient hydrogen atom  
327 donor compounds such as isopropanol are used as solvents, ketyl radicals are formed which dimerize  
328 leading to photopinacol analogue products as it has previously been reported for aromatic ketones  
329 such as benzophenone. A completely different intermediate is formed when ketone **1** is irradiated in  
330 acetonitrile. This intermediate possesses a zwitterionic character. A proton coupled electron transfer  
331 from this intermediate to **1** at its ground state is suggested to explain the formation of the unusual  
332 final product **2**.

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