

THE LACK OF PHOTOREACTIVITY FOR AN *ortho-tert*-BUTYLVALEROPHENONE

by William R. Bergmark\* and G. Davon Kennedy

Department of Chemistry, Ithaca College, Ithaca, NY 14850 USA

Summary: It is proposed that a rapid and reversible 1,6-hydrogen abstraction accounts for the lack of type II photoreaction in the title compound.

For some time we have been concerned about the question of how the mechanism of photoenolization (the hydrogen abstraction reaction of *o*-methylaryl ketones) contrasts with the general hydrogen abstraction photoreaction of ketones.<sup>1</sup> Ordinarily phenyl ketones undergo extremely rapid intersystem crossing so that photoreactions almost always derive from the triplet state.<sup>2,5</sup> One issue we wished to explore was the degree to which an *ortho* substituent might twist the carbonyl out of the phenyl plane, resulting in more aliphatic-like behavior--a slower intersystem crossing rate and a mix of singlet and triplet photoprocesses. This kind of effect is known in other systems, for example, anthryl ketones.<sup>3</sup> With these thoughts in mind we undertook an examination of the behavior of an *ortho-t*-butylaryl ketone. Previously the photoreduction of 2-*t*-butylbenzophenone was examined,<sup>4</sup> but insufficient data was collected to draw conclusions on this question. Because extensive data exists for the type II photoreduction of aryl ketones<sup>5</sup> we chose it to monitor the effects of the *o-t*-butyl group.

We were surprised to find that photolysis of 2,5-di-*t*-butylphenyl butyl ketone, 1, did not produce detectable type II products<sup>6</sup> nor could appreciable ketone disappearance be observed in *t*-butyl alcohol or benzene solvents ( $\phi < 10^{-3}$ ). In 2-propanol inefficient photoreduction ( $\phi \approx 5 \times 10^{-3}$ ) could be observed.<sup>7</sup> This reaction could be quenched by *cis*-dichloroethylene<sup>8</sup> and Stern-Volmer analysis (plot of  $\phi_0/\phi$  vs. quencher concentration) indicated a  $k_{qT}$  value of 0.4. If triplet quenching is involved a measured<sup>9</sup> rate constant of  $1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for phenyl alkyl ketones indicates a lifetime of 2.5 ns. If quenching of photoreduction were occurring by radical scavenging, the lifetime would be shorter.

How could such an unreactive aryl ketone have such a short lifetime? We concluded the most likely explanation for this was a very rapid and thermally reversible 1,6-hydrogen abstraction from the *o-t*-butyl group. The resulting 1,5 biradical did not produce an observable internal coupling product nor was there observable d-incorporation when the irradiation was carried out in deuterated methanol. Inefficient coupling relative to disproportionation was observed by Wagner<sup>10</sup> in other 1,6 hydrogen abstractions.

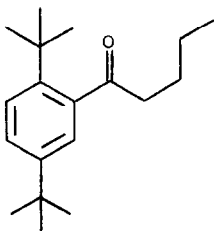
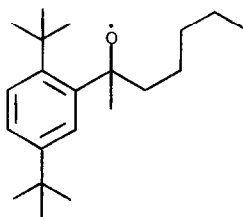
Support for the existence of such a biradical intermediate can be found from the behavior of a related alkoxy radical, 2. The radical 2 was generated by treatment of the corresponding alcohol with iodine and mercuric oxide.<sup>11</sup> The major product isolated from this reaction was assigned structure 3 on the basis of spectral data.<sup>12</sup> It is known that when considering hydrogen atom abstractions, a  $n, \pi^*$  ketone excited state and an alkoxy radical are very similar chemical species.<sup>13</sup> Although the alkoxy radical cannot be considered a perfect model for the excited ketone, nonetheless the major mode of 1,6-hydrogen abstraction indicated here supports the proposal above.

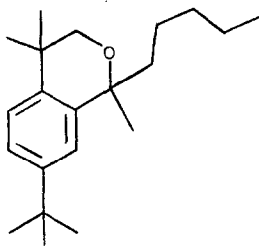
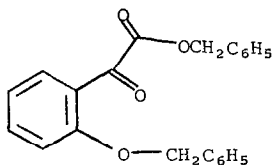
How could it be that the rate of 1,6-hydrogen abstraction exceeds that of 1,5? For hydrogen abstraction from a free alkyl chain, rate data indicate 1,5 exceeds that of 1,6 by a factor of 20.<sup>10</sup> Lewis,<sup>14</sup> in his studies on conformational effects in the type II photo-reaction, found that reducing the degrees of freedom of the bonds involved in the transition state resulted in substantial rate accelerations. Applying these observations to the present case, the considerable rigidity of the *tert.*-butyl-phenyl portion of the molecule plus the nine available hydrogens should provide a very large rate enhancement. Additional factors include the somewhat shorter bonds involved in the 1,6 route and any steric hindrance the *tert.*-butyl group provides for the 1,5 hydrogen abstraction.

There exists another example of this kind of overwhelming preference for 1,6 hydrogen transfer apparently because of rigidity. The ketone 4 apparently only abstracts hydrogen from the *ortho* group.<sup>15</sup> Also it is noteworthy that 1-benzoyl-8-benzyl-naphthalene undergoes a very rapid 1,6-hydrogen abstraction and the lowest excited state is distinctly  $\pi, \pi^*$ .<sup>16</sup>

It has been reported<sup>17</sup> that 2-methoxy-4,6-di-*t*-butylbenzophenone produces an indanol derived from H-abstraction from the *o-t*-butyl group followed by biradical coupling. Why coupling was observed here but not for 1 is not known.<sup>18</sup>

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### References and Notes

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6. The expected photoproduct, 2,5-di-*t*-butylphenyl methyl ketone, was synthesized separately and found stable to the photolysis conditions. The ketone 1 was synthesized by oxidation of the corresponding alcohol which was derived from treatment of pentanal with 2-lithio-1,4-di-*t*-butylbenzene which was prepared by the method of W. Theilacker and F. Koch, Chem. Ber., 102, 2023 (1969).
7. The apparent product is a pinacol which disproportionates in the glc injection port and produces ketone and alcohol.
8. Probably triplets are being quenched. The 2,5-di-*t*-butylphenyl methyl ketone sensitizes *cis-trans* isomerization of *cis*-pipyrylene half as efficiently as acetophenone.
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12. The identification of 3 is based on the following spectral data of a glc purified sample  
 pmr (CCl<sub>4</sub>, δ, 90 MHz) 7.10 (2H, s, Ar-), 6.91 (1H, s, Ar-), 3.55 (1H, d, J = 12 Hz, -O-CH<sub>2</sub>-), 3.38 (1H, d, J = 12 Hz, -O-CH<sub>2</sub>-), 1.65 (2H, m), 1.45 (3H, s), 1.35 (9H, s),

- 1.25 (3H, s), 1.20 (3H, s), 1.2 (8H, m), 0.90 (3H, t). m/e (rel. abundance): 287 (1.3, M-CH<sub>3</sub>), 231 (100.0, M-C<sub>5</sub>H<sub>11</sub>). Also satisfactory combustion analysis.
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  18. Unlike 1 the benzophenones have one phenyl group in the plane of the carbonyl group insuring rapid intersystem crossing.

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