

## Photoinduced Enolization of 2-(Ortho-tolyl)benzofuran-3-one<sup>†</sup>

Eunsook Koh, Bong Ser Park\*, Hyojeong Yoon<sup>1</sup> and Woo Ki Chae<sup>1</sup>

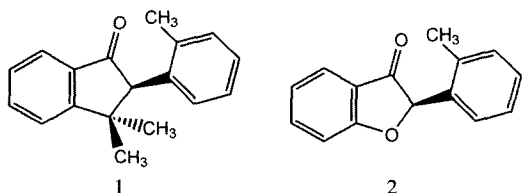
Department of Chemistry, Dongguk University, Seoul 100-715, Korea

<sup>1</sup>Department of Chemistry Education, Seoul National University, Seoul 151-742, Korea

The structurally rigid  $\alpha$ -(*o*-alkylphenyl)acetophenone derivatives lacking  $\beta$ -hydrogens, 3,3-dimethyl-2-*o*-tolylindanone-1-one and 2-*o*-tolyl-benzofuran-3-one, were prepared and their photochemical behaviors were examined. The former did not give any photoproduct while the latter turned into its enol tautomer. The difference of reactivity of two ketones was attributed to aromatic character of the enol of the benzofuranone. It was concluded that the reaction occurred via photoinduced 1,3-H transfer.

**key words:** enolization, benzofuranone

If there are several reaction pathways possible from a given molecule, selectivity in product distribution can be decided by various factors. Such behaviors can be found not only in ground state chemistry but also in excited state chemistry. We have recently shown such an example in the photochemistry of  $\alpha$ -(*o*-tolyl)acetophenone and its derivatives [1-3]. Without  $\alpha$ -substituents,  $\alpha$ -(*o*-alkylphenyl) acetophenones shows efficient photocyclization via 1,5-biradicals formed by hydrogen atom abstraction of carbonyl groups [4]. Putting an alkyl(or aryl) substituent at  $\alpha$  position, however, the efficiency of the hydrogen abstraction drops significantly and  $\alpha$ -cleavage reactions start to compete [5]. More recently, we have tested a conformational effect on the photochemistry of  $\alpha$ -(*o*-alkylphenyl)acetophenones using  $\alpha$ -(*o*-alkylphenyl)indanones [6]. These indanones have their  $\alpha$ -aryl groups always eclipsed with carbonyl group so the hydrogen abstraction reaction can occur at least from their geometrical point of view. However, these ketones still give  $\alpha$ -cleavage reactions predominantly presumably due to ring strain and facile disproportionation following the initial cleavage. Thus, we have designed the following indanone derivatives, **1** and **2**, in order to see how molecules respond as we block the efficient disproportionation pathway. Here we would like to report our preliminary results on the photochemical behaviors of these two ketones.



The ketones, **1** and **2**, were prepared by the literature procedure used in the synthesis of similar indanones and benzofuranones [7, 8, 9]. Photolysis of the ketones was done using the output of Pyrex filtered light of a Hanovia medium pressure mercury arc lamp. Either benzene or methanol was used as a solvent and typical concentration used was 0.01-0.02 M. Initial experiment did not show any sign of formation of new products even after prolonged irradiation of both ketones. Thus, a small scale irradiation was performed using an NMR tube containing 0.02 M of the ketone in deuterated benzene or methanol. The sample was monitored at regular intervals by <sup>1</sup>H NMR spectroscopy. The <sup>1</sup>H NMR spectrum of the ketone **1** remained unchanged throughout the irradiation, but the irradiation of the ketone **2** resulted in formation of a new product. Among other things, most noticeable were the growth of two new singlets at 6.95 ppm and 2.09 ppm having 1 to 3 integration ratio. The new peaks in the <sup>1</sup>H NMR spectrum disappeared slowly when the sample was kept in dark. If a single crystal of *p*-toluenesulfonic acid was added, the disappearance became instantaneous. Based on these facts, the new product observed was assigned as an enol form of the starting ketone.

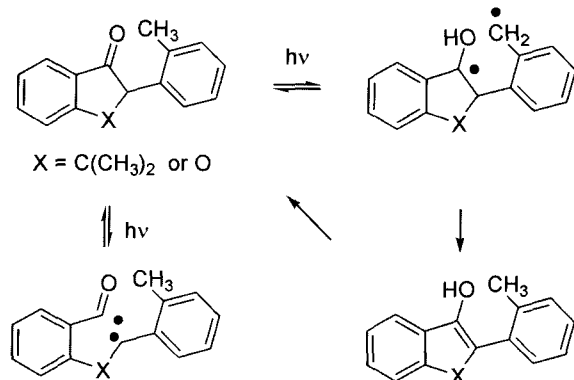
There are two major competing pathways possible for the ketones **1** and **2**, which are  $\alpha$ -cleavage and hydrogen abstraction. We believe that the  $\alpha$ -cleavage reactions actually occur for both ketones but become reversible due to the lack of product forming processes resulting from the absence of  $\beta$ -hydrogens. If hydrogen abstraction reactions can compete in the midst of the reversible  $\alpha$ -cleavage, the biradical intermediate shown in Scheme 1 can be formed as in the photochemistry of  $\alpha$ -(*o*-alkylphenyl)acetophenones. The biradical intermediates can either cyclize to form bicyclic products or go back to starting ketones *via* their enol forms. The cyclization products were not observed in our experiments, so we decided to look for the latter processes using  $\alpha$ -deuterated ketones. The deuteration was made by treating with sodium hydride followed by quenching with deuterium oxide. The deuterated ketones were irradiated under the same reaction condition as the above, but

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\*To whom correspondence should be addressed.

E-mail : parkbs@dongguk.edu

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Scheme 1.

the deuterium incorporation at the ortho-methyl of the tolyl moiety was not observed.

Photo-induced enolization is believed to occur from both ketones **1** and **2**, even though only one of them (an enol of **2**) is observed in our experiments. We think that the aromatic nature of the enol of **2** makes it more stable enough to be observed while the enol of **1** goes back to the keto form instantaneously. The enolization was not observed in the absence of light, so the process must be light induced. The fact that deuterium incorporation at the ortho-methyl of the tolyl moiety was not found rules out the reaction sequence involving hydrogen abstraction and disproportionation. The remaining mechanism to explain the observed enolization is the direct 1,3-shift, which is rare in photochemistry.

Tautomerism of parent molecules of **1** and **2**, 1-indanone and benzofuran-3-one, had been studied by Capon and coworkers [10,11]. The enolic forms of these ketones were reported to be highly unstable and they could only be generated by a special method, acidic hydrolysis of its trimethylsilyl ether. Even with this method, the enolic forms could be observed in a short period of time by NMR spectroscopy only in polar solvents. Our photochemical generation of the enolic form of **2** can be a promising alternative to the published method in investigations of unstable tautomers. We are currently looking into this matter using several analogues, which are structurally closely related.

As previously reported by us, photolysis of indanones containing  $\beta$ -hydrogens readily produced enals resulting from  $\alpha$ -cleavage followed by disproportionation [6]. Without  $\beta$ -hydrogens such as ketones **1** and **2**, the  $\alpha$ -cleavage seemed to become mostly 'energy funnel', which were reversible in nature. Even though our computation using Gaussian 98 showed that the molecules could easily form suitable geometries for hydrogen abstraction by minimal rotation along the bond connecting  $\alpha$ -carbon and  $\alpha$ -tolyl group, no evidences relating to such hydrogen abstraction reactions could be found in our experiments. The absence of the hydrogen abstraction reactions in the indanone system has been consistent throughout our studies on this skeleton [2,6]. The newly found photoinduced

enolization of benzofuranone system led us study the mechanistic origin of this reaction, which would require further investigation.

In summary, the structurally rigid  $\alpha$ -(*o*-alkylphenyl) acetophenone derivatives lacking  $\beta$ -hydrogens, 3,3-dimethyl-2-*o*-tolylindan-1-one and 2-*o*-tolyl-benzofuran-3-one, were prepared and their photochemical behaviors were examined. The former did not give any photoproduct while the latter turned into its enol tautomer. The difference of reactivity of two ketones was attributed to aromatic character of the enol of the benzofuranone. It was concluded that the reaction occurred via photoinduced 1,3-H transfer.

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- Spectroscopic data of **1**: <sup>1</sup>H NMR(CDCl<sub>3</sub>, 200 MHz)  $\delta$  7.81(d, 1H, J=7.0 Hz), 7.68(t, 1H, J=7.0 Hz), 7.55(d, 1H, J=7.0 Hz), 7.45(t, 1H, J=7.0 Hz), 7.28-7.10(m, 3H), 6.77(d, 1H, J=7.0 Hz), 4.07(s, 1H), 2.44(s, 3H), 1.61(s, 3H), 0.99(s, 3H), <sup>13</sup>C NMR(CDCl<sub>3</sub>, 50 MHz)  $\delta$  198.0, 145.1, 137.5, 136.4, 132.9, 131.1, 128.4, 127.1, 127.0, 126.8, 125.7, 124.7, 122.5, 64.8, 32.7, 25.4, 20.2, 15.5, IR(CCl<sub>4</sub>, cm<sup>-1</sup>) 1715, EI MS 77, 105, 250(M<sup>+</sup>). Spectroscopic data of **2**: <sup>1</sup>H NMR(CDCl<sub>3</sub>, 200 MHz)  $\delta$  7.75(d, 1H, J=7.0 Hz), 7.42(t, 1H, J=

- 7.0 Hz), 7.25-7.14(m, 3H), 7.11-6.90(m, 3H), 6.87(s, 1H), 2.40(s, 3H),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  196.9, 140.0, 134.7, 128.7, 127.9, 127.2, 125.2, 125.0, 124.9, 123.7, 123.1, 120.8, 117.8, 88.7, 16.9, IR( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ) 1720, EI MS 77, 105, 224( $\text{M}^+$ ).
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