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Photochemistry of α-(o-Alkylphenyl)indanones[1]

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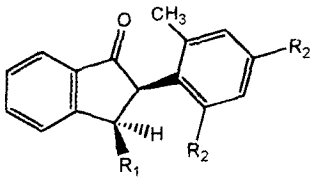
Photolysis of α-(o-alkylphenyl)indanones resulted in α-cleavage followed by disproportionation to form E-and Z- ortho-formyl stilbenes. No evidences of hydrogen abstraction reactions were collected from these indanones. The minimum rate constant of α-cleavage in the α-(o-alkylphenyl)indanones was estimated to be $5.5 \times 10^{10} s^{-1}$.

key words: α-cleavage, hydrogen abstraction, indanones

Like the ground state chemistry, reaction pathway of excited states can vary widely with changes of molecular structure and reaction condition. Understanding the relation between structure and reactivity has always been a main focus in the research of organic chemistry. Since several reactions are competing with each other, minor structural changes often lead to completely different reaction selectivity. One of the recent examples showing such a phenomenon is photochemical reactivities of α-(o-tolyl)acetophenone and its derivatives [2,3]. α-(o-Tolyl)acetophenone is one of many compounds showing efficient photocyclization *via* 1,5-biradicals formed by hydrogen atom abstraction of carbonyl groups. If the ketone has an alkyl(or aryl) substituent at α position, the efficiency of the hydrogen abstraction decreases and α-cleavage reactions start to compete. The result was rationalized by ground state conformational control of reactivity. For α-(o-tolyl)acetophenone, the most stable conformation has an α-aryl group eclipsing with the carbonyl group, which is very close to "reactive" geometry for hydrogen abstraction. For the substituted ones, however, an additional α-substituent makes the tolyl group twist away from the carbonyl group. In this "poor" geometry for hydrogen abstraction, the reaction rate drops and other reactions such as α-cleavage start to compete. Thus, it occurred to us that if the geometry of the α-arylacetophenone is fixed such that α-aryl group is always eclipsed with carbonyl group, the hydrogen abstraction reaction would be restored even with α-substituents. Such a candidate would be α-(o-alkylphenyl)indanone system. In this paper, we would like to report photochemical behaviors of three α-(o-alkylphenyl)indanones, **1-3**, and discuss our results in terms of relationship between molecular structure and reactivity.

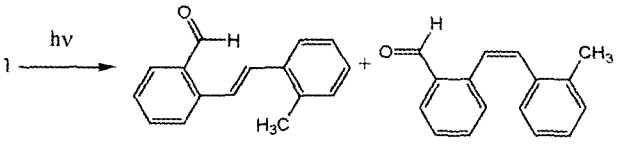
Compounds **1-3** [4] were prepared using modifications of the literature procedure [5,6]. The ketone derivatives in



1: $R_1 = R_2 = H$
2: $R_1 = CH_3$, $R_2 = H$
3: $R_1 = R_2 = CH_3$

benzene (typically 0.01-0.02 M) was irradiated in an immersion well using Pyrex-filtered light of a Hanovia medium pressure mercury arc lamp (450W) until all the starting material had disappeared. The solution was deaerated throughout by bubbling argon through. After evaporating all the volatiles and chromatographing over silica gel, two isomeric products were isolated, which were assigned to be ***E*** and ***Z*** ortho-formyl stilbenes shown below on the basis of their spectroscopic properties [7]. For stereochemical assignment, vicinal coupling constants of two olefinic protons in ^{1}H NMR spectra were particularly useful because the coupling constants of E-isomers were known to be larger than those of Z-isomers [8]. No other products were detected and the chemical yield of the sum of two isomers approached 100% within experimental errors. Outcome of the photolysis was also monitored at regular intervals by ^{1}H-NMR spectroscopy using sample solution in benzene-d_6 under the same irradiation condition.

The ratios of two isomers could be obtained by integrating two aldehydic proton peaks at around 10 ppm in ^{1}H-NMR of reaction mixtures. Under the irradiation condition the photoproducts absorbed the light, so *cis-trans* isomerization of stilbene moiety occurred during the photolysis. As a result, the ratios of two isomeric products changed until stationary



1P-*E* 1P-*Z*

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Table 1. *E/Z* ratios of Photoproducts from Ketones **1-3**.

Starting Ketones	E/Z Ratios
1	1:2
2	3:2
3	1:3

state was reached. The ratios of the photoproducts are summarized in Table 1.

There was no sign of the formation of expected cyclization products as evidenced by the absence of AB quartets at ca. 3 ppm, which were typical signals of such indanols. As mentioned above, the ketones **1-3** were designed to exploit the fact that the carbonyl group could stay eclipsed with α-aryl group in these ketones. With this rigid geometry, it was predicted that the Yang cyclization [9] could compete with the α-cleavage to form useful [3,3,0] bicyclic compounds. Contrary to this expectation, α-cleavage reactions still prevailed over hydrogen abstraction reaction routes in these indanones. The result indicates that incorporation of rings and creating rigidity in the molecules increase not only chances of hydrogen abstraction but also the rate of α-cleavage. Even though rotation around the bond between carbonyl carbon and α-carbon is fixed due to the skeleton of indanones, α-o-tolyl group still can rotate such that benzylic hydrogens being abstracted can be far away from the carbonyl group. Putting mesityl group instead of o-tolyl group should solve this problem. In fact, it is known that the rate of hydrogen abstraction in α-mesitylacetophenone is 3.4 times as fast as that of α-(o-tolyl)acetophenone [3]. However, no evidence of hydrogen abstraction was detected in the photolysis of the ketone **3**. The absence of the Yang cyclization products suggests that the rates of α-cleavage in ketones **1-3** are at least two orders of magnitude higher than those of hydrogen abstraction, which is 5.5×10^{8} s^{-1} for α-mesitylacetophenone [2]. The predominance of α-cleavage over hydrogen abstraction in these indanones may not be totally unexpected if we consider the relief of ring strain upon the cleavage of five membered ring that contains three sp^2 centers. In fact, the efficient α-cleavage of similar indanone system has been demonstrated in Baum's study on photochemistry of 2-phenyl- and 2,6-diphenyl-1-indanone, even though rate of the reaction was not described [10].

An alternative explanation of the above results is as follows: The hydrogen abstraction and the α-cleavage may in fact compete with comparable rates. In the former case the hydrogen atom shift becomes reversible due to significant barrier to form the [3,3,0] bicyclic product, whereas a stable energy sink from the biradical intermediate formed by the α-cleavage process exists in the latter case. Forming the stable enals by disproportionation makes whole process irreversible. Currently we are investigating photochemistry of other indanones in order to clarify this mechanistic puzzle.

In summary, photolysis of α-(o-alkylphenyl)indanones resulted in α-cleavage followed by disproportionation to form *E*- and *Z*-o-formyl stilbenes. No evidences of hydrogen abstraction reactions were collected from these indanones. From the results of this research the minimum rate constant of α-cleavage in the α-(o-alkylphenyl) indanones was set to be $5.5\times10^{10}s^{-1}$.

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4. The synthesis includes aldol condensation of the corresponding acetophenones with paraformaldehyde or acetaldehyde, followed by the Nazarov cyclization. Shown here are spectroscopic properties of a representative case, **1**. mp 94.0-95.0 °C, ^{1}H-NMR($CDCl_3$, 200 MHz) δ 7.87-6.92(m, 8H), 4.12(dd, 1H, J = 4.4, 7.7 Hz), 3.71(dd, 1H, J = 7.7, 17.5 Hz), 3.16(dd, 1H, J = 4.4, 17.5 Hz), 2.36(s, 3H). ^{13}C-NMR($CDCl_3$, 50 MHz) δ 207.2, 154.0, 140.0, 139.1, 137.2, 135.5, 131.3, 128.3, 128.0, 127.6, 127.1, 126.9, 124.8, 51.4, 36.1, 20.7.. IR(CCl_4, cm^{-1}) 1706. EIMS 77, 222(M^+).
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7. Shown here are spectroscopic properties of a representative case. Spectroscopic data of **1P-*E***: ^{1}H-NMR($CDCl_3$, 200 MHz) δ 10.38(s, 1H), 7.91(d, 1H, J = 16.0 Hz), 7.88(dd, 1H, J = 7.6, 1.4 Hz), 7.78-7.59(m, 3H), 7.45(t, 1H, J = 7.6 Hz), 7.32-7.13(m, 4H), 2.42(s, 3H). ^{13}C-NMR($CDCl_3$, 50 MHz) δ 192.7, 140.5, 136.2, 136.0, 135.0, 133.9, 133.1, 132.1, 130.6, 128.3, 127.7, 127.6, 126.5, 126.2, 126.0, 20.0. IR(KBr, cm^{-1}): 2963, 2925, 2854, 2733, 1694. EIMS 77, 105, 222(M^+); Spectroscopic data of **1P-*Z***: ^{1}H-NMR($CDCl_3$, 200 MHz) δ 10.23(s, 1H), 7.86-7.81(m, 2H), 7.65-6.80(m, 8H), 2.33(s, 3H). ^{13}C-NMR($CDCl_3$, 50 MHz) δ 192.1, 140.5, 136.6, 135.3. 133.6.

133.5, 132.8, 130.8, 130.2, 129.6, 128.4, 127.7, 127.6, 127.2, 125.6, 20.0. IR(KBr): 2959, 2925, 2854, 2745, 1694 cm^{-1}. EIMS 77, 105, 222(M^+).

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