Pergamon

Tetrahedron Letters 42 (2001) 711–713

TETRAHEDRON
LETTERS

Highly efficient photoinduced rearrangement of benzobicyclo[3.1.0]hexenones to 1-naphthols

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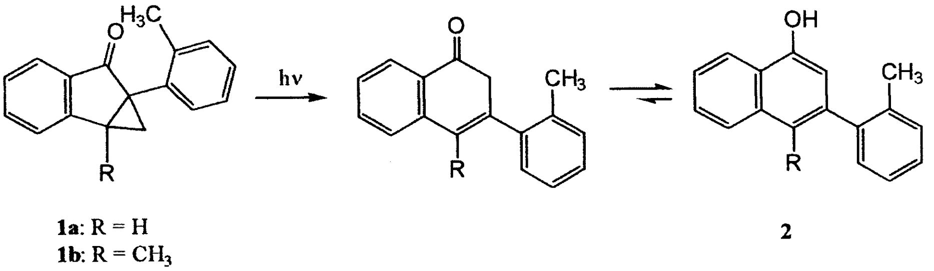
Received 21 September 2000; revised 7 November 2000; accepted 10 November 2000

Abstract—Irradiation of 1-(*o*-tolyl)-3,4-benzobicyclo[3.1.0]hexenones (**1**) in benzene at 365 nm has resulted in clean conversion to 3-(*o*-tolyl)-1-naphthols (**2**) via 3-(*o*-tolyl)-1(2*H*)-naphthalenones. The reaction is suggested to occur mainly from (n, π*)^3 state with a reaction rate higher than 10^{10} s^{-1}. © 2001 Elsevier Science Ltd. All rights reserved.

Photochemical conversion of linearly conjugated benzocyclohexadienones into benzobicyclo[3.1.0]hexenones has been studied by many research groups.[1] However, the reverse process is not known in the literature to date. In the course of our studies on the Yang photocyclization[2] of 1-benzoyl-1-(*o*-alkylphenyl)cyclopropanes,[3] we have recently investigated photoreactivity of the title compound to see the effect of conformational rigidity. Interestingly irradiation of this compound resulted in clean conversion to a single product, a naphthol, with high chemical and quantum efficiency (Scheme 1). Here we would like to report our preliminary result of the highly efficient transformation.

1-(*o*-Tolyl)-3,4-benzobicyclo[3.1.0]hexenones, **1**,[4] in benzene (typically 0.01–0.02 M) was irradiated in an immersion well using Pyrex (or Uranium) filtered light of a 450 W Hanovia medium pressure mercury arc lamp. After 30 min all the starting compound was replaced by a new adduct. The chemical yield of the isolated photoproduct was 80–90% (100% GC yield within experimental errors). The quantum yield of product formation at 5% conversion for **1a** and **1b** in benzene was 0.92 and 0.95, respectively.[5] The structure of the photoproduct was assigned as **2** according to usual spectroscopic measurements.[6] Substitution pattern of the photoproduct, particularly the position of the *o*-tolyl group within the naphthol skeleton, was not obvious at early stage, but the result of NMR scale photolysis supported our original structural assignment, vide infra. The reaction was not quenched by either 2,5-dimethyl-2,4-hexadiene (313 nm irradiation using potassium chromate filter solution[7]) or naphthalene (365 nm irradiation using a set of Corning 7–83 filters) up to 0.1 M concentration. The reaction proceeded in triplet sensitized condition using 20-fold excess of acetophenone as efficiently as in direct irradiation. In order to monitor the reaction more closely, a sample in an NMR tube containing **1a** in benzene-d_6 (0.02 M) was prepared and irradiated under the same condition as above. As in the case of preparative scale photolysis, a single product was formed, but its ^{1}H NMR spectrum



1a: R = H
1b: R = CH$_3$

2

Scheme 1. Photochemical rearrangement of ketones **1a**–**b**.

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PII: S0040-4039(00)02042-6

was different from that of **2a**. Particularly notable were a doublet at 2.96 ppm and a triplet at 6.40 ppm, which coupled with each other with a typical allylic coupling constant, 3.6 Hz. This compound was slowly changed to **2a** as standing at room temperature. The half life of the initially formed product was ca. 13 days. If a crystal of *p*-toluenesulfonic acid was added to the solution, only **2a** was left behind immediately. Thus, the initially formed product was assigned as the keto tautomer of **2a**, 3-(*o*-tolyl)-1(2*H*)-naphthalenone. When the reaction was run in methanol-d_4, no keto form of **2a** was observed, presumably due to the acidic nature of the solvent.

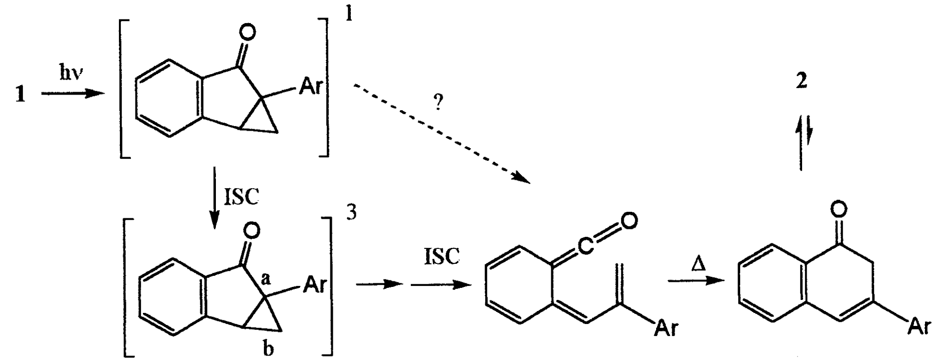
Zimmerman had studied photochemistry of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one and observed the formation of a carboxylic acid, a trapped product of a ketene intermediate by water, among other products.[8] In Chapman's study on photochemistry of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one, a ketene derived product was also observed along with several other products.[9] We postulated that the similar ketene intermediate could be responsible for the formation of **2** from **1**. However, several attempts to trap the possible ketene intermediate by irradiating in the presence of water, alcohols and amines were unsuccessful. We have also attempted to trap any radical species that may be formed during the reaction by performing the photolysis in the presence of dodecanthiol or tri-*n*-butyl tin hydride, but no other product but **2** was detected. The failure of trapping ketene or radical species still cannot exclude the possible involvement of such intermediates because it could simply mean that the product forming process is too rapid to be altered by any additives.

The clean conversion at 365 nm irradiation suggests that the reaction occurs from n, π* excited states.[10] Results from quenching and sensitization experiments indicate that more than one multiplicity excited states may be involved in the reaction of **1**. However, intersystem crossing ($S_1 \rightarrow T_1$) rates of phenyl ketones are known to be greater than 10^{10} s^{-1}.[11] Thus, it is likely that the reaction occurs mainly from triplet excited states. If the singlet reaction still can occur to compete with the ISC, the rate would be in the order of 10^{11} s^{-1}. Although there is no apparent quenching of product formation by triplet quenchers, a lower limit for the reaction rates of the triplet ketones can be estimated using the known rate of triplet energy transfer quenching by dienes or naphthalene in benzene, 5–6×10^9 M^{-1} s^{-1}.[12] With the highest quencher concentration being 0.1 M that was tried, the reaction rates must be in the order of 10^{10} s^{-1} for the product forming process to prevail over the quenching. Any bimolecular reactions and physical decays would be hard to compete with such a fast unimolecular process, which explains our experimental results of high quantum efficiency and failure of trapping any reaction intermediates.

Our proposed mechanism is summarized in Scheme 2. As discussed above, we think that the reaction occurs primarily from n, π* triplet excited states. How much the singlet reaction contributes to the total reactivity is, however, still an open question. In the triplet excited state, the reaction can start by cleavage of either bond a or bond b (Scheme 2),[13] which ultimately leads to the formation of the ketene intermediate.

It is also interesting to note that irradiation of **1** did not show any evidence of the Yang reaction which was the only reaction observed in the photolysis of structurally analogous 1-benzoyl-1-(*o*-alkylphenyl)cyclopropanes. The hydrogen abstraction reaction rate from n, π* triplet excited states of 1-benzoyl-1-(*o*-tolyl)cyclopropane has been measured to be 4×10^8 s^{-1} at ambient temperature.[3,14] Our estimated value for the reaction rate of **1** to **2** is much higher than this, which may explain the absence of the Yang reaction in the photolysis of **1**. By adjoining the cyclopropyl carbon with the *ortho* carbon of benzoyl group, photochemical reactivity changed completely from the Yang reaction to the observed rearrangement of current work.

In summary, the reverse process of the well-known photochemical transformation of 1(2*H*)-naphthalenones to benzobicyclo[3.1.0]hexenones has been found to occur in very high chemical and quantum efficiency. As noted above, the keto form of **2**, an 1(2*H*)-naphthalenone, is quite stable in benzene under our irradiation condition. We think that extra conjugation caused by the *o*-tolyl group at the 3 position of the 1(2*H*)-naphthalenone perturbs the electronic structures of the excited states, which renders whole process irreversible under the photolysis condition.[15] We are currently



Scheme 2. Proposed mechanism of photochemical transformation of **1** to **2**.

investigating the possible application of this system to photochromism.

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (98-0501-09-01-3), and in part by the Ministry of Education, Korea (BK21 program). We also thank Tae Young Kim and SooYoung Jeong for technical assistance.

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5. Valerophenone actinometer was used. Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. M.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506.
6. Spectroscopic properties of **2a**: ^{1}H NMR (CDCl$_3$, 200 MHz): δ 8.20 (m, 1H), 7.77 (m, 1H), 7.47–7.19 (m, 7H), 7.16 (d, 1H, $J=8.4$ Hz), 5.28 (s, 1H, -OH), 2.10 (s, 3H). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 148.3, 138.3, 136.4, 134.7, 131.5, 131.3, 129.2, 128.2, 128.1, 127.2, 126.8, 126.0, 124.7, 123.0, 121.4, 120.3, 20.4. IR (KBr) 3535, 3496, 3052, 2923, 1572, 1382, 1243. cm^{-1}; EI MS 234 (M$^+$), 115, 91, 89, 77, 63.
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13. For a similar transformation of 2,3-epoxy-2-methyl-3-phenylindanone to 3-methyl-4-phenylisocoumarin, the reaction was suggested to occur by the cleavage of bond a; Zimmerman, H. E.; Simkin, R. D. *Tetrahedron Lett.* **1964**, 1847.
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