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Photochemistry of α, α-Dihalovalerophenones

Sungsu Cho and Bong Ser Park*
Department of Chemistry, Dongguk University, Seoul 100-715, Korea

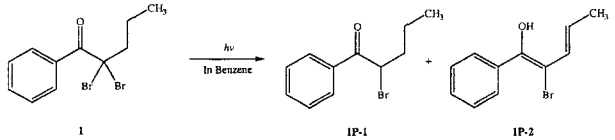
α,α-Dibromovalerophenone and α,α-dichlorovalerophenone were prepared and their photochemical behaviors were investigated. The former gives C-Br cleavage products and the latter gives mainly the Yang photocyclization products upon irradiation. The reactivity of the chlorine substituted ketone turned out to be quite different from that of α,α-difluorovalerophenone which gives both the cyclization and elimination products from the 1,4-biradical intermediate.

Key words: Yang photocyclization, substituent effects

Recently we have reported an interesting example of the substituent effect on photochemistry of carbonyl compounds, in which α-bromovalerophenone gives only the C-Br bond cleavage products, but α-chlorovalerophenone follows the classical Norrish/Yang reaction pathway predominantly. [1] As our continuing efforts to understand structure/reactivity relationship in photochemistry [2-5], we decided to extend our investigation on this system using α,α-dihalovalerophenones. Here we would like to report our findings in photochemical reactions of α,α-dibromovalerophenone, **1**, and α,α-dichlorovalerophenone, **2**, and compare those with the already known result of photolysis of α,α-difluorovalerophenone. [6-7]

The ketones **1** and **2** were prepared by di-halogenation of valerophenone using bromine in dichloromethane and sulfuryl chloride in dichloromethane, respectively. [8] Photolysis of the ketones was done using the output of Pyrex filtered light of a Hanovia medium pressure mercury arc lamp by hanging an NMR tube containing 0.02 M of the ketone in degassed benzene-d6 near the lamp. The sample was monitored at regular intervals by ^{1}H NMR spectroscopy.

At early stage of the photolysis of **1** the formation of two products was evident from the ^{1}H NMR spectrum and the TLC analysis. Large scale irradiation was performed in order to isolate each product and characterize its structure. The usual spectroscopic analysis of the products showed the two products were α-bromovalerophenone, **1P-1**, and 1-phenyl-2-bromopenta-1,3-dien-1-ol, **1P-2**, shown below. [9]



1 1P-1 1P-2

*To whom correspondence should be addressed.
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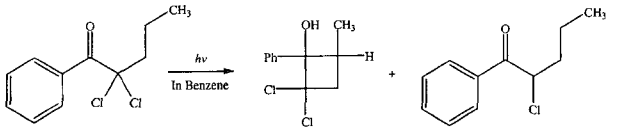
The prolonged irradiation of **1** resulted in complication of its ^{1}H NMR spectrum due to the secondary photoreactions of the initially formed photoproducts. Among those the most noticeable were valerophenone and β-bromovalerophenone, which resulted from photolysis of **1P-1**. [1] The ratio of **1P-1** and **1P-2** was time dependent, which can easily be explained by the occurrence of the secondary photoreactions. [10]

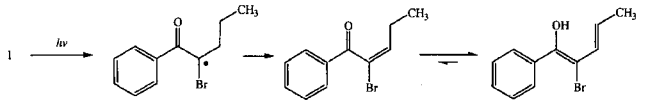
The ^{1}H NMR spectrum of **2** after irradiation also showed very complicated patterns. When the irradiation stopped before the secondary photolysis started, there were two major products in the reaction mixture, which were identified as 2,2-dichloro-4-methyl-1-phenylcyclobutanol, **2P-1**, and α-chlorovalerophenone, **2P-2**, shown below. [11]



2 2P-1 2P-2

The relative yields of **2P-1** and **2P-2** were 74 % and 26 %, respectively. Prolonged irradiation of **2** resulted in additional formation of 2-chloro-4-methyl-1-phenylcyclobutanol and 2-chloroacetophenone, which are the secondary photoproducts of **2P-2**.

Formation of **1P-1** from **1** can be explained by photoinduced C-Br bond cleavage followed by hydrogen atom transfer as evidenced by similar transformation of α-bromovalerophenone and other structural analogues. [12-14] More interesting is the finding of the photoproduct **1P-2** in the photolysis of **1**. In the photolysis of α-bromovalerophenone β-bromovalerophenone is formed as a photoproduct via the Michael addition of HBr to the α,β-unsaturated ketone intermediate. We believe the similar reaction occurs in the photolysis of **1**, which forms 2-bromo-1-phenylpent-2-en-1-one. At this stage, however, the α,β-unsaturated ketone tautomerizes rapidly to **1P-2** having the more extended conjugation instead of going through the Michael type reaction. The postulated reaction sequence is



Scheme 1.

shown in Scheme 1.

The photoproduct **2P-1** from **2** is the result of classical Yang photocyclization. [15-16] The reaction is well known to occur via 1,4-biradical intermediate. In the Norrish/Yang reaction the biradical intermediate normally gives both elimination and cyclization products. For example, valerophenone gives acetophenone, propene (elimination products), and diastereomeric mixtures of 1-phenyl-2-methylcyclobutan-1-ol (cyclization products). In photolysis of **2**, however, we could not detect α,α-dichloroacetophenone, which indicates that the biradical intermediate from **2** gives exclusively the cyclization product. The result is quite interesting considering α,α–difluorovalerophenone gives an equal amount of the elimination products and the cyclization products.[6] The origin of the different reaction selectivities of two compounds cannot be explained clearly at this stage and requires further investigation.

As in the case of photolysis of mono halogenated valerophenone, the bromine substituted ketone does not give the cyclization product presumably due to relatively fast C-Br bond cleavage reaction rate resulting from the weak bond energy. [1] We are currently looking into possibilities of photoinduced electron transfer in the photolysis of **1** and **2** in polar solvents.

In summary, photochemical properties of α,α-dibromovalerophenone and α,α-dichlorovalerophenone were investigated. The former gives C-Br cleavage products and the latter gives mainly the Yang photocyclization products upon irradiation. The reactivity of the chlorine substituted ketone turned out to be quite different from that of α,α-difluorovalerophenone which gives both the cyclization and elimination products from the 1,4-biradical intermediate.

REFERENCES

1. Park, B. S. and S. Cho. (2004) Substituent Effect in Photochemistry of Carbonyl Compounds: α-Halovalerophenones *Bull. Korean Chem. Soc.* **25**, 42-44
2. Park, B. S., D. J. Chang, and K. Nahm (2002) Reversed Diastereoselectivity in the Yang Photocyclization upon Introducing a Cyclopropyl Group at Alpha Position to Carbonyls *Terahedron Lett.* **43**, 4249-4252.
3. Park, B. S. and D. J. Chang (2001) Highly Efficient Photoinduced Rearrangement of Benzobicyclo[3,1,0]hexenones to 1-Naphthols. *Tetrahedron Lett.* **42**, 711-713.
4. Park, B. S., D. J. Chang, T. G. Kim, H, Kim, J. Hahn and D.-J. Jang (2001) Photolysis Dynamics of Cyclopropyl and Oxiranyl Aryl Ketones: Drastic Ring Activation Effect of Oxygen. *J. Phys. Chem. A.* **105**, 3555-3563.
5. Park, B. S. and S. Y. Jeong (2000) Photochemistry of α-(o-Alkylphenyl)indanones. *J. Photoscience* **7**, 35-37.
6. Wagner, P. J. and M. J. Thomas (1976) Enhanced Photocyclization of α-Fluoro Ketones *J. Am. Chem. Soc.* **98**, 241-243.
7. Wagner, P. J., M. J. Thomas, and A. E. Puchalski (1986) Photoreactivity of α-Fluorinated Phenyl Alkyl Ketones *J. Am. Chem. Soc.* **108**, 7739-7744.
8. Spectroscopic data of **1**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.34 (d, 2H, J = 7.0 Hz), 7.51 (m, 3H,), 2.65 (t, 2H, J = 7.6 Hz), 1.77 (tq, 2H, J = 7.4, 7.6 Hz), 1.06 (t, 3H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$) δ 188.7, 133.3, 132.8, 131.2, 128.0, 66.7, 48.9, 21.0, 13.6. IR(neat) : 1681(C=O str.) cm^{-1}. Spectroscopic data of **2**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.28 (d, 2H, J = 7.0 Hz), 7.52 (m, 3H), 2.48 (t, 2H, J = 7.4 Hz), 1.74 (tq, 2H, J = 7.5, 7.4 Hz), 1.04 (t, 3H, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 188.6, 133.5, 132.2, 131.0, 128.3, 87.6, 46.5, 18.3, 13.4. IR(neat) : 1685(C=O str.) cm^{-1}.
9. Spectroscopic properties of **1P-1**: ^{1}H NMR ($CDCl_3$, 200 MHz) 8.02 (m, 2H), 7.53 (m, 3H), 5.15 (dd, 1H, J = 7.1, 7.0 Hz), 2.15 (m, 2H), 1.51 (m, 2H), 0.98 (t, 3H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 193.4, 134.6, 133.8, 129.0, 128.9, 47.1, 35.5, 20.9, 13.7. IR(neat) : 1688(C=O) cm^{-1}, EI mass: 240 (M^+). Spectroscopic data of **1P-2**: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.77 (d, 2H, J = 7.0 Hz), 7.55 (m, 3H), 6.85 (d, 1H, J = 10.0 Hz), 5.21 (dq, 1H, J = 10.0, 6.6 Hz), 1.84 (d, 3H, J = 6.6 Hz). ^{13}C NMR($CDCl_3$) δ 145.4, 133.3, 129.9, 128.8, 128.7, 128.5, 128.3, 94.7, 24.8. IR(neat): 3321(O-H str.) cm^{-1}.
10. As the irradiation continues, the relative yield of **1P-2** increases in compensation for the loss of **1P-1**. The photochemical integrity was not changed in different reaction concentration.
11. Spectroscopic data of **2P-1**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.24 (d, 2H, J = 7.0 Hz), 7.55 (m, 3H), 2.70-1.80(m, 3H), 0.97 (d, 3H, J = 7.0 Hz). Spectroscopic properties of **2P-2**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.01 (m, 2H), 7.55 (m, 3H), 5.13 (dd, 1H, J = 8.0, 5.8 Hz), 2.03 (m, 2H), 1.53 (m, 2H), 0.98 (t, 3H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 193.8, 134.7, 133.8, 129.0, 128.9, 57.7, 35.7, 19.7, 13.7. IR(neat) : 1693 (C=O) cm^{-1} . EI mass: 196(M^+).
12. Izawa, Y., Y. Watoh, and H. Tomioka, (1984) Effect of Structure on Photoalcoholysis of Aromatic α-Halo Ketones. *Chem. Lett.* **1**, 33-36.
13. Purohit, P. C. and H. R. Sonawane, (1981) Photochemistry of α-Haloketones *Tetrahedron*, **37**, 873-877.
14. McGimpsey, J. C. and J. C. Scaiano (1988) Photochemistry of α-Chloro-and α-Bromoacetophenone, Determination of Extinction Coefficient for Halogen-benzene Complexes. *Can. J. Chem.* **66**, 1474-1478.
15. Wagner, P. J (2004) Yang Photocyclization: Coupling of Biradicals Formed by Intramolecular Hydrogen Abstraction of Ketones In *CRC Handbook of Organic Photochemistry and Photobiology*, Eds. Horspool, W. M. and Song, P. S., CRC Press, Boca Raton, FL., pp58-1-58-70
16. Wagner, P. J. and B. S. Park (1991) Photoinduced Hydrogen Atom Abstraction by Carbonyl Compounds *Org. Photochem.* **11**, 227-348