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Photodecarbonylation of 2-Phenyl-4-alkylidene-5(4H)-oxazolones

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Abstract: *The title compounds were prepared by the Erlenmeyer synthesis and irradiated with or without a Pyrex filter using 450 W medium pressure mercury arc lamp. Cis-trans isomerization was the major reaction under pyrex filtered condition, whereas irradiation without a Pyrex filter resulted in decarbonylation, followed by trapping of the ketenimine intermediate by protic solvents.*
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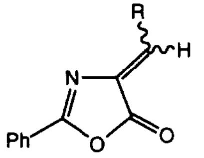
For decades, several papers describing photochemistry of 2-phenyl-4-alkylidene-5(4H)-oxazolones have been appeared in the literature[1]. Even though some of these compounds showed various photoreactivities depending upon their substituents and reaction media, most of them involved photoinduced cis-trans isomerization of the alkylidene moieties. Ullman and coworkers have studied the wavelength dependence on photochemistry of 2-phenyl-4-benzylidene-5(4H)-oxazolone, **1a**.[2] They reported that irradiation of **1a** at 365 nm resulted in cis-trans isomerization, while irradiation at 254 nm resulted in hydrogen atom abstraction from a solvent, 2-propanol. This report led us to study photobehavior of compounds **1b** and **1c** shown below, which we expected those E isomers to react by an intramolecular H-atom abstraction. Contrary to this expectation, these compounds showed different photoreactivities. Here we would like to report what we have found so far on this system.



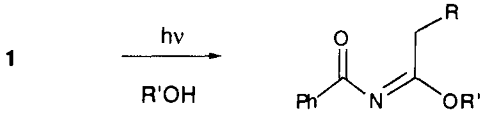
a: R = Ph
b: = Me
c: = Et

1

The title compounds were prepared by Erlenmeyer synthesis[3], which gave mixtures of Z- and E-isomers with a ratio of 3 to 1 for both **1b** and **1c**.[4] The amount of E-isomers could be increased by using known methods[5], but they were slowly isomerized to the more stable Z-isomers in solution at room temperature. Especially, the E-isomer of **1c** was not stable enough to be used for photolysis in pure form.

Irradiation was performed using 450 W Hanovia medium pressure mercury arc lamp with or without a Pyrex filter sleeve. Several different solvents were used for the photolysis; ethanol. 2-propanol, *tert*-butanol, benzene, THF and acetonitrile. With the Pyrex filter, the only reaction observed was cis-trans isomerization in all the solvents used. The E to Z ratios in photostationary mixtures were 3 to 1 and 1 to 1 for **1b** and **1c**, respectively.

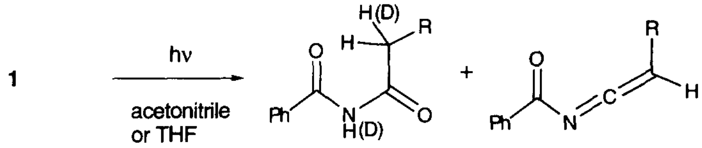
The photolysis of **1b** and **1c** in alcoholic solvents without a Pyrex filter resulted in formation of a sole product.[6] The product was identified as **2**, whose chemical yield was over 90 %.[7] We could not detect any products of hydrogen abstractions from solvents, which Ullman and coworkers had observed for **1a**.[2]



R = Me or Et R' = Et, i - Pr or *t* - Bu

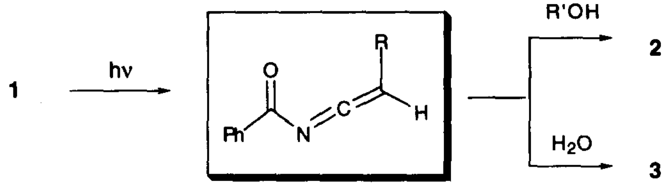
2

When **1b** and **1c** were irradiated in acetonitrile or THF containing a few percents of water, one product was formed predominantly, which was identified to be **3**.[8] Even if well dried solvents were used for photolysis, the same product was obtained, which we believe some moisture got involved during the workup. When D_2O was added in the reaction mixture, **3**-d_2 was obtained as a sole product after photolysis.[9] When **1b** was irradiated in a degassed quartz tube using CD_3CN as a solvent and transfered to an NMR tube, a new product was observed besides **3b**.[10] This product was tentatively assigned as **4b** based on its ^{1}H NMR spectroscopic data.[11] Further characterization of this compound could not be done due to its instability.



3 **4**

A plausible explanation based on our results is that **1b** and **1c** are decarbonylated and form ketenimine **4** on photolysis without a Pyrex filter. The ketenimine is rapidly trapped by protic solvents. Photodecarbonylation has been suggested as a reaction mechanism of N-(methylidene)acetamide formation from 2,4-dimethyl-4-phenyl-Δ^2-oxazoline-5-one in which an alkylidene moiety is absent at 4 position.[12] To our knowledge, however, our result is the first direct observation of photodecarbonylation from 4-alkylidene-2-phenyl-5(4H)-oxazolones. Our results are unique in that the photodecarbonylation forms reactive ketenimines, which can be further elaborated toward synthetic applications. Also it can be a good candidate for photoaffinity labeling.[13]



Ullman has discussed the wavelength dependent photoreactivity of **1a** in terms of involvement of different excited states. His theoretical views predicted that the upper excited state $T_2(n, \pi^*)$ was responsible for hydrogen abstraction reaction and the lower excited state $T_1(\pi, \pi^*)$ was the origin of cis-trans isomerization. In our experiments with **1b** and **1c**, decarbonylation is observed unlike hydrogen abstraction for **1a** on photolysis at the shorter wavelength.[14] The ultraviolet absorption spectra of **1a** and **1b** look similar, but the absorption maxima of **1a** is at the longer wavelength than those of **1b**; 259, 360 nm for **1a** and 236, 298 nm for **1b**. We think the excited state $T_2(n, \pi^*)$ is also responsible for decarbonylation reaction and the change of the reaction pathway may have resulted from the higher energy of **1b**.

In summary, irradiation of 2-phenyl-4-ethylidene(or propylidene)-5(4H)-oxazolone at short wavelength resulted in an efficient photodecarbonylation followed by trapping of the ketenimine intermediate by protic solvents, which was unprecedented for photochemistry of 2-phenyl-4-alkylidene-5(4H)-oxazolones so far. The detailed mechanistic picture of this reaction will be described in a full paper in due time.

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4. The structural assignment of each isomer is based on relative stability of each isomer and on Sidhu's general observations on the NMR spectra of oxazolones; Sidhu, G. S.; Venkataratnam, V.; Prassad, K. K.; Iyengar, D. S. *Ind. J. Chem.* **1972,** *10,* 448-451. **Z-1b:** ^{1}H NMR ($CDCl_3$, 200 MHz); δ 8.10 (d, 2H, J = 8.4 Hz), 7.60-7.51 (m, 3H), 6.76 (q, 1H, J = 7.4 Hz), 2.26 (d, 3H, J = 7.4 Hz); **E-1b:** ^{1}H NMR ($CDCl_3$, 200 MHz); δ 8.05 (d, 2H, J = 7.6 Hz), 7.59-7.45 (m, 3H), 6.91 (q, 1H, J = 7.9 Hz), 2.37 (d, 3H, J = 7.9 Hz); **Z-1c:** ^{1}H NMR ($CDCl_3$, 200 MHz); δ 8.10 (d, 2H, J = 7.4 Hz), 7.60-7.47 (m, 3H), 6.70 (t, 1H, J = 7.9 Hz), 2.71 (dq, 2H, J = 7.9, 7.7 Hz), 1.20 (t, 3H, J = 7.7 Hz); **E-1c:** ^{1}H NMR ($CDCl_3$, 200 MHz); δ 8.06 (d, 2H, J = 7.4 Hz), 7.60-7.45 (m, 3H), 6.83 (t, 1H, J = 7.9 Hz), 2.86 (dq, 2H, J = 7.9, 7.7 Hz), 1.18 (t, 3H, J = 7.7 Hz). Other physical properties of **1b** were the same as the reported values.(ref 3 and refs therein)
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6. Irradiation of one isomer only or the mixture gave the same result.
7. Shown here are two representative cases where R' is an isopropyl group; **2b:** ^{1}H NMR ($CDCl_3$, 200 MHz); δ 8.01 (d, 2H, J = 7.4 Hz), 7.60-7.40 (m, 3H), 5.19 (septet, 1H, J = 7.0 Hz), 2.38 (q, 2H, J = 7.4 Hz), 1.38 (d, 6H, J = 7.0 Hz), 1.12 (t, 3H, J = 7.4 Hz), IR(CCl_4) 1667, 1549, 1268 cm^{-1}, EI MS 219(M^+, 3), 105(100), 77(48), 59(34). **2c:** ^{1}H NMR ($CDCl_3$, 200 MHz); δ 8.00 (d, 2H, J = 7.4 Hz), 7.60-7.40 (m, 3H), 5.20 (septet, 1H, J = 7.0 Hz), 2.32 (t, 2H, J = 7.4 Hz), 1.59 (tq, 2H, J = 7.4, 7.5 Hz), 1.35 (d, 6H, J = 7.0 Hz), 0.88 (t, 3H, J = 7.5 Hz), IR(CCl_4) 1664, 1539, 1265 cm^{-1}, EI MS 233(M^+, 2), 105(100), 77(48). The stereochemistry of the product could not be determined by any methods that we had tried so far. It is possible that this compound exists as stereolabile E, Z isomers that interconvert with a low free energy of activation.(See Guerra, A.; Lunazi, L. *J. Org. Chem.* **1995**, *60*, 7959-7965.) We, however, failed to observe such a phenominon by low temperature NMR spectroscopy due to solubility problems.
8. **3b:** ^{1}H NMR ($CDCl_3$, 200 MHz); δ 9.01 (br s, 1H), 7.89 (d, 2H, J = 7.4 Hz), 7.55-7.45 (m, 3H), 3.01 (q, 2H, J = 7.4 Hz), 1.24 (t, 3H, J = 7.4 Hz). IR(CCl_4) 3297, 1712, 1682 cm^{-1}, EI MS 177(M^+, 13), 105(100), 77(47), 57(20), 51(21). **3c:** ^{1}H NMR ($CDCl_3$, 200 MHz); δ 8.43 (br s, 1H), 7.84 (d, 2H, J = 7.4 Hz), 7.60-7.45 (m, 3H), 2.99 (t, 2H, J = 7.4 Hz), 1.77 (tq, 2H, J = 7.4 Hz)), 1.03 (t, 3H, J = 7.4 Hz). IR(CCl_4) 3306, 1718, 1685 cm^{-1}, EI MS 191(M^+, 8), 105(100), 77(56).
9. **3b**-d_2: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.89 (d, 2H, J = 7.4 Hz), 7.55-7.45 (m, 3H), 3.01 (br, 1H), 1.24 (br d, 3H, J = 7.3 Hz).
10. The amounts of products varied from trace to ten percents depending upon the reaction time under this reaction condition. The reaction mixture became complicated at high conversion.
11. **4b:** ^{1}H NMR (CD_3CN, 200 MHz) δ 8.00 (d, 2H, J = 8.0 Hz), 7.71-7.45 (m, 3H), 4.70 (q, 1H, J = 8.0 Hz), 1.59 (d, 3H, J = 8.0 Hz).
12. Johnson, M. R.; Sousa, L. R. *J. Org. Chem.* **1977,** *42,* 2439-2443.
13. Fleming, S. A. *Tetrahedron* **1995**, *51*, 12479-12520.
14. When **1a** was irradiated under our reaction condition, no decarbonylation products were detected. The hydrogen abstraction product that Ullman had reported was observed together with some other unidentifiable products.

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