

NOTE

Photoinduced Rearrangement of 2-Phenyl-4-alkylidene-5(4H)-Oxazolones to Benzoyl Acetonitriles via 1,3-Benzoyl Shift of N-Benzoyl Ketenimines

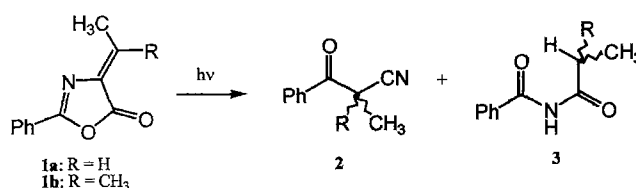
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Ketenimines are nitrogen analogues of ketenes that can be prepared by many different methods from various precursors [1]. Even though the chemistry of ketenimines shares in large portion with that of ketenes [1, 2], there is a unique reactivity for the ketenimines, so called 1,3-rearrangement to nitriles. The reaction involves thermal 1,3-dhift of *N*-substituent to terminal carbon. Various ketenimines have been tested for the reaction [3, 4] and a recent study has shown that the rearrangement occurs via homolytic cleavage followed by recombination of radical pairs [5].

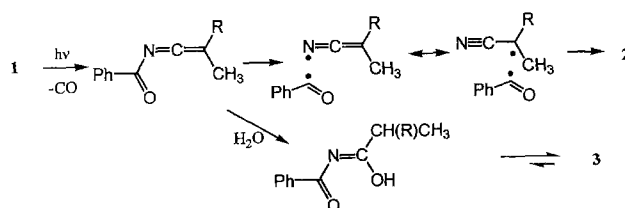
In the course of our studies on photochemistry of 2-phenyl-4-alkylidene-5(4H)-oxazolones, we have collected several evidences supporting the intermediacy of *N*-benzoyl ketenimines via photoinduced decarbonylation of the oxazolones [6-8]. The 1,3-acyl shift of *N*-acyl ketenimines has not been available in the literature mainly due to relative instability of the ketenimines. Here we would like to report one pot transformation of 2-phenyl-4-alkylidene-5(4H)-oxazolones to α -alkyl substituted benzoylacetonitriles involving the 1,3-acyl shift of *N*-benzoyl ketenimines.

The oxazolone (**1**) in dry organic solvents (typically 0.05 M solution in acetonitrile or methylene chloride) was irradiated at room temperature in a quartz vessel using an output of a 450 W Hanovia medium pressure mercury arc lamp. After concentrating the solution using a rotary evaporator, a major product was isolated by column chromatography over silica gel. From its spectroscopic properties, the product was assigned as α -alkyl substituted benzoylacetonitrile (**2**). The structural assignment was confirmed by comparing them with authentic samples prepared by α -alkylation of benzoylacetonitrile using NaH as a base. Chemical yields of the formation of **2** were strongly dependent upon the dryness of reacting solution, ranging from 10 to 75%. Even when a small amount of water was present in solution, an imide (**3**) in Scheme 1 became a major product.



Scheme 1. Photochemical Reactions of 2-phenyl-4-alkylidene-5(4H)-oxazolones.

The formation of **2** from **1** is initiated by photoinduced decarbonylation which gives *N*-benzoyl ketenimines. If any nucleophiles are present in the solution, the ketenimines are rapidly trapped by them. Thus, a small amount of water can intercept the ketenimine intermediates to give **3**. The quenching by water is so efficient that other reactions cannot compete with it unless the solution is completely dry. If the reaction condition is carefully controlled, the ketenimines can rearrange to **2** via 1,3-acyl shift. The exact reaction route of the rearrangement could not be determined in our experiments because the ketenimines could not be isolated despite several efforts. As noted above, the 1,3-rearrangement of most other ketenimines to nitriles has been believed to occur via homolytic decomposition and recombination of the resulting radical pairs. We think the same mechanism can be applied to our system. One distinct feature of our system is that the rearrangement occurs even at low temperature as efficiently as at ambient temperature. Previously known examples of such rearrangements are all thermal reactions. The temperature range that applied was 60 °C to 200 °C depending on *N*-substituents. Considering the fact that the same efficiency was maintained at -78 °C, the



Scheme 2. Reaction Mechanism for the Formation of **2** and **3** in Photolysis of **1**.

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rearrangement of **1** to **2** is believed to occur photochemically. Obviously more experiments would be required to get more clear picture of the reaction. Our proposed reaction mechanism is summarized in Scheme 2.

In summary, irradiation of 2-phenyl-4-alkylidene-5(4H)-oxazolones resulted in formation of α -alkyl substituted benzoylacetonitriles. The reaction mechanism involves photoinduced decarbonylation and 1,3-acyl shift of *N*-benzoyl ketenimines. The 1,3-shift reaction proceeds photochemically which is unprecedented in the literature up to now.

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