

**Photoinduced One Pot Transformation of 2-Phenyl-4-ethylidene-5(4*H*)-oxazolone and Allylic Alcohols to  $\gamma, \delta$ -Unsaturated *N*-benzoyl Amides<sup>1</sup>**

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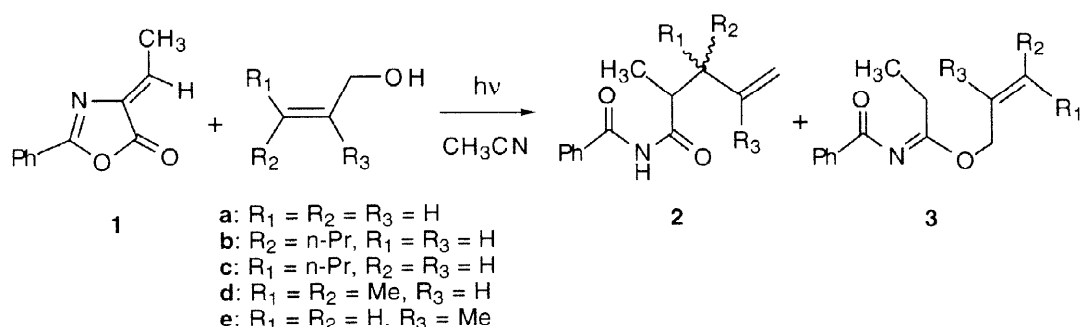
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**Abstract:** Photolysis of 2-Phenyl-4-ethylidene-5(4*H*)-oxazolones in the presence of allylic alcohols resulted in a novel one-pot transformation to  $\gamma, \delta$ -unsaturated *N*-benzoyl amides via decarbonylation, nucleophilic addition of allylic alcohols, photoinduced hydrogen transfer and the Claisen rearrangement. © 1998 Elsevier Science Ltd. All rights reserved.

The Claisen rearrangement has received a great deal of attentions because it provides an easy access to synthetically useful  $\gamma, \delta$ -unsaturated carbonyl compounds.<sup>2</sup> Recent studies show that allyl imidates also undergo the rearrangement. Metz and coworkers have reported several examples of such a rearrangement by treating various allyl imidates with appropriate bases.<sup>3</sup> If the base is not used, the thermal rearrangement requires high temperature such as decalin refluxing condition.<sup>4</sup> In the course of our studies on the photochemistry of 2-phenyl-4-ethylidene-5(4*H*)-oxazolones, **1**, we have found a convenient method to prepare *N*-benzoyl imidates<sup>5</sup>, which led us to investigate possibilities of the Claisen rearrangement of *O*-allyl *N*-benzoyl imidates under mild reaction condition without using bases. Here we would like to report a novel one-pot transformation of **1** and allylic alcohols to  $\gamma, \delta$ -unsaturated *N*-benzoyl amides by a photochemical method.

The oxazolone **1**<sup>6</sup> in dry acetonitrile (typically 0.01-0.02 M) containing an excess amount of allyl alcohol (2 to 3 eq.) was irradiated at room temperature for up to 48 hours in a quartz vessel using an output of a 450 W Hanovia medium pressure mercury arc lamp. After evaporating all the volatiles and chromatographing over silica gel, two major products were isolated together with varying amounts of one other product depending upon dryness of the solvent.



On the basis of their spectroscopic properties<sup>7</sup>, they were assigned to be **2**, **3** and N-benzoyl propionamide<sup>5</sup>, **4**. Other allylic alcohols except *cis*-2-hexenol gave similar results, *vide infra*. In case of *trans*-2-hexenol (entry b), anti- and syn isomers of **2** were formed in 5.1 to 1 ratio.<sup>8</sup> When the irradiation was stopped at low conversion, **3** was a major product. The amount of **4** was minimal in the crude reaction mixture if the solvent was carefully dried. We also noticed that **3** was easily converted into **4** during workup and purification step. Prolonged irradiation resulted in increased formation of other products including benzamide, which resulted from thermal decomposition and secondary photoreactions of primary photoproducts. The best yield of **2** was obtained at 50-60 % conversion. Results of the photolysis are summarized below.

Table 1. Product Yields of Photolysis of **1** in the Presence of Allylic Alcohols

Entry	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Yields <sup>a</sup> (%)	
				<b>2</b>	<b>3 + 4</b> <sup>b</sup>
a	H	H	H	28	48
b	H	n-Pr	H	42 <sup>c</sup>	29
c	n-Pr	H	H	trace	79
d	Me	Me	H	19	60
e	H	H	Me	24	58

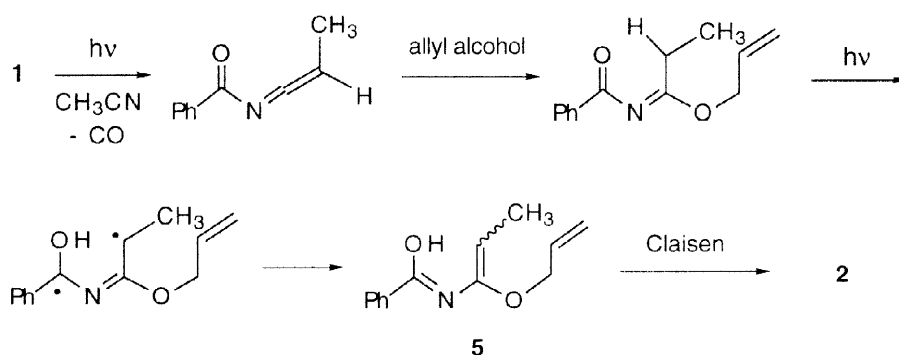
<sup>a</sup> Isolated yields at 50-60 % conversion; <sup>b</sup> Parts of **3** was hydrolyzed to give **4** after column chromatography. <sup>c</sup> Anti to syn product ratio was 5.1 to 1.

At the beginning of this study, we were trying to isolate **3** first and then investigate reactivities of **3** either thermally or photochemically. But it is apparent from the above results that the Claisen rearrangement product of **3**, **2**, can be obtained under the same irradiation condition as that of the photodecarbonylation of **1**. However, it was not still certain that **2** was formed from **3** thermally or photochemically. Thus we have irradiated the isolated **3** under the same reaction condition. It resulted in clean conversion to **2**. Refluxing **3** in either acetonitrile or toluene under dark condition for up to 24 hours did not provide **2** at all, which clearly indicated the formation of **2** resulted from photochemical reaction of **3**.

It is known that  $\alpha,\beta$ -unsaturated ketones or esters with appropriate substituents can be deconjugated photochemically *via* hydrogen transfer from  $\gamma$ -carbons to the carbonyl oxygen.<sup>9</sup> We believe that the N-benzoyl imidate **3** undergoes similar double bond shift process under the above reaction condition, which is then subject to the Claisen rearrangement to give **2**. But there still remains a question of how this Claisen rearrangement occurs. One possibility is that the biradical intermediate formed from hydrogen abstraction reaction of **3** cyclizes in 6-endo fashion which subsequently fragments to give the final product **2**. Or the dienol intermediate formed from the biradical may undergo the photo-Claisen rearrangement following similar reaction routes as that previously reported by Matlin and coworkers for 2-acyl-4-oxa-1,5-hexadienes<sup>10</sup> and 1-acyl-3-oxa-1,5-hexadienes<sup>11</sup>. The former mechanism seems unlikely considering that

the 6-endo cyclization of 5-hexenyl radical proceeds with a rate constant of  $<10^5 \text{ s}^{-1}$  at  $25 \text{ }^\circ\text{C}$ <sup>12</sup> and that lifetime of triplet dienol from *o*-methylacetophenone is only several hundred nanoseconds in wet acetonitrile.<sup>13</sup> We think that the biradical intermediate would rapidly collapse to a dienol once it is formed. In any event, we have attempted to trap possible radical intermediates but failed. The result still cannot exclude the radical mechanism because it could simply mean that the radical intermediate was so short-lived that it could not be trapped. We could not detect photochemical 2+2 adducts in either head to head or head to tail form, which Matlin and coworkers had observed in their studies.

Thermal [3,3] sigmatropic rearrangement from the dienol intermediate **5** can be another possible mechanism. Chemical yields given in Table 1 suggest that the thermal mechanism may in fact be operating here. Relative yields of entry b,c,d are similar to the corresponding results of thermal Claisen rearrangement of *N*-silyl ketene *N,O*-acetals from allyl *N*-phenylimidates studied by Metz and coworkers.<sup>14</sup> For example, in their studies an acetal from *cis*-hexenyl imidate required  $130 \text{ }^\circ\text{C}$  heating to isomerize while that from *trans*-hexenyl imidate isomerized efficiently at room temperature. In order to get further proof for the thermal mechanism, we have repeated entry b at  $0 \text{ }^\circ\text{C}$ , which resulted in formation of **3b** and **4**. At prolonged irradiation only a trace amount of **2b** was detected. Therefore, once **5** is formed *via* photoinduced hydrogen transfer, the rearrangement seems to follow the normal [3,3] sigmatropic pathways. Our proposed mechanism for the formation of **2** is summarized below.



Diastereoselectivity of entry b is worthy of further mentioning. The ratio of **5.1** to **1** is higher than 2 to 1 from an *N*-phenyl imidate used in Metz's study in decalin refluxing condition and lower than 10 to 1 from an *N*-silyl ketene *N,O*-acetal studied in the same research group at room temperature. Obviously steric demand at transition state of the rearrangement and the reaction temperature are the important factors determining the selectivity. Stereochemistry of the vinylic methyl group of **5** must play an important role dictating the stereochemical outcome of the rearrangement, but could not be determined in our cases. Our result is unique in that reasonably high diastereoselectivity is obtained directly from the imidate under mild condition without converting to enolates or ketene *N,O*-acetals.

In summary, photolysis of 2-Phenyl-4-ethylidene-5(4*H*)-oxazolone in the presence of allyl alcohol resulted in a novel one-pot transformation to  $\gamma,\delta$ -unsaturated *N*-benzoyl amides *via* decarbonylation, nucleophilic addition of allyl alcohol, photoinduced hydrogen transfer and the Claisen rearrangement. To our knowledge, this is the first example of the Claisen rearrangement induced by photodeconjugation. Our result will be a nice addition to known methods from the fact that the reaction can be done under mild

condition without using any bases. Currently, the scope and utility of this reaction is being studied using various substrates and reaction conditions in our laboratory.

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#### REFERENCES AND NOTES

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7. Structure of **2** was confirmed further by converting it into the corresponding lactones *via* iodolactonization using iodine and DME(ref. 3). As a representative example, spectroscopic data of **2a** and **3a** are given.: **2a**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz);  $\delta$  8.68 (broad s, 1H), 7.87 (d, 2H,  $J = 7.0$  Hz), 7.64-7.46 (m, 3H), 5.85 (dddd, 1H,  $J = 10.0, 17.2, 6.1, 7.1$  Hz), 5.18-5.02 (2nd order splitting, 2H), 2.57 (ddd, 1H,  $J = 6.6, 6.1, 13.8$ ), 2.22(ddd, 1H,  $J = 7.0, 7.1, 13.8$ ), 1.26(d, 3H,  $J = 6.9$  Hz), 3.69 (ddq, 1H,  $J = 6.9, 6.6, 7.0$  Hz)  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ , 50 MHz)  $\delta$  178.9, 165.4, 135.6, 133.2, 129.2, 129.0, 127.8, 117.1, 40.0, 37.5, 16.5. IR( $\text{CCl}_4$ ) 3268, 1731, 1681  $\text{cm}^{-1}$  Mass(EI) 77(45), 96(32), 105(100), 122(37), 175(3), 217( $\text{M}^+$ , 1.3); **3a**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  7.90 (d, 2H,  $J = 7.1$  Hz), 7.61-7.38 (m, 3H), 6.05 (ddt, 1H,  $J = 17.0, 10.0, 5.6$  Hz), 5.47 (br. d, 1H,  $J = 17.0$  Hz), 5.39 (br. d, 1H,  $J = 10.0$  Hz), 4.78 (d, 2H,  $J = 5.6$  Hz), 2.41 (2H, q,  $J = 7.6$  Hz), 1.14 (t, 3H,  $J = 7.6$  Hz).  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ , 50 MHz)  $\delta$  179.3, 168.4, 135.1, 134.9, 134.2, 131.6, 130.9, 120.2, 69.6, 28.0, 12.7.
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