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THE PHOTOCHEMICAL REACTION OF 3,4,5-TRIPHENYL-4-OXAZOLIN-2-ONE[1]

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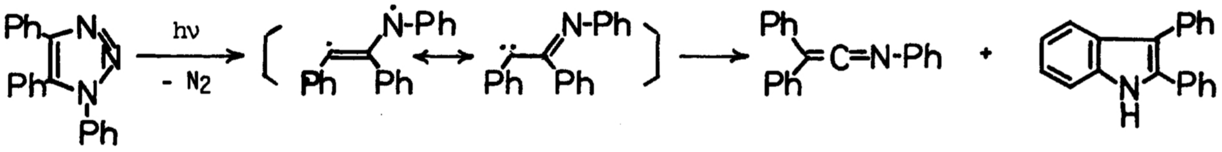
Irradiation of 3,4,5-triphenyl-4-oxazolin-2-one (**1**) in benzene, under nitrogen, with or without iodine gave benzanilide and phenanthroxazolinone **2**. However, in the presence of oxygen **1** was photochemically converted to benzanilide, benzoic acid, and benzamidobenzophenones. This photooxygenation is interpreted by the pathway proceeding via an initial attack of singlet oxygen to **1** forming a dioxetane, followed by ring cleavage to yield N,N-dibenzoylaniline (**6**) which gives final products.

The photochemical extrusion of carbon dioxide from heterocyclic compounds having $-O-\overset{O}{\overset{\|}{C}}-$ linkage as a part of the ring systems is a general reaction, and provides a useful method for the preparation of small ring compounds or for the generation of reactive intermediates which are capable of forming cycloadducts with multiple bonds.[2-4] As a potential route to the as yet unknown antiaromatic heterocycle, 1H-azirine, photolysis of 1H-1,2,3-triazoles have been investigated by Burgess et al.[5] However, irradiation of 1,4,5-triphenyl-1H-1,2,3-triazole in benzene afforded triphenylketenimine and 2,3-diphenylindole.



We had anticipated that the same intermediate as from the 1H-1,2,3-triazole might be produced from the photochemical loss of carbon dioxide from 3,4,5-triphenyl-4-oxazolin-2-one (**1**). Although this expectation was not realized, we now report novel findings concerning the photochemical reaction of **1**.

Irradiation of a benzene solution of oxazolinone **1** (1.3×10^{-2} mol/l), stirred by a stream of nitrogen, by a 300W high-pressure mercury lamp with a Pyrex filter afforded benzanilide and 3-phenylphenanthro[9,10-d]oxazolin-2-one (**2**) in low yeilds respectively, together with recovery of **1** (Table 1). The structure of **2** was assigned on the basis of microanalysis and its spectral data.

2: mp 229-230°C; colorless prisms; ir (KBr) 1760 cm^{-1} (CO); nmr ($CDCl_3$) δ 6.8-8.7 (m, aromatic protons); mass m/e 311 (M^+), 283 (M^+ - CO), 267 ($M^+ - CO_2$), 255 (283^+ - CO), 180 (283^+ - PhNC).

It is well known that irradiation of cis-stilbene[6] and other cis-1,2-diarylethenes in the presence of oxidizing agents such as oxygen and iodine produces condensed ring systems derived from cyclization followed by oxidation. Thus, irradiation of oxazolinone **1** in the presence of iodine was carried out; the results are also given in Table 1. As shown in Table 1, the yield of phenanthrene derivative **2** increased as the iodine content was increased.

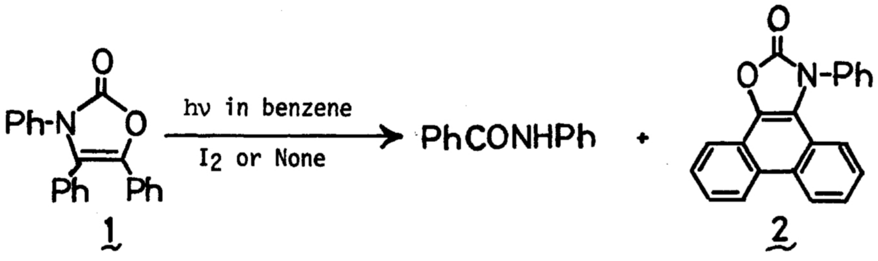
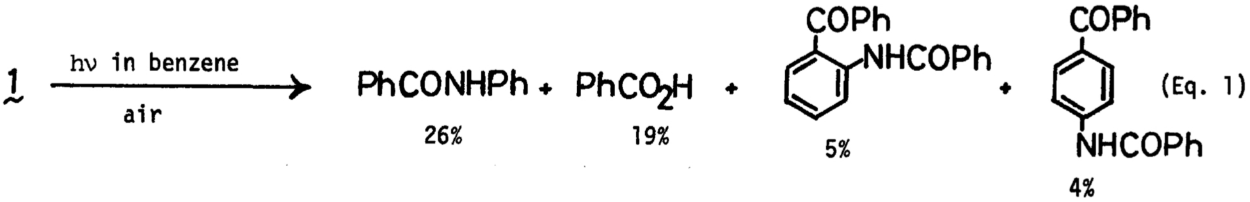


Table 1

Conditions		Products, %		Recovered **1** %
Irradiation time, hr	Iodine mole% to **1**	PhCONHPh	**2**	
43	0	8	3	37
5	2	8	20	43
5	10	trace	35	12
5	15	trace	52	0

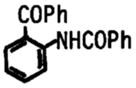
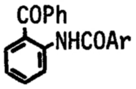
Recently, Padwa and Dehm[8] have reported that upon irradiation in the presence of oxygen 3,4-diphenyl- and 3,4,5-triphenyl-2(5H)-furanones were converted into the corresponding phenanthro[9,10-c]-furanones in high yields.

As commercial nitrogen was passed through a benzene solution of **1** during irradiation, it might be thought that oxygen contaminated in nitrogen would participate in the formation of benzanilide and phenanthrene derivative **2**. When a benzene solution of oxazolinone **1**, agitated by a stream of air, was irradiated for 10 hr, benzanilide, benzoic acid, and benzamidobenzophenones were obtained (Eq. 1).[9] The yield of benzanilide was significantly higher than that in irradiation under nitrogen. This clearly indicates that oxygen is involved in the formation of benzanilide. Contrary to expectation, however, no phenanthrene derivative **2** was formed.

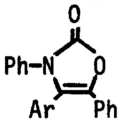


Our efforts were directed toward clarification of the reaction pathway for the photooxygenation of oxazolinone **1**. The photooxygenation of 4-p-anisyl-3,5-diphenyl-4-oxazolin-2-one (**3**) and 5-p-anisyl-3,4-diphenyl-4-oxazolin-2-one (**4**) was performed in the same manner as with **1**. As shown in Table 2, the yields in each case were almost equal with respect to all products. This indicates that the photooxygenation of oxazolinones 3 and 4 proceeds via a common intermediate.

Table 2

Oxazolinone	Products, %						
	ArCONHPh	PhCONHPh	ArCOOH	PhCOOH			
3	21	6	5	6	1	2	7
4	25	7	8	4	3	2	6

3:



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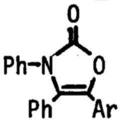
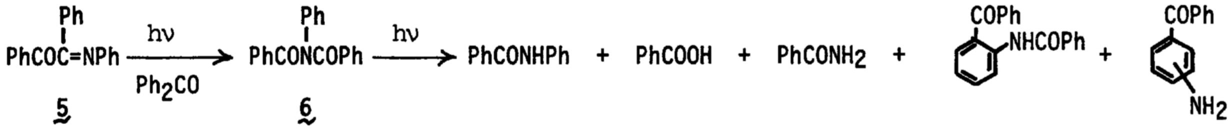


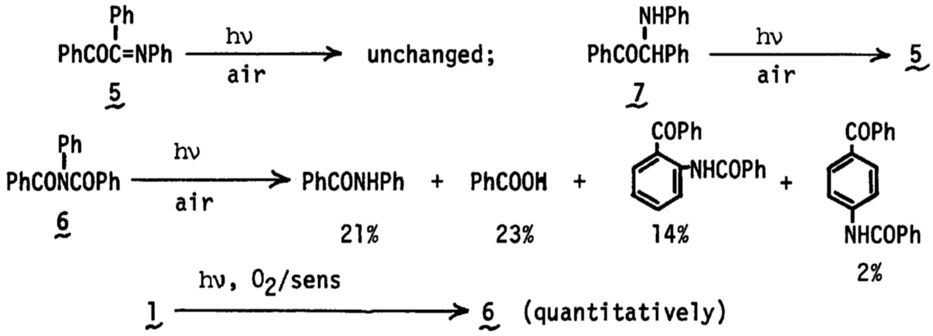
(Ar= p-anisyl)

Kan and Furey[10] have reported the formation of N,N-dibenzoylaniline (6) and benzanilide in the photolysis of an ethereal solution of benzil monophenylimine (5) in the presence of benzophenone as a sensitizer under nitrogen. They also found that upon irradiation in the absence of sensitizers 6 was transformed into benzanilides and other products (Eq. 2).



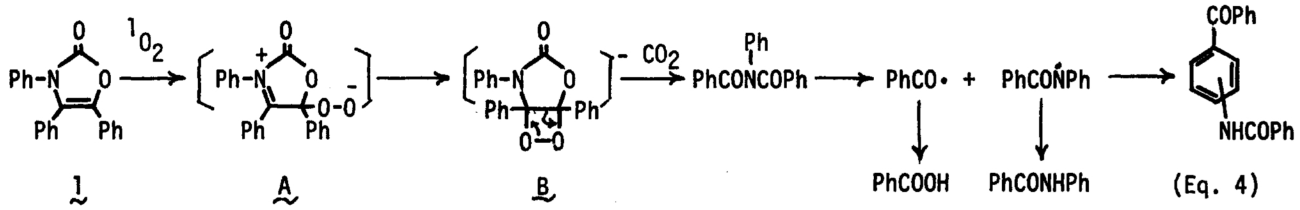
(Eq. 2)

However, it was proved that benzil monophenylimine (5) was not involved in the formation of photooxidized products from oxazolinone 1, because 5 was unchanged upon irradiation in benzene in the absence of a sensitizer. In addition, α-anilinodeoxybenzoin (7) which was formed by hydrolysis of 1, was transformed into 5, and no benzanilide was formed. On the other hand, when a benzene solution of 6 was irradiated under a stream of air for 3 hr, benzanilide, benzoic acid, and benzamidobenzophenones were obtained (Eq. 3). This result is similar to that in the photolysis of 1 under the same conditions. In addition, photooxygenation of oxazolinone 1 in benzene sensitized by hematophorphyrin with visible light for 5 hr gave N,N-dibenzoylaniline (6) quantitatively.[11]



(Eq. 3)

On the basis of the above facts, benzanilide, benzoic acid, and benzamidobenzophenones from the photolysis of oxazolinone **1** in the presence of oxygen can be concluded as arising via **6** in the same way as that proposed by Kan and Furey.[10] We propose the pathway for the formation of **6** from **1** as depicted in Eq. 4. In the same manner as with photooxygenations of enamines,[12] fully N-alkylated uric acids,[13] and tetraphenylimidazole,[14] oxazolinone **1** undergoes an initial attack of singlet oxygen to form a zwitterionic peroxide **A**, and then a dioxetane **B**. This is followed by ring cleavage with concurrent elimination of carbon dioxide from **B** to yield **6**. It seems worthwhile to note that in the photolysis under oxygen oxazolinone **1** itself behaves as a sensitizer for the generation of singlet oxygen.



(Eq. 4)

References and Notes

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9. After irradiation, the reaction mixture was chromatographed on alumina using n-hexane, benzene, and then chloroform as elents to give 2-benzamidobenzophenone, benzanilide, and then 4-benzamidobenzophenone respectively. Extraction of the adsorbent with 10% aqueous $NaHCO_3$ gave benzoic acid.
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