

PHOTOCYCLIZATION AND PHOTOOXYGENATION OF 1,3,4,5-TETRAARYLIMIDAZOLIN-2-ONES<sup>1</sup>

Otohiko Tsuge\*, Kōji Oe, and Hisataka Inoue

Research Institute of Industrial Science, Kyushu University 86,Hakozaki, Higashi-ku, Fukuoka 812, Japan

Irradiation of 1,3,4,5-tetraarylimidazolin-2-ones in benzene, under nitrogen, with or without iodine gave the corresponding phenanthroimidazolinones. In the presence of oxygen, however, the imidazolinone was photochemically converted to the corresponding benzanilide, N-benzoyl-N,N'-diphenylbenzamide and p-benzoyl-phenyl isocyanate, besides the phenanthroimidazolinone. On the other hand, the dye-sensitized photooxygenation afforded the benzanilide, amidine, N,N'-dibenzoyl-N,N'-diphenylurea, and/or 1,4-diaza-1,3-butadiene derivative, whose yields depended on the nature of substituents of the imidazolinone and of the solvent employed. Mechanistic consideration of the photooxygenation was also described.

Previously<sup>2</sup> we reported on the photocyclization and photooxygenation of 3,4,5-triphenyloxazolin-2-one; irradiation of the oxazolinone with or without iodine gave the phenanthrooxazolinone, whereas upon irradiation under oxygen the oxazolinone afforded benzanilide, benzoic acid, and benzamidobenzophenones through N,N-dibenzoylaniline which was arisen from a dioxetane intermediate with the elimination of carbon dioxide. Our attention was directed toward photochemical behaviour of 1,3,4,5-tetraarylimidazolin-2-ones (1)<sup>3</sup> whose structures are similar to that of the oxazolinone.

Irradiation without or with Iodine. When a benzene solution of 1,3,4,5-tetraphenylimidazolin-2-one (1a) was irradiated under stirring with nitrogen by a 300W high-pressure mercury lamp with a Pyrex filter for 10 h, 1,3-diphenylphenanthro[9,10-d]imidazolin-2-one (2a) was formed, together with a trace amount of benzanilide (3a) and recovery of 1a. Upon irradiation in the presence

of iodine (3 mol% to 1a) under nitrogen, the phenanthroimidazolinone (2a) was obtained in a high yield.

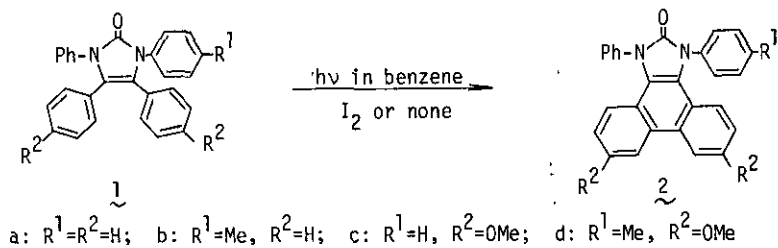


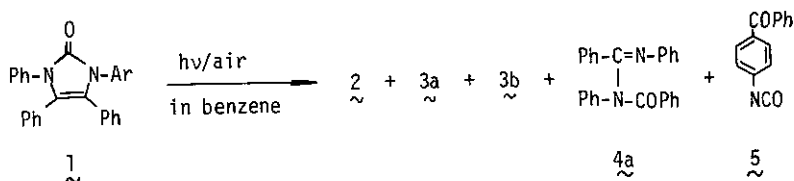
Table 1

Imidazolinone	I <sub>2</sub> mol% to <u>1</u>	Phenanthroimidazolinone <u>2</u>		
		Yield, %	Mp., °C	IR, cm <sup>-1</sup>
<u>1a</u>	0 <sup>a</sup>	6	>300	1690
<u>1a</u>	3	74		
<u>1b</u>	3	77	>300	1700
<u>1c</u>	3	93	280-282	1690
<u>1d</u>	3	90	277-278	1690

<sup>a</sup>Benzanilide (3a) was formed in a trace amount, together with an 85% recovery of 1a.

Similarly, irradiation of 1,4,5-triphenyl-3-p-tolyl- (1b), 1,3-diphenyl-4,5-bis(p-methoxyphenyl)- (1c), and 4,5-bis(p-methoxyphenyl)-1-phenyl-3-p-tolylimidazolin-2-one (1d) in the presence of iodine afforded the corresponding phenanthroimidazolinones, 2b-2d, in good yields (Table 1).<sup>4</sup>

Irradiation in the Presence of Oxygen. Irradiation of a benzene solution of 1a, stirred by a stream of air, for 2 h afforded 3a as the major product, together with 2a, N-benzoyl-N,N'-diphenylbenzamidine (4a), mp 177-178° (lit.<sup>5</sup> mp 174.5-175°), and p-benzoylphenyl isocyanate (5). The isocyanate 5 was identified as 1-p-benzoylphenyl-3-p-tolylurea, mp 207-208°.<sup>6</sup>



a: Ar=Ph	1%	11%	-	1%	trace
b: Ar=p-tolyl	6%	7%	5%	-	trace

Chart 1

A similar photooxygenation of **1b** gave **2b**, **3a**, *p*-benzoyltoluidine (**3b**), and **5**; but no amidines were detected (Chart 1). The pathway for the formation of photoproducts will be described below.

**Dye-sensitized Photooxygenation.** In connection with the above photooxygenation, **1** was photooxygenated at room temperature for 5 h using hematophorphyrin as sensitizer and a 500 W tungsten lamp. It has been reported that in both the dye-sensitized photooxygenation and the reaction with singlet oxygen, generated by non-photochemical means, **1a** gave sym-dibenzoyldiphenylurea (**6a**) as a sole product.<sup>7</sup> However, we found that benzanilide (**3a**) and the amidine **4a** were formed as well as the urea **6a**. The results in various solvents are

Table 2.

Solvent	$\text{1a} \xrightarrow{^1\text{O}_2} \text{PhCONHPh} + \begin{array}{c} \text{Ph-C=N-Ph} \\   \\ \text{Ph-N-COPh} \end{array} + \begin{array}{c} \text{Ph} \quad \text{Ph} \\ \diagdown \quad \diagup \\ \text{NCON} \\ \diagup \quad \diagdown \\ \text{PhCO} \quad \text{COPh} \end{array}$		
	<b>3a</b>	<b>4a</b>	<b>6a</b>
Benzene	29%	37%	25%
Dioxane	19	28	26
Chloroform	4	-	74
Dichloromethane	16	-	73
Dichloromethane <sup>a</sup>	5	3	50
Acetonitrile	9	-	81

<sup>a</sup>A Rose Bengal—18-Crown-6 complex was used.

given in Table 2; the yields of the products depended on the nature of solvent. Boden<sup>8</sup> reported that the photosensitization with a Rose Bengal—18-Crown-6 complex in dichloromethane can effectively generate singlet oxygen. The photooxygenation in dichloromethane using the complex gave also **3a**, **4a**, and **6a** as shown in Table 2.

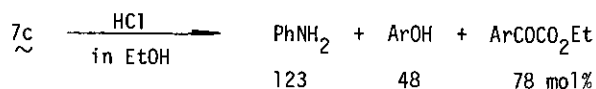
Next, the photosensitized oxygenation of imidazolinones, **1b**–**1d**, were carried out in benzene using hematophorphyrin as sensitizer. The photoproducts are shown in Chart 2. The imidazolinone **1b** afforded two isomeric benzamidines, **4b** and **4b'**,<sup>9</sup> and the urea **6b**, mp 188–190° [IR 1710, 1690, 1680 cm<sup>-1</sup>; m/e 434 (M<sup>+</sup>)], as major products, together with a mixture of **3a** and **3b** in low yield.



2-p-methoxyphenyl-3-p-methoxyphenoxy-1,4-diaza-1,3-butadiene on the basis of the following evidence.

$\underline{7c}$ : IR 1660, 1600  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  3.68, 3.76 (each 3H, s), 6.2-6.5 (2H, m), 6.7-7.4 (14H, m), 7.9-8.1 (2H, m); m/e 436 ( $\text{M}^+$ ), 313 ( $\text{M}^+ - \text{OC}_6\text{H}_4\text{OMe}$ ), 210, 195, 167, 136, 133, 123 ( $[\text{MeOC}_6\text{H}_4\text{O}]^+$ ), 107, 103, 91, 77.

Hydrolysis of  $\underline{7c}$  with hydrochloric acid in ethanol gave aniline, p-methoxyphenol and p-methoxyphenylglyoxylic acid ester.



Ar=p-methoxyphenyl

Similarly,  $\underline{1d}$  yielded the corresponding benzanilides,  $\underline{3c}$  and  $\underline{3d}$ ,<sup>10</sup> and urea  $\underline{6d}$ , mp 125-126° [IR 1710, 1695, 1675  $\text{cm}^{-1}$ ; m/e 494 ( $\text{M}^+$ )], as major products, accompanied by small amounts of the amidine and diazabutadiene, whose structures are either  $\underline{4d}$  or  $\underline{4d'}$  and either  $\underline{7d}$  or  $\underline{7d'}$ , respectively.

Amidine  $\underline{4d}$  or  $\underline{4d'}$ : mp 161-162°; IR 1650, 1620  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  2.20, 3.68, 3.75 (each 3H, s), 6.5-7.4 (15H, m), 7.9-8.1 (2H, m); m/e 450 ( $\text{M}^+$ ).

Diazabutadiene  $\underline{7d}$  or  $\underline{7d'}$ : mp 131-133°; IR 1665, 1600  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  2.20, 3.68, 3.76 (each 3H, s), 6.1-6.4 (2H, m), 6.6-7.3 (13H, m), 7.9-8.1 (2H, m); m/e 450 ( $\text{M}^+$ ).

In the cases of  $\underline{1c}$  and  $\underline{1d}$  having p-methoxyphenyl groups at 4- and 5-positions, the corresponding diazabutadienes  $\underline{7c}$  and  $\underline{7d}$  (or  $\underline{7d'}$ ) were newly formed. In order to compare with the photoproducts from  $\underline{1c}$  or  $\underline{1d}$ , the photosensitized oxygenation of 1,3,5-triphenyl-4-p-methoxyphenylimidazolin-2-one ( $\underline{1e}$ ) was examined under similar conditions.

As shown in Chart 3, the expected diazabutadiene  $\underline{7e}$  was also obtained, together with the corresponding benzanilides,  $\underline{3a}$  and  $\underline{3c}$ , amidine  $\underline{4e}$ , mp 160-161° [IR 1650, 1620  $\text{cm}^{-1}$ ; m/e 406 ( $\text{M}^+$ )], and urea  $\underline{6e}$ , mp 199-200° [IR 1710, 1700, 1680  $\text{cm}^{-1}$ ; m/e 450 ( $\text{M}^+$ )]. Hydrolysis of  $\underline{7e}$ , mp 94-95° [IR 1665, 1610  $\text{cm}^{-1}$ ; m/e 406 ( $\text{M}^+$ )], with hydrochloric acid in ethanol afforded aniline, p-methoxyphenol and phenylglyoxylic acid ester.

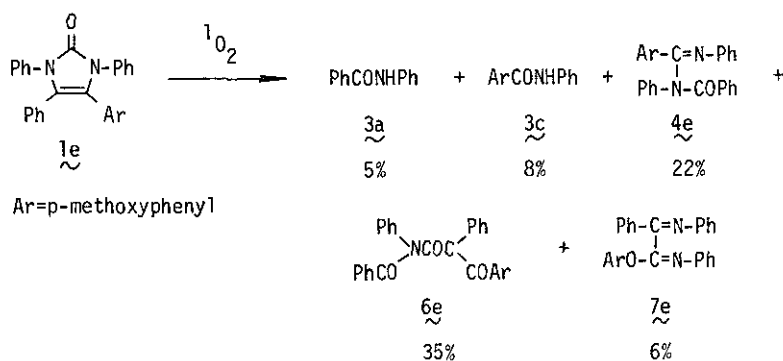
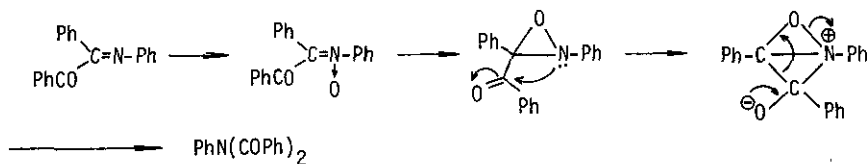


Chart 3

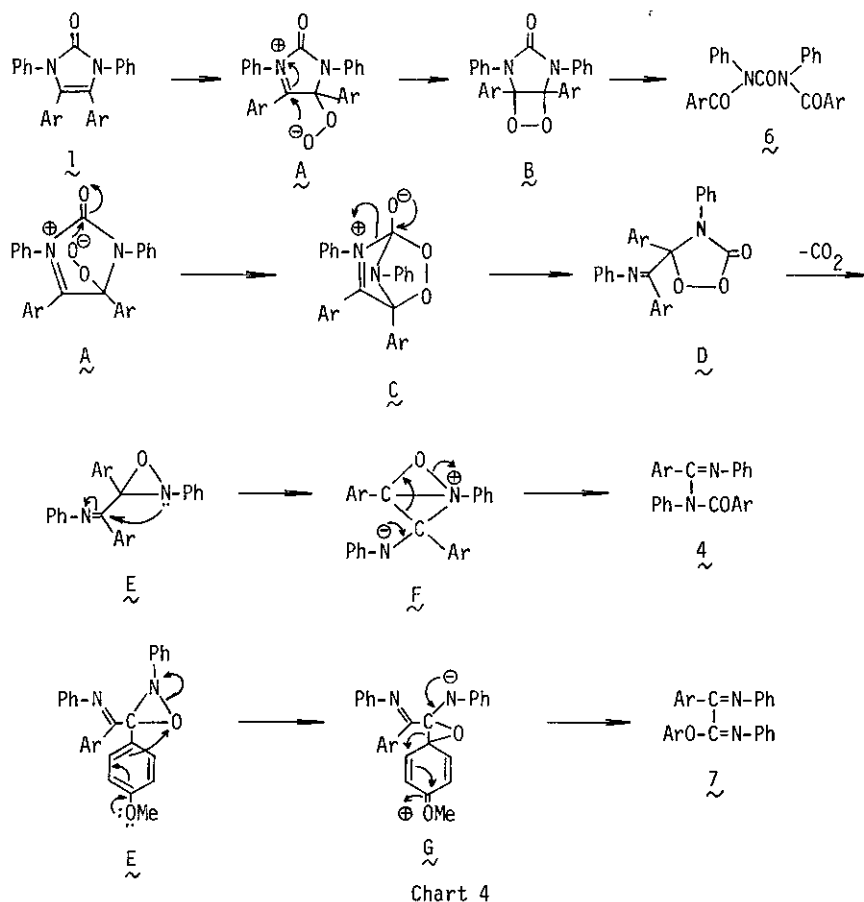
Reaction Pathways. We wish to propose the pathways for the formation of the amidine 4, urea 6, and diazabutadiene 7 as depicted in Chart 4. In the same manner as with photooxygenations of fully N-alkylated uric acids<sup>11</sup> and enamines,<sup>12</sup> the imidazolinone 1 undergoes an initial attack of singlet oxygen to form a zwitterionic peroxide A or a four-membered cyclic peroxide B.

The zwitterionic peroxide A decomposes to give the final products 4, 6, and/or 7. The rearrangement of A to the cyclic peroxide B, followed by ring cleavage gives the urea 6. On the other hand, a nucleophilic attack of the perhydroxy anion on the carbonyl carbon atom forms a cyclic tautomer C. This is followed by ring cleavage to yield a dioxazolidinone D, and subsequent elimination of carbon dioxide from D yields an oxazirane E. The oxazirane E seems to be a common key intermediate to produce 4 and 7.

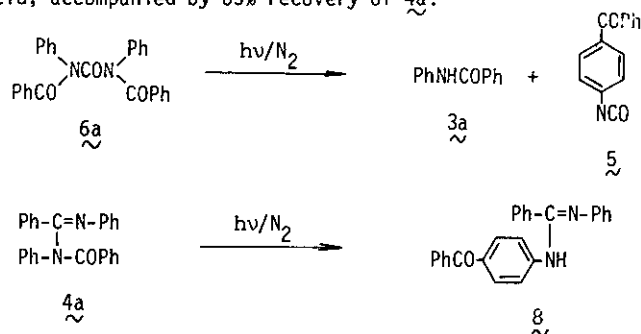
The oxazirane E rearranges to the amidine 4 through a 1-aza-2-oxabicyclo-[1.1.0]butane F. This process is very similar to that for the formation of



dibenzoylaniline from the photooxygenation of benzil monoanil.<sup>13,14</sup> When Ar is p-methoxyphenyl group, another rearrangement can be considered; a 1,2-shift of p-methoxyphenyl group through a spiro-oxirane G gives the diazabutadiene 7.



Both the amidine 4c and urea 6a were unchanged under conditions similar to those of dye-sensitized photooxygenation. On the other hand, irradiation of the urea 6a in benzene by a high-pressure mercury lamp (under nitrogen, 15 min) gave benzanilide (3a) and the isocyanate 5 in 5 and 1% yields respectively, together with 60% recovery of 6a. Upon irradiation for 1 h under similar conditions, the amidine 4a was transformed into N-p-benzoylphenyl-N'-phenylbenzamidine (8), mp 137-138° [IR 3350, 1630, 1620  $\text{cm}^{-1}$ ;  $m/e$  376 ( $M^+$ )], in 6% yield, accompanied by 65% recovery of 4a.



On the basis of the above facts, it seems reasonable to assume that, upon irradiation of 1a under conditions shown in Chart 1, the urea 6a and amidine 4a were also formed by the same routes as those depicted in Chart 4, and subsequent photolysis of 6a gave 3a and 5.<sup>15</sup>

#### REFERENCES AND NOTES

- 1 Photochemistry of Heterocyclic Compounds. IX. Part VIII: O. Tsuge, K. Oe, and M. Tashiro, Chem. Lett., 1977, 1207.
- 2 O. Tsuge, K. Oe, and Y. Ueyama, Chem. Lett., 1976, 425.
- 3 Imidazolinones 1a-1e were prepared by the reaction of the corresponding benzoin and aryl isocyanate. 1a: mp 212-213° (lit.<sup>16</sup> mp208-209°); 1b: mp 210-211°; 1c: mp 241-242°; 1d: mp 234-235°; 1e: mp 243-244°.
- 4 All new compounds gave elementary analyses in good accord with the assigned structures.
- 5 P. Oxley and W. F. Short, J. Chem. Soc., 1948, 1514.
- 6 After irradiation, the reaction mixture was concentrated in vacuo, and the residue was extracted with n-hexane. p-Toluidine was added to the extract to give 1-p-benzoylphenyl-3-p-tolylurea. The insoluble products were chromatographed on silica gel using benzene as an eluent.
- 7 H. H. Wasserman, J. R. Scheffer, and J. L. Cooper, J. Amer. Chem. Soc., 1972, 94, 4991.
- 8 R. M. Boden, Synthesis, 1975, 783.
- 9 Isolation of pure 4b and 4b' was unsuccessful, and it was found that the mixture was composed of equal amounts of two amidines on the basis of the methyl signals ( $\delta$  2.20, 2.25) in its NMR spectrum. The reaction of N-phenylbenzimidochloride with p-toluidine, followed by benzoylation gave a mixture of equal amounts of 4b and 4b'.
- 10 Quantitative estimation by the NMR spectrum showed a mixture of equal amounts of 3c and 3d.
- 11 T. Matsuura and I. Saito, Tetrahedron, 1969, 25, 549.
- 12 C. S. Foote, A. A. Dzakpasn, and J. W.-P. Lin, Tetrahedron Lett., 1975, 1247; H. H. Wasserman and S. Terao, ibid., 1975, 1735.
- 13 R. O. Kan and R. L. Furey, ibid., 1966, 2573.
- 14 A. Padwa, J. Amer. Chem. Soc., 1965, 87, 4365.



- 15 Since the amidines  $\overset{\sim}{4}$  and ureas  $\overset{\sim}{6}$  were partially converted into the corresponding benzanilides  $\overset{\sim}{3}$  on chromatography on silica gel, the benzanilides isolated from the photooxygenated products seems to be ascribed in part to hydrolysis of  $\overset{\sim}{4}$  and  $\overset{\sim}{6}$ .
- 16 H.-D. Becker, J. Org. Chem., 1970, 35, 2099.

Received, 20th September, 1978