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PHOTOCYCLIZATION AND PHOTOOXYGENATION OF 1,3,4,5-TETRAARYLIMIDAZOLIN-2-ONES[1]

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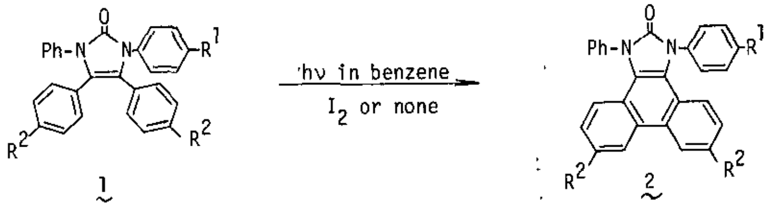
Irradiation of 1,3,4,5-tetraarylimidazolin-2-ones in benzene, under nitrogen, with or without iodine gave the corresponding phenanthroimidazolinones. In the presence of oxygen, however, the imidazolinone was photochemically converted to the corresponding benzanilide, N-benzoyl-N,N'-diphenylbenzamidine and p-benzoylphenyl 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[2] 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)[3] 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.



a: $R^1=R^2=H$; b: $R^1=Me$, $R^2=H$; c: $R^1=H$, $R^2=OMe$; d: $R^1=Me$, $R^2=OMe$

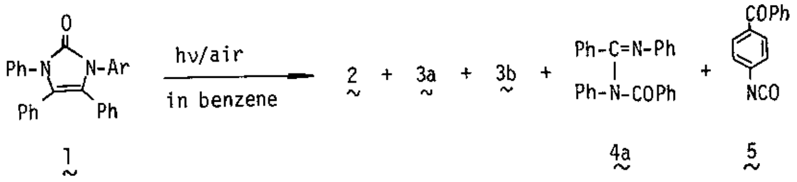
Table 1

Imidazolinone	I_2 mol% to 1	Phenanthroimidazolinone 2 Yield, %	Mp., °C	IR, cm^{-1}
1a	0[a]	6	>300	1690
1a	3	74		
1b	3	77	>300	1700
1c	3	93	280-282	1690
1d	3	90	277-278	1690

[a] 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).[4]

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.[5] mp 174.5-175°), and p-benzoylphenyl isocyanate (5). The isocyanate 5 was identified as 1-p-benzoylphenyl-3-p-tolylurea, mp 207-208°.[6]



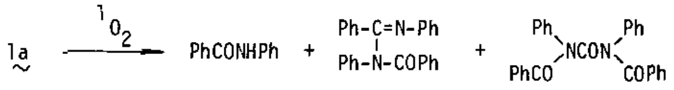
	2	3a	3b	4a	5
a: Ar=Ph	1%	11%	-	1%	trace
b: Ar=p-tolyl	6%	7%	5%	-	trace

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 decribed 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.[7] However, we found that benzanilide (3a) and the amidine 4a were formed as well as the urea 6a. The results in various solvents are given in Table 2; the yields of the products depended on the nature of solvent. Boden[8] 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.

Table 2.



$$\mathbf{1a} \xrightarrow{^1O_2} \mathrm{PhCONHPh} + \begin{matrix}\mathrm{Ph{-}C{=}N{-}Ph} \\ | \\ \mathrm{Ph{-}N{-}COPh}\end{matrix} + \begin{matrix}\mathrm{Ph} & & \mathrm{Ph} \\ & \mathrm{NCON} & \\ \mathrm{PhCO} & & \mathrm{COPh}\end{matrix}$$

Solvent	3a	4a	6a
Benzene	29%	37%	25%
Dioxane	19	28	26
Chloroform	4	-	74
Dichloromethane	16	-	73
Dichloromethane[a]	5	3	50
Acetonitrile	9	-	81

[a] A Rose Bengal—18-Crown-6 complex was used.

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',[9] and the urea 6b, mp 188-190° [IR 1710, 1690, 1680 cm^{-1}; m/e 434 (M$^+$)], as major products, together with a mixture of 3a and 3b in low yield.

In the case of 1c, however, a new type of compound 7c was obtained, besides the corresponding benzanilide 3c, mp 172-173°, amidine 4c, mp 152-153° [IR 1650, 1620 cm^{-1}; m/e 436 (M^{+})], and urea 6c, mp 161-162° [IR 1700, 1680 cm^{-1}; m/e 480 (M^{+})]. The compound 7c, mp 139-140°, was assigned to be 1,4-diphenyl-

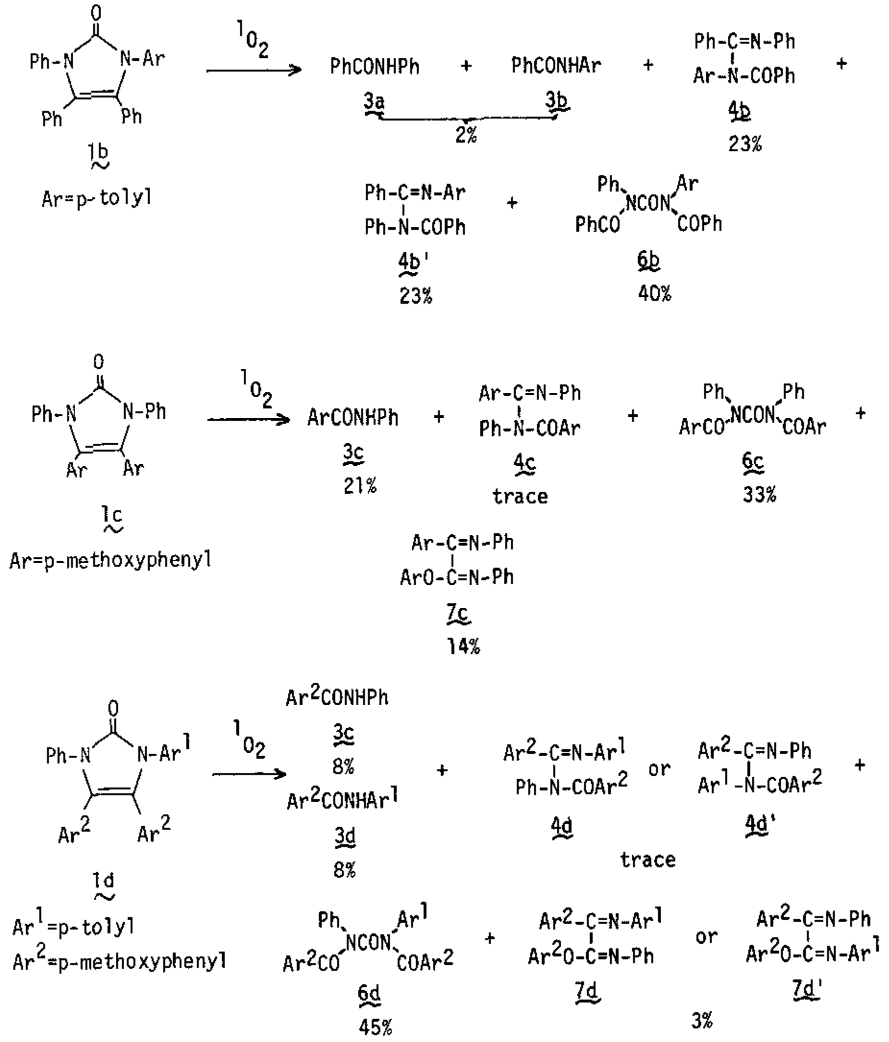


Chart 2

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

7c: IR 1660, 1600 cm^{-1}; NMR ($CDCl_3$) δ 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 (M^+), 313 ($M^+-OC_6H_4OMe$), 210, 195, 167, 136, 133, 123 ($[MeOC_6H_4O]^+$), 107, 103, 91, 77.

Hydrolysis of 7c with hydrochloric acid in ethanol gave aniline, p-methoxyphenol and p-methoxyphenylglyoxylic acid ester.

$$\begin{array}{lccc} 7c \xrightarrow[\text{in EtOH}]{\text{HCl}} & PhNH_2 & + \ ArOH & + \ ArCOCO_2Et \\ & 123 & 48 & 78\ \text{mol\%} \end{array}$$

Ar=p-methoxyphenyl

Similarly, 1d yielded the corresponding benzanilides, 3c and 3d,[10] and urea 6d, mp125-126° [IR 1710, 1695, 1675 cm^{-1}; m/e 494 (M^+)], as major products, accompanied by small amounts of the amidine and diazabutadiene, whose strucutres are either 4d or 4d' and either 7d or 7d', respectively.

Amidine 4d or 4d': mp 161-162°; IR 1650, 1620 cm^{-1}; NMR ($CDCl_3$) δ 2.20, 3,68, 3.75 (each 3H, s), 6.5-7.4 (15H, m), 7.9-8.1 (2H, m); m/e 450 (M^+).

Diazabutadiene 7d or 7d': mp 131-133°; IR 1665, 1600 cm^{-1}; NMR ($CDCl_3$) δ 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 (M^+).

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

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

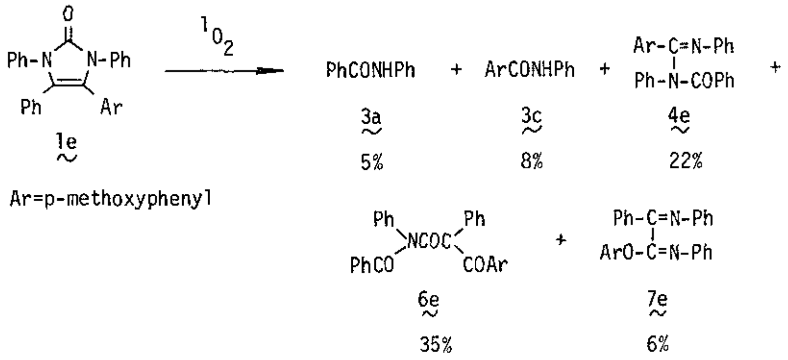
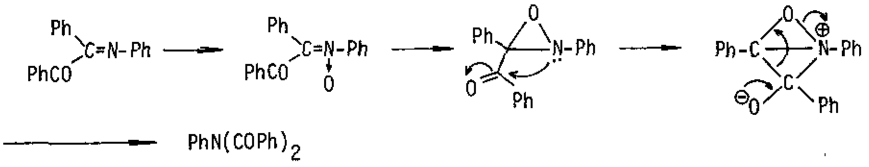


Chart 3

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[11] and *enamines,*[12] *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.[13,14] 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.

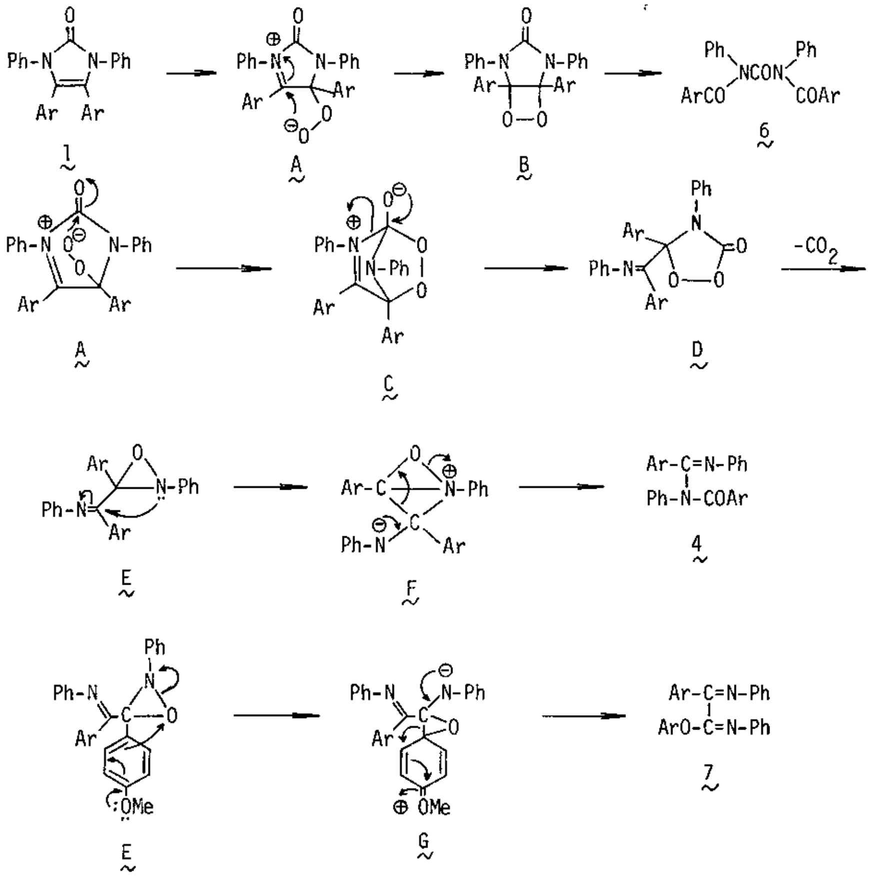
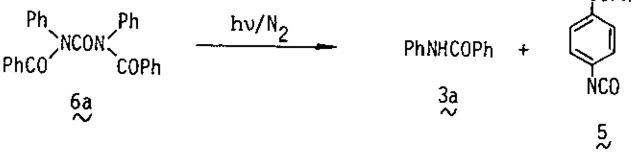
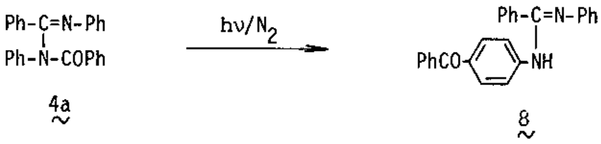


Chart 4

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 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**.[15]

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2 O. Tsuge, K. Oe, and Y. Ueyama, <u>Chem. Lett</u>., 1976, 425.

3 Imidazolinones **1a**-**1e** were prepared by the reaction of the corresponding benzoins and aryl isocyanate. **1a**: mp 212-213° (lit.[16] 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, <u>J. Chem. Soc</u>., 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.

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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 (δ 2.20, 2.25) in its NMR spectrum. The reaction of N-phenylbenziminochloride 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**.

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15 Since the amidines 4 and ureas 6 were partially converted into the corresponding benzanilides 3 on chromatography on silica gel, the benzanilides isolated from the photooxygenated products seems to be ascribed in part to hydrolysis of 4 and 6.

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