

## Regiospecific photochemical transformations of 4, 5-diaryl- $\Delta^4$ -imidazolin-2-ones: ketal formation and cyclodehydrogenation

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**Abstract.** 4, 5-Diaryl- $\Delta^4$ -imidazolin-2-ones undergo conversion to 2, 2-dialkoxy-4, 5-diaryl- $\Delta^4$ -imidazolines by a characteristic solvent interaction of the carbonyl group on irradiation in alcoholic solvents. The photochemical oxidative cyclization of the stilbene system in these compounds to the corresponding phenanthrene derivatives does not occur under the usual conditions. Acidic conditions hinder the ketal formation of the carbonyl group and favour the oxidative dehydrocyclization reaction to the phenanthrene derivatives. These reactions have been found to be general to the 4, 5-diaryl- $\Delta^4$ -imidazolin-2-ones and plausible mechanistic pathways have been suggested for the two different selective reactions.

**Keywords.** Regiospecific photochemical transformations; photochemical oxidative cyclization; ketal formation.

### 1. Introduction

Imidazolin-2-ones of the type **2** were reported to be photochemically inactive (Steffan and Schenck 1967). Under ordinary conditions in a neutral organic solvent, imidazolin-2-ones remain fully unchanged on irradiation with UV-visible light, both in the presence and absence of ketonic sensitizers. In contrast to simple imidazolin-2-ones the corresponding N, N'-diacetyl derivatives undergo typical carbonyl addition at the carbon-carbon double bond to form oxetanes (Steffan and Schenck 1967). In view of our interest in the selective photochemical reactions of bichromophoric heterocyclic systems containing a stilbene chromophore (Padwa and Hartman 1966; Copper and Wasserman 1969; Grimshaw and Manns 1977; Pillai and Ravindran 1977; Pillai and Purushothaman 1978) we undertook a study of the photochemistry of 4, 5-diaryl- $\Delta^4$ -imidazolin-2-ones (**2**). Contrary to our expectation (Pillai and Ravindran 1977; Pillai and Purushothaman 1978) that a regioselective photochemical cyclodehydrogenation reaction of the stilbene system to the phenanthrene system as in **4** would occur on irradiation, the imidazolin-2-ones chromophore underwent a facile conversion to the corresponding 2, 2-dialkoxy-4, 5-diaryl- $\Delta^4$ -imidazoline in alcoholic solvents. This observation prompted us to explore the possibility of formation of such ketals from the imidazolin-2-ones. The possibility that solvent addition to the carbonyl group leading to the formation of 2, 2-dialkoxy-4, 5-diaryl- $\Delta^4$ -imidazolines occurs through the low-energy excitation of the carbonyl group, prompted an

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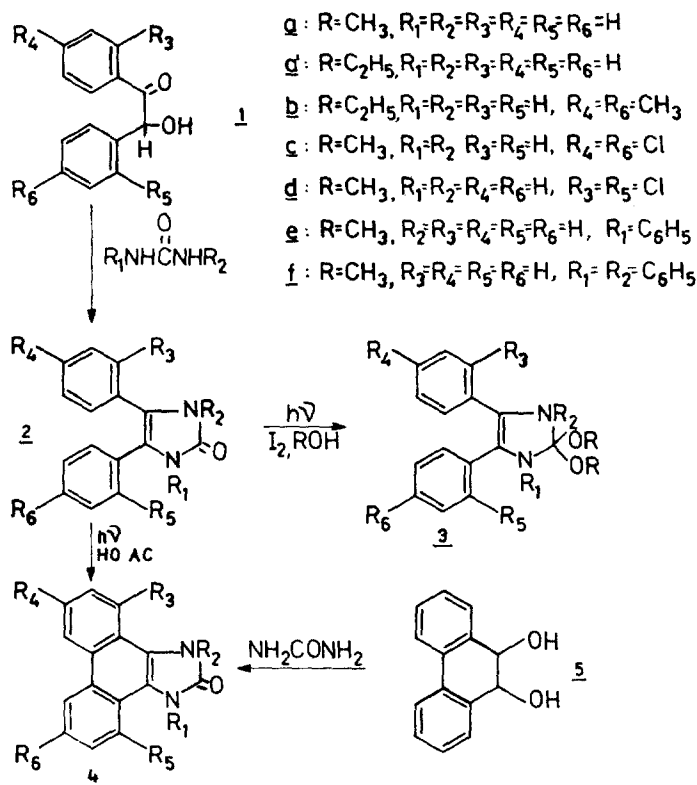


Chart 1.

investigation of the photolysis in a solvent which can prevent the low-lying excitation (Badger *et al* 1966). Thus, in this paper we describe the photolysis of some 4,5-diaryl- $\Delta^4$ -imidazolin-2-ones in alcoholic and acidic solvents to yield 2,2-dialkoxy-4,5-diaryl- $\Delta^4$ -imidazolines and phenanthro [9,10-d]-imidazolin-2-ones respectively.

## 2. Results and discussion

### 2.1 Synthesis of 4,5-diarylimidazolones

The 4,5-diarylimidazolones (**2**) were prepared by the reaction of substituted benzoin with urea or substituted urea in glacial acetic acid in 20–75% yields. The details of the preparation and analytical characteristics of the compounds are given in table 1.

### 2.2 Photolysis of 4,5-diaryl- $\Delta^4$ -imidazolin-2-ones in alcoholic solvents

For cyclodehydrogenation of stilbenes and related systems to the corresponding phenanthro derivatives, the general experimental condition involves (Mallory *et al* 1963; Wood and Mallory 1964; Pillai and Ravindran 1977; Pillai and Purushothaman 1978) irradiation in solutions in the presence of dissolved oxygen or iodine as oxidising agent. Thus, a solution (0.05 M) of 4,5-diphenyl- $\Delta^4$ -imidazolin-2-one (**2a**) in

**Table 1.** Preparative conditions and analytical details of 4,5-diarylimidazolin-2-ones **2a-f**.

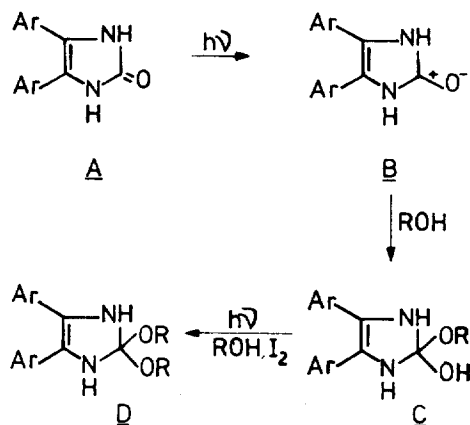
Compd.	Reaction time (h)	Yield (%)	m.p. (°C)	Mol. formula	C	H	N
					Found (calc.) (%) and [spectral data]		
<b>2a</b>	7	75	330	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O	76.42 (76.27)	5.13 (5.08)	11.44 (11.86)
					[IR (KBr): 3235 (NH), 1710 (NH-CO-NH)]		
<b>2b</b>	6	50	294	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O	77.06 (77.27)	6.14 (6.06)	10.47 (10.60)
					[MS: 264 (M <sup>+</sup> ), 221, 118, 91]		
<b>2c</b>	5	34	291	C <sub>15</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O	59.44 (59.01)	3.49 (3.27)	8.97 (9.18)
<b>2d</b>	7	42	248–250	C <sub>15</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O	58.89 (59.01)	3.45 (3.27)	9.01 (9.18)
<b>2e</b>	7	20	307	C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> O	81.04 (80.76)	5.15 (5.12)	8.99 (8.97)
<b>2f</b>	10	52	208 (Becker 1970) (208–209)	C <sub>27</sub> H <sub>20</sub> N <sub>2</sub> O	83.21 (83.50)	5.43 (5.15)	6.67 (7.21)
					[PMR (Acetone-d <sub>6</sub> ): 7.37–7.13 (m, aromatic)]		

methanol was irradiated in the presence of a trace of iodine using pyrex-filtered light from a Philips HPK 125 W high-pressure mercury-quartz lamp. The reaction was followed by thin layer chromatography. After complete disappearance of the starting material (15 h), the solvent was distilled off and the residue purified by crystallisation. Elemental and spectral analysis of the product showed it to be 2,2-dimethoxy-4,5-diphenyl- $\Delta^4$ -imidazoline (**3a**) and not the expected phenanthro[9,10-d]imidazolin-2-one (**4a**).

Since solvent incorporation is involved in the formation of the above product, we thought that it would be interesting to examine the irradiation in a different alcoholic solvent under identical conditions. Thus, irradiation of a solution of 4,5-diphenyl- $\Delta^4$ -imidazolin-2-one in ethanol (0.05 M) and a trace of iodine resulted in the formation of 2,2-diethoxy-4,5-diphenyl- $\Delta^4$ -imidazoline (**3a**) in 49% yield. Similarly irradiation of 4,5-di-*p*-tolyl- $\Delta^4$ -imidazolin-2-one (**2b**) in ethanol also resulted in the formation of 2,2-diethoxy-4,5-di-*p*-tolyl- $\Delta^4$ -imidazoline (**3b**).

The formation of the dialkoxyimidazolines from imidazolin-2-ones can be tentatively explained as proceeding through reaction of the excited carbonyl group with alcohols. It is likely that a charged species of the type (**B**) is formed in the photolysis. This species can undergo carbonyl-type addition with ROH to form the species (**C**). The hydroxyl group in (**C**) undergoes further photochemical alkylation in the presence of the alcohol and iodine. The tentative pathway suggested for the reaction from imidazolin-2-ones to dialkoxyimidazolines is depicted in scheme 1.

The generality of the photochemical formation of the 2,2-dialkoxyimidazolines from the corresponding imidazolin-2-ones was established by the photoconversion of 4,5-di-*p*-chlorophenyl- $\Delta^4$ -imidazolin-2-one (**2c**), 4,5-di-*o*-chlorophenyl- $\Delta^4$ -imidazolin-2-one (**2d**), 3,4,5-triphenyl- $\Delta^4$ -imidazolin-2-one (**2e**) and 1,3,4,5-tetraphenyl- $\Delta^4$ -imidazolin-2-one (**2f**) to the corresponding 2,2-dialkoxyimidazolines (**3c-f**) in 30–61% yield under different conditions.



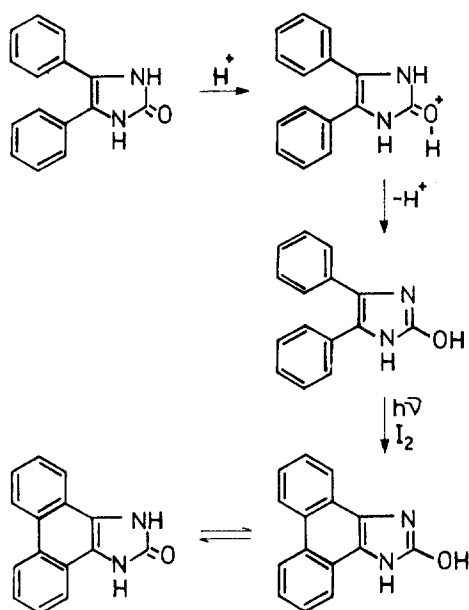
**Scheme 1.** Mechanism of the photolysis of 4,5-diaryl- $\Delta^4$ -imidazolin-2-ones in alcoholic solvents.

### 2.3 Photolysis of 4,5-diaryl- $\Delta^4$ -imidazolin-2-ones under acidic conditions

Ketal formation on irradiation in alcoholic solvents appears to proceed through the excited state carbonyl group in the imidazolones. This prompted an investigation of the photolysis in a solvent which can prevent the low-lying  $n \rightarrow \pi^*$  excitation. Thus, irradiation of 4,5-diphenyl- $\Delta^4$ -imidazolin-2-one (2a) in acetic acid in the presence of iodine with the HPK 125W mercury-quartz lamp for 7 h resulted in the formation of the cyclodehydrogenated product, phenanthro [9, 10-d] imidazolone (4a), though in low yield (30%). The yield of the cyclization could not be increased by prolonging the reaction period. The product deposits on the sides of the reaction vessel during irradiation. The photolysate became dark red on distillation and chromatography did not afford any other product; only decomposed resinous material was isolated. The structure of the product was established from elemental and spectral measurements. Phenanthro-[9, 10-d]imidazolin-2-one (4a) was also prepared by an independent thermal route starting from 9, 10-phenanthrenediol (5) and urea in presence of glacial acetic acid.

The observation that the selective cyclization of the stilbene system and subsequent oxidation of the resulting dihydrophenanthrene could be effected in the 4,5-diphenyl- $\Delta^4$ -imidazolin-2-one, prompted the extension of the reaction to other substituted 4,5-diaryl derivatives. Thus, irradiation of 4,5-di-*p*-tolyl- $\Delta^4$ -imidazolin-2-one (2b) and 4,5-di-*p*-chlorophenyl- $\Delta^4$ -imidazolin-2-one (2c) under identical conditions and work up of the photolysate gave the corresponding phenanthro derivatives.

The mechanism of the cyclodehydrogenation of 4,5-diaryl- $\Delta^4$ -imidazolin-2-ones to the corresponding phenanthro[9, 10-d] imidazolin-2-ones can be explained as follows. Under normal conditions of irradiation in a neutral alcoholic solvent, low-lying carbonyl excitation occurs and products result from the charged species of the carbonyl excited-state form. In the presence of acetic acid, the low-lying excitation of the carbonyl group is prevented by protonation of the carbonyl oxygen in addition to the protonation of the other basic sites present in imidazolones. Thus, it is possible that a  $\pi \rightarrow \pi^*$  excitation of the stilbene chromophore responsible for the cyclization occurs and the dehydrocyclization of the stilbene chromophore takes place by the usual mode



**Scheme 2.** Mechanism of the photolysis of 4,5-diaryl- $\Delta^4$ -imidazolin-2-ones under acidic conditions.

of formation of the phenanthrenes. The mechanistic pathways for the formation of the phenanthrimidazolones can be represented as in scheme 2.

#### 2.4 Conclusion and outlook

In conclusion, we have shown that the photolysis of 4,5-diaryl- $\Delta^4$ -imidazolin-2-ones, in alcoholic solvents proceeds in a preparative scale to the hitherto unreported 2,2-dialkoxy-4,5-diaryl- $\Delta^4$ -imidazolines. The ease with which this photochemical conversion takes place points to the synthetic potential of this reaction for the formation of ketals from an amide carbonyl group under neutral alcoholic conditions.

### 3. Experimental

#### 3.1 General

All the melting points are uncorrected and recorded on a Toshniwal capillary melting point apparatus. Irradiations were carried out with a Philips HPK 125 W mercury-quartz lamp in a water-cooled Pyrex photochemical apparatus or in a Hanovia one-litre photochemical reactor with quartz thimbles. Precoated silica gel sheets (0.2 mm thick EM/BDH reagent) were used for analytical TLC. All solvents were distilled and dried according to literature procedures.

#### 3.2 Synthesis of 4,5-diaryl- $\Delta^4$ -imidazolin-2-ones

The synthesis of 4,5-diaryl- $\Delta^4$ -imidazolin-2-ones was carried out following the method of Winans and Adkins (1933). A mixture of acyloin (20 mmol), urea or

substituted urea (36 m mol) and glacial acetic acid (16 ml) was heated under reflux for 5–10 h for different compounds. The reaction mixture was then allowed to cool for some time or kept overnight. The crystallised material was filtered and dried. The unreacted acyloin and urea were removed by repeatedly washing with ether and water. The products were then purified by redissolving in glacial acetic acid and reprecipitating with cold water followed by crystallisation to afford white crystals of the imidazolin-2-ones.

### 3.3 Photolysis of 4,5-diaryl- $\Delta^4$ -imidazolin-2-ones: Formation of 2,2-dialkoxy-4,5-diaryl- $\Delta^4$ -imidazolines

Details of procedure are as follows: A solution of 4,5-diphenyl- $\Delta^4$ -imidazolin-2-one (1g, 4.2 m mol) and iodine ( $\approx 15$  mg) in methanol (150 ml) was irradiated with a Philips HPK 125 W mercury-quartz lamp in a water-cooled preparative photo-chemical reactor with a pyrex immersion well. The reaction was followed by TLC. On completion of the reaction (15 h) the reaction mixture was worked up by distillation. The crystals were filtered, washed with a small amount of methanol and dried. The residue was redissolved in hot methanol, decolourised with animal charcoal and crystallised to obtain 2,2-dimethoxy-4,5-diphenyl- $\Delta^4$ -imidazoline (**3a**): yield 0.7 g (59%), m.p. 232–233°C; Analysis, found: C, 72.43; H, 6.21; N, 9.92; calculated for  $C_{17}H_{18}N_2O_2$  (mol. wt. 282) C, 72.34; H, 6.38; N, 9.92%; PMR: (90 MHz, DMSO- $d_6$ )  $\delta$  8.32 (s, 2H,  $-\text{NH}$ ); 7.38–7.23 (m, 10H, aromatic), 2.77 ppm (s, 6H, methoxy); MS:  $M^+$  ion: 282. The ketal **3a** gave no characteristic carbonyl absorption frequency. Details of the other photolytic reactions are shown in table 2.

### 3.4 Photolysis of 4,5-diaryl- $\Delta^4$ -imidazolin-2-ones in acetic acid and iodine: Formation of phenanthro [9,10-d] imidazolin-2-ones

4,5-Diphenyl- $\Delta^4$ -imidazolin-2-one (1g, 4.2 m mol) and iodine (10 mg) in glacial acetic acid (200 ml) were irradiated with a Philips HPK 125 W mercury-quartz lamp in a water-cooled photochemical reactor with a quartz immersion well. The reaction was followed by TLC. Crystals were found to deposit on the sides of the reaction vessel and the photolysate turned dark red. When the reaction was complete (7 h), the photolysate was worked up by distillation. The residue crystallised from glacial acetic acid to afford light yellow needles of phenanthro [9,10-d] imidazolin-2-one (**4a**): yield 0.3 g (30%), m.p. above 360°C (Rees and Sale 1973, m.p. above 350°C); Analysis, found: C, 76.54; H, 4.63; N, 12.04; calculated for  $C_{15}H_{10}N_2O$  (mol. wt. 234) C, 76.92; H, 4.27; N, 11.97%; IR (KBr): 3176 ( $-\text{NH}$ ), 1700  $\text{cm}^{-1}$  ( $\text{NH}-\text{CO}-\text{NH}$ ); MS:  $m/z$  (relative intensity) 234 ( $M^+ 100$ ), 206 (31), 178 (8). Details of the photolytic reactions are given in table 3.

### 3.5 Thermal synthesis of phenanthro[9,10-d] imidazolin-2-one (**4a**)

In a typical procedure 9,10-phenanthrenediol (0.7 g, 3.3 m mol), urea (0.4 g, 6.7 m mol) and glacial acetic acid (16 ml) were heated under reflux for 2 h. The product which separated in the reaction flask was filtered, washed repeatedly with acetic acid and dried. Recrystallisation from acetic acid afforded light yellow needles of phenanthro [9,10-d] imidazolin-2-one (**4a**): yield 0.5 g (64%), m.p. and mixed m.p. above 360°C; Analysis found: C, 76.54; H, 4.42; N, 12.12; Calcd. for  $C_{15}H_{10}N_2O$  (mol. wt. 234) C, 76.92; H, 4.27; N, 11.27%.

Table 2. Photolysis of 4, 5-diarylimidazolin-2-ones in alcoholic solvents.

Compd. irradiated	Solvent	Time of irradiation (h)	Product	Yield (%)	m.p. (°C)	Mol. formula	C H N		
							Found (calc.) (%) and [spectral data]		
<u>2a</u>	Methanol	15	2,2-Dimethoxy-4,5-diphenyl- $\Delta^4$ -imidazoline ( <u>3a</u> )	59	232-233	$C_{17}H_{18}N_2O_2$	72.43 (72.34)	6.21 (6.38)	9.92 (9.92)
<u>2a</u>	Ethanol	15	2,2-Diethoxy-4,5-diphenyl- $\Delta^4$ -imidazoline ( <u>3a</u> )	46	260	$C_{19}H_{22}N_2O_2$	[PMR (DMSO- $d_6$ ): 8.32 (NH), 7.38-7.23 (aromatic) 2.77 (methoxy) MS: 292 ( $M^+$ )] 73.01 6.88 9.28		
<u>2b</u>	Ethanol	9	2,2-Diethoxy-4,5-di- <i>p</i> -tolyl- $\Delta^4$ -imidazoline ( <u>3b</u> )	57	265	$C_{21}H_{26}N_2O_2$	(73.54) 74.87 (74.55)	(7.08) 7.98 (7.69)	(9.03) 9.21 (8.28)
<u>2c</u>	Methanol	4	4,5-Di- <i>p</i> -chlorophenyl-2,2-dimethoxy- $\Delta^4$ -imidazoline ( <u>3c</u> )	61	345	$C_{17}H_{16}Cl_2N_2O_2$	[MS: 338 ( $M^+$ ), 264, 118, 91] 58.86 (58.11)	3.98 (4.55)	8.01 (7.97)
<u>2d</u>	Methanol	20	4,5-Di- <i>o</i> -chlorophenyl-2,2-dimethoxy- $\Delta^4$ -imidazoline ( <u>3d</u> )	43	283	$C_{17}H_{16}Cl_2N_2O_2$	57.65 (58.11)	4.35 (4.55)	7.79 (7.97)
<u>2e</u>	Methanol	13	2,2-Dimethoxy-3,4,5-triphenyl- $\Delta^4$ -imidazoline ( <u>3e</u> )	26	212	$C_{23}H_{22}N_2O_2$	78.07 (77.09)	5.66 (6.14)	7.64 (7.82)
<u>2f</u>	Methanol	18	2,2-Dimethoxy-1,3,4,5-tetraphenyl- $\Delta^4$ -imidazoline ( <u>3f</u> )	30	328	$C_{29}H_{26}N_2O_2$	[PMR (Acetone- $d_6$ ): 8.15 (NH), 7.54-7.27 (aromatic) 3.43 (methoxy)] 80.68 (80.18)	5.90 (5.99)	6.27 (6.45)

Table 3. Photolysis of 4,5-diarylimidazolin-2-ones under acidic conditions.

Comps. irradiated	Time of irradiation (h)	Product	Yield (%)	m.p. (°C)	Mol. formula	C H N		
						Found (Calc)% and Spectral data		
<u>2a</u>	7	Phenanthro [9,10- <i>d</i> ] imidazolin-2-one ( <u>4a</u> )	30	> 350	$C_{13}H_{10}N_2O$	76.54 (76.92)	4.63 (4.27)	12.04 (11.97)
					•	IR (KBr): 3176 (NH), 1700 (NH-CO-NH) MS: 234 (M <sup>+</sup> ), 206, 178		
<u>2b</u>	11	6,9-Dimethylphenanthro [9,10- <i>d</i> ] imidazolin-2-one ( <u>4b</u> )	30	> 360	$C_{17}H_{14}N_2O$	76.71 (77.0)	5.50 (5.34)	10.34 (10.69)
<u>2c</u>	9	6,9-Dichlorophenanthro [9,10- <i>d</i> ] imidazolin-2-one ( <u>4c</u> )	25	348-350	$C_{13}H_8Cl_2N_2O$	58.83 (59.40)	2.81 (2.64)	8.92 (9.24)



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