Synthesis of New Photochromic Compounds from the Dimer of Arylphenanthroimidazoles

Yoshiko Sakaino

Department of Chemistry, Faculty of Education, Gunma University, Maebashi, Japan

and

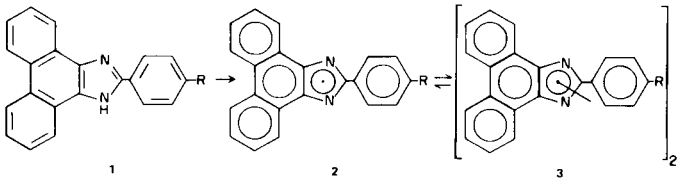
Hiroshi Kakisawa and Takenori Kusumi

Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo, Japan

Received March, 19, 1975

Treatment of the dimer of 2-arylphenanthro[9,10-*d*]imidazoles with nucleophilic compounds such as alcohols, aliphatic amines, and carboxylic acids afforded 2-substituted-2*H*- and 4-substituted-4*H*-2-arylphenanthro[9,10-*d*]isoimidazoles. These products showed a characteristic photochromism by dissociation to a stable imidazolyl radical.

In the course of our studies on oxidation of 2-arylphenanthro[9,10-*d*]imidazoles (**1**), various derivatives (**1**, R = H, CH_3, and Cl) were found to give the dimers (3) of corresponding imidazoles (1). The dimers showed characteristic thermochromism by reversible dissociation to the imidazolyl radicals (1). Contrary to these compounds, a ferricyanide oxidation of 2-anisylphenanthro[9,10-*d*]imidazole (**1**, R = OCH_3) in ethanol did not afford a corresponding dimer, but yielded 2-ethoxy-2-anisylphenanthro[9,10-*d*]-2*H*-isoimidazole (**4b**) and 4-ethoxy-4*H*-isoimidazole (**5b**) (2). These two isoimidazoles showed a remarkable photochromism, but showed no thermochromism (2). This paper describes a convenient method for preparation of these photochromic compounds and the other new photochromic compounds. The ferricyanide



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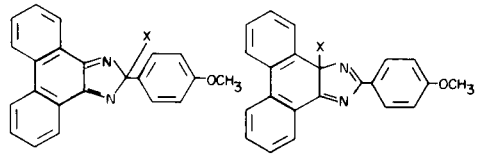
oxidation of the anisylphenanthroimidazole (**1**, R = OCH_3) in ethanol afforded the ethoxyisoimidazoles (**4b** and **5b**), whereas the oxidation in *t*-butyl alcohol produced a yellow compound (2). The same compound was conveniently available by the oxidation in alkaline tetrahydrofuran. The benzene solution of the product exhibited a thermochromism; the intensity of absorption maximum at 655 nm of the solution was enhanced with an increase of temperature and the intensity decreased at low temperature. These spectra showed isosbestic points at 355 and 451 nm, and the change of absorption intensities obeyed the equation of reversible dissociation of a dimer to monomer (2). The esr spectrum of the benzene solution showed the same hyperfine structures as those which had been identified as the anisylphenanthroimidazolyl radical (**2**, R = OCH_3) (3). The similarity of these properties to those of the dimer (1b) obtained from phenylphenanthroimidazole (**1**, R = H) suggested that the oxidation product in tetrahydrofuran was a dimer (**3**, R = OCH_3) of imidazole, which dissociated easily to the imidazolyl radical. The MS spectrum showed a characteristic pattern to the dimer of imidazole (1).

Treatment of the blue benzene solution of the dimer with methanol at room temperature afforded a mixture composed of 2-methoxy-2*H*-, 4-methoxy-4*H*-isoimidazoles, and the original imidazole (**4a**, **5a**, and **1**, R = OCH_3). 2-Ethoxy-2*H*- and 4-ethoxy-4*H*-isoimidazoles were also obtained by the treatment of the dimer with ethanol. These observations show that the ferricyanide oxidation of anisylphenanthroimidazole in ethanol solvent produces first the dimer (**3**, R = OCH_3), which then reacts with chtanol to give the ethoxyisoimidazoles. This reaction accommodates a new method for preparation of 2- or 4-substituted imidazolyl derivatives. Although **4a** and **5a** had been prepared by direct oxidation of the anisylimidazole (**1**, R = OCH_3) in methanol (2), the derivatives carrying an amino or acyloxy substituent at 2- or 4-position in the imidazole could not be prepared by the oxidative method. We found that the dimer (**3**, R = OCH_3) reacted with nucleophilic substances such as alcohols, aliphatic amines, and carboxylic acids to afford substituted isoimidazoles (**4b**, **4c**, **4d**, **5b**, and **5c**) and an equivalent amount

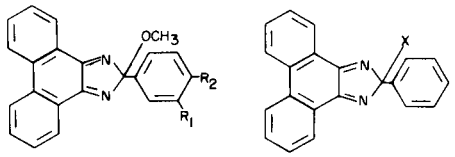
of the anisylimidazole (**1**, R = OCH_3). Chloro, nitro, and methyl derivatives (**6a**, **6c**, and **6d**) were also prepared by this method. The structures of these products were determined from elemental analyses and spectral properties [Tables I and II].

Parent dimer (**3**, R = H), m.p. 203°, also reacted with methanol to afford 2-methoxy-2*H*-isoimidazole (**7a**). Although the *o*-chlorodimer (**8**) was neither dissociative to the corresponding radical at room temperature nor reactive to a nucleophilic reagent such as alcohol, the addition of a catalytic amount of hydrochloric acid made feasible the reaction with methanol and afforded 2-methoxy-2*H*-2′-chloroisoimidazole (**9**). These facts showed that the formation of the substituted isoimidazoles (**4**, **5**, and **6**) from the dimers (**3**) was not through a homolytic but a heterolytic process, and the dimer which is more dissociative to the corresponding radicals is susceptible in greater cast to the heterolytic reaction.



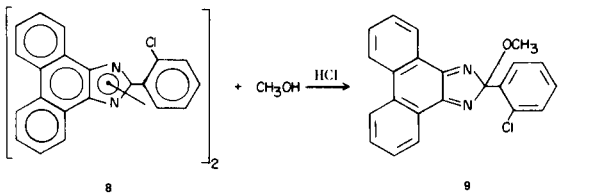
4a X = OCH_3
4b X = OC_2H_5
4c X = $N(C_2H_5)_2$
4d X = $OCOCH_3$

5a X = OCH_3
5b X = OC_2H_5
5c X = $N(C_2H_5)_2$

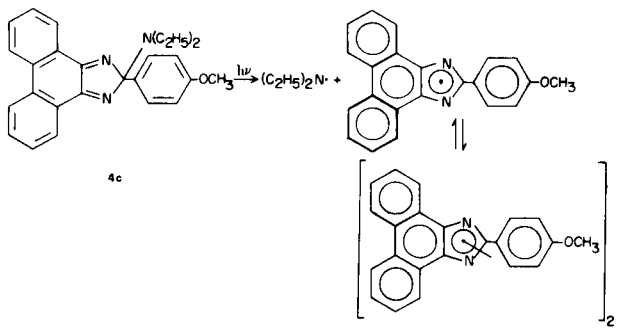


6a R_1 = Cl, R_2 = H
6b R_1 = NO_2, R_2 = H
6c R_1 = H, R_2 = Cl
6d R_1 = H, R_2 = CH_3

7a X = OCH_3
7b X = OAc
7c X = $N(C_2H_5)_2$
7d X = O_2CCH_2Ph



8 **9**

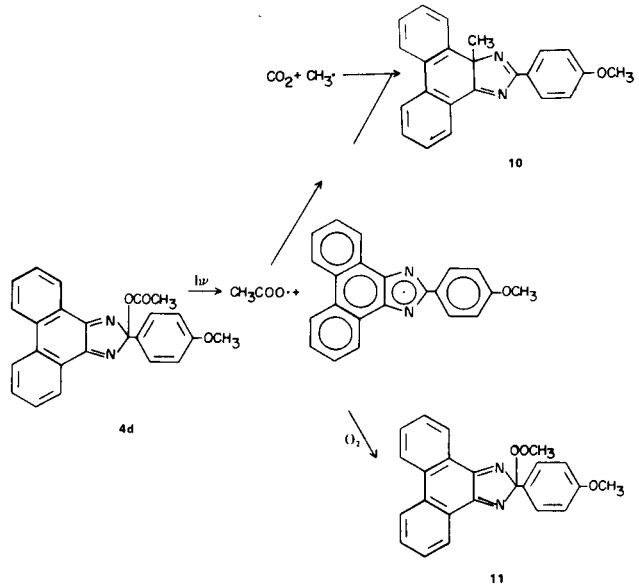


4c

Two series of isoimidazoles, 2-substituted-2*H*- and 4-substituted-4*H*-isoimidazoles (**4**, **6**, **7**, and **5**), showed a photochromic property: light yellow benzene solution of these compounds became blue on exposure to the sun or a mercury lamp, and the colored solution showed the characteristic absorption spectra of the imidazolyl radicals. The colored solution faded to light blue on standing in a cold dark place. The decolorized solution showed thermochromism: the colorless solution changed to a blue solution having the same absorption spectrum as that of radicals **2**. This color change of compounds **4**, **5**, **6** and **7** can be accounted for by (i) photo-chemical cleavage of the compound to two kinds of radicals, an alcoxyl, amino, or carboxyl radical, and an arylphenanthroimidazolyl radical, (ii) combination of the latter radical to the dimer, and (iii) thermal dissociation of the dimer to the radical as represented with the amino compound (**4c**):

From the irradiated solution of the acetoxy compound (**4d**) in a nitrogen atmosphere were detected carbon dioxide and the 4-methyl-4*H*-isoimidazole (**10**). The formation of the methyl compound (**10**) was anticipated from decomposition of acetoxyl radical to carbon dioxide and methyl radical, and recombination of the latter radical with imidazolyl radical (**2**, R = OCH_3). Compound (**10**) exhibited neither photochromism nor thermochromism. Irradiation in an oxygen atmosphere afforded a peroxide (**11**) besides the methylisoimidazole (**10**). The structure of the peroxide was determined from an elemental analysis and spectral properties.

These reactions, preparation of substituted isoimidazoles **4**, **5**, **6**, and **7** from the dimers **3** and nucleophilic substances, and subsequent photoirradiation appear to be useful for the generation of appropriate radicals.



10

4d

11

EXPERIMENTAL

Preparation of Photochromic Compounds (**6a**, **6b**, **6c**, **6d**, and **7a**) by Direct Oxidation.

A cold 10% aqueous solution of potassium ferricyanide (200 ml.) was added to a solution of 2-(substituted-phenyl)phenanthro-[9,10-*d*]imidazole (1 g.) dissolved in 99% methanol (100 ml.) containing potassium hydroxide (6.0 g.). During the addition the mixture was maintained at 15° and vigorously agitated by a stream of oxygen. After the completion of addition (2 hours), precipitates were collected by suction filtration, washed with water repeatedly and dried. The product was recrystallized from the solvent shown in Table I.

Preparation of 2-Substituted 2-(*p*-Anisyl)phenanthro-2*H*- and 4-Substituted 4-(*p*-Anisyl)phenanthro-4*H*-isoimidazoles from the Dimer.

To a solution of 2-(*p*-anisyl)phenanthroimidazole (**1**, R = OCH_3) (1 g.) in THF (50 ml.) was added a mixture of 1*N* potassium hydroxide (50 ml.) and 10% aqueous potassium ferricyanide solution (200 ml.) with stirring by a stream of oxygen at 5°. A deep blue color first appeared and blue precipitates were separated. The precipitates were collected, washed with water and THF, and dried to get a compound, m.p. 142-146°. A benzene solution of the product exhibited a thermochromism. An esr spectrum of the benzene solution showed the same hfs pattern as the esr spectrum of the substance identified as the *p*-anisylphenanthroimidazolyl radical.

To a benzene solution (100 ml.) of the bis(2-(*p*-anisyl-)phenanthroimidazolyl) (1 g.) was added methanol (100 ml.) with stirring under a nitrogen atmosphere at room temperature. A deep blue color first appeared in the course of the addition and colorless precipitates were separated. After the precipitates were removed, the evaporation of the filtrate gave a yellow oil which crystallized on addition of a small amount of methanol. The product was recrystallized from methanol to afford 2-methoxy-2-(*p*-anisyl)-phenanthro[9,10-*d*]-2*H*-isoimidazole (**5a**). The colorless precipitates (450 mg.) obtained from the reaction were recyrstallized from a mixture of acetone and water to give crystals, m.p. 255-256°. An ir spectrum and m.p. of the crystals were coincident with those of 2-(*p*-anisyl)phenanthroimidazole (**1**). The other substituted 2*H*- or 4*H*-isoimidazoles (**4b**, **4c**, and **5c**) were also prepared by the same methods using ethanol or diethylamine instead of methanol.

2-Acetoxy-2-(*p*-anisyl)phenanthro[9,10-*d*]-2*H*-isoimidazole (**4d**).

A mixture of bis(2-(*p*-anisyl)phenanthroimidazolyl) (2 g.) and acetic acid (20 ml.) in 200 ml. of benzene was stirred at room temperature. The deep blue color of the solution slowly disappeared and colorless precipitates were separated. After the removal of the precipitates by filtration, the filtrate was evaporated to give a reddish yellow oil which was crystallized by addition of a small amount of acetic acid. Dark yellow crystals were recrystallized from acetic acid to yield yellow prisms (814 mg.) of acetoxy-2*H*-isoimidazole (**4d**).

2-Diethylamino-2-phenylphenanthro[9,10-*d*]-2*H*-isoimidazole (**7c**).

Diethylamine (200 mg.) was added to a benzene solution of bis(2-phenylphenanthro[9,10-*d*]imidazolyl) (**3**, R = H) (600 mg.), and the solution was stirred at room temperature for 2 hours. The reaction mixture was filtered to remove the 2-phenylphenanthroimidazole (**1**, R = H), and the filtrate was evaporated to dryness. The residue was purified by preparative thin layer chromatography on silica gel developing with benzene-ethyl acetate (10:1). A main yellow band (R_f 0.41) on the chromatogram was collected and extracted with ethyl acetate to obtain 210 mg. of 2-diethylamino-2-phenylphenanthro-2*H*-isoimidazole (**7c**).

2-Acetoxy-2-phenylphenanthro[9,10-*d*]-2*H*-isoimidazole (**7b**).

To a solution of bis(2-phenanthroimidazolyl) (**3**, R = H) (1 g.) in 30 ml. of benzene was added acetic acid (10 ml.) with stirring at room temperature. After 2 hours the reaction mixture was filtered to remove precipitates of 2-phenylphenanthroimidazole (**1**, R = H), and the filtrate was evaporated to dryness. The residue was recrystallized from benzene to obtain 500 mg. of 2-acetoxy-2*H*-isoimidazole (**7b**).

2-Phenylacetoxy-2-phenylphenanthro[9,10-*d*]-2*H*-isoimidazole (**7d**).

A solution of 1 g. of bis(2-phenylphenanthroimidazolyl) (**3**, R = H) and 300 mg. of phenylacetic acid dissolved in 60 ml. of benzene was stirred at room temperature for 2 hours. The reaction mixture was filtered to remove the precipitates (300 mg.) of 2-phenylphenanthroimidazole (**1**, R = H) and the filtrate was evaporated to give a dark yellow residue. The residue was crystallized by treating with a mixture of ethyl acetate and ethanol (1:1), and the crystals were recrystallized from benzene to yield 300 mg. of 2-phenylacetoxy-2*H*-isoimidazole (**7d**).

2-Methoxy-2-(*p*-chlorophenyl)phenanthro[9,10-*d*]-2*H*-isoimidazole (**9**).

To a solution of 1 g. of dimer of 2-(*p*-chlorophenyl)phenanthro-[9,10-*d*]imidazole (**8**) and ethanol (20 ml.) in benzene (80 ml.) was added a drop of concentrated hydrochloric acid and the mixture was refluxed for 1 hour. After the solvent was evaporated *in vacuo*, 50 ml. of benzene was added to precipitate 2-(*o*-chlorophenyl)-phenanthro[9,10-*d*]imidazole (400 mg.). The filtrate was evaporated and the residue was subjected to purification by preparative thin layer chromatography developing with a mixture of benzene and ethyl acetate (10:1). A yellow band was eluted by ethyl acetate to yield 2-methoxy-2-(*o*-chlorophenyl)-2*H*-isoimidazole (**9**).

4-Methyl-2-(*p*-anisyl)phenanthro[9,10-*d*]-4*H*-isoimidazole (**10**) and 2-methylperoxy-2-(*p*-anisyl)phenanthro[9,10-*d*]-2*H*-isoimidazole (**11**).

A solution of 2-acetoxy-(*p*-anisyl)phenanthro-2*H*-isoimidazole (**4d**, 700 mg.) in benzene (100 ml.) was irradiated with a 100 w Hg-lamp (high pressure) under a stream of nitrogen at 10° for 2 hours. The nitrogen stream was conducted into lime water to detect carbon dioxide. Although the benzene solution initially changed to a green color by irradiation, the color gradually turned to reddish yellow and precipitates of calcium carbonate appeared. After 2 hours, the benzene solution was evaporated to dryness *in vacuo*, and the residue was separated by column chromatography on silica gel to yield yellow substance, 4*H*-isoimidazole (**10**), which was recrystallized from methanol, m.p. 155-156°, λ max 263 (log ε 4.67), 290 (4.21) and 300 nm (4.20), M^+ 228.1416 (Calcd. for $C_{23}H_{18}N_2O$; 338.1418). When the benzene solution of the acetoxy compound (**4d**) was irradiated in the usual atmosphere, yellow needles of peroxide (**11**) were obtained in addition to the methyl compound (**10**), m.p. 170-171°, λ max 264, 273, 325 nm, δ 7.89 (d, 2H, J = 9 Hz), 6.82 (d, 2H, J = 9), 3.85 (s, 3H), 3.77 (s, 3H), 8.44 (2H, m), 7.65-7.30 (m, 6H).

Anal. Calcd. for $C_{23}H_{18}N_2O_3$: C, 74.57; H, 4.91; N, 7.56. Found: C, 74.20; H, 4.89; N, 7.45.

TABLE I

Properties of Substituted 2*H*- and 4*H*-Isoimidazoles

Compound	Recryst solvent (a)	M.p. °C	Formula	C% Found	C% Calcd.	H% Found	H% Calcd.	N% Found	N% Calcd.
4c	DA	147	$C_{26}H_{25}N_3O$	78.74	78.95	6.42	6.38	10.57	10.62
4d	A	141	$C_{24}H_{18}N_2O_3$	75.55	75.37	4.50	4.75	7.16	7.33
5c	DA	137	$C_{26}H_{25}N_3O$	78.87	78.95	6.40	6.38	10.54	10.62
6a (b)	M	140	$C_{22}H_{15}ClN_2O$	73.52	73.63	4.23	4.22	7.82	7.81
6b	M	169	$C_{22}H_{15}N_3O_3$	71.50	71.53	4.24	4.10	11.21	11.38
6c (b)	M	186	$C_{22}H_{15}ClN_2O$	73.26	73.63	4.30	4.22	7.60	7.81
6d	M	189	$C_{23}H_{18}N_2O$	81.63	81.62	5.39	5.37	8.06	8.28
7a	M	165	$C_{22}H_{16}N_2O$	81.19	81.45	5.10	4.97	8.41	8.64
7b	B	202	$C_{23}H_{16}N_2O_2$	78.42	78.38	4.66	4.59	7.91	7.95
7c	DA	210	$C_{25}H_{23}N_3$	82.13	82.15	6.36	6.36	11.58	11.50
7d	B	166	$C_{29}H_{20}N_2O_2$	81.52	81.28	4.86	4.71	6.37	6.54
9 (b)	M	159	$C_{22}H_{15}ClN_2O$	73.61	73.63	3.93	4.22	7.83	7.81

(a) A: acetic acid; B: benzene; DA: diethylamine; E: ethanol; M: methanol. (b) Chlorine content; **6a**: Found: 9.76. Calcd.: 9.88%. **6c**: Found: 9.88. Calcd.: 9.88%. **9**: Found: 9.82. Calcd.: 9.88%.

TABLE II

NMR and UV Spectra of Substituted 2*H*- and 4*H*-Isoimidazoles, and UV Spectrum of Imidazolyl Radicals

Compound	δ (ppm from TMS)	λ max (log ε) in Ethanol	λ max after Irradiation
4c	1.02 (t, 3H), 2.75 (q, 2H, 7), 3.80 (s, 3H) 6.90 (d, 2H, 8), 7.85 (d, 2H, 8)	264 (4.56), 272 (4.56) 325 (3.81)	655
4d	2.20 (s, 3H), 3.88 (s, 3H), 6.95 (d, 2H, 8) 7.90 (d, 2H, 8)	264 (4.49), 270 (4.50) 329 (3.87)	655
5c	0.75 (t, 3H, 7), 2.50 (m, 2H), 3.85 (s, 3H) 6.96 (d, 2H, 8), 8.35 (d, 2H, 8)	264 (4.59), 292 (4.09), 306 (4.09)	655
6a	3.28 (s, 3H)	265 (4.54), 272 (4.54), 320 (3.91), 390 (3.23)	587
6b	3.28 (s, 3H)	267 (4.65), 272 (4.65) 320 (4.02), 390 (3.46)	570
6c	3.25 (s, 3H), 7.15 (d, 2H, 7), 7.45 (d, 2H, 7)	264 (4.52), 272 (4.53) 321 (3.85), 388 (3.18)	605
6d	2.30 (s, 3H), 3.30 (s, 3H)	264 (4.55), 272 (4.57), 323 (3.89), 382 (sh)	617
7a	3.30 (s, 3H)	264 (4.09), 272 (4.51) 321 (3.89), 388 (3.18)	585
7b	2.10 (s, 3H), 7.25 (m, 5H)	268 (sh), 270 (4.51) 323 (3.90), 390 (3.32)	585
7c	1.00 (t, 6H, 7), 2.75 (q, 4H, 7)	263 (4.50), 271 (4.47) 317 (3.80), 374 (3.34)	585
7d	3.75 (s, 2H)	262 (4.52), 269 (4.53), 323 (3.97), 392 (3.16)	585
9	3.30 (s, 3H)	266 (4.56), 272 (4.55) 321 (3.90)	

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