SYNTHESIS OF NAPHTHO[2,3-*b*]INDOLIZINE-6,11-DIONE DERIVATIVES BY IODINE OXIDATION OF 2-ALKYL-1,4-NAPHTHOQUINONES IN THE PRESENCE OF SUBSTITUTED PYRIDINES

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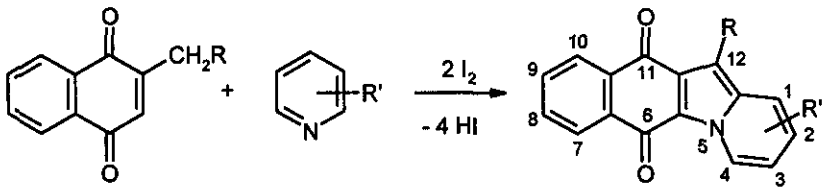
Abstract - Iodine oxidation of 2-alkyl-1,4-naphthoquinones (**1**) in the presence of substituted pyridines (**2**) afforded naphtho[2,3-*b*]indolizine-6,11-dione derivatives (**3**). Other oxidant systems (MnO_2/I^- or $Fe(ClO_4)_3/I_2$) can be used and 2-alkylbenzoquinones reacted in lower yield. Iodination of **3** by I_2 and dibenzoyl peroxide occurred selectively at position 12.

The α,β-unsaturated carbonyl system of quinones has provided several examples of Michael addition of neutral and charged nucleophiles. The main preparative use of these processes is that the quinol addition products can be oxidized back to quinones; the overall process being a direct substitution of the quinone by an electronegative atoms.[1] Under acidic oxidative conditions, the addition/oxidation sequence can be easily performed in synthetically useful yields until polysubstitution.[1,2] The use of basic oxidative conditions was less extensively investigated, but it should provide access to a wide variety of symmetrical and unsymmetrical polysubstituted quinones. In fact, the electronegative atoms firstly introduced in the oxidation step can undergo fast nucleophilic substitution by appropriate bases present in the reaction medium. We have recently reported an example of this strategy in the four electron oxidation of 1,4-naphthoquinone by wet iodine or hydrogen peroxide in the presence of substituted pyridines to give 2-oxy-3-(pyridinium-1'-yl)-1,4-naphthoquinones (N/O substitution).[3] However, under these conditions, aliphatic α,β-unsaturated carbonyl compounds gave vinylic α-substitution through a nucleophilic addition/electrophilic capture/elimination pathway.[4] This different behavior prompted us to investigate the reactivity of 2-alkylquinones under basic oxidative conditions. In this paper, we report that 2-alkyl-1,4-

naphthoquinones (**1a-e**) are oxidized by iodine in the presence of substituted pyridines (**2a-d**) to naphtho[2,3-*b*]indolizine-6,11-dione derivatives (**3a-h**) in a reaction which exhibits quinonoid addition and intramolecular substitution involving the heterocyclic base (eq.1, Table 1).



eq. 1

1a-e **2a-d** **3a-h**

1a ; R = H
1b ; R = CO_2Et
1c ; R = COPh
1d ; R = Ph
1e ; R = CN

2a ; R' = H
2b ; R' = 4-CO_2Et
2c ; R' = 3-CO_2Et
2d ; R' = 3,4-C_4H_4

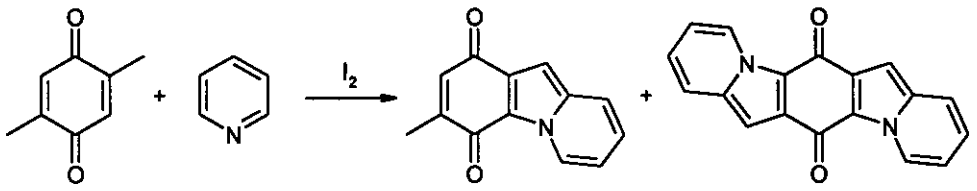
3a ; R = R' = H
3b ; R = H, R' = 2-CO_2Et
3c ; R = H, R' = 3-CO_2Et
3d ; R = H; R' = 1,2-C_4H_4
3e ; R = CN, R' = H
3f ; R = Ph, R' = H
3g ; R = CO_2Et, R' = H
3h ; R = COPh, R' = H

Heterocyclic quinones (**3**) were previously synthesized by condensation of 2,3-dichloro-1,4-naphthoquinone with 2-alkyl substituted pyridines[5,6] or with methylene active compounds in the presence of R'-substituted pyridines,[7] but only traces of **3** were observed in similar reactions with 1,4-naphthoquinone.[5,8] The new type of condensation was performed by adding iodine to a freshly prepared cold solution of 2-alkyl-1,4-naphthoquinone in excess of substituted pyridine and heating the mixture at 60-90 °C for 12-24 h. Compounds (**3**) were usually isolated from the reaction mixture by addition of an appropriate solvent and filtration. Representative results of isolated yields are shown in Table 1 (HPLC analytical yields were 7-12 % higher than the isolated one).[9] With menadione (**1a**), pyridines substituted by electron-withdrawing groups (**2b** and **2c**) afforded **3** in lower yield than pyridine or isoquinoline. By contrast, quinoline did not react also at higher temperatures,[10] and a mixture of isoquinoline and quinoline (1:10) afforded only the addition product to isoquinoline (**3d**). Quinones (**1b-1e**), carrying unsaturated substituents (i.e. CN, COPh, CO_2Et, Ph), reacted even more successfully. Moreover, 2,5-dimethyl-1,4-benzoquinone (**1f**) gave small amounts of the indolizine (**4a**) and traces of the diindolizine (**4b**) (eq. 2). Structural assignment for compounds (**3**) and (**4**) was carried out by spectroscopic analysis (IR, ^{1}H-NMR and ^{13}C-NMR, MS) and confirmed by comparison with compounds obtained by known procedures.[5,6]

Table 1. Naphtho[2,3-*b*]indolizine-6,11-dione derivatives (3a-h) by iodine oxidation of 2-alkyl-1,4-naphthoquinones (1) in the presence of substituted pyridines (2).

1	2	3	mp °C [a]	1 conv. %	3 [b] yield %	Molecular Formula	Analysis % Calcd/Found		
							C	H	N
1a	**2a**	**3a** [c]	239-240[h]	98	71	$C_{16}H_9NO_2$	77.72	3.67	5.66
							77.58	3.82	5.81
1a	**2b**	**3b** [d]	235-236	85	51	$C_{19}H_{13}NO_4$	71.47	4.10	4.39
							71.66	4.23	4.37
1a	**2c**	**3c** [e]	223-224	75	60	$C_{19}H_{13}NO_4$	71.47	4.10	4.39
							71.28	4.25	4.21
1a	**2d**	**3d** [f]	302-304 [i]	96	55	$C_{20}H_{11}NO_2$	80.80	3.73	4.71
							80.94	3.65	4.92
1e	**2a**	**3e** [d]	309-310 [j]	95	70	$C_{17}H_8N_2O_2$	75.00	2.96	10.29
							74.88	3.04	10.13
1d	**2a**	**3f** [c]	248-249 [k]	79	61	$C_{22}H_{13}NO_2$	81.72	4.05	4.33
							81.90	4.19	4.46
1b	**2a**	**3g** [c]	157-158 [l]	88	68	$C_{19}H_{13}NO_4$	71.47	4.10	4.39
							71.40	3.95	4.31
1c	**2a**	**3h** [c]	257-258 [m]	90	53	$C_{23}H_{13}NO_3$	78.62	3.73	3.99
							78.48	3.61	4.11
1f [g]	**2a**	**4a** [d]	178-180	100	18	$C_{13}H_9NO_2$	73.92	4.29	6.63
							74.11	4.41	6.52

[a] Melting points were not corrected. [b] isolated product. [c] 90 °C, 24 h. [d] 60 °C, 24 h. [e] 60 °C, 48 h. [f] 80 °C, 48 h. [g] 2,5-dimethylbenzoquinone. [h] lit.,[11] mp 238-9 °C. [i] lit.,[5] mp 296-297 °C. [j] lit.,[5] mp 307.5-308.5. [k] lit.,[4] mp 244.5-245.5 °C. [l] lit.,[8] mp 157-158 °C. [m] lit.,[5] mp 256-257.5 °C (decomp)



1f **4a** **4b** eq. 2

The yield of **3** was approximately proportional to the amount of iodine used and was systematically higher in the presence of oxygen (air) than in a nitrogen atmosphere. Molecular oxygen is responsible for the formation of **3** in very low yield in reactions with the same substrates in the absence of iodine,[8] but attempts to use catalytic amounts of iodine in the presence of oxygen under various conditions were unsuccessful. In order to determine whether iodine could be replaced by other less expensive oxidants, a combination of metal oxidants and iodine (10 %) as catalyst, or metal oxidants alone, were examined.

Table 2. Naphtho[2,3-*b*]indolizine-6,11-dione derivatives (3) by metal oxidation of 2-alkyl-1,4-naphthoquinones (1) in the presence of substituted pyridines (2).

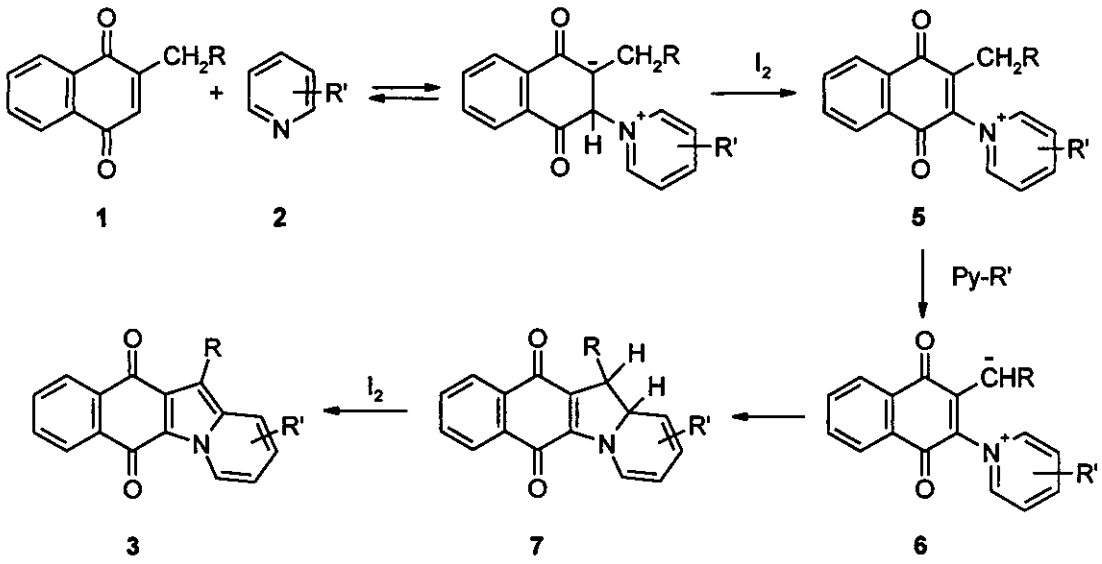
Compound	1	2	Metal Oxidant (mol %) [a]	Additive (mol %) [a]	1 conv. % [b]	3 yield % [b]
3a [c]	**1a**	**2a**	MnO_2 (3)	I_2 (0.1)	80	69
3h [c]	**1h**	**2a**	MnO_2 (3)	I_2 (0.1)	86	74
3a [d]	**1a**	**2a**	FEP (4) [e]	-	91	68
3b [d]	**1a**	**2b**	FEP (4) [e]	-	86	60
3b [d]	**1a**	**2d**	FEP (4) [e]	-	12	-
3a [f]	**1a**	**2a**	FEP (0.08) [e]	O_2 (5-6)	58	35

[a] for mol of **1** (0.2 M solutions). [b] determined by HPLC. [c] 90 °C, 24 h. [d] 50 °C, 5 h. [e] $Fe(ClO_4)_3 \cdot 6H_2O$. [f] 60 °C, 24 h with O_2 flow of 0.5 mL/min

Typical results obtained are shown in Table 2. The procedure with iodine as catalyst turned out to be successful with manganese dioxide (3 mol) but a more complex work-up was necessary. In the absence of iodine, the oxidation of **1a** to **3a** occurred also in comparable yield with $Fe(ClO_4)_3 \cdot 6H_2O$ (FEP) in pyridine, but the reaction was less general than with iodine as oxidant (isoquinoline did not reacts). On the contrary, other oxidants, i.e. $Mn(OAc)_3$, PbO_2, CAN, were inefficient, whereas molecular oxygen in the presence of catalytic amount of FEP showed some potentiality.

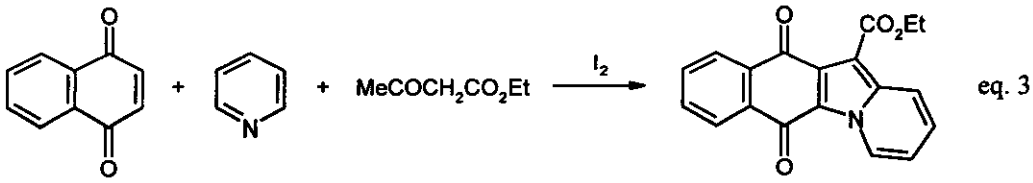
A mechanistic interpretation of this complex transformation is shown in Scheme 1. Nucleophilic addition of substituted pyridine to quinone and oxidation by iodine of the intermediate anion would produce the pyridinium-quinone (**5**), which is deprotonated by the base to the conjugated heteroaromatic betaine (**6**). Intramolecular addition of the anion to the pyridinium moiety affords the dihydro derivative (**7**), which undergo dehydrogenation by iodine to **3**. With unsymmetrical heteroaromatic bases (**2b** and **2d**) only compounds (**3c**) and (**3d**) were obtained, respectively. This suggests a charge-transfer transition state for the cyclization step which involves selectively the more soft carbon atom of betaine (**6**) in alpha position to nitrogen, in analogy to other additions of soft nucleophiles to pyridinium cations. On the other hand, steric factors in the addition of the base to the quinone and in the cyclization of the corresponding non planar betaine (**6**) should work against the quinoline reaction.

Support to the mechanism of Scheme 1 arises from the high yield of the 2-(pyridinium-1'-yl)-1,4-naphthoquinone obtained under quite similar conditions in the reaction of **1a** with pyridine and iodine,[1] and from previous results of condensation of active methylene compounds with 2,3-dichloroquinone in the presence of pyridine.[3-6]

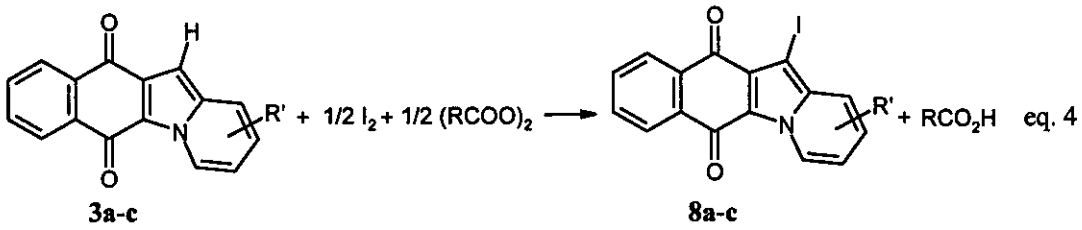


Scheme 1

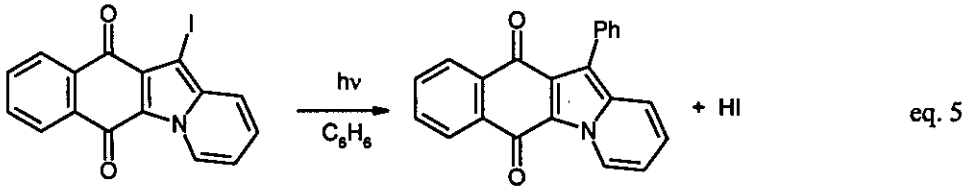
On this basis, the reaction of 1,4-naphthoquinone with ethyl acetoacetate in the presence of pyridine (eq. 3) (previously reported in the absence of any oxidant to give **3g** in 11 % yield)[6] was easy improved to 80 % yield in the presence of one mole of iodine.



A specific feature of the reaction with ethyl isonicotinate (**2b**) was the formation of the side product 12-iodo derivative (**8b**). Checking carefully the details of the reaction, we identified appropriate conditions to convert compounds (**3**) to the corresponding 12-iodo derivative (**8**) by iodine in acidic medium. Diacyl peroxides proved to be valuable co-oxidants in these processes (eq. 4, Table 3).



3a-c **8a-c**



8a **3f**

Table 3. Synthesis of 12-iodonaphtho[2,3-*b*]indolizine-6,11-dione derivatives (8a-c) by reaction of compounds (3a-c) with iodine in the presence of dibenzoyl peroxide (BP).

Compound	3	Additive	3 conv. %	8 yield % [a]	Molecular Formula	Analysis % Calcd/Found			
						C	H	N	I
8a [b]	**3a**	-	20	13	$C_{16}H_8NO_2I$	51.50	2.16	3.75	34.01
						51.41	2.31	3.66	34.40
8a [c]	**3a**	BP	93	93	$C_{16}H_8NO_2I$	51.50	2.16	3.75	34.01
						51.52	2.19	3.90	33.91
8b [d]	**3b**	BP	92	88	$C_{19}H_{12}NO_4I$	51.26	2.72	3.15	28.50
						51.15	2.85	3.11	28.70
8c [e]	**3c**	BP	88	79	$C_{19}H_{12}NO_4I$	51.26	2.72	3.15	28.50
						51.36	2.79	3.04	28.36

[a] isolated product. [b] 90 °C, 24 h. [c] 60 °C, 24 h. [d] 60 °C, 48 h. [e] 80 °C, 48 h

Compounds (**8a-c**) are useful starting material for cross coupling and nucleophilic substitution reactions, affording a variety of 12-substituted naphtho[2,3-*b*]indolizine-6,11-dione derivatives. For example, the structure of phenyl derivative (**3f**), whose previous analytical data were uncertain,[6] was confirmed by comparison with the product of photolysis (300 nm, 24 h) of **8a** in benzene (eq. 5, see experimental part). The methodology here reported, combined with the easy functionalization of quinones by a variety of carbon nucleophiles or by carbon centered radicals, opens a direct efficient access to benzo[*b*]indolizine derivatives.

EXPERIMENTAL

Melting points were determined on a Büchi melting point apparatus and are not corrected. ^{1}H-NMR spectra were recorded on a Bruker AM 400 and AC 250 instruments. MS were obtained on a Finnigan TSQ 70 instrument. IR spectra were taken on a Perkin Elmer FT-IR 2000 instrument. Satisfactory combustion analysis were obtained in the microanalytical Redox laboratory (Milan). HPLC analyses were performed on a Hewlett Packard 1100 instrument with autosample and photodiode array detector.

General Procedure with Iodine. Quinone (**1**) (5.8 mmol) was dissolved in the substituted pyridine (**2**) (29.0 mmol) at 5-10 °C under magnetic stirring, and I_2 (2.95 g, 11.6 mmol) was added to the solution. The mixture was heated at 60-90 °C under stirring for 24-48 h. The cold mixture was diluted with $CHCl_3$ (2-4 mL), the red-orange precipitate was filtered and the organic phase was washed with 10 % HCl (5 mL), water (5 mL) and 5 % $Na_2S_2O_3$ solution (15 mL), dried on Na_2SO_4 and concentrated. The residue was flash silica gel chromatographed (1:50) with hexane/ethyl acetate 8:2. With insoluble compounds (**3d** and **3e**) DMSO (20 ml) was added to the reaction mixture under stirring in 15 min and the resulting red solid was filtered and dried at 60 °C/1 mmHg for 6 h.

General Procedure with MnO_2. To a flask charged with pyridine (5 mL), MnO_2 (1.9 g, 4.1 mmol) and iodine (0.03 g, 0.12 mmol) were added under stirring at 5-10 °C. After 15 min the quinone (**1**) (1.2 mmol) was added and the mixture was heated at 50 °C for 8 h. Then, the flask was cooled at 0-5 °C for 1 h, the solid was filtered and extracted in Soxhlet with boiling chloroform (50 mL). Concentration of the extract to 5 mL and filtration afforded **3**.

General Procedure with FEP. $Fe(ClO_4)_3 \cdot 6H_2O$ (FEP) (1.9 g, 4.1 mmol) was added to the substituted pyridine (5 mL) cooled at 0 °C. The mixture was stirred for 15 min at 0 °C and, after addition of the quinone (1.2 mmol), it was heated at 50 °C for 5 h. The mixture was cooled at 10 °C and filtered. The filtrate was washed with ether (2 x 5 mL). Concentration under reduced pressure and flash silica gel chromatography gave **3**.

Improved condensation of 1,4-Naphthoquinone with Ethyl Acetoacetate in the presence of Iodine and Pyridine. 1,4-Naphthoquinone (1.0 g, 6.33 mmol) and ethyl acetoacetate (1.7 mL, 13.34 mmol) were added in sequence at 20 °C under stirring to a solution of pyridine (5 mL) and 35 % HCl (0.17 mL). After 10 min, iodine (3 g, 11.8 mmol) was added and the mixture was stirred for 8 h at 20 °C, then poured into $CHCl_3$ (100 mL) and 10 % HCl (25 mL), the organic phase was separated, washed with 10 % NaOH and

water, and concentrated to afford crude **3g**, which was crystallized from 1,2-dichloroethane (1,61 g, 80 % yield).

Naphtho[2,3-*b*]indolizine-6,11-dione (3a). ^{1}H NMR ($CDCl_3$) (δ, ppm): 9.66 (1H, dddd, J = 6.9, 1.2, 1.2, and 1.2 Hz), 8.26 (1H, dd, J = 7.5 and 1.5 Hz), 8.21 (1H, dd, J = 7.5 and 1.5 Hz), 7.75-7.61(3H, m), 7.22 (1H, ddd, J = 1.2, 6.9 and 9.1 Hz), 7.08 (1H, d, J = 1.2 Hz), 7.05 (1H, ddd, J = 1.3, 6.9 and 6.9 Hz). MS (EI) (m/z) (int. rel.): 247 (M, 100), 218 (35), 189 (60), 190 (74), 163 (21), 95 (19). MS (FAB) (m/z) (rel. int.): 248 (M+1, 100). IR (KBr) (ν_{max}; cm^{-1}): 1674, 1625, 1627, 1494, 1393, 1349, 1231.

2-Ethoxycarbonylnaphtho[2,3-*b*]indolizine-6,11-dione (3b). ^{1}H NMR ($CDCl_3$) (δ, ppm): 9.53 (1H, dd, J = 1.07 and 0.8 Hz), 8.33 (1H, dd, J = 1.74 and 1.07 Hz), 8.22-8.11 (2H, m), 7.78-7.67 (2H, m), 7.56 (1H, dd, J = 7.36 and 1.74 Hz), 7.30 (1H, d, J = 0.8 Hz), 4.48 (2H, q, J = 7.4 Hz), 1.44 (3H, t, J = 7.4 Hz). MS (EI) (m/z) (rel. int.): 319 (M, 68), 291 (100), 275 (20), 246 (23), 218 (8), 190 (41), 163 (12), 150 (8), 95 (15), 83 (18). IR (KBr) (ν_{max}; cm^{-1}): 1716, 1634,1391, 1229.

3-Ethoxycarbonylnaphtho[2,3-*b*]indolizine-6,11-dione (3c). ^{1}H NMR ($CDCl_3$) (δ, ppm): 9.73 (1H, m), 9.21 (1H, dd, J = 1.2 and 7.9 Hz), 8.20-8.10 (2H, m), 7.80-7.69 (2H, m), 7.66 (1H, d, J = 7.9 and 0.5 Hz), 7.30 (1H, d, J = 0.9 Hz), 4.48 (2H, q, J = 7.4 Hz), 1.44 (3H, t, J = 7.4 Hz). MS (EI) (m/z) (rel. int.): 319 (M, 22), 291 (31), 190 (100), 274 (20), 247 (19). IR (KBr) (ν_{max}; cm^{-1}): 1720, 1644,1396, 1230.

12-Cyanonaphtho[2,3-*b*]indolizine-6,11-dione (3e). ^{1}H NMR ($CDCl_3$) (δ, ppm): 9.92 (1H, ddd, J = 7.2, 1.3 and 1.3 Hz), 8.34 (1H, ddd, J = 9.3, 1.3 and 1.3 Hz), 8.27-8.23 (2H, m), 7.78-7.68 (2H, m), 7.45 (1H, ddd, J = 9.3, 6.8 and 1.3 Hz), 7.15 (11H, ddd, J = 7.2, 6.8 and 1.3 Hz). MS (EI) (m/z) (rel. int.): 272 (M, 61), 255 (100), 254 (23), 253 (40), 219 (61), 163 (21), 95 (19).

12-Phenylnaphtho[2,3-*b*]indolizine-6,11-dione (3f). ^{1}H NMR ($CDCl_3$) (δ, ppm): 9.82 (1H, ddd, J = 6.9, 1.2, 1.2 and 1.2 Hz), 8.27 (1H, dd, J = 7.6 and 1.5 Hz), 8.15 (1H, dd, J = 7.6 and 1.5 Hz), 7.75-7.61 (5H, m), 7.55-7.42 (3H, m), 7.22 (1H, ddd, J = 1.3, 6.9 and 1.2 Hz), 7.11 (1H, ddd, J = 1.2, 6.9 and 6.9 Hz). MS (EI) (m/z): 323 (M, 100), 293 (30), 265 (86), 264 (43), 239 (20), 161 (62), 133 (70), 120 (22).

12-Ethoxycarboylnaphtho[2,3-*b*]indolizine-6,11-dione (3g). ^{1}H NMR ($CDCl_3$) (δ, ppm): 9.85 (1H, ddd, J = 7.15, 1.3 and 1.3 Hz), 8.32 (1H, ddd, J = 9.1, 1.3 and 1.3 Hz), 8.25-8.21 (2H, m), 7.75-7.67 (2H, m), 7.42 (1H, ddd, J = 9.1, 6.8 and 1.3 Hz), 7.16 (11H, ddd, J = 7.1, 6.8 and 1.3 Hz), 4.52 (2H, q, J = 7.0 Hz), 1.50 (3H, t, J = 7.0 Hz). MS (EI) (m/z) (rel. int.): 319 (M, 52), 274 (61), 247 (98), 218 (20), 191 (32), 190 (100), 163 (49).

12-Benzoylnaphtho[2,3-*b*]indolizine-6,11-dione (3h). ^{1}H NMR ($CDCl_3$) (δ, ppm): 9.92 (1H, ddd, J = 7.11, 1.5 and 1.3 Hz), 8.32 (1H, ddd, J = 9.1, 1.3, 1.3 Hz), 8.25-8.21 (2H, m), 7,92 (2H, d, J = 7,3 Hz), 7.75-7.67 (2H, m), 7.5-7.1 (5H, m). MS (EI) (m/z) (rel. int.): 351 (M, 83), 246 (21), 218 (18), 191 (32), 190 (100), 163 (11).

Benz[5,6]indole[1,2-*a*]isoquinoline-8,13-dione. ^{1}H NMR ($CDCl_3$) (δ, ppm): 9.39 (1H, dd, J = 7.5 and 0.7 Hz), 8.27-8.20 (3H,), 7.76-7.56 (5H, m), 7.57 (1H, d, J = 0.7 Hz), 7.25 (1H, d, J = 7.5 Hz). MS (EI) (m/z) (rel. int.): 297 (M, 100), 240 (58), 213 (25), 164 (22), 120 (23), 76 (22), 57 (35), 43 (25). IR (KBr) (ν_{max}; cm^{-1}): 1668, 1626, 1594, 1463, 1396, 1354, 1245.

3-Methylpyrido[1,2-*a*]indole-1,4-dione (4a). mp 133-134 °C. ^{1}H NMR ($CDCl_3$) (δ, ppm): 9.44 (1H, dddd, J = 7.1, 1.1, 1.1 and 1.1 Hz), 7.63 (1H, ddd, J = 8.9, 1.2 and 1.2 Hz), 7.18 (1H, ddd, J = 8.9, 6.8 and 1.1 Hz), 7.02 (1H, ddd, J = 8.9, 6.8 and 1.2 Hz), 6.89 (1H, d, J = 1.0 Hz), 6.48 (1H, q, J = 1.6 Hz), 2.17 (3H, d, J = 1.6 Hz). MS (EI) (m/z) (rel. int.): 211 (M, 100), 183 (57), 154 (60), 79 (56), 50 (82).

Indolizino[3,2-*f*]pyrido[1,2-*a*]indole-6,13-dione (4b). mp > 350 °C (lit.,[12] mp > 360 °C). ^{1}H NMR ($CDCl_3$) (δ, ppm): 9.41 (1H, dddd, J = 7.2, 1.0, 1.1 and 1.1 Hz), 7.65 (1H, ddd, J = 8.7, 1.1 and 1.0 Hz), 7.16 (1H, ddd, J = 8.8, 6.9 and 1.1 Hz), 7.03 (1H, ddd, J = 8.9, 6.8 and 1.1 Hz), 6.86 (2H, d, J = 1.1 Hz). MS (EI) (m/z) (rel. int.): 286 (M, 100), 258 (21), 154 (13), 79 (20).

12-Iodo-2-ethoxycarbonylnaphtho[2,3-*b*]indolizine-6,11-dione (8b). mp 203-205 °C (decomp.). ^{1}H NMR ($CDCl_3$) (δ, ppm): 9.71 (1H, dd, J = 7.36 and 1.07 Hz), 8.43 (1H, dd, J = 1.07 and 1.74 Hz), 8.24-8.28 (2H, m), 7.69-7.77 (2H, m), 7.63 (1H, dd, J = 7.36 and 1.74 Hz), 4.47 (2H, q, J = 7.4 Hz), 2.49 (3H, t, J = 7.4 Hz). MS (EI) (m/z) (rel. int.): 445 (M, 37), 417 (40), 297 (20), 256 (20), 417 (411), 243 (49), 188 (32), 149 (41), 107 (47), 91 (50), 71 (88), 44 (100).

12-Iodonaphtho[2,3-*b*]indolizine-6,11-dione (8a). mp 228 °C. ^{1}H NMR ($CDCl_3$) (δ, ppm): 9.75 (1H, dd, J = 7.0 and 1.0 Hz), 8.28-8.24 (m, 2H), 7.78-7.67 (3H, m), 7.34 (1H, ddd, J = 9.1, 6.9 and 1.2 Hz), 7.13 (1H, ddd, J = 7.0, 7.1 and 1.3 Hz), MS (EI) (m/z) (rel. int.): 373 (M, 100), 345 (2), 218 (4), 190 (20), 95 (10).

Photolysis of 8a in Benzene. A solution of **8a** (373 mg, 1,0 mmol) in benzene (20 mL) was irradiated at 300 nm in a Rayonet reactor equipped with 4 medium pressure mercury lamps for 24 h at 25-28 °C. The solution was evaporated in the presence of SiO_2 (3 g) and the solid was silica gel chromatographed

(hexane/ethyl acetate 8:2) to give **8a** (55 mg, conversion 85 %), **3f** (mp 265-6 °C, 195 mg, yield 60 %) and **3a** (70 mg. 29 %).

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