

Article

The Photochemistry of Benzotriazole Derivatives. Part 2: Photolysis of 1-Substituted Benzotriazole Arylhydrazones: New Route to Phenanthridin-6-yl-2-phenyldiazines

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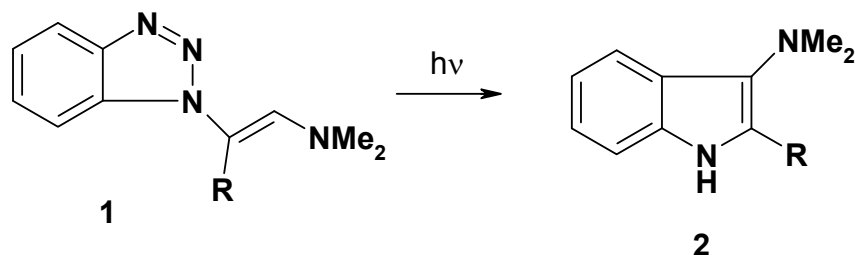
Received: 11 November 2011; in revised form: 23 November 2011 / Accepted: 28 November 2011 / Published: 8 December 2011

Abstract: Irradiation of 1-substituted benzotriazole arylhydrazones **3a–c**, **4a,b** and **5a,b** with a 16 W low pressure mercury arc-lamp (254 nm) for 24 h gave phenanthridin-6-yl-2-phenyldiazines **9a–c**, phenanthridin-6(5*H*)-ones **10a–c**, 1-anilinobenzimidazoles **11a–c**, 2-aryl-1*H*-benzimidazoles **12a–c**, 1-arylamino-1*H*-benzimidazol-2-carboxylic acid ethyl esters **14a,b**, 1-aryl-1*H*, 9*H*-benzo [4,5][1,2,3] triazolo[1,2-*a*]tetrazole-3-carboxylic acid ethyl esters **16a,b**, 1-arylamino-2-benzoylbenzimidazoles **18a,b** and 2-benzoylbenzoxazole **21**.

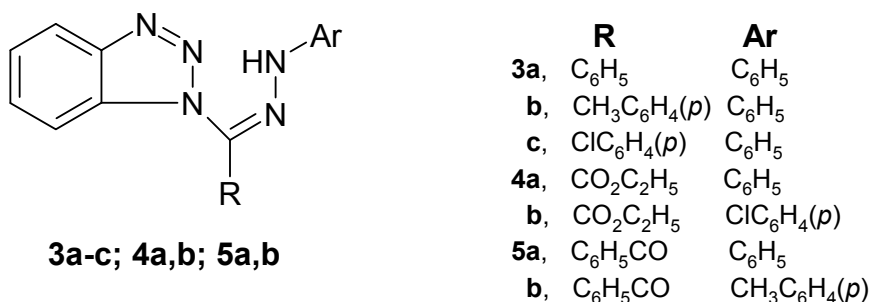
Keywords: 1,2,3-benzotriazole; phenanthridin-6-yl-2-phenyldiazine; phenanthridin-6(5*H*)-one; 1-anilinobenzimidazole; 1*H*-benzimidazole; 2-benzoyl-1*H*-benzoxazole; photolysis

1. Introduction

The behavior of benzotriazole and its derivatives under pyrolytic and photolytic conditions has already received considerable attention. In particular, 1-substituted-1*H*-benzotriazoles pyrolyze via elimination of N₂ to give a 1,3-diradical intermediate which can interact with aromatic or unsaturated substituents to give cyclic and rearranged products [1–10]. In the earlier paper in this series, we have reported the photolysis of *N*-vinylsubstituted benzotriazole derivatives **1** into 2-acyl-3-dimethylaminoindoles **2** [11].

Scheme 1. Photolysis of *N*1-vinylsubstituted benzotriazoles **1** into 2-acylindoles **2**.

This investigation is now extended to include seven 1-substituted benzotriazole arylhydrazones **3a–c**, **4a,b** and **5a,b** (Figure 1).

Figure 1. 1-substituted benzotriazole arylhydrazones **3a–c**, **4a,b** and **5a,b**.

2. Results and Discussion

Compounds **3a–c** and **5a,b** were obtained by the procedures described earlier and were fully characterized [12–14]. The UV spectra of these compounds display two absorption maxima in the region 243–392 nm wavelength regions.

Irradiation of compounds **3a–c** in a quartz tube with a 16 W low pressure mercury arc-lamp (254 nm) in acetonitrile for 24 hours at room temperature produced phenanthridin-6-yl-2-phenyldiazines **9a–c** (48–51%), phenanthridin-6(5*H*)-ones **10a–c** (15–18%), 1-anilino-2-arylbenzimidazoles **11a–c** (10–14%) and 2-aryl-1*H*-benzimidazoles **12a–c** (8–10%). The formation of these products can be explained by a mechanistic pathway presented in Scheme 2, involving initial photo-extrusion of N₂ to form the corresponding diradical intermediate **6**, which cyclizes to diradical **7** and is then converted to **8**, and the latter is photooxidized to **9a–c**. Partial hydrolysis of **9a–c** in the reaction media produces **10a–c**. Concurrently, cyclization of the tautomer of diradical intermediate **6** affords compounds **11a–c** which are further converted to **12a–c**. To confirm that **9a–c** and **11a–c** are the likely precursors of **10a–c** and **12a–c** respectively, **9a** and **11a** were isolated and then subjected to irradiation for 24 hours. In each case the corresponding reaction products **10a** and **12a** were obtained in quantitative yield. The structures of all isolated products were confirmed based on their full ¹H-NMR, ¹³C-NMR, and mass spectral data. Moreover, an X-ray crystal structure of compound **9a** was obtained (Figure 2 and Table 1).

Scheme 2. Mechanism of photolysis of *N*-(benzotriazol-1-yl-phenylmethylene)-*N'*-arylhydrazines **3a–c**.

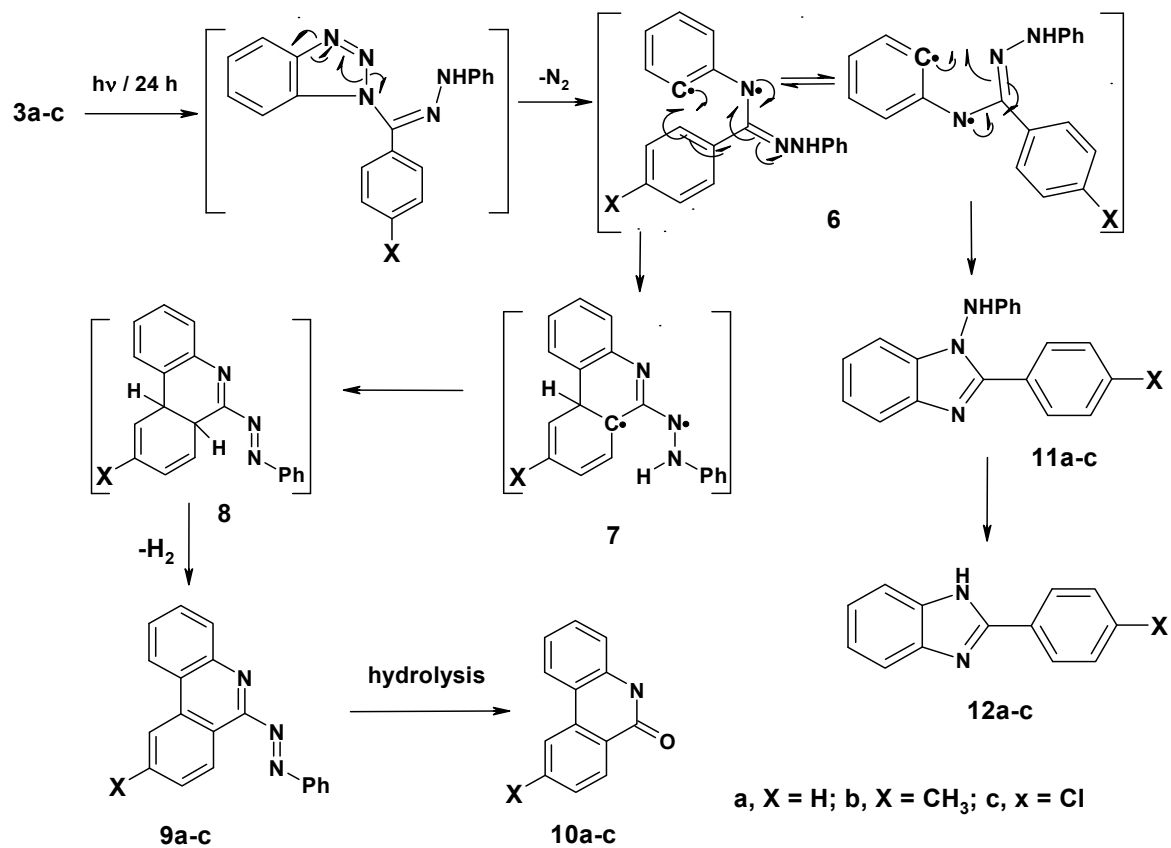


Figure 2. X-ray structure of compound **9a** (thermal ellipsoids).

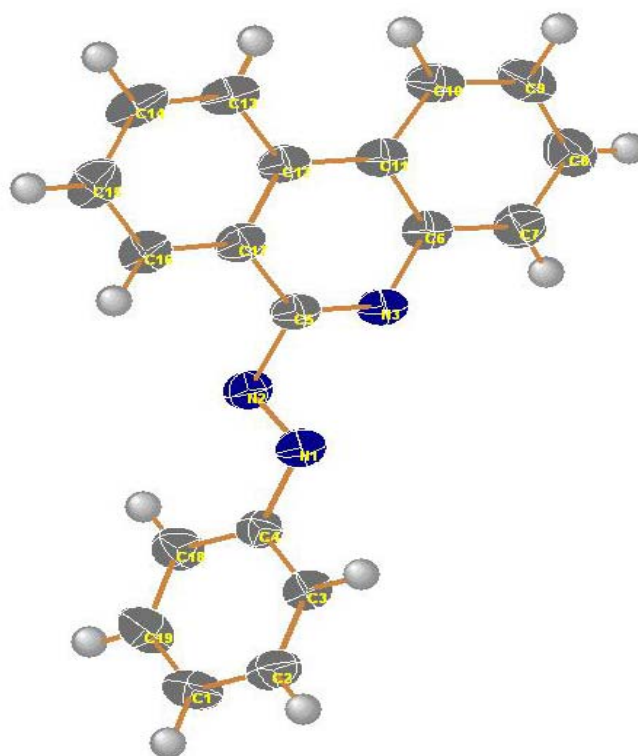


Table 1. Selected bond lengths and bond angles for compound **9a**.

Bond	Bond lengths (Å)	Bond	Bond angles (°)
N1-N2	1.2462 (13)	N1-N2-C5	112.58 (9)
N2-C5	1.4368 (14)	N3-C5-N2	117.90 (10)
N3-C6	1.3857 (15)	N2-C5-N17	116.62 (10)
N3-C5	1.2949 (15)	C5-N3-C6	117.99 (10)
C5-C17	1.4400 (16)	C6-C11-C12	118.27 (11)
N1-C4	1.4286 (14)	C10-C11-C12	124.11 (11)
C11-C12	1.4450 (18)	N3-C6-C11	122.68 (11)

Benzotriazol-1-yl-(2-arylhydrazono) acetic acid ethyl esters **4a,b** were prepared in 75–77% yield by stirring 1,2,3-benzotriazole with ethyl 2-chloro-2-(2-arylhydrazono)acetate in DCM/TEA for 24 hours at room temperature. Irradiation of **4a,b** in acetonitrile for 24 hour afforded 1-aryl-1*H*-benzimidazol-2-carboxylic acid ethyl esters **14a,b** (45–48% yield) and 1-aryl-1*H*,9*H*-benzo[4,5][1,2,3]triazolo[1,2-*a*]tetrazole-3-carboxylic acid ethyl esters **16a,b** (35–36% yield). It is assumed that initial N₂ extrusion affords the biradical intermediate **13** which then cyclized into **14a,b**. On the other hand, formation of photoproducts **16a,b** may be explained by assuming a intramolecular 1,6-H shift (Scheme 3). Single crystal X-ray structure analysis (Figures 3 and 4, Table 2) confirmed the structures of new compounds **4b** and **14b**.

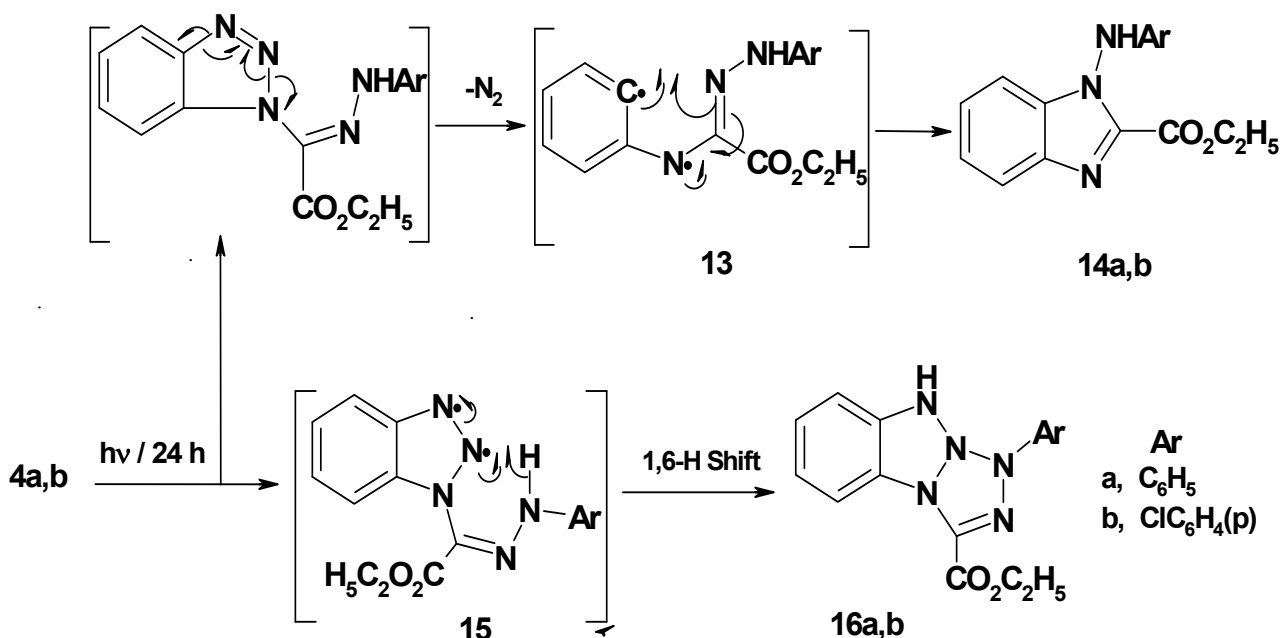
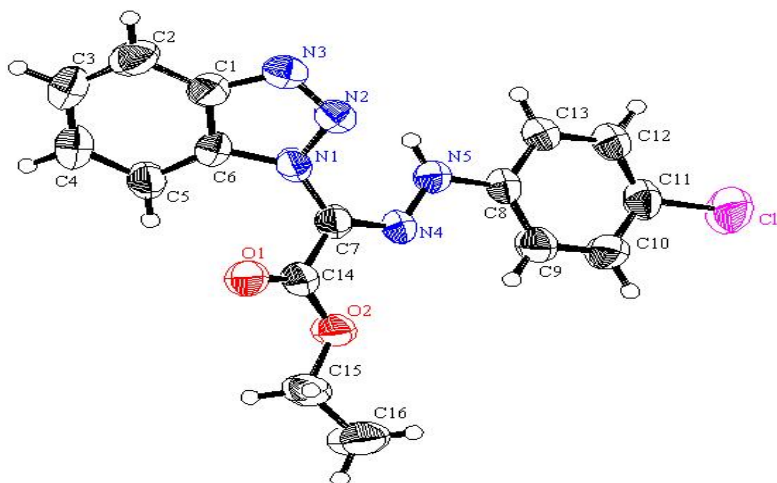
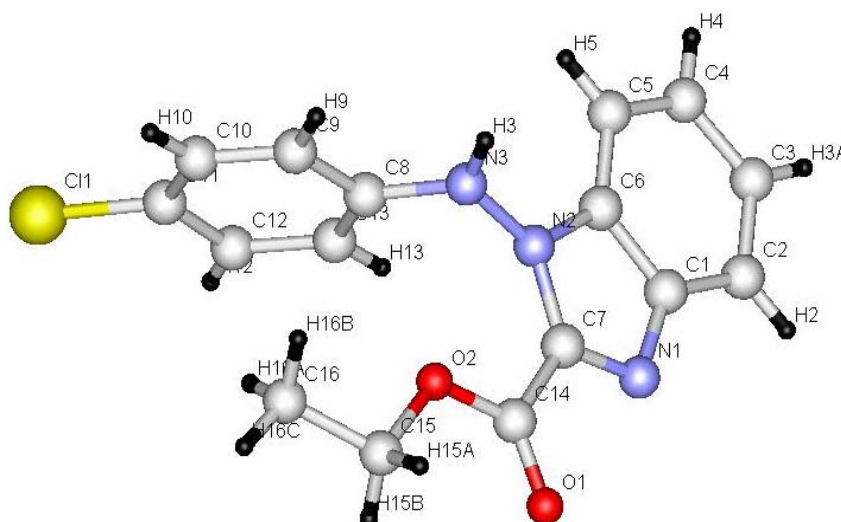
Scheme 3. Mechanism of photolysis of benzotriazol-1-yl-(2-arylhydrazono)-acetic acid ethyl esters **4a,b**.

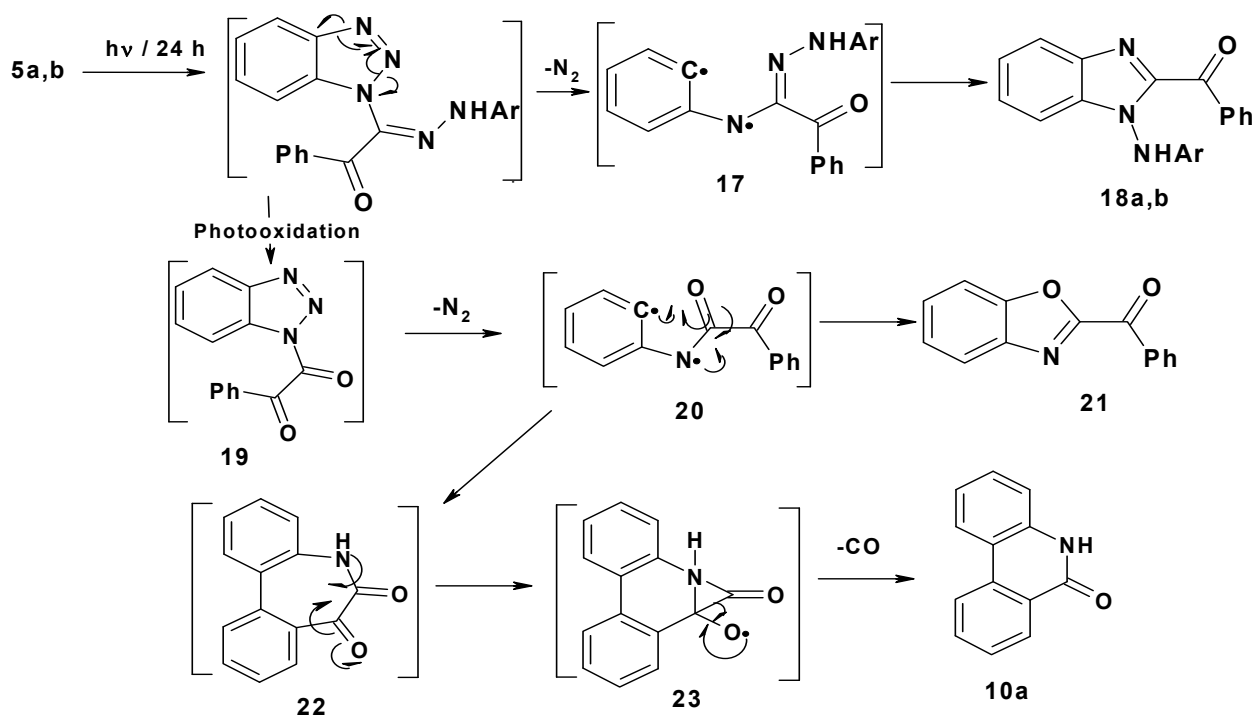
Figure 3. ORTEP drawing of **4b**.**Figure 4.** Ball and stick drawing of **14b**.**Table 2.** Selected bond lengths and bond angles for compounds **4b** and **14b**.

4b Bond	Bond lengths (Å)	Bond	Bond angles (°)	14b Bond	Bond lengths (Å)	Bond	Bond angles (°)
N1-C6	1.375 (6)	N1-C6-C1	104.8 (4)	N1-C1	1.380 (10)	C1-N1-C7	104.4 (6)
N1-C7	1.409 (6)	N1-C7-C14	117.1 (4)	N1-C7	1.318 (10)	N1-C7-N2	114.1 (7)
N4-C7	1.301 (6)	N1-C7-N4	125.3 (4)	N2-C7	1.375 (9)	N3-N2-C7	130.6 (6)
C7-C14	1.477 (7)	N1-N2-N3	108.5 (4)	N2-N3	1.372 (9)	N2-C6-C5	131.6 (8)
N5-C8	1.408 (6)	N2-N1-C7	120.3 (4)	N2-C6	1.405 (10)	N2-C7-C14	126.8 (7)
N4-N5	1.328 (6)	N5-C8-C13	118.2 (5)	C7-C14	1.495 (11)	N1-C1-C6	111.1 (7)
N3-C1	1.386 (7)	N3-C1-C6	109.2 (4)	N3-C8	1.409 (10)	O2-C14-C7	112.7 (7)

Finally, irradiation of 2-arylhydrazono-2-(benzotriazol-1-yl)-1-phenylethanones **5a,b** afforded 1-arylamino-2-benzoylbenzimidazoles **18a,b** (25–30%), 2-benzoylbenzoxazole **21** (24–27%) and phenantheridin-6(5*H*)-one **10a** (15–17%). The suggested mechanism proposed for this photoreaction is shown in Scheme 4. Initial photo-extrusion of N₂ forms the corresponding diradical intermediate **17**,

followed by cyclization to yield **18a,b**. On the other hand, photooxidation of **5a,b** afforded 1-benzotriazole-2-phenylethan-1,2-dione **19**, which upon elimination of N_2 formed diradical **20**, which either cyclizes to yield 2-benzoylbenzoxazole **21** in (24–27%) or cyclizes to **22**, which spontaneously loses CO through intermediate **23** to produce phenanthradin-6(5*H*)-one **10a** in 15–17% yield.

Scheme 4. Mechanism of photolysis of 2-arylhydrazono-2-(benzotriazol-1-yl)-1-phenylethanones **5a,b**.



The structure of all new compounds were assigned by spectroscopic and analytical methods. The structure of **21** is readily assigned based on 2D-NMR results. The 1H - and ^{13}C -NMR signal assignments and the H-C correlation from the HMBC 2-D experiments are displayed in Figure 5. Table 3 summarizes the absorption maxima (λ_{max}) and the photoproducts of substrates **3a–c**, **4a,b** and **5a,b**. The fact that the substituents R affected the nature of the products much more than the substituted Ar may be attributed to the strong influence of the substituents on the formed biradicals.

Figure 5. H-C Correlations in the HMBC 2-D experimental of compound **21**.

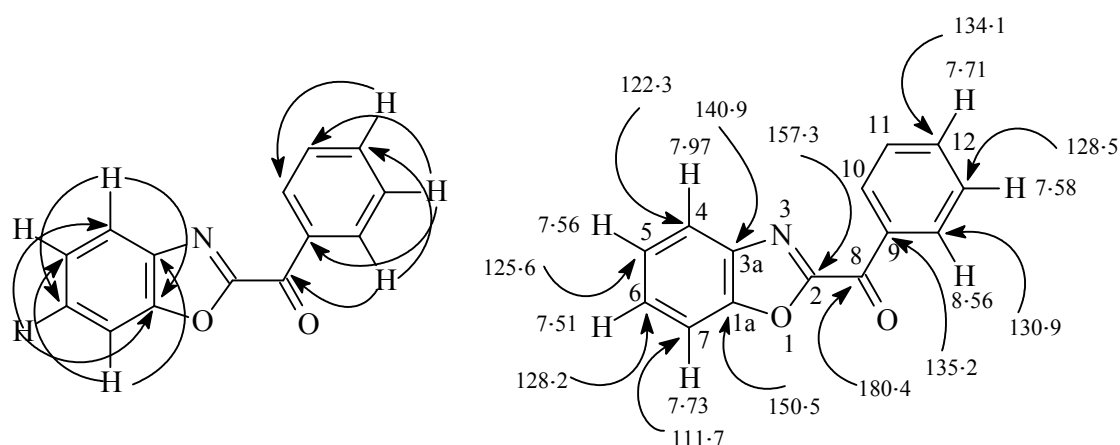


Table 3. Photoproducts formed by irradiation of compounds **3a–c**, **4a,b** and **5a,b** and yield.

Comp	R	Ar	$\lambda_{\max}$	Photo-products and yields (%)							
				9	10	11	12	14	16	18	21
3a	C ₆ H ₅	C ₆ H ₅	244, 338	51	16	12	10	-	-	-	-
3b	CH ₃ C ₆ H ₄ (<i>p</i>)	C ₆ H ₅	247, 347	48	18	14	8	-	-	-	-
3c	ClC ₆ H ₄ (<i>p</i>)	C ₆ H ₅	243, 392	50	15	10	9	-	-	-	-
4a	CO ₂ C ₂ H ₅	C ₆ H ₅	244, 370	-	-	-	-	48	36	-	-
4b	CO ₂ C ₂ H ₅	ClC ₆ H ₄ (<i>p</i>)	245, 355	-	-	-	-	45	35	-	-
5a	COC ₆ H ₅	C ₆ H ₅	253, 345	-	15	-	-	-	-	25	27
5b	COC ₆ H ₅	CH ₃ C ₆ H ₄ (<i>p</i>)	256, 379	-	17	-	-	-	-	30	24

3. Experimental

3.1. General

All melting points were recorded on a Gallenkamp apparatus. IR spectra were recorded using KBr pellets on a Perkin-Elmer System 2000 FT-IR spectrophotometer. ¹H- and ¹³C-NMR spectra were recorded on Bruker DPX 400 MHz or Avance^{II} 600 MHz super-conducting NMR spectrometers with proton spectra measured at 400, 600 MHz and carbon spectra at 100 and 150 MHz, respectively. Mass spectra were measured on a VG Auto-spec-Q (high resolution, high performance, tri-sector GC/MS/MS) and with LCMS using Agilent 1100 series LC/MSD with an API-ES/APCI ionization mode. Microanalyses were performed on LECO CH NS-932 Elemental Analyzer. The UV/VIS absorption spectra were recorded using a Varian Cary 5 instrument in the wave length range 200–450 nm using dry clean quartz cuvette of 1.0 cm path length. X-Ray analysis were performed using a Rigaku Rapid II diffractometer.

3.2. Synthesis of Starting Compounds **4a,b**

To a solution of 1,2,3-benzotriazole (3.57 g, 30 mmol), in DCM (50 mL), TEA (5 drops) and ethyl 2-chloro-2-(2-arylhydrazono)acetate (30 mmol) were added [15]. The mixture was stirred at room temperature for 24 hours, and then diluted with CH₂Cl₂ (150 mL), washed successively with dil. HCl (6 M, 20 mL), satd. aq. NaHCO₃ (150 mL), and water and then dried over anhydrous Na₂SO₄. The solvent was then evaporated *in vacuo*, and the residue was crystallized from ethanol to give **4a,b**.

Benzotriazol-1-yl-phenylhydrazono-acetic acid ethyl ester (4a). Colorless crystals, yield 7.2 g (77%), m.p. 183–184 °C. MS: *m/z* (%) = 309 (M⁺, 15), 281 (35), 208 (80). IR (KBr, cm⁻¹): 3060, 2982, 1683, 1598, 1540, 1501, 1414, 1312, 1235, 1187, 1019, 759. ¹H-NMR (400 MHz, CDCl₃): δ 9.69 (br, 1H, NH), 8.01 (d, 1H, *J* = 8.4 Hz), 7.59 (t, 1H, *J* = 8.0 Hz), 7.49 (d, 1H, *J* = 8.4 Hz), 7.43 (t, 1H, *J* = 8.0 Hz), 7.38–7.32 (m, 4H), 7.09 (t, 1H, *J* = 8.4 Hz), 4.41 (q, 2H, *J* = 7.0 Hz), 1.40 ppm (t, 3H, *J* = 7.0 Hz). ¹³C-NMR (100 MHz, CDCl₃): δ 160.3, 144.9, 141.6, 132.5, 129.4, 128.9, 125.0, 123.8, 119.9, 118.5, 115.0, 111.2, 62.3, 14.3 ppm. Anal. Calcd. for C₁₆H₁₅N₅O₂ (309.3): C, 62.13; H, 4.89; N, 22.64. Found: C, 62.10; H, 4.80; N, 22.55.

Benzotriazol-1-yl-p-chlorophenylhydrazono-acetic acid ethyl ester (4b). Pale yellow crystals, yield 7.80 g (75%), m.p. 156–158 °C. MS: m/z (%) = 343 (M^+ , 10), 315 (30), 286 (35). IR (KBr, cm^{-1}): 3094, 2986, 1686, 1571, 1547, 1489, 1401, 1282, 1235, 1172, 1148, 1092, 1061, 832. ^1H -NMR (400 MHz, CDCl_3): δ 9.77 (br, 1H, NH), 8.03 (d, 1H, $J = 8.4$ Hz), 7.60 (dt, 1H, $J = 7.8, 1.2$ Hz), 7.49 (d, 1H, $J = 8.4$ Hz), 7.44 (dt, 1H, $J = 7.8, 1.2$ Hz), 7.32 (d, 2H, $J = 8.4$ Hz), 7.24 (d, 2H, $J = 8.4$ Hz), 4.40 (q, 2H, $J = 6.8$ Hz), 1.24 ppm (t, 3H, $J = 6.8$ Hz). ^{13}C -NMR (100 MHz, CDCl_3): δ 160.1, 145.0, 140.4, 132.4, 129.5, 129.1, 128.7, 125.2, 120.0, 119.1, 116.2, 111.3, 62.4, 14.3 ppm. (HRMS = 343.0831, requires $\text{C}_{16}\text{H}_{14}\text{ClN}_5\text{O}_2$ 343.0830).

3.3. Irradiation Using a Low Pressure Mercury Arc-Lamp

Each of the substrates **3a–c**, **4a,b** and **5a,b** (10.0 mmol) was dissolved in acetonitrile (250 mL) in a number of quartz tubes (10×25 mL) and introduced to irradiate for 24 hours at room temperature (RT). The progress of each reaction was monitored by using TLC. The solvent was removed *in vacuo* and the resulting residue was subjected to column chromatography on silica gel using ethyl acetate/petroleum ether (b.p. 60–80 °C) as the eluent to give the corresponding products.

Phenanthridin-6-yl-2-phenyldiazine (9a). Red crystals from ethanol, m.p. 158–160 °C. MS: m/z (%) = 283 (M^+ , 10), 254 (100), 178 (70). IR (KBr, cm^{-1}): 3061, 3004, 2957, 1611, 1562, 1527, 1484, 1349, 1193, 925, 763. ^1H -NMR (600 MHz, $\text{DMSO}-d_6$): δ 8.98 (d, 1H, $J = 7.8$ Hz), 8.88 (d, 1H, $J = 8.4$ Hz), 8.55 (d, 1H, $J = 8.0$ Hz), 8.18 (d, 1H, $J = 8.0$ Hz), 8.15 (dd, 2H, $J = 7.8, 1.2$ Hz), 8.07 (t, 1H, $J = 7.6$ Hz), 7.88 (t, 1H, $J = 7.8$ Hz), 7.84 (t, 1H, $J = 7.6$ Hz), 7.81 (t, 1H, $J = 7.6$ Hz), 7.73–7.70 ppm (m, 3H). ^{13}C -NMR (150 MHz, $\text{DMSO}-d_6$): δ 159.6, 152.5, 142.4, 133.8, 133.0, 131.9, 130.5, 129.7, 129.6, 128.3, 127.9, 125.7, 124.5, 123.4, 123.0, 122.9, 122.1 ppm. Anal. Calc. for $\text{C}_{19}\text{H}_{13}\text{N}_3$ (283.3): C, 80.54; H, 4.62; N, 14.83. Found: C, 80.50; H, 4.60; N, 14.79.

9-Methylphenanthridin-6-yl-2-phenyldiazine (9b). Red crystals from ethanol, m.p. 140–142 °C. MS: m/z (%) = 297 (M^+ , 10), 268 (100), 192 (40). IR (KBr, cm^{-1}): 3056, 2918, 1617, 1509, 1483, 1373, 1308, 1189, 1022, 822, 760. ^1H -NMR (400 MHz, CDCl_3): δ 8.62 (dd, 2H, $J = 8.4, 2.0$ Hz), 8.50 (s, 1H), 8.31 (d, 1H, $J = 8.0$ Hz), 8.21 (dd, 2H, $J = 8.4, 2.0$ Hz), 7.76 (t, 1H, $J = 7.8$ Hz), 7.70 (t, 1H, $J = 7.8$ Hz), 7.63–7.58 (m, 4H), 2.70 ppm (s, 3H, CH_3). ^{13}C -NMR (150 MHz, $\text{DMSO}-d_6$): δ 159.5, 153.3, 143.3, 141.9, 134.9, 132.4, 131.6, 129.4, 129.2, 129.1, 127.4, 126.3, 125.0, 124.0, 122.1, 121.9, 121.7, 22.5 ppm. Anal. Calc. for $\text{C}_{20}\text{H}_{15}\text{N}_3$ (297.4): C, 80.78; H, 5.08; N, 14.13. Found: C, 80.70; H, 5.00; N, 14.10.

9-Chlorophenanthridin-6-yl-2-phenyldiazine (9c). Red crystals from ethanol, m.p. 136–138 °C. MS: m/z (%) = 319 (M^{+2} , 10), 317 (M^+ , 20), 268 (100). IR (KBr, cm^{-1}): 3062, 3007, 2957, 1605, 1512, 1486, 1380, 1309, 1143, 1015, 910, 761. ^1H -NMR (400 MHz, CDCl_3): δ 8.70 (d, 1H, $J = 8.4$ Hz), 8.66 (s, 1H), 8.53 (d, 1H, $J = 8.0$ Hz), 8.33 (d, 1H, $J = 7.8$ Hz), 8.19 (dd, 2H, $J = 7.8, 1.2$ Hz), 7.81 (t, 1H, $J = 7.8$ Hz), 7.73 (t, 1H, $J = 8.0$ Hz), 7.70 (dd, 1H, $J = 8.0, 1.2$ Hz), 7.62–7.58 ppm (m, 3H). ^{13}C -NMR (100 MHz, CDCl_3): δ 158.9, 153.3, 143.6, 138.0, 135.9, 132.7, 131.7, 129.9, 129.2, 128.3, 128.2, 127.9, 127.3, 124.1, 124.0, 122.2, 122.0 ppm. Anal. Calc. for $\text{C}_{19}\text{H}_{12}\text{ClN}_3$ (317.8): C, 71.81; H, 3.81; N, 13.22. Found: C, 71.75; H, 3.80; N, 13.17.

Phenanthridin-6(5H)-one (10a). White crystals, mp. 289–290 °C (lit. [13] m.p. 290–292 °C). MS: m/z (%) = 195 (M^+ , 100), 167 (20), 139 (15). $^1\text{H-NMR}$ (400 MHz, DMSO- d_6): δ 11.70 (br, 1H, NH), 8.52 (d, 1H, J = 8.0 Hz), 8.40 (d, 1H, J = 8.0 Hz), 8.33 (dd, 1H, J = 8.0, 1.2 Hz), 7.82 (dt, 1H, J = 8.0, 1.2 Hz), 7.65 (t, 1H, J = 8.0 Hz), 7.49 (dt, 1H, J = 8.0, 1.4 Hz), 7.36 (dd, 1H, J = 8.0, 1.4 Hz), 7.27 ppm (dt, 1H, J = 8.0, 1.4 Hz). $^{13}\text{C-NMR}$ (100 MHz, DMSO- d_6): δ 160.9, 136.6, 134.3, 132.9, 129.6, 128.0, 127.5, 125.7, 123.3, 122.7, 122.3, 117.6, 116.1 ppm.

9-Methylphenanthridin-6(5H)-one (10b). Colorless crystals, m.p. 251–253 °C (lit. [16] m.p. 250–251 °C). MS: m/z (%) = 209 (M^+ , 100), 180 (25). $^1\text{H-NMR}$ (600 MHz, DMSO- d_6): δ 11.58 (br, 1H, NH), 8.36 (d, 1H, J = 7.8 Hz), 8.32 (s, 1H), 8.19 (d, 1H, J = 8.0 Hz), 7.46 (dt, 2H, J = 8.4, 1.6 Hz), 7.34 (dd, 1H, J = 8.0, 1.4 Hz), 7.25 (dt, 1H, J = 8.4, 1.2 Hz), 2.51 ppm (s, 3H, CH_3). $^{13}\text{C-NMR}$ (150 MHz, DMSO- d_6): δ 160.8, 143.0, 136.7, 134.2, 129.4, 129.1, 127.5, 123.4, 123.2, 122.5, 122.1, 117.5, 116.1, 21.5 ppm.

9-Chlorophenanthridin-6(5H)-one (10c). Colorless crystals, m.p. 268–270 °C. LCMS: m/z = 232 ($M + 3$), 230 ($M + 1$). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 11.53 (br, 1H, NH), 8.43 (d, 1H, J = 8.0 Hz), 8.25 (d, 1H, J = 8.0 Hz), 8.14 (d, 1H, J = 8.4 Hz), 7.80 (t, 1H, J = 7.8 Hz), 7.64 (t, 1H, J = 7.8 Hz), 7.45 (d, 1H, J = 8.0 Hz), 7.38 ppm (t, 1H, J = 7.8 Hz) [13].

1-Anilino-2-phenylbenzimidazole (11a). Colorless crystals, m.p. 211–212 °C (lit. [14] m.p. 210–212 °C). LCMS: m/z = 286 ($M + 1$). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.07 (m, 2H), 7.86 (d, 1H, J = 8.0 Hz), 7.46–7.43 (m, 3H), 7.34 (t, 1H, J = 7.8 Hz), 7.32–7.24 (m, 3H), 7.21 (t, 1H, J = 8.4 Hz), 7.00 (t, 1H, J = 7.6 Hz), 6.81 (br, 1H, NH), 7.72 ppm (d, 2H, J = 7.8 Hz).

1-Anilino-2-p-tolylbenzimidazole (11b). Colorless crystals, m.p. 233–235 °C (lit. [14] m.p. 234–236 °C). LCMS: m/z = 300 ($M + 1$). $^1\text{H-NMR}$ (CDCl_3): δ 8.05 (d, 2H, J = 8.0 Hz), 7.82 (d, 1H, J = 8.0 Hz), 7.44 (d, 2H, J = 8.4 Hz), 7.33 (t, 1H, J = 7.8 Hz), 7.28 (m, 2H), 7.17 (d, 1H, J = 7.8 Hz), 7.02 (t, 2H, J = 7.8 Hz), 6.81 (br, 1H), 6.67 (d, 2H, J = 8.0 Hz), 2.40 ppm (s, 3H, CH_3).

1-Anilino-2-p-chlorophenylbenzimidazole (11c). Colorless crystals, m.p. 230–233 °C (lit. [14] m.p. 232–234 °C). LCMS: m/z = 321 ($M + 2$), 320 ($M + 1$). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.05 (dd, 2H, J = 8.4, 1.6 Hz), 7.86 (d, 1H, J = 8.4 Hz), 7.43 (dd, 2H, J = 8.4, 1.6 Hz), 7.35 (t, 1H, J = 8.0 Hz), 7.30–7.25 (m, 3H), 7.17 (d, 1H, J = 8.0 Hz), 7.02 (t, 1H, J = 7.8 Hz), 6.81 (br, 1H, NH), 6.67 ppm (d, 2H, J = 8.0 Hz).

2-Phenyl-1H-benzimidazole (12a). Colorless crystals, m.p. 290–292 °C (lit. [14] m.p. 289–290 °C). LCMS: m/z = 195 ($M + 1$). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.12 (m, 2H), 7.68 (m, 2H), 7.45 (m, 3H), 7.29 ppm (m, 3H, J 7.8 Hz).

2-p-Tolyl-1H-benzimidazole (12b). Colorless crystals, m.p. 271–272 °C (lit. [14] m.p. 269–272 °C). LCMS: m/z = 209 ($M + 1$). $^1\text{H-NMR}$ (400 MHz, DMSO- d_6): δ 12.78 (br, 1H, NH), 8.06 (d, 2H, J = 8.0 Hz), 7.56 (m, 2H), 7.32 (d, 2H, J = 8.0 Hz), 7.16 (m, 2H), 2.33 ppm (s, 3H, CH_3).

2-p-Chlorophenyl-1H-benzimidazole (12c). Colorless crystals, m.p. 291–292 °C (lit. [14] m.p. 289–291 °C). LCMS: m/z = 231 ($M + 3$), 229 ($M + 1$). $^1\text{H-NMR}$ (400 MHz, DMSO- d_6): δ 12.98 (br, 1H, NH), 8.18 (d, 2H, $J = 8.4$ Hz), 7.58 (d, 2H, $J = 8.4$ Hz), 7.56 (m, 2H), 7.18 ppm (m, 2H).

1-Anilino-1H-benzimidazole-2-carboxylic acid ethyl ester (14a). Colorless crystals from ethanol, m.p. 142–144 °C. MS: m/z (%) = 281 (M^+ , 70), 253 (35), 208 (80). IR (KBr, cm^{-1}): 3244, 3054, 2973, 1683, 1600, 1556, 1490, 1392, 1240, 1157, 1053, 734. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 7.95 (d, 1H, $J = 8.4$ Hz), 7.76 (br, 1H, NH), 7.56 (dd, 1H, $J = 8.4, 1.2$ Hz), 7.45 (d, 1H, $J = 8.4$ Hz), 7.36 (dt, 1H, $J = 7.8, 1.4$ Hz), 7.12 (t, 2H, $J = 8.4$ Hz), 6.98 (t, 1H, $J = 7.8$ Hz), 6.54 (d, 2H, $J = 8.0$ Hz), 4.43 (q, 2H, $J = 6.8$ Hz), 1.42 ppm (t, 3H, $J = 6.8$ Hz). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 159.8, 144.7, 141.2, 132.1, 128.9, 128.4, 124.5, 123.3, 119.6, 118.1, 114.5, 110.7, 61.7, 13.7 ppm. Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_2$ (281.3): C, 68.30; H, 5.37; N, 14.94. Found: C, 68.25; H, 5.35; N, 14.89.

1-p-Chloroanilino-1H-benzimidazole-2-carboxylic acid ethyl ester (14b). Colorless crystals from ethanol, m.p. 146–148 °C. MS: m/z (%) = 315 (M^+ , 100), 242 (65), 149 (80). IR (KBr, cm^{-1}): 3224, 3032, 2979, 1723, 1599, 824. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 7.97 (d, 1H, $J = 8.4$ Hz), 7.76 (br, 1H, NH), 7.56 (dd, 1H, $J = 8.4, 1.4$ Hz), 7.53 (dt, 1H, $J = 8.4, 1.4$ Hz), 7.45 (dt, 1H, $J = 7.8, 1.4$ Hz), 7.18 (d, 2H, $J = 8.4$ Hz), 6.48 (d, 2H, $J = 8.4$ Hz), 4.43 (q, 2H, $J = 6.8$ Hz), 1.42 ppm (t, 3H, $J = 6.8$ Hz). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 159.2, 145.6, 138.9, 138.8, 135.5, 129.5, 127.6, 126.9, 124.7, 122.1, 115.1, 110.8, 62.7, 14.1 ppm. (HRMS = 315.0769; requires 315.0768).

1-Phenyl-1H,9H-benzo[4,5][1,2,3]triazolo[1,2-a]tetrazole-3-carboxylic acid ethyl ester (16a). Pale yellow crystals from ethanol, m.p. 152–154 °C. MS: m/z (%) = 309 (M^+ , 25), 295 (10), 281 (50). IR (KBr, cm^{-1}): 3036, 2982, 1683, 1598, 1540, 1501, 1458, 1312, 1235, 1187, 1063, 1019, 759. $^1\text{H-NMR}$ (CDCl_3): δ 12.44 (s, 1H, NH), 8.16 (d, 1H, $J = 8.4$ Hz), 7.60–7.54 (m, 2H), 7.45 (tt, 1H, $J = 8.4, 1.6$ Hz), 7.37 (t, 2H, $J = 8.0$ Hz), 7.28 (d, 2H, $J = 8.4$ Hz), 7.12 (t, 1H, $J = 7.8$ Hz), 4.31 (q, 2H, $J = 7.2$ Hz), 1.22 ppm (t, 3H, $J = 7.2$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 161.9, 145.8, 142.3, 134.6, 130.1, 130.0, 128.83, 124.80, 124.76, 120.6, 115.5, 110.8, 62.9, 14.5 ppm. Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_5\text{O}_2$ (309.3): C, 62.13; H, 4.89; N, 22.64. Found: C, 62.07; H, 4.82; N, 22.65.

1-p-Chlorophenyl-1H,9H-benzo[4,5][1,2,3]triazolo[1,2-a]tetrazole-3-carboxylic acid ethyl ester (16b). Yellow crystals from ethanol, m.p. 156–158 °C. MS: m/z (%) = 343 (M^+ , 15), 315 (30), 126 (100). IR (KBr, cm^{-1}): 3094, 2986, 1680, 1571, 1547, 1489, 1401, 1282, 1235, 1172, 1148, 1062, 832. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 12.43 (s, 1H, NH), 8.15 (d, 1H, $J = 8.0$ Hz), 7.58–7.55 (m, 2H), 7.48–7.44 (m, 1H), 7.32 (d, 2H, $J = 8.4$ Hz), 7.22 (d, 2H, $J = 8.4$ Hz), 4.31 (q, 2H, $J = 7.2$ Hz), 1.23 ppm (t, 3H, $J = 7.2$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 161.3, 145.2, 140.3, 133.9, 129.6, 129.2, 128.3, 124.2, 120.1, 119.2, 116.1, 110.1, 62.4, 13.9 ppm. (HRMS = 343.0830; requires $\text{C}_{16}\text{H}_{14}\text{ClN}_5\text{O}_2$ 343.0831).

1-Anilino-2-benzoylbenzimidazole (18a). Yellow crystals, m.p. 216–218 °C. MS: m/z (%) = 313 (M^+ , 60), 279 (20), 167 (40), 149 (100). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.33 (dd, 2H, $J = 8.4, 1.6$ Hz), 8.12 (br, 1H, NH), 7.96 (d, 1H, $J = 8.0$ Hz), 7.70 (dt, 1H, $J = 8.4, 1.6$ Hz), 7.60 (dt, 1H, $J = 8.0, 1.4$ Hz), 7.53–7.42 (m, 3H), 7.34 (t, 1H, $J = 7.8$ Hz), 7.16 (t, 2H, $J = 8.0$ Hz), 6.90 (t, 1H, $J = 8.2$ Hz), 6.54 ppm

(d, 2H, $J = 7.8$ Hz). ^{13}C -NMR (100 MHz, CDCl_3): δ 185.7, 147.2, 144.7, 139.1, 135.7, 134.0, 131.2, 129.4, 128.3, 127.6, 126.9, 124.4, 122.4, 122.3, 113.8, 111.1 ppm. (HRMS = 313.1209; requires $\text{C}_{20}\text{H}_{15}\text{N}_3\text{O}$ 313.1207).

2-Benzoyl-1-*p*-toluidinobenzimidazole (18b). Pale yellow crystals, m.p. 226–228 °C. MS: m/z (%) = 327 (M^+ , 100), 223 (40), 195 (100). IR (KBr, cm^{-1}): 3331, 3061, 1648, 730. ^1H -NMR (400 MHz, CDCl_3): δ 8.34 (dd, 2H, $J = 8.4, 1.6$ Hz), 8.12 (br, 1H, NH), 7.99 (d, 1H, $J = 8.0$ Hz), 7.73 (d, 1H, $J = 8.4$ Hz), 7.64–7.50 (m, 3H), 7.34 (t, 1H, $J = 7.8$ Hz), 7.06 (t, 1H, $J = 8.0$ Hz), 6.99 (d, 2H, $J = 8.8$ Hz), 6.49 (d, 2H, $J = 8.8$ Hz), 2.22 ppm (s, 3H, CH_3). ^{13}C -NMR (100 MHz, CDCl_3): δ 185.4, 144.5, 137.8, 136.2, 134.6, 132.1, 131.5, 130.0, 129.8, 129.3, 128.9, 127.4, 126.1, 122.3, 114.1, 111.5, 20.6 ppm. (HRMS = 327.1366, requires $\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}$ 327.1366).

2-Benzoylbenzoxazole (21). Colorless crystals from ethanol, m.p. 136–138 (lit. [17] m.p. 139 °C). MS: m/z (%) = 223 (M^+ , 75), 195 (40), 105 (100). ^1H -NMR (600 MHz, CDCl_3): δ 8.56 (dd, 2H, $J = 8.4, 1.6$ Hz), 7.97 (d, 1H, $J = 8.4$ Hz), 7.73 (d, 1H, $J = 8.4$ Hz), 7.71 (t, 1H, $J = 8.0$ Hz), 7.58 (t, 2H, $J = 7.8$ Hz), 7.56 (t, 1H, $J = 7.8$ Hz), 7.51 ppm (t, 1H, $J = 7.8$ Hz). ^{13}C -NMR (150 MHz, CDCl_3): δ 180.4 (C), 157.3 (C), 150.5 (C), 140.9 (C), 135.2 (C), 134.1 (CH), 130.9 (2CH), 128.5 (2CH), 128.2 (CH), 125.6 (CH), 122.3 (CH), 111.7 (CH) ppm. Anal. Calcd. for $\text{C}_{14}\text{H}_9\text{NO}_2$ (223.3): C, 75.33; H, 4.06; N, 6.27. Found: C, 75.23; H, 4.05; N, 6.29.

4. Conclusions

The present study offers a new route for the synthesis of some new heterocyclic phenanthridin-6-yl-2-phenyldiazines. Some of these photoproducts **10a–c** have been shown to have efficient complexation properties with transition metals and exhibit interesting photo-emission and fluorescence properties [18,19]. It also shows that 1-substituted benzotriazole arylhydrazones behave photochemically in a different manner than in flash vacuum pyrolysis (FVP) or static pyrolysis (STP) reactions [12–14].

Acknowledgements

The support of the University of Kuwait received through research grant # SC 04/08 and the facilities of ANALAB/SAF (grants no. GS01/01, GS02/01, GS03/08) are gratefully acknowledged.

References and Notes

1. Hubert, A.J. Photochemistry of benzotriazole. *J. Chem. Soc. C* **1969**, *10*, 1334–1336.
2. Kazuo, T.; Mamoru, O.; Teijiro, Y. Thermal and photochemical decomposition of 4,5,6,7-tetrahydro-1,2,3-benzotriazole analogs. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3605–3607.
3. Kazuo, T.; Mamoru, O.; Teijiro, Y. Photochemical decomposition of benzotriazole. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 515–519.
4. Crow, W.D.; Wentrup, C. Cyanocyclopentadienes by pyrolysis of isatain and 1*H*-benzotriazole. *Chem. Commun.* **1968**, *17*, 1026–1027.

5. Mærky, M.; Doppler, Th.; Hansen, H.; Schmid, H. Photoreactions of 1-alkylbenzotriazoles with aromatic compounds. *Chimia* **1969**, *23*, 230-231.
6. Mærky, M.; Schmid, H.; Hansen, H. Photoreactions of 1-alkylbenzotriazoles. *J. Helv. Chim. Acta* **1979**, *62*, 2129-2153.
7. Booker-Milburn, K.I.; Wood, P.M.; Dainty, R.F.; Urquhart, M.W.; White, A.J.; Lyon, H.J.; Charmant, J.P. Photochemistry of benzotriazole: Unprecedented tautomer-selective intermolecular [2 + 2] photocycloaddition. *Org. Lett.* **2002**, *4*, 1487-1489.
8. Wander, P.A.; Cooper, C.B. The photochemistry of 1-alkenylbenzotriazoles: Methodology for the synthesis of indoles. *Tetrahedron* **1986**, *42*, 2985-2991.
9. Androsov, D.A.; Neckers, D.C. Photochemical study of tris(benzotriazol-1-yl)methane. *J. Org. Chem.* **2007**, *72*, 1148-1152 and references therein.
10. Katritzky, A.R.; Lan, X.; Yang, J.; Denisko, O. Properties and synthesis utility of *N*-substituted benzotriazoles. *Chem. Rev.* **1998**, *98*, 409-548.
11. Al-Jalal, N.; Al-Awadi, N.A.; Ibrahim, M.R.; Elnagdi, M.H. The photochemistry of 1-alkenyl-substituted-1,2,3-benzotriazoles leading to formation of indole and fused indole derivatives. *ARKIVOC* **2011**, *x*, 288-297.
12. Dib, H.H.; Al-Awadi, N.A.; Ibrahim, Y.A.; El-Dusouqui, O.M. Gas-phase thermolysis of benzotriazole derivatives. Part 2: Synthesis of benzimidazo[1,2-*b*] cinnolines, a novel heterocyclic ring system, by pyrolysis of benzotriazole derivatives, kinetics and mechanistic study. *Tetrahedron* **2003**, *59*, 9455-9464.
13. Al-Awadi, N.A.; George, B.; Dib, H.H.; Ibrahim, M.R.; Ibrahim, Y.A.; El-Dusouqui, O.M. Gas-phase thermolysis of benzotriazole derivatives. Part 3: Kinetic and mechanistic evidence for biradical intermediates in pyrolysis of aroylbenzotriazoles and related compounds. *Tetrahedron* **2005**, *61*, 8257-8263.
14. Al-Awadi, H.; Ibrahim, M.R.; Ibrahim, Y.A.; Al-Awadi, N.A. Gas-phase thermolysis of benzotriazole derivatives. Part 4: Pyrolysis of 1-acylbenzotriazole phenylhydrazones. Interesting direct route towards *N*-aminobenzimidazole. *J. Heterocycl. Chem.* **2008**, *45*, 723-727.
15. Shawali, A.S.; Eweiss, N.F.; Hassaneen, H.M.; Sami, M. Synthesis and rearrangement of ethyl aryloxyglyoxalate arylhydrazones. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 365-366.
16. Dubost, E.; Magnelli, R.; Cailly, T.; Legay, R.; Fabis, F.; Rault, S. General methods for the synthesis of substituted phenanthradin-6(5H)-ones using a KOH-mediated anionic ring closure as the key step. *Tetrahedron* **2010**, *66*, 5008-5016.
17. Xiao-Feng, W.; Pazhamala, A.; Helfried, N.; Matthias, B. Palladium-catalyzed carbonylative C-H activation of heteroarenes. *Angew. Chem. Int. Ed.* **2010**, *49*, 7316-7319.
18. Oliver, M.; Christian, L.; Evelyn, F.; Klaus, K.; Nicolle, L.; Christian, S.; Jens, R.; Gerhard, W.; Soichi, W. Transition metal cyclometalated complexes with chelating bidentate *N*-heterocyclic carben-heterocycle ligands as light-emitting materials for organic light-emitting devices. WO 2008-EP64064 20081017, 2008 (*Chem. Abstr.* **2009**, *150*, 472908).
19. Morgan, A.R.; Severini, A.; James, M.N.G. Methods for assaying proteinases and proteinase inhibitors. WO 1992-CA18 19920115, 1992 (*Chem. Abstr.* **1992**, *117*, 187290).

20. Crystallographic data of (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 852370 (**9a**), CCDC 852374 (**4b**) and CCDC 852389 (**14b**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Sample Availability: Samples of the compounds **4**, **9**, **14**, **18** and **21** are available from the authors.

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