New Unexpected Products during Heteroannulation of 1,4-Naphthoquinone Derivatives

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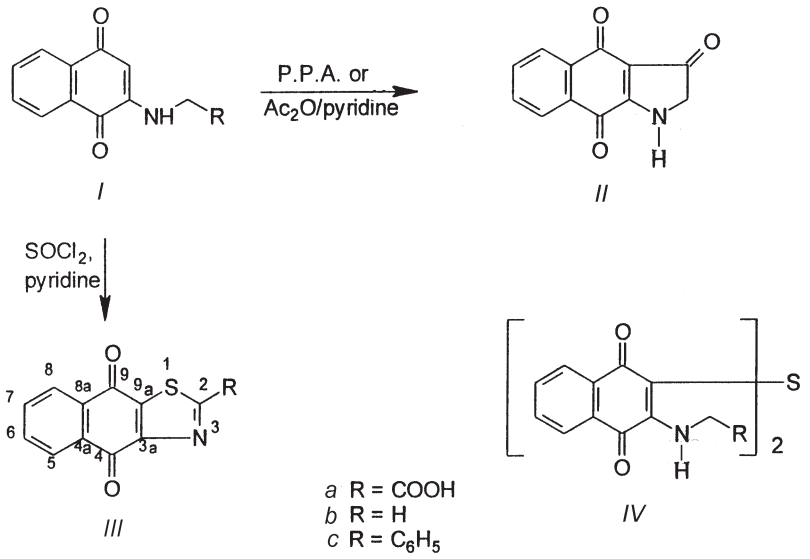
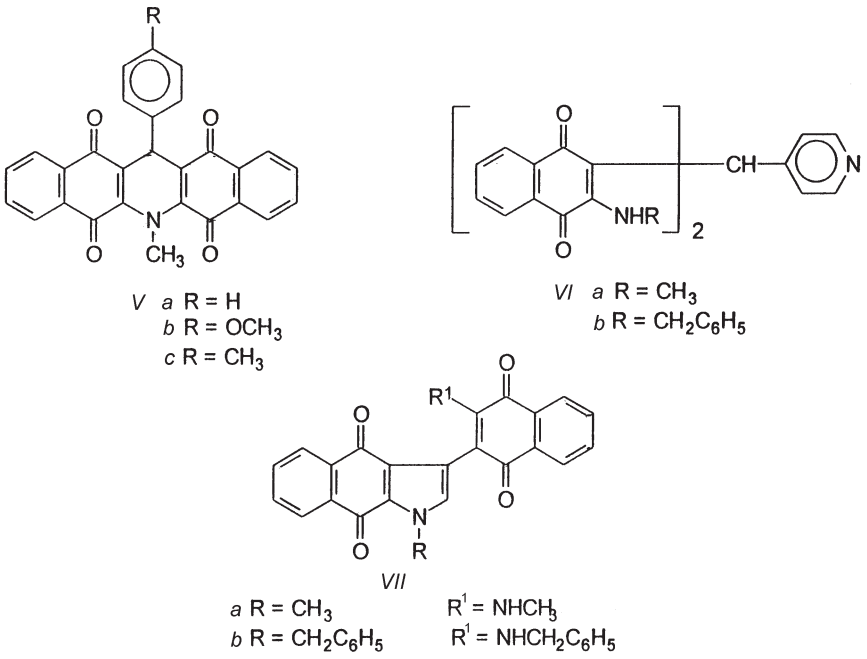
A series of substituted heterocyclic 1,4-naphthoquinones as naphthothiazoles, dinaphthopyridines, benzoindoles, benzoquinolines, naphthoimidazoles, naphthoimidazolines, and benzothioxoquinazoline were synthesized from 2-alkylamino-1,4-naphthoquinone. The structures of these products were established by means of spectral data. Some of these compounds were unexpected.

During the past few years, a number of interesting articles which report on the importance of heterocyclic quinones have been published [1—9]. Especially in the last ten years, some programs directed towards the synthesis of annulated heterocyclic naphthoquinones have been reported [10—13].

Attempted intramolecular cyclodehydration of 2-(carboxymethylamino)-1,4-naphthoquinone [14] (*Ia,* Scheme 1) with polyphosphoric acid or acetic anhydride in pyridine met with failure to give compound *II* and the starting material was recovered unchanged. This result disagrees with that reported [15]. Hence, attention was turned to finding another mode of cyclization for *Ia.* This compound was treated with thionyl chloride in pyridine to give the corresponding acid chloride which subsequently could be cyclized to *IIa*, but an interesting rearranged product which was shown to be naphthothiazole derivative *IIIa* was achieved. The conspicuous absence of the signals of NH and CH_2 protons in the ^{1}H NMR spectrum, the presence of twelve different carbons in the ^{13}C NMR spectrum, disappearance of NH band in IR spectrum and a molecular ion peak in mass spectrum at m/z = 259 (68 %) corroborated the structure *IIIa* for this compound. This elegant reaction and appearance of *IIIa* prompted us to widen this reaction with suitable 2-alkylamino-1,4-naphthoquinones [16, 17] such as *Ib* and *Ic* which also gave the corresponding *IIIb* and *IIIc*, respectively by the same manner. On the other hand, when the reaction was tried in the absence of pyridine, thiazole derivatives were not formed, but the sulfide derivatives *IV* were achieved. The literature survey



Scheme 1

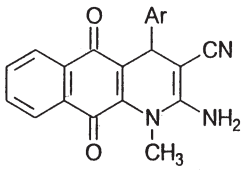


Scheme 2

presented an analogous behaviour and it is mechanistic rationale [18]. Elemental analysis, IR, ^{1}H NMR, ^{13}C NMR, and mass spectra were consistent with all structures.

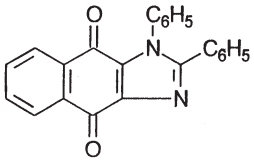
In continuation of the investigations for preparation of annulated heterocyclic naphthoquinone, dinaphthopyridine derivatives *V* (Scheme 2) were obtained from the reaction of *Ib* with aromatic aldehydes in methanolic hydrochloric acid. ^{1}H NMR spectra of *Va* and *Vb* showed two singlets at δ = 3.2—3.8 (NCH_3), 5.41—5.92 (CH) and multiplet at 7.11—7.96 (H_{arom}). The ^{13}C NMR spectra of *Va* and *Vb* were characterized by the presence of signals at 138.61, 138.59 and 23.11, 22.95 due to C-8 and NCH_3, respectively, beside all other carbons in their expected regions. Also, the mass spectrum of *Va* showed the molecular ion peak at m/z = 431 (80 %). In case of using 4-pyridinecarbaldehyde the cyclization reaction did not occur, but bis[3-(alkylamino)naphthoquinon-2-yl]-(4-pyridyl)methane *VI* was obtained. ^{1}H NMR of compound *VI* showed an A_2B_2 system at 9.02—9.25 due to the pyridyl protons and signal at 6.21—6.33 due to CH protons, beside all other expected signals of the products *VIa* and *VIb*. Also, ^{13}C NMR spectrum supported the structure *VIa*. Mass spectrum of *VIb* showed molecular ion peak at m/z = 616 (60 %). Unexpectedly, reaction of *Ib* or *Ic* with glyoxal sodium bisulfide in aqueous ethanolic sodium carbonate yielded 1-alkyl-3-[2-(alkylamino)naphthoquinon-3-yl]benzo[*f*]indole-4,7-dione derivatives *VII*. Similar type of other synthesis has been recorded [19]. ^{1}H NMR spectra of *VII* exhibited broad signals at 2.33—2.41 due to C-2—H of indole ring. The mass spectral studies of *VIIa* showed a molecular ion peak at m/z = 396 (70 %) and other characteristic peaks at 211 (90 %) and 187 (39 %).

The reaction of *Ib* with arylidene malononitrile in the presence of triethylamine afforded benzo[*g*]quinoline derivatives *VIII* (Scheme 3) in excellent yields. Analogous other synthesis has been reported [20]. The structure *VIII* was assigned on the basis of elemental and spectral studies. The ^{1}H NMR spectra revealed amino protons at δ = 3.81—4.0, methinyl protons at 4.60—4.73. Also, IR spectra showed bands for both conjugated cyano group at $\tilde{\nu}$ = 2220 cm^{-1} and amino group at 3200—3300 cm^{-1}, in addition to carbonyl band around 1680 cm^{-1}. ^{13}C NMR spectrum of *VIIIa* showed signals characteristeristic of all carbons in its structure. Equimolecular quantity of *Ic* and nitrosobenzene in acetic anhydride was heated in oil bath at 200 °C for 1 h to give naphtho[2,3-*d*]imidazole derivative *IX* in 50 % yield, improved yield (80 %) of *IX* was obtained when nitrosobenzene was taken in excess (three-fold). Similar other synthesis was recorded [21]. The structure *IX* was assigned by satisfactory spectral data, especially the presence of the molecular ion peak in its mass spectrum at m/z = 350 (70 %), also, ^{1}H NMR spectrum was devoid from signals of NH, CH_2, and vinylic proton which are present at 8.61, 3.51, and 5.82, respectively in *Ic*. Also, IR spectrum of this compound does not contain absorption in the region of NH band. ^{13}C NMR spectrum confirms this assignment which is shown by nonequivalent substituted benzenoid systems. As an analogous case [22] to prepare another azole ring annulated with naphthoquinone, *Ia* was reacted with azobenzene in chlorobenzene at 150—160 °C for 10 h to give naphtho[2,3-*d*]imidazoline

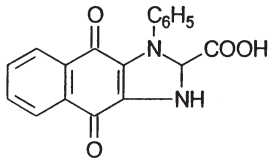


VIII

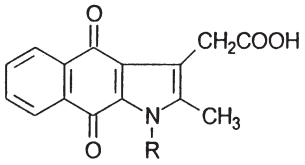
a Ar = C_6H_5
b Ar = $C_6H_4(p\text{-}CH_3)$
c Ar = $C_6H_4(p\text{-}OCH_3)$



IX

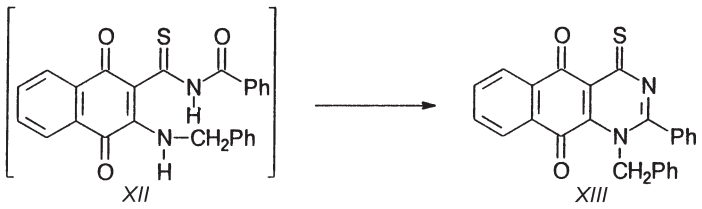


X



XI

a R = CH_3
b R = $CH_2C_6H_5$



XII *XIII*

Scheme 3

derivative *X*. The structure *X* was assigned by elemental analysis, mass, ^{1}H NMR, ^{13}C NMR, and IR spectra.

Reaction of both *Ib* and *Ic* with maleic acid in the presence of acetic anhydride and ammonium acetate, furnished benzo[*f*]indole-3-acetic acid derivatives *XI*. Other synthesis of similar type has been obtained by *Vince* [23]. Structure *XI* was established on the basis of elemental analysis and spectral data, ^{1}H NMR spectra showed two singlet signals in the regions of δ = 3.66—3.72 and 2.03—2.11 for CH_2 and $C_2C\underline{H}_3$, respectively. ^{13}C NMR spectrum of *XIa* exhibited signals at 16.4, 22.3, 40.8, 102.3, 124.6, and 175.6 due to CH_3, NCH_3, CH_2, C-3, C-2, and COOH, respectively, beside of naphthoquinonoide carbons.

Moreover, benzothioxoquinazoline derivative *XIII* was formed from cyclocondensation of compound *Ic* with benzoyl isothiocyanate in dioxane *via* the initial formation of thioamide *XII*. Other synthesis of similar type reaction was reported [24]. The structure *XIII* was assigned on the basis of mass spectrum which showed the molecular ion peak at m/z = 408 (100 %) and peak at m/z = 410 ((M^+ + 2); (4 %)) revealing the presence of sulfur atom, both ^{13}C NMR and ^{1}H NMR spectra of *XIII* showed the presence of characteristic sharp signals.

In conclusion, we report here on a synthesis of both expected and unexpected derivatives related to 1,4-naphthoquinone which is not recorded in literature, further, these derivatives possess good antibacterial activity. The experimental details and results of the antibacterial activity of the title compounds will be published later on.

EXPERIMENTAL

Melting points were measured on GallenKamp apparatus. IR spectra (KBr) were recorded on Perkin—Elmer 1430 spectrometer. ^{1}H NMR spectra were measured on Varian EM-90 MHz spectrometer with TMS as internal standard in DMSO-d_6 and $CDCl_3$. ^{13}C NMR spectra were performed on Varian VX75 MHz spectrometer. The mass spectra were obtained on Varian Atlas CH-7 spectrometer at 70 eV ionizing beam. Elemental analyses were carried out at the Microanalytical Unit, Faculty of Science, Cairo University, Egypt.

2-Substituted Naphtho[2,3-*d*]thiazole-4,9-diones *III*

Thionyl chloride (10 cm^3) and pyridine (1 cm^3) were added to *I* (0.01 mol) and the mixture was refluxed for 1 h. Excess thionyl chloride and pyridine were removed under reduced pressure. Ethanol was added to destroy residual thionyl chloride and then removed under reduced pressure. The residue was recrystallized from ethanol to give *III*.

IIIa: M.p. = 221 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 3340 (OH), 1690, 1685 (C═O), 1670 (C═N), 1633, 1614 (C═C). ^{1}H NMR spectrum, δ: 7.01—7.98 (m, 4H, H_{arom}), 12.90 (s, 1H, COOH, D_2O exchangeable). ^{13}C NMR spectrum, δ: 182.3 (C-9), 181.4 (C-4), 175.1 (COOH), 153.4 (C-2), 140.5 (C-9a), 139.9 (C-3a), 133.8 (C-8), 133.3 (C-5), 131.8 (C-4a), 130.9 (C-8a), 126.1 (C-6), 125.8 (C-7). Mass spectrum, m/z (I_r/%): 259, M^+ (68), 261, [M^+ + 2] (2). For $C_{12}H_5NO_4S$ (M_r = 259.24) w_i(calc.): 55.59 % C, 1.94 % H, 5.41 % N; w_i(found): 55.95 % C, 2.31 % H, 5.63 % N.

IIIb: M.p. = 239 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 1685, 1680 (C═O), 1670 (C═N), 1635, 1620 (C═C). ^{1}H NMR spectrum, δ: 7.0—7.81 (m, 4H, H_{arom}), 8.91 (s, 1H, C-2—H). ^{13}C NMR spectrum, δ: 182.1 (C-9), 181.3 (C-4), 153.8 (C-2), 140.3 (C-9a), 140.0 (C-3a), 133.7 (C-8), 133.4 (C-5), 131.9 (C-4a), 130.8 (C-8a), 126.2 (C-6), 125.9 (C-7). For $C_{11}H_5NO_2S$ (M_r = 215.23) w_i(calc.): 61.38 % C, 2.34 % H, 6.51 % N; w_i(found): 61.56 % C, 2.56 % H, 6.32 % N.

IIIc: M.p. = 256 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 1685, 1680 (C═O), 1670 (C═N), 1650, 1630 (C═C). ^{1}H NMR spectrum, δ: 7.57—8.11 (br, 9H, H_{arom}). For $C_{17}H_9NO_2S$ (M_r = 291.32) w_i(calc.): 70.08 % C, 3.11 % H, 4.81 % N; w_i(found): 69.88 % C, 2.33 % H, 4.60 % N.

Bis[3-(alkylamino)-1,4-naphthoquinon-2-yl]-sulfides *IV*

Thionyl chloride (20 cm^3) was added to *I* (0.01 mol) and the mixture was refluxed for 20 min. Thionyl chloride was removed under reduced pressure and the residue was treated with ethanol as above, the residue was then recrystallized from benzene to give *IV*.

IVa: M.p. = 252 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 3330 (OH), 3250 (NH), 1690, 1685, 1680 (C═O). ^{1}H NMR spectrum, δ: 3.03 (d, 4H, 2CH_2, J = 5.5 Hz), 7.41—7.86 (br, 8H, H_{arom}), 8.67 (br, 2H, 2NH), 11.80 (s, 2H, 2COOH, D_2O exchangeable). ^{13}C NMR spectrum, δ: 182.3 (C-1), 181.4 (C-4), 140.5 (C-3), 139.8 (C-2), 133.8 (C-8), 133.3 (C-5), 131.7 (C-9), 130.7 (C-10), 126.1 (C-6), 125.8 (C-7), 68.2 (C$\underline{H}_2$), 1782 (C$\underline{O}$OH). Mass spectrum, m/z (I_r/%): 492, M^+ (80), 494, [M^+ + 2] (2). For $C_{24}H_{16}N_2O_8S$ (M_r = 492.46) w_i(calc.): 58.53 % C, 3.27 % H, 5.69% N; w_i(found): 58.72 % C, 3.48 % H, 5.55 % N.

IVb: M.p. = 281 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 3230 (NH), 1685, 1680 (C═O), 1640, 1635 (C═C). ^{1}H NMR spectrum, δ: 3.03 (br, 6H, 2CH_3), 6.96—7.65 (m, 8H, H_{arom}), 8.07 (br, 2H, 2NH). For $C_{22}H_{16}N_2O_4S$ (M_r = 404.44) w_i(calc.): 65.33 % C, 3.99 % H, 6.93 % N; w_i(found): 65.49 % C, 4.11 % H, 6.81 % N.

IVc: M.p. = 278 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 3310 (NH), 1680 (C═O), 1645, 1640 (C═C). ^{1}H NMR spectrum, δ: 7.93 (br, 2H, 2NH). For $C_{34}H_{24}N_2O_4S$ (M_r = 556.62) w_i(calc.): 73.36 % C, 4.35 % H, 5.03 % N; w_i(found): 73.45 % C, 4.46 % H, 5.23 % N.

1-Methyl-8-aryl-1,2,7,8,9,14-hexahydrodi-naphtho[2,3-*b*:2′,3′-*e*]pyridine-2,7,9,14-tetrone *V*

A mixture of *Ib* (0.02 mol), drops of HCl and aromatic aldehyde (0.01 mol) in methanol (30 cm^3) was heated under reflux for 1 h. The mixture was cooled and the separated solid was filtered, washed with methanol and recrystallized from ethanol to give *V*.

Va: M.p. = 190 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 1685, 1680 (C═O), 1600 (C═C). ^{1}H NMR spectrum, δ: 3.80 (s, 3H, NCH_3), 5.43 (s, 1H, C-8—H), 7.11—7.24 (br, 13H, H_{arom}). Mass spectrum, m/z (I_r/%): 431, M^+ (100). For $C_{28}H_{17}NO_4$ (M_r = 431.43) w_i(calc.): 77.95 % C, 3.97 % H, 3.25 % N; w_i(found): 78.19 % C, 4.21 % H, 3.16 % N.

Vb: M.p. = 210 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 1685, 1680 (C═O), 1600 (C═C), 1230 (Ar-OCH_3), 820 (*p*-disubs. benzene). ^{1}H NMR spectrum, δ: 3.36 (s, 3H, NCH_3), 3.63 (s, 3H, OCH_3), 5.81(s, 1H, C-8—H), 7.21—7.93 (br, 12H, H_{arom}). For $C_{29}H_{19}NO_5$ (M_r = 461.45) w_i(calc.): 75.48 % C, 4.15 % H, 3.03 % N; w_i(found): 75.61 % C, 4.28 % H, 3.29 % N.

Vc: M.p. = 235 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 1685, 1680 (C═O), 1620 (C═C), 830 (*p*-disubs. benzene). ^{1}H NMR spectrum, δ: 1.91 (s, 3H, Ar-CH_3), 3.22 (s, 3H, NCH_3), 5.72 (s, 1H, C-8—H), 7.10—7.83 (br, 12H, H_{arom}). Mass spectrum, m/z (I_r/%): 445, M^+ (100). For $C_{29}H_{19}NO_4$ (M_r = 445.45) w_i(calc.): 78.19 % C, 4.30 % H, 3.15 % N; w_i(found): 78.30 % C, 4.51 % H, 3.33 % N.

Bis[3-(alkylamino)naphthoquinon-2-yl]-4-(pyridyl)methane *VI*

To a mixture of *I* (0.02 mol) and 4-pyridinecarbaldehyde (0.01 mol) in ethanol (100 cm^3) concentrated HCl (20 cm^3) was added and the mixture was refluxed for 1 h. The milky suspension was neutralized with concentrated ammonium hydroxide, the precipitate was filtered and crystallized from ethanol to give *VI*.

VIa: M.p. = 175 °C. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3310 (NH), 1685, 1680 (C═O), 1640 (C═C). ^{1}H NMR spectrum, δ: 2.51 (br, 6H, $2CH_3$), 3.33 (s, 2H, CH_2), 6.52 (s, 2H, 2NH), 7.31—7.73 (br, 8H, H_{arom}), 9.02 (AB_q, 4H, $H_{pyridyl}$, J_{AB} = 6 Hz). Mass spectrum, m/z (I_r/%): 464, M^+ (80). For $C_{28}H_{22}N_3O_4$ (M_r = 464.48) w_i(calc.): 72.40 % C, 4.77 % H, 9.05 % N; w_i(found): 72.61 % C, 4.62 % H, 8.91 % N.

VIb: M.p. = 187 °C. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3320 (NH), 1680 (C═O), 1645 (C═C), 720 (monosubs. benzene). ^{1}H NMR spectrum, δ: 3.36 (s, 1H, $CH_{pyridine}$), 3.58 (s, 1H, CH_2-Ar), 6.43 (s, 2H, 2NH), 7.11—7.56 (br, 18H, H_{arom}), 8.98 (AB_q, 4H, $H_{pyridyl}$, J_{AB} = 6 Hz). For $C_{40}H_{30}N_3O_4$ (M_r = 616.66) w_i(calc.): 77.91 % C, 4.91 % H, 6.81 % N; w_i(found): 78.11 % C, 4.82 % H, 6.99 % N.

1-Alkyl-3-[2′-(alkylamino)naphthoquinon-3′-yl]-benzo[*f*]indole-4,7-dione *VII*

A mixture of *Ib* or *Ic* (0.01 mol), glyoxal sodium bisulfide (0.01 mol), and anhydrous potassium carbonate (10 g) was stirred in absolute ethanol for 2 h, then refluxed for 6 h, the mixture was acidified with 3 M-HCl. The precipitate was filtered off and recrystallized from methanol to afford *VII*.

VIIa: M.p. = 270 °C. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3320 (NH), 1685, 1680 (C═O), 1660, 1655 (C═C). ^{1}H NMR spectrum, δ: 2.33 (s, 1H, C-2—H), 2.52 (s, 3H, NCH_3), 3.91 (s, 3H, NCH_3), 6.89—7.34 (m, 8H, H_{arom}), 7.89 (s, 1H, NH). Mass spectrum, m/z (I_r/%): 396, M^+ (80). For $C_{24}H_{16}N_2O_4$ (M_r = 396.39) w_i(calc.): 72.72 % C, 4.07 % H, 7.07 % N; w_i(found): 72.57 % C, 4.23 % H, 7.31 % N.

VIIb: M.p. = 293 °C. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3330 (NH), 1685, 1680 (C═O), 1650 (C═C), 830 (*p*-disubs. benzene). ^{1}H NMR spectrum, δ: 2.41 (s, 1H, C-2—H), 4.82 (s, 2H, CH_2-Ar), 5.11 (s, 2H, NCH_2-Ar), 7.10—7.34 (br, 13H, H_{arom}), 8.10 (s, 1H, NH). For $C_{36}H_{24}N_2O_4$ (M_r = 548.57) w_i(calc.): 78.82 % C, 4.41 % H, 5.11 % N; w_i(found): 78.98 % C, 4.66 % H, 4.98 % N.

2-Amino-4-aryl-3-cyano-1-methyl-1,4,5,10-tetrahydrobenzo[*g*]quinoline-5,10-dione *VIII*

A mixture of *Ib* (0.01 mol), appropriate arylidene malononitrile (0.01 mol), and triethylamine (3 drops) in ethanol (30 cm^3) was refluxed for 1 h. The solid product formed on standing was collected by filtration and crystallized from ethanol to give *VIII*.

VIIIa: M.p. = 185 °C. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3330 (NH_2), 2170 (CN), 1680 (C═O), 1620 (C═C). ^{1}H NMR spectrum, δ: 2.41 (s, 3H, NCH_3), 3.81 (s, 2H, NH_2), 4.73 (s, 1H, C-4—H of pyridine), 7.11—7.71 (br, 9H, H_{arom}). ^{13}C NMR spectrum, δ: 182.1 (C═S), 181.8 (C-10), 151.2 (C-2), 140.2 (C-4), 139.9 (C-11), 139.1 (C-11a), 133.9, 133.3, 131.8, 130.9, 126.1, 125.8, 125.7, 125.6, 125.5, 125.4, 125.3 (aromatic carbons), 113.2 (C≡N), 81.8 (C-3), 22.3 (CH_3). Mass spectrum, m/z (I_r/%): 341, M^+ (60). For $C_{21}H_{15}N_3O_2$ (M_r = 341.35) w_i(calc.): 73.89 % C, 4.43 % H, 12.31 % N; w_i(found): 74.03 % C, 4.61 % H, 12.13 % N.

VIIIb: M.p. = 210 °C. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3200 (NH_2), 2220 (C≡N), 1630 (C═C), 820 (*p*-disubs. benzene). ^{1}H NMR spectrum, δ: 1.92 (s, 3H, Ar-CH_3), 2.43 (s, 3H, NCH_3), 4.00 (s, 2H, NH_2), 4.66 (s, 1H, C-4—H of pyridine), 6.98—7.56 (br, 8H, H_{arom}). For $C_{22}H_{17}N_3O_2$ (M_r = 355.38) w_i(calc.): 74.03 % C, 4.82 % H, 11.82 % N; w_i(found): 74.21 % C, 5.00 % H, 11.72 % N.

1,2-Diphenyl-4,9-dihydronaphtho[2,3-*d*]-imidazole-4,9-dione (*IX*)

A solution of *Ic* (0.01 mol) and nitrosobenzene (0.03 mol) in acetic anhydride was heated in a sealed tube at about 200 °C for 1 h. Acetic anhydride was removed under reduced pressure and the residue diluted with water (50 cm^3), extracted with chloroform (3 × 250 cm^3), dried with Na_2SO_4 and evaporated to give crude product which was purified by column chromatography over silica gel using benzene—hexane (φ_r = 1:4) as eluent to give *IX*. M.p. = 210 °C. IR spectrum, $\tilde{\nu}/cm^{-1}$: 1680 (C═O), 1660 (C═N), 1620 (C═C). ^{1}H NMR spectrum, δ: 7.23—7.91 (br, 14H, H_{arom}). ^{13}C NMR spectrum, δ: 184.6 (C-4), 184.3 (C-9), 139.1 (C-10), 138.8 (C-10a), 136.2 (C-2), 132.3, 132.0, 131.6, 131.4, 130.2, 127.1, 126.8, 126.6, 126.3, 126.1, 125.8, 125.4, 125.2, 125.0 (aromatic carbons). Mass spectrum, m/z (I_r/%): 350, M^+ (100). For $C_{23}H_{14}N_2O_2$ (M_r = 350.36) w_i(calc.): 78.84 % C, 4.03 % H, 8.00 % N; w_i(found): 78.61 % C, 4.33 % H, 7.83 % N.

1-Phenyl-2-carboxy-2,3,4,9-tetrahydro-naphtho[2,3-*d*]imidazole-4,9-dione (*X*)

A stirred suspension of *Ia* (0.01 mol) in a mixture of azobenzene (0.01 mol) and chlorobenzene (100 cm^3) was heated to reflux in an oil bath maintained at 150—160 °C for 10 h. The reaction mixture was then filtered, the filtrate cooled, and the formed solid crystallized from benzene to give *X*. M.p. = 200 °C. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3360 (OH), 3280 (NH), 1690, 1680 (C═O), 1620 (C═C). ^{1}H NMR spectrum, δ: 2.16 (s, 1H, C-

2—H), 7.13—7.90 (br, 9H, H_{arom}), 9.81 (s, 1H, NH), 12.23 (s, 1H, COOH, D_2O exchangeable). ^{13}C NMR spectrum, δ: 184.1 (C-4), 183.8 (C-9), 175.6 (COOH), 160.3 (C-2), 139.8 (C-10), 139.1 (C-10a), 133.7, 133.1, 131.8, 131.6, 127.4, 127.1, 126.3, 126.2, 125.3, 125.1 (aromatic carbons). For $C_{18}H_{12}N_2O_4$ (M_r = 320.30) w_i(calc.): 67.50 % C, 3.78 % H, 8.73 % N, w_i(found): 67.66 % C, 3.97 % H, 8.58 % N.

1-Alkyl-2-methyl-4,9-dihydrobenzo[*f*]indole-4,9-dion-3-ylacetic Acid (*XI*)

A mixture of *I* (0.01 mol), maleic acid (0.01 mol), and excess ammonium acetate (0.03 mol) in acetic anhydride (100 cm^3) was heated under reflux for 5 h. Acetic anhydride was removed under reduced pressure. The residue was crystallized from ethanol to give *XI*.

XIa: M.p. = 230 °C. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3350 (OH), 1710, 1685, 1680 (C=O), 1620 (C=C). ^1H NMR spectrum, δ: 2.11 (s, 3H, C-2—CH_3), 3.66 (s, 2H, CH_2), 3.95 (s, 3H, NCH_3), 7.12—7.65 (m, 4H, H_{arom}), 12.11 (hump, 1H, COOH, D_2O exchangeable). ^{13}C NMR spectrum, δ: 182.3 (C-4), 182.1 (C-9), 175.6 (COOH), 124.6 (C-2), 140.3 (C-10a), 140.1 (C-10), 133.9, 133.3, 131.8, 130.9, 126.1, 125.8 (aromatic carbons), 102.3 (C-3), 40.8 (CH_2), 22.3 ($NC\underline{H}_3$), 16.4 (C-2—$\underline{C}H_3$). Mass spectrum, m/z (I_r/%): 283, M^+ (70). For $C_{16}H_{13}NO_4$ (M_r = 283.27) w_i(calc.): 67.84 % C, 4.62 % H, 4.95 % N; w_i(found): 67.67 % C, 4.82 % H, 5.26 % N.

XIb: M.p. = 262 °C. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3320 (OH), 1700, 1685, 1680 (C=O), 1630 (C=C). ^1H NMR spectrum, δ: 2.03 (s, 3H, C-2—$C\underline{H}_3$), 3.72 (s, 2H, CH_2), 4.89 (s, 2H, $NC\underline{H}_2$—Ph), 7.0—7.61 (br, 9H, H_{arom}), 12.66 (br, 1H, $COO\underline{H}$, D_2O exchangeable). For $C_{22}H_{17}NO_4$ (M_r = 359.37) w_i(calc.): 73.53 % C, 4.77 % H, 3.89 % N; w_i(found): 73.38 % C, 4.89 % H, 4.03 % N.

1-Benzyl-2-phenyl-4-thioxobenzo[*g*]-quinazoline-5,10-dione (*XIII*)

A mixture of benzoylisothiocyanate (0.01 mol) and *Ic* (0.01 mol) in dioxane (20 cm^3) was heated under reflux for 5 h, poured onto water and the solid product so formed was collected by filtration and crystallized from ethanol to give *XIII*. M.p. = 300 °C. IR spectrum, $\tilde{\nu}/cm^{-1}$: 1685, 1680 (C=O), 1640 (C=N), 1620 (C=C), 1250 (C=S). ^1H NMR spectrum, δ: 4.61 (s, 2H, $NC\underline{H}_2$), 7.10—7.32 (br, 14H, H_{arom}). ^{13}C NMR spectrum, δ: 196.1 (C=S), 182.7 (C-5), 182.1 (C-10), 160.2 (C-2), 139.9 (C-11), 139.7 (C-11a), 133.9, 133.3, 131.8, 131.2, 128.2, 127.8, 127.3, 126.8, 126.5, 126.2, 126.1, 126.0, 125.8, 125.4, 125.3, 125.2 (aromatic carbons), 71.8 (CH_2). Mass spectrum, m/z (I_r/%): 408 (M^+; 100 %). For $C_{25}H_{16}N_2O_2S$ (M_r = 408.47) w_i(calc.) 73.51 % C, 3.95 % H, 6.86 % N; w_i(found): 73.68 % C, 4.21 % H, 6.58 % N.

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