Reaction of Chloronaphthoquinones with Phenylhydrazones as Azaenamines in Pyridine

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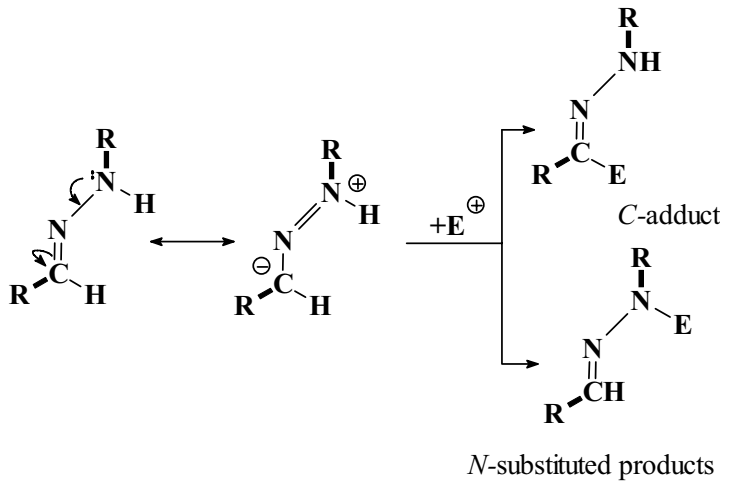
The behaviour of chloronaphthoquinones towards phenylhydrazones in pyridine and resulting *N*-substituted products are reported. Cyclization of these *N*-substituted adducts gave different heterocyclic systems. The heterocyclic products were directly formed from the same reaction with the reactive chloronaphthoquinone without detecting the corresponding *N*-substituted products.

Recently, it was reported that enamines react with quinones to give heterocyclic systems [1]. Hydrazones react similarly to enamines and can be regarded as azaenamines [2—4]. Hydrazones are formally considered bidentate ambident nucleophiles. Accordingly, the electrophilic substitution reactions of hydrazones may occur at methine carbon or at amino nitrogen (Scheme 1).

Gramik et al. [5] discovered that the interaction of benzaldehyde phenylhydrazone with chlorobenzoquinone *I* in the presence of acetic acid occurred at methine carbon to give the so-called hydroquinone *C*-adduct *II*, followed by ring closure to interesting indazole derivative *III* (Scheme 2).

In contrast to the latter of the previous facts, the compounds *VII* (Scheme 3) were formed as the only detectable products (TLC), when 2-chloro-1,4-naphthoquinone *IV* was reacted with aromatic aldehyde phenylhydrazones *V* as azaenamines in pyridine. The corresponding *C*-adducts *VI* were not formed. Proofs of the structure *VII* were based firmly on ^{1}H NMR spectra, in which N=CH proton at $\delta = 6.91$—6.98 appeared as a singlet signal. IR spectra revealed also the absence of NH band. ^{13}C NMR spectrum of the compound *VIIa* is in good agreement with this structure.

In addition, the cyclization process of *VII* in acetic acid to benzindazole quinones *VIII* met with failure and the naphthoxadiazines *IX* were formed. The disfavoured cyclization of *VII* to indazoles *VIII* is due to stereochemical reasons [6], where the ring closure in this case can be regarded as a 5-*endo-trig* reaction



Scheme 1

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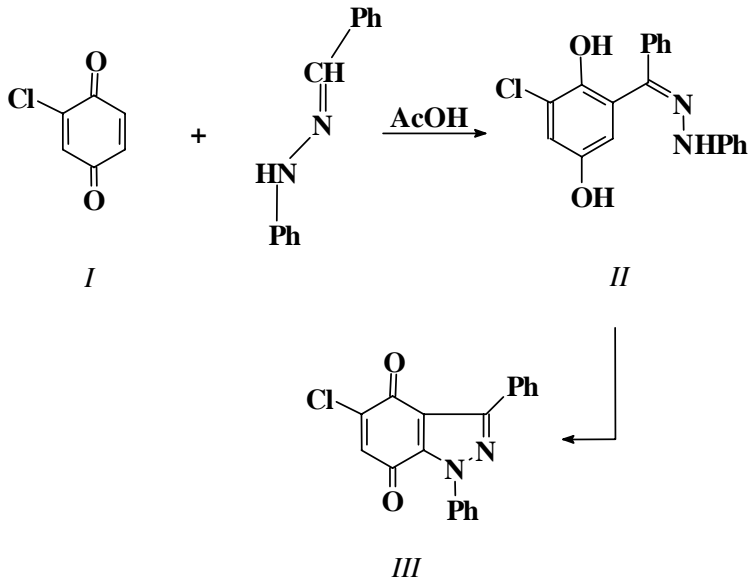


Scheme 2

which is known to be an unfavourable process. Moreover, the electrophilic character of C-3 in *VII* is very weak due to the presence of electron-rich nitrogen substituent in position 2. The proposed mechanism of formation of *IX* was shown by the similar intramolecular hetero Diels—Alder reaction (Scheme 4). The structure of *IX* was proved by spectral data. ^{1}H NMR spectrum of *IXa* showed the absence of N=C<u>H</u> signal initially present in *VIIa* and an additional signal for OH proton at $\delta = 9.07$ appeared. IR spectra of *IX* revealed the absence of C=O band, and the presence of a broad OH band at $\tilde{\nu} = 3335$—3398 cm^{-1}. The mass spectra of *IXa* and *IXc* are in a good agreement with the structure. The characteristic fragment ion peaks of *IXa* occur at 352, 275, 248, and 232 due to M^+, ($M^+ - C_6H_5$), [M^+ − (C_6H_5C=N)], and [M^+ − (C_6H_5—CNO)], respectively.

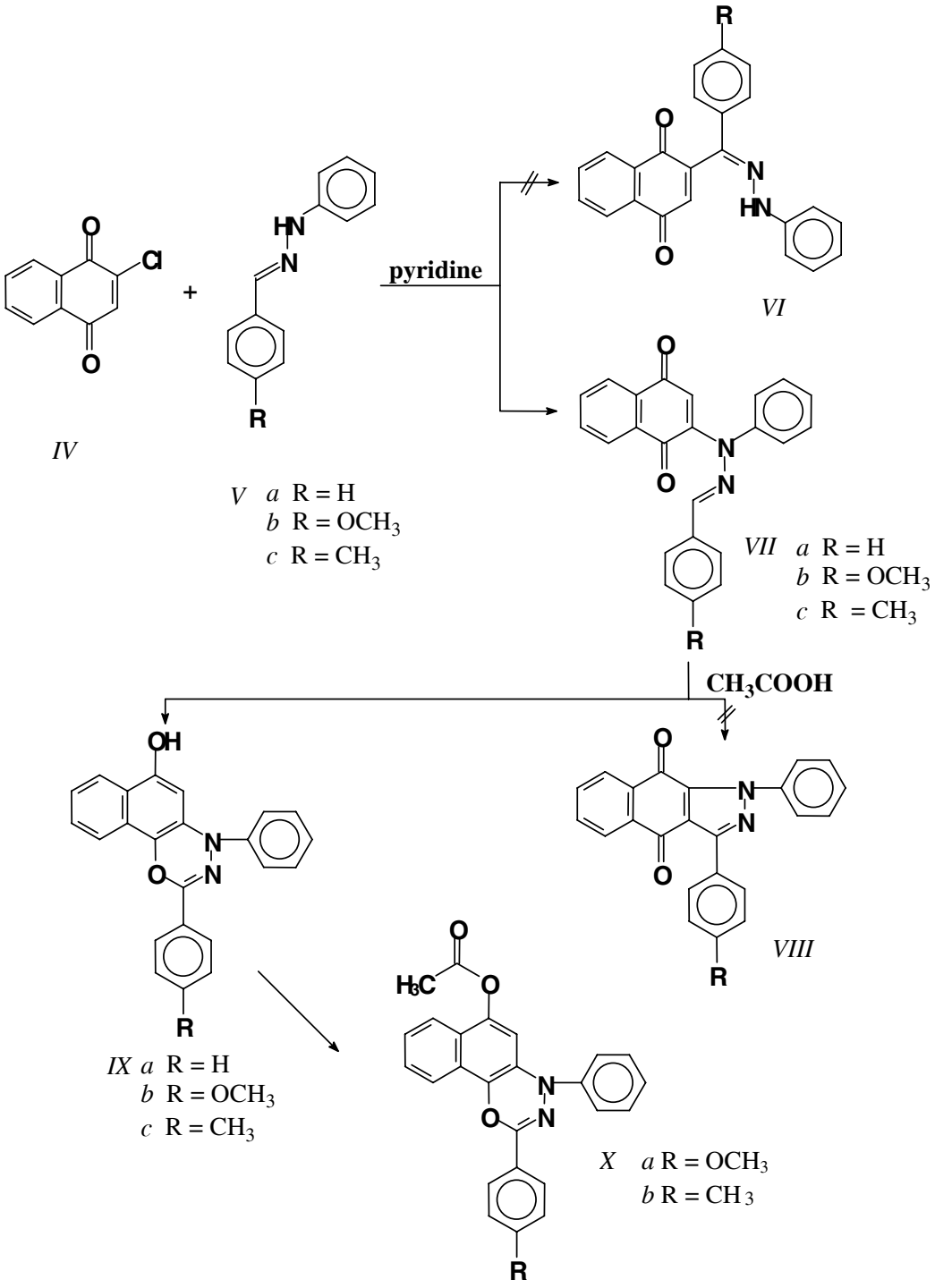
Compounds *IXb* and *IXc* were transformed into acetoxy derivatives *Xa* and *Xb*, respectively. This transformation was important to prove the structure of compounds *IXb* and *IXc* which are not soluble enough for ^{1}H and ^{13}C NMR measurements.

When the same reaction was carried out with 2,3-dichloro-1,4-naphthoquinone (*XI*), the compounds *XII* were also successfully obtained (Scheme 5). The ^{1}H NMR spectra of *XII* revealed the absence of NH signal and the presence of two singlet signals at δ = 7.71—7.76 and 10.08—10.21 due to N=C<u>H</u> and O<u>H</u> protons, respectively. Besides the carbonyl band at $\tilde{\nu}$ = 1673—1680 cm^{-1} a broad band at $\tilde{\nu} = 3326$—3408 cm^{-1} appeared in IR spectra of *XII* due to OH group, both NH and CCl bands were absent. The structure *XIIa* was confirmed by mass and ^{13}C NMR spectra. The reliable reaction mechanism for formation of the products *XII* under these basic conditions is presented in Scheme 5.

According to this mechanism, the quaternary pyridinium chloride A is the first and main intermediate [7]. The chlorine atom in this intermediate is highly reactive due to the pyridinium moiety [8—10]. Consequently, the intermediate A readily underwent nucleophilic attack with phenylhydrazones to give another intermediate of type B which is transformed by hydrolysis to *XII*.

Ring closure of the product *XII* to benzindazole quinones *XIII* was possible in this case under drastic conditions. Refluxing *XII* and drops of acetic anhydride in xylene for 48 h, benzindazoles *XIII* were formed in low yields. Formation of oxadiazines *XIV* easily took place by the refluxing of *XII* with methanolic sodium methoxide for 2 h. The smooth cyclization of *XII* to *XIV* is due to the favoured nature of the corresponding 6-*endo-trig* process [11]. Structures *XIII* and *XIV* were established by the spectral data. ^{1}H NMR spectra of both *XIII* and *XIV* revealed the absence of N=CH proton signal initially present in *XII*. Also, OH band disappeared in IR spectra of *XIII* and *XIV*. ^{13}C NMR spectra of *XIIIb* and *XIVa* are in good agreement with the structures, *XIIIb* showed a singlet signal at $\delta = 148.12$ for C-3 of indazole ring and *XIVa* at $\delta = 168.81$ for C-3 of oxadiazine ring. The mass spectra showed M^+ for *XIIIa* at $m/z = 350$, while for *XIV* at $m/z = 366$.

Finally, we have carried out the same reaction with 2-acetylamino-3-chloro-1,4-naphthoquinone (*XV*). This reaction gave good yields (70—80 %) of the triazine derivatives *XVI*, and we were not able to detect the corresponding *N*-substituted products as usual in the previous reactions (Scheme 6). The direct preferential formation of *XVI* may be due to the higher reactivity of both NH and Cl in the compound *XV*. ^{1}H NMR spectra of *XVI* showed the absence of

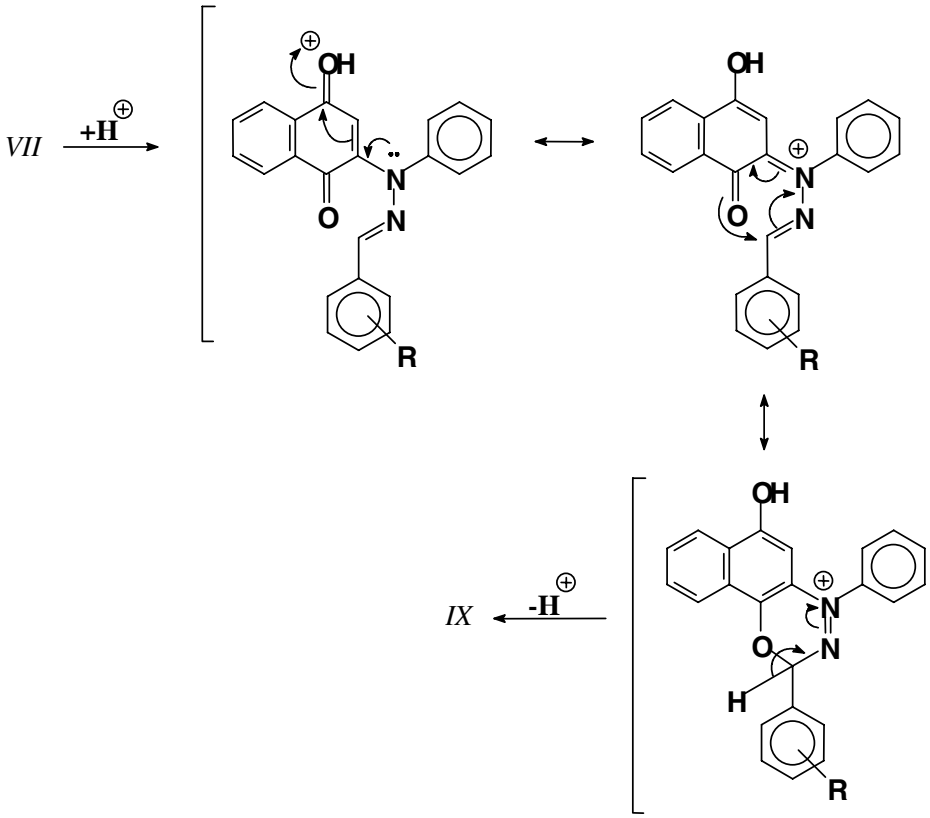


Scheme 3

N=C<u>H</u> and N<u>H</u> proton signals. Both CCl and NH bands disappeared in the IR spectra. Structure *XVIa* was confirmed by ^{13}C NMR spectrum.

Unlike to the previous case, 2,4-dinitrophenylhydrazones did not react with *IV* and *XI*, and with *XV* at all and the starting compounds were recovered. This is due to the lower nucleophilicity of the nitrogen atom in 2,4-dinitrophenylhydrazones in comparison with phenylhydrazones.

In summary, we have demonstrated that the reaction of chloroquinones with phenylhydrazones in pyridine yielded *N*-substituted products instead of *C*-adducts which were obtained from the similar type reaction in acetic acid. These *N*-substituted products open new ways to the synthesis of naphthoxadiazines, benzindazoles, and naphthotriazines.



Scheme 4

EXPERIMENTAL

Melting points were measured on a Gallenkamp apparatus. IR spectra (KBr, $\tilde{\nu}/\mathrm{cm}^{-1}$) were recorded using Perkin—Elmer 1600 spectrophotometer. Mass spectra were taken using Finnigan 4000 mass spectrometer (70 eV). ^{1}H NMR spectra were recorded using Varian FT80A instrument (80 MHz). ^{13}C NMR spectra (30 MHz) were taken with TMS as an internal standard; chemical shifts are given in δ values. Microanalyses were determined by a microanalytical unit of Cairo and Tanta Universities. TLC was performed on silica gel plates (thickness 0.2 mm). UV detection (Silufol UV-254) was used for TLC control.

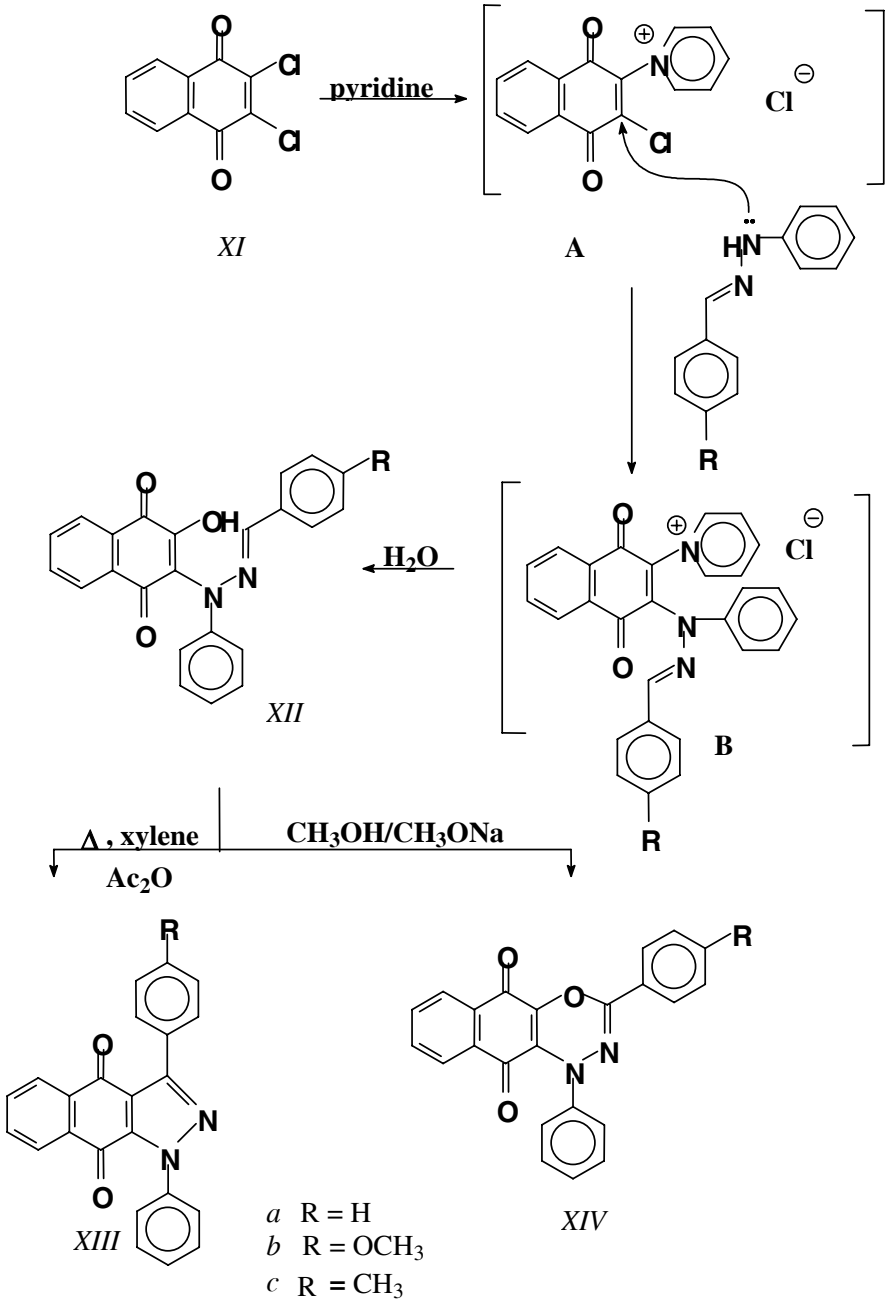
2-(N′-Arylidene-*N*-phenylhydrazino)-1,4-naphthoquinones *VII*

A phenylhydrazone of aromatic aldehyde *V* (0.01 mol) was added to a solution of 2-chloro-1,4-naphthoquinone *IV* (0.01 mol) in pyridine (20 cm^3) under stirring. The mixture was refluxed for 4—5 h and left to cool overnight. The precipitate was washed with water, filtered off, dried and crystallized from benzene to give reddish-brown crystals.

VIIa: M.p. = 163 °C. IR spectrum, $\tilde{\nu}/\mathrm{cm}^{-1}$: 2929, 1678, 1635, 1590, 1582. MS, m/z (I_r/%): 352 (14) [M$^+$], 324 (7), 296 (6), 248 (38), 220 (49), 192 (24), 158 (38), 130 (33), 106 (100), 102 (30), 77 (71), 51 (35). ^{1}H NMR spectrum ($CDCl_3$), δ: 6.98 (s, 1H, H-3), 7.21—7.68 (br, 12H, 2C_6H_5, H-6,7), 7.81 (s, 1H, N=CH), 7.96—8.13 (m, 2H, H-5,8). ^{13}C NMR spectrum ($CDCl_3$), δ: 182.82 (s, C-1 or C-4), 182.11 (s, C-4 or C-1), 153.37 (s, C_6H_5—N), 151.21 (s, C-2), 142.29 (d, N=CH), 134.66 (s, C-4a), 133.37 (d, C-6 or C-7), 133.18 (d, C-7 or C-6), 132.53 (s, C_6H_5—), 132.28 (s, C-8a), 129.78 (d, C-5 or C-8), 129.23 (d, C-8 or C-5), 129.11, 129.03, 128.89, 128.77, 128.51, 128.43, 128.36, 128.14, 127.71, 127.30 (d, C_phenyl), 118.92 (d, C-3). For $C_{23}H_{16}N_2O_2$ (M_r = 352.4) w_i(calc.): 78.39 % C, 4.58 % H, 7.95 %N; w_i(found): 78.12 % C, 4.71 % H, 8.13 % N.

VIIb: M.p. = 167 °C. IR spectrum, $\tilde{\nu}/\mathrm{cm}^{-1}$: 2938, 1675, 1624, 1593, 1510. MS, m/z (I_r/%): 382 (49) [M$^+$], 361 (10), 354 (13), 326 (7), 249 (36), 214 (24), 186 (41), 158 (100), 130 (20), 106 (72), 102 (38), 77 (34), 51 (8). ^{1}H NMR spectrum ($CDCl_3$), δ: 3.78 (s, 3H, OCH_3), 6.91 (s, 1H, H-3), 7.70—7.85 (m, 11H, C_6H_5—, C_6H_4—, H-6,7), 7.85 (s, 1H, N=CH), 7.91—8.14 (m, 2H, H-5,8). For $C_{24}H_{18}N_2O_3$ (M_r = 382.4) w_i(calc.): 75.38 % C, 4.74 % H, 7.33 % N; w_i(found): 75.52 % C, 4.93 % H, 7.18 % N.

VIIc: M.p. = 193 °C. IR spectrum, $\tilde{\nu}/\mathrm{cm}^{-1}$: 2958, 1676, 1625, 1607, 1596, 1512. ^{1}H NMR spectrum ($CDCl_3$), δ: 2.11 (s, 3H, CH_3), 6.96 (s, 1H, H-3), 7.21—7.67 (br, 11H, C_6H_5—, C_6H_4—, H-6,7), 7.79 (s, 1H,



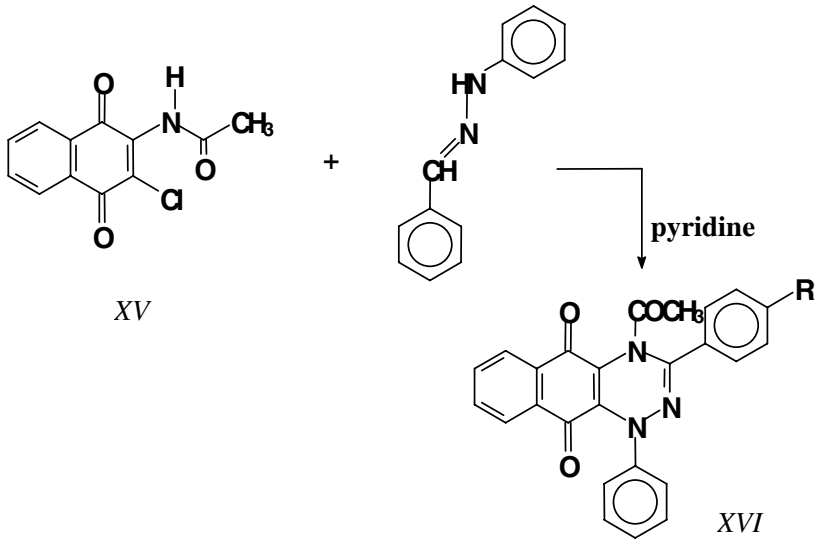
Scheme 5

N=CH), 7.99—8.03 (m, 2H, H-5,8). For $C_{24}H_{18}N_2O_2$ (M_r = 366.4) w_i(calc.): 78.67 % C, 4.95 % H, 7.65 % N; w_i(found): 78.46 % C, 5.21 % H, 7.43 % N.

9-Hydroxy-1-phenyl-3-aryl-1*H*-naphtho[1,2-*e*]-[1,3,4]oxadiazines *IX*

A solution of *VII* (0.01 mol) in methanol (50 cm^3) was refluxed under stirring with acetic acid (20 cm^3) for 4—6 h. The solvent was evaporated and the mixture left overnight at room temperature. The residue was filtered, dried, and crystallized from petroleum ether to give white-yellow crystals.

XIa: M.p. = 185 °C. IR spectrum, $\tilde{\nu}/cm^{-1}$: 3375, 2964, 2938, 1610, 1598, 1570. MS, m/z (I_r/%): 352 (38) [M^+], 275 (10), 248 (27), 232 (62), 220 (42), 204 (85), 124 (100), 108 (8), 96 (15), 82 (63), 67 (13), 42 (51). ^{1}H NMR spectrum (DMSO-d_6), δ: 6.11 (s, 1H, H-10), 7.44—7.85 (m, 14H, H_{arom}), 9.07 (s, 1H, OH). ^{13}C NMR spectrum (DMSO-d_6), δ: 166.01 (s, C-4a), 164.32 (s, C-9), 162.66 (s, C-10a, 160.87 (s, C-3), 148.29 (s, C_6H_5—N), 134.80 (s, C_6H_5—), 132.13 (s, C-8a), 132.08 (C-4b), 132.0, 131.13 (s, C-8a), 132.08 (C-4b), 132.0, 131.98, 129.87, 128.76, 128.18, 127.65, 126.38, 126.19, 125.13, 124.88 (d, C_{phenyl}). For $C_{23}H_{16}N_2O_2$ (M_r = 352.4) w_i(calc.): 78.39 % C, 4.58 % H, 7.95 % N; w_i(found): 78.51 % C, 4.32 % H, 8.09 % N.



XV

XVI

a R = H
b R = OCH_3
c R = CH_3

Scheme 6

IXb: M.p. = 148 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 3398, 2961, 2924, 1620, 1610, 1577. For $C_{24}H_{18}N_2O_3$ (M_r = 382.4) w_i(calc.): 75.38 % C, 4.74 % H, 7.33 % N; w_i(found): 75.57 % C, 4.91 % H, 7.13 % N.

IXc: M.p. = 210 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 3335, 2980, 2930, 1610, 1605, 1580. MS, m/z (I_r/%): 366 (39) [M$^+$], 289 (10), 262 (17), 246 (63), 234 (58), 218 (7), 124 (100), 108 (9), 82 (18), 67 (31), 42 (25). For $C_{24}H_{18}N_2O_3$ (M_r = 366.4) w_i(calc.): 78.67 % C, 4.95 % H, 7.65 % N; w_i(found): 78.76 % C, 4.76 % H, 7.51 % N.

3-Aryl-1-phenyl-1*H*-naphtho[1,2-*e*]oxadiazin-9-yl Acetate *X*

IXb or *IXc* (0.01 mol) was dissolved in acetic anhydride (20 cm^3), and drops of pyridine were added. The mixture was refluxed for 1 h. The solvent was removed, and the residue was crystallized from benzene to give yellow needles.

Xa: M.p. = 156 °C. IR spectrum, $\tilde{\nu}$ /cm^{-1}: 2972, 2908, 1692, 1612, 1604, 1505. ^{1}H NMR spectrum ($CDCl_3$), δ: 2.58 (s, 3H, $COCH_3$), 3.78 (s, 3H, OCH_3), 6.23 (s, 1H, H-10), 7.11—7.63 (m, 13H, H_{arom}). For $C_{26}H_{20}N_2O_4$ (M_r = 426.4) w_i(calc.): 73.57 % C, 4.75 % H, 6.6 % N; w_i(found): 73.85 % C, 5.03 % H, 6.73 % N.

Xb: M.p. = 182 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 2968, 2934, 1691, 1623, 1608, 1510. MS, m/z (I_r/%): 408 (21) [M$^+$], 365 (68), 304 (65), 288 (13), 276 (53), 260 (41), 124 (89), 108 (6), 96 (10), 82 (48), 67 (16), 42 (56). ^{1}H NMR spectrum ($CDCl_3$), δ: 2.11 (s, 3H, CH_3), 2.43 (s, 3H, $COCH_3$), 6.12 (s, 1H, H-10), 7.02—7.84 (m, 13H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ: 169.21 (s, CO), 167.32 (s, C-4a), 166.11 (s, C-9), 163.63 (s, C-10a), 161.76 (s, C-3), 147.82 (s, C_6H_5—N), 135.11 (s, C_6H_5—), 133.0 (s, C-8a), 132.24 (s, C-4b), 132.16 (d), 131.83 (d), 124.92 (d), 128.71 (d), 128.23 (d), 127.81 (d), 126.44 (d), 126.33 (d), 125.91 (d), 125.75 (d), 125.56 (d), 125.41 (d), 125.31 (d), 125.22 (d), 124.81 (s, C_{arom}), 23.12 (q, $COCH_3$), 21.23 (q, CH_3). For $C_{26}H_{20}N_2O_3$ (M_r = 408.4) w_i(calc.): 76.46 % C, 4.92 % H, 6.86 % N; w_i(found): 76.76 % C, 5.08 % H, 7.03 % N.

2-(N′-Arylidene-*N*-phenylhydrazino)-3-hydroxy-1,4-naphthoquinones *XII*

A phenylhydrazone of aromatic aldehyde (0.01 mol) was added to a solution of 2,3-dichloro-1,4-naphthoquinone (*XI*) (0.01 mol) in pyridine (10 cm^3) under stirring. The mixture was refluxed for 2—3 h and left to cool overnight. The precipitate was washed with water, filtered off, and recrystallized from aqueous ethanol to give brownish-red crystals.

XIIa: M.p. = 140 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 3326, 3281, 2998, 1675, 1626, 1590, 1560. MS, m/z (I_r/%): 368 (70) [M$^+$], 351 (8), 340 (12), 312 (60), 286 (53), 264 (42), 175 (28), 158 (100), 130 (40), 106 (22), 104 (10), 77 (3), 51 (9). ^{1}H NMR spectrum ($CDCl_3$), δ: 7.21—7.67 (m, 12H, $2C_6H_5$, H-6,7), 7.76 (s, 1H, N=CH), 7.80—8.0 (m, 2H, H-5,8), 10.11 (s, 1H, OH). ^{13}C NMR spectrum ($CDCl_3$), δ: 182.21 (s, C-1 or C-4), 182.02 (s, C-4 or C-1), 156.33 (s, C-3), 154.21 (s, C-2), 144.61 (d, N=CH), 134.53 (s, C-4a), 133.66 (d, C-6 or C-7), 133.34 (d, C-7 or C-6), 132.56 (s, C-8a),

132.12 (s, C_6H_5—N), 129.21 (s, C_6H_5—), 128.61 (d, C-5 or C-8), 128.24 (d, C-8 or C-5), 127.81, 127.31, 126.91, 126.53, 126.33, 125.32, 125.21, 124.91, 124.63 (d, C_{arom}). For $C_{23}H_{16}N_2O_3$ (M_r = 368.3) w_i(calc.): 74.99 % C, 4.38 % H, 7.61 % N; w_i(found): 74.83 % C, 4.51 % H, 7.87 % N.

XIIb: M.p. = 138 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 3368, 3342, 3005, 1680, 1673, 1620, 1595, 1560. ^{1}H NMR spectrum ($CDCl_3$), δ: 3.78 (s, 3H, OCH_3), 7.12—7.56 (br, 11H, $2C_6H_5$, H-6,7), 7.71 (s, 1H, N=CH), 7.82—8.10 (m, 2H, H-5,8), 10.21 (s, 1H, OH). For $C_{24}H_{18}N_2O_4$ (M_r = 398.4) w_i(calc.): 72.35 % C, 4.52 % H, 7.03 % N; w_i(found): 72.48 % C, 4.31 % H, 6.83 % N.

XIIc: M.p. = 122 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 3408, 3393, 2993, 1680, 1677, 1623, 1589, 1562. ^{1}H NMR spectrum ($CDCl_3$), δ: 2.1 (s, 3H, CH_3), 7.01—7.66 (br, 11H, $2C_6H_5$, H-6,7), 7.75 (s, 1H, N=CH), 7.81—8.12 (m, 2H, H-5,8), 10.08 (s, 1H, OH). For $C_{24}H_{18}N_2O_3$ (M_r = 382.4) w_i(calc.): 75.38 % C, 4.74 % H, 7.33 % N; w_i(found): 75.11 % C, 4.46 % H, 7.23 % N.

3-Aryl-1-phenyl-1*H*-benzo[*f*]indazole-4,9-dione *XIII*

XII (0.01 mol) was suspended in xylene (30 cm^3) and drops of acetic anhydride were added. The mixture was refluxed for 48 h. The solvent was removed and the residue treated with dichloromethane (1 cm^3) and chromatographed on silica gel with eluent dichloromethane. Yellow crystals were formed after cooling at (10 °C—0 °C) overnight.

XIIIa: M.p. = 252 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 2888, 1678, 1664, 1621, 1598, 1590. MS, m/z (I_r/%): 350 (80) [M$^+$], 322 (18), 494 (9), 259 (14), 247 (43), 158 (20), 129 (44), 102 (46), 76 (73), 50 (54), 43 (22). ^{1}H NMR spectrum ($CDCl_3$), δ: 7.10—7.36 (br, 10H, $2C_6H_5$), 7.67—7.81 (m, 2H, H-6,7), 7.92—8.16 (m, 2H, H-5,8). For $C_{23}H_{14}N_2O_2$ (M_r = 350.4) w_i(calc.): 78.84 % C, 4.03 % H, 8.00 % N; w_i(found): 79.08 % C, 3.88 % H, 8.16 % N.

XIIIb: M.p. = 180 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 2892, 1667, 1608, 1593, 1578. ^{1}H NMR spectrum ($CDCl_3$), δ: 3.78 (s, 3H, OCH_3), 6.97—7.43 (m, 9H, H_{arom}), 7.57—7.84 (m, 2H, H-6,7), 7.93—8.21 (m, 2H, H-5,8). ^{13}C NMR spectrum ($CDCl_3$), δ: 180.11 (s, C-9 or C-4), 179.31 (s, C-4 or C-9), 156.21 (s, C_6H_5—O), 155.14 (s, C-9a), 152.31 (s, C_6H_5—N), 150.11 (s, C-4a), 148.12 (s, C-3), 134.18 (d, C-6 or C-7), 133.82 (d, C-7 or C-6), 132.42 (s, C-8a), 131.83 (s, C_6H_5—C=N), 126.32, 126.11, 125.80, 125.52, 125.22, 125.0, 124.91, 124.63, 124.32 (d, CH_{arom}). For $C_{24}H_{16}N_2O_3$ (M_r = 380.4) w_i(calc.): 75.77 % C, 4.24 % H, 7.37 % N; w_i(found): 75.81 % C, 4.42 % H, 7.52 % N.

XIIIc: M.p. = 202 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 2992, 1678, 1620, 1610, 1592, 1567. ^{1}H NMR spectrum ($CDCl_3$), δ: 2.32 (s, 3H, CH_3), 7.10—7.43 (br, 9H, H_{arom}), 7.51—7.73 (m, 2H, H-6,7), 7.88—8.02 (m, 2H, H-5,8). For $C_{24}H_{16}N_2O_2$ (M_r = 364.4) w_i(calc.): 79.90 % C, 4.43 % H, 7.69 % N; w_i(found): 80.12 % C, 4.62 % H, 7.52 % N.

3-Aryl-1-phenyl-4*H*-naphtho[2,3-*e*][1,3,4]oxadiazine-5,10-dione *XIV*

Sodium metal (0.01 mol) was allowed to react with methanol (50 cm^3), *N*-substituted product *XII* (0.01 mol) was added. The solution was heated at reflux for 2—3 h. The reaction mixture was cooled and adjusted to pH 5 with 1 M-HCl. The mixture was poured into water (100 cm^3) and extracted with ether. The extracts were dried by $MgSO_4$, and the solvent was removed to afford a solid material, recrystallized from ethanol.

XIVa: M.p. = 256 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 2889, 1673, 1670, 1622, 1592. MS, m/z (I_r/%): 366 (61) [M$^+$], 338 (28), 310 (43), 263 (16), 247 (9), 172 (8), 158 (80), 130 (32), 106 (23), 102 (36), 77 (24), 51 (43). ^{1}H NMR spectrum ($CDCl_3$), δ: 6.98—7.41 (m, 10H, H_{arom}), 7.52—7.68 (m, 2H, H-6,7), 7.73—7.98 (m, 2H, H-5,8). ^{13}C NMR spectrum ($CDCl_3$), δ: 181.31 (s, C-5 or C-10), 180.72 (s, C-10 or C-5), 168.81 (s, C-3), 155.64 (s, C-4a), 153.93 (s, C-10a), 151.82 (s, C_6H_5—N), 134.55 (s, C-9a), 133.38 (s, C-5a), 133.22 (d, C-7 or C-8), 133.11 (d, C-8 or C-7), 133.00 (s, C_6H_5—), 129.91 (d, C-6 or C-9), 129.3 (d, C-9 or C-6), 128.00, 126.72, 126.62, 125.83, 125.31, 124.86, 124.68, 124.44, 124.38 (d, CH_{arom}). For $C_{23}H_{14}N_2O_3$ (M_r = 366.4) w_i(calc.): 75.40 % C, 3.82 % H, 7.65 % N; w_i(found): 75.23 % C, 4.09 % H, 7.38 % N.

XIVb: M.p. = 243 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}:2909, 1680, 1672, 1623, 1591. ^{1}H NMR spectrum ($CDCl_3$), δ: 3.33 (s, 3H, OCH_3), 7.12—7.67 (m, 9H, H_{arom}), 7.76—7.81 (m, 2H, H-6,7), 7.93—8.20 (m, 2H, H-5,8). For $C_{24}H_{16}N_2O_4$ (M_r = 396.4) w_i(calc.): 72.27 % C, 4.07 % H, 7.07 % N; w_i(found): 72.98 % C, 4.26 % H, 6.82 % N.

XIVc: M.p. = 274 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 2993, 1678, 1663, 1628, 1591. ^{1}H NMR spectrum ($CDCl_3$), δ: 2.18 (s, 3H, CH_3), 7.02—7.62 (m, 11H, H_{arom}, H-6,7), 7.83—7.98 (m, 2H, H-5,8). For $C_{24}H_{16}N_2O_3$ (M_r = 380.4) w_i(calc.): 75.78 % C, 4.24 % H, 7.36 % N; w_i(found): 76.01 % C, 4.03 % H, 7.21 % N.

4-Acetyl-3-aryl-1-phenyl-1,4-dihydronaphtho-[2,3-*e*][1,2,4]-triazine-5,10-dione *XVI*

To a solution of 2-acetylamino-3-chloro-1,4-naphthoquinone (*XV*) (0.01 mol) in pyridine (10 cm^3), aromatic aldehyde phenylhydrazone (*V*) (0.01 mol) was added under stirring. The mixture was refluxed for 6 h. The precipitate was filtered off, washed with ethanol, dried, and recrystallized from benzene.

XVIa: M.p. = 260 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 1758, 1677, 1671, 1623, 1590. ^{1}H NMR spectrum ($CDCl_3$), δ: 2.61 (s, 3H, $COCH_3$), 7.01—7.43 (m, 10H, H_{arom}),

7.59—7.72 (m, 2H, H-6,7), 7.81—8.02 (m, 2H, H-5,8). ^{13}C NMR spectrum ($CDCl_3$), δ: 182.20 (s, C-5 or C-10), 181.81 (s, C-10 or C-5), 169.33 (s, $COCH_3$), 165.2 (s, C-3), 155.23 (s, C-4a), 154.34 (s, C-10a), 152.13 (s, C_6H_5—N), 134.82 (s, C-9a), 133.26 (d, C-7 or C-8), 133.00 (d, C-8 or C-7), 131.82 (s, C-5a), 131.25 (s, C_6H_5—), 129.99 (d, C-9 or C-6), 129.73 (d, C-6 or C-9), 126.38, 126.00, 125.83, 125.72, 125.63, 125.36, 124.92, 124.63, 124.31, 124.22 (d, CH_{arom}), 22.62 (q, CH_3). For $C_{25}H_{17}N_3O_3$ (M_r = 407.4) w_i(calc.): 73.70 % C, 4.21 % H, 10.31 % N; w_i(found): 73.93 % C, 4.45 % H, 10.18 % N.

XVIb: M.p. > 360 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 1760, 1673, 1670, 1620, 1593. ^{1}H NMR spectrum ($CDCl_3$), δ: 2.41 (s, 3H, $COCH_3$), 3.28 (s, 3H, OCH_3), 7.21—7.76 (br, 11H, H_{arom}, H-6,7), 7.83—8.10 (m, 2H, H-5,8). For $C_{26}H_{19}N_3O_4$ (M_r = 437.4) w_i(calc.): 71.38 % C, 4.38 % H, 9.61 % N; w_i(found): 71.21 % C, 4.17 % H, 9.49 % N.

XVIc: M.p. > 360 °C. IR spectrum, $\tilde{\nu}$/cm^{-1}: 1755, 1670, 1668, 1623, 1592. ^{1}H NMR spectrum ($CDCl_3$), δ: 2.23 (s, 3H, CH_3), 2.44 (s, 3H, $COCH_3$), 7.11—7.57 (m, 11H, H_{arom}, H-6,7), 7.80—7.92 (m, 2H, H-5,8). For $C_{26}H_{19}N_3O_3$ (M_r = 421.4) w_i(calc.): 74.10 % C, 4.54 % H, 9.97 % N; w_i(found): 73.88 % C, 4.62 % H, 10.08 % N.

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