Transformations of 1-amino-2-(3-hydroxyalk-1-ynyl)-9,10-anthraquinones in the presence of amines

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When heated in piperidine, 1-amino-2-(3-hydroxyalk-1-ynyl)-9,10-anthraquinones undergo cyclization into 2-(1-hydroxyalkyl)naphtho[2,3-*g*]indole-6,11-diones. In contrast, 1-amino-2-(3-hydroxy-3-phenylpropynyl)-9,10-anthraquinone reacts with primary and secondary amines to give the corresponding 1-amino-2-(1-amino-2-benzoylvinyl)-9,10-anthraquinones, which undergo cyclization into 4-dialkylamino- or 4-alkylamino-2-phenylnaphtho[2,3-*h*]quinoline-7,12-diones. Heating of the starting phenylpropynol with Et_3N causes its dehydrogenation and isomerization.

Key words: 1-amino-2-(3-hydroxyalk-1-ynyl)-9,10-anthraquinones, addition of amines, dehydrogenation, isomerization, cyclization, 2-(1-hydroxyalkyl)naphtho[2,3-*g*]indole-6,11-diones, 4-dialkylamino-2-phenylnaphtho[2,3-*h*]quinoline-7,12-diones.

Fused quinoid heterocycles are interesting as substances with potential biological activity.[1—3] A general approach to their synthesis is based on the use of alkynyl derivatives of simple quinones (anthra-, naphtho-, and benzoquinones) as key intermediates.[4—8] Earlier,[5,9—11] it was shown that the addition of amines to alkynylquinones containing a functional group vicinal to the alkynyl substituent changes the geometry of the unsaturated fragment and, in most cases, allows easy cyclization of the adducts obtained. Depending on the structure and/or the reaction conditions, the resulting heterocycle can either lose or retain the amino group. We have developed methods for the synthesis of naphthoquinoline- and naphthoindolediones from amino adducts of different vicinal oxo-, alkoxycarbonyl-, alkyl-, and arylacetylenic derivatives of aminoanthraquinones.[5,12—14]

In the present work, the possibility and specific features of the formation of adducts and the heterocyclization of 1-amino-2-(3-hydroxyalk-1-ynyl)-9,10-anthraquinones (**1**—**3**) in their reactions with amines were studied.

Results and Discussion

It was found that, when heated in piperidine at 80—106 °C, 1-amino-2-(3-hydroxyprop-1-ynyl)- (**1**) and 1-amino-2-(3-hydroxyhex-1-ynyl)-9,10-anthraquinones (**2**) undergo intramolecular cyclization into 2-(1-hydroxyalkyl)naphtho[2,3-*g*]indole-6,11-diones (**4**, **5**) in 58 and 77% yields, respectively (Scheme 1).

Closure of the pyrrole ring in the heterocyclization of alcohols **1** and **2** under these conditions is hardly possible without prior addition of the amine to the triple bond. At the same time, no intermediates were detected chromatographically during the cyclization. This suggests that the multistep reaction includes the addition of the amine to compounds **1** and **2**, cyclization proper of the adduct, and elimination of the amine, the formation of the adduct being the rate-limiting step.

Unlike alcohols **1** and **2**, phenyl analog **3** reacts with piperidine, as well as with diethylamine and butylamine, at 40—80 °C in dioxane or without a solvent to give aminovinyl ketones **6a**—**c** rather than expected substituted aminoallyl alcohols.

Such an unusual outcome of the reaction of compound **3** with amines prompted us to search for additional confirmation of the structures of adducts **6a**—**c**. The cyclization of amino ketones **6a**—**c** in the presence of small amounts of H_2SO_4 in benzene at 20 °C gave dialkyl(or alkyl)amino-2-phenylnaphtho[2,3-*h*]quinoline-7,12-diones (**7a**—**c**). In addition, heating of alcohol **3** in morpholine at 120 °C for 1 h yielded naphthoquinolinedione **7d**. Adducts **6a**—**c** and cyclization products **7a**—**c** and **7d** were compared with authentic compounds synthesized[13] from 1-amino-2-benzoylethynyl-9,10-anthraquinone (**8**). The substances obtained by two independent methods were identical, which unambiguously proves the correctness of structures **6a**—**c** for the adducts of amines to alcohol **3**.

While studying the way in which alcohol **3** is transformed into amino ketones **6**, we found that heating of **3** in Et_3N (8 h, 80 °C) — unlike secondary and primary amines, it cannot add to the triple bond—affords two products, namely, 1-amino-2-benzoylethynyl- (**8**) and *E*-1-amino-2-(2-benzoylvinyl)-9,10-anthraquinones (**9**) in virtually quantitative yield in the ratio 1 : 1 (Scheme 2).

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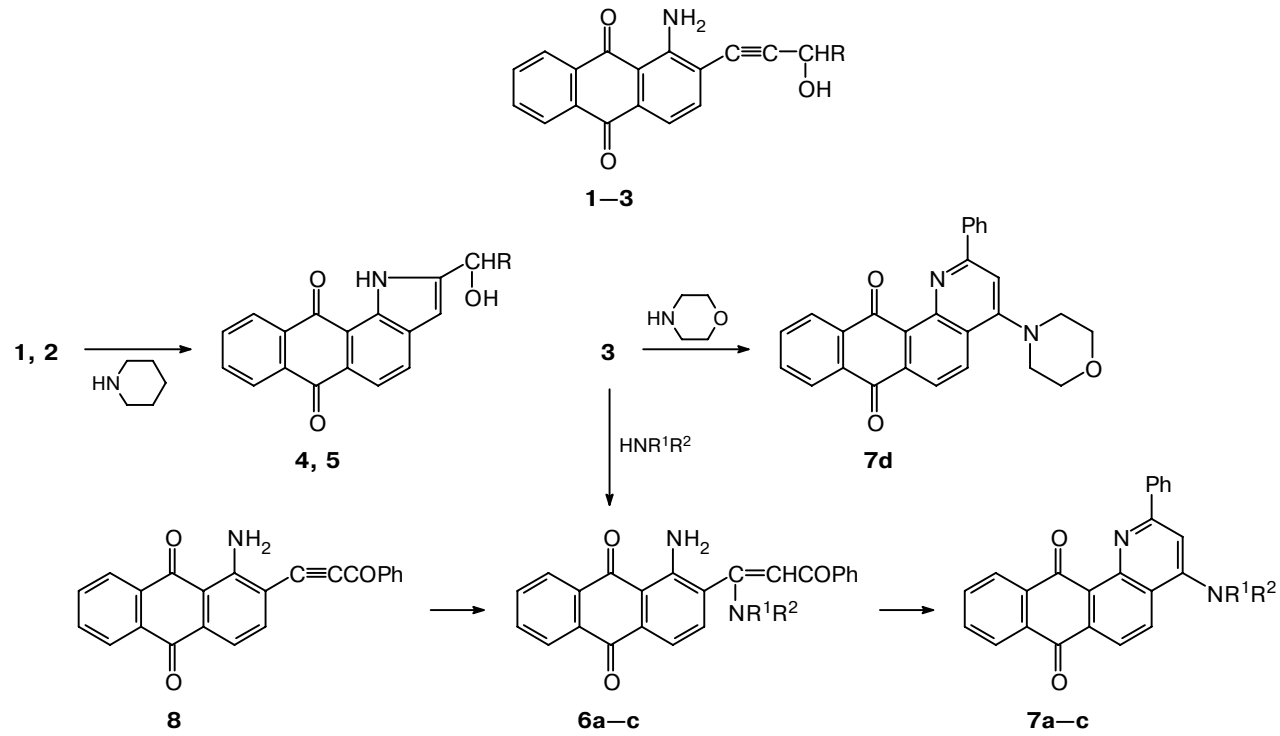
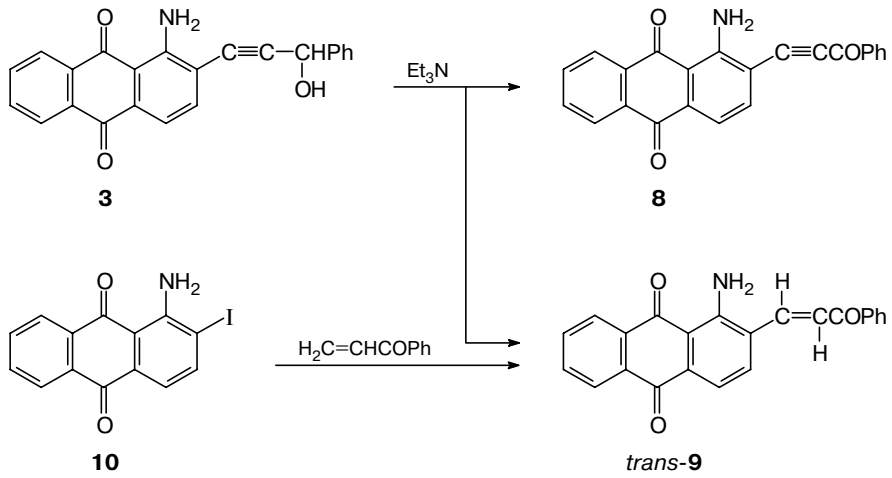
Scheme 1



Scheme 2

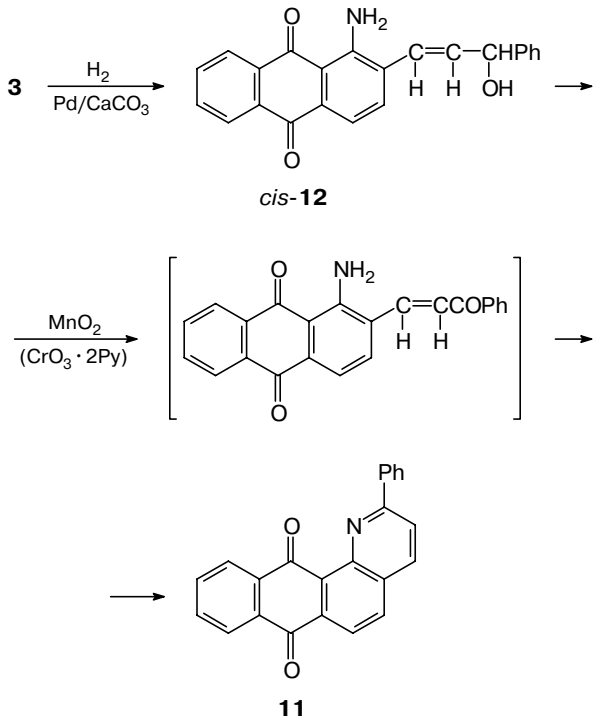


The structure of vinyl ketone **9** was confirmed by an independent Pd-catalyzed synthesis from 1-amino-2-iodo-9,10-anthraquinone (**10**) and phenyl vinyl ketone ($Pd(PPh_3)_2Cl_2$, MeCN, refluxing for 6 h); the yield of **9** was 53%. Amino ketone **9** in conc. H_2SO_4 undergoes no intramolecular cyclization into 2-phenylnaphtho[2,3-*h*]quinoline-7,12-dione (**11**), which proved unambiguously its *E*-configuration.

Alkynol **3** was selectively hydrogenated on $Pd/CaCO_3$ to give allylic alcohol **12**, which was then oxidized with

active MnO_2 in $CHCl_3$ or with $CrO_3 \cdot 2Py$ in CH_2Cl_2 at 20 °C. The resulting *Z*-isomer of vinyl ketone **9** underwent cyclization into naphthoquinoline **11** under reaction conditions (Scheme 3).

Scheme 3



Thus, it was found that heating of alcohol **3** in Et_3N induces its oxidation into ethynyl ketone **8** and isomerization into *E*-vinyl ketone **9**.

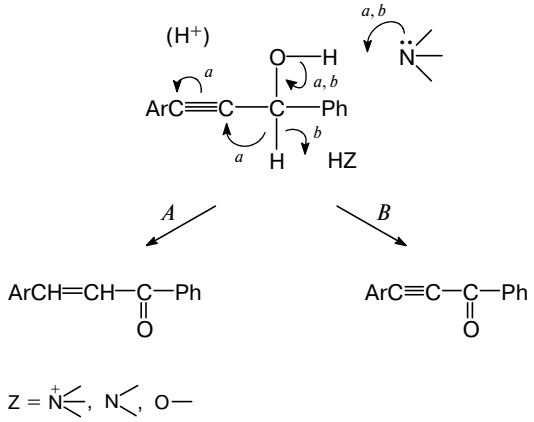
Information on the oxidation of secondary alkynols under similar conditions is lacking. It is known that primary and secondary alkynols isomerize into α,β-enones in the presence of metallocomplex catalysts.[15,16] It has also been shown that 1,3-diarylprop-2-yn-1-ols isomerize in boiling aqueous-ethanolic KOH.[17] The resulting enones were not isolated because of their scission into simpler carbonyl compounds. Under these conditions, primary β-alkynols and purely aliphatic secondary alcohols did not isomerize.

Later, it was found that hydroxyalkynoates and hydroxyethynyl ketones of the general formula $RCH(OH)C{\equiv}CCOR^1$ (R = Ar, Het, or $R^2CH{=}CH$— and R^1 = Ar or OEt) isomerize under the action of Bu_3N into the corresponding 4-oxoalk-2-enoates and 2-alkene-1,4-diones.[18]

Cross-linking of some substituted iodoazines containing the N atom linked to the C—I fragment with 1-phenylprop-2-yn-1-ol in Et_3N in the presence of $Pd(PPh_3)_2Cl_2$—CuI was reported to give anomalous products, namely, *E*-enones.[19] Presumably, the Pd-catalyzed condensation is accompanied by amine-catalyzed isomerization of the product.

Comparison of the literature data on the isomerization of alkynols with our experimental results suggests that the anomalous formation of dehydro adducts **6** in the reaction of alcohol **3** with amines is due to a high hydride mobility of the hydrogen at the C atom bearing the OH group of compound **3**. This is associated with the presence of both the phenyl group at this carbon atom and an aromatic (electron-acceptor quinone) fragment bound to the acetylenic group. This provides the structural basis for the formation of a long conjugated system upon H^- abstraction and facilitates the process itself, which occurs already when a base accepts the OH proton. Indeed, secondary alkynols of this structural type isomerize into vinyl ketones in the presence of bases,[17—19] whereas in other cases more efficient metallocomplex catalysts are required.[15,16] In our opinion, the mechanism of the base-catalyzed isomerization of such alcohols includes the abstraction of the OH proton by a base and the migration of the hydride ion to the nearest C atom of the ethynyl group, which are accompanied by proton transfer from the conjugated acid of the base used, *e.g.*, amine, to the second acetylene C atom (pathway *a*). The isomerization is a redox process, whereupon the secondary alcohol group of the molecule oxidizes, while the triple bond is reduced. At the same time, the hydride ion can apparently be accepted not only by the triple bond, but also by the acid functions (HO, HN, and HN^+) of the reaction components with evolution of hydrogen (pathway *b*) or by the quinone CO group with subsequent oxidation of the resulting hydroquinone by atmospheric oxygen (Scheme 4).

Scheme 4



The mechanism of the dehydrogenation of alcohol **3** into ethynyl ketone **8** is not proved, the acceptor of the hydride ion remaining unknown. Obviously, this reaction pathway becomes dominant in the presence of secondary amine, while with tertiary amine the rates of dehydrogenation and isomerization of alcohol **3** are comparable.

The starting alcohols **1**—**3** were synthesized by the coupling of 1-amino-2-iodo-9,10-anthraquinone (**10**) with the corresponding hydroxyacetylenes in aqueous pyridine in the presence of $Pd(PPh_3)_2Cl_2$, CuI, and Na_2CO_3 according to the known procedure.[20] Ketone **8** was obtained by the oxidation of alcohol **3** by the Collins reagent ($CrO_3 \cdot 2Py$) in CH_2Cl_2 at 20 °C.

Experimental

^{1}H NMR spectra were recorded on Bruker AM-250 and JEOL-FX-90 spectrometers in $CDCl_3$ at 25 °C. IR spectra were recorded on a UR-20 spectrophotometer in $CHCl_3$. The course of the reaction was monitored by TLC on Silufol plates in a benzene—ether solvent system.

1-Amino-2-(3-hydroxyprop-1-ynyl)-9,10-anthraquinone (1). Propargyl alcohol (0.04 g, 0.7 mmol) was added with stirring in an atmosphere of Ar at 75 °C to anthraquinone **10** (0.20 g, 0.6 mmol), $Pd(PPh_3)_2Cl_2$ (5 mg), and CuI (3 mg) in 4 mL of pyridine. Then a solution of Na_2CO_3 (0.06 g, 0.6 mmol) in 1.9 mL of water preheated to 80 °C was rapidly added, and stirring was continued at 75 °C for 5 min. The reaction mixture was diluted with 100 mL of $CHCl_3$ and washed with dilute HCl and water. Chromatography on SiO_2 in $CHCl_3$ gave compound **1** (0.13 g, 81.8%), m.p. 225—227 °C ($CHCl_3$—pentane). Found (%): C, 73.70; H, 3.94; N, 5.01. $C_{17}H_{11}NO_3$. Calculated (%): C, 73.64; H, 4.00; N, 5.05. ^{1}H NMR (DMSO-d_6), δ: 4.40 (d, 2 H, CH_2, J = 5.8 Hz); 5.45 (t, 1 H, OH, J = 5.8 Hz); 7.39 (d, 1 H, C(3/4)H, J = 7.7 Hz); 7.65 (d, 1 H, C(4/3)H, J = 7.7 Hz); 7.75—7.95 (m, 2 H, C(6)H, C(7)H); 8.05—8.25 (m, 2 H, C(5)H, C(8)H).

The same procedure was used to obtain **1-amino-2-(3-hydroxyhex-1-ynyl)-9,10-anthraquinone (2)** (15 min, 80 °C), yield 91.2%, m.p. 161.5—162.5 °C (benzene). Found (%): C, 75.13; H, 5.26; N, 4.28. $C_{20}H_{17}NO_3$. Calculated (%): C, 75.22; H, 5.37; N, 4.39. ^{1}H NMR, δ: 1.02 (t, 3 H, CH_3, J = 7.0 Hz); 1.40—2.00 (m, 4 H, CH_2CH_2); 2.10 (d, 1 H, OH, J = 5.3 Hz); 4.74 (m, 1 H, CHO—); 7.59 (s, 2 H, C(3)H, C(4)H); 7.50—8.00 (m, 2 H, C(6)H, C(7)H); 8.15—8.40 (m, 2 H, C(5)H, C(8)H). IR, ν/cm^{-1}: 1650, 1675 (C=O); 3345, 3485 (NH_2); 3600 (OH).

1-Amino-2-(3-hydroxy-3-phenylprop-1-ynyl)-9,10-anthraquinone (3) (7 min, 85 °C), yield 90.8%, m.p. 172.5—173.5 °C ($CHCl_3$). Found (%): C, 78.07; H, 4.56; N, 3.87. $C_{23}H_{25}NO_3$. Calculated (%): C, 78.17; H, 4.28; N, 3.96. ^{1}H NMR, δ: 2.38 (br.s, 1 H, OH); 5.79 (br.s, 1 H, CHO—); 7.30—7.50 (m, 3 H, 3 HPh); 7.61 (s, 2 H, C(3)H, C(4)H); 7.50—8.05 (m, 4 H, C(6)H, C(7)H, 2 HPh); 8.10—8.40 (m, 2 H, C(5)H, C(8)H). IR, ν/cm^{-1}: 1660, 1675 (C=O); 3345, 3495 (NH_2); 3600 (OH).

1-Amino-2-benzoylethynyl-9,10-anthraquinone (8). Alcohol **3** (0.80 g, 2.3 mmol) was oxidized with $CrO_3 \cdot 2Py$ (3.00 g, 11.6 mmol) in 225 mL of anhydrous CH_2Cl_2 at 20 °C for 1.5 h. The yield of **8** was 0.77 g (96.8%), m.p. 254—256 °C ($CHCl_3$).[13]

***Z*-1-Amino-2-(3-hydroxy-3-phenylprop-1-enyl)-9,10-anthraquinone (12).** Alcohol **3** (0.11 g, 0.3 mmol) in 12 mL of peroxide-free dioxane was hydrogenated in the presence of $Pd/CaCO_3$ at 20 °C until the starting compound **3** disappeared; 0.7 mmol of H_2 was absorbed. Chromatography on SiO_2 in a mixture of toluene and ether (7 : 3) gave compound **12** (0.09 g, 81.4%), m.p. 161—162 °C (benzene—hexane). Found (%): C, 77.67; H, 4.70; N, 4.20. $C_{23}H_{17}NO_3$. Calculated (%): C, 77.73; H, 4.70; N, 3.94. ^{1}H NMR, δ: 2.05 (br.s, 1 H, OH); 5.33 (d, 1 H, CHO—, J = 8.3 Hz); 6.05—6.60 (m, 2 H, CH=CH); 7.05 (br.s, 2 H, NH_2); 7.25—7.45 (m, 6 H, 5 HPh, C(3/4)H); 7.65 (d, 1 H, C(4/3)H, J = 8.0 Hz); 7.50—7.85 (m, 2 H, C(6)H, C(7)H); 8.10—8.40 (m, 2 H, C(5)H, C(8)H). IR, ν/cm^{-1}: 1645, 1675 (C=O); 3335, 3495 (NH_2); 3600 (OH).

2-Hydroxymethylnaphtho[2,3-*g*]indole-6,11-dione (4). Alcohol **1** (0.12 g, 0.4 mmol) in 5 mL of piperidine was stirred at 80 °C for 3 h 15 min and poured into 400 mL of water. The products were extracted with 150 mL of benzene. The extract was washed with water and concentrated *in vacuo* to 5 mL. Pentane was added (20 mL), and the crystals that formed were filtered off. The yield of product **4** was 0.07 g (58.3%), m.p. 222—223 °C (benzene). Found (%): C, 73.55; H, 3.93; N, 5.08. $C_{23}H_{17}NO_3$. Calculated (%): C, 73.64; H, 4.00; N, 5.05. ^{1}H NMR (DMSO-d_6), δ: 4.72 (d, 2 H, CH_2, J = 5.0 Hz); 5.46 (t, 1 H, OH, J = 5.0 Hz); 6.50 (s, 1 H, C(3)H); 7.60—7.95 (m, 4 H, C(4)H, C(5)H, C(8)H, C(9)H); 7.95—8.40 (m, 2 H, C(7)H, C(10)H); 11.57 (br.s, 1 H, NH). IR, ν/cm^{-1}: 1670 (C=O); 3450 (NH).

2-(1-Hydroxybutyl)naphtho[2,3-*g*]indole-6,11-dione (5) was obtained analogously (refluxing for 18 h), yield 76.7%, m.p. 135—137 °C (benzene). Found (%): C, 75.31; H, 5.34; N, 4.35. $C_{20}H_{17}NO_3$. Calculated (%): C, 75.22; H, 5.37; N, 4.39. ^{1}H NMR, δ: 1.00 (t, 3 H, CH_3, J = 7.3 Hz); 1.20—2.20 (m, 4 H, CH_2CH_2); 2.57 (d, 1 H, OH, J = 4.2 Hz); 4.94 (m, 1 H, CHO—); 6.31 (d, 1 H, C(3)H, J = 1.9 Hz); 7.55—8.00 (m, 4 H, C(4)H, C(5)H, C(8)H, C(9)H); 8.00—8.45 (m, 2 H, C(7)H, C(10)H); 10.53 (br.s, 1 H, NH). IR, ν/cm^{-1}: 1670 (C=O); 3450 (NH); 3600 (OH).

1-Amino-2-(2-benzoyl-1-piperidinovinyl)-9,10-anthraquinone (6a). Alcohol **3** (0.40 g, 1.2 mmol) and piperidine (0.50 g, 5.8 mmol) were heated in 10 mL of dioxane at 75 °C for 7 h. The solvent and the excess of piperidine were removed *in vacuo*. The residue was dissolved in 30 mL of benzene, and 30 mL of pentane was added. The precipitate that formed was separated to give compound **6a** (0.33 g, 66.8%), decomp. < 195 °C (ether). The product is identical to anthraquinone **6a** synthesized by the addition of piperidine to ketone **8**.[13]

1-Amino-2-(2-benzoyl-1-butylaminovinyl)-9,10-anthraquinone (6c) was obtained analogously from alcohol **3** and $BuNH_2$ (refluxing for 2.5 h), yield 66.7%, m.p. 193—195 °C (ether). The product is identical to that synthesized from ketone **8**.[13]

1-Amino-2-(2-benzoyl-1-diethylaminovinyl)-9,10-anthraquinone (6b). Alcohol **3** (0.60 g, 1.7 mmol) in 10 mL of Et_2NH was heated at 40 °C for 3.5 h (monitoring by TLC on Silufol in $CHCl_3$), concentrated *in vacuo* to 4 mL, and diluted with 60 mL of pentane. The precipitate that formed was filtered off and chromatographed on SiO_2 in $CHCl_3$ to give compound **6b** (0.55 g, 76.3%), m.p. 193—195 °C (benzene—pentane). The product is identical to that synthesized according to the known procedure.[13]

4-Piperidino-2-phenylnaphtho[2,3-*h*]quinoline-7,12-dione (7a). Ketone **6a** (0.15 g, 0.3 mmol) was vigorously stirred with conc. H_2SO_4 (0.1 mL) in 40 mL of benzene at 20 °C for 30 min. The precipitate that formed was separated and treated with aqueous $NaHCO_3$, and compound **7a** was extracted with benzene (100 mL), yield 0.10 g (69.5%), m.p. 233—235 °C (benzene—pentane). The product is identical to that synthesized according to the known procedure.[13]

The same procedure was used to obtain **4-diethylamino-2-phenylnaphtho[2,3-*h*]quinoline-7,12-dione (7b)**, yield 99.2%, m.p. 168—169 °C (benzene—pentane)[13] and **4-butylamino-2-phenylnaphtho[2,3-*h*]quinoline-7,12-dione (7c)**, yield 55.0%, m.p. 190—192 °C (benzene).[13]

4-Morpholino-2-phenylnaphtho[2,3-*h*]quinoline-7,12-dione (7d). Alcohol **3** (0.15 g, 0.4 mmol) was heated in 5 mL of morpholine at 120 °C for 1 h and diluted with 50 mL of water.

The precipitate that formed was filtered off and chromatographed on Al_2O_3 and SiO_2 in benzene to give compound **7d** (0.10 g, 56.2%), m.p. 207—208 °C (benzene—ether). The product is identical to that obtained according to the known procedure.[13]

Isomerization and dehydrogenation of 1-amino-2-(3-hydroxy-3-phenylprop-1-ynyl)-9,10-anthraquinone (3). Alcohol **3** (0.40 g, 1.1 mmol) was refluxed for 8 h in a mixture of Et_3N (5 mL) and benzene (50 mL). The precipitate that formed on cooling was filtered off and thoroughly washed with benzene and boiling $CHCl_3$. The solvent was removed from the combined filtrate, and the residue was chromatographed on Al_2O_3 in $CHCl_3$ to give ethynyl ketone **8** (0.19 g, 47.8%) and ***E*-1-amino-2-(2-benzoylvinyl)-9,10-anthraquinone (9)** (0.02 g). The latter was combined with the washed precipitate (0.18 g) of virtually pure compound **9**; the total yield of vinyl ketone **9** was 50.0%, m.p. 269—271 °C (dioxane). Found (%): C, 77.93; H, 4.09; N, 3.90. $C_{23}H_{15}NO_3$. Calculated (%): C, 78.17; H, 4.28; N, 3.96.

Vinyl ketone **9** was obtained independently by the condensation of 1-amino-2-iodoanthraquinone (**10**) with phenyl vinyl ketone. Phenyl vinyl ketone was added in two equal portions (each 0.64 g, 4.8 mmol) in 18 mL of MeCN at an interval of 3 h to a boiling solution of iodide **10** (0.56 g, 1.6 mmol), $Pd(PPh_3)_2Cl_2$ (40 mg), and Et_3N (5.6 mL) in 28 mL of MeCN. The reaction mixture was stirred for 6 h 15 min overall (TLC monitoring on Silufol in benzene). The yield of vinyl ketone **9** was 0.30 g (53.0%).

2-Phenylnaphtho[2,3-*h*]quinoline-7,12-dione (11). ***A.*** Alcohol **12** (0.22 g, 0.6 mmol) was stirred with active MnO_2 (3.40 g) in 35 mL of $CHCl_3$ at 20 °C for 28 h. Chromatography on SiO_2 in toluene gave product **11** (0.11 g, 54.6%), m.p. 237—238 °C (benzene). Found (%): C, 82.32; H, 4.01; N, 4.40. $C_{23}H_{13}NO_2$. Calculated (%): C, 82.37; H, 3.91; N, 4.18. ^{1}H NMR, δ: 7.45—7.70 (m, 3 H, 3 HPh); 7.70—7.95 (m, 2 H, C(9)H, C(10)H); 7.95—8.80 (m, 6 H, C(5)H, C(6)H, C(8)H, C(11)H, 2 HPh). IR, ν/cm^{-1}: 1680 (C=O).

B. Alcohol **12** (0.13 g, 0.4 mmol) and $CrO_3 \cdot 2Py$ (0.48 g, 1.9 mmol) in 40 mL of anhydrous CH_2Cl_2 were stirred at 20 °C for 7 h and poured into a solution of $NaHCO_3$ (6.0 g) in 200 mL of water. Compound **11** was extracted with 200 mL of toluene and purified by chromatography on SiO_2 in toluene, yield 0.05 g (40.8%).

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