A new heterocyclization in the series of acetylenic derivatives of anthraquinone

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2-Alkynyl-1-amino-9,10-anthraquinones react with HNO_2 in a mixture of dilute HCl and dioxane at 20 °C to give 1,1-dichloroalkyl-1*H*-3-naphtho[2,3-g]indazole-6,11-diones. This reaction differs from the known cyclization of *ortho*-alkynylbenzenediazonium salts involving the formation of a pyridazine ring (the Richter synthesis of 4-hydroxy- and 4-halocinnolines).

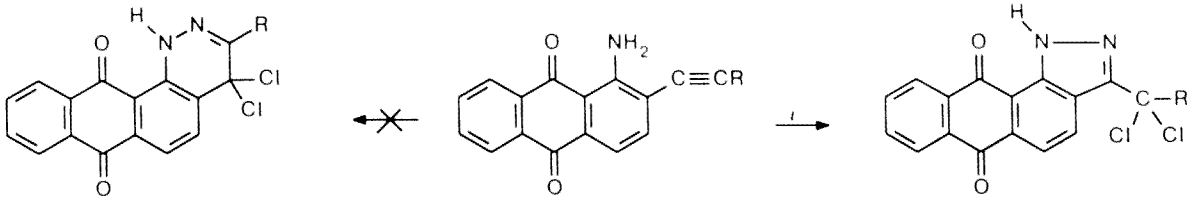
Key words: the Richter reaction, 2-alkynyl-1-amino-9,10-anthraquinones, cyclization, 3-substituted 1*H*-naphtho[2,3-g]indazole-6,11-diones.

In a continuation of our investigations dealing with the synthesis of fused polycyclic structures,[1–5] we studied the cyclization of 2-alkynyl-1-amino-9,10-anthraquinones under the action of nitrous acid (for the previous communication, see Ref. 6). *Ortho*-alkynylbenzenediazonium salts and some of their heterocyclic analogs are known to undergo cyclization to give 4-hydroxy- and 4-halocinnolines or, correspondingly, heteroanalogs of these compounds (the Richter reaction).[7,8] In the series of alkynylanthraquinones, no such reactions have been described, and their possibility is not at all obvious, since the nucleophilicity of the acetylenic residue in the quinoid nucleus is low,[9] and the functional group, which adds intramolecularly at the triple bond in the Richter reaction, is electrophilic.

2-Alkynyl-1-amino-9,10-anthraquinones **1a—c** were introduced into a reaction with a 1.7—2-fold excess of $NaNO_2$ in a mixture of dilute HCl and dioxane at 20 °C. Under these conditions, compounds **1a—c** were completely consumed over a period of 10—30 min to afford in each case one major product, containing one more H atom and one more Cl atom than the expected 4-chloronaphtho[2,3-*h*]cinnoline-7,12-dione (yields 65—82 %). Formation of dihalides has not been observed previously in the Richter reaction. Nevertheless, the presence of a ^1H NMR signal at 11.85 ppm (in $CDCl_3$) or at 14.25 ppm (in DMSO-d_6) corresponding to the NH-group and the possibility of stabilization of the molecule by an intramolecular hydrogen bond seemed to give grounds for attributing the structure of 4,4-dichloro-1,4-dihydronaphtho[2,3-*h*]cinnoline-7,12-diones (**2**) (Scheme 1) to the compounds obtained.

However, when we attempted to carry out dehydrochlorination of these compounds under the action of bases, we found that the dichloroalkyl group is located in the α-position of the side chain. This implies that cyclization of the intermediate diazonium salts or, possibly, of other intermediates having a similar structure, affords a five-membered pyrazole ring rather than a six-membered pyridazine ring (which is formed in known

Scheme 1



2 **1a—c** **3a—c**

i. $NaNO_2$, dilute HCl, dioxane, 20 °C

a: R = Bu, **b**: R = CH_2OPh, **c**: R = H

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examples of the Richter reaction), and thus the reaction yields 3-substituted 1*H*-naphtho[2,3-*g*]indazole-6,11-diones (**3a—c**) (Table 1).

In fact, when dichlorides **3a,b** react with BuLi, they lose an HCl molecule and are converted into monochlorides **4a,b** in 72 and 63 % yields, respectively. Dehydro-

Table 1. Yields and characteristics of 3-substituted 1*H*-naphtho[2,3-*g*]indazole-6,11-diones **3—9**

Starting compound	Product	Yield (%)	M.p./°C (solvent)	Molecular formula	Found / Calculated (%)			^{1}H NMR ($CDCl_3$, δ, *J*/Hz)
					C	H	N	
1a	**3a**	65.4	190—191 (dioxane —hexane)	$C_{20}H_{16}Cl_2N_2O_2$	62.15 / 62.03	4.15 / 4.16	18.30 / 18.31	1.00 (t, 3 H, CH_3, *J* = 7.0); 1.20—2.00 (m, 4 H, β- and γ-CH_2); 2.93 (t, 2 H, α-CH_2, *J* = 7.0); 7.70—7.90 (m, 2 H, H-8,9); 8.20—8.45 (m, 2 H, H-7,10); 8.12 (d, 1 H, H-5(4), *J* = 8.3); 8.62 (d, 1 H, H-5(4), *J* = 8.3); 11.85 (br.s, 1 H, NH)
1b	**3b**	76.9	235—236 (toluene)	$C_{23}H_{14}Cl_2N_2O_3$	62.95 / 63.17	3.22 / 3.23	16.01 / 16.21	—
1c	**3c**	82.4	279—281 (with decomp., benzene)	$C_{16}H_8Cl_2N_2O_2$	57.97 / 58.03	2.63 / 2.43	21.10 / 21.41	7.90—8.35 (m, 6 H, H-4(5),7—10, $CHCl_2$); 8.50 (d, 1 H, H-5(4), *J* = 9.0); 14.25 (br.s, 1 H, NH)*
3a	**4a**	72.0	223—224 (dioxane —hexane)	$C_{20}H_{15}ClN_2O_2$	68.61 / 68.48	4.31 / 4.32	10.11 / 9.96	1.05 (t, 3 H, CH_3, *J* = 7.7); 1.65 (sextet, 2 H, CH_2CH_3, *J* = 7.7); 2.50 (κ, 2 H, CH_2CH=, *J* = 7.7); 6.63 (t, 1 H, CH=, *J* = 7.7); 7.70—7.90 (m, 2 H, H-8,9); 8.12 (d, 1 H, H-4(5), *J* = 8.4); 8.20—8.40 (m, 2 H, H-7,10); 8.45 (d, 1 H, H-5(4), *J* = 8.4); 11.87 (br.s, 1 H, NH)
3b	**4b**	72.0	223—224 (dioxane —hexane)	$C_{20}H_{15}ClN_2O_2$	68.61 / 68.48	4.31 / 4.32	10.11 / 9.96	7.10—7.55 (m, 6 H, CH=, Ph); 7.80—8.10 (m, 2 H, H-8,9); 8.15—8.40 (m, 2 H, H-7,10); 8.20 (d, 1 H, H-4(5) *J* = 8.5); 8.55 (d, 1 H, H-5(4), *J* = 8.5); 14.15 (br.s, 1 H, NH)*
3a	**5a**	82.0	164—165 (ethanol)	$C_{22}H_{22}N_2O_4$	70.02 / 69.83	5.84 / 5.86	7.54 / 7.40	0.77 (t, 3 H, CH_3, *J* = 6.5); 0.95—1.30 (m, 4 H, β- and γ-CH_2); 2.15 (t, 2 H, α-CH_2, *J* = 6.5); 3.30 (s, 6 H, OCH_3); 7.70—7.90 (m, 2 H, H-8,9); 8.20—8.35 (m, 2 H, H-7,10); 8.08 (d, 1 H, H-4(5), *J* = 8.4); 8.43 (d, 1 H, H-5(4), *J* = 8.4); 11.88 (br.s, 1 H, NH)
3b	**5b**	84.6	167—168 (benzene —hexane)	$C_{25}H_{20}N_2O_5$	70.10 / 70.08	4.83 / 4.71	6.57 / 6.54	3.45 (s, 6 H, OCH_3); 4.45 (s, 2 H, CH_2O); 6.70—7.00 (m, 3 H, Ph); 7.05—7.20 (m, 2 H, Ph); 7.70—7.90 (m, 2 H, H-8(9)); 8.20—8.40 (m, 2 H, H-7,10); 8.10 (d, 1 H, H-4(5), *J* = 9.0); 8.60 (d, 1 H, H-5(4), *J* = 9.0); 11.95 (br.s, 1 H, NH)
3c	**5c**	84.6	196—198 (benzene —hexane)	$C_{18}H_{14}N_2O_4$	67.52 / 67.07	4.42 / 4.38	8.78 / 8.69	3.48 (s, 6 H, OCH_3); 5.82 (s, 1 H, OCHO); 7.70—7.90 (m, 2 H, H-8,9); 8.20—8.35 (m, 2 H, H-7,10); 8.08 (d, 1 H, H-4(5), *J* = 9.0); 8.40 (d, 1 H, H-5(4), *J* = 9.0); 11.88 (br.s, 1 H, NH)

(*to be continued*)

Table 1 (*continued*)

Starting compound	Product	Yield (%)	M.p./°C (solvent)	Molecular formula	Found / Calculated (%)			^{1}H NMR ($CDCl_3$, δ, *J*/Hz)
					C	H	N	
1a **5a** **3a**	**6a**	65.6 92.8 47.4	255—256 (toluene)	$C_{20}H_{16}N_2O_3$	72.17 72.28	4.91 4.85	8.23 8.43	0.95 (t, 3 H, CH_3, *J* = 6.7); 1.20—1.90 (m, 4 H, β- and γ-CH_2); 3.28 (t, 2 H, α-CH_2, *J* = 6.7); 7.75—7.95 (m, 2 H, H-8,9); 8.25—8.45 (m, 2 H, H-7,10); 8.23 (d, 1 H, H-4(5), *J* = 8.5); 8.80 (d, 1 H, H-5(4), *J* = 8.5); 12.20 (br.s, 1 H, NH)
5b	**6b**	~100	249—251 (dioxane —hexane)	$C_{23}H_{14}N_2O_4$	72.24 72.25	3.77 3.69	7.14 7.33	—
5c	**6c**	94.0	296—298 (toluene)	$C_{24}H_{15}NO_4$	69.73 69.56	3.03 2.92	10.05 10.14	7.85—8.05 (m, 2 H, H-8,9); 8.10—8.35 (m, 3 H, H-4(5),7,10); 8.59 (d, 1 H, H-5,(4), *J* = 8.5); 10.30 (s, 1 H, CHO); 14.70 (br.s, 1 H, NH)*
7	**8****	86.6	281—282 (toluene)	$C_{17}H_{10}N_2O_4$	66.81 66.67	3.49 3.29	9.32 9.15	4.00 (s, 3 H, OCH_3); 7.85—8.05 (m, 2 H, H-8,9), 8.05—8.30 (m, 3 H, H-4(5),7,10); 8.50 (d, 1 H, *J* = 8.5, H-5(4)); 14.43 (br.s, 1 H, NH)*
5a	**10**	83.3	133—135 (benzene —hexane)	$C_{23}H_{24}N_2O_4$	70.42 70.39	5.97 6.16	6.93 7.14	0.75 (t, 3 H, CH_3, *J* = 6.7); 0.90—1.35 (m, 4 H, β- and γ-CH_2); 2.07 (t, 2 H, α-CH_2, *J* = 6.7); 3.25 (s, 6 H, OCH_3); 4.45 (s, 3 H, NCH_3); 7.65—7.85 (m, 2 H, H-8,9); 7.97 (d, 1 H, H-4(5), *J* = 8.3); 8.15—8.45 (m, 3 H, H-5(4),7,10)
10 **6a**	**9**	83.3 84.2	284—286 (benzene —hexane)	$C_{21}H_{18}N_2O_3$	72.57 72.82	5.26 5.24	7.96 8.09	1.00 (t, 3 H, CH_3, *J* = 6.7); 1.20—1.95 (m, 4 H, β- and γ-CH_2); 3.18 (t, 2 H, α-CH_2, *J* = 6.7); 4.63 (s, 3 H, NCH_3); 7.70—7.95 (m, 2 H, H-8,9); 8.15—8.45 (m, 4 H, H-4,5,7,10)

* In DMSO-d_6. ** MS, *m*/*z* 306.

chlorination with weak bases such as $NaHCO_3$ occurs in a similar way but with greater difficulties.

The structures of **4a,b** were confirmed by the data of elemental analysis and by NMR spectra (Table 1). For example, the spectrum of **4a** exhibits a triplet at 6.63 ppm (CCl=CH).

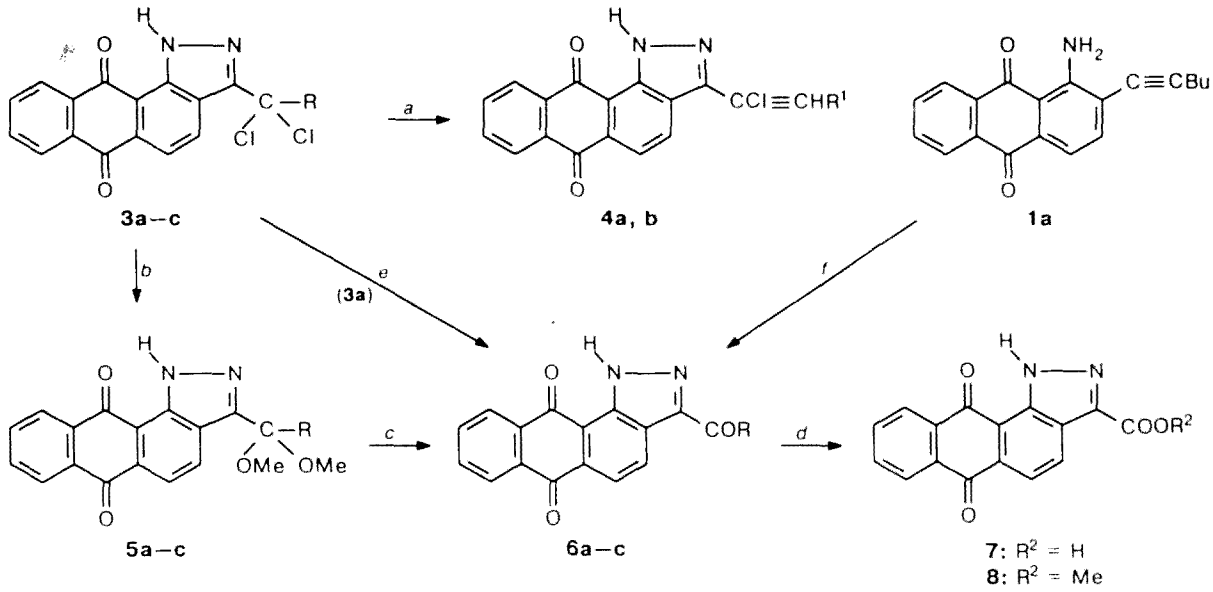
As should be expected, dichloromethylindazole **3c** does not undergo dehydrochlorination. Instead, it reacts with BuLi slowly and ambiguously (Scheme 2).

Both Cl atoms in **3a—c** are readily replaced by methoxy groups on treatment with MeONa in MeOH (20 °C, 5 min); the yields of the corresponding ketals **5a,b** and of acetal **5c** are 82—85 %. The ^{1}H NMR spectra of compounds **5a—c** contain a singlet corresponding to the two equivalent methyl groups in the 3.30—3.48 ppm region; the chemical shift of CH in **5c** is 5.82 ppm. Under the conditions normal for the hydrolysis of acetals (treatment with dilute H_2SO_4 in dioxane, 20 °C, 30 min), compounds **5a—c** afford the corresponding carbonyl compounds **6a—c** in >90 % yields. The formation of aldehyde **6c** proves unambiguously that dichloride **3c**, like dichlorides **3a,b**, is a 3-substituted 1*H*-naphtho[2,3-*g*]indazole-6,11-dione. The CHO group in compound **6c** is responsible for a doublet at 186.7 ppm in the ^{13}C NMR spectrum (with incomplete proton decoupling) and for a singlet at 10.30 ppm in the ^{1}H NMR spectrum.

Like ketone **6a**, aldehyde **6c** is oxidized by chromic acid to give 1*H*-6,11-dioxonaphtho[2,3-*g*]indazole-3-carboxylic acid **7** (yield 80 %); the latter was converted into the corresponding methyl ester **8** without purification.

It should be noted that in the case of dichlorides **3**, the acid hydrolysis typical of 4-chlorocinnolines occurs with great difficulty, and **3a** can be hydrolyzed to **6a** only by boiling in a mixture of 50% H_2SO_4 and dioxane for 51 h, and the yield of **6a** being less than 50 %. However, using this particular ketone **6a** as an example, it has been shown that 3-acylnaphthoindazoles **6** can be synthesized directly from alkynylanthraquinones **1** by

Scheme 2



a: R = Bu, R¹ = Pr; **b**: R = CH_2OPh, R¹ = OPh; **c**: R = H

a. BuLi, dioxane—hexane, 20 °C.

b. MeONa, MeOH, 20 °C, 5 min.

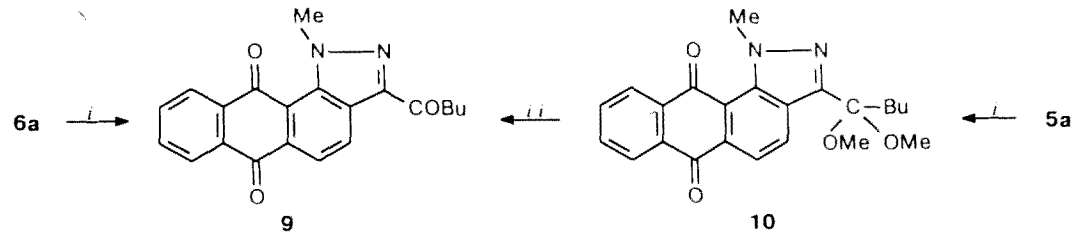
c. H_2SO_4 (dilute), dioxane, 20 °C, 30 min.

d. 1) $K_2Cr_2O_7$, H_2SO_4—AcOH, boiling for 1—3 h (for **7**); 2) MeOH, H_2SO_4, boiling for 12 h (for **8**).

e. 50% H_2SO_4, dioxane, boiling for 51 h.

f. $NaNO_2$, H_2SO_4 (разб.), dioxane, 20 °C, 40 min.

Scheme 3



i. BuLi, dioxane—hexane, 20 °C; Me_2SO_4, 15—120 min.

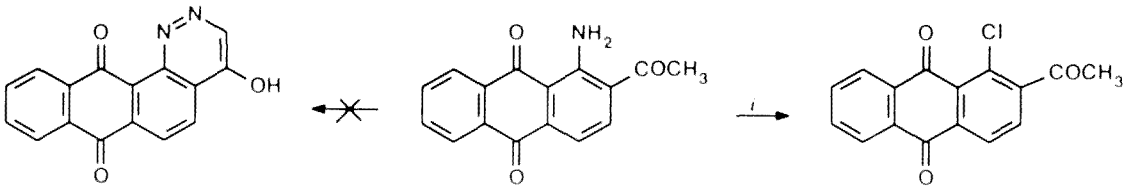
i i. HCl (diluted), dioxane, 20 °C, 2 h.

using dilute H_2SO_4 instead of HCl for cyclization, the other conditions remaining the same.

After conversion into the conjugated bases by the reaction with BuLi, 2-acylnaphtho-1*H*-[2,3-g]indazole-6,11-diones **6** can be methylated at the N atom by treatment with Me_2SO_4. The structure of the *N*-methylation product **9a** obtained from **6a** was confirmed by the data of the ^1H NMR spectrum and by its alternative synthesis by methylation of ketal **5a** under the same conditions followed by hydrolysis of *N*-methylketal **10** (Scheme 3).

Intramolecular cyclization of *ortho*-acylarenediazonium salts (Borsche reaction)[7] is similar in essence to the Richter reaction. However, in contrast to the cyclization of acetylene derivatives, this reaction can in principle yield only a six-membered heterocyclic compound. Therefore, it was of interest to compare the behavior of 1-amino-2-ethynyl- (**1c**) and 2-acetyl-1-amino-9,10-anthraquinone (**11**) under the conditions of the reaction considered. It was found that, unlike acetylene **1c**, ketone **11** does not undergo cyclization in the reaction with excess HNO_2 in a mixture of dilute HCl and dioxane at 20 °C. Instead, it is slowly (over a period of 30 h) converted into 2-acetyl-1-chloro-9,10-anthraquinone **12** in 77.5 % yield (Scheme 4).

Scheme 4



i. $NaNO_2$, dilute HCl, dioxane, 20 °C, 30 h.

Experimental

NMR spectra were recorded on Jeol FX-90Q and Bruker 400 spectrometers in $CDCl_3$, and IR spectra were obtained on a UR-20 spectrophotometer in $CHCl_3$. The reactions were monitored by TLC using Silufol UV 254 plates in $CHCl_3$. Physicochemical characteristics of the 3-substituted 1*H*-naphtho[2,3-*g*]-indazole-6,11-diones synthesized are presented in Table 1.

1-Amino-2-hexyn-1-ylanthraquinone (1a) was prepared by condensation[3] of 1-amino-2-iodoanthraquinone (1.75 g, 5.0 mmol) with copper butylacetylenide (1.10 g, 7.5 mmol) in 80 mL of pyridine under Ar (115 °C, 5 min) in a yield of 1.20 g (80.0 %); m.p. 124—125 °C (benzene—hexane). Found (%): C, 78.92; H, 5.50; N, 4.47. $C_{20}H_{17}NO_2$. Calculated (%): C, 79.19; H, 5.65; N, 4.62. ^1H NMR, δ: 0.95 (t, 3 H, CH_3), 1.40—1.65 (m, 4 H, β- and γ-CH_2), 2.55 (t, 2 H, α-CH_2), 7.55 (s, 2 H, H-3,4), 7.60—7.80 (m, 2 H, H-6,7), 8.15—8.35 (m, 2 H, H-5,8). IR, ν/cm^{-1}: 3345, 3490 (NH_2); 2230 (C≡C); 1640, 1675 (C=O).

Acetylenes **1b,c** were synthesized by the known procedure.[10]

3-(1,1-Dichloropentyl)-1*H*-naphtho[2,3-*g*]indazole-6,11-dione (3a). Dilute HCl (12 mL) (1 : 1) and a solution of $NaNO_2$ (0.48 g, 7.0 mmol) in 6 mL of water were added successively to **1a** (1.20 g, 4.0 mmol) in 80 mL of dioxane. The mixture was stirred for 7 min at 20 °C, diluted with 500 mL of $CHCl_3$, and washed with water. The solvent was evaporated *in vacuo*, and the residue was crystallized in ether and filtered off to give **3a** in 1.00 g (65.4 %) yield.

Compounds **3b,c** were obtained in a similar way.

3-(1-Chloropenten-1-yl)-1*H*-naphtho[2,3-*g*]indazole-6,11-dione (4a). At 20 °C, 0.92 mL of a 1.45*N* solution of BuLi (1.3 mmol) in hexane was added under Ar to compound **3a** (130 mg, 0.3 mmol) in 20 mL of anhydrous dioxane. The mixture was stirred for 5 min, diluted with 200 mL of $CHCl_3$, and washed with water. Chromatography on silica gel (ASKG) in benzene gave 85 mg (72.0 %) of **4a**.

Compound **4b** was obtained from dichloride **3b** in a similar way.

3-(1,1-Dimethoxypentyl)-1*H*-naphtho[2,3-*g*]indazole-6,11-dione (5a). A solution of MeONa in MeOH (0.60 g Na, 15 mL of MeOH) was added to a suspension of **3a** (0.62 g, 1.6 mmol) in 30 mL of MeOH. The mixture was stirred for 5 min at 20 °C, diluted with 300 mL of $CHCl_3$, and washed with water. The solvent was evaporated *in vacuo*, and a benzene solution of the residue was filtered through a layer of silica gel (ASKG) and reprecipitated from benzene with hexane to give 0.50 g (82.0 %) of **5a**.

Compounds **5b,c** were prepared in a similar way.

3-Valeryl-1*H*-naphtho[2,3-*g*]indazole-6,11-dione (6a). **a.** A solution of ketal **5a** (1.0 g, 2.9 mmol) in 150 mL of dioxane, 18 mL of 36% HCl, and 15 mL of water was stirred for 30 min at 20 °C to give 0.90 g (92.8 %) of compound **6a**.

Compounds **6b,c** were prepared in a similar way by the hydrolysis of **5b,c**.

b. A mixture of 160 mg (0.4 mmol) of compound **3a**, 15 mL of dioxane, 4 mL of water, and 2 mL of conc. H_2SO_4 was boiled for 51 h. The indazoledione **6a** (83 mg) isolated by the usual workup was additionally purified by chromatography on silica gel (40—100 mm) in $CHCl_3$, yield 65 mg (47.7 %).

c. Concentrated H_2SO_4 (0.1 mL) diluted with 0.5 mL of water and a solution of $NaNO_2$ (0.04 g, 0.6 mmol) in 0.5 mL of water were added successively to compound **1a** (0.10 g, 0.3 mmol) in 6 mL of dioxane, and the mixture was stirred for 40 min at 20 °C. After isolation by the usual workup, compound **6a** was recrystallized from ether and filtered off. Yield 0.07 g (65.6 %).

Methyl 6,11-dioxo-1*H*-naphtho[2,3-*g*]indazole-3-carboxylate (8). Potassium dichromate (2.60 g, 8.8 mmol) in dilute H_2SO_4 (5 mL conc. H_2SO_4 and 30 mL of water) was added at 40 °C over a period of 20 min to compound **6a** (0.60 g, 1.8 mmol) in 150 mL of AcOH; the mixture was heated to boiling (105 °C), stirred at this temperature for 3 h, and cooled. Half of the mother liquor was carefully decanted, 100 mL of water was added, and the precipitate was filtered off, washed with water, and dried in air. The resulting acid **7** (0.43 g; 81.1 %) was extracted without additional purification. Compound **7** (0.32 g, 1.1 mmol) in 20 mL of MeOH, containing 3 mL of conc. H_2SO_4, was boiled for 12 h, diluted with 300 mL of $CHCl_3$, and washed with water, and the solvent was evaporated *in vacuo* to give 0.20 g (86.6 %) of ester **8**.

Compound **6c** was oxidized in a similar way.

1-Methyl-3-(1,1-dimethoxypentyl)naphtho[2,3-*g*]indazole-6,11-dione (10). 1.6 mL of a 1.45 *N* hexane solution of BuLi (2.3 mmol) and Me_2SO_4 (0.40 g, 3.2 mmol; 0.3 mL) were added successively to compound **5a** (0.46 g, 1.2 mmol) in 35 mL of anhydrous dioxane under Ar. The mixture was heated to 50 °C, stirred for 15 min, cooled, diluted with 300 mL of $CHCl_3$, and washed with water. Chromatography on silica gel (ASKG) in benzene gave 0.40 g (83.3 %) of compound **10**.

1-Methyl-3-valerylnaphtho[2,3-*g*]indazole-6,11-dione (9). **a.** Compound **10** (0.14 g, 0.4 mmol) in 30 mL of dioxane and 9 mL of dilute HCl (2 : 1) was stirred for 2 h at 20 °C. The mixture was diluted with 200 mL of $CHCl_3$ and washed with water until the solution was neutral, and the solvent was evaporated *in vacuo*. Chromatography on silica gel (ASKG) in $CHCl_3$ gave 0.10 g (83.3 %) of compound **9**.

b. Compound **6a** (0.18 g, 0.5 mmol) in 40 mL of anhydrous dioxane was methylated as described for compound **5a** to give 0.16 g (84.2 %) of compound **9**.

2-Acetyl-1-chloro-9,10-anthraquinone (12). Dilute HCl (1 : 1) (6 mL) and a solution of $NaNO_2$ (0.24 g, 3.5 mmol) in

3 mL of water were added successively to ketone **11** (0.37 g, 1.4 mmol) in 40 mL of dioxane. The mixture was stirred for 30 h at 20 °C, diluted with 300 mL of $CHCl_3$, and washed, and the solvent was evaporated *in vacuo*. The residue was triturated with ether, and the mixture was cooled and filtered; the yield of **12** was 0.31 g (77.5 %), m.p. 165—167 °C (benzene—pentane). Found (%): C, 67.49; H, 3.33; Cl, 12.14. $C_{16}H_9ClO_3$. Calculated (%): C, 67.50; H, 3.19; Cl, 12.45. ^{1}H NMR, δ: 2.65 (s, 3 H, MeCO), 7.65 (d, 1 H, H-4, J = 7.8 Hz), 7.70—7.90 (m, 2 H, H-6,7), 8.15—8.35 (m, 2 H, H-5,8), 8.35 (d, 1 H, H-3, J = 7.8 Hz). IR, ν/cm^{-1}: 1680, 1710 (C=O).

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References

1. I. D. Ivanchikova, A. A. Moroz, and M. S. Shvartsberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1447 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1286 (Engl. Transl.)].
2. M. A. Mzhel'skaya, A. A. Moroz, and M. S. Shvartsberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1656 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1469 (Engl. Transl.)].
3. I. D. Ivanchikova, G. E. Usubalieva, P. V. Schastnev, A. A. Moroz, and M. S. Shvartsberg, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2138 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1672 (Engl. Transl.)].
4. M. S. Shvartsberg, A. V. Piskunov, M. A. Mzhel'skaya, and A. A. Moroz, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1423 [*Russ. Chem. Bull.*, 1993, **42**, 1357 (Engl. Transl.)].
5. A. V. Piskunov and M. S. Shvartsberg, *Mendeleev Commun.*, 1995, 155.
6. M. S. Shvartsberg, I. D. Ivanchikova, and L. G. Fedenok, *Tetrahedron Lett.*, 1994, **35**, 6749.
7. A. E. A. Porter, *Diazines and Benzodiazines*. In *Comprehensive Organic Chemistry*, Eds D. H. R. Barton and W. D. Ollis, Pergamon Press: Oxford, 1979, **4**, 123.
8. S. F. Vasilevsky and E. V. Tretyakov, *Liebigs Ann.*, 1995, 775.
9. A. V. Piskunov, A. A. Moroz, and M. S. Shvartsberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 864 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 785 (Engl. Transl.)].
10. A. V. Piskunov, A. A. Moroz, and M. S. Shvartsberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 828 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 755 (Engl. Transl.)].

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