Reactions of 9-chloro-1,10-anthraquinone 1-dichlorophosphorylimine with N- and C-nucleophiles

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9-Chloro-1,10-anthraquinone 1-dichlorophosphorylimine formed in the reaction of 1-amino-9,10-anthraquinone with PCl_5 followed by dehydrochlorination reacts with primary amines with substitution of chlorine atoms. In the case of aliphatic amines, the reaction occurs further concurrently in two directions: the addition of the amine molecule with the formation of 9,9-di(alkylamino) derivatives of the anthrone and the substitution of hydrogen atom at position 4 with the formation of 4,9-di(alkylamino) derivatives of 1,10-anthraquinone 1-imine. In the case of aromatic amines, 1-amino-9,10-anthraquinone 9-arylimines are the end products. Reactions with the anions of CH-acids containing an alkoxycarbonyl or cyano group occur with substitution in position 9 followed by intramolecular cyclization with the formation of 2-alkoxy- or 2-amino-7*H*-dibenzo[*f,ij*]isoquinolin-7-one derivatives, respectively.

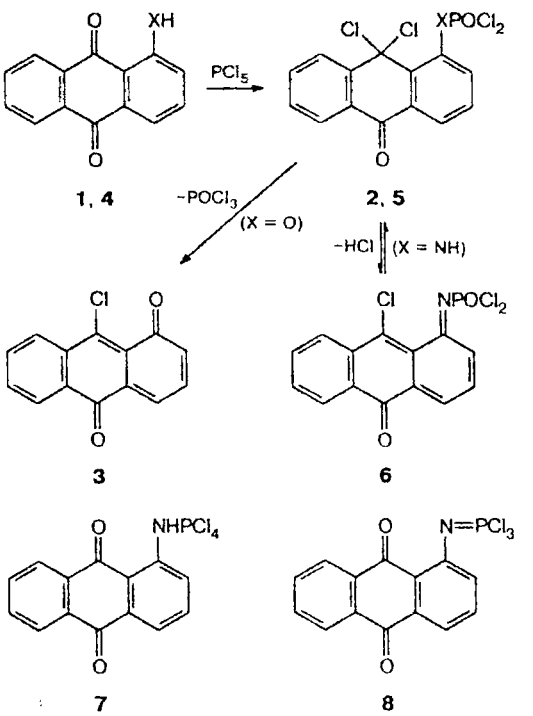
Key words: 9-chloro-1,10-anthraquinone 1-dichlorophosphorylimine; amines; addition, substitution; CH-acids, cyclization, 7*H*-dibenzo[*f,ij*]isoquinolin-7-ones.

In our preceding communication[2] we have shown that 9,9-dichloro-1-dichlorophosphoryloxyanthrone (**2**) obtained by reaction of 1-hydroxyanthraquinone (**1**) with PCl_5 reacts with primary amines in benzene with substitution of chlorine atoms and retention of the phosphoryloxy group, whereas the latter is eliminated to generate 9-chloro-1,10-anthraquinone (**3**) in DMF. Compound **3** undergoes alkylamination with substitution of the hydrogen atom at position 4 rather than the chlorine atom at position 9, as could be expected.

This work deals with the study of compounds **5** and **6** formed in the reaction of 1-aminoanthraquinone (**4**) with PCl_5 followed by dehydrochlorination (Scheme 1). At first, it was assumed that these products have the structure of aminotetrachlorophosphorane (**7**) and phosphazoanthraquinone (**8**), respectively;[3] however, it was established later by X-ray analysis that the first compound has the same structure as 9,9-dichloro-1-dichlorophosphorylaminoanthrone (**5**) and, as a consequence, the structure of 9-chloro-1,10-anthraquinone 1-dichlorophosphorylimine (**6**) was ascribed to the second compound.[4]

The structural similarity of dichloroanthrones **2** and **5** is confirmed by similarity of their ^1H and ^{13}C NMR spectra. In contrast to the transformation of anthrone **2** into 1,10-anthraquinone **3**, the transformation of anthrone **5** into 1,10-anthraquinone imine **6** requires no elimination of phosphoryl group and occurs reversibly *via* the proton abstraction from the NH group followed by elimination of chloride anion. For this reason, anthrone **5** reacting with basic nucleophilic reagents is first transformed into quinonimine **6** that undergoes the nu-

Scheme 1



X = O (**1**, **2**, **3**), NH (**4**, **5**, **6**)

* For preliminary communication, see Ref. 1.

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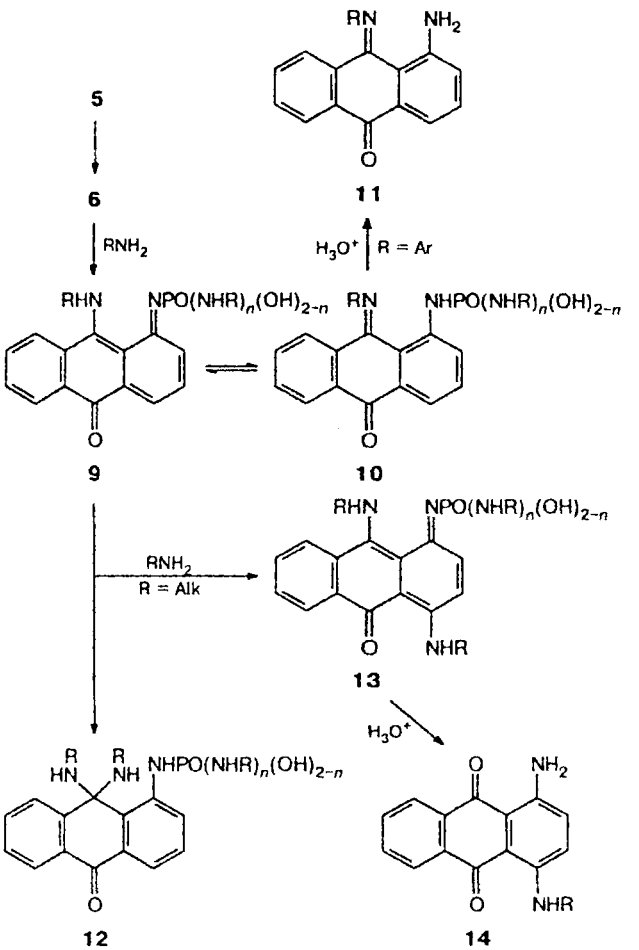
cleophilic attack. The results obtained are independent of whether the preliminarily isolated quinonimine **6** or dichloroanthrone **5** itself is introduced into reaction. We used the second version that not only includes fewer steps but also provides higher yields. Aromatic (aniline and 2,4,6-trimethylaniline) and nonaromatic (cyclohexylamine and *tert*-butylamine) primary amines were used as N-nucleophiles, and anions of CH-acids (diethylmalonate, malononitrile, and ethyl cyanoacetate) were used as C-nucleophiles.

It is known that the reaction of 1,10-anthraquinone imine **6** with aniline leads to a product of substitution of all three chlorine atoms for the amine residue. According to the reported data,[4] such a product is formed in benzene upon boiling and has the structure of 9-phenylamino-1,10-anthraquinone 1-di(phenylamino)phosphorylimine (**9a**, n = 2); according to the data reported in Ref. 3, it is formed in benzene at 20 °C (Scheme 2). We found that the substitution of chlorine atoms occurs without heating with the formation of 1-di(phenylamino)phosphorylamino-9,10-anthraquinone 9-phenylimine (**10a**, n = 2), whereas boiling results in the formation of a mixture of compound **10a** (n = 2) and 1-amino-9,10-anthraquinone-9-phenylimine (**11a**), which is a product of elimination of phosphoryl group. The conclusion that the compounds in question have tautomeric 9,10-anthraquinoid structures (**10a**, **11a**) rather than the 1,10-anthraquinoid structure (**9a**) follows from consideration of electronic spectra, since the spectra of quinones and their imines are similar. The electronic spectra of compounds **10a** and **11a** are close to those of 1-acylamino- and 1-amino-9,10-anthraquinones, respectively,[5] and differ from those of much more deeply colored 9-amino-1,10-anthraquinones.[6] The reaction with 2,4,6-trimethylaniline occurs in a similar way; however, only one chlorine atom in the dichlorophosphoryl group (apparently, due to steric hindrances) is substituted by the arylamine residue with the formation of monoamide **10b** (n = 1) which is transformed into aminoimine **11b**.

Reaction of anthrone **5** with cyclohexylamine in benzene at 20 °C leads to the formation of two major products (a colorless and a blue one) of similar composition obtained in a 2 : 1 ratio. Both compounds contain no chlorine atoms and have three cyclohexylamine residues in their molecules. The absence of absorption in the visible region makes it possible to ascribe the structure of 9,9-di(cyclohexylamino)-10-anthrone derivative (**12c**, n = 1) to the colorless compound. This compound is partially transformed into the blue substance upon heating with excess cyclohexylamine while in concentrated sulfuric acid it gives 1-aminoanthraquinone. Treatment of the blue substance with hydrochloric acid gives 1-amino-4-cyclohexylamino-9,10-anthraquinone (**14c**) identical to that obtained by independent synthesis from 4-bromo-1-cyclohexylaminoanthraquinone,[7] which means that the blue substance contains a cyclohexylamino group at position 4 and is a derivative of 4,9-di(cyclohexylamino)-1,10-anthraquinone 1-imine (**13c**, n = 1).

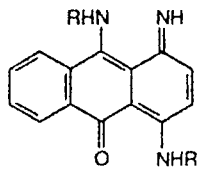
Scheme 2



R = Ph (**a**), 2,4,6-$Me_3C_6H_2$ (**b**), *cyclo*-C_6H_{11} (**c**), Bu^t (**d**); n = 2, 1, 0

The presence of only one cyclohexylamine residue in the phosphorylamino groups of isolated compounds **12c** and **13c** is a consequence of a secondary hydrolytic process. This can be clearly seen by the example of the reaction of anthrone **5** with *tert*-butylamine, where hydrolysis occurs especially easily due to steric factors. Colored derivatives of 4,9-di(*tert*-butylamino)-1,10-anthraquinone 1-imine (**13d**) differing in the number of alkylamide groups (n = 2, 1, 0) were obtained as individual substances in solutions and characterized by electronic spectra and TLC data; however, they have not been isolated in the crystalline state. The sequence of their interconversions indicates changes in the phosphoryl residue. Chromatography of the reaction mixture gave a fraction containing compound **13d** (n = 2) (λ_{max} 614 and 668 nm) that is completely transformed into compound **13d** (n = 1) (λ_{max} 568 and 608 nm) within several days. After treatment of the solution of compound **13d** with HCl and then with an aqueous solution of Na_2CO_3, the sodium salt of compound **13d** (n = 0) (λ_{max} 576 and 620 nm), whose molecule contains no alkylamide groups,

passes into the aqueous layer. After acidification, the aqueous layer gradually decolorizes and 1-amino-4-*tert*-butylamino-9,10-anthraquinone (**14d**), which was isolated in the crystalline form, is accumulated in the organic layer. Noteworthy is that 4,9-di(alkylamino)-1,10-anthraquinone 1-imine (**15c,d**) was not detected even under such mild conditions. The reason for the easy exchange of the 9-alkylamino group in 4,9-di(alkylamino)-1,10-anthraquinone 1-imines (**15**) in acidic medium compared to its stability in 4,9-di(alkylamino)-1,10-anthraquinones (**16**)[2] and 4,9-di(arylamino)-1,10-anthraquinones[8] deserves special study.



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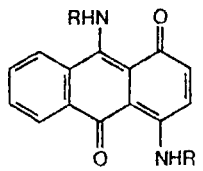

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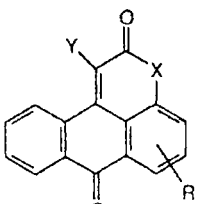
The absence of products of amination exclusively in the phosphoryl residue in the case of reaction of imine **6** indicates that the mobility of the chlorine atom in the carbocycle of molecule **6** is comparable to that of the chlorine atoms in the halophosphoryl residue. The substitution of chlorine atoms results in 9-amino-1,10-anthraquinone 1-aminophosphorylimines **9** which also can exist in tautomeric 9,10-anthraquinoid form **10**. Tautomeric equilibrium is dependent on the relative proton affinity of *peri* nitrogen atoms in positions 1 and 9. In the case of aromatic amines, the 9,10-anthraquinoid form **10** of low reactivity is predominant. In the case of aliphatic amines having higher basicities, the equilibrium is shifted to a greater extent toward the 1,10-anthraquinoid tautomer **9** which is responsible for further reactions of addition of amine and substitution of hydrogen atom. 1,4-Addition of an alkylamine molecule to 1,10-anthraquinoneimine **9** and substitution of the hydrogen atom result in the formation of 9,9-di(alkylamino)anthrone **12** and 4,9-dialkylamino-1,10-anthraquinone 1-imine **13**, respectively.

It could be expected for reactions between 9-chloro-1,10-anthraquinone imine (**6**) and anions of CH-acids that nucleophilic substitution in position 9 will be followed by cyclization involving the *peri* heteroatom. In the case of 2,4,9-trichloro-1,10-anthraquinone, cyclization involving the oxygen atom in position 1 results in anthra[1,9-*bc*]pyran-2,7-dione (pyronanthrone) (**17**) derivatives.[9] By analogy, cyclization involving a nitrogen atom in the case of reaction of 9-chloro-1,10-anthraquinone 1-imine **6** (Scheme 3) can lead to the formation of 7*H*-dibenzo[*f,ij*]isoquinoline-2,7-dione (pyridoanthrone) system (**18**).

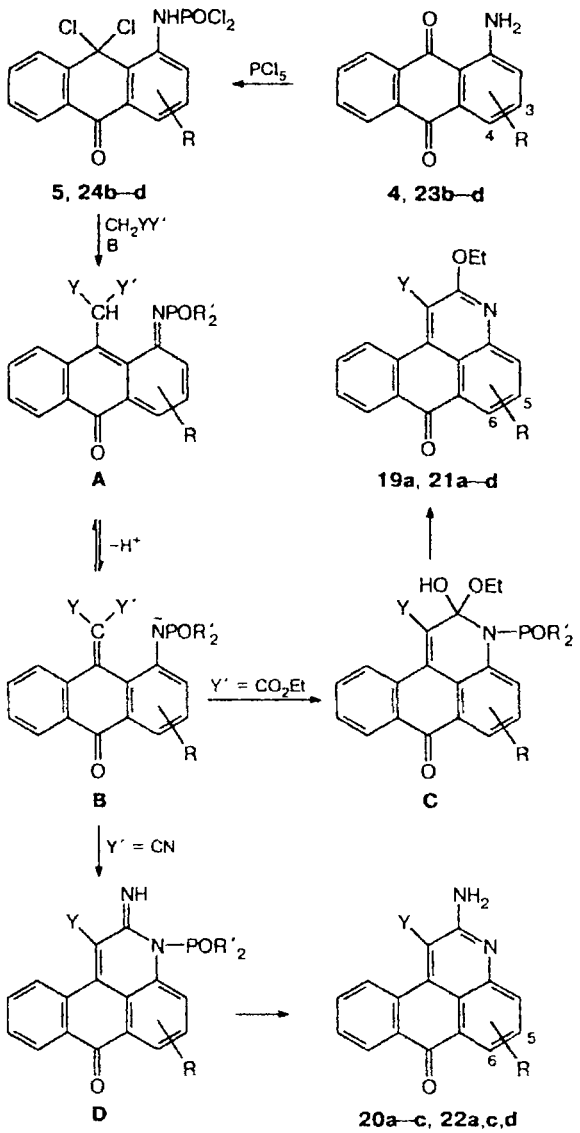


17, 18

X = O (**17**), NH (**18**)

The closure of the heterocycle does occur in reactions with carbanions generated from diethyl malonate, malononitrile, and ethyl cyanoacetate containing ethoxycarbonyl, nitrile, or simultaneously both these electrophilic groups, respectively.

Scheme 3



19–22: R = H (**a**), 5-Me (**b**), 5-Cl (**c**), 6-Cl (**d**)
Y = CO_2Et (**19**, **22**), CN (**20**, **21**);
23, **24:** R = 3-Me (**b**), 3-Cl (**c**), 4-Cl (**d**)
R' = OH or CHYY',
B — base, Y' = CO_2Et, CN

Cyclization occurs following substitution of the chlorine atom at position 9 of 1,10-anthraquinone imine **6**

by the CH-acid residue (A) most likely through the deprotonation and transfer of the negative charge in carbanion **B** to the nitrogen atom that attacks the electrophilic center of the CH-acid residue. CH-Acidity of the substitution product **A** is higher than that of the original CH-acid because of the electron-accepting effect of the anthrone system and additional stabilization of the carbanion due to transformation of 1,10-anthraquinoid structure **A** into 9,10-anthraquinoid structure **B**.

Two variants of stabilization of intermediate **C** are possible after closure of the C—N bond of the heterocycle in the case of cyclization involving ethoxycarbonyl group, namely, the elimination of the ethoxy group with the formation of pyridoanthrone system **18** or the elimination of hydroxyl group with the formation of the 2-ethoxypyridoanthrone system **19**. The experiment shows that only the latter variant occurs. The reaction of anthrone **5** with the potassium salt of diethyl malonate in benzene yielded 2-ethoxy-1-ethoxycarbonyl-7*H*-dibenzo[*f,ij*]isoquinolin-7-one (**19a**). At the same time, the reaction between 1-aminoanthraquinone itself and diethyl malonate (when the initial formation of C—N bond is followed by the formation of the C—C bond) leads to 1-ethoxycarbonyl-7*H*-dibenzo[*f,ij*]isoquinoline-2,7-dione (pyridoanthrone) (**18**, Y = CO_2Et).[10]

Cyclization involving a nitrile group occurs with the intermediate formation of pyridoanthrone 2-imines (**D**) that are transformed into 2-aminopyridoanthrones **20** by losing the phosphoryl group. Thus, the reaction of anthrone **5** with malononitrile in benzene in the presence of triethylamine results in 2-amino-1-cyano-7*H*-dibenzo[*f,ij*]isoquinolin-7-one (**20a**), which was also obtained recently by condensation of malononitrile with 1-aminoanthraquinone followed by cyclization.[10]

If both the ethoxycarbonyl and nitrile group are present simultaneously in the CH-acid residue, then cyclization involving the ethoxycarbonyl group appears to be preferred. Reaction of anthrone **5** with carbanion generated from ethyl cyanoacetate results mainly in 1-cyano-2-ethoxypyridoanthrone (**21a**). The alternative cyclization product, 2-amino-1-ethoxycarbonylpyridoanthrone (**22a**), is formed in a much lesser amount than the main product **21a**.

Among the compounds with a tetracyclic dibenzo[*f,ij*]isoquinoline skeleton, the derivatives containing a *peri*-annelated pyridine ring have been described much less than those containing pyridone ring **18**. In particular, no procedures for the preparation of 2-alkoxypyridoanthrones have been developed. For this reason, the syntheses presented above can be of certain practical importance. Among their drawbacks are large reagent—substrate mole ratios and relatively low yields (30—67%) while among their advantages are experimental simplicity and ready availability of starting compounds. Transformation of 1-aminoanthraquinone **23**, which can contain substituents in the carbocyclic system, occurs in one preparative stage by heating in an organic solvent with PCl_5 and mixing the formed solution of dichloroanthrone **24** with a solution of a base and CH-acid. Thus, substituted 1-cyano-2-ethoxypyridoanthrones **21b—d** and 2-amino-1-ethoxycarbonylpyridoanthrones **22c,d** formed in parallel were obtained by reactions of 3-methyl-, 3-chloro- or 4-chloro-1-aminoanthraquinone (**23b—d**) with ethyl cyanoacetate, while the reactions of 3-methyl- or 3-chloro-1-aminoanthraquinone **23b,c** with malononitrile result in 2-amino-5-methyl-1-cyano- and 2-amino-5-chloro-1-cyanopyridoanthrones (**20b,c**), respectively. The characteristics of the synthesized pyridoanthrone derivatives are listed in Table 1.

In summary, 9,9-dichloro-1-dichlorophosphoryl-aminoanthrone undergoes an easy dehydrochlorination with the formation of 9-chloro-1,10-anthraquinone 1-dichlorophosphorylimine, which reacts with nucleophilic reagents at position 9 and with primary aliphatic amines at position 4. Reactions with anions of CH-acids are accompanied by cyclization into 7*H*-dibenzo[*f,ij*]isoquinolin-7-one derivatives.

Experimental

Electronic spectra were recorded on a Specord M 40 spectrophotometer, IR spectra were recorded on a Perkin-Elmer 598 spectrometer in KBr pellets, mass spectra were recorded on a MX-1013 instrument, ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-360 spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. 1-Aminoanthraquinone ("pure" grade) was a commercial product (Shostka Chemical Plant). The reactions and purity of the compounds were monitored by TLC on Silufol UV-254 plates. Chromatographic separation of the substances was performed on columns with Al_2O_3 ("For chromatography" grade) or with silica gel (40/100 μm). The substances were identified by TLC, melting points of mixed samples, and IR spectra.

1-Dichlorophosphorylamino-9,9-dichloro-10-anthrone (5). A mixture of 1-aminoanthraquinone (**4**) (4.46 g, 20 mmol) and PCl_5 (4.16 g, 20 mmol) was boiled in 50 mL of benzene for 30 min until starting compound **4** disappeared, then activated carbon was added, the mixture was filtered, the filtrate was diluted with hexane (100 mL), and the precipitate was separated, yield 6.78 g (78%), m.p. 153—155 °C (from a benzene—hexane mixture) (*cf.* Ref 4: m.p. 153 °C). ^1H NMR (δ): 7.61 (t, 1 H, H(6), J = 7 Hz); 7.67 (t, 1 H, H(3), J = 7 Hz); 7.84 (t, 1 H, H(7), J = 8 Hz); 8.07 (d, 1 H, H(2), J = 7 Hz); 8.26 (d, 1 H, H(5), J = 7 Hz); 8.24 (d, 1 H, H(8), J = 7 Hz); 8.27 (d, 1 H, H(4), J = 7 Hz). ^{13}C NMR (δ): 79.2 (C(9)), 124.0 (C(4)), 127.6 (C(2)), 126.4 (C(5)), 129.8 (C(8)), 130.6 (C(6)), 131.4 (C(3)), 134.8 (C(7)), 180.0 (C(10)).

1-Di(phenylamino)phosphorylamino-9,10-anthraquinone 9-phenylimine (10a, *n* = 2) and 1-amino-9,10-anthraquinone 9-phenylimine (11a). A solution of aniline (1.63 g, 17.5 mmol) in 12 mL of benzene was added to a solution of anthrone **5** (1.0 g, 2.5 mmol) in 25 mL of benzene at 0—5 °C, the mixture was stirred for 4 h at 20 °C, and the precipitate was filtered off and washed with water to remove anilinium chloride. Compound **10a** (0.70 g, 53%) was obtained as orange prisms (from benzene), m.p. 138—140 °C (*cf.* Refs. 3 and 4: m.p. 137—140 °C and 205 °C, respectively). IR, ν/cm^{-1}: 1650 (C=O), 3140, 3330 (NH). Electronic spectrum ($CHCl_3$), λ_{max}/nm: 415 (log ε 3.76). Found (%): C, 73.00; H, 4.89; N, 10.34. $C_{32}H_{25}N_4O_2P$. Calculated (%): C, 72.72; H, 4.77; N, 10.60.

Table 1. Characteristics of 7*H*-dibenzo[*f,ij*]isoquinolin-7-one derivatives **19—22**

Compound	M.p. /°C[a]	IR spectrum, ν/cm^{-1}			Electronic spectrum, λ_{max}/nm (log ε)	Found / Calculated (%)			Empirical formula
		C=O	C=N	NH		C	H	N	
19a	160—161	1650, 1715	—	—	354(4.16), 392(3.75)	72.43 / 72.61	5.19 / 4.93	4.14 / 4.03	$C_{21}H_{17}NO_4$
20a	308—310 (decomp.)	1650	2200	3350, 3420	368(4.08), 442(3.74), 460(3.64)	75.16 / 75.27	3.30 / 3.34	15.31 / 15.49	$C_{17}H_9N_3O$
20b	290—292	1630	2180	3270, 3330	345(4.22), 421(3.86), 442(3.82)	75.59 / 75.78	4.12 / 3.89	14.55 / 4.73	$C_{18}H_{11}N_3O$
20c	318—320	1650	2190	3300, 3460	375(4.05), 420(3.75), 440(3.78)	66.68 / 66.79	2.90 / 2.64	13.86 / 13.74	$C_{17}H_8ClN_3O$[b]
21a	210—211	1655	2210	—	363(3.97), 398(3.79), 417(3.78)	75.82 / 75.99	4.17 / 4.03	9.58 / 9.33	$C_{19}H_{12}N_2O_2$[c]
21b	210—211	1650	2200	—	370(4.13), 400(3.87), 419(3.84)	76.25 / 76.42	4.60 / 4.49	9.02 / 8.91	$C_{20}H_{14}N_2O_2$
21c	210—212	1650	2210	—	371(4.15), 398(3.86), 417(3.85)	67.94 / 68.17	3.18 / 3.32	8.28 / 8.37	$C_{19}H_{11}ClN_2O_2$
21d	222—223	1650	2210	—	360(4.03), 403(3.68), 423(3.98)	68.15 / 68.17	3.20 / 3.32	8.35 / 8.37	$C_{19}H_{11}ClN_2O_2$[d]
22a	221—223	1630, 1700	—	3300, 3450	361(4.03), 428(3.63)	71.40 / 71.69	4.56 / 4.43	8.91 / 8.80	$C_{19}H_{14}N_2O_3$
22c	252—253	1640, 1695	—	3240, 3460	367(3.87), 410 пл(3.87)	64.57 / 64.69	3.95 / 3.71	7.74 / 7.94	$C_{19}H_{13}ClN_2O_2$
22d	234—235	1650, 1700	—	3280, 3460	358(4.09), 437(3.84)	64.45 / 64.69	4.03 / 3.71	7.67 / 7.94	$C_{19}H_{13}ClN_2O_2$

[a] Compounds **19a**, **20a** were purified by recrystallization from propan-2-ol, **20b,d** from a toluene—hexane mixture, **21a,c**, **22a,c** from a $CHCl_3$—hexane mixture, **21b** from $CHCl_3$, and **21d**, **22d** from butanol.
[b] Found (%): Cl, 11.48. Calculated (%): Cl, 11.60. MS, *m/z* 271 [M$^+$].
[c] MS, *m/z* 300 [M$^+$].
[d] Found (%): Cl, 10.52. Calculated (%): Cl, 10.59.

After separation of compound **10a**, an additional 0.50 g of aniline was added to the filtrate, the mixture was boiled for 2 h, the solvent was removed, and the residue was treated with propan-2-ol to give phenylimine **11a** (0.25 g, 33%) as red-brown needles (from a propan-2-ol—water mixture), m.p. 168—170 °C. IR, ν/cm^{-1}: 1650, 1640 sh (C=O), 3250, 3380 (NH). Electronic spectrum ($CHCl_3$), λ_{max}/nm: 442 (log ε 3.81). Found (%): C, 80.87; H, 4.83; N, 9.45. $C_{20}H_{14}N_2O$. Calculated (%): C, 80.52; H, 4.73; N, 9.39.

1-(2,4,6-Trimethylphenylamino)phosphorylamino-9,10-anthraquinone 9-(2,4,6-trimethylphenylimine) (10b, *n* = 1) and 1-amino-9,10-anthraquinone 9-(2,4,6-trimethylphenylimine) (11b). A solution of 2,4,6-trimethylaniline (mesidine) (2.36 g, 17.5 mmol) in 12 mL of benzene was added to a solution of anthrone 5 (1.0 g, 2.5 mmol) in 25 mL of benzene at 0—5 °C; the mixture was stirred for 3 h at 20 °C and allowed to stand for 15 h. After separation of mesidine hydrochloride, the benzene solution was chromatographed on a column with silica gel (over a period no longer than 2 h, with $CHCl_3$ as eluent) to isolate compound **10b** (0.80 g, 59%), m.p. 178—180 °C (decomp.) (from a benzene—hexane mixture), which partially decomposes upon boiling in benzene to give imine **11b** and 1-aminoanthraquinone (**4**). IR, ν/cm^{-1}: 1660 (C=O), 3150, 3360 (NH). Electronic spectrum ($CHCl_3$), λ_{max}/nm: 408 (log ε 3.64). Found (%): C, 72.03; H, 5.86; N, 7.76. $C_{32}H_{32}N_3O_3P$. Calculated (%): C, 71.49; H, 6.00; N, 7.82.

In a similar experiment, mesidine (0.60 g) was added to the benzene solution after separation of mesidine hydrochloride and the mixture was boiled for 1 h, and then chromatography of the solution on a column with silica gel with chloroform as eluent was used to isolate compound **11b** (0.40 g, 47%), m.p. 193—195 °C (decomp.) (from a benzene—hexane mixture). IR, ν/cm^{-1}: 1650 (C=O), 3300, 3430 (NH). Electronic spectrum ($CHCl_3$), λ_{max}/nm: 448 (log ε 3.70). Found (%): C, 81.27; H, 5.85; N, 8.01. [M$^+$], 340. $C_{23}H_{20}N_2O$. Calculated (%): C, 81.15; H, 5.92; N, 8.23. M, 340.

9,9-Di(cyclohexylamino)-1-cyclohexylaminohydroxyphosphorylamino-10-anthrone (12c, *n* = 1) and 4,9-di(cyclohexylamino)-1,10-anthraquinone 1-cyclohexylaminohydroxyphosphorylimine (13c, *n* = 1). A solution of cyclohexylamine (7.0 g, 70 mmol) in 50 mL of benzene was added dropwise over a period of 1 h to a solution of anthrone 5 (3.95 g, 10 mmol) in 100 mL of benzene at 0—5 °C and the mixture was allowed to stay for 15 h at ~20 °C. The precipitate was filtered off, washed with benzene, dried in air, and treated with water to dissolve cyclohexylamine hydrochloride. The undissolved colorless residue was identified as compound **12c** (*n* = 1), yield 2.37 g (42%), m.p. 245—247 °C (from toluene). IR,

ν/cm^{-1}: 1660 (C=O), 3140 (NH). UV ($CHCl_3$), λ_{max}/nm: 357 (log ε 3.31). Found (%): C, 67.84; H, 8.22; N, 9.65. $C_{32}H_{45}N_4O_3P$. Calculated (%): C, 68.06; H, 8.03; N, 9.92.

Chromatography of the filtrate on a column with silica gel (over a period no longer than 4 h, with $CHCl_3$ as eluent) afforded blue compound **13c** (1.20 g, 21%), m.p. 205—207 °C (from benzene). IR, ν/cm^{-1}: 1623 (C=O). Electronic spectrum ($CHCl_3$), λ_{max}/nm: 593 (log ε 3.97), 640 (log ε 4.03). Found (%): C, 68.28; H, 7.61; N, 10.24. $C_{32}H_{43}N_4O_3P$. Calculated (%): C, 68.31; H, 7.70; N, 9.96. Aminoanthraquinone **4** (0.15 g, 76%) was isolated after stirring of compound **12c** (0.50 g) for 15 min in 10 mL of conc. H_2SO_4, pouring of the mixture into water, and neutralization. Upon boiling of the benzene solution of compound **12c** with 10-fold molar excess of cyclohexylamine for 5 h, a blue compound, **13c**, was chromatographically detected in the solution, whereas most of compound **12c** did not enter into the reaction.

1-Amino-4-cyclohexylamino-9,10-anthraquinone (14c). Hydrochloric acid (32 %, 2 mL) was added to a solution of compound **13c** (0.30 g) in 50 mL of $CHCl_3$ and the mixture was allowed to stand for 15 h at ~20 °C. The solution was treated with an aqueous solution of Na_2CO_3 to neutralize the acid, washed with water, and chromatographed on a column with silica gel (with $CHCl_3$ as eluent) to give 1-amino-4-cyclohexylaminoanthraquinone **14c** (0.16 g, 94%), m.p. 160—161 °C (from benzene), identical to that synthesized from 4-bromo-1-cyclohexylaminoanthraquinone (*cf.* Ref. 7: m.p. 161 °C).

4,9-Di(*tert*-butylamino)-1,10-anthraquinone 1-di(*tert*-butylamino)-, 1-*tert*-butylaminohydroxy- and 1-dihydroxyphosphorylimines (13d, *n* = 2, 1, 0), and 1-amino-4-*tert*-butylamino-9,10-anthraquinone (14d). A solution of *tert*-butylamine (1.53 g, 21 mmol) in 15 mL of benzene was added to a solution of anthrone **5** (1.19 g, 3 mmol) in 30 mL of benzene over a period of 40 min at 0—5 °C, and the mixture was stirred for 3 h and allowed to stand for 15 h at 20 °C. The residue of amine hydrochloride was filtered off, and the benzene solution was rapidly passed through a column with silica gel (with $CHCl_3$ as eluent) to obtain a solution that contained only compound **14d** (*n* = 2) (TLC-monitoring), λ_{max} 614, 668 nm. After 120 h, complete conversion of this compound into compound **13d** (*n* = 1) with a smaller R_f, λ_{max} 568 and 608 nm, occurred in the same solution. Then a solution of HCl in chloroform was added to the above solution and after 10 min the mixture was neutralized by shaking with an aqueous solution of Na_2CO_3. The organic layer decolorized, and the aqueous layer turned blue because of the formation of a sodium salt of amidophosphonic acid **13d** (*n* = 0), λ_{max} 576, 620 nm. After neutralization with acetic aid, the aqueous layer gradually decolorized, and the organic layer became colored. The organic layer was evaporated and chromatography on a column with silica gel (with $CHCl_3$ as eluent) gave 1-amino-4-*tert*-butylamino-9,10-anthraquinone (**14d**), m.p. 193—195 °C (from a benzene—hexane mixture). Electronic spectrum ($CHCl_3$), λ_{max}/nm: 575 (log ε 4.12), 618 (log ε 4.15). Found (%): C, 73.10; H, 6.17; N, 9.19. [M^+], 294. $C_{18}H_{18}N_2O_2$. Calculated (%): C, 73.45; H, 6.16; N, 9.52. M, 294.

2-Ethoxy-1-ethoxycarbonyl-7*H*-dibenzo[*f,ij*]isoquinolin-7-one (19a). A solution of Et_3N (0.30 g) in 5 mL of benzene was added to a solution of anthrone **5** (1.19 g, 3 mmol) in 50 mL of benzene at 0—5 °C and the obtained mixture was introduced at 10—15 °C into a suspension of a potassium salt of diethyl malonate prepared by boiling diethyl malonate (4.80 g, 30 mmol) and KOH (1.70 g, 30 mmol) in 50 mL of benzene, the mixture was stirred for 15 h at 20 °C, and benzene was evaporated *in vacuo*. The residue was dissolved in 50 mL of acetone and then water (150 mL) was added to filter pyridoanthrone **21a** (0.365 g, 35%) (Table 1).

2-Amino-1-cyano-7*H*-dibenzo[*f,ij*]isoquinolin-7-one (20a). Malononitrile (0.66 g, 10 mmol) and Et_3N (1.0 g) were introduced into a solution of anthrone **5** (0.396 g, 1 mmol) in 25 mL of benzene, the mixture was stirred for 15 min at 20 °C and then for an additional 30 min on boiling, and the solvent was evaporated *in vacuo*. Acetone (10 mL) and then water (50 mL) was added to the residue, the mixture was heated for 10 min at 60 °C, and pyridoanthrone **20a** that precipitated was separated, yield 0.186 g (67%) (Table 1).

2-Amino-5-methyl-1-cyano-7*H*-dibenzo[*f,ij*]isoquinolin-7-one (20b). A solution prepared by boiling 1-amino-3-methylanthraquinone **23b** (0.474 g, 2 mmol) and PCl_5 (0.420 g) in 20 mL of benzene for 1 h was introduced at 0—5 °C into a solution of malononitrile (1.32 g, 20 mmol) and Et_3N (2.23 g, 22 mmol) in 20 mL of benzene, the mixture was stirred for 20 min at 20 °C, benzene was evaporated *in vacuo*, the residue was dissolved in 20 mL of acetone, water (60 mL) was added, and pyridoanthrone **20b** that precipitated was separated (0.310 g, 54%) (Table 1).

2-Amino-5-chloro-1-cyano-7*H*-dibenzo[*f,ij*]isoquinolin-7-one (**20c**) was synthesized analogously using 1-amino-3-chloroanthraquinone (**23c**) as starting compound.

2-Amino-6-chloro-1-ethoxycarbonyl-7*H*-dibenzo[*f,ij*]isoquinolin-7-one (22d) and 6-chloro-1-cyano-2-ethoxy-7*H*-dibenzo[*f,ij*]isoquinolin-7-one (21d). A mixture of 1-amino-4-chloroanthraquinone (**23d**) (1.29 g, 5 mmol), PCl_5 (1.04 g), and 25 mL of benzene was boiled for 1 h and then introduced at 0—5 °C into a mixture of $NCCH_2CO_2Et$ (5.65 g, 50 mmol), Et_3N (5.57 g, 55 mmol), and 20 mL of benzene, the mixture was stirred for 20 min at 20 °C, benzene was evaporated *in vacuo*, the residue was dissolved in 50 mL of acetone, and water (150 mL) was added. The precipitate (1.36 g) was separated, dissolved in $CHCl_3$, and chromatographed on a column with Al_2O_3 (with $CHCl_3$ as eluent). 2-Amino-6-chloro-1-ethoxycarbonylpyridoanthrone (**22d**) (0.64 g, 38%) and 6-chloro-1-cyano-2-ethoxypyridoanthrone (**21d**) (0.15 g, 8.5%) were obtained as the first and second fraction, respectively (Table 1).

2-Amino-, 2-amino-5-methyl- and 2-amino-5-chloro-1-ethoxycarbonyl-7*H*-dibenzo[*f,ij*]isoquinolin-7-ones (**22a—c**), 1-cyano-2-ethoxy-7*H*-dibenzo[*f,ij*]isoquinolin-7-one (**21a**), and 5-chloro-1-cyano-2-ethoxy-7*H*-dibenzo[*f,ij*]isoquinolin-7-one (**21c**) (Table 1) were synthesized analogously using 1-aminoanthraquinone (**4**), 1-amino-3-methylanthraquinone (**23b**), and 1-amino-3-chloroanthraquinone (**23c**), respectively, as starting compounds. The minor component **21b** of the reaction with 1-amino-3-methylanthraquinone (**23b**) was not isolated as individual substance.

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