# Synthesis of 9-chloro-1,10-anthraquinone and its reactions with amines

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1-Dichlorophosphoryloxy-9,9-dichloroanthrone, a product of the reaction between 1-hydroxyanthraquinone and $PCl_5$, reacts with primary amines in benzene to give first 1-(diaminophosphoryloxy)-9,9-dichloroanthrones and then the corresponding 9-imines. The reaction in DMF occurs with elimination of the phosphoryloxy group and generation of 9-chloro-1,10-anthraquinone that undergoes amination followed by substitution of the hydrogen atom in position 4 rather than a chlorine atom in position 9, which is the most active position in 2,4,9-trichloro-1,10-anthraquinone. The second step of amination results in 4,9-di(alkylamino)-1,10-anthraquinone. The literature data on obtaining individual 9-chloro-1,10-anthraquinone under the action of bases on 1-dichorophosphoryloxy-9,9-dichloroanthrone were not experimentally supported.

**Key words:** 9-chloro-1,10-anthraquinone; amines; 9,9-dichloro-1-phosphoryloxyanthrones; nucleophilic substitution of hydrogen.

The first stable compound of the 1,10-anthraquinone series, 2,4,9-trichloro-1,10-anthraquinone (**2**) which is incapable of tautomeric transformation into 9,10- or 1,4-anthraquinones,[2] was obtained by the action of $SOCl_2$ on 1,4-dihydroxy-9,10-anthraquinone or 1-hydroxy-9,10-anthraquinone (**1**) in the presence of $Et_3N$. Reactions involving a nucleophilic attack on position 9, for instance, the reversible HCl addition followed by conversion into 1-hydroxy-2,4,9,9-tetrachloroanthrone **3**, are mostly characteristic of quinone **2**. It is likely that substitution of the carbonyl oxygen atom by the chlorine atom in quinone **1** occurs by a route involving the formation of a cyclic intermediate (**A** → **B**) generated due to nucleophilic *peri*-interaction (Scheme 1).[3,4] It has been postulated that the formation of 1-dichlorophosphoryloxy-9,9-dichloroanthrone (**4**) upon heating hydroxyanthraquinone (**1**) with $PCl_5$ in an inert solvent occurs by a similar mechanism with participation of cyclic intermediate (**C** → **D**).[5,6]

It was reported[5,7] that it is possible to obtain 9-chloro-1,10-anthraquinone (**5**) in high yield and isolate it in pure form upon boiling compound **4** in benzene in the presence of several reagents ($Et_3N$, MeOH, *etc.*). However, no chemical properties of **5** were described. It was only pointed out that quinone **5** forms no individual products in reactions with amines and alcohols. At first the objective of our work was to repeat the synthesis of 9-chloride **5** and study its reactivity toward amines as compared to that of 2,4,9-trichloride **2**.

It turned out that the synthesis of compound **5**[5,7] appeared to be irreproducible. Boiling of anthrone **4** in benzene in the presence of $Et_3N$, filtration and removal of the solvent as described[5,7] for the preparation of 9-chloro-1,10-anthraquinone (**5**) resulted in a residue that was not an individual substance. We did not observe its complete dissolution in benzene on attempted recrystallization, whereas the fractions isolated from the solution were not colored red, which is characteristic of 1,10-anthraquinones, and contained phosphorus. The experiments performed in the presence of other reagents specified in Ref. 5 also failed. It should be noted that for the product, to which the structure **5** was ascribed, the band of the carbonyl group at 1690 $cm^{-1}$ was reported[5] in the IR spectrum, as for 9,10-anthraquinones and anthrones, whereas a shift of the band toward lower frequencies is typical of 1,10-anthraquinones (νCO 1647 $cm^{-1}$ for quinone **2**);[2,3] there is no data on the absorption in the visible region ($\lambda_{max}$ 476—504 nm),[3,8] which is specific to 1,10-anthraquinones. We believe that information[5] on obtaining 9-chloro-1,10-anthraquinone (**5**) in pure form does not represent the facts. For this reason, we studied the interaction of the product of the reaction between hydroxyanthraquinone **1** and $PCl_5$ with aromatic and aliphatic amines considering the possibility of forming quinone **5** *in situ* in this case.

The structure of the product of the reaction between hydroxyanthraquinone **1** and $PCl_5$ identified as 1-dichlorophosphoryloxy-9,9-dichloroanthrone (**4**) is confirmed by $^1H$ and $^{13}C$ NMR spectra. The action of aromatic amines on anthrone **4** (Scheme 2) leads to the substitution of all chlorine atoms with the formation of 9-imines. Thus, treatment with aniline in benzene at room temperature leads (most likely, through the intermediate formation of dichloride **6** (R = Ph)) to

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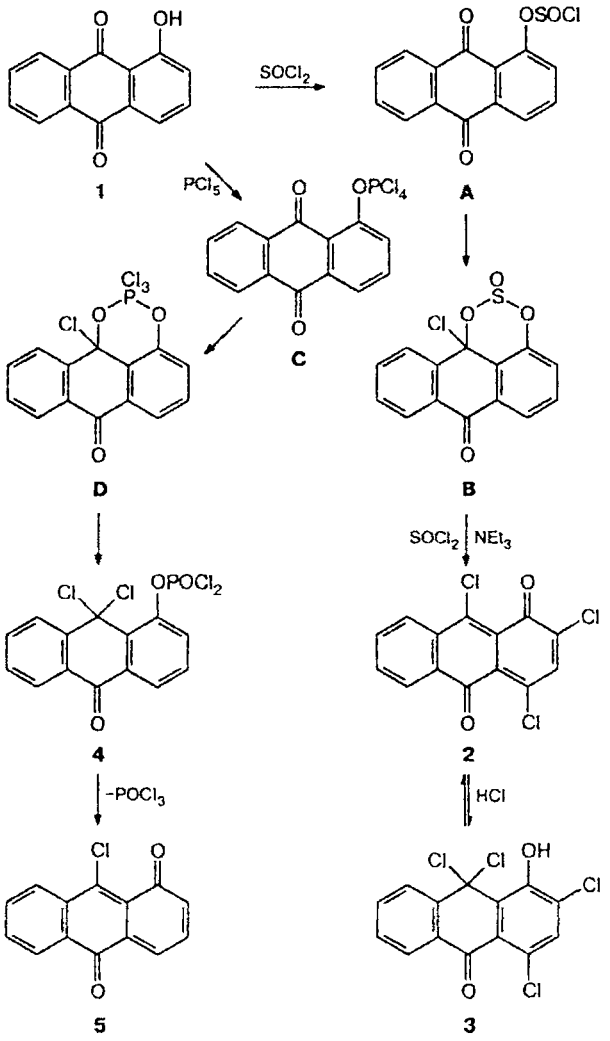
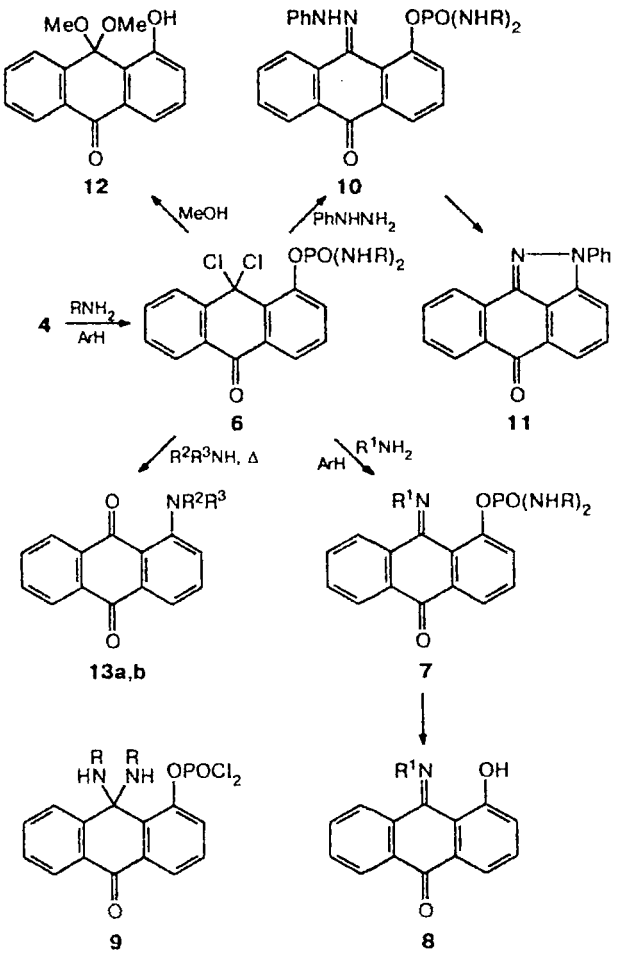
**Scheme 1**



1-di(phenylamino)phosphoryloxy-9,10-anthraquinone 9-phenylimine (**7**, R = $R^1$ = Ph) and 1-hydroxy-9,10-anthraquinone 9-phenylimine (**8**, $R^1$ = Ph) in a total yield of 93%. The first compound is readily transformed into the second one (upon heating at temperatures above 100 °C as well). The similarity of the electronic spectrum of compound **8** to that of 1-hydroxy-9,10-anthraquinone (**1**) and its distinction from the spectra of much more deeply colored 9-amino-1,10-anthraquinones[3] indicates that compound **8** has the 9,10-anthraquinone imine structure rather than a tautomeric 1,10-anthraquinone structure.

A colorless product of substitution of two chlorine atoms by amine residues precipitates out of benzene solution in a yield of approximately 90% in the reaction of anthrone **4** with nonaromatic amine (cyclohexylamine) under the same conditions. In this case the 1-di(alkylamino)phosphoryloxy-9,9-dichloroanthrone structure (**6**) rather than 1-dichlorophosphoryloxy-9,9-di(alkylamino)anthrone structure (**9**) was chosen based on the fact that compound **6** (R = *cyclo*-$C_6H_{11}$) is transformed, with the loss of chlorine atoms but with the retention of cyclohexylamino groups, into 9-phenylhydrazone **10** that undergoes cyclization into 2-phenylanthra[1,9-*cd*]-pyrazol-6-one (**11**) in an alcoholic solution of KOH. Compound **6** is transformed into 1-hydroxy-9,9-dimethoxyanthrone (**12**) upon heating in MeOH with $Na_2CO_3$ and into the corresponding *N*-substituted 1-aminoanthraquinone **13** upon heating with amine (cyclohexylamine, morpholine).

**Scheme 2**



R, $R^1$ = Ph, *cyclo*-$C_6H_{11}$; $R^2$ = *cyclo*-$C_6H_{11}$, $R^3$ = H (**a**); $R^2$, $R^3$ = $(CH_2)_2O(CH_2)_2$ (**b**)

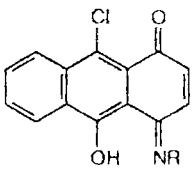
As can be seen, in compound **4** the chlorine atoms in the phosphoryl group are more mobile than those in the *meso*-position of the anthrone system. It is likely that in the reaction with aniline they are substituted first as well. Formation of the products of substitution of all chlorine atoms (compound **7**) and of those substituted only in the phosphoryl group (compound **6**) in the reaction with aniline and cyclohexylamine, respectively,

is likely due to the lower solubility of 1-di(cyclohexylamino)phosphoryloxyderivative **6** that precipitates, thus leaving the reaction sphere. In fact, compound **6** (R = *cyclo*-$C_6H_{11}$) dissolved in toluene easily reacts upon heating with both aniline and cyclohexylamine to give corresponding 1-di-(cyclohexylamino)phosphoryloxy 9-imines (**7**).

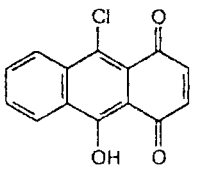
The results of the reactions of 1-dichlorophosphoryloxy-9,9-dichloroanthrone (**4**) with nonaromatic amines in DMF are distinct from those in benzene. 1-Hydroxyanthraquinone **1** and a violet substance identified as 9-chloro-4-cyclohexylamino-1,10-anthraquinone (**14**) were isolated as main products in a 2 : 1 ratio in a total yield of 83% after reaction of anthrone **4** with cyclohexylamine in DMF upon slight heating and dissolution with water (Schemre 3). The molecule of compound **14** contains a chlorine atom and a cyclohexylamino group. After hydrolysis in $H_2SO_4$, it is transformed into 1-hydroxy-4-cyclohexylamino-9,10-anthraquinone (**15**) identical to that synthesized from 1,4-dihydroxy-9,10-anthraquinone (**16**). A small amount of the same substance is formed in the reaction of anthrone **4** with cyclohexylamine in benzene. Among other impurities, 1-cyclohexylamino-9,10-anthraquinone (**13a**) and 1,4-di(cyclohexylamino)-9,10-anthraquinone were found in both cases.

Upon heating with cyclohexylamine in benzene, substitution of the chlorine atom at position 9 occurs and compound **14** is transformed into 4,9-di(cyclohexylamino)-1,10-anthraquinone (**17**) that partially undergoes cyclization into 6-cyclohexylaminoanthra[9,1-*de*]-[1,3]oxazine-7-one-2-spirocyclohexane (**18**) under experimental conditions. The independent synthesis of diamino derivative **17** was performed using the acylotropic rearrangement[9] starting from 1-acetoxy-4-cyclohexylamino-9,10-anthraquinone (**19**) that is transformed into compound **17** upon short-term boiling in methanol with potassium acetate and cyclohexylamine. Cyclization into anthra[9,1-*de*][1,3]oxazinones in the presence of bases is characteristic of 9-alkylamino-1,10-anthraquinones.[10]

The question in which tautomeric form the amination products **14** and **17** exist can be resolved from the data of electronic spectroscopy. The existence of the monoamination product in the form of 9-chloro-4-cyclohexylamino-1,10-anthraquinone (**14**) rather than 10-hydroxy-9-chloro-1,4-anthraquinone 4-cyclohexylimine (**20**) follows from the marked distinction of its electronic spectrum (Fig. 1) from that of 10-hydroxy-9-chloro-1,4-anthraquinone (**21**) formed upon heating of 1,4-dihydroxyanthraquinone (**16**) in $SOCl_2$.[11] The spectrum of compound **14** contains a long-wavelength band with two maxima in the range

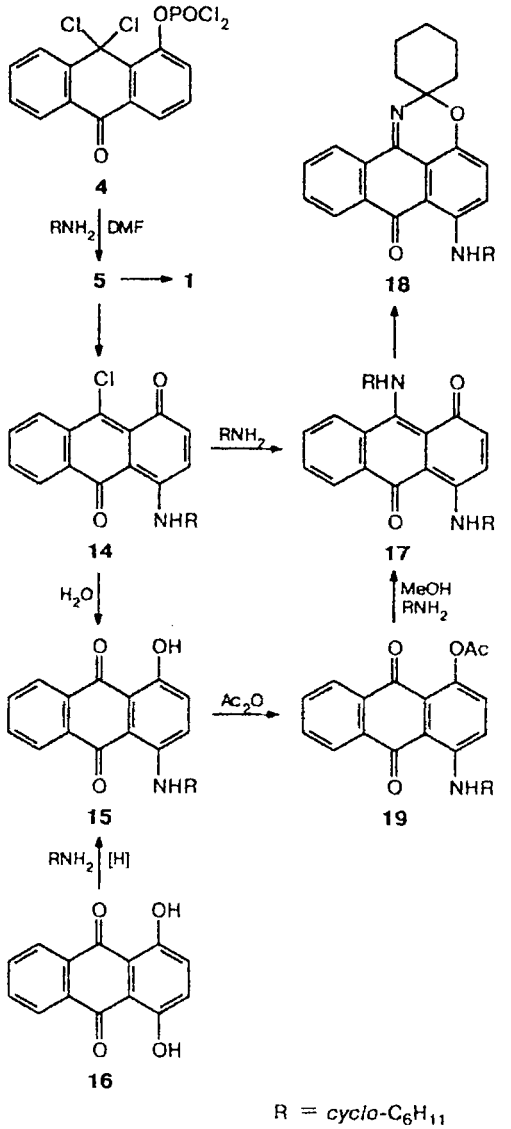



**20**




**21**

**Scheme 3**




R = *cyclo*-$C_6H_{11}$

560—600 nm, whereas that of compound **21** contains a band with a maximum at 462 nm. In the case of the 1,4-anthraquinone structure of the monoamination product the spectra of these compounds would be similar.

The spectrum of bisamination product **17** also contains a band with two maxima in the visible region, which is more intense and shifted by 30-35 nm toward the long-wavelength region (Fig. 1) as compared to the spectra of monoamino derivative **14** and 1-hydroxy-4-cyclohexylamino-9,10-anthraquinone (**15**) that can be taken as a model for the 9,10-anthraquinone form of the bisamination product, 1-hydroxy-4-cyclohexylamino-9,10-anthraquinone 9-cyclohexylimine. Previously,[12] it has been shown on the basis of spectral analysis and quantum-chemical calculations that two of four possible tautomeric forms of 4,9-di(arylamino) derivatives are

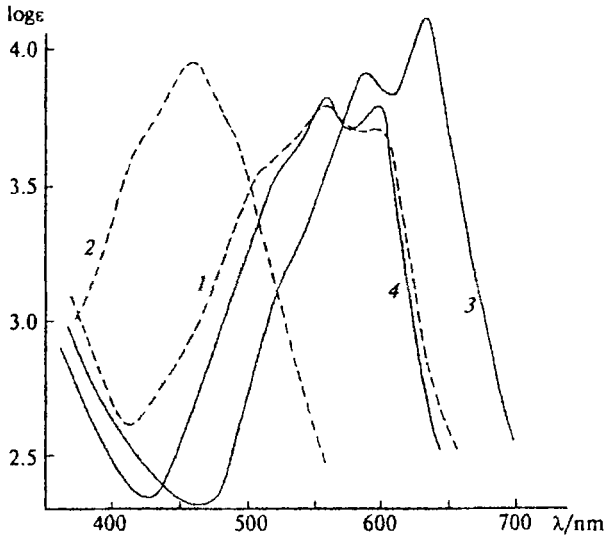



**Fig. 1.** Electronic spectra in EtOH: *1*, 9-chloro-4-cyclohexylamino-1,10-anthraquinone (**14**); *2*, 10-hydroxy-9-chloro-1,4-anthraquinone (**21**); *3*, 4,9-di(cyclohexylamino)-1,10-anthraquinone (**17**); *4*, 1-hydroxy-4-cyclohexylamino-9,10-anthraquinone (**15**).

actually observed, namely, the 1,10-anthraquinone and 9,10-anthraquinoneimine forms, which are in a tautomeric equilibrium that can be shifted toward the 1,10-anthraquinone form in polar solvents. In the case of 4,9-dialkylamino derivatives the 1,10-anthraquinone form must be much more favorable, since the nitrogen atom of alkylamino group has greater proton affinity than arylamino group. In fact, while the spectrum of 4,9-di(*p*-tolylamino) derivative changes on going from a polar solvent to a nonpolar one due to the appearance of the 1,4-quinone tautomer, no such change is observed in the case of 4,9-di(cyclohexylamino) derivative **17**, which is indicative of the predominance of the 1,10-anthraquinone tautomer irrespective of the solvent nature.

9-Chloro-1,10-anthraquinone (**5**), which undergoes amination at position 4 with substitution of the hydrogen atom, is responsible for the formation of 9-chloro-4-cyclohexylamino-1,10-anthraquinone (**14**) in the reaction of anthrone **4** with amine in DMF. It is likely that the unsubstituted quinone acts as an oxidant, being reduced to hydroquinone and regenerated further by oxidation with atmospheric oxygen. The appearance of the impurity 1,4-di(cyclohexylamino)-9,10-anthraquinone, the formation of which from 1-hydroxy-4-cyclohexylamino-9,10-anthraquinone (**15**) under such mild conditions requires transformation into the 2,3-dihydro derivative,[13] is indirect evidence of the presence of a reducing agent in the reaction medium. A competitive process is the transformation of quinone 5 into 1-hydroxyanthraquinone (**1**). The difference of the reaction in DMF is that the nucleophilic attack of amine on the phosphorus atom results in the cleavage of the P—O bond, whereas in the case of reaction in benzene the P—O bond is retained, and after substitution of chlorine atoms at the phosphorus atom the carbon atom in position 9 undergoes attack.

The fact that the hydrogen atom in position 4 rather than the chlorine atom in position 9 is substituted first in the amination of 9-chloro-1,10-anthraquinone (**5**) deserves special attention. In the case of amination of 2,4,9-trichloro-1,10-anthraquinone (**2**), where all active positions are occupied by chlorine atoms, the chlorine atom in position 9 is substituted first.[2] According to quantum-chemical calculation of the 1,10-anthraquinone molecule (see Ref. 13, p. 80), the π-electron density at this position is minimum. The chloride anion is incomparably a better leaving group than the hydride ion that formally acts as a nucleofuge in the substitution of hydrogen atom. The fact that in spite of this the hydrogen atom does undergo substitution reflects the specific mechanism of quinone reactions, when a nucleophilic attack on an unoccupied position is accompanied by intramolecular transfer of the electron pair from the reaction center to the quinone group, which is reduced to hydroquinone, followed by abstraction of a proton and oxidation rather than the abstraction of hydride ion. The attack on an unoccupied position is preferable to that on the position occupied by a halogen atom because the former is less sterically hindered.

9-Chloro-1,10-anthraquinone is a labile compound that was not isolated in individual form. In reactions with amines, compound 5 generated *in situ* undergoes nucleophilic attack on unsubstituted position 4, followed by position 9.

## Experimental

Electronic spectra were recorded on a Specord M 40 spectrophotometer in EtOH, 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-Hydroxyanthraquinone was obtained from 1-aminoanthraquinone by diazotization followed by substitution of the diazonium group[14] and recrystallized from acetic acid. 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-Dichlorophosphoryloxy-9,9-dichloro-10-anthrone (4).** A mixture of hydroxyanthraquinone **1** (2.24 g, 10 mmol) and $PCl_5$ (2.08 g, 10 mmol) was boiled in 25 mL of anhydrous benzene for 30 min until starting compound **1** disappeared, then activated carbon was added, the mixture was filtered, the precipitate was washed with benzene, the filtrate was concentrated in part and diluted with hexane, and the precipitate was separated to give anthrone **4** (2.64 g, 67%), m.p. 152 °C (from heptane) (*cf.* ref. data:[5] 150 °C). $^1H$ NMR (δ): 7.57 (t, 1 H, H(6), $J$ = 7 Hz); 7.67 (t, 1 H, H(3), $J$ = 7 Hz); 7.80 (t, 1 H, H(7), $J$ = 8 Hz); 7.98 (d, 1 H, H(2), $J$ = 7 Hz); 8.21 (d, 1 H, H(5), $J$ = 7 Hz); 8.25 (d, 1 H, H(8), $J$ = 7 Hz); 8.27 (d, 1 H,

H(4), $J$ = 7 Hz). $^{13}C$ NMR (δ): 75.5 (C(9)); 125.1 (C(4)); 125.3 (C(2)); 126.3 (C(5)); 129.8 (C(8)); 130.1 (C(6)); 131.4 (C(3)); 134.8 (C(7)); 179.6 (C(10)). Found (%): C, 42.31; H, 1.98; Cl, 35.40. $C_{14}H_7Cl_4O_3P$. Calculated (%): C, 42.46; H, 1.78; Cl, 35.81.

**1-Di(cyclohexylamino)phosphoryloxy-9,9-dichloro-10-anthrone (6, R = *cyclo*-$C_6H_{11}$).** Cyclohexylamine (4.0 g, 40 mmol) was added to a solution of anthrone (**4**) (4.17 g, 8 mmol) in 40 mL of dry benzene, the mixture was stirred for 4 h and then allowed to stay for 15 h at ~20 °C. The precipitate was filtered off and washed with benzene and water; yield 3.79 g (90%), m.p. 228—230 °C (from chlorobenzene). IR, ν/cm$^{-1}$: 1660 (C=O), 2840, 2900 ($CH_2$), 3190 (NH). UV, $\lambda_{max}$/nm: 229 (log ε 4.26), 266 (log ε 3.95), 285 (log ε 4.05). Found (%): C, 59.84; H, 6.09; Cl, 13.32; N, 5.42. $C_{26}H_{31}Cl_2N_2O_3P$. Calculated (%): C, 59.89; H, 5.99; Cl, 13.60; N, 5.37. Chromatography of the filtrate on a column with $Al_2O_3$ (with $CHCl_3$ as eluent) resulted in successive elution of small amounts of 1-cyclohexylamino-9,10-anthraquinone (**13a**), m.p. 145—145.5 °C (*cf.* ref. data:[5] 145—146 °C), 1,4-di(cyclohexylamino)-9,10-anthraquinone, m.p. 234—235 °C (*cf.* ref. data:[5] 235—235.5 °C) and 4-cyclohexylamino-9-chloro-1,10-anthraquinone (**14**). When water (2 mL) was added to the benzene solution of anthrone **4** prior to the reaction with cyclohexylamine the yield of compound **6** decreased to 72%, while the amount of impurities **13** and **14** increased.

**1-Di(phenylamino)phosphoryloxy-9,10-anthraquinone 9-phenylimine (7, R = R$^1$ = Ph) and 1-hydroxy-9,10-anthraquinone 9-phenylimine (8, R$^1$ = Ph).** Aniline (6.0 g, 64 mmol) in 10 mL of benzene was added to a solution of anthrone **4** (3.17 g, 8 mmol) in 40 mL of benzene, the mixture was stirred for 3 h at 20 °C, then anilinium chloride was filtered off and hexane (150 mL) was added to precipitate compound **7** (2.76 g, 65%), m.p. 201—202 °C (with decomp., from a benzene—hexane mixture). IR, ν/cm$^{-1}$: 1655 (C=O), 3140, 3320 (NH). UV, $\lambda_{max}$/nm: 274 (log ε 4.27), 338 (log ε 3.77). Found (%): C, 72.33; H, 4.44; N 7.70; P, 6.16. $C_{32}H_{24}N_3O_3P$. Calculated (%): C, 72.58; H, 4.57; N, 7.94; P, 5.85.

After separation of compound **7**, the filtrate was concentrated *in vacuo*, the residue was washed with hexane and water, and recrystallized from propan-2-ol to give phenylimine **8** (0.70 g, 28%), m.p. 174—175 °C (from propan-2-ol) (*cf.* ref. data:[16] 174.5—176 °C). The same substance was obtained in 85% yield by heating compound **7** for 20 min at 100—120 °C followed by extraction with propan-2-ol.

**1-Di(cyclohexylamino)phosphoryloxy-9,10-anthraquinone 9-phenylimine (7, R = *cyclo*-$C_6H_{11}$, R$^1$ = Ph).** A mixture of anthrone **4** (0.26 g, 0.5 mmol), toluene (8 mL), and aniline (0.19 g, 2 mmol) was boiled for 30 min, then anilinium chloride (0.125 g, ~1 mmol) was filtered off, and hexane was added to the filtrate to precipitate imine **7** (0.20 g, 73%), m.p. 268—270 °C (from a benzene—hexane mixture). IR, ν/cm$^{-1}$: 1610 (C=N), 1665 (C=O), 2840, 2920 ($CH_2$); 3200, 3360 (NH). UV, $\lambda_{max}$/nm: 224 (log ε 4.33), 253 (log ε 4.52). Found (%): C, 70.87; H, 6.69; N, 7.68. $C_{32}H_{36}N_3O_3P$. Calculated (%): C, 70.96; H, 6.70; N, 7.76.

**1-Di(cyclohexylamino)phosphoryloxy-9,10-anthraquinone 9-cyclohexylimine (7, R = R$^1$ = *cyclo*-$C_6H_{11}$).** This compound was synthesized analogously to the preceding one using cyclohexylamine. The yield was 64%, m.p. 180—182 °C (from aqueous solution of EtOH). IR, ν/cm$^{-1}$: 1605 (C=N), 1665 (C=O), 2840, 2920 ($CH_2$); 3190, 3350 (NH). UV, $\lambda_{max}$/nm: 248 (log ε 4.40). Found (%): C, 70.42; H, 6.86; N, 7.67. $C_{32}H_{42}N_3O_3P$. Calculated (%): C, 70.18; H, 7.73; N, 7.67.

**1-Di(cyclohexylamino)phosphoryloxy-9,10-anthraquinone 9-phenylhydrazone (10).** A solution of anthrone **4** (0.26 g, 0.5 mmol) and phenylhydrazine (0.22 g, 2 mmol) in 7 mL of toluene was boiled for 10 min, phenylhydrazine hydrochloride (0.14 g) was filtered off, then hexane (50 mL) was added to the filtrate, and the precipitate was separated. The yield was 0.24 g (87%), m.p. 220 °C (from a benzene—hexane mixture). IR, ν/cm$^{-1}$: 1640, 1650 sh. (C=O, C=N), 2840, 2910 ($CH_2$); 3320, 3380 (NH). UV ($CHCl_3$), $\lambda_{max}$/nm: 342 (log ε 3.78), 442 (log ε 4.09). Found (%): C, 69.01; H, 6.87; N, 9.89. $C_{32}H_{37}N_4O_3P$. Calculated (%): C, 69.05; H, 6.70; N, 10.07.

**2-Phenylanthra[1,9-*cd*]pyrazol-6-one (11).** Phenylhydrazone **10** (56 mg) was added to a solution of KOH (100 mg) in 5 mL of EtOH, the mixture was boiled for 10 min, poured into 50 mL of water, acidified to pH 3, and the precipitate was separated to obtain pyrazole **11** (27 mg, 91%), m.p. 211—212 °C (from AcOH) identical to that synthesized by arylation of anthra[1,9-*cd*]pyrazol-6-one with bromobenzene (*cf.* ref. data:[17] m.p. 211—212 °C).

**1-Hydroxy-9,9-dimethoxy-10-anthrone (12).** A mixture of anthrone **4** (0.52 g, 1 mmol), $Na_2CO_3$ (2 g), and 20 mL of MeOH was boiled for 30 min and poured into 100 mL of water. Extraction with benzene followed by evaporation of the solvent and recrystallization from hexane gave compound **12** (0.20 g, 74%), m.p. 119—120 °C (*cf.* Ref. 10: m.p. 119—120 °C).

**1-Cyclohexylamino-9,10-anthraquinone (13a).** A solution of anthrone **6** (0.52 g, 1 mmol) in 5 mL of cyclohexylamine was boiled for 5 h, diluted with 50 mL of benzene, washed with diluted HCl and water, and chromatographed on a column with $Al_2O_3$ to elute with benzene a red band of 1-cyclohexylaminoanthraquinone (0.24 g, 56%), m.p. 145—146 °C (*cf.* Ref. 15: m.p. 145—146 °C).

**1-Morpholino-9,10-anthraquinone (13b).** 1-Morpholinoanthraquinone was obtained analogously in 89% yield by boiling anthrone **6** in morpholine, m.p. 151—152 °C (*cf.* Ref. 18: m.p. 152 °C).

**9-Chloro-4-cyclohexylamino-1,10-anthraquinone (14).** A solution of cyclohexylamine (4.32 g, 40 mmol) in 10 mL of DMF was added to a solution of anthrone **4** (3.17 g, 8 mmol) in 75 mL of DMF heated to 50 °C, the mixture was stirred for 1 h at 20 °C, poured into 1 L of water, and compound **14** that precipitated was rapidly separated, yield 1.10 g (46%), m.p. 188—189 °C (from *n*-butanol). IR, ν/cm$^{-1}$: 1625 (C=O), 2840, 2910 ($CH_2$); 3370 (NH). Electronic spectrum, $\lambda_{max}$/nm: 561 (log ε 3.80), 602 (log ε 3.70). Found (%): Cl, 10.21; N, 4.20. [M$^+$], 340. $C_{20}H_{18}ClNO_2$. Calculated (%): Cl, 10.43; N, 4.12. M, 339.8. After 20 h, 1-hydroxyanthraquinone (**1**) (1.24 g, 55%) that precipitated was separated from the filtrate.

**1-Hydroxy-4-cyclohexylamino-9,10-anthraquinone (15).** *A.* A solution of compound **14** (0.34 g) in 10 mL of conc. $H_2SO_4$ was heated for 20 min at 100 °C and poured into 100 mL of water after cooling, then anthraquinone **15** that precipitated was filtered off and recrystallized from aqueous EtOH, yield 0.27 g (83%), m.p. 170—171 °C, IR, ν/cm$^{-1}$: 1605 w (C=O), 2840, 2910 ($CH_2$); 3380 (NH). Electronic spectrum, $\lambda_{max}$/nm: 561 (log ε 3.83), 602 (log ε 3.80). Found (%): C, 74.70; H, 5.89; N, 4.40; [M]$^+$, 321. $C_{20}H_{19}NO_3$. Calculated (%): C, 74.75; H, 5.96.; N, 4.36; M, 321.

*B.* A mixture of 1,4-dihydroxy-9,10-anthraquinone (**16**) (2.4 g, 10 mmol), 2,3-dihydro-1,4,9,10-anthradiquinone (2.42 g, 10 mmol), and 50 mL of cyclohexylamine was stirred for 5 min at 80 °C, cooled, and poured into 500 mL of 3 % HCl. The precipitate was filtered, washed with water, and chromatographed on a column with $Al_2O_3$ to elute with $CHCl_3$ a compound (2.50 g, 39%) identical to that isolated in case *A*.

**4,9-Di(cyclohexylamino)-1,10-anthraquinone (17) and 6-cyclohexylaminoanthra[9,1-*de*][1,3]oxazin-7-one-2-spiro-**

**cyclohexane (18).** ***A.*** Compound **14** (204 mg, 0.6 mmol) and 1 mL of cyclohexylamine were boiled for 1 h in 10 mL of benzene, then cyclohexylamine hydrochloride that precipitated was filtered off, and the solution was chromatographed on a column with $Al_2O_3$ to elute with benzene a violet band of oxazine **18** (51 mg, 21%), m.p. 154—155 °C (from aqueous propan-2-ol). Electronic spectrum ($CHCl_3$), $\lambda_{max}$/nm: 300 (log ε 3.84); 327 (log ε 3.76); 555 (log ε 3.81). Found (%): N, 6.75. $[M]^+$, 400. $C_{26}H_{28}N_2O_2$. Calculated (%): N, 6.99. M, 400. Elution of the next (blue) band afforded compound **17** (57 mg, 23%), m.p. 167—168 °C (from a benzene—hexane mixture). Electronic spectrum, $\lambda_{max}$/nm: 590 (3.92); 635 (4.13). Found (%): N, 7.09. $[M]^+$, 402. $C_{26}H_{30}N_2O_2$. Calculated (%): N, 6.96. M, 402.

***B.*** Quinone **19** (0.73 g, 2 mmol) and 1 mL of cyclohexylamine were added to a mixture of MeOH (40 mL) and AcOK (1 g), the mixture was heated to boiling, stirred for 10 min, and poured into 100 mL of 0.5 % HCl, the precipitate was filtered and chromatographed on a silica gel column (benzene) to elute 1-hydroxy-4-cyclohexylaminoanthraquinone (**15**) (0.39 g, 60%) and compound **17** (0.23 g, 28%) identical to that synthesized in case ***A***. Oxazine **18** was found as a small impurity.

**1-Acetoxy-4-cyclohexylamino-9,10-anthraquinone (19).** A mixture of quinone **15** (1.61 g), $Ac_2O$ (20 mL), and pyridine (10 mL) was stirred for 1 h at 100 °C, poured into 200 mL of water, and the precipitate was separated and recrystallized from EtOH, yield 1.45 g (80%), m.p. 133 °C (*cf.* Ref. 19: m.p. 133—134 °C).

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