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Solvent effect on the reactivity of 1,10-phenanthroline-5,6-dione towards diazomethane

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Abstract—In an aprotic medium, such as THF, Et_2O or CH_2Cl_2, the reaction of 1,10-phenanthroline-5,6-dione with diazomethane gave 5,6-methylenedioxy-1,10-phenanthroline as the only product. In contrast, in a protic solvent, such as 2-propanol or ethanol, the nucleophilic attack of CH_2N_2 occurred on carbonyl carbons, resulting in the formation of dispiro[5,6-dihydro-1,10-phenanthroline-5,6-dioxirane] as the main product. When the reaction with CH_2N_2 was carried out in methanol, the only product which could be isolated from the reaction mixture, dimethyl 2,2′-bipyridine-3,3′-dicarboxylate, resulted from a break of the C(5)–C(6) bridge.

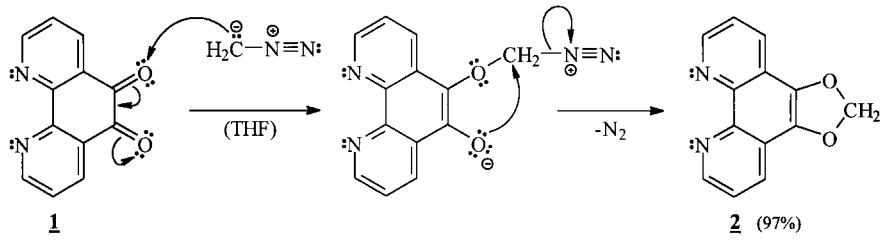
1. Introduction

1,10-Phenanthroline and a number of its derivatives, substituted mainly at the 2,9, the 4,7 or the 5,6 positions, play an important role in complex chemistry because of their unique properties as chelating agents.[1,2,3] 1,10-Phenanthroline-5,6-dione (**1**) is of particular interest, since two nucleophilic centers (nitrogen and oxygen lone pairs) are composed in a molecule of such a quinone, with all the atoms, except hydrogens, being of sp^2 hybridization.[4] The presence of two electronegative heteroatoms creates not only the basic properties in the Lewis sense but also, because of the resonance conjugation, make it possible to alter the electron density in different parts of the molecule, especially by the interaction of an external electrophile with the unshared pairs of electrons of the heteroatom. As a consequence, a dramatic change in reactivity can occur, which is not observed in the case of the corresponding aromatic homocyclic analogue, phenanthrenequinone.[5] This is also seen in the reaction with CH_2N_2, in which, contrary to the heterocyclic **1**, as we found later on, the homocyclic quinone gave a spiro-oxirane derivative in an aprotic solvent, while in methanol it is transformed into a product of the enlarged middle ring to a seven-membered one.[6,7]

2. Results and discussion

We have found[8] that 1,10-phenanthroline-5,6-dione (**1**), when dissolved in THF and treated with diazomethane, gave 5,6-methylenedioxy-1,10-phenanthroline (**2**) as the only product (Scheme 1). Neither the formation of a product of an enlarged dione ring[6,9] by a methylene insertion via a rearrangement of the preliminary diazomethane addition intermediate, nor the formation of oxirane or dioxirane derivatives was observed.

The formation of the 1,3-dioxolene ring in this reaction resembled the result of a phenanthrolinequinone treatment with an anion generated from 2-nitropropane[10] or



Scheme 1.

Keywords: 1,10-phenanthroline; quinones; diazo compounds; solvents and solvent effects.
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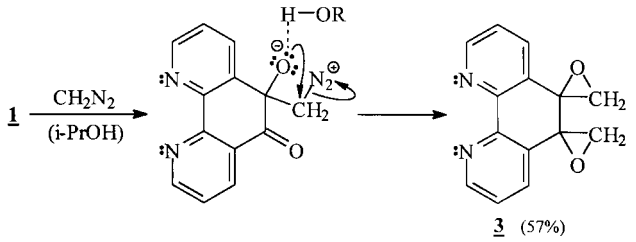
nitroethane,[11] in which either 5,6-isopropylidenedioxy-1,10-phenanthroline or an ethylidene derivative, respectively, was obtained. Our attempts to adopt this method in the synthesis of 5,6-methylenedioxy-1,10-phenanthroline by using nitromethane anion instead of nitropropane failed and we were not able to find the desired compound in the product mixture. The formation of the 1,3-dioxolene system by the treatment of quinones with diazomethane derivatives had already been reported but with reference to 9,10-phenanthrenedione and 4,7-phenanthroline-5,6-dione, and in the reaction with diazoethane[6] or phenyl- and diphenyldiazomethane,[12] respectively. However, both the reaction conditions leading to the dioxolene formation as well as the stability of the resulting products towards hydrolytic agents differed from those relating to 1,10-phenanthroline-5,6-dione.

In an aprotic solvent, the unsolvated carbonyl oxygens are exposed to the diazomethane attack, but, because of the conjugated system of both carbonyls, the nucleophilic attack is preferred with a consequent shift of π electrons towards the second oxygen and enolate anion formation; the intermediate product of addition then underwent an intramolecular cyclization with a simultaneous loss of a nitrogen molecule.

When 1,10-phenanthrolinequinone was dissolved in 2-propanol (or ethanol, but the results in such a case were less satisfying) and treated with an ethereal solution of diazomethane, the reaction occurred differently, yielding dispiro[5,6-dihydro-1,10-phenanthroline-5,6-dioxirane] (**3**) as the main product. In the case of both dioxolene **2** as well as dispirodioxirane **3**, the structure suggestions which were based on the spectral data were confirmed by an X-ray analysis.[13]

Protic solvents change the environmental situation of the quinone molecule, because of the solvation ability of heteroatoms by hydrogen bonding. While the carbonyl oxygen is shielded by the rather bulky isopropyl alcohol molecules, the carbonyl carbon is the atom most sensitive to a nucleophilic attack and, in the competition between the alcohol and diazomethane molecules, it appeared that the latter was more effective. As a result, dispirodioxirane **3** is formed by the mechanism generally accepted for similar reactions (Scheme 2).

However, when, as a solvent for **1**, methanol was used instead of a higher homologue, the post-reaction mixture composition differed dramatically and the only product, which could be isolated in a fair yield, had the structure of

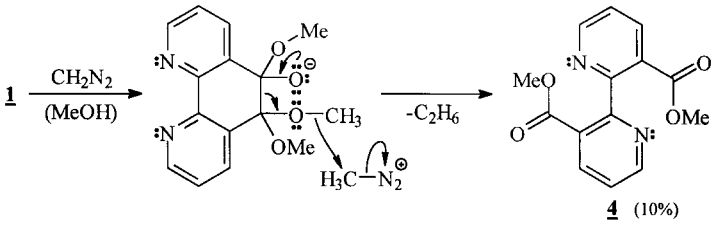


Scheme 2.

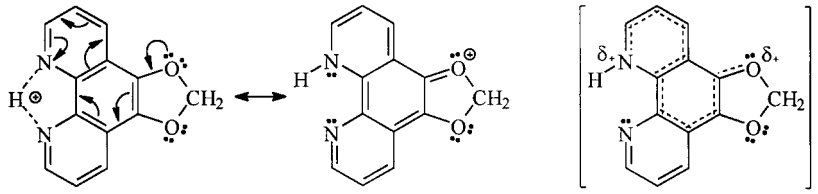
dimethyl 2,2′-bipyridine-3,3′-dicarboxylate (**4**). A similar result, thought with a better yield of **4** (about 30%), was obtained when **1** was treated with *N*-methyl-*N*-nitrosourea in the presence of potassium carbonate in methanol following the procedure described for 4,7-phenanthroline-5,6-dione, which, however, led to the formation of dispiro[5,6-dihydro-4,7-phenanthroline-5,6-dioxirane].[14]

Unexpectedly, the use of methanol instead of a higher alcoholic homologue caused a change in the course of the reaction, leading mainly to the formation of dimethyl 2,2′-bipyridine-3,3′-dicarboxylate (**4**). It seems most probable that, in this case, the small methanol molecules not only solvate the oxygen, but also act effectively as nucleophiles attacking carbon faster than those of diazomethane. As a result, a hemiacetal or even a double full acetal is formed. When the bridge carbons gained the sp^3 hybridization, it is most probable that, partly at least because of the crowdedness, a rearrangement occurs with a simultaneous reduction of diazomethane at the expense of the C(5)–C(6) bridge electrons (Scheme 3). Actually, the exact mechanism of this transformation is not yet proved and the observations are difficult to interpret without further experimental evidence.

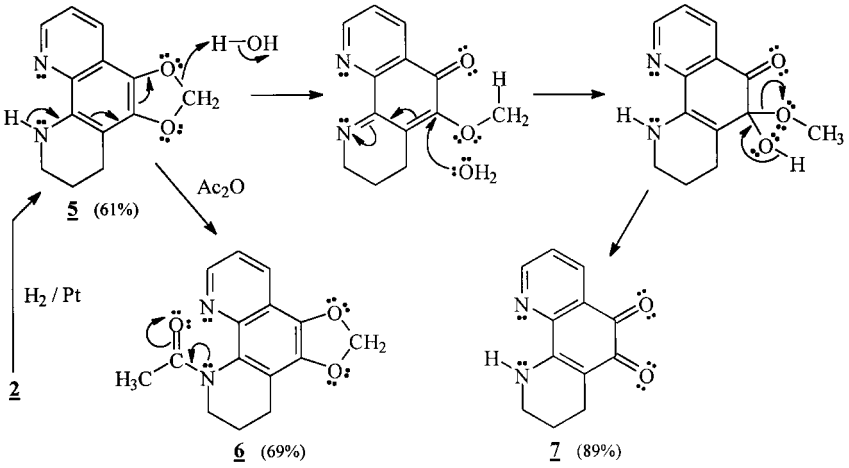
Contrary to the reactivity, which is characteristic for acetals, of 1,3-dioxolene derived from 9,10-phenanthrenedione[12] or other quinone systems reported in the literature, 5,6-methylenedioxy-1,10-phenanthroline was found to be extremely resistant to hydrolysis by aqueous acids, even when kept in 40% HBr·aq at 90°C for 1 h. The removal of the protecting methylene group was only possible by an oxidative treatment with bromine, which yielded 1,10-phenanthroline-5,6-dione. The enhanced stability revealed by the acetal in an acidic medium is probably the result of the intramolecular electron density shift towards the electron-withdrawing protonated nitrogen, which makes the oxygen less nucleophilic and, thus, less sensitive to protonation (Scheme 4, in which the participation of only one nitrogen is shown for simplicity).



Scheme 3.



Scheme 4.



Scheme 5.

The non-reactivity of the dioxolene system changed dramatically when 5,6-methylenedioxy-1,10-phenanthroline was subjected to a catalytic hydrogenation in the presence of Adams' catalyst, as a result of which 1,2,3,4-tetrahydro-5,6-methylenedioxy-1,10-phenanthroline (**5**) was obtained.[†] The resulting tetrahydro derivative, by immediate treatment with acetic anhydride and storing the reaction mixture overnight at room temperature, was easily transformed into a stable 1-acetyl-1,2,3,4-tetrahydro-5,6-methylenedioxy-1,10-phenanthroline (**6**).

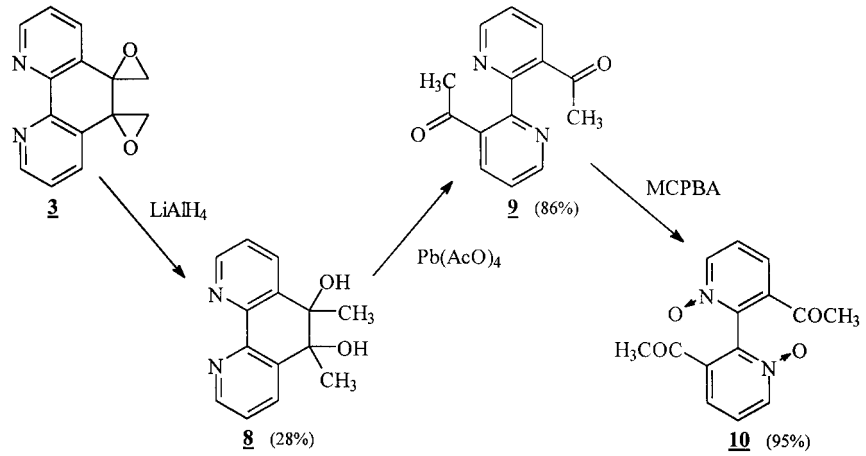
However, when the parent free amine **5** was stored for a few hours, either in a neat state or in a polar solvent, such as chloroform (most likely by the contribution of a trace of moisture), it changed spontaneously into 1,2,3,4-tetrahydro-1,10-phenanthrolino-5,6-dione (**7**). The regeneration of the quinone system resembles the deprotection of **2** by bromine, but this time it occurred at the expense of the internal fragment, which had been derived from CH_2N_2, instead of the external reagent. This transformation was not stimulated by acids or bases.

These observations, as shown in Scheme 5, can be interpreted as being the result of a change in the intramolecular availability of electrons in different parts of the molecule, by long-distance nucleophilic assistance exerted by the nitrogen's unshared pair of electrons via the π electron system.

The acetylation of 1,2,3,4-tetrahydro-5,6-methylenedioxy-1,10-phenanthroline (**5**) to **6** causes the nitrogen electrons to be more tightly bound to the amide system and, thus, less available for the intramolecular long distance assistance by resonance in hydrolysis, accompanied by oxidation (Scheme 5). The planarity of both the acetamide group itself, because of the partly C–N double bond character of the resonance amide structure (1639 cm^{-1}), as well as of its arrangement with the aromatic fragment of the molecule [though unfavourable due to the steric (CH_3, N-10) or dipole–dipole (C=O, N-10) repulsion], can be concluded from the molecular model analysis and the NMR data. The chemical shift of pseudo-axial and pseudo-equatorial protons located in the C-2 position, close to the amide nitrogen, revealed a distinct difference (up to 1.81 ppm), which shows the different magnetic environment of both hydrogens as a result of a different anisotropic interaction caused mainly by the acetyl group [for H(3p-e)-H(3p-a), being in a similar relationship to the aromatic system Δ=0.35 ppm]. Such a conformation makes it possible to withdraw the electrons effectively by the resonance from the acetal region. It seems very likely that, because of similar reasons, this time caused by an additional protonation of nitrogens, no accelerating effect of the reaction rate was observed when **5** was attempted to be hydrolysed in aqueous acid.

To prove the structure of dispirodioxirane **3** obtained by the diazomethane treatment of phenanthrolinequinone in 2-propanol, the dioxirane derivative, as shown in Scheme 6, was subjected to a reduction by $LiAlH_4$, which yielded 5,6-dihydro-5,6-dihydroxy-5,6-dimethyl-1,10-phenanthroline (**8**). The product was then oxidized, first by $Pb(OAc)_4$ to 3,3′-diacetyl-2,2′-bipyridine (**9**) and, next, by MCPBA to

[†] In similar conditions, the hydrogenation of 1,10-phenanthroline, in the presence of PtO_2, gave, in good yield, the corresponding 1,2,3,4-tetrahydro derivative as the only product, the physical properties of which were identical with those reported for that compound synthesized by different methods.[15,16]



Scheme 6.

3,3′-diacetyl-2,2′-bipyridine 1,1′-dioxide (**10**). The structures of all these products were proved by spectroscopic data.

3. Experimental

3.1. General

Melting points were determined by a hot plate method (only occasionally a Büchi 535 capillary apparatus was used) and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a VARIAN GEMINI 300 spectrometer. The chemical shift values are in ppm measured from TMS as a standard. Proton and carbon assignments were based on COSY and HETCOR experiments. IR spectra were measured on an FT-IR BRUKER IFS 113v instrument for KBr discs. MS spectral data were obtained on an AMD 402 mass spectrometer.

TLC analyses were carried out using MERCK DC-Alufolien, Kieselgel 60 WF_{254}s and AcOEt–*i*PrOH–conc. NH_3·aq. (8:4:1) or AcOEt–MeOH (7:3) as a developing system. Column chromatography was carried out using MERCK Kieselgel 60 (230–400 mesh) as the stationary phase, while hexane, benzene, AcOEt, CH_2Cl_2, $CHCl_3$ and 5% MeOH in $CHCl_3$ were the eluting solvents.

3.1.1. 5,6-Methylenedioxy-1,10-phenanthroline (2). A stirred solution of 1,10-phenanthroline-5,6-dione[3] (**1**, 226 mg, 1.08 mmol) in 60 mL of anhydrous tetrahydrofuran was treated with an ethereal solution of diazomethane prepared from *N*-methyl-*N*-nitrosourea (2.315 g, 22.48 mmol) in 80 mL of diethyl ether. The yellow solution was stirred at room temperature overnight and, next, the resulting non-homogeneous reaction mixture was concentrated under diminished pressure yielding 234 mg (97%) of a solid residue, which contained almost pure **2** of R_f 0.7. The crude product, when recrystallized from methanol, gave as a first crop 108 mg (45%) of bright yellow needles melting at 274–276°C, while the recrystallization of an analytical sample from anhydrous ethanol furnished thin plates of mp 280–281°C. IR (cm^{-1}): 3022, 1661, 1590, 1550, 1515, 1460, 1398, 1365, 1302, 1136, 1065, 1027, 965, 795, 733, 622; ^{1}H NMR (DMSO) δ: 9.05 (2H, dd, J=4.4, 1.9 Hz, H-2 and H-10), 8.38 (2H, dd, J=8.2, 1.9 Hz, H-4 and H-7), 7.82 (2H, dd, J=8.2, 4.4 Hz, H-3 and H-8), 6.47 (2H, s, CH_2); ^{1}H NMR (CD_2Cl_2) δ: 9.04 (2H, dd, J=4.3, 1.8 Hz, H-2 and H-9), 8.27 (2H, dd, J=8.3, 1.8 Hz, H-4 and H-7), 7.64 (2H, dd, J=8.3, 4.3 Hz, H-3 and H-8), 6.34 (2H, s, CH_2); ^{13}C NMR (CD_2Cl_2) δ: 148.32 (C-2 and C-9), 142.97 (C-5 and C-6), 137.35 (C-10a and C-10b), 127.93 (C-4 and C-7), 123.09 (C-3 and C-8), 118.24 (C-4a and C-6a), 103.27 (CH_2); MS: 224 (100%, M^+), 196 (7%), 168 (10%), 166 (29%), 139 (15%), 112 (13%); HRMS for M^+, $C_{13}H_8N_2O_2$, calcd: 224.0586, found: 224.0571; for (M−28), $C_{12}H_8N_2O$, calcd: 196.0637, found: 196.0647.

3.1.2. Dispiro[5,6-dihydro-1,10-phenanthroline-5,6-dioxirane] (3). To a suspension of 1,10-phenanthroline-5,6-dione (**1**, 100 mg, 0.48 mmol) in 50 mL of anhydrous isopropyl alcohol was added a solution of diazomethane in diethyl ether (25 mL) obtained from 550 mg (5.34 mmol) of *N*-methyl-*N*-nitrosourea. Stirring at room temperature was continued overnight and then the resulting clear solution was concentrated under diminished pressure yielding 133 mg of crude residue, which, according to the TLC pattern, was composed of a main product, R_f 0.7, accompanied by two others, R_f 0.5 and 0.6, respectively. The main product **3** was obtained in a pure state (65 mg, 57%) by chromatography on SiO_2, when the column was washed with an AcOEt–benzene (4:1) mixture; the colourless solid product did not melt when heated up to 360°C. IR (cm^{-1}): 3071, 2992, 1578, 1561, 1421, 949, 895, 853, 805, 744, 607; ^{1}H NMR ($CDCl_3$) δ: 8.82 (2H, dd, J=4.7, 1.6 Hz, H-2 and H-9), 7.65 (2H, dd, J=8.0, 1.6 Hz, H-4 and H-7), 7.37 (2H, dd, J=8.0, 4.7 Hz, H-3 and H-8), 3.42 (2H, d, J=6.3 Hz, CH_2), 2.73 (2H, d, J=6.3 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ: 151.09 (C-10a and C-10b), 150.38 (C-2 and C-9), 131.22 (C-4 and C-7), 130.83 (C-4a and C-6a), 124.38 (C-3 and C-8), 56.77 (CH_2), 55.1 (C-5 and C-6); MS: 238 (M^+, 41%), 220 (70%), 208 (68%), 193 (69%), 180 (100%), 164 (18%), 154 (20%), 44 (23%); HRMS for M^+, $C_{14}H_{10}N_2O_2$, calcd: 238.0742, found: 238.0754.

3.1.3. Dimethyl 2,2′-bipyridine-3,3′-dicarboxylate (4) from 1. A suspension of 1,10-phenanthroline-5,6-dione (**1**, 500 mg, 2.38 mmol) in 60 mL of anhydrous methanol, when stirred in a 2-propanol/solid CO_2 bath, was supplied with a

precooled down to −75°C diethyl ether solution of diazomethane prepared from 2.6 g (25.24 mmol) of *N*-methyl-*N*-nitrosourea. Stirring at that temperature was continued for a further 15 min, then the cooling bath was removed, and the reaction mixture was first allowed to reach room temperature overnight and, next, concentrated under diminished pressure. The resulting brown oil (656 mg) was composed, according to the TLC pattern, of three compounds from which one revealed R_f 0.6, that resembled the value of the starting quinone. From a silica gel column, using an AcOEt–benzene (4:1) mixture, was eluted a homogeneous product **4** as colourless crystals (64 mg, 10%) of R_f 0.7 and mp 153–156°C, which is consistent with the lit.[17,18] IR (cm^{-1}): 3004, 2954, 1718, 1582, 1561, 1454, 1434, 1415, 1309, 1300, 1216, 1135, 1053, 961, 766; ^1H NMR ($CDCl_3$) δ: 8.78 (2H, dd, J=4.7, 1.6 Hz, H-6 and H-6′), 8.37 (2H, dd, J=8.0, 1.6 Hz, H-4 and H-4′), 7.45 (2H, dd, J=8.0, 4.7 Hz, H-5 and H-5′), 3.69 (6H, s, 2×C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ: 165.86 (CO), 159.29 (C-2 and C-2′), 151.52 (C-6 and C-6′), 138.08 (C-4 and C-4′), 125.25 (C-3 and C-3′), 122.62 (C-5 and C-5′), 52.27 (2×$\underline{C}H_3$); MS: 272 (9%, M^+), 257 (9%), 241 (100%), 213 (17%), 199 (11%), 182 (7%), 170 (8%); HRMS for M^+, $C_{14}H_{12}N_2O_4$, calcd: 272.0797, found: 272.0782.

3.1.4. Oxidative hydrolysis of 2 by bromine. A stirred solution of 5,6-methylenedioxy-1,10-phenanthroline (**2**, 29 mg, 0.12 mmol) in 1 mL of glacial acetic acid was supplied with 0.02 mL of bromine which caused an immediate separation of an orange precipitate. The subsequent addition of water (10 mL) gave a homogeneous solution from which the product was isolated by extraction with CH_2Cl_2 (3×10 mL). The organic layer, when dried over anhydrous Na_2SO_4 and concentrated, yielded 25 mg (92%) of pure 1,10-phenanthroline-5,6-dione (**1**). A trace of a further amount of the quinone was additionally recovered when the remaining aqueous layer was neutralized by means of solid $NaHCO_3$ and, next, re-extracted with CH_2Cl_2.

3.1.5. 1,2,3,4-Tetrahydro-5,6-methylenedioxy-1,10-phenanthroline (5). A solution of 5,6-methylenedioxy-1,10-phenanthroline (**2**, 200 mg, 0.89 mmol) in 50 mL of anhydrous methanol was supplied with 10 mg of PtO_2 (Adams' catalyst) and the resulting suspension was shaken at room temperature in a hydrogen atmosphere under pressure of 0.055 MPa for 3 h. After removing the catalyst by filtration, the resulting bright yellow solution (the colour of which changed quickly to brown when kept in open air) was concentrated yielding 185 mg of a brown oil. The crude product was then subjected to column chromatography on silica gel (4 g). The use of benzene as an eluting solvent furnished a yellow solidifying oil of **5** (124 mg, 61%, R_f 0.9). IR (cm^{-1}): 3402 (br.), 2929, 2859, 1722, 1703, 1655, 1493, 1445, 1387, 1341, 1276, 1104, 1067, 970; ^1H NMR ($CDCl_3$) δ: 8.51 (1H, dd, J=4.1, 1.6 Hz, H-9), 7.98 (1H, dd, J=8.5, 1.6 Hz, H-7), 7.25 (1H, dd, J=8.5, 4.1 Hz, H-8), 6.04 (2H, s, C$\underline{H}_2$), 5.75 (1H, br., N$\underline{H}$), 3.49 (2H, t, J=5.5 Hz, H-2), 2.85 (2H, t, J=6.5 Hz, H-4), 2.07 (2H, m, H-3); ^{13}C NMR ($CDCl_3$) δ: 145.27 (C-9), 143.96, 138.67, 132.72, 129.47, 128.01 (C-7), 121.72 (C-8), 114.74, 103.97, 102.11 ($\underline{C}H_2$), 41.57 (C-2). 21.85 (C-3), 21.47 (C-4); MS: 228 (100%, M^+), 213 (15%), 211 (12%), 199 (23%), 185 (8%), 170 (15%), 167 (8%), 149 (14%), 142 (37%), 115 (11%); HRMS for M^+, $C_{13}H_{12}N_2O_2$, calcd: 228.0899, found: 228.0916, for (M−15), $C_{12}H_9N_2O_2$, calcd: 213.0664, found: 213.0646; MIKES for M^+: 213, 211, 200 for (M−CH_3): 185.

The final elution of the column by ethyl acetate gave a red solid (25 mg, 13%), which was identified as quinone **7**.

3.1.6. 1-Acetyl-1,2,3,4-tetrahydro-5,6-methylenedioxy-1,10-phenanthroline (6). A yellow solution of 1,2,3,4-tetrahydro-5,6-methylenedioxy-1,10-phenanthroline (**5**, 33 mg, 0.14 mmol) in 1 mL of acetic anhydride was left overnight at ambient temperature which caused a change of the colour to red. After an addition of 20 mL of water, the reaction mixture was first neutralized by solid $NaHCO_3$ and then extracted with CH_2Cl_2 (3×10 mL). The organic layer was dried over Na_2SO_4 and concentrated. From the red oily residue, the pure amide **6** was obtained in the form of a solidifying oil (27 mg, 69%) by purification over a silica gel (0.5 g) column when 30% AcOEt in PhH was used as eluant. Mp 180–181°C. IR (cm^{-1}): 3080, 3006, 2956, 2933, 2901, 1639, 1461, 1420, 1382, 1374, 1329, 1282, 1211, 1068, 1032, 999, 809, 786; ^1H NMR ($CDCl_3$) δ: 8.78 (1H, dd, J=4.1, 1.9 Hz, H-9), 8.13 (1H, dd, J=8.5, 1.9 Hz, H-7), 7.32 (1H, dd, J=8.5, 4.1 Hz, H-8), 6.22 (2H, d, J=3.3 Hz, C$\underline{H}_2$), 4.86 (1H, m, H-2), 3.05 (1H, m, H-2), 3.00 (1H, m H-4), 2.74 (1H, m, H-4), 2.28 (1H, m, H-3), 1.93 (1H, m, H-3), 1.92 (3H, s, C$\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ: 172.29 (CO), 148.01 (C-9), 141.42, 138.14, 137.77, 131.85, 128.26 (C-7), 120.63, 120.46 (C-8), 113.48, 102.39 ($\underline{C}H_2$), 42.86 (C-2), 23.46 ($\underline{C}H_3$), 23.39 (C-3), 20.76 (C-4); MS: 270 (30%, M^+), 228 (100%), 213 (12%), 211 (9%), 199 (16%), 185 (4%), 170 (10%), 142 (20%), 115 (6%); HRMS for M^+, $C_{15}H_{14}N_2O_3$, calcd: 270.1004, found: 270.0989, for (M−42), $C_{13}H_{12}N_2O_2$, calcd: 228.0899, found: 228.0896.

3.1.7. 1,2,3,4-Tetrahydro-1,10-phenanthroline-5,6-dione (7). A solution of 1,2,3,4-tetrahydro-5,6-methylenedioxy-1,10-phenanthroline (**5**, 37 mg) in 20 mL of $CHCl_3$ was supplied with 1 g of silica gel (Kieselgel 60) and the suspension was stirred for 6 days, which caused a change of its colour to brown, but, according to TLC, no significant progress of the reaction occurred. Next, 5 drops of water were added and stirring was continued for a further 3 days, after which a completion of the reaction was checked by TLC (developed by AcOEt–MeOH, 7:3), according to which the product of R_f 0.6 was only contaminated by a trace of the starting material. The reaction mixture, when supplied with 20 mL of 5% methanol in CH_2Cl_2, was filtered through a thin layer of SiO_2 and concentrated under diminished pressure yielding a red solid of **7** (31 mg, 89%), not melting up to 280°C. IR (cm^{-1}): 3294, 2919, 2850, 1687, 1586, 1551, 1518, 1432, 1333, 1199; ^1H NMR ($CDCl_3$) δ: 8.70 (1H, dd, J=4.9, 1.9 Hz, H-9), 8.33 (1H, dd, J=8.0, 1.9 Hz, H-7), 7.60 (4.81 after D_2O was added, 1H, s, N$\underline{H}$), 7.50 (1H, dd, J=8.0, 4.9 Hz, H-8), 3.61 (2H, m, H-2), 2.72 (2H, t, J=6.3 Hz, H-4), 2.00 (2H, m, H-3); ^{13}C NMR ($CDCl_3$) δ: 181.04 (C-5 or C-6), 173.14 (C-5 or C-6), 152.24 (C-9), 149.67, 147.83, 134.95 (C-7), 127.07, 125.47 (C-8), 109.77, 41.35 (C-2), 20.30 (C-3), 19.14 (C-4); MS: 214 (37%, M^+), 186 (62%), 157,

(100%), 130 (34%); HRMS for M^+, $C_{12}H_{10}N_2O_2$, calcd: 214.0742, found: 214.0749.

3.1.8. 5,6-Dihydro-5,6-dihydroxy-5,6-dimethyl-1,10-phenanthroline (8). To a stirred solution of dispiro[5,6-dihydro-1,10-phenanthroline-5,6-dioxirane] (**3**, 335 mg, 1.41 mmol) in 10 mL of CH_2Cl_2 was added 175 mg of $LiAlH_4$ and then the resulting suspension was diluted with 10 mL of anhydrous THF, which caused a vigorous reaction and a change of the colour to brown. After storing the suspension overnight, while kept in an ice-bath, it was treated with 5 mL of water and, next, the organic solvents were removed under diminished pressure. The residue was extracted with a $CH_2Cl_2/CHCl_3$ mixture (3×75 mL) and the obtained solution was first dried over Na_2SO_4 and then concentrated, yielding 126 mg of a light brown residue. The crude product was purified by column chromatography on silica gel using 3–6% of MeOH in $CHCl_3$ as the eluant, which yielded 94 mg (28%) of a slightly coloured solid of **8**. An analytically pure sample, in the form of a colourless material not melting up to 280°C, was prepared by treating the chromatographically purified product with a small amount of methanol followed by decantation. IR (cm^{-1}): 3250 (br.), 2986, 2931, 1582, 1564, 1419, 1210, 1069, 1043, 955, 812, 752; ^1H NMR (DMSO) δ: 8.58 (2H, dd, J=4.7, 1.6 Hz, H-2 and H-9), 8.03 (2H, dd, J=7.8, 1.6 Hz, H-4 and H-7), 7.43 (2H, dd, J=7.8, 4.7 Hz, H-3 and H-8), 5.46 (2H, s, O<u>H</u>, exchangeable with D_2O), 1.18 (6H, s, 2×C<u>H</u>$_3$); ^1H NMR ($CDCl_3+CD_3OD$) δ: 8.63 (2H, dd, J=4.5, 1.8 Hz, H-2 and H-9), 8.13 (2H, dd J=7.7, 1.8 Hz, H-4 and H-7), 7.42 (2H, dd, J=7.7, 4.5 Hz, H-3 and H-8), 4.72 (s, O<u>H</u>), 1.35 (6H, s, 2×C<u>H</u>$_3$): ^{13}C NMR ($CDCl_3+CD_3\underline{O}D$) δ: 147.94 (C-10a and C-10b), 147.85 (C-2 and C-9), 140.34 (C-4a and C-6a), 132.51 (C-4 and C-7), 124.10 (C-3 and C-8), 75.88 (C-5 and C-6), 23.88 (2×<u>C</u>H$_3$); MS: 242 (M^+, 30%), 225 (100%), 209 (7%), 207 (7%), 199 (54%), 181 (26%), 157 (16%), 122 (26%); HRMS for M^+, $C_{14}H_{14}N_2O_2$, calcd: 242.1055, found: 242.1039.0.

3.1.9. 3,3′-Diacetyl-2,2′-bipyridine (9). A solution of 5,6-dihydro-5,6-dihydroxy-5,6-dimethyl-1,10-phenanthroline (**8**, 139 mg, 0.57 mmol) in 4 mL of glacial AcOH when stirred was supplied with $Pb(OAc)_4$ (279 mg, 0.63 mmol). When stirred for 3 h, the resulting turbid solution, according to TLC, contained none of the starting material, but, instead, only one product of R_f 0.7. After storing overnight, the reaction mixture was diluted with 10 mL of H_2O, then neutralized by solid $NaHCO_3$ and, finally, extracted with CH_2Cl_2 (3×30 mL). The organic layer, when dried over Na_2SO_4 and concentrated, gave 158 mg of a pale brown residue, which was purified by a silica gel (3 g) column, from which, using 30–60% AcOEt in PhH as an eluant, 118 mg (86%) of colourless crystals of **9** were obtained. Mp 174–176°C. IR (cm^{-1}): 3363, 3061, 2967, 1693, 1579, 1553, 1409, 1354, 1277, 1253, 1208, 1106, 1046, 974, 817, 749, 637; ^1H NMR ($CDCl_3$) δ: 8.66 (2H, dd, J=4.7, 1.6 Hz, H-6 and H-6′), 7.95 (2H, dd, J=8.0, 1.6 Hz, H-4 and H-4′), 7.41 (2H, dd, J=8.0, 4.7 Hz, H-5 and H-5′), 2.42 (6H, s, 2×C<u>H</u>$_3$); ^{13}C NMR ($CDCl_3$) δ: 201.08 (2×CO), 155.18 (C-2 and C-2′), 149.78 (C-6 and C-6′), 136.26 (C-3 and C-3′), 135.84 (C-4 and C-4′), 123.03 (C-5 and C-5′), 29.95 (2×<u>C</u>H$_3$); MS: 241 (1%, M+1), 240 (0.1%, M^+), 239 (0.5%), 226 (15%), 225 (100%), 197 (22%), 183 (46%), 168 (5%), 155 (6%), 141 (2%), 128 (5%), 101 (3%), 78 (5%), 51 (4%), 43 (30%); HRMS for (M+1), $C_{14}H_{13}N_2O_2$, calcd: 241.0977, found: 241.0963.

3.1.10. 3,3′-Diacetyl-2-2′-bipyridine 1,1′-dioxide (10). To a solution of 3,3′-diacetyl-2,2′-bipyridine (**9**, 38 mg, 0.16 mmol) in 3 mL of CH_2Cl_2, while stirred and kept in a cooling bath (*i*PrOH/solid CO_2), a commercial 85% 3-chloroperoxybenzoic acid (250 mg, 1.23 mmol) dissolved in 5 mL of CH_2Cl_2 was added. Stirring at −75°C was continued for 1 h and then the reaction mixture was allowed to reach the room temperature overnight. The resulting solution was introduced on 1 g of silica gel and the column was washed, first, with CH_2Cl_2 by which almost all of the *m*-chlorobenzoic acid was removed. By using 3% MeOH in $CHCl_3$, almost pure **10** was obtained, the rechromatography of which gave 41 mg (95%) of a colourless solid not melting up to 370°C (R_f 0.2 when AcOEt–MeOH 7:3 was used as a developing phase). IR (cm^{-1}): 3088, 2927, 1693, 1420, 1368, 1295, 1248, 1189, 1015, 917, 903, 801, 721; ^1H NMR ($CDCl_3+CD_3OD$) δ: 8.38 (2H, dd, J=6.6, 1.1 Hz, H-6 and H-6′), 7.89 (2H, dd, J=8.0, 1.1 Hz, H-4 and H-4′), 7.58 (2H, dd, J=8.0, 6.6 Hz, H-5 and H-5′), 2.60 (6H, s, 2×C<u>H</u>$_3$); ^{13}C NMR ($CDCl_3+CD_3OD$) δ: 195.47 (2×<u>C</u>O), 141.35 (C-6 and C-6′), 141.19 (C-2 and C-2′), 136.81 (C-3 and C-3′), 126.86 (C-4 and C-4′), 125.92 (C-5 and C-5′), 26.72 (2×<u>C</u>H$_3$); MS: 273 (1%, M+1), 272 (5%, M^+), 257 (3%), 241 (10%), 230 (12%), 229 (86%), 226 (15%), 225 (100%), 214 (11%), 213 (72%), 197 (36%), 194 (19%), 183 (69%), 171 (74%), 168 (20%), 155 (16%), 143 (26%), 131 (13%), 128 (15%), 120 (9%), 116 (18%), 78 (25%), 51 (21%); HRMS for M^+, $C_{14}H_{12}N_2O_4$, calcd: 272.0797, found: 272.0783.

3.1.11. 5,6-Isopropylenedioxy-1,10-phenanthroline. When the reaction of quinone **1** with 2-nitropropane anion was carried out by us following the literature procedure,[10] it appeared that the reaction was already complete at room temperature and after 15 min (instead of 60°C and 24 h); the product obtained in almost quantitative yield (instead of 67%), when recrystallized from ethyl ether, gave yellow needles of mp 160–165°C (hot plate method), 158–160°C (capillary method) (lit.[10] 140–143°C), revealing identical spectral properties with those already reported.[10]

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