ON THE CHLORINE ADDITION TO THE C(5)-C(6) BRIDGE AND THE *N*-OXIDATION OF 1,10-PHENANTHROLINE

Róża Antkowiak and Wiesław Z.Antkowiak*

Faculty of Chemistry, A.Mickiewicz University, Grunwaldzka 6, 60-780 Poznań,
Poland

This paper is dedicated to Dr Koji Nakanishi on the occasion of his 75th birthday.

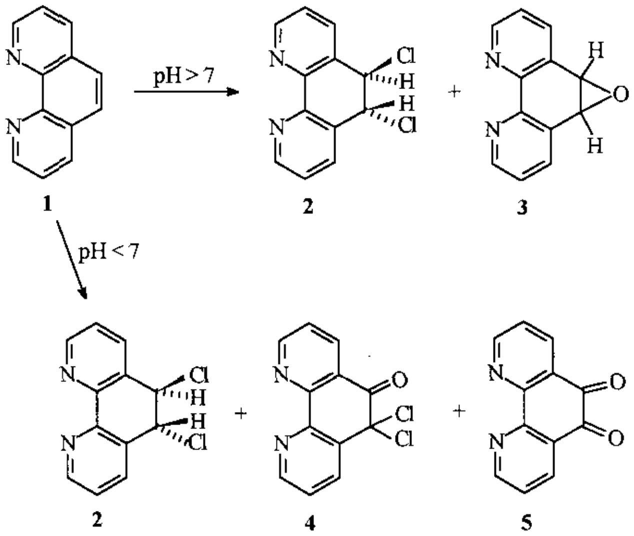
Abstract - It was found that under the influence of aqueous hypochlorite 1,10-phenanthroline (**1**) is initially transformed into 5,6-dichloro-5,6-dihydro-1,10-phenanthroline (**2**) and 5-chloro-6-hydroxy-5,6-dihydro-1,10-phenanthroline (**8**). The latter readily undergoes subsequent transformations either into a mixture of 5,5-dichloro-6-oxo-5,6-dihydro-1,10-phenanthroline (**4**) and 5,6-dioxo-5,6-dihydro-1,10-phenanthroline (**5**) or into the known 5,6-epoxy-1,10-phenanthroline (**3**) depending on the acidic or alkaline conditions, respectively. In contrast to the flat molecule of the starting **1**, that of the dichloro derivative (**2**) being twisted at the central bond of the bipyridine system can be easily *N*-oxidized to di-*N*-oxide (**11**). Both **2** and its di-*N*-oxide (**11**) in the presence of sodium isopropoxide at 0°C freely lost hydrogen chloride and returned to the fully aromatic system of 5-chloro-1,10-phenanthroline (**9**) and its di-*N*-oxide (**13**), respectively.

The nitration[1] and the bromination[2] of 1,10-phenanthroline (**1**), the electrophilic substitutions requiring both oleum as a medium and an elevated temperature, together with the oxidation to quinone[3] and the epoxidation,[4a,b] are the only published methods allowing the direct functionalization of **1** in the C-5 and/or C-6 positions. The last process, in which oxirane is formed and the aromaticity of the middle benzene ring is destroyed, can be carried out by a two-phase reaction using a slightly alkaline aqueous hypochlorite solution and a phase transfer catalyst.

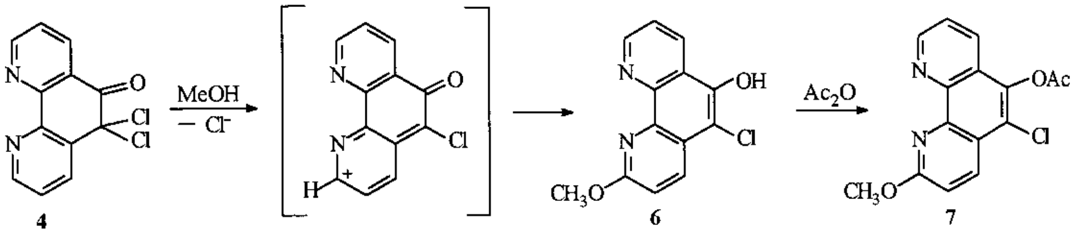
Following the literature procedure,[4a,b] we found by experiment that the last reaction is almost always accompanied though in a variable range by a chlorine molecule addition with the formation of

5,6-dichloro-5,6-dihydro-1,10-phenanthroline (**2**),[5] a side reaction not reported previously.[6] As in the case of 5,6-epoxy-1,10-phenanthroline (**3**), the ^{1}H NMR spectrum showed the molecules of the chlorine addition product (**2**) to be symmetrical yet the most diagnostic two-proton peak of H-5 and H-6 appeared at 5.43 ppm instead of at 4.64 ppm.[7]

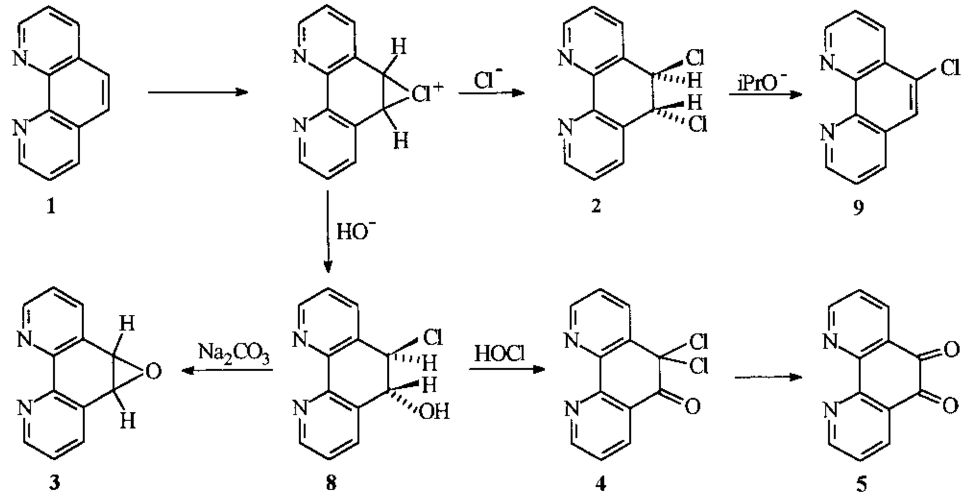
The chlorination process appears to be especially effective by the use of the sodium hypochlorite solution, which is of lower pH than that originally recommended for the epoxide (**3**) formation, and, according to our findings, with the optimum value being in the approximate range between 6 and 7. The spontaneous decomposition of an aqueous hypochlorite solution, which, according to the literature report,[8] is fastest at pH 6.7, caused an additionally strong acidification of the solution, resulting in the formation of a more contaminated dichloro derivative (**2**). The maintenance of pH on a roughly steady, slightly acidic level at which the starting **1** remains still dissolved in the chloroform layer was achieved when the two-phase reaction was buffered with sodium acetate.



However, the increase in the hydrogen ion concentration of the reaction medium caused the change of the chemical composition of the product mixture. The epoxide was almost the sole product when pH was about or fractionally higher than 9. At pH lower than that, the presence of the dichloro derivative (**2**) was always found, but above 7 it was accompanied with epoxide (**3**) while below 7 with both 5,5-dichloro-6-oxo-5,6-dihydro-1,10-phenanthroline (**4**) and 5,6-dioxo-5,6-dihydro-1,10-phenanthroline (**5**),[9] the last two compounds being the product of further oxidation, chlorination and hydrolysis reactions. Additionally, the dichloro ketone (**4**), which can be easily separated because of its inertness towards hydrochloric acid, in the presence of methanol spontaneously and quantitatively underwent transformation into 5-chloro-6-hydroxy-2-methoxy-1,10-phenanthroline (**6**), the structure of which was established by spectroscopic data. The location of methoxyl at C-2 instead of at C-9 resulted from the observed change of the chemical shifts of H-7 and H-8 (shielded by -1.05 ppm and -0.53 ppm, respectively, while the change for H-4 and H-3 was only +0.23 ppm and -0.05 ppm, respectively) when the hydroxyl at C-6 in **6** was transformed into the acetoxy group as a result of the formation of 6-acetoxy-5-chloro-2-methoxy-1,10-phenanthroline (**7**).



In accordance with the electrophilic mechanism of the hypochlorite action on the bridge double bond of **1**, the corresponding chlorohydrine intermediate, 5-chloro-6-hydroxy-5,6-dihydro-1,10-phenanthroline (**8**),[10] was additionally isolated as a by-product by us when the reaction was carried out under epoxide formation conditions (slightly alkaline) and the product mixture was not treated with sodium carbonate when worked up .



Chlorohydrine (**8**) is quite sensitive to the sodium carbonate treatment forming the corresponding epoxide (**3**) and, thus, can be omitted during the originally recommended work up procedure for the last compound preparation. When treated with an aqueous, slightly acidic solution prepared from commercial sodium hypochlorite and sodium acetate, chlorohydrine (**8**) underwent the rapid oxidation-chlorination reactions yielding a product mixture composed mainly of dichloro ketone (**4**) contaminated by quinone (**5**).

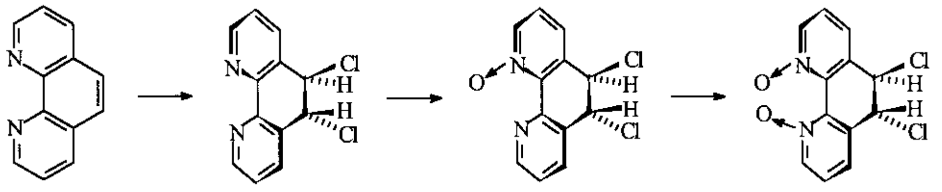
The dependence of the course of the reaction towards either an epoxidation or a chlorination upon pH is most likely the result of a competition between the nucleophiles: the strongest HO^- in the presence of Cl^-

or Cl^- versus H_2O when pH is alkaline or slightly acidic, respectively, the competition taking place in the attack on the chloronium ion intermediate in the second step of the reaction.

Furthermore, the different product composition when the reaction is carried out above or below pH 7 is the result of the subsequent transformation of the chlorohydrine intermediate. In the alkaline solution, chlorohydrine (**8**) eliminates hydrogen chloride yielding epoxide (**3**) while in the acidic medium, it successively underwent oxidation and chlorination to dichloro ketone (**4**) and, finally, hydrolysis to quinone (**5**). Additionally, it was found that, while in alkaline medium, the quaternary ammonium catalyst is essential for the transfer of the hypochlorite ions into the chloroform phase and initiate the addition process, in the acidic conditions the reaction towards the dichloro, dichloro keto and diketo derivatives also occurred in the absence of the tetrabutylammonium catalyst but with a slightly smaller contribution of the former in the product mixture. These observations suggest that at pH below 7 the undissociated hypochlorous acid is extracted from the aqueous phase to chloroform and serves as the main interphase carrier of positive chlorine needed for the chloronium ion formation while the quaternary ammonium catalyst is above all instrumental in supplying the organic phase with chloride ions.[11]

The dichloro derivative (**2**) was found to be stable against either aqueous sodium carbonate or triethylamine in refluxing glyme (DME), but it easily lost hydrogen chloride when treated with sodium isopropoxide in 2-propanol at 0°C with the quantitative formation of 5-chloro-1,10-phenanthroline (**9**).[12] The procedure provides a new synthetic route to this chlorophenanthroline derivative, a synthesis which can be carried out in a simpler way than the one commonly used hitherto, namely, the multi-step synthesis based on the Skraup reaction.[13]

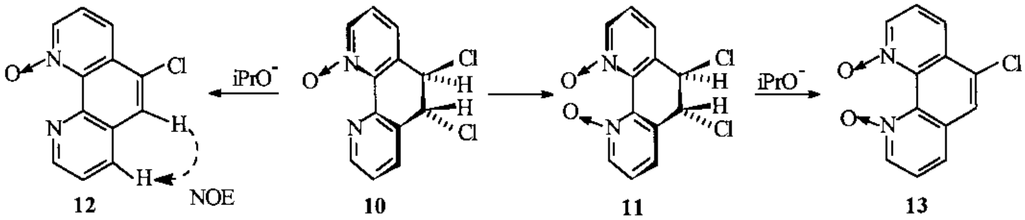
The change in the hybridization of phenanthroline's C-5 and C-6 orbitals due to the addition of chlorine atoms in those positions caused the molecules of **2** to be twisted at the bond between the two pyridine rings. Sterically this created a new chance to introduce substituents to the cavity of the molecule and attach them to the nitrogens. Indeed, contrary to the literature reports on the reactivity of phenanthroline towards *N*-oxidation,[14-18] the dichloro derivative (**2**) readily reacted with m-CPBA at -70°C to yield, first, mono-*N*-oxide of 5,6-dichloro-5,6-dihydro-1,10-phenanthroline (**10**) and, next, di-*N*-oxide of 5,6-dichloro-5,6-dihydro-1,10-phenanthroline (**11**). Unfortunately, even at -70°C the formation of di-*N*-oxide (**11**) is so fast that the mono-*N*-oxide (**10**) was always accompanied either with the starting **2** or the final **11** depending on the time of the oxidation treatment.[19] Both of the *N*-oxidation products can be



1 **2** **10** **11**

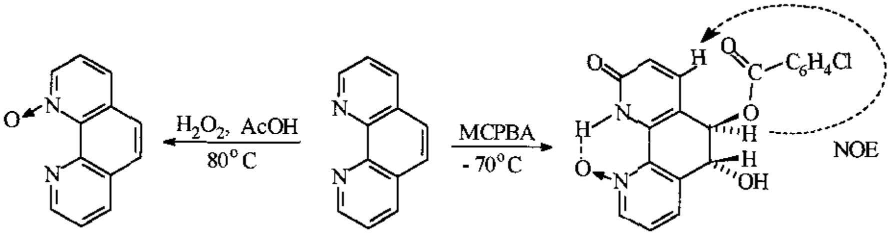
easily differentiated on the basis of the presence or absence of the symmetry features revealed by their proton and carbon NMR spectra (e.g. H-5 and H-6 of the dichloro-di-*N*-oxide derivative (**11**) gave a singlet at 5.24 ppm and only two multiplets of the aromatic protons) and the nitrogen resonance absorption which appeared for non-oxidized and *N*-oxidized ^{14}N at -71.4 ppm and -91.2 ppm, respectively.

When treated with a sodium alkoxide solution in alcohol at 0°C, both mono-*N*-oxide (**10**) and di-*N*-oxide (**11**) easily gave 5-chloro-1,10-phenanthroline-1-oxide (**12**)[20] and 5-chloro-1,10-phenanthroline-1,10-dioxide (**13**), respectively. The last case is especially interesting since it provides evidence that two oxygen atoms can be accommodated in the cavity of a flat molecule of the 1,10-phenanthroline skeleton in spite of the sterical crowdedness and the dipol-dipol repulsion. For a long time the argument of steric hindrance in the space between *N*-1 and *N*-10 was used to explain the difficulties in the preparation of 1,10-phenanthroline di-*N*-oxide.[21] As shown by our experiments, this obviously is not the case.



The hereby presented chemical changes around the "back" carbons C-5 and C-6 of the central ring of phenanthroline or its dihydro derivative are responsible for the conformational transformations of molecules between planar and twisted, respectively, (e.g. **1** → **2** → **11**→ **13**). These, in turn, forced the two nitrogens, *N*-1 and *N*-10, to be either in a juxtaposition or held them clearly separated, which allowed two *N*-oxide oxygens instead of only one to be introduced into the bay of the molecule. To some extent, the stereochemical behaviour of the investigated system resembled the allosteric transitions observed in protein chemistry and, thus, can be seen as a model of such changes.

For comparative purposes the *N*-oxidation of 1,10-phenanthroline by hydrogen peroxide in acetic acid was carried out by us following the literature procedure.[17] Indeed, this resulted in the formation of mono-*N*-oxide only but of somewhat different NMR characteristics (see Tables) from those reported in the literature.[16] Contrary to that, we found that when m-CPBA was used instead of hydrogen peroxide, the reaction proceeded differently consuming more than the calculated amount of the reagent. Even at -70°C a very rapid reaction occurred and it was completed within 5 min consuming 3 molar equivalents of the peracid as found by iodometric assay. While monitoring the reaction by TLC, it was found that a colourless product of significant polarity, intially formed at -70°C, is readily transformed in contact with water into a yellow, less polar 6-(3-chlorobenzoyloxy)-5-hydroxy-9-oxo-5,6,9,10-tetrahydro-1,10-



15 **1** **14**

phenanthroline-1-oxide (**14**), which in the product mixture was accompanied by 1,10-phenanthroline-1-oxide (**15**) as a by-product and by some of the starting **1** (in spite of the significant excess of the reagent used).

Table 1: ^{1}H NMR chemical shifts (ppm) and J(Hz) coupling constans (in parentheses) of selected 1,10-phenanthroline derivatives in $CDCl_3$*.

Compound	H-2	H-9	H-3	H-8	H-4	H-7	H-5	H-6
1	9.19 (4.4, 1.8)	9.19 (4.4, 1.8)	7.65 (8.1, 4.4)	7.65 (8.1, 4.4)	8.27 (8.1, 1.8)	8.27 (8.1, 1.8)	7.81	7.81
15	8.75 (6.3, 1.1)	9.27 (4.4, 1.8)	7.48 (8.1, 6.3)	7.67 (8.1, 4.4)	7.79 (8.1, 1.1)	8.24 (8.1, 1.8)	7.75 and 7.80 AB system (9.0)	
9	9.24 (4.3, 1.6)	9.19 (4.4, 1.7)	7.77 (8.4, 4.3)	7.66 (8.1, 4.4)	8.71 (8.4, 1.6)	8.20 (8.1, 1.7)	-	7.93
12	8.79 (6.3, 1.1)	9.29 (4.4, 1.9)	7.57 (8.5, 6.3)	7.68 (8.0, 4.4)	8.24 (8.5, 1.1)	8.17 (8.0, 1.9)	-	7.94
13	8.62 (6.4, 1.0)	8.57 (6.1, 1.3)	7.56 (8.2, 6.4)	7.48 (8.0, 6.1)	7.99 (8.2, 1.0)	7.52 (8.0, 1.3)	-	7.72

*In the case of *N*-oxides the $CDCl_3$ solution was supplied with a drop of CD_3OD.

The NMR studies of the examined compounds revealed some interesting relationships between their structure and the spectral data. As was shown in Tables 1 and 2 the mono- and di-*N*-oxide derivatives in the series of 1,10-phenanthroline can readily be differentiated from the corresponding free amines on the basis of proton and carbon NMR data. The resonance peak of proton being in the neighbouring (2 and 9) or the gamma (4 and 7) position to the nonoxidized nitrogen, which usually can be found in the range of 9.0 to 9.4 ppm and 8.2 to 8.7 ppm, are shifted up-field by 0.44 ppm and 0.48 ppm, respectively, when transforming the free amine of the pyridine fragment into the corresponding *N*-oxide. In the case of 5,6-dihydro-1,10-phenanthroline derivatives, the range of such a structurally dependent change of the chemical shift can amount even up to 0.7 ppm. Additionally, the value of the coupling constant of the neighbouring protons ($J_{2,3}$ and $J_{9,8}$) is dependent on the oxidation state of nitrogen; for the free base and the *N*-oxide it amounts to about 4.5 Hz and ≥ 6 Hz, respectively. Finally, besides the previously mentioned nitrogen chemical shift, the carbon chemical shift can be very useful for structural assignments since the transformation of a free amine into its *N*-oxide results in an increase in the chemical shift of C-2 (C-9) by ~10 ppm and of C-4 (C-7) by ~15 ppm.

Table 2: ^{13}C NMR chemical shifts (ppm) of 3° C atoms of selected 1,10-phenanthroline derivatives in $CDCl_3$*.

Compound	C-2	C-9	C-3	C-8	C-4	C-7	C-5	C-6
1	149.74	149.74	122.56	122.56	135.49	135.49	125.99	125.99
15	140.72	149.84	122.93	123.37	125.37	136.02	129.15	126.49
9	150.87	150.52	123.52	123.62	133.20	135.13	-	125.67
12	141.31	150.07	123.07	123.73	121.5	135.11	-	128.39
13	139.83	139.53	123.14	123.5	118.49	120.30	-	126.69

*In the case of *N*-oxides the $CDCl_3$ solution was supplied with a drop of CD_3OD.

EXPERIMENTAL

Melting points were determined by a Bűchi 535 capillary apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a VARIAN GEMINI 300 spectrometer while ^{14}N and ^{15}N NMR on BRUKER AM 500 at 36.142 MHz and 50.698 MHz, respectively. Proton and carbon assignments were based on COSY and HETCOR experiments. UV spectra were measured on a SHIMADZU UV-160 spectrophotometer and IR spectra on a FT-IR BRUKER IFS 113v instrument. MS spectral data were obtained on an AMD 402 mass spectrometer. All pH values were taken using microcomputer pH-meter CP-315.

TLC analyses were carried out using Analtech silica gel plates and AcOEt-iPrOH-conc.$NH_3 \cdot aq$ (8:4:1) as a developing system. To estimate the Rf value, the distance between the starting point and the middle of the spot was measured. Column chromatography was mostly carried out using a 3:1 mixture of Whatman cellulose-silica gel (MN-Kieselgel 60, 100-200 mesh) as the stationary phase, while hexane, benzene, CH_2Cl_2, AcOEt, $CHCl_3$ and 5% MeOH in $CHCl_3$ were the eluting solvents.

The concentration of both active chlorine and active oxygen in commercial aqueous sodium hypochlorite and m-CPBA reagents, respectively, were determined by iodometric assay. In most cases of $CHCl_3$ or CCl_4 solutions, the homogenity of the mixture with an aqueous starch-iodide solution had to be improved by an ethanol or acetone addition before it was titrated with sodium thiosulphate. Mono-*N*-oxide of 1,10-phenanthroline, prepared according to the literature procedure,[15,17] melted at 172°C (instead of at 182°C) but only when the product, being purified by chromatography on SiO_2 followed by recrystallization from chlorobenzene, was kept for a long time under diminished pressure and elevated up to about 50°C temperature to remove the strongly coordinated water. For UV examinations of the $CHCl_3$ solutions of the reagents containing electrophilic chlorine, a stirred mixture of commercial, aqueous NaOCl [10 mL, supplied or not with Bu_4NHSO_4 (340 mg) and/or AcONa (500 mg)] and $CHCl_3$ (5 mL) was treated at 0°C with ~17% aqueous HCl till pH of the aqueous layer reached the required value. Then, the chloroform layer was kept over Na_2SO_4 (300 mg) for 5 min and used immediately in one mL samples to determine the active chlorine concentration (usually the value close to 0.55N was found) and, when diluted 100 times, to record the UV spectra.

Treatment of 1,10-phenanthroline with aqueous hypochlorous acid. Formation of 2, 4, and 5. The aqueous solution of sodium hypochlorite (70 mL of about 13%, but commercial products of a higher or smaller concentration were also used with a proportional modification of the volume of the reagent) was supplied with 10 mL of $CHCl_3$[22] and a solution of sodium acetate (10 g), sodium chloride (5 g), and 40% aqueous tetrabutylammonium hydroxide (2 mL; instead, 860 mg of Bu_4NHSO_4 was sometimes used) in 50 mL of water and for 30 min treated dropwise at 0°C with glacial acetic acid (about 5.5 mL) till its pH dropped to a value close to 6.5 or less. The resulting solution was added to a solution of 1,10-phenanthroline hydrate (990 mg, Rf 0.72) in 90 mL of chloroform while being stirred and cooled in an ice-bath. After about a quarter of an hour, the reaction was completed as showed by TLC and ^1H NMR. The separated chloroform layer was washed successively with two 150 mL portions of 3% aqueous Na_2CO_3, two 200 mL portions of water (to remove Bu_4N^+ ions), kept for 15 min over anhydrous Na_2CO_3 and, finally, concentrated yielding 1.23 g of a solidifying material. According to NMR, the crude product mixture was composed of **2** (70%), **4** (20%) and **5** (~ 10%, including the contaminating by-products). The components can be separated by shaking the crude product mixture in about 20 mL of $CHCl_3$ successively with two 4 mL portions of 5% aqueous HCl and 2 mL of H_2O and the resulting solutions treated as follows:

5,5-Dichloro-6-oxo-5,6-dihydro-1,10-phenanthroline (**4**). The chloroform solution, when dried over Na_2CO_3 and concentrated, gave 5,5-dichloro-6-oxo-5,6-dihydro-1,10-phenanthroline (**4**) of mp 151-157°C and Rf 0.75 (a brick coloured spot under a UV long wavelength). The product was readily decomposable when being chromatographed on silica gel or alumina column. IR(KBr): 1709, 1605, 1576, 1291, 1227, 1120, 926, 822, 724, 693, 619, 540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.15 (1H, dd, J 4.8, 1.7, H-2), 8.96 (1H, dd, J 4.4, 1.5, H-9), 7.56-7.62 (2H, m, H-3 and H-8), 8.53 (1H, dd, J 7.8, 1.7, H-4), 8.50 (1H, dd, J 8.2, 1.5, H-7); MS: 264 (78%, M^+), 266 (52%), 268 (10%), 236 (83%, M−CO), 238 (54%), 240 (10%), 201 (100%, M−CO, −Cl), 203 (34%).

5,6-Dichloro-5,6-dihydro-1,10-phenanthroline (**2**). The combined aqueous acidic solutions were kept under vacuum to remove the dispersed chloroform and, next, while being cooled in an ice-bath, was treated with 10% aqueous Na_2CO_3 till all of the precipitate of the 5,6-dichloro derivative (**2**) of Rf 0.84 separated. When air dried, the crude product (**2**) was quickly filtered through a layer of neutral aluminium oxide (a second grade activity) using large amounts of a 30% AcOEt-hexane mixture. The concentration of the eluent to a small volume yielded colourless needles (they can be recrystallized from AcOEt or CCl_4) of mp 164.5-165°C (with decomp). IR(KBr): 2969, 1581, 1562, 1425, 1193, 1123, 1069, 750, 707, 680, 623 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.91 (2H, dd, J 4.8, 1.7, H-2 and H-9), 7.83 (2H, dd, J 7.7, 1.7, H-4 and H-7), 7.44 (2H, dd, J 7.7, 4.8, H-3 and H-8), 5.43 (2H, s, H-5 and H-6); ^{13}C NMR ($CDCl_3$) δ 151.55 (C-2 and C-9) 149.11 (C-10a and C-10b), 137.23 (C-4 and C-7), 129.34 (C-4a and C-6a), 124.46 (C-3 and C-8), 57.26 (C-5 and C-6); ^{14}N NMR ($CDCl_3$) δ -71.4 (N-1 and N-10); MS: 250 (24%, M^+), 252 (25%), 254 (4%), 215 (100%, M−Cl), 217 (30%), 180 (76%), 179 (54%); HRMS for $C_{12}H_8N_2{}^{35}Cl_2$ calcd 250.00645, found 250.005239, and for $C_{12}H_8N_2{}^{35}Cl$ calcd 215.03760, found 215.03773.

5,6-Dioxo-5,6-dihydro-1,10-phenanthroline (**5**). The alkalized aqueous solution remaining after **2** separation was extracted with $CHCl_3$, the organic layer then being dried over Na_2CO_3 and concentrated yielding quinon **5** of Rf 0.68 (a green spot under a UV long wavelength) slightly contaminated by **2**. A small sample was chromatographed on a cellulose-SiO_2 column yielding, when CH_2Cl_2 as eluant was used, pure **5** of mp 258-259°C (lit.,[4b,23,3] 246-248°C, 271-272°C). ^{13}C NMR ($CDCl_3$ + CD_3OD) δ 178.69 (C-5 and C-6), 156.29 (C-2 and C-9), 152.82 (C-10a and C-10b), 137.37 (C-4 and C-7), 128.17 (C-4a and C-6a), 125.76 (C-3 and C-8); MS: 210 (10%, M^+), 182 (100%), 154 (45%); HRMS for M^+ $C_{12}H_6N_2O_2$ calcd 210.04292, found 210.04426; for M - CO, $C_{11}H_6N_2O$ calcd 182.04802, found 182.04818.

5-Chloro-6-hydroxy-2-methoxy-1,10-phenanthroline (**6**). 5,5-Dichloro-6-oxo-5,6-dihydro-1,10-phenanthroline (**4**) (264 mg, 1 mmol) was dissolved in warm methanol and left at rt overnight to give yellow needles (185 mg, 70%), mp 239-239.5°C. The product of Rf 0.37 was found to have the structure of **6**. IR (KBr): 3353, 3085, 2950, 1599, 1535, 1445, 1369, 1281, 1241, 1123, 1004, 812, 740, 666 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CD_3OD) δ 9.55 (1H, dd, J 5.4, 1.4, H-9), 9.28 (1H, dd, J 8.5, 1.4, H-7), 8.34 (1H, d, J 9.0, H-4), 8.18 (1H, dd, J 8.5, 5.4, H-8), 7.26 (1H, d, J 9.0, H-3), 4.39 (3H, s, OCH_3); ^{1}H NMR (DMSO-d_6) δ 9.41 (1H, dd, J 8.4, 1.4, H-7), 9.38 (1H, dd, J 5.3, 1.4, H-9), 8.41 (1H, d, J 9.0, H-4), 8.29 (1H, dd, J 8.4, 5.3, H-8), 7.40 (1H, d, J 9.0, H-3), 4.23 (3H, s, OCH_3) and a broad singlet centered at 11.4 (OH); ^{13}C NMR ($CDCl_3$ + CD_3OD) δ 162.66 (C-2), 144.11 (C-9), 143.78 (C-7), 140.90, 134.83 (C-4), 124.76, 123.83, 123.13, 118.19 (C-3), 55.71 (OCH_3); MS: 260 (100%, M$^+$), 262 (34%), 259 (94%, M−1), 261 (45%), 231 (58%, M−29), 233 (17%), 230 (67%), 232 (29%); HRMS for $C_{13}H_9N_2O_2{}^{35}Cl$ calcd 260.03525, found 260.03455, and for $C_{13}H_9N_2O_2{}^{37}Cl$ calcd 262.03232, found 262.03189. For (M−1), $C_{13}H_8N_2O_2{}^{35}Cl$ calcd 259.02744, found 259.02780.

6-Acetoxy-5-chloro-2-methoxy-1,10-phenanthroline (7). When a solution of **6** (52 mg, 0.2 mmol) in 2.5 mL of Ac_2O was supplied with 8 drops of pyridine and kept overnight at rt, its colour changed from orange-yellow to violet and no starting material was left according to TLC. The reaction mixture was treated with ice-water and, next, the product was taken into $CHCl_3$ from which 39 mg of a cream-coloured solid residue of Rf 0.84 was obtained. When filtered through a silica gel layer in CH_2Cl_2 and recrystallized from AcOEt, the crude product gave colourless needles of mp 188.5-189.5°C. IR(KBr): 3393, 3283. 2948, 1764, 1679, 1615, 1593, 1493, 1373, 1364, 1280, 1207, 1113, 1063, 1017, 836, 814, 800, 753 cm^{-1} ; ^{1}H NMR ($CDCl_3$) δ 9.20 (1H, dd, J 4.4, 1.5, H-9), 8.57 (1H, d, J 8.8, H-4), 8.23 (1H, dd, J 8.4, 1.5, H-7), 7.65 (1H, dd, J 8.4, 4.4, H-8), 7.23 (1H, d, J 8.9, H-3), 4.33 (3H, s, OCH_3), 2.57 (3H, s, $COCH_3$); ^{13}C NMR ($CDCl_3$) δ 168.10 (C=O), 163.56 (C-2), 150.54 (C-9), 144.23, 143.36, 138.85, 136.03 (C-4), 129.99 (C-7), 124.09, 123.13 (C-8), 122.25, 122.03, 114.78 (C-3), 54.18 (OCH_3), 20.50 ($COCH_3$); MS: 302 (14%, M$^+$), 304 (5%), 260 (100%, M−CH_2CO), 262 (34%), 259 (67%, M−CH_3CO), 261 (37%), 231 (38%), 233 (12%), 230 (37%), 232 (18%), 149 (25%); HRMS for $C_{15}H_{11}N_2O_3{}^{35}Cl$ calcd 302.04581, found 302.04780, for M−42, $C_{13}H_9N_2O_2{}^{35}Cl$ calcd 260.03525, found 260.03395 and for $C_{13}H_9N_2O_2{}^{37}Cl$ calcd 262.03232, found 262.03168.

5-Chloro-6-hydroxy-5,6-dihydro-1,10-phenanthroline (**8**). An aqueous solution of commercial (~ 12%) sodium hypochlorite (100 mL) was diluted with water (100 mL) and its pH was adjusted to 7.47 by a dropwise addition of 17% aqueous HCl. Next, the resulting solution was immediately added to a stirred solution of 1,10-phenanthroline hydrate (990 mg, 5 mmol) and tetrabutylammonium hydrogen sulfate (680 mg, 2 mmol) in 100 mL of $CHCl_3$ kept in a tap-water bath. Stirring was continued for about 1 h till no more of the starting **1** was shown by TLC.[9] The chloroform solution was separated, washed with five portions of water, dried over Na_2SO_4 and concentrated. The residue was chromatographed on a cellulose-

SiO_2 (7:1) mixture [using hexane-CH_2Cl_2 (4:1) as the eluant] mainly giving epoxide (**3**) which when recrystallized from CCl_4 melted at 187.5-188°C (with decomp, lit.,[4a,b] 165°C) in addition to chlorohydrine **8** of mp 157°C (EtOH) and dichloro derivative **2** of mp 164.5°-165°C.

1. **Epoxide** (**3**): IR (KBr): 2999, 2894, 1579, 1560, 1432, 1428, 1215, 1188, 1131, 1080, 1012, 882, 799, 750, 706 cm^{-1} ; ^1H NMR ($CDCl_3$) δ 8.92 (2H, dd, J 4.7, 1.7, H-2 and H-9), 8.02 (2H, dd, J 7.7, 1.7, H-4 and H-7), 7.42 (2H, dd, J 7.7, 4.7, H-3 and H-8), 4.64 (2H, s, H-5 and H-6); ^{13}C NMR ($CDCl_3$) δ 150.77 (C-2 and C-9), 149.53 (C-10a and C-10b), 130.08 (C-4 and C-7), 129.02 (C-4a and C-6a), 123.60 (C-3 and C-8); ^{14}N NMR: −73 ppm (N-1 and N-10); MS: 196 (55%, M^+), 197 (13%), 180 (28%), 168 (100%), 167 (17%); HRMS for $C_{12}H_8N_2O$ calcd 196.06366, found 196.06371 and for $C_{11}H_8N_2$ calcd 168.06870, found 168.065901.

2. **Chlorohydrine** (**8**): ^1H NMR (CD_3OD) δ 8.74 (2H, m, H-2 and H-9), 8.00 (2H, m, H-4 and H-7), 7.48 (2H, m, H-3 and H-8), 5.29 (1H, d, J 4.2, H-5 or H-6) and 5.03 (1H, d, J 4.2, H-5 or H-6); ^1H NMR (DMSO-d_6) δ 8.73 (2H, m, H-2 and H-9), 8.05 (1H, dd, J 7.7, 1.6, H-4 or H-7) and 7.95 (1H, dd, J 7.6, 1.7, H-4 or H-7), 7.49 (2H, m, H-3 and H-8), 5.52 (1H, d, J 4.0, H-5 or H-6) and 5.00 (1H, d, J 4.0, H-5 or H-6), 6.35 (br s, 1H, OH); ^{13}C NMR (DMSO-d_6) δ 150.41, 150.03, 149.87, 149.38, 137.81, 137.62, 132.69, 131.24, 124.58,124.42, 70.67, 58.36; ^{15}N NMR (CD_3OD) δ -81.24 and -81.83 (N-1 and N-10); MS: 250 (20%, M + HOH), 252 (7%), 232 (8%, M^+), 234 (3%), 215 (72%), 217 (12%), 214 (20%), 216 (9%), 197 (40%, M − Cl), 180 (100%, M − Cl, − OH); HRMS for $C_{12}H_9N_2O^{35}Cl$ calcd 232.04034, found 232.04049; for $C_{12}H_9N_2O^{37}Cl$ calcd 234.03739, found 234.037178; for $C_{12}H_8N_2{}^{35}Cl$ calcd 215.03755, found 215.036143; for $C_{12}H_9N_2O$ calcd 197.07149, found 197.07150; for $C_{12}H_8N_2$ calcd 180.06875, found 180.068573.

Hydrogen chloride elimination from 8. To a solution of chlorohydrine (**8**, 46 mg, 0.2 mmol) in 5 mL of waterless methanol, anhydrous sodium carbonate (63 mg, 0.6 mmol) was added and the resulting suspension was stirred at rt overnight. The reaction mixture, the TLC of which showed not even traces of the starting **8**, was concentrated under diminished pressure, the residue supplied with water and extracted with $CHCl_3$ from which 32 mg of epoxide (**3**) was obtained. The structure was confirmed by TLC, MS and NMR.

Oxidation of 8. Chlorohydrine **8** (60 mg) dissolved in 10 mL of $CHCl_3$ was treated with an aqueous sodium hypochlorite solution, additionally containing $Bu_4N^+Cl^-$ (50 mg) and NaOAc (100 mg), the pH of which was adjusted by aqueous HCl treatment to 6.6. After stirring for the first two min, the TLC spot of starting **8** (Rf 0.65) vanished and was replaced by a spot of Rf 0.74 which, after the next 10 min, was additionally accompanied by a spot of Rf 0.67. The NMR spectrum of the product isolated from the chloroform layer showed the presence of dichlorooxo derivative (**4**) contaminated only with quinone (**5**).

5-Chloro-1,10-phenanthroline (**9**). While being stirred at 0°C, a solution of **2** (145 mg, 0.58 mmole) in 7 mL of 2-propanol was supplied dropwise for 6 min with 20 mg of sodium metal dissolved in 6 mL of iPrOH. Then the turbid reaction mixture was allowed to warm to rt and stirred for an additional hour to complete the reaction as shown by TLC. Next, the solvent was removed under reduced pressure and the white solid residue was extracted with $CHCl_3$. The chloroform solution was washed with water, dried and concentrated yielding 121 mg (97.5%) of a solid material melting at 122-123°C when recrystallized from AcOEt (lit.,[13a] 123°C). ^1H NMR ($CDCl_3$) - Table 1 and ref. 13b, ^1H NMR ($CDCl_3$ + TFA-d) δ 9.36 (1H, dd, J 4.7, 1.5) H-2, 9.33 (1H, dd, J 4.5, 1.6) H-9), 8.83 (1H, dd, J 8.4, 1.5) H-4, 8.49 (1H, dd, J 8.1, 1.6) H-7, 8.05 (1H, s) H-6, 7.93 (1H, dd, J 8.1, 4.5) H-8, 7.91 (1H, dd, J 8.4, 4.5) H-3; ^{13}C NMR ($CDCl_3$) - Table 2; ^{15}N NMR ($CDCl_3$) δ -76.47 and -76.63 (N-1 and N-10). MS: 214 (100%, M^+), 216 (35%), 213 (21%), 215 (22%), 179 (11%); HRMS for $C_{12}H_7N_2{}^{35}Cl$ calcd 214.02977, found 214.02897; for $C_{12}H_7N_2$ calcd 179.06093, found 179.06039.

***N*-oxides of 5,6-dichloro-5,6-dihydro-1,10-phenanthroline** (**10** and **11**). While being stirred at -75°C, a solution of **2** (224 mg, mp 164.5-165°C, 0.89 mmol) in 10 mL of $CHCl_3$ and 10 mL of CH_2Cl_2 was treated dropwise with a solution of 220 mg of commercial ~80% m-CPBA (1 mmol, 1.12 molar equiv.) in 5 mL of $CHCl_3$ for 5 min and the stirring was continued for a further 55 min. As shown by TLC and NMR, the reaction mixture consisted mainly of mono-*N*-oxide of 5,6-dichloro-5,6-dihydro-1,10-phenanthroline (**10**) (a blue spot under UV long wavelength, Rf. 0.58) contaminated with starting **2** (Rf 0.82) and di-*N*-oxide of 5,6-dichloro-5,6-dihydro-1,10-phenanthroline (**11**, brick-coloured under long UV waves, Rf 0.48).[19] The reaction was quenched by pouring the cold solution into aqueous $NaHCO_3$. Next the organic layer was additionally washed with three 50 mL portions of saturated solution of aqueous $NaHCO_3$, dried and concentrated. Since most attemps to isolate pure mono-*N*-oxide by means of chromatography on Al_2O_3 or SiO_2 were unsuccessful and caused the decomposition of the product, the crude material containing about 80% of **10** was used for further transformation into 5-chloro-1,10-phenanthroline-*N*-oxide (**12**). A sample of pure mono-*N*-oxide **10** of mp 207-210°C (followed by decomposition) was obtained in low yield when the crude product was successively filtered through a thin layer of cellulose-silica gel in CH_2Cl_2 and recrystallized from CH_2Cl_2. IR (KBr): 1239 cm^{-1} (N→O); ^1H NMR ($CDCl_3$) δ 8.43 (1H, dd, J 6.0, 1.9, H-2), 8.97 (1H, dd, J 4.7, 1.6, H-9), 7.81 (1H, dd, J 7.7, 1.6, H-7), 7.43 (1H, dd, J 7.7, 4.7, H-8), 7.28-7.34 (2H, m, H-3 and H-4), 5.25 and 5.30 (an AB system, J 3.0, H-5 and H-6); ^{13}C NMR ($CDCl_3$) δ 150.68 (C-9), 143.54 (C-2), 136.90 (C-7), 125.24 (C-3), 125.13 (C-4), 124.59 (C-8), 56.69 and 56.62 (C-5 and C-6); MS: 266 (0.3%), 230 (70%), 232 (23%), 214 (100%); HRMS for M^+- HCl, $C_{12}H_7N_2O^{35}Cl$ calcd 230.02469, found 230.02488and for $C_{12}H_7N_2O^{37}Cl$ calcd 232.02174, found 232.02178.

When the reaction was carried out overnight instead of in one hour and with 2.4 molar equivalent of m-CPBA, the di-*N*-oxide derivative (**11**) was found as the sole product after the removal of the acidic components. Di-*N*-oxide prepared in this way in 90% yield when recrystalized from AcOEt melted at 228-229°C. IR (KBr): 3417, 3102, 3073, 2980, 1594, 1482, 1432, 1418, 1314, 1284, 1252 (N→O), 1217, 1194, 1053, 1016, 967, 821, 799, 787, 718, 712, 678, 650, 598, 536, 499 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.38 (2H, dd,J 6.1, 1.8, H-2 and H-9), 7.39-7.46 (4H, sym. m, H-3, H-4, H-7 and H-8), 5.28 (2H, s, H-5 and H-6); ^{14}N NMR ($CDCl_3$ + CD_3OD) δ -91.17 (N-1 and N-10); MS: 282 (18%, M^+), 284 (11%), 246 (10%,M − HCl), 248 (3%), 230 (10%) 214 (49%), 215 (54%), 216 (22%), 217 (16%), 212 (21%), 196 (23%), 180 (100%).

5-Chloro-1,10-phenanthroline-1-oxide (12). 5,6-Dichloro-5,6-dihydro-1,10-phenanthroline-1-oxide (**10**), obtained as the crude product (197 mg) of mono-*N*-oxidation of **2**, was dissolved in 5 mL of absolute MeOH and 10 mL of iPrOH and the solution, while being stirred at 0°C, was treated dropwise for 3 min with a solution of 33 mg of sodium metal dissolved in iPrOH (14 mL). According to TLC, the reaction was completed within 10 min. The reaction mixture was concentrated at rt under diminished pressure and the brown residue (170 mg) was extracted, first, with AcOEt and, next, with $CHCl_3$ from which 48 mg of pure **12** was obtained (a further 70 mg of **12**, though more contaminated, was found in the AcOEt extract). Total yield 118 mg (69%). For ^{1}H NMR and ^{13}C NMR see Table 1 and Table 2. MS: 230 (18%, M^+), 232 (6%), 214 (100%, M − O), 216 (32%).

5-Chloro-1,10-phenanthroline-1,10-dioxide (13). A solution of 5,6-dichloro-5,6-dihydro-1,10-phenanthroline-1,10-dioxide (**11**, 117 mg, 0.41 mmol) in 5 mL of MeOH and 10 mL of iPrOH, when stirred and kept in an ice-bath, was treated dropwise for 2 mins with sodium isopropoxide (prepared from 17 mg of Na, 0.73 mmol, and 7 mL of iPrOH). The stirring at 0°C was continued for an additional 80 min. Then the reaction mixture was concentrated at rt under diminished pressure and the residue treated with $CHCl_3$ from which 99 mg (97%) of crude solid **13** was obtained. The product in CH_2Cl_2 or $CHCl_3$ was found to decompose easily on a silica gel column. ^{1}H NMR ($CDCl_3$ + TFA-d) δ 9.24 (1H, d, J 8.6, 1.2, H-7), 9.23 (1H, dd, J 6.3, 1.1, H-2), 9.17 (1H, dd, J 6.2, 1.2, H-9), 8.76 (1H, dd, J 8.4, 1.1, H-4), 8.41 (1H, dd, J 8.6, 6.2, H-8), 8.32 (1H, dd, J 8.4, 6.3, H-3), 8.46 (1H, s, H-6). For ^{1}H NMR and ^{13}C NMR see Table 1 and Table 2.

Reaction of 1,10-phenanthroline (1) with 3-chloroperoxybenzoic acid. Formation of 14. 1,10-Phenanthroline hydrate (198 mg, 1 mmol) was successively dissolved in three 50 mL portions of $CHCl_3$ and the solvent removed each time under reduced pressure to the initial dryness (to avoid a loss of the material by sublimation). A solution of **1**, dehydrated in this way, was dissolved in 10 mL of CH_2Cl_2 and the resulted solution, while being stirred at -75°C (bath temperature), was treated dropwise with a solution of 971 mg of ~ 80% *m*-CPBA (4.5 mmol of neat reagent) in 10 mL of CH_2Cl_2 for 2.5 min. After a further 2-3 min, when no starting material was left according to TLC, the iodometric assay for the active oxygen concentration showed the consumption of 3 mmol of the reagent. When stirring was continued, no further significant progress of the reaction was observed. After 30 min on average, the cold methylene chloride solution was poured into 2% aqueous HCl (10 mL), the CH_2Cl_2 layer, when separated, was extracted with an additional 10 mL of 2% aqueous HCl, then, washed successively with 10 mL of water, three 20 mL portions of 5% aqueous Na_2CO_3 and 10 mL of brine and, finally, dried over Na_2SO_4 and concentrated yielding 6-(3-chlorobenzoyloxy)-5-hydroxy-9-oxo-5,6,9,10-tetrahydro-1,10-phenanthroline-1-oxide (**14**) in a form of a glassy yellow-brown material (187 mg) of Rf 0.62 (as compared with Rf 0.73 for **1**). The product (**14**) when recrystallized from $CHCl_3$-Et_2O softened at 120°C and melted at 143-144°C (followed by decomp). IR (KBr): 3650-2500 cm^{-1} (O–H), 1727 cm^{-1} (OC=O), 1696 cm^{-1} (NC=O); ^1H NMR ($CDCl_3$) δ 13.29 (1H, s, N_{10}-H), 8.42 (1H, dd, J 6.1, 0.8, H-2), 7.91 (1H, t, J 1.8, m-CBz), 7.84 (dt, J 7.9, 1.3, m-CBz), 7.83 (1H, d, J 8.5, H-7), 7.78 (1H, d, J 8.5, H-4), 7.52 (1H, d, J 8.5, H-8), 7.49 (1H, ddd, J 8.0, 2.2, 1.2, m-CBz), 7.35 (1H, dd, J 8.5, 6.1, H-3), 7.33 (1H, t, J 8.0, m-CBz), 6.36 (1H, d, J 4.0, H-5 or H-6), 4.71 (1H, d, J 4.0, H-5 or H-6); ^{13}C NMR ($CDCl_3$) δ 168.58 (C-9), 164.81, 137.76 (C-2), 134.61, 133.48, 133.21, 131.19 (C-7), 131.05 (129.81), 129.78, 129.51, 128.38 (C-4), 120.02, 122.28 (C-3), 122.21 (C-8), 122.16, 119.83, 71.44 (C-6), 68.11 (C-5); MS: 384 (1%, M^+), 356 (4%, M–CO), 358 (1%), 228 (8%, M–ClC_6H_4CO), 212 (6%), 201 (39%), 200 (23%), 199 (32%), 183 (15%), 173 (48%), 139 (100%, ClC_6H_4CO), 141 (45%), 111 (51%) 113 (41%); HRMS: for $C_{12}H_8N_2O_3$ calcd 228.05343, found 228.05339 and for $C_{12}H_8N_2O_2$ calcd 212.05852, found 212.05766.

The acidic aqueous solutions were combined, then washed once with 3 mL of CH_2Cl_2 and, while being cooled in an ice-bath, treated with 10% aqueous Na_2CO_3 till the solution gave an alkaline reaction. Next, the aqueous solution was successively extracted, first, with AcOEt and, then, with $CHCl_3$ and when the organic solutions were separately dried and concentrated, 23 mg of starting **1** and 48 mg of 1,10-phenanthroline-1-oxide (**15**) of Rf 0.35, the crystallizing solids, were obtained, respectively. For ^1H NMR and ^{13}C NMR data of **1** and **15** see Table 1 and Table 2. *N*-oxide (**15**): For ^1H NMR and ^{13}C NMR see Table 1 and Table 2, respectively. IR (KBr): 3408 cm^{-1} (broad, HO-H), 1256 cm^{-1} (N→O); MS: 196 (100%, M^+), 180 (82%), 168 (56%), 141 (30%), 140 (31%); HRMS: for $C_{12}H_8N_2O$ calcd 196.06366, found 196.06405 and for $C_{12}H_8N_2$ calcd 180.06874, found 180.06886.4

5,6-Epoxy-1,10-phenanthroline-1-oxide. A solution of 5,6-epoxy-1,10-phenanthroline (**3**, 124 mg, 0.63 mmol) in 8 mL of CH_2Cl_2 while being stirred at 0°C was treated dropwise with commercial ~80% *m*-CPBA (411 mg, 1.9 mmol of neat peracid) in 10 mL of CH_2Cl_2 for 5 min and, then, stirring in an ice-bath was continued for 1 h. Next, the reaction mixture was diluted with $CHCl_3$, washed successively with two 20 mL portions of aqueous Na_2CO_3 and water, then, the chloroform solution was dried over Na_2SO_4 and concentrated yielding 102 mg of solidifying light-brown oil which gave on TLC plate a fluorescent spot (under long UV wavelength) of Rf 0.22 (as compared with 0.63 for starting **3**). The product was purified by filtration its chloroform solution through a cellulose-silica gel (7:1) layer which yielded 81 mg (60%). ^{1}H NMR ($CDCl_3$ + CD_3OD) δ 9.00 (1H, dd, J 4.7, 1.8, H-9), 8.45 (1H, dd, J 6.6, 1.3, H-2), 8.02 (1H, dd, J 7.7, 1.8, H-7), 7.54 (1H, dd, J 7.6, 1.3, H-4), 7.45 (1H, dd, J 7.7, 4.7, H-8), 7.28 (1H, dd, J 7.6, 6.6, H-3), 4.58 and 4.61 (2H, an AB system, J 3.9, H-5 and H-6); ^{15}N NMR ($CDCl_3$ + CD_3OD) δ –68.99 (N-10), –87.89 (N-1); HRMS: for M^+ $C_{12}H_8N_2O_2$ calcd 212.05858 found 212.05761.

ACKNOWLEDGEMENT

This work was supported by the Research Committee's KBN Grant PB-0912/P3/94/06.

REFERENCES AND NOTES

1. G.F.Smith and F.W.Cagle, Jr., *J.Org.Chem.*, 1947, **12**, 781.
2. J.Młochowski, *Roczniki Chem.*, 1974, **48**, 2145.
3. M.Yamada, Y.Tanaka, Y.Yoshimoto, S.Kuroda, and I.Shimao, *Bull.Chem.Soc.Jpn.*, 1992, **65**, 1006.
4. (a) S.Krishnan, D.G. Kuhn, and G.A.Hamilton, *J.Am.Chem.Soc.*, 1977, **99**, 8121; (b). C.J.Moody, C.W. Rees, and R.Thomas, *Tetrahedron*, 1992, **48**, 3589.
5. The lack of selectivity of this two-phase reaction is probably responsible for the reported melting point value of epoxide (**3**) which is more than 20 degrees lower than that estimated by us. The product mixture formation can be easily followed on TLC since dichloro derivative (**2**) reveals a higher Rf value as opposed to the lower one of epoxidation product (**3**) when compared with that of the starting material (**1**). Dichloro derivative (**2**) was also obtained when a solution of dehydrated **1** (1 mmol) and Bu_4NCl (0.6 mmol) in CCl_4 (60 mL) was treated overnight with a 1.79 N solution of Cl_2 in CCl_4 (5 mL). However, the yield of **2** was only about 40% mainly because of the insolubility of phenanthroline hydrochloride separating from the reaction mixture. When $CHCl_3$ was used, the salt Phen·HCl was formed in a quantitative yield. The reaction was found to occur also in the absence of an ammonium catalyst though the addition of Bu_4NCl resulted in a faster completion of the reaction and a quantitative consumption of the starting base (**1**).

6. The formation of the dichloro derivative (**2**) as a by-product of the phenanthroline epoxidation was preliminarily reported by R.Antkowiak and W.Z.Antkowiak, *Tetrahedron Lett.*, 1997, **38**, 1857.
7. Neocuproine was found to react similarly yielding the corresponding 5,6-dichloro-5,6-dihydro derivative for which the NMR signal of the 5 and 6 protons appeared as a singlet at 5.38 ppm.
8. R.M.Chapin, *J.Am.Chem.Soc.*, 1934, **56**, 2211.
9. J.E.Dickeson and L.A.Summers, *Aust.J.Chem.*, 1970, **23**, 1023.
10. Chlorohydrine (**8**) appeared on a TLC plate just above the phenanthroline spot but distinctly below that of the dichloro derivative (**2**) and revealed the bridge proton absorption as a couple of doublets of an AB system with J 4.2 Hz at 5.03 ppm and 5.29 ppm, respectively.
11. To verify the supposition expressed in the equation, UV spectra of the chlorinating agent

    $$\underset{\text{in } CHCl_3}{HOCl} \xleftarrow[\text{pH} < 7 \qquad \text{pH} > 7]{H^+,\ CHCl_3} \underset{Na^+\ ClO^-}{\text{aqueous}} \xrightarrow{Bu_4N^+,\ CHCl_3} \underset{\text{in } CHCl_3}{Bu_4N^+ClO^-}$$

    in $CHCl_3$ were examined. The chloroform extracts of the aqueous sodium hypochlorite solutions of different pH containing or not the quaternary ammonium ions, showed in the spectrum the presence of a band with a maximum at ~ 245 nm which was always strong when Bu_4N^+ ions in the medium of ClO^- were present. Additionally, when the $CHCl_3$ solution was prepared based on aqueous NaOCl, the pH of which was adjusted to a neutral or weak acidic reaction, a band of significant intensity appeared at ~ 328 nm independent of the presence or absence of the Bu_4N^+ ions. The addition of AcOH revealed no influence on the UV pattern. These observations suggest that the participation of $Bu_4N^+ClO^-$ in the inter-phase transfer of the electrophilic chlorine is even possible in an acidic medium. Unlike what we found for chloroform solutions, the absorption bands for aqueous solutions at 292 nm and 230 nm for ClO^- and HOCl, respectively, were reported by M.Anbar and I.Dostrovsky *J.Chem.Soc.*, 1954, 1105.

    A reagent containing a very electrophilic chlorine separated on the surface as a neat yellow oil which readily decomposed at rt when a weak basic NaOCl solution was treated with an aqueous solution of Bu_4N^+ ions. The yellow product was found to be insoluble in CCl_4 and water but can easily be taken into chloroform. The $CDCl_3$ solution of the product (containing n-butyl groups according to NMR) gave a strong absorption at 245 nm, the band which in the spectrum of HOCl in a chloroform solution (without any amount of the quaternary ammonium base) appeared as a shoulder peak of low intensity only.
12. When melted at 164.5-165°C, the dichloro derivative (**2**) is purely transformed into a pink coloured hydrochloride of 5-chloro-1,10-phenanthroline (**9** · HCl) of mp 264-265°C. As with most of the compounds dealt with in this paper, **2** was found to decompose spontaneously even at rt when kept in chloroform or a methylene chloride solution, especially when wet.

13. (a) F.Richter and G.F.Smith, *J.Am.Chem.Soc.*, 1944, **66**, 396; (b) M.Yamada, Y.Nakamura, T.Hasegawa, A.Itoh, S.Kuroda, and I.Shimao, *Bull.Chem.Soc.Jpn.*, 1992, **65**, 2007.

14. G. Maerker and F.H.Case, *J.Am.Chem.Soc.*, 1958, **80**, 2745.

15. E.J.Corey, A.L.Borror, and T.Foglia, *J.Org.Chem.*, 1965, **30**, 288.

16. J.Młochowski, *Roczniki Chem.*, 1977, **51**, 665.

17. J.Młochowski and K.Kloc, *Roczniki Chem.*, 1973, **47**, 727.

18. D.Wenkert and R.B.Woodward, *J.Org.Chem.*, 1983, **48**, 283.

19. While monitoring the reaction by TLC, a formation at the very beginning of an additional extremely reactive intermediate of Rf similar to that of di-*N*-oxide (**11**) was observed. The spot, which was clearly separated from those of mono-*N*-oxide (**10**) and starting **2**, disappeared within the initial 10 min at -70°C and appeared again later when di-*N*-oxide (**11**) was formed. The *N*-oxides (**10**) and (**11**) can easily be reduced to the starting **2** by an aqueous sodium sulfite treatment.

20. The aromatization of the central ring by hydrogen chloride elimination appeared to be regioselective in the formation of 5-chloro-1-oxide derivative (instead of 6-chloro-1-oxide) the structure of which was proved by NOE experiment. The irridation of H-6 at 7.94 ppm of product (**12**) resulted in an enhancement of the H-7 signal intensity at 8.17 ppm by 5.44%.

21. P.G.Sammes and G.Yahioglu, *Chem.Soc.Rev.*, 1994, **23**, 327. The formation of di-*N*-oxide, as reported by F.Linsker and R.L.Evans (*J.Am.Chem.Soc.*, 1946, **68**, 403), when 1,10-phenanthroline was treated with H_2O_2 in AcOH, was not confirmed later by other authors.

22. The addition of $CHCl_3$ caused the dissolving of the chlorinating agent which separated when formed during the acid treatment, see ref. 11.

23. R.D.Gillard and R.E.E.Hill, *J.Chem.Soc.,Dalton Trans.*, **1974**, 1217.

Received, 1st July, 1997