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Is the Formation of 1,10-Phenanthroline Di-N-oxide Possible ?

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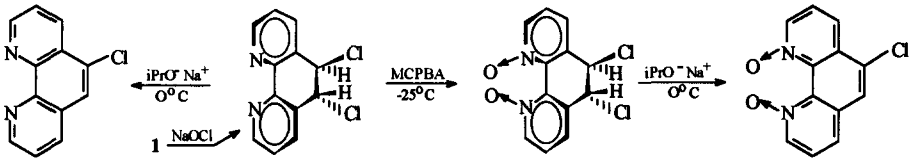
Abstract: *5,6-Dichloro-5,6-dihydro-1,10-phenanthroline (2) was found as an additional product of the hypochlorous acid action on 1,10-phenanthroline. When treated with MCPBA the product of the chlorine addition yielded a corresponding di-N-oxide 3, which readily lost hydrogen chloride under the influence of sodium isopropoxide. The resulting monochloro di-N-oxide 5 molecules (assumed to be flat) revealed a satisfactory stability unless the neutral or basic solution was made acidic.* © 1997, Elsevier Science Ltd. All rights reserved.

According to the literature reports,[1-5] 1,10-phenanthroline (**1**) can be N-oxidized to a mono-N-oxide derivative only. This was interpreted as a result of crowding due to steric hindrance in the cavity of the flat molecule. Whether this is the real cause could be checked by twisting the molecule around the central bond of the bipyridine fragment by changing the hybridization of the atomic orbitals of carbon C-5 and C-6 into sp^3 before returning to the coplanarity of the molecule when both nitrogens are N-oxidized.

To test this strategy we took advantage of our observation that 5,6-dichloro-5,6-dihydro-1,10-phenanthroline (**2**) is formed as a by-product when one is following the procedure[6,7] for **1** epoxidation in chloroform using a slightly alkaline aqueous sodium hypochlorite solution and a phase transfer catalyst.[8] Indeed, the twisted molecules of derivative **2** reacted readily with MCPBA at -25°C to yield, first, mono-N-oxide and, next, di-N-oxide of 5,6-dichloro-5,6-dihydro-1,10-phenanthroline (**3**). Both of these products can be easily differentiated on the basis of the presence or absence of the symmetry features revealed on their proton and carbon NMR spectra — H-5 and H-6 of the dichloro-di-N-oxide derivative gave a singlet at 5.24 ppm — and a 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 sodium isopropoxide in isopropanol at 0°C, both **2** and **3** readily yielded the products of hydrogen chloride elimination, 5-chloro-1,10-phenanthroline (**4**)[9] and di-N-oxide of 5-chloro-1,10-phenanthroline (**5**), respectively, the latter with the two N-oxide functions untouched.[10] It follows from these observations that, as in the sterically similar case of 4,5-dimethoxyphenanthrene,[11] the 1,10-phenanthroline molecule is also able to accommodate two oxygens in its cavity in spite of the resulting interaction between the two dipols. Such a possibility was assumed 50 years ago in the first and only report on the controversial o-phenanthroline di-N-oxide synthesis by Linsker and Evans.[12]



4 2 3 5

However, the hitherto reported procedures towards the phenanthroline N-oxide synthesis were based on the use of different oxidation agents but in acidic conditions in all cases. Therefore, once we had carried out the last step of our synthesis of di-N-oxide **5** in a basic medium, it was reasonable to check the stability of our product against an acidic reagent. We found that even silica gel in methylene chloride was active enough to force some structural change of **5** causing the appearance of the low-field absorption at above 9 ppm - the position characteristic for an *alpha* proton of the free base (deshielded by about 0.5 ppm in relation to that of the starting di-N-oxide **5**). The observation indicated oxygen elimination from one of the N-oxide functions. This conformed with our previous supposition[13] that protonation of such a di-N-oxide forms a system which probably creates a new opportunity to discharge the strain by the operation of a special mechanism of deoxidation.

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