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Phenanthroline Di-N-oxides

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The structural analogy of phenanthrene and the phenanthrolines is not evident through any similarity in chemical behavior. Phenanthrene can be nitrated, sulfonated and chlorinated under comparatively mild conditions, but the phenanthrolines resist all such attempts. The Friedel-Crafts reaction which leads to a variety of phenanthrene derivatives cannot be applied to the nitrogenous analogs. This inactivity of the phenanthrolines is partly explained through their dipyridobenzene nature. We would therefore not expect substitution to take place on the pyridine rings, but the inertness of the two available benzenoid positions is, however, quite surprising. Although in the cases of phenanthrene and 7,8-benzoquinoline,¹ chromic acid oxidation leads to the formation of orthoquinones, we failed to observe any oxidation of *m*- and *p*-phenanthroline under identical conditions, and the starting material was recovered in both instances. Other oxidizing agents such as selenium dioxide, vanadium pentoxide, iodic acid and periodic acid were equally ineffective. Hydrogen peroxide in acetic acid at boiling temperature converted the phenanthrolines into the corresponding di-N-oxides in good yields, and this reagent seems preferable to the commonly used perbenzoic acid. The latter was used recently to convert *m*-phenanthroline into the N¹-oxide.²

Phenanthroline di-N-oxides are bright yellow crystalline solids, which melt at considerably higher temperatures than the corresponding phenanthrolines. They are soluble in dilute mineral acids and dilute acetic acid with formation of salts. In the course of this investigation 2,3-diphenylquinoxaline di-N-oxide was also prepared by the same method.

Experimental Part

***m*-Phenanthroline Di-N-oxide.**—Six grams of *m*-phenanthroline dihydrate was dissolved in 40 g. of glacial acetic acid and 20 g. of hydrogen peroxide (100 volumes) was added. The solution was boiled two hours under reflux, cooled to room temperature, diluted with 150 ml. of water, and made alkaline by the slow addition of a 30% caustic soda solution. The alkaline mixture was allowed

to remain at 0° during three hours, the precipitate was filtered and washed with water. The crude product was recrystallized from boiling water and dried over calcium chloride in a desiccator. The yield was 4.2 g. (71%) of fine yellow needles, m. p. 192°; soluble in hot water and hot alcohol; insoluble in cold water, cold alcohol and most organic solvents.

Anal. Calcd. for C₁₂H₈N₂O₂: C, 67.92; H, 3.77. Found: C, 68.23; H, 4.00.

***p*-Phenanthroline Di-N-oxide.**—The procedure was the same as in the foregoing example. Starting from five grams of *p*-phenanthroline a yield of 4 g. (68%) of di-N-oxide was obtained. It was crystallized from water in yellow needles, m. p. 308°; soluble in boiling water, insoluble in most organic solvents.

Anal. Calcd. for C₁₂H₈N₂O₂: C, 67.92; H, 3.77. Found: C, 68.04; H, 3.79.

***o*-Phenanthroline Di-N-oxide.**—Three grams of *o*-phenanthroline monohydrate was dissolved in 24 cc. of glacial acetic acid and 12 g. of hydrogen peroxide (100 volumes) was added. The solution was boiled under reflux for one hour, cooled, and an excess of 5% caustic soda was added slowly. After cooling, the precipitate, consisting of the product together with large amounts of sodium acetate, was filtered and dried in a desiccator. The isolation of pure *o*-phenanthroline di-N-oxide base proved to be difficult because it is so readily soluble in water. The crude precipitate was therefore extracted with ethyl alcohol and the solution was precipitated with picric acid. The picrate was purified through repeated crystallization from ethyl alcohol; yellow prisms, m. p. 191–192°.

Anal. Calcd. for C₁₂H₈N₂O₂·C₆H₃N₃O₇: C, 48.98; H, 2.48. Found: C, 49.29; H, 2.82.

2,3-Diphenylquinoxaline Di-N-oxide.—A solution of 5 g. of 2,3-diphenylquinoxaline in 40 g. of glacial acetic acid and 20 g. of hydrogen peroxide (100 vol.) was heated for two hours to reflux temperature. After cooling, the reaction mixture was poured into 500 cc. of water and the resulting voluminous light yellow precipitate was filtered. After thorough washing with water, it was dried and recrystallized from ethanol; short thick yellow needles, m. p. 210°, yield 5 g. (90%).

Anal. Calcd. for C₂₀H₁₄N₂O₂: C, 76.43; H, 4.46. Found: C, 76.77; H, 4.71.

Summary

Phenanthroline di-N-oxides and 2,3-diphenylquinoxaline di-N-oxide were obtained by oxidizing the bases with hydrogen peroxide in acetic acid solution.

Attempts to oxidize phenanthrolines to phenanthroline quinones were unsuccessful.

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(1) Skraup and Cobenzl, *Monatsh.*, **4**, 460 (1883).

(2) Kermack and Tebrich, *J. Chem. Soc.*, 375 (1945).