

研 究 主 論 文 抄 録

論文題目

テトラミン酸とテトロン酸誘導体の Mn(III)に基づく酸化反応とその関連反応に関する研究

(Study on the Mn(III)-Based Oxidation of Tetramic Acid and Tetric Acid Derivatives and the Related Reactions)

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主論文要旨

《本文》

Tetramic acid (pyrrolidine-2,4-dione) derivatives, one of the most important nitrogen heterocycles, have attracted a great deal of interest because of majority of the compounds isolated to date exhibit biological function, usually antibiotic, antiviral and antiulcerative properties, cytotoxicity, mycotoxicity, and the inhibition of tumors as well as fungicidal action.

On the other hand, tetric acid (4-hydroxybutenolide) moiety occurs in the structure of many natural products having important biological activities. This is the case of ascorbic acid (vitamin C). Various terpenes, alkaloids, antibiotics, and the mushroom pigments pulvinic acids also contain a tetric acid-derived fragment.

On the basis of the importance of the biological activities of the tetramic acid and tetric acid derivatives, the candidate had interest for the synthesis of some new derivatives of tetramic acid and tetric acid derivatives having peroxide functional group.

The interested points are:

- (1) The direct hydroperoxidation of the tetramic acid derivatives in the Mn(III)-catalyzed aerobic oxidation followed by the characterization of the rearrangement products.
- (2) The alkylhydroperoxidation of the tetramic acid derivatives in the Mn(III)-catalyzed aerobic oxidation in the presence of alkenes, although the corresponding endoperoxides were formed.

(3) The Mn(III)-catalyzed aerobic oxidation of tetronic acid and its derivatives for the investigation of peroxy lactone derivatives and also the reaction at elevated temperature for the formation of Hagen's gland lactones, although the Hagen's gland lactones were formed by the Pd-C catalyzed hydrogenolysis of the peroxy lactones not by the reaction at elevated temperature.

The formation of carbon-centered radicals and their additions to molecular oxygen in the presence of manganese(III) acetate at room temperature for the production of hydroperoxides, and to alkenes in the presence of manganese(III) acetate at room temperature to produce endoperoxides and peroxy lactones were focused in *Chapter 2*, *3*, and *4*. And also the Pd-C catalyzed hydrogenolysis of peroxy lactones for the formation of Hagen's gland lactones was described in *Chapter 4*.

In *Chapter 2*, it was explained that the reaction of various 2,4-pyrrolidinediones in the presence of manganese(III) acetate at room temperature in air gave the 3-hydroperoxy-2,4-pyrrolidinediones in excellent yields. In addition, it was also observed that the rearrangement of the 3-hydroperoxy-2,4-pyrrolidinediones gave 5-hydroxyoxazolidin-4-ones.

In *Chapter 3*, it was described the aerobic oxidation of a mixture of alkenes and 2,4-pyrrolidinediones using a catalytic amount of manganese(III) acetate at room temperature gave the corresponding endoperoxides not the expected alkylhydroperoxides due to the presence of active *keto*-carbonyl center.

In *Chapter 4*, it was described the Mn(III)-catalyzed aerobic oxidation of tetronic acid and its derivatives for the formation of peroxy lactone derivatives, and also the reaction at elevated temperature for the formation of ethyl and/or ethenyl-tetronic acids along with a peroxypropellane. The Hagen's gland lactones were formed by the Pd-C catalyzed hydrogenolysis of the peroxy lactones.

The synthetic utilities and the plausible mechanism of the reactions were also discussed in detail, and finally the general procedure for the reactions, the spectroscopic data as well as physical properties of the new compounds were given in each chapter.