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

# Study on the Mn(III)-Based Oxidation of Tetramic Acid and Tetronic Acid Derivatives

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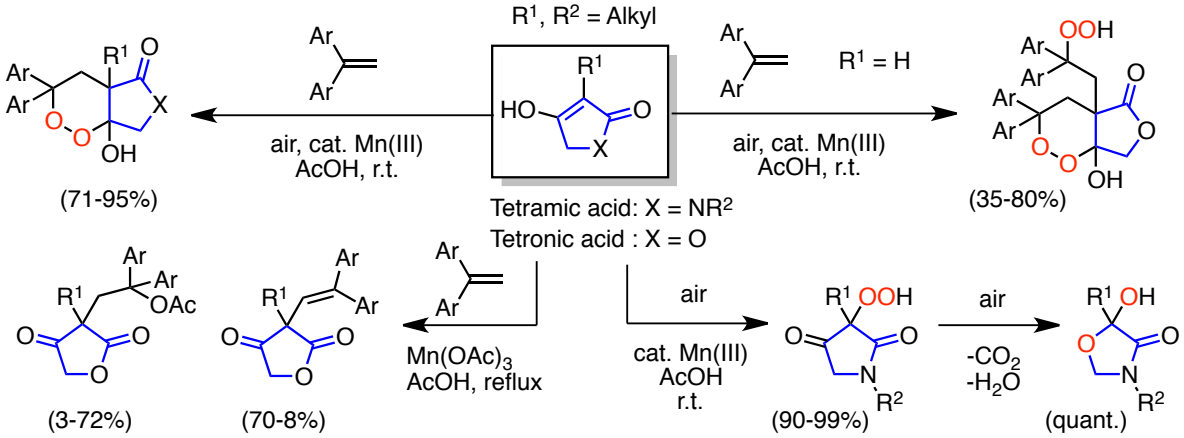
Natural products containing tetramic acid (2,4-pyrrolidinedione) or tetronic acid (tetrahydrofuran-2,4-dione) moieties continue to attract the interest of chemists due to their challenging structures and wide range of biological activities which they display. Endoperoxides and hydroperoxides also exist in nature, and many of them are drugs with therapeutic values. Specifically, some of the endoperoxides and heterocyclic hydroperoxides show antimalarial and anticancer activities. Mn(III) acetate acts as an excellent oxidizing agent to produce endoperoxides or hydroperoxides by oxidizing a variety of 1,3-dicarbonyl heterocyclic compounds.[1] Therefore, the synthesis of some tetramic acid and tetronic acid derivatives containing peroxide functional group would be a good selection for the new aspect of synthetic chemistry. To search some new biologically active peroxide derivatives of tetramic and tetronic acids, we investigated Mn(III)-catalyzed aerobic oxidation of tetramic and tetronic acid derivatives. The Mn(III)-catalyzed direct aerobic oxidation of 3-substituted tetramic acids (X = $NR^2$) at room temperature in acetic acid produced the corresponding hydroperoxy derivatives in excellent yields. The hydroperoxytetramic acids spontaneously decomposed to give oxazolidin-4-ones.[2] A similar oxidation of tetronic acid (X = O, $R^1$ = H) in the presence of 1,1-disubstituted alkenes gave the corresponding tetronic acid derivatives which contain both alkylhydroperoxy and endoperoxy functional group, in moderate to good yields. The reaction of both 3-substituted tetramic and tetronic acids with 1,1-disubstituted alkenes under similar aerobic conditions resulted in the production of the bicyclic endoperoxides in good to excellent yields. On the other hand, the tetronic acids underwent oxidative addition with 1,1-diarylethenes at elevated temperature to afford the corresponding ethyl- and ethenyl-tetronic acid derivatives.[3] The results of the Mn(III)-based oxidation and the mechanism for the formation of the products will be discussed.

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