

研 究 主 論 文 抄 録

論文題目

Study on the Mn(III)-Based Oxidative Radical Reaction of Polycarbonyl  
Compounds with Alkenes

(ポリカルボニル化合物とアルケン類の Mn(III)に基づく酸化的ラジカル反応に関する研究)

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主論文要旨

In this thesis, the synthesis of 2,3,3a,6a-tetrahydrofuro[2,3-*b*]furans, 3,4-dihydro-2*H*-pyrans, 3-(2-aryl-2-oxoethyl)-5,5-diaryl-2-oxotetrahydrofuran-3-carboxylates, 7-aza-2-oxaspiro[4.4]nonane-8,9-diones and 2,7-dioxa[4.4]nonan-1-ones by the Mn(III)-based oxidative reaction is described. These reactions are presented in the chapters 2-4. All the synthesized compounds were new and fully characterized by spectroscopic methods, elemental analysis, and X-ray crystallography. Each reaction mechanism was proposed and discussed. The detailed results of the studies are given in *Chapters 2-4*, and the general procedure for these reactions and the spectroscopic data as well as physical properties of the products are given in each chapter.

In *Chapter 1*, the background of the research project and the purpose of the thesis were described.

In *Chapter 2*, the Mn(III)-based oxidation of 1,1-disubstituted ethenes with 2-(2-aryl-2-oxoethyl)malonates, 2-acetyl-4-aryl-4-oxobutanoates, and 3-acetyl-1-aryl-pentane-1,4-diones was evaluated. It was found that the reaction using the malonates mainly gave the 2,3-dihydro-4*H*-pyran-4,4-dicarboxylates along with  $\gamma$ -lactones, and a similar reaction using the acetyloxobutanoates and acetylpentanediones produced the 2,3,3a,6a-tetrahydrofuro[2,3-*b*]furans and the corresponding dihydropyrans. As a result, the cyclization was strongly affected by the nucleophilicity of the carbonyl oxygen in the carbocation intermediate, and the kinetic and thermodynamic controls of the following reaction. Finally, the relative feasibility of the 5-*endo-trig* tandem cyclization, 6-*endo-trig* cyclization, and 5-*endo-trig* lactonization in the carbocation intermediate was estimated as 24:13:8:1 for the reaction of 1,1-diphenylethene with 3-acetyl-1-phenylpentane-1,4-dione, ethyl 2-acetyl-4-phenyl-4-oxobutanoate, and

dimethyl 2-(2-phenyl-2-oxoethyl)malonate. The structure determination and the mechanisms for the formation of the products were also discussed.

In *Chapter 3*, the Mn(III)-based reaction of a mixture of 1,1-diarylethenes and 4-acylpyrrolidine-2,3-diones was studied, and nine 2-oxa-7-azaspiro[4.4]nonane-8,9-diones were newly synthesized in good yields. It was found that the pyrrolidinedione ring remained intact and became one of the two rings of the 2-oxa-7-azaspiro[4.4]nonanedione scaffold under the stated reaction conditions. It was proved that the reaction was straightforward, the reaction time was significantly short, the procedure was simple, and the products were easily separated to obtain the desired azaspiro compounds. In addition, the structure determination of the azaspiro compounds using 2D NMR technique and an X-ray crystallography, and the mechanism for the formation of the 2-oxa-7-azaspiro[4.4]-nonanediones were also discussed.

In *Chapter 4*, the cyclization of 3-acylbutyrolactones with 1,1-diarylethenes in the presence of manganese(III) acetate as a free-radical oxidant was explored. The reaction successfully occurred and eight novel spiro compounds, 2,7-dioxa[4.4]nonan-1-ones, containing a tetrahydrofuran skeleton were obtained in 40-79% yields. The synthetic procedure was considerably simple, and the products were easily separated to purify. In addition, the structure determination of the spiro compounds using 2D NMR technique and the mechanism for the formation of the 2,7-dioxa[4.4]nonan-1-ones were also discussed.

In *Chapter 5*, the general conclusion was written. That is, it was proved that the Mn(III)-based oxidative radical reaction was one of the convenient methods to prepare complex and structurally crowded oxygen-heterocycles and *exo*-methylene-spiro compounds. It was found that the nucleophilicity of the carbonyl oxygen in the carbocation intermediate, and the kinetic and thermodynamic controls of the following reaction played an important role in the oxidative cyclization.