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Synthesis of dioxapropellanes using Mn(III)-based oxidative tandem cyclization of tetracarbonyl compounds with diarylethenes

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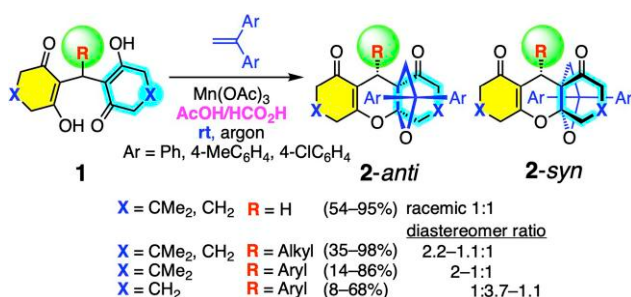
Hiroshi Nishino obtained his bachelor (1979) and MS degree in chemistry at Kumamoto University under the supervision of Professor Kazu Kurosawa, and was appointed Assistant Professor (1981), Department of Chemistry, Faculty of Science, Kumamoto University. He received his Ph.D. degree (1988) in chemistry from Tohoku University supervised by Professor Sho Ito, and joined Professor Jay K. Kochi's group (1988 to 1989), University of Houston, U.S.A., then Associate Professor Tohru Fukuyama's group (1989 to 1990), Rice University, U.S.A. He returned to Kumamoto University in 1990, and was promoted to Associate Professor in 1996, then full Professor (1999 to 2021), and is now Specially Appointed Professor of Kumamoto University.

Abstract

The Mn(III)-based oxidation of tetracarbonyl compounds with 1,1-diarylethenes formed dioxapropellanes. The use of methylenebis(3-hydroxycyclohex-2-en-1-one)s as a tetracarbonyl compound led to the production of 3,4,5,6,7,9-hexahydro-8*H*-4a,9a-(epoxyethano)xanthene-1,8(2*H*)-diones in good yields. Although the reaction competed with self-cyclization to form 3,5,6,7-tetrahydro-4*H*-spiro[benzofuran-2,1'-cyclohexane]-2',4,6'-triones, it could be controlled by adding the co-solvent formic acid at room temperature. The reactions of alkyl- and aryl-substituted methylenebis(3-hydroxycyclohex-2-en-1-one)s resulted in the corresponding dioxapropellanes as a diastereomixture. The formation of diastereomers is explained by the steric hindrance of the intermediate carbocations during tandem cyclization. The reactions using 2-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)butane-1,4-diones and 2,2'-methylenebis(3-hydroxycyclopent-2-en-1-one)s also produced the corresponding dioxapropellanes. The structure determination of the products and the reaction pathway for the formation of dioxapropellanes are discussed.

Keywords: dioxapropellanes, manganese(III) acetate, oxidative tandem cyclization.

Graphical Abstract



The Mn(III)-based oxidation of tetracarbonyl compounds with 1,1-diarylethenes formed dioxapropellanes. The use of methylenebis(3-hydroxycyclohex-2-en-1-one)s led to the production of 3,4,5,6,7,9-hexahydro-8*H*-4a,9a-(epoxyethano)xanthene-1,8(2*H*)-diones in good yields. The reactions of alkyl- and aryl-substituted methylenebis(3-hydroxycyclohex-2-en-1-one)s resulted in the corresponding dioxapropellanes as a diastereomixture. The formation of the diastereomers is explained by the steric hindrance of the intermediate carbocations during the tandem cyclization.