Chiral 7-Oxabicyclo[2.2.1]heptane Building Blocks for Prostanoids

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Abstract—Methyl (*Z*)-3-[(2*R*,3*R*,4*S*,5*S*)-5-(2-methoxy-2-oxoethyl)-3,4-(isopropylidenedioxy)tetrahydrofuran-2-yl]-prop-2-enoate was synthesized, and its intramolecular carbocyclization was studied. This reaction proceeds smoothly and quickly under the action of *t*-BuOK in THF, leading to three cycles with the methoxy and methoxycarbonylmethyl side substituents *trans* to each other. A stepwise route for the formation of methyl (1*R*,2*R*,6*S*,7*R*,8*R*,9*R*)-9-(2-methoxy-2-oxoethyl)-4,4-dimethyl-3,5,10-trioxatricyclo[5,2,1,$0^{2,6}$]decane-8-carboxylate and methyl (1*R*,2*R*,6*S*,7*R*,8*S*,9*S*)-9-(2-methoxy-2-oxoethyl)-4,4-dimethyl-3.5,10-trioxatricyclo-[5,2,1,$0^{2,6}$]decane-8-carboxylate with the *trans* orientation of the side substituents is proposed. The observed stereochemical result of the reaction is interpreted in terms of epimerization in the C^1 and C^4 centers of methyl (*Z*)-3-[(2*R*,3*R*,4*S*,5*S*)-5-(2-methoxy-2-oxoethyl)-3,4-(isopropylidenedioxy)-tetrahydrofuran-2-yl]prop-2-enoate, which ultimately leads to the cyclized β,β'-*cis* diastereomer of methyl (*Z*)-3-[(2*R*,3*R*,4*S*,5*S*)-5-(2-methoxy-2-oxoethyl)-3,4-(isopropylidenedioxy)-tetrahydrofuran-2-yl]prop-2-enoate and the corresponding α,α'-*cis* diastereomer, a precursor of methyl (1*R*,2*R*,6*S*,7*R*,8*S*,9*S*)-9-(2-methoxy-2-oxoethyl)-4,4-dimethyl-3,5,10-trioxatricyclo[5,2,1,$0^{2,6}$]decane-8-carboxylate.

Keywords: D-ribose, (methoxycarbonylmethylidene)triphenylphosphorane, Wittig reaction, intramolecular carbocyclization, functionalized 7-oxabicyclo[2.2.1]heptanes

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