Synthesis, Structure, and Keto–Enol Tautomerism of 3-R^1-5,5-R^2,R^2-6-R^3-2,3,5,6-Tetrahydropyran-2,4-diones

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Abstract — Ethyl esters of 2,4-dibromo-2-R^1-4-R^2-3-oxopentanoic and -hexanoic acids react with zinc and aliphatic or aromatic aldehydes under the conditions of the Reformatskii reaction to give 3-R^1-5,5-R^2,R^2-6-R^3-2,3,5,6-tetrahydropyran-2,4-diones, which are obtained in three forms: keto, enol with enolization of the keto group, and enol with enolization of the ester group. The keto form is isolated by crystallization from a mixture of CCl_4 and petroleum ether; the first enol form, from MeOH, EtOH, and polar aprotic solvents; and the second enol form, from $CHCl_3$. The second enol form is oxidized in DMSO to form a keto compound containing a hydroxy group at the 3-position of the heteroring.