

Zinc-catalyzed cycloisomerizations. Synthesis of substituted furans and furopyrimidine nucleosides.

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5-*Endo-dig* cycloisomerization of 1,4- and 1,2,4- mostly aryl-substituted but-3-yn-1-ones in the presence of a catalytic amount of zinc chloride etherate (10 mol %) in dichloromethane at room temperature gave 2,5-di- and 2,3,5-trisubstituted furans in high yields (85–97%). DSC studies confirmed that a solely thermal process does not take place. A relevant catalytic process, employing μ -oxo-tetranuclear zinc cluster $\text{Zn}_4(\text{OCOCF}_3)_6\text{O}$, yielded bicyclic furopyrimidine nucleosides, when starting from acetyl-protected 5-alkynyl-2'-deoxyuridines (85–86%). Furopyrimidine was deprotected or simultaneously converted into pyrrolopyrimidine nucleoside. The time/concentration dependence for the reaction of 1-phenyl-4-(4-methylphenyl)butynone to 2-(4-methylphenyl)-5-phenylfuran displayed first-order kinetics with the rate dependent on catalyst concentration. The plot of $\ln k_{\text{obs}}$ versus $\ln[\text{ZnCl}_2]$ indicated first-order cycloisomerization, as referred to ZnCl_2 concentration, using both NMR and UV–vis reaction monitoring. The crystal structure of propyl furopyrimidine nucleoside (orthorhombic, $P2_12_12_1$, $a/b/c = 5.684(2)/6.682(2)/36.02(2)$ Å, $Z = 4$) shows C2'-*endo* deoxyribose puckering, and the base is found in the *anti* position in crystalline form.

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