Levoglucosenone Transformation to Anhydroglycosidic Bond

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Levoglucosenone - 1,6-anhydro-3,4-dideoxy- β -D-pyranosen-2-on - is the main product, forming on thermolysis of various cellulose containing materials with catalysts of acid type on temperature of 300 $^{\circ}$ C and higher and attracts researchers attention by unique constitution and receiving possibility on its base various compounds containing the structural fragments of natural compounds.

Levoglycosenone is the reactive substance, as it contains olefinic C=C bond, carbonylic C=O group and anhydroglycosidic bond in its composition. In spite of the fact that the literature gives reasonably many examples of levoglucosenone reactions where C=C and C=O bond. Levoglucosenone reactions with anhydroglycosidic bond are not practically investigated. It is clear that such reactions will proceed in acid medium with ions of H_3O^+ . Considering that the literature has showed the forming possibility hydroxymethylfurfural from levoglucosenone, one could expect that the nature of forming products from levoglucosenone with catalysts of acid type would be determined by medium in which transformation is carried out, and by the conditions of test conducting.

Accordingly levoglucosenone transformations in the presence of strong organic and mineral acids in different solvents, by way of which it was used trifluoroacetic acid (TFAA), water and lower aliphatic alcohols - methanol, ethanol and propanol have been investigated in this work.

On the base of NMR ¹H data, chromato-mass-spectrometry and GLC it is established, that levoglucosenone on temperature of 150-200°C in the presence of sulphuric acid in the water medium quantitatively (yield of 80 mol.%) are changed into levulinic acid. Kinetic investigations of the process with analysis of all forming products showed, that the levulinic acid from levoglucosenone are run through the formation stage of hydroxymethylfurfural. From the obtained data the result is that you can receive hydroxymethylfurfural derivative in other medium capable to interact with hydroxymethylfurfural, and in medium, interacting with levulinic acid, you can receive levulinic acid derivative. Indeed, on the NMR ¹H, ¹⁹F, chromato-mass-spectrometry, and GLC data, levoglucosenone in the TFAA medium in the temperature interval of 25-60°C has been estimated to transform into trifluoroacetate of hydroxymethylfurfural. In the presence of phosphoric acid the TFA HMF yield is reached 94,1 mol.%.

At the same time, in the medium of lower aliphatic alcohols, levoglucosenone in the temperature interval of 100-130°C is able to change into consistent ether of levulinic acid, and its yield is 94-95 mol.%.

levoglucosenone----> hydroxymethylfurfural----> levulinic acid----> levulinic acid ether

Forming conditions of different derivatives where determined, and the base of kinetic investigations and studies accordingly to composition of intermediate compounds the possible mechanisms of the running reactions were discussed.

So the studied in this work chemical levoglucosenone transformation widens the concepts about reactivity of this substance and opens new possibilities for synthesis on its base of different chemical substances including biologically active substances.