

Michael's reaction of levoglucosenone with α -alkylcycloalkanone enamines of CH-acids and linear nitroesters

© Lilia Kh. Faizullina,⁺ Yulia A. Khalilova, Yulia S. Galimova,
Shamil M. Salikhov, and Farid A. Valeev*

Ufa Institute of Chemistry of the Russian Academy of Sciences. Oktober Ave., 71.

Ufa, 450054. Russia. Fax: +7 (3472) 35-60-66. E-mail: sinvmet@anrb.ru

*Supervising author; ⁺Corresponding author

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Abstract

Reactions of Michael levoglucosenone with nucleophiles are differentiated by high regio and stereoselectivity. When using binucleophiles, these reactions occur with the participation of C=C and C=O bonds and allow to obtain condensed heterocyclic systems containing a carbohydrate moiety.

On the basis of the Michael adducts of levoglucosenone and cycloalkanones obtained through the enamines of the latter, a scheme for the synthesis of medium and large chiral lactones has been developed. In order to expand the arsenal of Michael adducts used in the synthesis of lactones, the possibilities of obtaining 1,4-addition products of cyclopentenone dienolate to levoglucosenone using α -allylcyclohexenamines, CH-acids, including nitro compounds, have been studied. The synthesis of the Michael adduct levoglucosenone and allyl cyclohexanone was carried out by the enamine method. An attempt to obtain the lithium enolate by acting on the Michael adduct of levoglucosenone and cyclohexanone LiNH₂ led to the selective reduction of the keto group of the cyclohexanone fragment to obtain 4 diastereomers and minor amounts of α '-allylated Michael adduct. Adducts of levoglucosenone with ethoxycarbonylcyclopentanone and -cyclododecanone were prepared using CH-acids in the presence of tetramethylguanidine (TMG) in CH₂Cl₂. Michael's linear nitro adducts were synthesized in toluene under the action of TBA-OH – K₂CO₃. In all cases, the reaction is accompanied by the formation of a diastereomeric mixture of adducts. The structure of the compounds obtained was established on the basis of the ¹H and ¹³C NMR spectra using two-dimensional standard correlation methods HHCosy, HSQC, HMBC, NOESY.

New Michael adducts are promising for subsequent use in the synthesis of medium and large modified lactones according to the previously developed scheme, as well as carbocyclic compounds for the synthesis of terpenoids and their analogues.

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