Reference Object Identifier – ROI: jbc-02/16-45-3-11 Subsection: Organic Chemistry. Publication is available for discussion in the framework of the on-line Internet conference "Butlerov readings". http://butlerov.com/readings/ Submitted on May 26, 2016.

Interaction of levoglucosenone with enamine of cyclohexanone at high pressure

© Yulia A. Khalilova, Lilia Kh. Faizullina, Yulia S. Galimova, Vadim A. Schamukaev, Rustam L. Safiullin, Leonid V. Spirikhin, and Farid A. Valeev^{*+}

Ufa Institute of Chemistry of the Russian Academy of Sciences. Prospect Oktyabrya, 71. Ufa, 450054. Fax: +7 (3472) 35-60-66. E-mail: sinvmet@anrb.ru

*Supervising author; ⁺Corresponding author

Keywords: levoglucosenone, 1,6-anhydro sugar, Michael reaction, high pressure, aldol condensation enamines.

Abstract

Enamines ketones react with electrophiles lead to the formation of α -alkylated derivatives. Reactions of pirrolidinenamines with acrylonitrile or ethyl acrylate can be accompanied by obtainment of dialkylation products. In the interaction of pirrolidinenamine and acrolein proceeds by tandem MIRC-conversion to form of a bicyclic compound containing of carbonyl bridge.

Interaction of levoglucosenone with linear 1,3-dicarbonyl compounds in some cases may also be accompanied by MIRC-transformations. Our attempts to carry out such of transformation by reacting levoglucosenone with pyrrolidine enamines of cyclopentanone or hexanone with good yields led to the realization of only the first step - the formation of Michael adducts.

Alternative intermolecular interaction adducts under the action of bases is also not observed.

It is known, that for to overcome of steric counteraction in reactions between activated cycloalkanone and a sterically hindered of ketones successfully uses high static pressure. Considering the in our case, the significance of this transformation for exit to the chiral carbocyclic compounds of medium and large sizes cycles we studied the possibility of using of high static pressure.

In carrying out the reaction between levoglucosenone and by pirollidincyclohexene in acetonitrilediazobicycloundecene (DBU) and a pressure of 10.000 atm. for 24 hours from a reaction mixture, consisting, mostly the degradation products of reacting compounds, isolated of Michael adducts with a yield of 7%. An analogous result with a yield of 4% was obtained using morpholine enamine of cyclohexanone. Changing of the reaction time and lowering the applied pressure to 6000 atm. did not lead to a fundamental change of the composition of the reaction mixture.

When trying to realization of the second stage of the theoretically possible of MIRC-transformation in the adducts under pressure of 6000 atm. in toluene in the presence of diazobicycloundecene (DBU) was isolated from the reaction mixture of product of intermolecular aldol condensation with 17% yield. The transformation also proceeds with a significant expansion of the reactants.

References

- [1] A.R. Tagirov, L.Kh. Faizullina, Sh.M. Salikhov, F.A. Valeev. Levoglucosenone in the synthesis of chiral benzodecanolide. Butlerov Communications, 2014. Vol.39. No.10. P.48-50. ROI: jbc-02/14-39-10-48
- [2] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, R. Terrell. The Enamine Alkylation and Acylation of Carbonyl Compounds. J.Am. Chem. Soc. 1963. Vol.85. P.207.
- [3] G. Opitz, H. Mildenberger, H. Suhr. Alkylierun von enaminen aus cyclischen ketonen. Liebigs Ann. Chem. 1961. Vol.649. No.26. P.47.
- [4] G. Stork, H.K. Landesman. A new ring enlargement sequence. J.Am. Chem. Soc. 1956. Vol.78. P.5129.
- [5] N.F. Firrell, P.W. Hickmott. 2,2-versus 2,6-Dialkylation of the Pyrrolidine Enamine of 2-Methylcyclohexanone with Electrophilic Olefins. Chem. Comm. 1969. P.544.
- [6] Y.A. Khalilova, L.V. Spirikhin, Sh.M. Salikhov, F.A. Valeev. Ehleutezides and their analogs. V. Lactones medium and large cycles based on levoglucosenone. J.OrgChem. 2014. Vol.50. P.125-135. (russian)
- [7] Y.A. Khalilova, A.R. Tahirov, O.Yu. Doronina, L.V. Spirikhin, Sh.M. Salikhov, F.A. Valeev. Reaction of 1,2- and 1,4-addition of cycloalkanes to levoglucosenone. J.OrgChem. 2014. Vol.50. P.118-124. (russian)

Kazan. The Republic of Tatarstan. Russia. © Butlerov Communications. 2016. Vol.45. No.3. 11

Full Paper _____ Yu.A. Khalilova, L.Kh. Faizullina, Yu.S. Galimova, V.A. Schamukaev, R.L. Safiullin, L.V. Spirikhin, and F.A. Valeev

- [8] L.Kh. Faizullina, I.M. Biktagirov, I.A. Zagreeva, M.G. Safarov, F.A. Valeev. Michael reaction of levoglucosenone and α -bromolevoglucosenone with nitroalkanes. Butlerov Communications. 2016. Vol.45. No.2. P.64-67. ROI: jbc-02/16-45-2-64
- [9] W.G. Dauben, R.A. Bunce. Organic Reactions at High Pressure. A Robinson Annulation Sequence Initiated by Michael Addition of Activated Cycloalkanones with Hindered Enones'. J.Org. Chem. 1983. Vol.48. P.4642.