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СИНТЕЗ ИНГИБИТОРОВ ДЛЯ НЕФТЕГАЗОВОЙ ОТРАСЛИ НА ОСНОВЕ ЭНАНТИОСЕЛЕКТИВНОГО АЛКИНИЛИРОВАНИЯ БЕНЗАЛЬДЕГИДА И ЕГО ПРОИЗВОДНЫХ ФЕНИЛАЦЕТИЛЕНОМ

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SYNTHESIS OF INHIBITORS FOR THE OIL AND GAS INDUSTRY BASED ON THE PROCESS OF ENANTIOSELECTIVE ALKYNATION OF BENZALDEHYDE AND ITS DERIVATIVES WITH THE PARTICIPATION OF PHENYLACETYLENE

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АННОТАЦИЯ

Сегодня особое внимание уделяется разработке методов синтеза биологически активных веществ на основе взаимодействия алкинов с органическими соединениями, содержащими в своих молекулах карбонильные, карбоксильные и гидроксильные группы, а также разработке технологий производства нового поколения местных лекарственных препаратов, способных заменить импорт. В данной работе впервые изучена энантиоселективная реакция алкинилирования бензальдегида и ряда его производных с использованием фенилацетилена в каталитической системе $Zn(OTf)_2/TBAF\cdot 3H_2O/NEt_3/MeCN$. *Систематически проанализировано влияние природы и количества растворителей, катализаторов, реагентов и субстратов на выход продукта при синтезе ароматических ацетиленовых спиртов.*

ABSTRACT

Today, special attention is paid to the development of methods for the synthesis of biologically active substances based on the interaction of alkynes with organic compounds containing carbonyl, carboxyl and hydroxyl groups in their molecules, and the development of technologies for the production of a new generation of local drugs that can replace imports. In this work, for the first time, the enantioselective alkynylation reaction of benzaldehyde and a number of its derivatives using phenylacetylene in the $Zn(OTf)_2/TBAF\cdot 3H_2O/NEt_3/MeCN$ *catalytic system was studied. The effect of the nature and amounts of solvents, catalysts, reagents and substrates on the yield of the product in the synthesis of aromatic acetylene alcohols was systematically analyzed.*

Ключевые слова: *ингибиторы коррозии, нефтегазовая отрасль, энантиоселективное алкинилирование, бензальдегид, фенилацетилен, ацетиленовые спирты, органический синтез.*

Key words: *corrosion inhibitors, oil and gas industry, enantioselective alkynylation, benzaldehyde, phenylacetylene, acetylenic alcohols, organic synthesis.*

INTRODUCTION

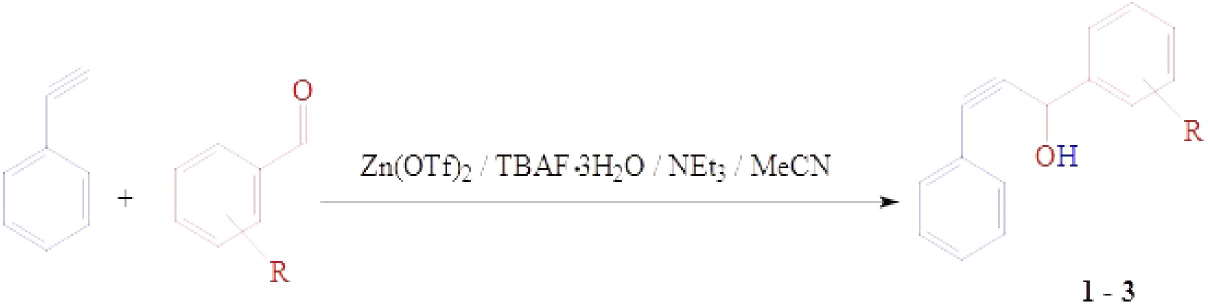
Today, the production of highly demanded preparations is increasing year by year in the world through the introduction of new innovative technologies in the synthesis of organic substances based on hydrocarbons. The use of active catalysts in the synthesis of acetylene alcohols from natural raw materials, the implementation of technological calculations for process control, the use of acetylene alcohols in the production of high-quality preparations in the rubber and technical, paint and varnish industries, in the medical field and in agriculture, and the synthesis of many new substances by introducing functional groups into their composition are of great importance. The presence of a triple bond in the molecule of acetylene alcohols, a hydroxyl group, a mobile active hydrogen in the hydroxyl group, as well as substituents and functional groups of various nature, gives them important properties. It is known that acetylene alcohols undergo an exchange reaction at the expense of hydrogen in the hydroxyl group, therefore, valuable organic compounds necessary for various industries are synthesized from such alcohols.

LITERATURE REVIEW AND METHODS

In the world, research is being conducted in a number of priority areas in the field of acetylene compound chemistry, including the synthesis of acetylene alcohols by catalytic ethynylation of elemental organic compounds, amines, aldehydes, and ketones with terminal alkynes using selective nanocatalysts NaOH/EtOH/DMSO, $InNTf_2/BuOH/CH_2Cl_2$, and $Pd(Ph_3P)_2Cl_2/CuI/Et_3N$ [1-4].

Asymmetric alkynylation of some aldehydes of various nature, including 3-methylbutanal, cyclohexanal, benzaldehyde, *p*-fluorobenzaldehyde, *m*-methoxybenzaldehyde, *3*-furancarbaldehyde and *3*-thiophenaldehydes, was carried out in a weakly acidic medium at 40 °C in a complex catalytic system $InBr_3/BINOL/Cu_2NMe/CH_2Cl_2$ at intervals of 9-48 hours using phenylacetylene and its homologues, and the corresponding acetylenic alcohols were synthesized in 80-95% yield [5].

Based on the data presented in the literature, the following scheme of the alkynylation reaction of the aldehydes selected as the object of the study in the presence of phenylacetylene was proposed [6].



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R= – $_{о}$Me (**1**); – $_{о}$ OMe (**2**); – $_{м}$ OMe (**3**).

Results and discussion

According to the purpose of the study, the effect of the nature of the selected aldehydes, the spatial structure of their molecules, optical activity and the nature of the substituents on the yield of acetylenic alcohols was studied. The effect of temperature, reaction time, nature of solvents and catalysts, concentration and molar amounts of starting materials on the course of chemical processes and product yield was systematically analyzed. Initially, the effect of the amount of catalyst on the yield of acetylenic alcohols was studied. In this case, the total amount of $Zn(OTf)_2$ and $TBAF\cdot 3H_2O$ selected as catalysts was taken in the ratio of 0.025 ÷ 0.075 mol.

When the total amount of $Zn(OTf)_2/TBAF\cdot 3H_2O$ was increased from 0.025 to 0.05 mol, the yield of acetylenic alcohols increased, including from **1**– 52 to 74%, from **2**– 44 to 68% and from **3**– 57 to 79%. The amount of NEt_3 was taken in a ratio of 1.78:1 to the total amount or mass of $Zn(OTf)_2/TBAF\cdot 3H_2O$ (0.05 mol), and in this case, the catalytic activity of the catalysts and the susceptibility of the molecules in the system to the reaction passed through a maximum.

The duration of the reaction for the synthesis of acetylenic alcohols was also studied. The nature of the substituents in the molecule of the selected aldehydes, including the spatial effect of the shift of the electron cloud of the carbonyl group towards the oxygen atom, and the strong (high) polarization of the carbonyl group, resulted in an increase in the electron density at the oxygen atom.

This condition, in addition to determining the reactivity of aldehydes (facilitating the formation of the C-O bond under the influence of polar particles in the system), created sufficient conditions for the rapid and complete completion of the reaction or the addition of phenylacetylene. The reaction was initially carried out for 60 minutes, and the synthesized aromatic acetylenic alcohols were formed in high yield.

The effect of the molar amounts of substrate and reagents on the alkynylation reaction of selected aldehydes was studied.

According to the results of the study, acetylenic alcohols were synthesized with the highest yield when the phenylacetylene:aldehyde ratio was 2:1. During the reaction, when the amount of phenylacetylene was increased threefold compared to the amount of aldehydes, a large amount of intermediate products (π-complex) and triethylamine were completely consumed in the system, resulting in the formation of the trifluoromethylsulfonate salt of phenylacetylene, which sharply reduced the ability of $TBAF\cdot 3H_2O$ to fully demonstrate its catalytic ability, which led to the formation of a relatively low amount of aromatic acetylenic alcohols.

In addition, $TBAF\cdot 3H_2O$ was insufficient to activate almost half of the phenylethynyltrifluoromethylsulfonate alcohol with fluorine to form the $[Ph{\equiv}ZnFOTf]\text{-}[NBu_4]^+$ complex, resulting in an increase in the amount of by-products (mainly alcohol compounds) in the system. Similar to the above cases, the unreacted phenylacetylene partially combined with the aromatic acetylene alcohols formed as a result of the reaction to form vinyloxy compounds, which reduced the selectivity of the reaction.

Although the starting materials were taken in equimolar ratios, it was not possible to convert the starting materials into complete alcohols, but a sharp decrease in product yield was not observed. It was also found that a change in the process regime was required to convert the by-products formed in the system into the expected substances.

CONCLUSIONS

For the first time, 3-phenyl-1-o-tolylpropyn-2-ol-1, 1-(2-methoxyphenyl)-3-phenylpropyn-2-ol-1, and 1-(3-methoxyphenyl)-3-phenylpropyn-2-ol-1 were synthesized in the $Zn(OTf)_2/TBAF \cdot 3H_2O/NEt_3/MeCN$ catalytic system.

Based on the yield of acetylenic alcohols, the following relative activity series was determined according to the nature, location, and steric interaction of the substituents in the aldehyde molecule in the alkynylation reactions: 1-(2-methoxyphenyl)-3-phenylpropyn-2-ol-1 < 3-phenyl-1-*o*-tolylpropyn-2-ol-1 < 1-(3-methoxyphenyl)-3-phenylpropyn-2-ol.

REFERENCES

1. Sobenina L.N., Petrova O.V., Tomilin D.N., Ivanov A.V., Shcherbakova V.S., Mikhaleva A.I., Trofimov B.A. First example of Favorskii ethynylation of pyrrolecarbaldehydes: Synthesis of 1-(1-methyl-1*H*-pyrrol-2-yl)prop-2-yn-1-ol. Russian Journal of Organic Chemistry, 2015, Volume 51, Issue 1, pp 51-53.

2. Roger Fassler, Craig Tomooka, Doug Frantz, Erick Carreira Infrared spectroscopic investigations on themetallation of terminal alkynes by $Zn(OTf)_2$. PNAS, 2004, Volume 101, Issue 16, pp. 5843-5845.

3. Chandrasekar Praveen, Paramasivan T. Perumal Extrapolation of the gold-catalyzed cycloisomerization to the palladium-catalyzed cross-coupling cycloisomerization of acetylenic alcohols for the synthesis of polysubstituted furans: Scope and application to tandem processes. Chinese Journal of Catalysis 2016, Volume 37, №2. rr. 288-299.

4. Barry M. Trost, Andrew H. Weiss The Enantioselective Addition of Alkyne Nucleophiles to Carbonyl Groups. Advanced Synthesis & Catalysis, 2009, Volume 351, Issue 7-8, rr.963-983.

5. Ryo Takita, Kenichiro Yakura, Takashi Ohshima, Masakatsu Shibasaki Asymmetric Alkynylation of Aldehydes Catalyzed by an In(III)/BINOL Complex. Journal of the American Chemical Society, 2005, Issue 127, pp. 13760-13761.

6. Jarryl M D'Oyley, Abil E Aliev, Tom D Sheppard Regioselective Dihalohydration Reactions of Propargylic Alcohols: Gold-Catalyzed and Noncatalyzed Reactions. Angewandte Chemie International Edition, 2014, Volume 53, Issue 40, pp. 10747–10750.

7. Vladimir V. Voronin, Maria S. Ledovskaya, Alexander S. Bogachenkov, Konstantin S. Rodygin, Valentine P. Ananikov Acetylene in Organic Synthesis: Recent Progress and New Uses. Molecules 2018, Issue 23, pp. 2442-2448.