# SYNTHESIS OF ACETYLENE ALCOHOLS IN DIFFERENT CATALYTIC SYSTEMS

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**Abstract:** In this study, with the participation of such complex catalytic systems as 3,3'-$Ph_2$BINOL-2Li/Ti($O^iPr$)$_4$/$Et_2Zn$ and Zn(OTf)$_2$/TBAF•3$H_2O$, some ketones with a carbonyl group in the molecule - cyclopentanone, cyclohexanone, camphor , adamantanone, methyl butyl ketone, methyl ethyl ketone, methyl isopropyl ketone, methyl tert-butyl ketone, acetophenone, methyl *p*-tolyl ketone, methyl mesityl ketone, methyl *β*-naphthyl ketone, methyl furyl ketone, methyl thienyl ketone, methyl pyridinyl ketone and methyl 2-chlorothiophenyl ketone terminal alkynes – acetylene, hexine, octine and phenylacetylene by alkynylation reaction acetylene alcohols with high biological activity were synthesized. The relative efficiency of acetylenic alcohols synthesis was established based on the structure, nature, and chemical activity of ketone molecules, the nucleophilic addition reaction of ketones, and their influence on the product yield. The process of synthesizing acetylenic alcohols in selected systems and the factors affecting the reaction, such as temperature, reaction duration, catalyst, promoter and solvent nature, quantities of reagents and substrates, types and quantities of intermediate and by-products, were systematically studied and analyzed based on the obtained results. The activation energies of the performed reactions were determined, and the kinetics of chemical changes were analyzed. The efficiency, selectivity, and stability of catalytic systems were determined, and a relative catalytic efficiency sequence was proposed based on their influence on the reaction and product yield. The purity and structure of the synthesized compounds were investigated using modern physical and chemical research methods, specific constants were determined, and energetic and quantum chemical characteristics were calculated, including the charges of atoms in the molecules, electron density, and optical properties. The synthesized acetylenic alcohols were also applied in practice as components for anti-foaming agents in oil and gas industries and as inhibitors for complexation of heavy metals in natural gas compositions.

**Keywords:** Terminal alkynes, aliphatic, aromatic, cyclic and heterocyclic ketones, nucleophilic coupling, product yield.

## 1 INTRODUCTION

In the world, the oil and gas, chemical, rubber-technical, textile, and pharmaceutical industries are considered the main driving forces of the economy, and the synthesis of numerous new preparations for the development of these fields is of great importance. In particular, the wide utilization of acetylenic alcohols in the oil and gas, chemical, rubber-technical, textile, and pharmaceutical industries for obtaining high-quality preparations is highly significant. Currently, in developed countries, systematic research is being conducted on the synthesis methods [1-4] and production technologies of acetylenic alcohols and their derivatives that possess biological activity, including aliphatic, aromatic, cyclic, and heterocyclic substituents. The research aims to investigate their physical, chemical, energetic, and mechanical properties, chemical transformations, and activities, as well as to improve the methods for producing new ionites, biocides, inhibitors, solvents, and polymers based on them in the industry [5-8].

## 2. RESEARCH METHODOLOGY

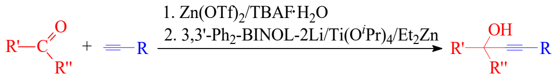
$^1H$ and $^{13}C$ NMR spectra were recorded on Bruker Avance (400 and 100.6 MHz, respectively) spectrometer at 20-25 $^oC$ in $CDCl_3$, acetone-$d_6$, $C_6D_6$, solution using the solvent line as an internal reference; IR specta of the synthesized compounds were recorded on The Thermo Scientific Nicolet iS50 FT-IR spectrometer (Raman module, USA). Progress of reactions and purity of the synthesized compounds were examined by means of TLC analysis on Merck Silica gel 60 $GF_{254}$ plates and visualization in UV light.

## 3 ANALYSIS OF WORKS RELATED TO THE TOPIC

Nowadays, various complex catalytic systems are being utilized by world scientists to synthesize acetylenic alcohols through enantioselective alkynylation reactions of compounds containing a carbonyl group in their molecular structure [9-13]. For instance, Lin Pu and his research team have investigated the enantioselective alkynylation reactions of benzaldehyde and its derivatives with terminal alkynes using a complex catalytic system prepared with 1,1'-bi-2-naphthol ((*S*)-BINOL) and titanium tetraisopropoxide ($Ti(O^iPr)_4$) as catalysts. Under room temperature conditions, after a 4-hour reaction time, acetylenic alcohols were synthesized with a minimum yield of 92% when using various solvents such as TGF, PhMe, or dichloromethane, and a maximum yield of 71-81% when using diethyl ether. Additionally, the formation of secondary products, namely cyclic ethers, was identified [14-15]. X. Fu carried out the alkyne reaction of N-benzylisatin with phenylacetylene in the presence of AgCl complex salts of N-heterocyclic carbenes and diisopropylethylamine as catalysts at a temperature of 40 °C for 120 minutes, resulting in the synthesis of 3-hydroxy-3-ethynylindolin-2-one with a yield of 98% [16-18]. Karen and his research team employed a mechanochemical method with KOH as a catalyst to carry out the alkyne reaction of diphenylketone with $CaC_2$, leading to the synthesis of 1,1,4,4-tetraphenylbutane-2,3-diol-1,4 with a yield of [19-20].

## 4 ANALYSIS AND RESULTS

In this work, the synthesis of acetylenic alcohols in a controlled manner was carried out using selected ketones - cyclopentanone, cyclohexanone, camphor, adamantane, methylbutanone, methyl ethyl ketone, methyl isopropyl ketone, methyl cyclobutyl ketone, acetophenone, methyl-*p*-tolyl ketone, methyl mesityl ketone, methyl-*β*-naphthyl ketone, methyl furyl ketone, methyl thienyl ketone, methyl pyridinyl ketone, and methyl-2-thioxophenyl ketone - as nucleophilic reactants with the assistance of complex catalytic systems such as 3,3'-$Ph_2$BINOL-2Li/$Ti(O^iPr)_4$/$Et_2Zn$ and $Zn(OTf)_2$/TBAF•$3H_2O$. The general scheme of the reaction, proposed based on literary sources, is as follows:

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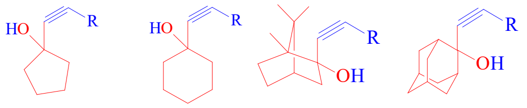

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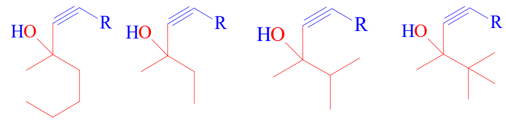

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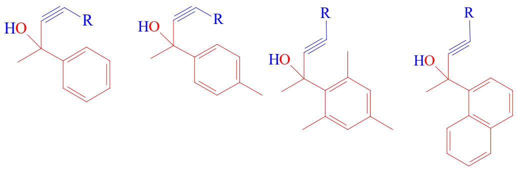

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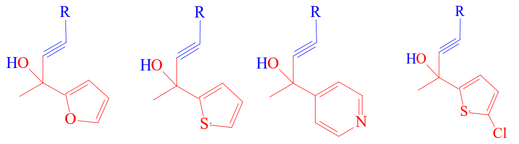

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Various factors such as temperature, reaction duration, solvent nature, and the initial amount of starting materials were analyzed in a systematic manner to understand their influence on the process of synthesizing acetylenic alcohols using complex catalytic systems. The importance of catalysts employed to enhance product yield and reaction efficiency was investigated [21-22]. Based on the results obtained, a relative catalytic activity sequence for the complex catalytic systems was established as follows:

3,3'-$Ph_2$BINOL-2Li/$Ti(O^iPr)_4$/$Et_2Zn$ < $Zn(OTf)_2$/TBAF•$3H_2O$

The structure of ketone molecules, the size and conformation of cyclic radicals attached to the >C=O group, the influence of their solubility and phase location on the progress of the reaction, the reactivity sequence of ketones, and the regularities in the formation of aromatic acetylenic alcohols were determined, along with suggested reaction mechanisms. The relationship between the number of rings in the ketone molecule, the size of radicals, and their impact on the reaction and product yield was established. According to the findings, the reactivity decreased in the order of acetophenone < methyl ethyl ketone < cyclopentanone < cyclohexanone < methylbutanone < methyl isopropyl ketone < methyl-β-naphthyl ketone < methyl-p-tolyl ketone < methyl cyclobutyl ketone < methyl furyl ketone < methyl pyridinyl ketone < camphor < adamantane < methyl thienyl ketone < methyl mesityl ketone < methyl-2-thioxophenyl ketone. Kinetic parameters of the investigated reactions were determined, the activation energies for the formation of aromatic acetylenic alcohols were identified, the specific properties of the synthesized compounds were characterized, including their electronic structure, distribution of charges within the molecule, quantum chemical, and molecular dynamics properties.

The synthesized terminal acetylenic alcohols were utilized as inhibitors to separate sulfur compounds from the composition of natural gas products at the “Muborak Gas Processing Plant” JSC. This method enabled the separation of 42-58% of elemental sulfur, hydrogen sulfide, mercaptans, sulfides, and disulfides, which are hazardous sulfur compounds, from the composition of natural gas products, thus improving the quality of natural gas, reducing the amount of toxic sulfur compounds emitted into the environment, and increasing the operational reliability and durability of technological equipment and facilities. The application of the synthesized acetylenic alcohols was also recommended for their use as agents in the rubber and technical industry, providing an effective means of suppressing the agglomeration of sulfur compounds and improving resource efficiency and ecological safety.

The inhibitory properties of the synthesized aromatic acetylenic alcohols against components that form salt deposits in circulating water systems in industrial plants were investigated. The water hardness of the “Ohangaron Cement” JSC circulating water systems was determined. Experiments were conducted with solutions of aromatic acetylenic alcohols at concentrations of 5.0-25.0 mg/l. The results indicated the effective inhibitory activity of aromatic acetylenic alcohols against components that form salt deposits in circulating water systems, with a selective retention of metal cations (87.0%). Aromatic acetylenic alcohols were utilized as inhibitors against the formation of salt deposits in circulating water systems at the "Ohangaron Cement" JSC.

**CONCLUSION AND RECOMMENDATIONS**

In this study, the nucleophilic addition reaction of various natural ketones with aliphatic and aromatic terminal alkynes was investigated, and the influence of different catalysts under specific conditions was studied. Based on the obtained results, a new catalytic system, $Zn(OTf)_2/TBAF \cdot 3H_2O$, is proposed for the efficient synthesis of acetylenic alcohols.

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