SYNTHESIS AND DEMETALLIZATION OF 1-ETHYNYLCYCLOHEXANOL

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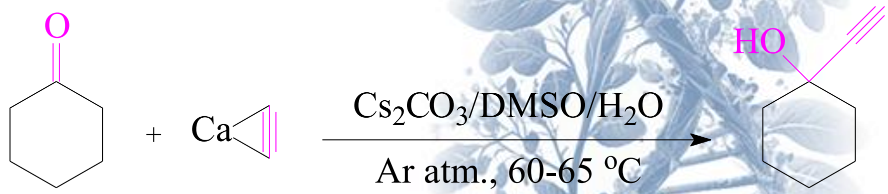
KALIT SO'ZLAR:
cyclohexanone, calcium carbide, acetylene alcohol, demirization process, diols, reaction scheme, product yield.

ANNOTATSIYA:

Nowadays, fields such as pharmacology, medical chemistry, and organic synthesis are developing rapidly in order to create new pharmacological drugs and valuable biologically active organic compounds. In this work, acetylene alcohol with high chemical activity - 1-ethinylcyclohexanol was synthesized in the catalytic system Cs2CO3/DMSO/H2O and the effect of the amount of substance on the product yied was studied. As well as for the first time in the CuCl/TMEDA/CCl4/MeOH catalytic system of 1-ethynylcyclohexanol, an demirization process was carried out to synthesize containing two to three bonds and hydroxyl groups, unsaturated diol – 1-(4-(1-hydroxycyclohexyl)butadiynyl-1,3)cyclohexanol.

The presence of triple bonds and hydroxyl groups in acetylenic alcohols and diols enables them to readily and easily undergo nucleophilic substitution reactions [1]. Therefore, these compounds have been widely used as key reagents in the synthesis of a range of valuable biologically active organic substances, including alkaloids, pheromones, prostaglandins [2] and vitamins, as well as in the production of lipoxygenase inhibitors that are employed as potential therapeutic agents against serious human diseases such as asthma and cancer, which further increases the significance of this class of compounds [3].

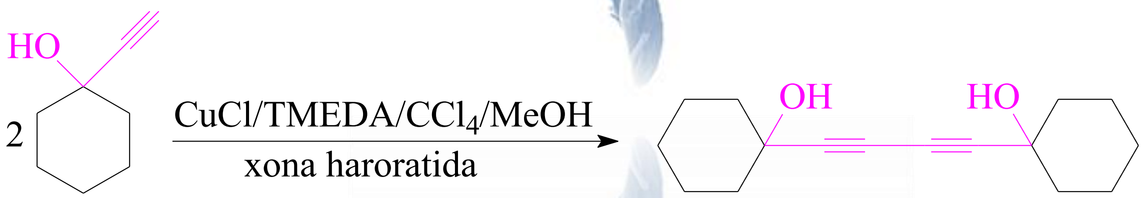
In this work, the synthesis of terminal acetylene alcohols and the formation of their conversion into diols through a demerization process, driven by the mobile hydrogen atom at the sp–C–H bond, were envisaged. Acetylene alcohols were synthesized via nucleophilic addition to cyclohexanone using calcium carbide as an acetylene source under mild conditions. The reaction was carried out in a highly basic Cs_2CO_3/DMSO/H_2O catalytic system under an argon atmosphere at 60–65 °C, resulting in the efficient synthesis of 1-ethynylcyclohexanol. The optimal molar ratio of cyclohexanone to calcium carbide was determined to be 1:2.7, respectively. The reaction scheme is proposed as follows [4].



When cyclohexanone and calcium carbide were used in a 2:2.7 molar ratio, the 1-ethynylcyclohexanol formed in the process was observed to further react with the ketone, leading to the formation of an additional by-product,

1-(2-(1-hydroxycyclohexyl)ethynyl)cyclohexanol

The demetallization of the synthesized 1-ethynylcyclohexanol was carried out at room temperature in the CuCl/TMEDA/CCl_4/MeOH catalytic system, resulting in the formation of 1-(4-(1-hydroxycyclohexyl)butadiyn-1,3)cyclohexanol with a yield of 64.7%. The proposed reaction scheme is as follows [5].



The synthesized acetylene alcohol, its diol, and demetallization products were characterized in terms of some physical properties, composition, and structure using IR, ^{1}H NMR, and ^{13}C NMR spectroscopy on a Bruker UltraShield™ 400 MHz instrument.

1-etinilsiklogeksanol – colorless liquid, R_f = 0,67. ^{1}H – YaMR (400 MHz, $CDCl_3$) □□2.71 (s, C≡CH), 2.44 (s, OH), 1.89-1.85 (t, 2H), 1.67-1.61 (m, 2H), 1.54-1.43 (m, 5H), 1.21 (m, 1H). ^{13}C – YaMR (101 MHz, $CDCl_3$) □ 87.35, (C≡CH), 76.37, 68.07, 39.27, 24.64, 23.1.

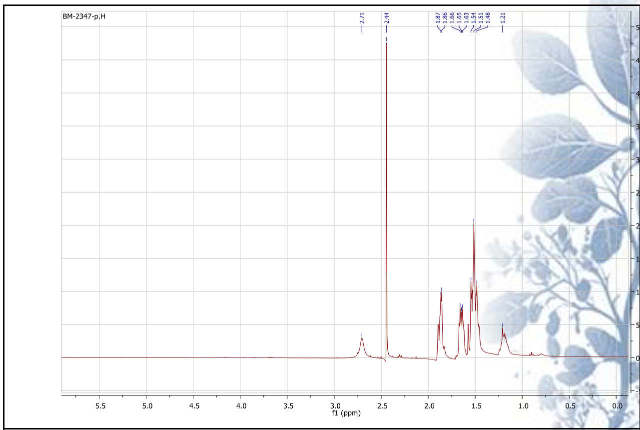
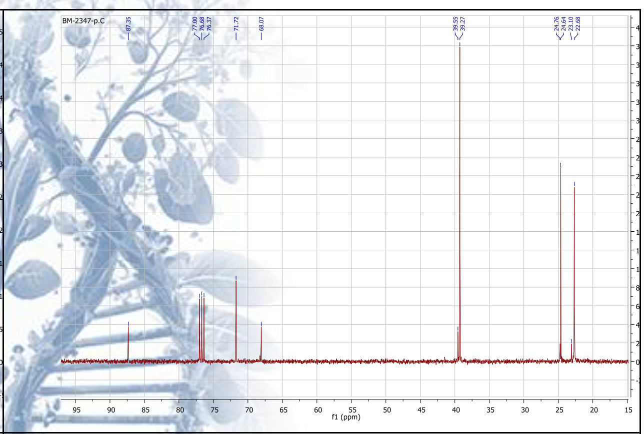
	

Figure-1. ^{1}H - NMR spectrum of 1-etinilsiklogeksanol	**Figure-2. ^{13}C - NMR spectrum of 1-etinilsiklogeksanol**

1-(2-(1-gidroksosiklogeksil)etinil)siklogeksanol – colorless liquid, R_f = 0,54. ^{1}H – YaMR (400 MHz, $CDCl_3$) □□2.67-2.61 (d, OH), 1.93-1.69 (t, 8H), 1.59-1.47 (m, 8H), 1.24-0.82 (m, 4H). ^{13}C – YaMR (101 MHz, $CDCl_3$) □ 87.53, (C≡CH), 76.94, 68.13, 40.41, 39.80, 24.81, 23.11.

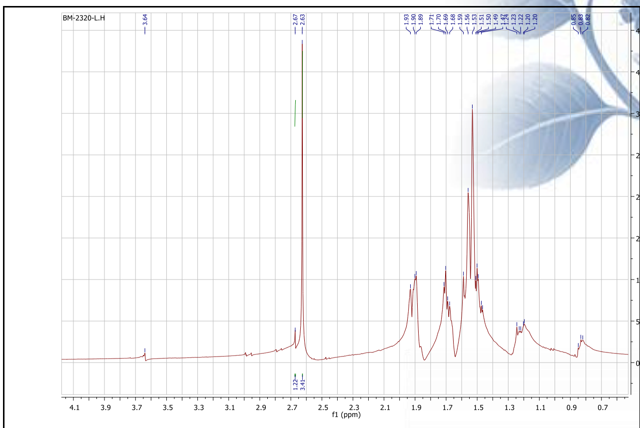
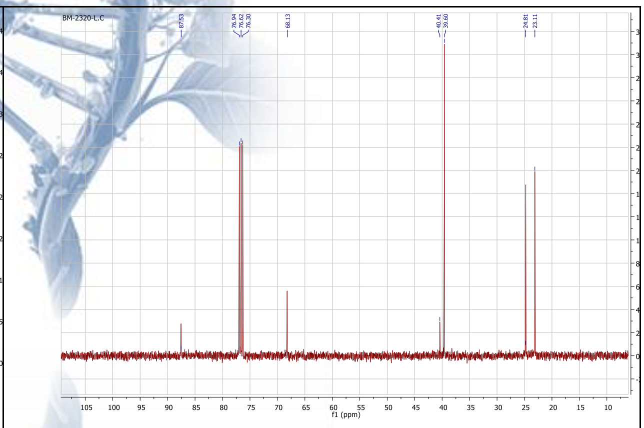
	

Figure-3. ^{1}H - NMR spectrum of 1-(2-	**Figure-4. ^{13}C - NMR spectrum of 1-(2-**

(1-gidroksosiklogek-sil)etinil)siklogeksanol	**(1-gidroksosiklogek-sil)etinil)siklogeksanol**

1-(4-(1-gidroksosiklogeksil)butadinil-1,3)siklogeksanol - yellow-colored oily liquid, R_f = 0,54. ^{1}H – YaMR (400 MHz, $CDCl_3$) □□3.71-3.24 (dd, 2OH), 3.02-2.25 (m, 8H), 1.90-1.62 (m, 8H), 1.59-1.25 (m, 4H). ^{13}C – YaMR (101 MHz, $CDCl_3$) □ 87.52-82.66 (C≡CH), 76.92, 68.72, 39.64, 39.24, 24.76, 23.09, .

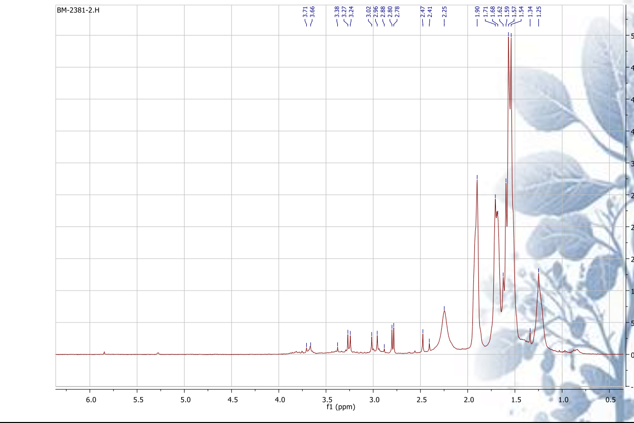
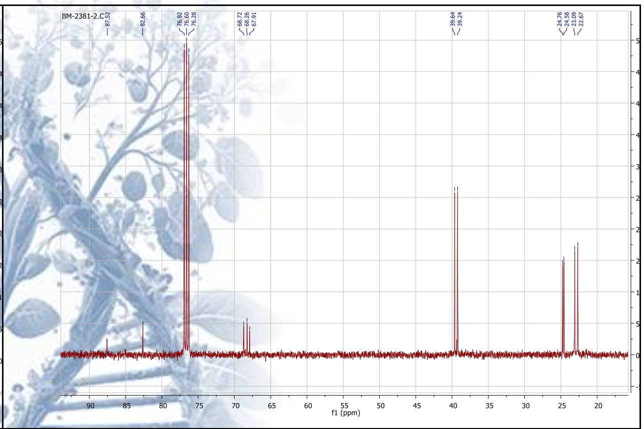
	

Figure-5. ^{1}H - NMR spectrum of 1-(4-(1-gidroksosiklogek-sil)butadinil-1,3)siklogeksanol	**Figure-6. ^{13}C - NMR spectrum of 1-(4-(1-gidroksosiklogek-sil)-butadinil-1,3)siklogeksanol**

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