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REACTION OF 3,5-DIMETHYLHEPTADIINE-1,6-DIOL-3,5 WITH ACETYLENE BY HETEROGENEOUS-CATALYTIC METHOD

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Abstract:

The catalyst was obtained by impregnating an alkaline solution with activated carbon. The vinylation process with 3,5-dimethylheptadiine-1,6-diol-3,5 with acetylene was carried out in a heterogeneous catalytic manner. The influence of the catalytic nature of the starting materials on the yield of vinyl ethers, the molecular ratio, the temperature and duration of the reaction was investigated.

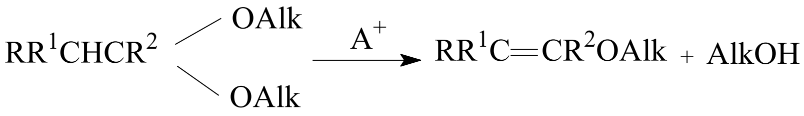
Keywords: Acetylene, heterogeneous catalysis, 3,5-dimethylheptadiine-1,6-diol-3,5, activated carbon, catalyst.

INTRODUCTION

Many inorganic and organic substances are synthesized using heterogeneous catalysis. In heterogeneous catalysis, the catalyst and the reagent form different phases, and in this case the reaction proceeds at the boundary surface. Now many scientists synthesize new organic substances heterogeneously catalytically [1,4].

For the synthesis of various vinyl esters for research purposes, Watanabe's method of transvinylation of available vinyl esters of alcohols and acids with other alcohols and diols in the presence of mercury, palladium, or iridium salts is widely used [5].

The second most important method for the synthesis of vinyl alkyl ethers is the acetal dealkoxylation reaction [6], which is usually accelerated by using various acid catalysts:



$$RR^1CHCR^2(OAlk)_2 \xrightarrow{A^+} RR^1C{=}CR^2OAlk + AlkOH$$

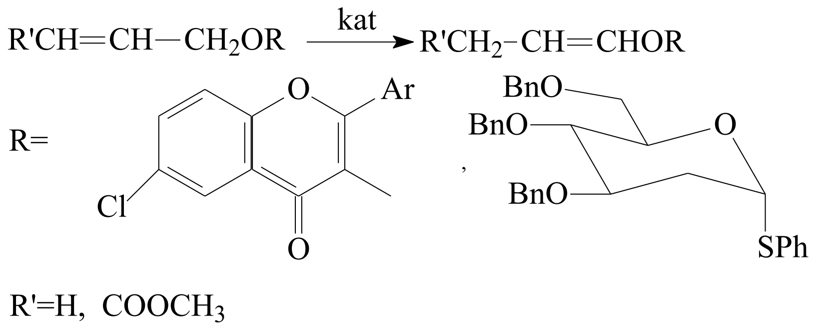
R,R^1,R^2=H,Alk, OAlk,ClAlk; R=H, R^1+R^2=cyclo-Alk

$$A^+ = H_3PO_4,\quad H_3PO_4 + C_5H_5N,\quad CF_3SO_3SiMe_3 + Et_3N,$$

$$p\text{-}MeC_6H_4SO_3H,\quad AlCh,\quad FeCl_3$$

1,2-divinyloxy-1- and 1.2-divinyloxy-2-propenes (I), (II) were first obtained with a total yield of 68% upon heating (100-110 ° C) glycerol and acetylene in the superbasic KOH-DMSO, successfully proven in vinylation reactions. The synthesis of propenes (I) and (II) was carried out in an autoclave under acetylene pressure using a significant excess (90-130 mol/%) of KOH with respect to glycerol. Under these conditions, 4-vinyloxymethyl-2-methyl-1.3-dioxolane is also formed with a yield of up to 9% [7].

β-substituted vinyl ethers can also be obtained by isomerization of allyl ethers under the action of strong bases [8] or metal complex catalysts [9]. According to this method, in the presence of ruthenium complexes, monoallyl ethers of diols are easily isomerized to the corresponding monovinyl (1-propenyl) ethers of diols [10]:



kat= BuOK-DMSO, $(Ph_3P)_3RhCl_2$, $(Ph_3P)_3RhCl$ n-BuLi, hv

For the synthesis of various vinyl esters for research purposes, Watanabe's method of transvinylation of available vinyl esters of alcohols and acids with other alcohols and diols in the presence of mercury, palladium, or iridium salts is widely used [5].

It is known that the vinylation of saturated alcohols has been well studied, while that of acetylenic alcohols and diols has been insufficiently studied. Our research goal is to develop a technology for producing acetylenic diols and their vinyl esters.

OBJECTS AND RESEARCH METHODS

Method for preparing heterogeneous catalysts.

To obtain heterogeneous vinyl 3,5-dimethylheptadiine-1,6-diol-3,5 impregnated with activated carbon as a catalyst, KOH and NaOH were used. The catalyst was prepared by adsorption on activated carbon. For this, 21.43 g of KOH was added to 50 ml of water and a 30% solution was prepared. The prepared KOH solution was added to 50 g of activated carbon (AC-U) in a porcelain crucible and slowly heated with a glass rod, stirring constantly. Water evaporates when heated. Then the prepared catalyst was dried in an oven at 160 °C for 4 hours. The resulting catalyst is purified from small particles. The prepared catalyst was used for the reaction.

Method of heterogeneous catalytic vinylation of 3,5-dimethylheptadiine-1,6-diol-3,5. The process of obtaining vinyl 3,5-dimethylheptadiine-1,6-diol-3,5 by the heterogeneous catalytic method was carried out in a vertical reactor. In this process, potassium hydroxide (C_{active}/KOH) absorbed by activated carbon was used as a catalyst, and acetylene was used as a vinyl agent.

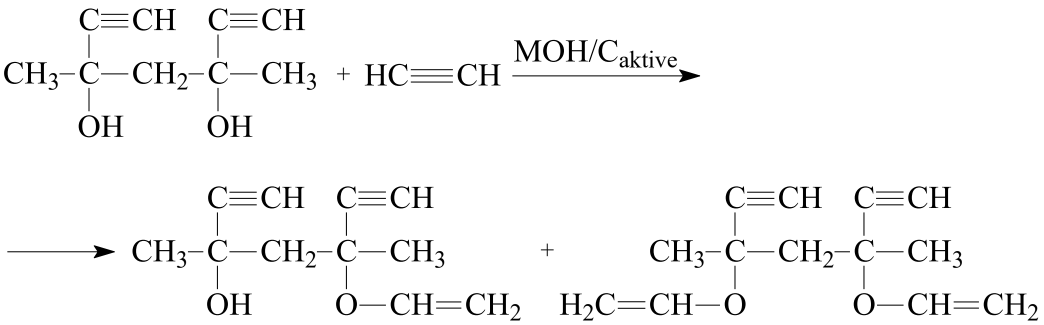
Acetylene is fed from a graduated gasholder to a mixer, and then to a reactor through suction filters and a rheometer. 3,5-dimethylheptadiine-1,6-diol-3,5 is dissolved in the presence of a dissolving dimethyl sulfoxide through a dispenser and fed through a mixer into the reactor. A vapor-gas mixture formed at a high temperature is fed to the catalyst when the inert bed reaches a predetermined temperature in the upper bed of the filled reactor. In this case, diffusion of acetylene over the catalyst surface is observed. The temperature in the reactor is controlled by a thermocouple and regulated by an autotransformer. The resulting product is cooled to room temperature in a refrigerator and sent to an extraction device. The recovered product is heated to a certain temperature in a rectifier to separate the target product and organic particles formed during the reaction.

The catalyst formed during the synthesis is extracted three times with diethyl ether, the solvent is distilled off from the organic portion, and the residue is separated into fractions in a vacuum.

RESULTS AND DISCUSSION

The reactions of the combination of acetylene with other substances, in which the role of predominantly homogeneous and heterogeneous catalysts is important, have been studied. The process of synthesis of vinyl esters based on the catalytic component 3,5-dimethylheptadiine-1,6-diol-3,5, formed by alkalis with activated carbon, has been investigated.

At the same time, the process of heterogeneous catalytic synthesis of 3,5-dimethylheptadiine-1,6-diol-3,5 in vinyl ethers was studied, while a slightly higher yield of vinyl ethers was observed. The reaction scheme of the process is presented as follows.



The nature and mass fraction of catalysts, the ratio of the moles of the starting materials, the effect of temperature and reaction time on the yield of vinyl esters in the heterogeneous vinyl reaction of 3,5-dimethylheptadiine-1,6-diol-3,5 were studied. Acetylene feed rate, the rate of introduction of the 3,5-dimethylheptadiine-1,6-diol-3,5 system, energy consumption, accumulation of starting materials, including acetylene, in catalysts, process control, cooling, separation, drying, purification, the formed catalyst was studied and separation, recovery of catalysts, the duration of their operation, instrumental accounting, simultaneously occurring several chemical transformations. The influence of the nature of the catalyst on the yield of vinyl esters and the ratio of the amount of starting materials to mole was studied using NaOH/C_{active} and KOH/C_{activ} as catalysts. The reaction was carried out at a temperature of 160 °C for 2 hours. The table shows that the yield increases with increasing acetylene content compared to 3,5-dimethylheptadiine-1,6-diol-3,5. For example, in the presence of a NaOH/C_{active} catalyst, the formation of vinyl esters increased by 21.8% with an increase in the amount of 3,5-dimethylheptadiine-1,6-diol-3,5 and acetylene in a ratio of 1:1 to 1:4.

Table 1

Influence of 3,5-dimethylheptadiine-1,6-diol-3,5 on the yield of vinyl esters by the nature of the catalyst and the molecular weight of the starting materials

diol: acetylene *μ*	**Yield of 3,5-dimethylheptadiine-1,6-diol-3,5-vinyl ethers,%**	
	Monovinyl ether	**Divinyl ether**
Catalyst KOH/C_{aktive}		
4:1	36.4	12.1
3:1	32.3	19.2
1:1	14.2	53.1
1:3	8.7	76.2
1:4	6.2	76.8
Catalyst NaOH/C_{aktive}		
1:1	49.2	18.2
1:3	70.1	10.3
1:4	71.0	8.2

From table. 1 shows that an increase in the amount of 3,5-dimethylheptadiine-1,6-diol-3,5 in relation to acetylene has a negative effect on the product yield, i.e. the object of research is 53.1%. yield 49.2% in equimolar ratio of diol and acetylene. Mono- and divinyl ethers of 3,5-dimethylheptadiine-1,6-diol-3,5 in the ratio of 3,5-dimethylheptadiine-1,6-diol-3,5 to acetylene 4 times more (1:4), synthesized with high yield.

As the amount of acetylene increases in relation to 3,5-dimethylheptadiine-1,6-diol-3,5, its vinyl esters are formed in high yield, diffusion of acetylene to the catalyst, acetylene first undergoes physical adsorption and then to chemical adsorption. The adsorbed acetylene molecule forms a π-complex with a metal cation, the active site of the catalyst, to form an intermediate compound, which combines with 3,5-dimethylheptadiine-1,6-diol-3,5 to form mono- and divinyl ethers. Saturation of 3,5-dimethylheptadiine-

1,6-diol-3,5 alcohols with acetylene forms a compound with the catalyst fed to the reactor with 3,5-dimethylheptadiine-1,6-diol-3,5, which prevents the action of acetylene on vinyl esters low yields were observed.

Based on the data on the influence of the molar ratios of the catalysts and starting materials used on the product yield, the ratios of 3,5-dimethylheptadiine-1,6-diol-3,5 and acetylene 1:3 process were chosen as alternative conditions for the reaction. According to his data, the yield of 3,5-dimethylheptadiine-1,6-diol-3,5 in KOH/C_{active} compared to $NaOH/C_{active}$ was 70.1% and 76.2%, respectively.

When the amount of 3,5-dimethylheptadiine-1,6-diol-3,5 and acetylene was taken as 1:4, it was found that the yield of vinyl esters did not increase significantly, but an increase in the consumption of acetylene leads to an increase in the cost of vinyl esters. The starting material for the heterogeneous catalytic vinyl reaction of 3,5-dimethylheptadiine-1,6-diol-3,5 was obtained as the most alternative variant of the process, in which the molar ratio was 1: 3. The effect of temperature and reaction time on the yield of mono- and divinyl ethers of 3,5-dimethylheptadiine-1,6-diol-3,5 was studied. The reaction was carried out in the temperature range 150-250 °C, in the presence of a $NaOH/C_{active}$ catalyst, the molar ratio of the starting materials was 1:3. Since the solubility of gases increases with increasing temperature, which, in turn, accelerates their activity, the efficiency of the formation of vinyl esters of 3,5-dimethylheptadiine-1,6-diol-3,5 also increases.

Table 2

Influence of temperature and reaction time of 3,5-dimethylheptadiine-1,6-diol-3,5 on the yield of vinyl esters

Temperature, °C	**Reaction time, hour**	**Output 3,5-dimethyl-5-vinyloxy-heptadiin-1,6-ola-3, %**	**Output 3,5-dimethyl-3,5-divinyloxy-heptadiine-1,6, %**
150	2	3.0	44
	4	3.3	50
	6	3.1	40
	8	2.8	34
170	2	4.2	50
	4	5.1	60
	6	6.2	55
	8	5.1	40
200	2	5.3	64
	4	8.7	76.2
	6	4.5	62
	8	3.2	51
220	2	5.1	54
	4	5.8	61
	6	5.0	53
	8	4.5	40
250	2	3.1	26
	4	2.9	34
	6	2.3	24
	8	2.0	22

Table 2 shows that the yield of vinyl esters 3,5-dimethylheptadiine-1,6-diol-3,5 increases, since the adsorption of acetylene by the catalyst reaches a maximum when the temperature rises from 150 to 200 °C, the product yield slightly decreases, and at 250 °C it leads to to a decrease in adsorption due to desorption of acetylene and a decrease in the yield of vinyl ether. The limiting stage of the process is the formation of an internal salt of the metal cation on the active site of the catalyst. In addition, the vinyl process 3,5-dimethylheptadiine-1,6-diol-3,5 is carried out in the temperature range 20÷40 °C above the boiling point of 3,5-dimethylheptadiine-1,6-diol-3,5. We can talk about a high yield of the product as a result of the conversion of 5-dimethylheptadiine-1,6-diol-3,5 into a bound state. The duration of the reaction developed with the greatest yield when carrying out 4 hours. Polymerization of vinyl esters of 3,5-dimethylheptadiine-1,6-diol-3,5 during the reaction after 6-8 hours. Decrease in the yield of 3,5-dimethylheptadiine-1,6- diol-3,5-vinyl ether is observed as a result of rearrangement to acetylene. The effect of the amount of catalytically active components on the vinyl process 3,5-dimethylheptadiine-1,6-diol-3,5 was studied. Various amounts (5-25 wt.%) Of KOH/C$_{active}$ samples were prepared. The process was carried out at a temperature of 200 °C for 4 hours in a ratio of 3,5-dimethylheptadiine-1,6-diol-3,5: acetylene 1:3. The resulting 3,5-dimethylheptadiine-1,6-diol-3,5 was determined by vinyl ethers by the gravity method, in some cases by gas-liquid chromatography.

Table 3

Influence of 3,5-dimethylheptadiine-1,6-diol-3,5 on the yield of vinyl esters by the amount of KOH catalyst

Number of KOH, C$_{active}$ mass, %	**Yield, 3,5-dimethyl-5-vinyloxyheptadiine-1,6-ol-3, %**	**Yield 3,5-dimethyl-3,5-divinyloxyheptadiine-1,6, %**
5	4.2	64.0
10	5.2	75.0
15	8.7	76.2
20	6.2	76.7
25	6.8	76.9

According to the results of scientific research, an increase in the yield of the product was noted with an increase in the amount of the active substance KOH/C$_{active}$ in the composition of catalysts for the production of vinyl esters of 3,5-dimethylheptadiene-1,6-diol. (5÷15 wt.%), In those cases when the yield of vinyl esters increases, the amount of KOH is within 20÷25 wt. %, the product yield increases very slightly.

The process of vinyl 3,5-dimethylheptadiine-1,6-diol-3,5 with acetylene at a temperature of 200 °C in the ratio of diol: acetylene 1:3 for 4 hours 3,5-dimethylheptadiine-1,6-diol-3,5 with an increase in the amount of catalyst in the yield of vinyl esters, as a result of scientific research, an increase in the amount of active potassium alcohol in the system and a decrease in the amount of polymers and intermediates were revealed.

In addition to control and regulation of a heterogeneous process, safety, relative stability of primary and intermediate products, their polymerization, formation of intermediate complex

The reaction of vinyl 3,5-dimethylheptadiine-1,6-diol-3,5 with acetylene in a heterogeneous catalytic method at a temperature of 200 °C, in the KOH/C$_{active}$ system, the amount of KOH, mass Cactive, 15%, starting from 4 hours. Diol:acetylene 1: When carried out in 3 ratios, the substances were synthesized with the product 3,5-dimethyl-5-vinyloxyheptadiine-1,6-ola-3, 8.7%, 3,5-dimethyl-3,5-divinyloxyheptadiine-1.6 product, 76.2% product and as an alternative process condition. When synthesizing the reaction of vinyl-3,5-dimethylheptadiine-1,6-diol-3,5 with acetylene by a heterogeneous catalytic method, those skilled in the art found that there were relatively few cost-effective, convenient, environmentally friendly intermediates and β-products. The synthesis of vinyl esters by a homogeneous catalytic method leads to an increase in the cost of production due to some inconveniences.

metal salts, rearrangement, acetylation of acetone, enolacetal, less effective than the homogeneous method, due to the observed low alcohol content.

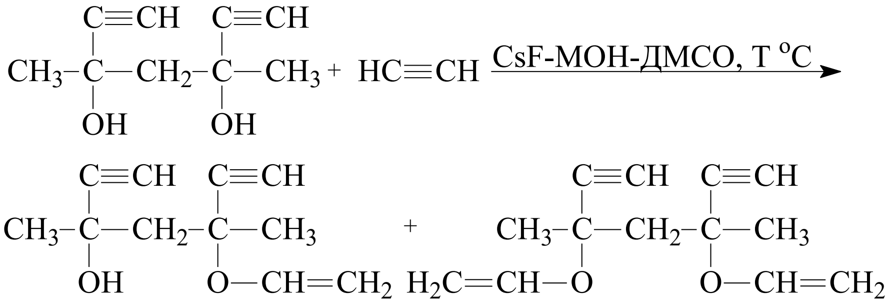
Table 4

Physicochemical values of 3,5-dimethylheptadiine-1,6-diol-3,5 and its vinyl esters

Synthesized substances	**General formula**	**Molecular weight, g/mol**	**T boiling, °C**	n_D^{20}	d_{20}^{4} **g/cen³**
3,5-dimethylheptadiine-1,6-diol-3,5	$C_9H_{12}O_2$	152	159	1.010	1.12
3,5-dimethyl-5-vinyloxyheptadiine-1,6-ola-3	$C_{11}H_{14}O_2$	178	118	1.4130	0.9420

3,5-dimethyl-3,5-divinyloxyheptadiine-1,6	$C_{13}H_{16}O_2$	204	95	1.3817	0.9215

Although the process of vinylation of acetylene by representatives of different classes, retained by the group on in the molecule, has been studied for decades, the mechanism of their reaction has not been scientifically studied enough. It is assumed that the reactions currently taking place in the MOH-CsF-DMSO system are the formation of solvates of alkali metals, which transform into an intermediate metal complex with an active center, forming a catalytic active center and alternating the catalytic function. Based on the literature, the mechanism of the catalytic scheme for the vinylation of acetylene in the highly basic system NaOH-CsF-DMSO 3,5-dimethylheptadiine-1,6-diol-3,5 is proposed below.

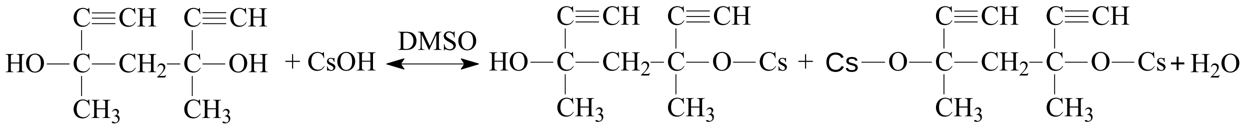


$$CH_3-\underset{OH}{\overset{C\equiv CH}{C}}-CH_2-\underset{OH}{\overset{C\equiv CH}{C}}-CH_3 + HC\equiv CH \xrightarrow{\text{CsF-MOH-ДМСО, T }^{o}C}$$

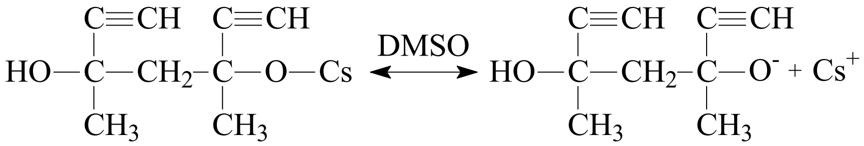
$$CH_3-\underset{OH}{\overset{C\equiv CH}{C}}-CH_2-\underset{O-CH=CH_2}{\overset{C\equiv CH}{C}}-CH_3 + CH_3-\underset{H_2C=CH-O}{\overset{C\equiv CH}{C}}-CH_2-\underset{O-CH=CH_2}{\overset{C\equiv CH}{C}}-CH_3$$

On the basis of the literature, it has been suggested that the reaction of vinyl-3,5-dimethylheptadiine-1,6-diol-3,5 with acetylene in a highly basic system proceeds in the following stages. It reacts initially with NaOH-CsF to form CsOH, which is considered catalytically active.

$$NaOH + CsF \longrightarrow NaF + CsOH$$

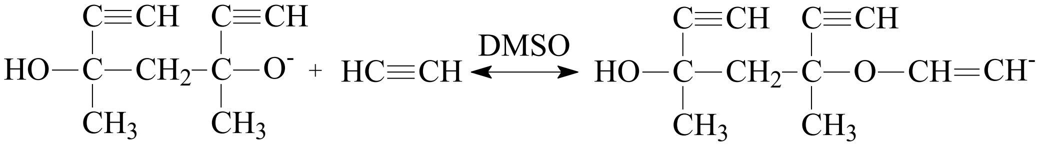


$$HO-\underset{CH_3}{\overset{C\equiv CH}{C}}-CH_2-\underset{CH_3}{\overset{C\equiv CH}{C}}-OH + CsOH \overset{DMSO}{\longleftrightarrow} HO-\underset{CH_3}{\overset{C\equiv CH}{C}}-CH_2-\underset{CH_3}{\overset{C\equiv CH}{C}}-O-Cs + Cs-O-\underset{CH_3}{\overset{C\equiv CH}{C}}-CH_2-\underset{CH_3}{\overset{C\equiv CH}{C}}-O-Cs + H_2O$$

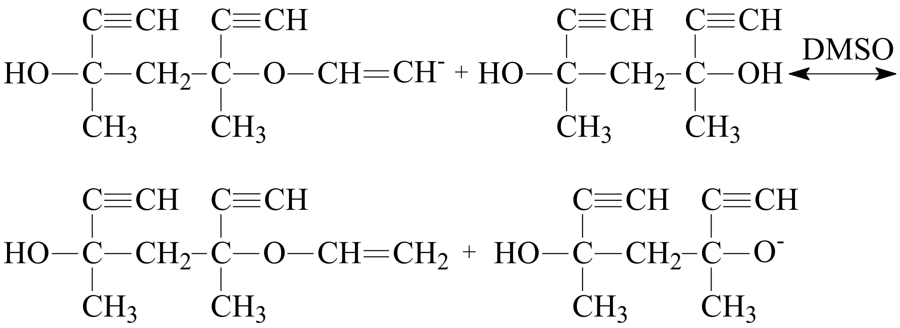


$$HO-\underset{CH_3}{\overset{C\equiv CH}{C}}-CH_2-\underset{CH_3}{\overset{C\equiv CH}{C}}-O-Cs \overset{DMSO}{\longleftrightarrow} HO-\underset{CH_3}{\overset{C\equiv CH}{C}}-CH_2-\underset{CH_3}{\overset{C\equiv CH}{C}}-O^- + Cs^+$$

Cesium hydroxide reacts with 5-dimethylheptadiine-1,6-diol-3,5 to form alcohols in solution. Alcohols readily dissociate in solution with DMSO, converting 5-dimethylheptadiine-1,6-diol-3,5 into cesium anions and cations. When acetylene is added to the process, 3,5-dimethylheptadiine-1,6-diol-3,5 anions in the system combine with acetylene in DMSO solution to form an intermediate compound and form the corresponding vinyl ester.



$$HO-\underset{CH_3}{\overset{C\equiv CH}{C}}-CH_2-\underset{CH_3}{\overset{C\equiv CH}{C}}-O^- + HC\equiv CH \overset{DMSO}{\longleftrightarrow} HO-\underset{CH_3}{\overset{C\equiv CH}{C}}-CH_2-\underset{CH_3}{\overset{C\equiv CH}{C}}-O-CH=CH^-$$

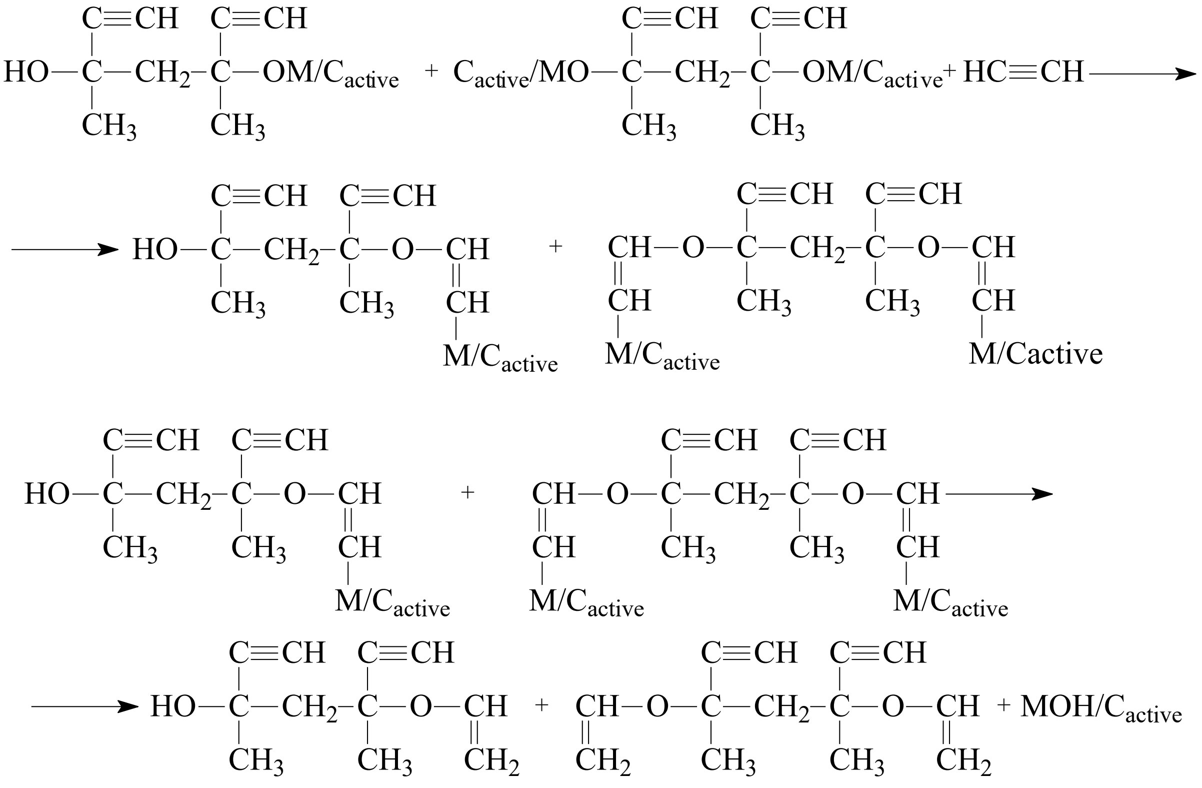


$$HO-\underset{CH_3}{\overset{C\equiv CH}{C}}-CH_2-\underset{CH_3}{\overset{C\equiv CH}{C}}-O-CH=CH^- + HO-\underset{CH_3}{\overset{C\equiv CH}{C}}-CH_2-\underset{CH_3}{\overset{C\equiv CH}{C}}-OH \xleftrightarrow{DMSO}$$

$$HO-\underset{CH_3}{\overset{C\equiv CH}{C}}-CH_2-\underset{CH_3}{\overset{C\equiv CH}{C}}-O-CH=CH_2 + HO-\underset{CH_3}{\overset{C\equiv CH}{C}}-CH_2-\underset{CH_3}{\overset{C\equiv CH}{C}}-O^-$$

In the process of vinylation in a highly basic system, 3,5-dimethylheptadiine-1,6-diol-3,5 acetylene is converted to 3,5-dimethylheptadiine-1,6-diol-3,5 anions. in the system are completely converted to vinyl esters and high yields are achieved.

The stable and reactive complex of 3,5-dimethylheptadiine-1,6-diol-3,5 of the intermediate metal undergoes a strong nucleophilic action of acetylene, forms an intermediate compound and forms mono- and divinyl ethers 3,5-dimethylheptadiine-1,6-diol-3,5 due to hydrolysis under the action of water vapor in the system.



In heterogeneous catalytic reactions in vinyl reactions of 3,5-dimethylheptadiine-1,6-diol-3,5 with acetylene, a high yield and low cost were obtained.

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