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VINYL ESTERS BASED ON ACETYLENE AND THEIR SYNTHESIS

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The aim of the research work elaboration of technology of obtaine of acetylene diols and their vinyl ethers. Reaction of formation mono di vinyl ethers as a result vinyl 3.6-dimetyloktin-4-diol-3.6 by acetylene, and also influence of solvents, the catalyst and its quantity, duration of reaction, temperatures is investigated. Are defined speed of reaction. Recommended vinyl 3.6-dimetyloktin-4-diol-3.6 acetylene in the presence of highly basic systems at atmospheric pressure.

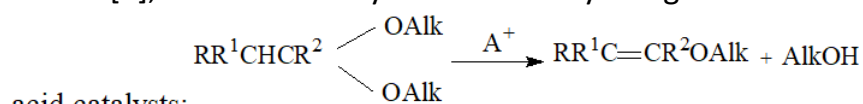
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INTRODUCTION

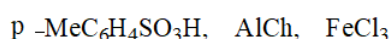
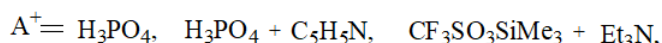
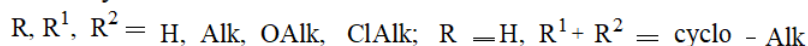
At present, acetylene-based products are used in chemical production and engineering, medicine, to obtain the growth of regulatory drugs and pesticides, light industry, perfumery, food and other fields. Particular attention is paid to the technology for the production of vinyl ethers and, on their basis, new drugs, unique polymeric materials, high-quality solvents for radio engineering, as well as reagents for directed organic synthesis [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 [2], which is usually accelerated by using various



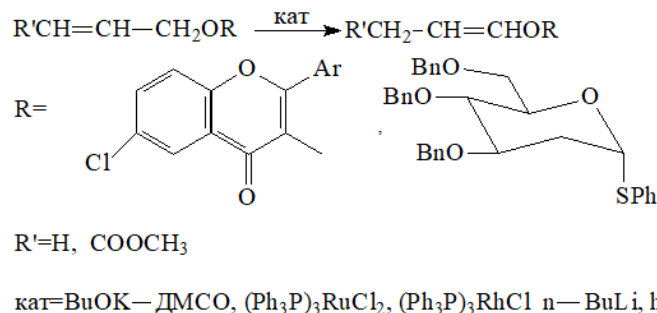
acid catalysts:



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%.

β -Substituted vinyl ethers can also be obtained by isomerization of allyl ethers under the action of strong bases [6] or metal complex catalysts [6, 7]. 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:



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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

In a four-necked flask equipped with a reflux condenser, a thermometer and a tube for supplying acetylene, 0.85 g of KOH (20% of the amount of diol) and 100 ml of DMSO were placed, heated to 100 °C with stirring, then slowly cooled to a temperature of 35-40 °C. Added 4.25 g (0.025 mol) of 3,6-dimethyloctane-4-diol-3,6 and after the formation of the alcoholate acetylene was passed.

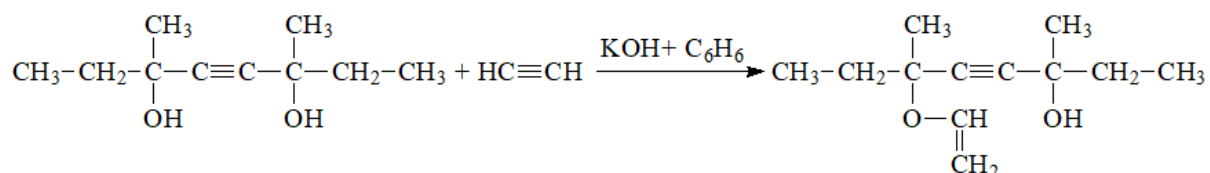
Vinylation was carried out with constant vigorous stirring of the solution at a temperature of 100 °C. After 6 hours, the reaction mixture was cooled, extracted with ether, the ether extracts were dried, the solvent was distilled off by vacuum distillation at room temperature, and then 2.76 g of the product (yield 53%) with bp = 130-133 °C at 15 mm was collected in a cooled trap. rt.st; g / cm³. This reaction was also studied in a benzene solution (KOH catalyst in an amount of 20% of the amount of diol) at various temperatures according to the above described method.

The reliability of the research results is confirmed by the fact that the composition and structure of the synthesized substances have been proven by gas-liquid (GLC "CHROM 5") and thin layer chromatography (TLC), PMR ("100 MGs") and IR ("SF-4A") -spectroscopy.

Results and discussion

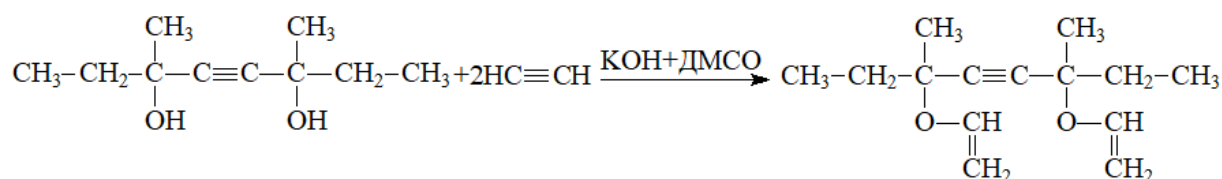
The synthesized 3,6-dimethyloctane-4-diol-3,6 was vinylated with acetylene in a benzene solution in the presence of KOH as a catalyst and in the KOH-DMSO system.

In a benzene solution, the vinylation reaction proceeds due to one OH - group with the formation of a monovinyl ether of acetylene diol:



The product yield was 25.6%. In the course of the reaction, divinyl ether of acetylene diol is also formed in an amount of 5-10%. The reason for the low yield is that KOH does not dissolve in the solvent and cannot fully function as a catalyst.

When the reaction is carried out in a superbasic medium in the KOH - DMSO system, the divinyl ether of the studied diol is mainly formed:



In the presence of KOH 20% of the amount of diol, divinyl ether is formed with a yield of 53%, and in the presence of KOH of 50% of the amount of diol, the yield of the ether increases to 57% at a temperature of 97-100 °C. With an increase in the reaction temperature to 120-125 °C, the yield of divinyl ether decreases insignificantly and amounts to 55%. which is explained by the fact that at high temperatures, under the action of alkali, the partial decomposition of the acetylene diol into the starting ketone and acetylene begins; The obtained experimental results on the synthesis of vinyl esters of acetylene diols are shown in Table 1.

Table 1
Some physicochemical constants of mono- and divinyl derivatives
3.6-dimethyloctine-4-diol-3.6

<u>Mono - and divinyl ethers</u>	<u>Dissolve tel: benzene</u>	<u>Dissolve tel: DMSO</u>	<u>Output, %</u>	<u>n_{20}^D</u>
$\text{H}_3\text{C}-\text{CH}_2-\underset{\text{OH}}{\overset{\text{CH}_3}{\text{C}}}-\text{C}\equiv\text{C}-\underset{\text{O}-\underset{\text{CH}_2}{\text{CH}}}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{CH}_3$	25.6		25.6	1.4700
$\text{H}_3\text{C}-\text{CH}_2-\underset{\text{O}-\underset{\text{CH}_2}{\text{CH}}}{\overset{\text{CH}_3}{\text{C}}}-\text{C}\equiv\text{C}-\underset{\text{O}-\underset{\text{CH}_2}{\text{CH}}}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{CH}_3$	13.1	57	57	1.4788

To clarify the effect of temperature on the course of vinylation of 3.6-dimethyloctine-4-diol-3.6, the reaction was carried out in the temperature range 60-120 °C, the amount of catalyst was 45% by weight of the diol.

The results at lower temperatures (60-70 °C) a mixture of mono - and divinyl ethers of 3.6-dimethyloctine-4-diol-3.6 is formed. Moreover, in all cases, the yield of divinyl ether

is greater than that of monovinyl ether. It is observed that with an increase in temperature in the range of 60-80 °C, the yield of monovinyl ether increases from 11.3 to 14.5%, and an increase in temperature to 90 °C decreases its yield to 9.6%. At temperatures above 90 °C, monovinyl ether is not formed. With an increase in temperature, the formation of divinyl ether passes through a maximum at 100 °C and is 46.4%. The formation of mainly divinyl ether is explained by the fact that in the catalytic vinylation of 3.6-dimethyloctine-4-diol-3.6, in our opinion, the rate-limiting stage of the reaction is the formation of monovinyl ether. It should be noted that in the literature there is evidence that with an increase in the acidity of alcohols, their vinylation becomes more difficult. The acidity of a diol is greater than that of a monohydric alcohol. When the diol is vinylated, as the acidity is higher, the first hydroxyl group is difficult to vinyl with the formation of a monovinyl ether (i.e., a monohydric acetylene alcohol). After that, the acidity of the molecule changes and divinyl ester is formed at a higher rate than monovinyl ester. At high temperatures (above 90 °C), monovinyl ether is not formed, i.e. completely transforms into divinyl ether. With an increase in temperature to 100 °C, the reaction rate and the yield of divinyl ether increase. A further increase in temperature (at 120 °C) leads to a decrease in the solubility of acetylene, as well as a partial decomposition of DMSO (the smell of hydrogen sulfide), due to these phenomena, the product yield sharply decreases.

In the processes carried out, a special place is occupied by the study of the kinetic parameters of the reaction. Based on this, the kinetics of vinylation of 3.6-dimethyloctine-4-diol-3.6 was investigated. The process was carried out in the temperature range 80-110 °C, duration 2-4 hours, the amount of catalyst was 45% by weight of the diol. The data obtained are shown in Table 3.

The results showed that with increasing temperature, the yield of divinyl ether increased. By studying the reaction at 2, 3, 4 hours at different temperatures, it was found that at lower temperatures (80-100 °C) with an increase in the reaction time, the yield of divinyl ether increases, and at 110 °C its yield passes through a maximum and in 3 hours is 48, 0%.

CONCLUSION

The optimal conditions for vinylation of 3.6-dimethyloctine-4-diol-3.6 providing the maximum yield of 3.6-dimethyloctine-4-diol-3.6 divinyl ether were determined. The best effect as a solvent among the investigated benzene, dimethyl sulfoxide, is dimethyl sulfoxide. With an increase in the reaction time, the yield of divinyl ether increases, reaching a maximum after 3 hours. The relatively low value of the calculated activation energy, equal to 39.8 kJ/mol, indicates a fairly high rate of the vinylation reaction of 3.6-dimethyloctine-4-diol-3.6.

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