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SYNTHESIS REACTIONS VINYL ETHERS OF AROMATIC ACETYLENE ALCOHOLS IN THE ALKALI PHASE

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ABSTRACT

Vinylation reaction was investigated by catalytic system in the presence of aromatic acetylene alcohols (AAA) with acetylene. Theoretically proposed factors affecting the process of the reaction. The influence of the nature and amount of catalyst, the molar ratio of the starting materials during the reaction temperature on the yield of the product. Definitely purity, structure, elemental composition and physical constants and quantum chemical calculations of the synthesized compounds. The optimal conditions for the synthesis of a product with a high yield.

KEYWORDS: acetylene, alcohols, catalysis, vinyl ethers, technological scheme.

INTRODUCTION

Vinyl ethers, among the organic compounds, are used as initial products in different fields such as in the fine organic syntheses and in the manufacture. Influence of nature of catalysts and solvents on these reactions was investigated, and also role of high-based system KOH-DMSO was determined. It can be explained the coming out of AAA vinyl ethers (VE) with higher yield in the presence of DMFA than DMSO. DMFA is considered as a solution in average solidity. Recently, scientific investigations on the creation of ecological safety and waste less technology, also, on the synthesis of economically cheap chemical preparations with higher yield and to introduce them into the practice have been carried out. Quantum-chemical and molecular-dynamical calculations of molecules of different vinyl ethers were carried out; also the vinylation process was modulated and the mechanisms of formation new compounds were proposed. In JSC "Navoiyazot-Uzbekistan" the plant for their synthesis has been constructed and also the test samples of 1-phenyl-3-methylbutyn-1-ol-3 and its vinyl ether were obtained and also the technological regalement and economical effect of there synthesis was elaborated.

MATERIALS AND METHODS

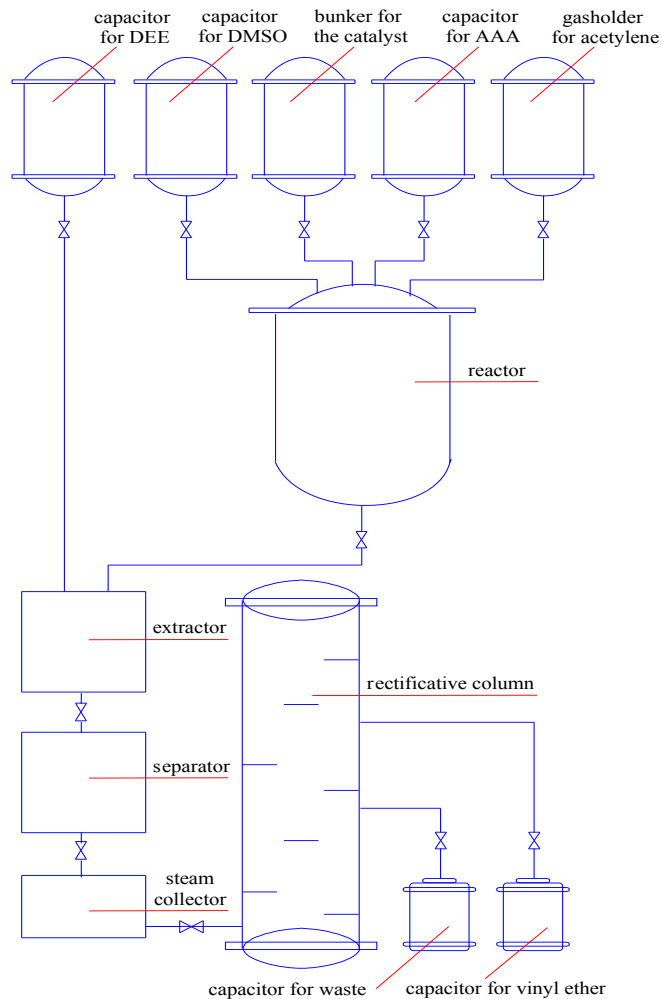
Experimental Section: PMR spectra of the structure of synthesized compounds have been studied in the spectrophotometer Jeol FX-90Q (90 millihertz), and IR structure has been studied in the spectrophotometer Bruker JFS-25. In the room temperature NMR ¹H structure has been determined with the help of spectrophotometer Bruker DPX-400 (working frequency 400.13 millihertz, solvent – CDCl₃, inner standard – GMDs). The content of mixture has been analyzed GLCh with the help of device LXM-80 (gas – carrier – helium, (column) geysir 3000×3 mm, 1% solution of liquid phase polyethylene glycol in NaCl).

Phase structure of synthesized AAA molecules, distribution of charges and electron density in the molecules, quantum – chemical granularity of compounds have been determined with the help of quantum-chemical half-empiric PM3 of STAT program Hyper Chem Activation 7.0 packet and the processes have been mathematical modeled, also AAA physical-chemical value (amount), including boiling and liquefaction temperatures, density, specific refraction indexes, their solubility in water or in which solutions and acceptable poisonous degrees have been investigated [1]. Vinylation of AAA with acetylene: First of all 3,76 g. alkali (for analyze 2KOH•H₂O, □ 15% H₂O with pure grade) and 150 ml., solvent (DMCO 0,2% H₂O of chemical pure grade) are poured into a 500 – millimeter – flask that mechanic stirrer, thermometer and reverse cooler are installed in, and heating under the temperature of 100 oC, it is prepared suspension. Product suspension is cooled to the temperature of 30– 35 oC. It is saturated with acetylene for 30 minutes, then as acetylene is running, ether solution (0,1 mole) is sent to the system for 6 hours at temperature 120

oC. Having been cooled the mixture is hydrolyzed and it is extracted, organic part is separated and dried with the help of $MgSO_4$. The mixture purified from water is refined of ether through distillation in common situation, then vacuum distillation is fulfilled. In this case aromatic acetylene alcohol, its vinyl ether, secondary and interval products are rectified and refined [2, 3, 11].

Experimental Set Up: In the process of vinylation of AAA acetylene in the reactor at constant mechanical mixing from capacitor moves DMCO, and from the bunker potassium hydroxide. Contents heat up to the dissolution of potassium hydroxide and from capacitor move AAA. After that from gasholder in a reactionary mix through gas measuring tank without discontinuous acetylene moves with a speed 0,541 m³/hour. In 4 hours after cooling it extracted in capacitor, forming catalysate is sent to separator, and then diethyl ether extracted. The organic layer moves into steam collector. At the same time reacted acetylene is allocated. Residuum moves in rectificative column. At the same time reacted acetylene is allocated, vinyl ether of AAA is allocated and gathered in capacity. The resinous residuum pours out in capacitor [4].

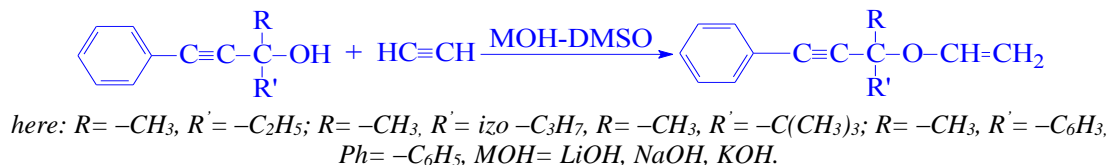
Technological process of manufacture of vinyl ether of AAA is developed together with employees of JSC "Navoiazot-Uzbekistan".



The basic technological scheme of obtaining process of vinyl ether of AAA

RESULTS AND DISCUSSION

Vinylation reaction of AAA containing phenyl group in its molecule in the presence of acetylene has been investigated and properly VE have been synthesized.



The influence of temperature, catalyst and solutions nature on the yield of AAA VE has been studied systematically and analyzed. On the basis of received results DMSO solution in the presence of catalyst KOH, when acetylene influences on AAA at temperature 120 oC, for 6 hours it has been determined that VE comes out with highest yield (Table.).

We can clarify the influence of temperature, catalyst and solutions nature on the AAA VE yield as following:

– it has been determined that VE comes out with maximum yield when catalyst KOH, which with higher base among the used catalysts, is used. During the process at first AAA: having interacted 1-phenyl-3-methylpentyn-1-ol-3 (I), 1-phenyl-3,4-dimethylpentyn-1-ol-3 (II), 1-phenyl-3,4,4-trimethylpentyn-1-ol-3 (III) and 1,3-diphenylbutyn-1-ol-3 (IV) with alkalis, interval compounds changes into alcoholates and accompanying with acetylene VE is yielded. Herein, because of potassium alcoholate's activity being higher than lithium and sodium alcoholates. During this reaction it has been determined the yield of product is higher because of having higher catalytic activity potassium alcoholate than lithium and sodium alcoholates [5, 6].

– at selected temperatures (80 – 140 oC) product is synthesized with higher yield at temperature 120 oC haroratda. When the process is carried out at 80 oC, on account of dissolving coefficient of acetylene is lower, solutions couldn't dissolve alcoholates normally, also acetylene escapes from the system not fully combining with alcoholates, product comes out with minimum yield. Also when the temperature is raised up to 140 oC, in the result of partly polymerization of VE being synthesized, escaping of AAA from the system with water vapour, the rise in the amount of metal complexes formed AAA VE with alkalis, it has been determined the decrease in the product yield.

– theoretically, when the temperature rises, it can be explained the decrease of AAA VE yield as follows. Orientation polarity of hydrogen positive charged in AAA hydroxyl group towards triple bond of acetylene depends on the exchanging of catalysts metal cations with active hydrogen of acetylene and acetylenides forming. It is known, it is determined the fall down in the product yield on account of the orientation polarity, having decreased alongside with rising of temperature, intensifying of acetylene molecule motion, as a result, on account of the damage of its special regulated arrangement.

– taking into consideration the medium in the process of catalytic organic reactions, that's to say, selecting right solution is of great importance. Hence, the vinylation process of AAA is carried out in the presence of aprotion solutions DMSO and DMFA. It has been observed the yield of product is higher in the presence of DMSO among the selected solutions. In the process DMSO is reacted with alkalis. It forms the system which partly acts as catalyst that is interval complex bounded through donor-acceptor in it and private solvation comes into being.

Table. To AAA VE's fertility temperature, catalyst and influence of solvents' character

Catalyst	Temperature, °C	I	II	III	IV
solvent DMFA					
LiOH	80	17,3	14,0	7,20	21,1
	100	19,6	15,1	9,50	24,8
	120	22,6	19,6	14,5	30,2
NaOH	80	23,1	18,4	13,6	27,3
	100	24,8	19,9	18,4	30,4
	120	30,1	26,0	22,0	35,3
KOH	80	29,5	25,5	23,4	33,2

	100	34,2	32,5	26,6	37,8
	120	41,3	34,0	29,5	44,2
	140	26,4	16,3	14,8	27,4
solvent DMSO					
LiOH	80	29,6	26,3	22,8	30,4
	100	33,5	32,0	29,6	39,2
	120	40,8	39,6	35,4	44,5
NaOH	80	33,4	29,6	24,4	34,2
	100	36,0	35,2	31,4	38,3
	120	40,5	42,7	37,4	46,0
	140	22,6	24,7	21,1	27,2
KOH	80	40,7	36,6	33,3	44,5
	100	41,7	42,4	35,4	46,4
	120	44,1	43,6	37,3	56,3
	140	26,4	25,3	20,1	35,3

here: I- VE 1-phenyl-3-methylpentin-1-ol-3;
 II- VE 1-phenyl-3,4-dimethylpentyn-1-ol-3;
 III- VE 1-phenyl-3,4,4-trimethylpentyn-1-ol-3;
 IV- VE 1,3-diphenylbutyn-1-ol-3.

Having reacted into nucleophile joining reaction with acetylene, alcoholates form VE in suitable way with higher yield.

– it can be explained the coming out of AAA VE with higher yield in the presence of DMFA than DMSO. DMFA is considered as a solution in average solidity. Positive charge in the nitrogen atom allows DMFA reacting as a weak proton acid. Owing to the presence of autoprotolysis in DMFA, it can't create convenient homogeneous medium for the process of reaction, as a result product is synthesized with partly low yield [7, 8]. And DMSO possesses two nucleophile consisting of solid-oxygen and soft sulphur atoms. Because of relatively strong protonation of hydrogen atoms in it, having been drawn with the help of alkalis, catalytic active interval complexes are formed. It causes the rise of product yield, at the same time creating convenient medium for the acetylene connection.

– it has been observed the decrease in the product yield on account of the increase of the number of carbon atoms or the increase of radicals branching in the main chain of AAA molecule and obstacle spacial them to compound with acetylene [9, 10]. Also, the number of carbon atoms in the main change are equal asosiy zanjirida uglerod atomlari soni bir xil (II and III), but the formation of VE goes worse with radicals branching (ethyl, isopropyl and tertiary butyl). Besides, it has been observed the product yield will be maximum on account of drawing more electron butyls of phenyl radicals in the presence of 1,3-diphenylbutin-1-ol-3 containing two aromatic nucleus. The cause of this is that the electronegateness of phenyl group is higher than the electronegateness of ethyl, isopropyl and tertiary butyl. In the hydroxyl oxygen negative charge falls down, acidity of alcohol goes up; as a result alcoholate is formed with higher yield. Formation of alcoholates with more high yield causes being convenient medium for acetylene joining. And it may synthesize the product with higher yield.

– in the presence of II and III containing isopropyl and tertiary butyl radicals positive induction effect (+I) increases alongside with the increase of the number of carbon atoms and branching that's on account of the increase of radicals electronegateness electron cloud of alcohols' hydroxyl group moves towards carbon atom more, joining metal atoms into itself becomes harder and forms alcoholates in respect of amount. It has been observed the influence of shortage of alcoholates amount on the product yield.

– it has been determined the decrease of solubilization of alcoholates alongside with the increase of their molecular weight, and this opposes acetylene joining and it has been observed the decrease in the formation of VE [11, 12]. If acetylene and solution are sent into the system with extra amount for the purpose of increasing product yield it will bring to rise in price of the cost of the product synthesizing. Extra expenditure of acetylene and solution causes lasting of reaction duration and recycling demands to implement complicated technological processes.

Theoretically, we can recommend the increase of formation yield of AAA VE on the row I > II > III basing on free radicals theory approximately as follows.

Free radicals are considered the group inclined to electron. Their stability become higher on the row primary < secondary < triple [10]. It was said that C←H polarity though it is very few, that's positive induction effect (+I) is causer for the stability of alkyl radicals. But it is explained the alkyl radicals stability through δ-p- adjoining, that's hyperconjugation. Ethyl radical and odd electron clouds in δ- orbital are covered each-other "from afar". So, it is considered that ethyl radical possesses four resonances. As a result of covering, shortening a little, C-H bonds become double-bonded partly. That's the stability of ethyl radical forming is more fewer than allil radical because of resonance structures $\text{CH}_3\text{-C}\cdot\text{H}_2\leftrightarrow\text{H}\cdot\text{H}_2\text{C}=\text{CH}_2$. As radical chain is becoming larger and branching, the stability of radical increases owing to the increase of the number of resonance structures too. Isopropyl processes six resonance structures and in triple butyl radical they are nine. It should be noted, the stability of radicals is a relative notion, none of them hasn't been separated in free state [13, 14].

CONCLUSION

To sum up, it has been observed the decrease in vinyl ethers productivity owing to the formation of acetylenids reacting with metals and their hydrolysis, the increase of alcolates stability formed by joining AAA containing ethyl, isopropyl and triple radicals with metals.

Conclusion, in order to synthesize AAA VE with higher yield 6 hour's process at 100 oC temperature in the system of NaOH-C₆F₆-DMSO has been chosen [15]. In this case it has been determined that very maximum yield of product is I=84,8%; II=77,1%; III=72,3% and IV=88,0%.

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