

Reactions for obtaining monomers for the synthesis of polymers with dielectric properties

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ABSTRACT: Today, there are many ways to obtain polymer membranes. In particular, part of the production of target materials is the processing of plastic waste, the production of composite, copolymer and other materials using industrial waste generated in the production of polymer products. The article presents the results of a study of the conditions, reactions and yield of aryl vinyl ether synthesis for the production of polymer composite materials with membrane properties.

KEY WORDS: aryl vinyl ethers, acetylene, vinylation reactions, terpenoids, menthol, thymol.

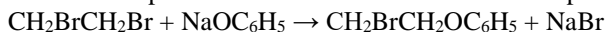
I. INTRODUCTION

Among the vinyl ethers, aryl-substituted vinyl ethers such as phenol, cresol, naphthol and alkyl aromatic alcohol derivatives are of particular importance due to the presence of vinyl, oxygen and aromatic groups in these compounds. Vinyl aryl ethers can be summarized as follows:

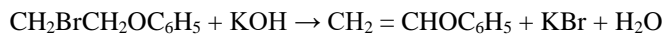


where Ar is an aromatic group of varying complexity.

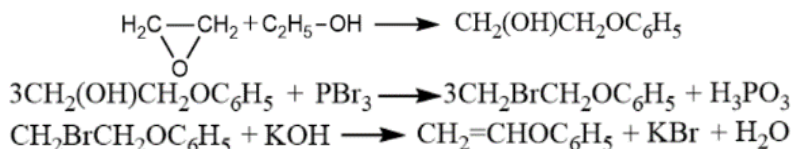
The first representative of this type of vinyl ether - phenylvinyl ether was synthesized in 1882 by A. Sabaneev. In this case, 1,2-dibromoethane and sodium phenolate were subjected to interaction in an alcohol solution, and then the reaction mixture was treated in an alcohol solution of potassium alkali. The method can be represented by the following scheme:



By 1910, A. Vol and E. Berthold synthesized phenylvinyl ether directly from β -bromophenetol:



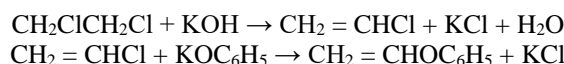
In 1932, V. Chalmers obtained vinylphenyl ether by the following processes:



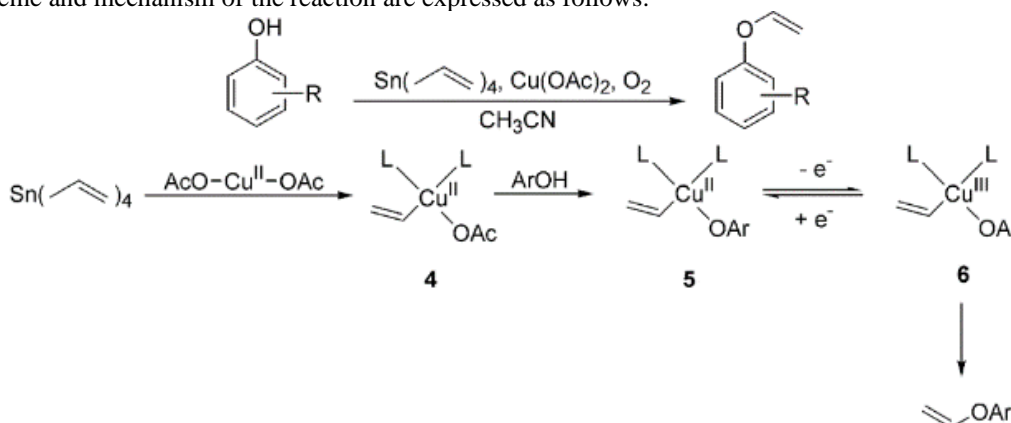
Apparently, this method was very labor-intensive and the yield of the product was low. In subsequent years, the Butlerov-Eltekov method was also used in the synthesis of phenylvinyl ethers. According to this method, the action of vinyl chloride and phenolate salts was used:



Later, this method was modified to convert vinyl chloride into 1,2-dichloroethane and phenolates into a mixture of phenol and alkali, with the reaction being carried out in various solvent environments. When using dichloroethane, it was necessary to obtain a sufficient amount of alkali to completely bind the chlorine. In this case, the synthesis of phenyl vinyl ether occurs in 2 stages:

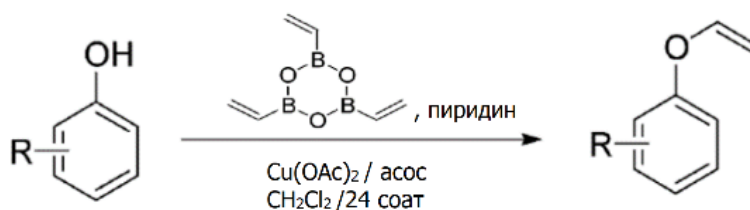


The destructive factor is the formation of water and chloride salts together with vinyl ethers in the reaction medium. Because vinyl ethers are subject to hydrolytic decomposition under the influence of these salts [1]. In 2001, Canadian scientists M. Bluen and R. Frenette synthesized more than 10 types of aryl vinyl ethers with a yield of more than 90% on a copper(II) acetate catalyst in gaseous oxygen and acetonitrile. They used tetravinyltin as a vinylizing agent [2]. The general scheme and mechanism of the reaction are expressed as follows:

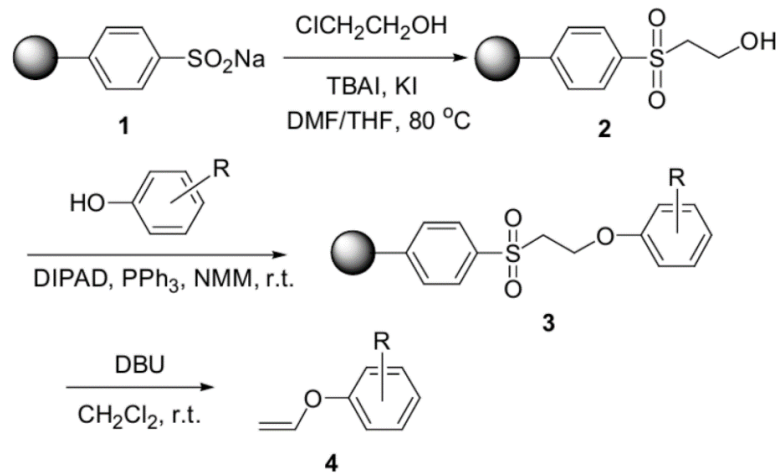


where R are different radicals; L – ligand (acetonitrile).

The reaction proceeds at room temperature. The main disadvantages of the method are the absence of a vinylizing agent, toxicity of residual tin compounds and a long process time (from 22 to 96 hours). After some time, N. McKenley and D. O'Shea (Ireland, 2004) used 2,4,6-trivinylcyclotriboroxane in the synthesis of aryl vinyl ethers. In this method, the 2,4,6-trivinylcyclotriboroxane-pyridine complex is presented as an effective (up to 100% conversion) vinylizing agent and 21 types of aryl vinyl ethers are synthesized. The reaction proceeds at room temperature for 24 hours. The reaction scheme is as follows:

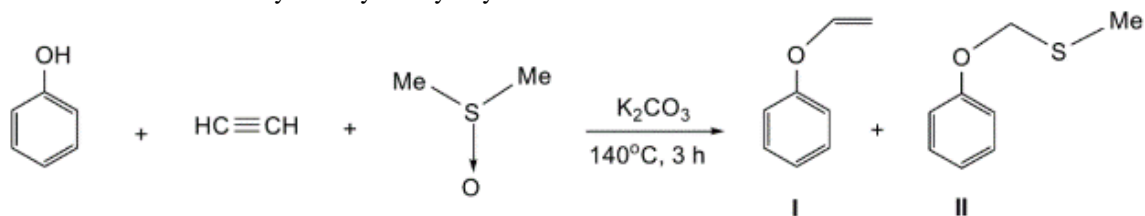


In 2012, a group of Chinese scientists [3] developed a method for solid-phase organic synthesis of aryl vinyl ethers via sulfone bonding. The main advantage of the method is the high yield of the product (88-95%) and purity (95-98%). However, the process takes place in several stages and uses many chemicals. A brief description of the method is as follows:

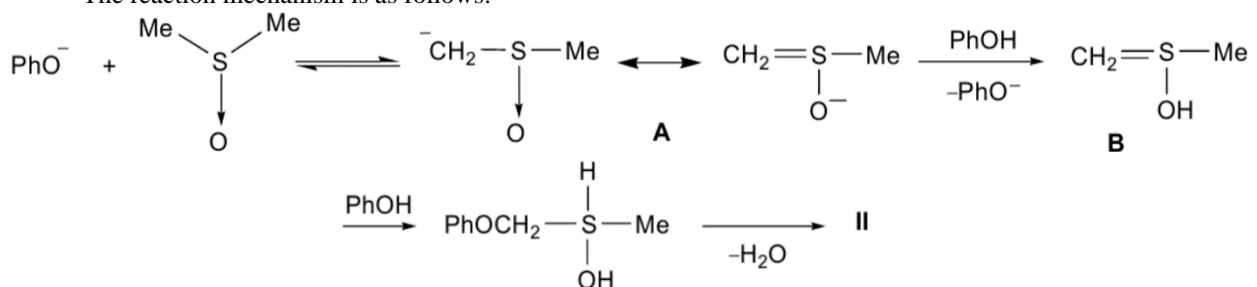


TBAI - tetrabutylammonium iodide, KI - potassium iodide, DMF - dimethylformamide, THF - tetrahydrofuran, DIPAD - diisopropylazadicarboxylate, PPh₃ - triphenylphosphine, NMM - N-methylmorpholine, r.t. - room temperature, DBU - 1,8-diazabicyclo- [5.4.0] undec-7-ene; R – H, 4-CH₃O, 2-CH₃O, 4-t-C₄H₉, 4-Br, 4-Cl, 4-NO₂, 4-CN, 4-CO₂CH₃, 1-naphthol.

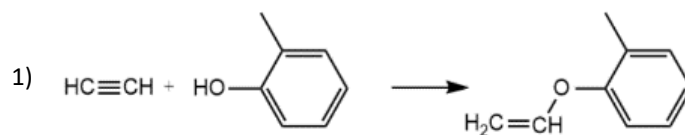
It is known from the methods mentioned that vinylization by heating in the presence of potassium alkali based on acetylene is also desirable in the synthesis of aryl vinyl ethers. This method was developed by A.E. Favorsky and improved by M.F. Shostakovskiy, later by B.A. Trofimov and others [2, 4]. It should be noted here that during the synthesis of aryl vinyl ethers at high temperature in a superbasic medium, a significant number of additional reactions occur, as a result of which methylsulfanyl methyl aryl ethers are also formed:

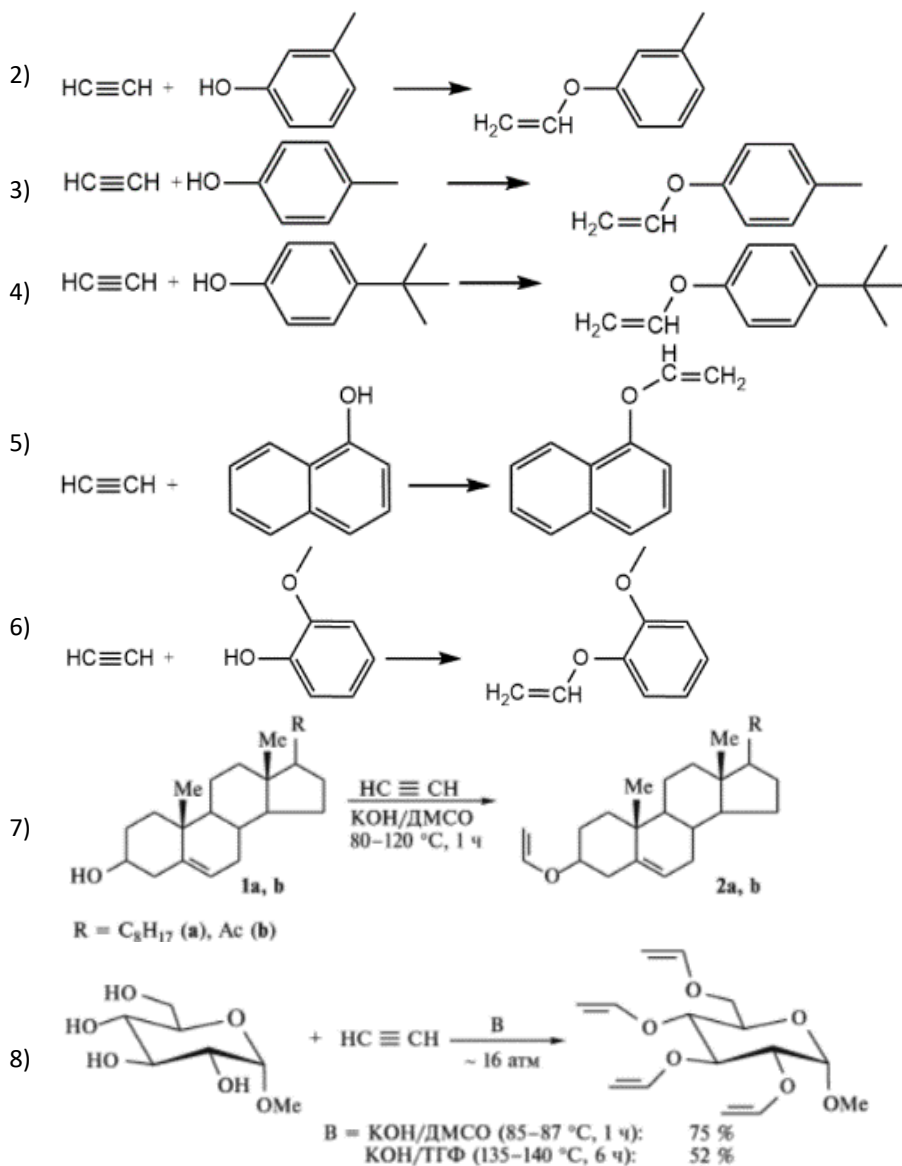


The reaction mechanism is as follows:



So far, several aryl vinyl ethers have been synthesized based on the Favorsky-Shostakovskii method. Here are some of them:





From the above reactions it is evident that the reaction of acetylene with phenols in the presence of alkali produces simple aryl vinyl ethers.

V. EXPERIMENTAL RESULTS

Aryl vinyl ethers have many new properties compared to alkyl vinyl ethers. In particular, aryl vinyl ethers differ sharply from alkyl vinyl ethers in chemical activity. For example, aryl vinyl ethers are prone to thermal polymerization, which can be observed even during the synthesis of vinyl ether. During the synthesis of phenyl vinyl ether from acetylene and phenol using dry substances together with vinyl ether, resinous or solid glassy products are formed. Adding water in an amount of 15-20% of the phenol mass before the reaction eliminates thermal polymerization and increases the yield of vinyl ether. The differences in the properties of aryl vinyl and alkyl vinyl ethers are also expressed in their tendency to form oxone compounds with halides, inorganic and organic acids and their salts. This is especially noticeable by the differences in the heat of formation of these compounds.

It is also noted in the literature that aryl vinyl ethers are stable to heating in acidic and alkaline media [2, 4]. It is known that alkalis are mainly used as catalysts in the synthesis of phenol derivatives and aryl vinyl ethers from acetylene. These

reactions were carried out at high pressure (30-50 atm) and high temperatures (150-200 °C) [5, 6]. Recently, many studies have been conducted to "soften" the reaction conditions, and it was possible to synthesize various aryl vinyl ethers at lower pressures [7, 8, 9, 10].

In this work, the effects of various factors on the vinylation of thymol, menthol and 3-hydroxymethyl-hamazulenes in the presence of acetylene in KOH-DMSO environment were investigated, and the optimal conditions of the process were determined. During the research, the experiments were conducted at a pressure of 14-16 atm.

In particular, the effect of temperature and time on the vinylation reaction of thymol with acetylene in the presence of 50 mol% KOH compared to the mass of thymol was investigated. The obtained results are presented in Table 1.

Table 1. Effect of temperature and duration of reaction on the reaction of thymol with acetylene (catalyst KOH - 50 mol%)

Temperature, °C	Reaction time, hours	Yield of vinyl ether, %
100	3	47,3
100	6	48,1
110	3	50,5
110	6	52,8
120	3	64,1
120	6	67,0
120	8	67,3
130	3	79,5
130	6	76,8
130	8	51,5
140	3	58,4
140	6	51,7

The results showed that temperature has a significant effect on the yield of thymol vinyl ether. Its yield increases from 47.3 to 79.5% depending on the temperature. A further increase in temperature will negatively affect the yield of the product. For example, at 140 °C, its yield is 51.5%. This situation is explained by a decrease in the solubility of acetylene in the solvent at very high temperatures, which results in a decrease in its concentration, a decrease in the reaction rate and the yield of the resulting product. In addition, at high temperatures, it is observed that dimethyl sulfoxide forms resinous substances with vinyl ethers and other intermediates of the reaction.

In order to study the effect of the nature of the substance on the vinylation process, the reaction of acetylene with menthol in the presence of the KOH-DMSO system was studied. The effect of temperature on the yield of menthol was studied in the range of 80-140 °C, the reaction duration was 3 hours. The results obtained are presented in Table 2.

Table 2. Effect of temperature on the yield of menthol vinyl ether (KOH catalyst amount - 50 mol%, reaction time - 3 hours)

Temperature, °C	Yield of vinyl ether, %
80	0
90	<1
100	46,4
110	49,0
120	61,0
130	79,0
140	77,6

The results showed that with increasing temperature, as in the thymol reaction, the yield of the product reached a maximum of 130 °C, and the yield was 79.0%.

Table 3. Effect of the amount of KOH catalyst on the yield of menthol (temperature 130 °C, solvent - DMSO, reaction time - 3 hours)

Amount of KOH catalyst, mol% (relative to the mass of menthol)	Yield of vinyl ether, %
15	50,5
25	72,4
50	79,0
75	78,1
100	76,2

Then, at 130 °C (as the optimum temperature), the effect of the amount of catalyst (KOH) on the yield of the product was studied in the range of 15-100 mol% (of the mass of menthol) (Table 3).

From Table 3, it is evident that a significant increase in the amount of catalyst affects the yield of menthol vinyl ether, and its optimum amount is 50 mol% relative to the mass of menthol. The yield of the product is 79.0% menthol.

Further increase in the amount of catalyst increases the yield at low values. This phenomenon means that up to a certain ratio (by weight) of catalyst and substrate, the active centers of the catalytic system are fully active, and when this ratio increases, the active centers of the catalytic system remain free.

Thus, the study of the reaction of menthol with acetylene showed that its optimal conditions are: temperature - 130 °C, the amount of catalyst KOH - 50 mol% (from the mass of menthol), the reaction duration - 3 hours. The maximum yield of menthol vinyl ether is 79.0%.

The effect of NaOH and KOH catalysts on the yield of vinyl ethers in DMSO solution was studied in the course of the research. For example, the yield of menthol vinyl ether is 75.7% with the maximum amount of NaOH; and in KOH – 79.0% (Table 4).

Table 4. Dependence of the yield of vinyl ethers on the amount and nature of the catalyst (temperature 130 °C, solvent - DMSO, reaction time - 3 hours)

Solvent	Catalyst	Amount of catalyst, % (relative to terpenoid mass)	Yield of vinyl ethers, %		
			Menthol	Thymol	3-Hydroxymethylhamazulene
DMSO	NaOH	25	60,1	59,0	56,7
		50	75,7	74,4	71,9
		100	72,5	71,0	68,3
	KOH	15	50,5	49,3	45,0
		25	72,4	71,0	67,7
		50	79,0	79,5	75,8
		75	78,1	77,6	74,3
		100	76,2	76,6	73,0

A similar dependence was observed for the yield of thymol vinyl ether and 3-vinyloxymethyl chamazulene, for which the maximum yield was 74.4 and 71.9% with sodium hydroxide catalysis and 79.5 and 75.8% with potassium hydroxide catalysis, respectively. Of the intermediate values determined by the amount of catalyst, the activity of the KOH catalyst was the highest. Based on this, the amount of catalyst participating in the reaction was studied in the range of 15-100 mol% relative to the terpenoid mass. The results showed that with an increase in the amount of KOH to 50 mol%, the yield of menthol vinyl ether increased to a maximum value of 79.0%. During thymol vinylation, the yield of its vinyl ether also passes through a maximum, this value is 79.5% in an amount of 50 mol% KOH, and during the synthesis of 3-vinyloxymethyl chamazulene - 75.8%. In both cases, increasing the amount of catalyst leads to a decrease in the yield of the corresponding vinyl ethers.

Physicochemical constants of new synthesized substances - menthol and thymol vinyl ethers, 3-hydroxymethylhamazulene and 3-vinyloxymethylhamazulene were determined (Table 5).

Table 5. Physico-chemical parameters of synthesized substances

№	Substance name	Boiling temperature, °C, 1 atm	Density, g/cm ³	Molecular refraction, cm ³	Refractive index, n_D^{20}
1	vinyl ether of menthol	180	0,85	56,97	1,449
2	vinyl ether of thymol	205	0,87	56,29	1,500
3	3-Hydroxy methyl-hamazulene	-	1,057	69,74	1,604
4	3-vinyloxy-methyl-hamazulene	160	1,032	78,94	1,572

VI. CONCLUSION AND FUTURE WORK

The work studies the reactions of vinylization of menthol, thymol and 3-hydroxymethyl chamazulenes in the presence of acetylene in a superbasic medium, the optimal conditions for carrying out the process, and the dependence of the yield of products on various factors.

In particular, it was shown that the optimal conditions for vinylation of the listed raw materials based on acetylene are: temperature - 130 °C, the amount of KOH catalyst - 50 mol% (relative to the molecular weight of the terpenoid), the reaction duration - 3 hours. The effect of sodium hydroxide and potassium hydroxide as a catalyst on the reaction yield was also studied and it was found that the product yield is higher in the case of using potassium hydroxide as a catalyst. In the experiments conducted, it was found that the maximum yield of vinyl ethers is 79.0, 79.5 and 75.8%, respectively, in menthol, thymol and 3-hydroxymethyl chamazulene.

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